Treating filtered final effluent from the Cape Flats Wastewater Treatment Plant with Ozone and Biologically Activated Carbon Filtration to remove pathogens and organic micropollutants

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Executive summary

Final effluent is widely recognised as a risky water source for human consumption given the organic micropollutants and pathogens it can contain. Hence, multi-barrier treatment trains and advanced processes are required. However, these are costly and therefore it is necessary to investigate how their cost can be optimized. Plumlee *et al.* (2014) asserted that quantifying the cost of advanced treatment processes can help compare treatment alternatives and utilities' planning.

The focus of the current study has been the cost optimisation of treatment processes in the treatment train of the Managed Aquifer Recharge (MAR) scheme of the Cape Flats Aquifer, one of the new bulk water schemes that originated out of the Cape Town drought peak during the period spanning between 2015–2017. It is an indirect potable reuse scheme that consists in injecting advanced treated final effluent from the Cape Flats MAR WRP into the Cape Flats Aquifer.

Within the Cape Flats MAR WRP is the O_3/BAC process, which is one of the advanced treatment processes at the facility. This process is essential given its ability to remove pathogens and organic micropollutants, i.e. it doubles as a disinfection step and an organic micropollutant removal step. However, the downside of the O_3/BAC process is its costs, particularly its capital and operating costs given the many variables affecting the removal efficiencies, and hence, the costs. Among these variables are the treatment objectives, energy usage and liquid oxygen usage. The main factors impacting the removal efficiency are the water quality (O_3 decay and instantaneous ozone demand [IOD]) and contact time. Therefore, the challenge is to carefully optimise the process without influencing the treatment objectives.

In light of this, the main research question that the current study tries to answer is about the optimum cost of the O_3/BAC filtration process for various treatment objectives to help produce safe drinking water in a treatment train. The aim of the current research is to study the interdependencies between the varying treatment objectives, the optimum operating conditions, and the efficiency of the O_3/BAC process to inactivate pathogens and remove organic micropollutants. The optimisation focusses on the filtered secondary effluent of the Cape Flats Wastewater Treatment Works (WWTW) with the aim to produce safe drinking water.

The research uses the O_3 process assessment methods, i.e. the T_{10} method and CSTR methods, and the O_3/TOC dose ratio as the main parameters to compare and relate the treatment objectives and the assessment methods with one another. The use of the O_3/TOC dose ratio is motivated by the findings of Snyder et al. (2014), which stated that the O_3/TOC dose ratio produces similar

treatment results, particularly oxidation, even with high variations in water quality. Gamage et al. (2013) also asserted that the O_3/TOC dose ratio relates the O_3 dose required for disinfection and the O_3 dose required for organic micropollutants oxidation. On one hand, the CT-value (product of residual O_3 concentration and contact time) guarantees that the O_3 process achieves its objectives concerning the removal of pathogens. On the other hand, the O_3/TOC dose ratio together with each pollutants O_3 and hydroxyl radical second-order reaction rates, k_{O3} and k_{OH}, allow the quantification of the removal of organic micropollutants. Additionally, the current research uses capital and operation and maintenance (O&M) costing models, including process performance regression models, applied to various treatment objectives of the O_3/BAC filtration process and to organic micropollutants found in the Cape Flats WWTW final effluent.

The current study finds that the O_3/BAC process of the Cape Flats MAR WRP can theoretically reduce more than 87% of the organic micropollutants in the Cape Flats WWTW final effluent, taking it from medium risk to low risk. The optimum contact time, in terms of cost for 2–4 Log virus inactivation by ozone and 1–3 Log giardia inactivation by ozone, is between 5–7 minutes as determined by the CSTR method, and it is 5 minutes as determined by the T_{10} method. The optimum contact time, in terms of cost for 1–3 log inactivation of cryptosporidium by ozone, is between 8–18 minutes for the CSTR method and between 6–13 minutes for the T_{10} method depending on the treatment objective and O_3 transfer efficiency. No apparent correlations between international concept costing models and actual Southern African O_3/BAC project costs were evident. The process assessment method, i.e. T_{10} or CSTR, affects the cost of the process and the performance objective that can be validated. Hence, the treatment of filtered final effluent by the O_3/BAC process can be optimized for specific treatment objectives to produce safe drinking water. A summary of the optimum O_3 contact times found in the current study are presented in Table 1-1.

Table 1-1 – Summary of the optimum O_3 contact times identified.

	Treatment Objectives optimum contact time (minutes)								
Process validation method	**2-log Virus**	**3-log Virus**	**4-log Virus**	**1-log Giardia**	**2-log Giardia**	**3-log Giardia**	**1-log Crypto***	**2-log Crypto***	**3-log Crypto***
T_{10}	5	5	5	5	5	5	6–7	9–10	12–13
CSTR	5–7	5–7	5–7	5–7	5–7	5–7	8–10	11–14	14–18

* Short for Cryptosporidium

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Acronyms and abbreviations

AADD	Annual Average Daily Demand
AOC	Assimilable Organic Carbon
AOP	Advanced Oxidation Process
AWTP	Advanced Water Treatment Plant
AWWA	American Water Works Association
BAC	Biological Activated Carbon
BAF	Biological Active Filter
BCA	Benefit-Cost Analysis
BOD	Biological Oxygen Demand
BOM	Biodegradable Organic Matter
BS	The British Standards
CCP	Critical Control Point
CCPP	Calcium Carbonate Precipitation Potential
CEA	Cost-Effectiveness Analysis
CEC	Contaminants/Chemicals of Emerging Concern
CIDB	Construction Industry Development Board
CoCT	City of Cape Town
COD	Chemical Oxygen Demand
CoR	Cost of Replacement
CP	Cathodic Protection
CPAF	Contract Price Adjustment Formulae
CSIR	Council for Scientific and Industrial Research
CSTR	Continuously Stirred Tank Reactor
CSWRCB	California State Water Resources Control Board
CT	Concentration x Time
CUA	Cost-Utility Analysis
CVM	Contingent Valuation Method
DAF	Dissolved Air Floatation
BMF	Biological Media Filtration
DBP	Disinfection By-Product
DEADP	Department of Environmental Affairs and Development Planning

DMF	Decision Making Framework
DOC	Dissolved Organic Carbon
DOL	Direct-On-Line
DPR	Direct Potable Reuse
DWS	Department of Water and Sanitation
EBCT	Empty Bed Contact Time
E.coli	Escherichia Coli
EDC	Endocrine-disrupting compounds
EIA	Environmental Impact Assessment
ES	Effective Size
GAC	Granular Activated Carbon
HCL	Hydrochloric Acid
HDT	Hydraulic Detention Time = Volume/volumetric flow
IPR	Indirect Potable Reuse
ISO	International Organization for Standardization
LCC	Life Cycle Cost
LOX	Liquid Oxygen
MAP	Mean Annual Precipitation
MAR	Managed Aquifer Recharge
MBR	Membrane Bioreactor
MF	Micro-Filtration
MLD	Megaliter per day
PV	Present Value
NPV	Net Present Value
NTU	Nephelometric Turbidity Units
NWRI	National Water Research Institute
O_3	Ozone
O&M	Operation and Maintenance
OEM	Original Equipment Manufacturer
OH·	Hydroxyl Radical
P&ID’s	Piping & Instrumentation Diagrams
PAC	Powder Activated Carbon
PLC	Program Logic Controller

PSA	Pressure Swing Adsorption
PST	Primary Settling Tank
RDP	Reconstruction and Development Program
RMU	Ring Main Unit
RO	Reverse Osmosis
SABS	South African Bureau of Standards
SANS	South African National Standards
SAR	South African Rands
SAT	Soil Aquifer Treatment
SST	Secondary Settling Tank
SCADA	Supervisory Control and Data Acquisition
SS 304	Stainless Steel Grade 304
STP	Sewage Treatment Plant
SWTR	Surface Water Treatment Rule
TBC	To Be Confirmed
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TOrC	Trace Organic Contaminants
UC	Uniformity Coefficient
UF	Ultra-Filtration
UPS	Uninterruptible Power Supply
US	United States
USA	United States of America
USEPA	The United States Environmental Protection Agency
UV	Ultraviolet light
$UV_{absorbance}$	Ultraviolet light absorption
UV_{a254}	Ultraviolet absorbance at 254nm
UVT	Ultraviolet Transmittance
WHO	World Health Organisation
WRC	Water Research Commission
WRP	Water Reclamation Plant
WRRF	Water Resource Recovery Facility

WTP	Water Treatment Plant
WTW	Water Treatment Works
WUL	Water Use Licence
WULA	Water Use Licence Application
WWTP	Wastewater Treatment Plant
WWTW	Wastewater Treatment Works

Symbols

A	Area (m^2)
AC	Annualised cost
CC	Capital cost
CCK	Capital Cost per kiloliter
d	Days
Df	Discount factor
EBCT	Empty Bed Contact Time
ft	Feet
Gal	United States Gallon
kg/m2.d	Kilogram per Square Meter per Day
kgO3/hr	Kilogram Ozone per hour
kl	Kiloliter
kl/d	Kiloliter per Day
kV	Kilovolt
kVA	Kilovolt-Ampere
kW	Kilowatt
kWhr	Kilowatt Hour
l/c/day	Liter per Capita per Day
m	Meter
m/h	Meter per Hour
m/s	Meter per Second
m2	Square Meter
m3/h.m	Cubic Meter per Hour per Meter
m3/hr	Cubic Meter per Hour
MGD	Mega Gallon per Day
mg-min/l	Milligram minutes per Liter
mg/L	Milligram per Liter
min	Minute
ml	Milliliter
Ml/day	Mega Liter per Day
MLD	Mega Liter per Day

MLSS	Mixed Liquor Suspended Solids
mm	Millimeter
mM	Millimole
mS/m	Micro Siemens per Meter
nm	Nanometers
ng/l	Nanogram per Liter
$UV_{absorbance}$	Ultraviolet light absorption
UV_{a254}	Ultraviolet absorbance at 254nm
UVT	Ultraviolet Transmittance
µg/L	Microgram per Liter
λ	Likelihood of consuming a micropollutant
μ	Consequence of consuming a micropollutant
$	United States Dollar

Chapter 1 : Introduction

1.1 Background

In a 1986 study on water reclamation, Schutte (1986) highlighted the increasing stresses that water resources in South Africa experience due to industrialisation and population growth and noted the need for alternative water sources. The recent drought in South Africa (2015–2017) proved his statements correct as certain parts of the country experienced periodical water shortfalls and placed the water supply under significant stress. Schutte (1986) further asserted that the increase in water usage causes more water to end up at wastewater treatment plants and ultimately in rivers and oceans. Moreover, according to Jiménez Cisneros (2014), increase in irrigation usage, water scarcity and urbanisation are also big motivators behind the need for alternative water sources, a problem which he posited could be solved by more wastewater reuse by the year 2025. Another factor that has become more prominent of late is climate change. Climate change impacts rainfall patterns, while the world population is rapidly increasing, placing significant stress on the current water supply. All the above indicate the need for wastewater reuse, which is not fully utilised at present.

The growing water shortage in South Africa, the requirement for alternative water resources and the rising cost of electricity creates a need for the optimisation of treatment processes that can be implemented in wastewater reuse treatment trains to produce water that is safe for consumption. Water utilities have found that water reuse is a very cost-effective source of alternative water, much more so than its counterpart, desalination (Turner *et al.*, 2015). Cost-effective and safe alternative water sources are affected by the following factors:

i) The universal changing paradigms around water sources (e.g., conversion of WWTPs to water and resource recovery facilities, WRRFs) (Sundaram *et al.*, 2020);

ii) The rising concern of the effects of organic micropollutants in wastewater (Plumlee *et al.*, 2014);

iii) The multi barrier approach adopted by most water utilities for wastewater reuse to reduce pathogens to acceptable levels, resulting in many costly treatment processes (Gerrity *et al.*, 2013); and

iv) The increasing costs of water treatment due to advanced treatment processes required to remove organic contaminants (Plumlee *et al.*, 2014). For example, Ozone/biological activated carbon (O_3/BAC) filtration can double the costs of treatment compared to a conventional treatment plant (Neukrug *et al.*, 1984).

The nature of wastewater treatment final effluent, the source water for water reuse treatment facilities, is that of a high biological organic content in the form of total organic carbon (TOC) and pathogens. Conventional wastewater treatment targets the reduction of the active portion of the biological organic content, the reduction of nutrients (nitrogen and phosphorous) and the reduction of E.coli to produce a final effluent that is safe for environmental release. Given its source and content, the final effluent of WWTP systems has a high health risk (acute and chronic) and needs advanced treatment to get it to drinking water standards. The organic portion (micro-organics) that contains organic micropollutants at microscale, can pose long term (chronic) health effects if consumed for long periods. The pathogens in the final effluent pose immediate (acute) health effects if ingested.

The global scale of the problems caused by organic micropollutants in wastewaters and the need for cost-effective and adequate treatment of micropollutants in water was highlighted by Schwarzenbach *et al*. (2006), especially given that wastewater treatment plant processes are unable to remove organic micropollutants (Bui *et al.*, 2016). Furthermore, Bui *et al.* (2016) attributed the inability of conventional treatment processes to adequately remove organic micropollutants to their diverse nature and their existence in wastewater at low concentrations. Advanced treatment processes like adsorption onto activated carbon or oxidation by ozonation are required for organic micropollutant removal (Guillossou *et al.*, 2019). There are, therefore, increasing concerns regarding the extensive presence of organic micropollutants in water given the damages they can have on reproductive systems (Cisneros, 2014), central nervous system and the risk of cancer (Derco *et al.*, 2015). The potential impacts on human health are the most significant forces behind the need for advanced alternative treatment processes to remove organic micropollutants from reused water (Derco *et al.*, 2015).

Waterborne pathogens have immediate and severe health effects and are considered to be acute (World Health Organisation, 2017). The World Health Organisation (WHO) furthermore recognises that a single microorganism, that can be transmitted by infected persons, has the potential to cause harm and illness. The effects caused by waterborne pathogens (as listed by the WHO) include an upset stomach, diarrhoea, cholera, typhoid fever and hepatitis-A among other health concerns and, in severe cases, even death (Department of Water and Sanitation, 2013). With Cape Town (similar to other major cities) depending on water-borne sanitation, water-stressed conditions such as those experienced during the 2015–2018 drought can lead to city-wide waste accumulation and the spreading of diseases.

Waterborne pathogens can generally be grouped into four categories (World Health Organisation, 2017):

i) Viruses (e.g. Hepatitis-A virus, Rotavirus, etc.);

ii) Protozoa (e.g. Giardia, Cryptosporidium, etc.);

iii) Bacteria (e.g. E.coli, salmonella, shigella, etc.); and

iv) Helminths (e.g. Roundworm, Tapeworm, etc).

Organic micropollutants can include a wide range of constituents originating from human activity or they can be naturally occurring. Organic contaminants are not considered acute but can lead to chronic health problems in those exposed to them for long periods of time and at high concentrations. The total quantity of organic chemicals can be grouped into a collective contaminant group known as total organic carbon (TOC) and measured in mg/l. Various organic micropollutants are present in low concentrations in wastewater, ranging from micro-g/l to nano-g/l. The composition of chemical mixtures in wastewater is continually changing depending on the activities that are happening in the catchment, such as the quantity and nature of industrial activities and local circumstances.

Organic micropollutants can be subdivided into the following main categories (Swartz *et al.*, 2015):

i) Volatile organic compounds (e.g. petrochemical products, industrial solvents, etc.);

ii) Synthetic industrial chemicals (e.g. plasticizers, polymers, dyes, etc.);

iii) Pesticides;

iv) Steroidal hormones;

v) Personal care products;

vi) Pharmaceuticals;

vii) Antiseptics;

viii) Per- and Polyfluoroalkyl substances (e.g. household products like non-stick coatings); and

ix) Dioxins and polychlorinated biphenyls (e.g. industrial discharges).

Organic micropollutants in small quantities are harmless but persistent exposure to these contaminants can potentially cause the following deleterious health conditions (Swartz *et al.*, 2015):

i) Industrial chemicals are identified as being carcinogenic;

ii) Pesticides and herbicides are identified as being endocrine disrupting;

iii) Pharmaceuticals or household chemicals are identified as being endocrine disrupting; and

iv) Personal care products are identified as causing liver problems.

Concentrations of pathogens and organic micropollutants (also known as contaminants of emerging concern – CECs) in wastewater must therefore be reduced to guideline levels before the water is safe for potable use.

Successful removal of antibiotics, i.e. greater than 95%, from wastewater by the combined process of Ozone (O_3) dosing and BAC filtration was reported in a wastewater-reuse pilot plant study done by Li *et al.* (2015). The combination of O_3 and BAC filtration is attractive because it inactivates pathogens and oxidises organic micropollutants (Mosher *et al.*, 2016) and it can produce a similar high quality water compared to reverse osmosis (RO) (Vatankhah *et al.*, 2019)**.** Moreover, increased TOC removal occurs in a biological activated filter (BAF) due to the biodegradation of organic matter formed in an O_3 process, installed before the BAFs (Zhu *et al.*, 2015). Besides, when Lee *et al.* (2012) compared the O_3/BAC filtration combined processes with the highly effective process of reverse osmosis, they recommended the O_3/BAC filtration combined process given that it had no waste stream, a lower energy cost, and also given that it removed micropollutants more efficiently. This finding was supported by a similar study from Bui *et al*. (2016).

Despite the fact that the O_3/BAC filtration process has lower energy costs compared to RO, advanced treatment technologies, like O_3 disinfection in wastewater reuse treatment trains, puts a high demand on energy usage and can increase the costs associated with water production by 20–40% (Dimitriou, 2007). The increase in cost can be attributed to how O_3 gas is produced. O_3 gas is produced in an O_3 generator when oxygen is passed through an electrical current, where O_2 is converted to O_3 (Arn *et al.*, 2011), but this conversion requires high amounts of energy and oxygen (Letterman, 1999), thus making the process costly. Nevertheless, the operational costs of replacing activated carbon can be reduced by extending the life of activated carbon when O_3 and a granular activated carbon (GAC) filter is combined (Neukrug *et al.*, 1984). GAC filters conventionally operating on the principle of adsorption of organic micropollutants, are converted to a BAC filter when an oxidation step (O_3) is put in place before the GAC filter (Ross *et al.*, 2019).

When designing treatment facilities, treatment objectives are the first priority and the optimisation of costs, the second priority. The most necessary design aspects of an O_3 system are ideal system performance, with regards to treatment objectives, and optimised costs implementation (Rakness, 2005). It is essential to find the right balance between treatment efficiency (removal of contaminants) and costs efficiency without compromising on sufficient removal of pollutants (Feng & Chu, 2004).

The City of Cape Town has experienced water shortages over the past four years, mainly due to the following reasons:

i) On the supply side: A continuous 3-year drought (2015–2017) that represented a 1:400-year drought (Department of Water and Sanitation, 2018); and

ii) On the demand side: Urbanisation, resulting in increased water demand.

Given the above conditions, the City of Cape Town embarked on finding alternative and sustainable water sources. A task team managing the *New Water Programme*, was set up. The New Water Programme's aim is to secure new bulk water resources as alternatives to conventional surface water (Department of Water and Sanitation, 2018). The objective, furthermore, is to improve the City's water resilience. The New Water Programme identified the Managed Aquifer Recharge (MAR) scheme of the Cape Flats Aquifer as one of the most viable alternative sources.

Treated final WWTP effluent is a large water source that usually ends up in the ocean, especially in the Cape Town context, where final effluent is discharged into short river streams close to the sea around the city. According to the Department of Water and Sanitation (2018), the unconstrained daily demand of the City of Cape Town is 888MLD (in the drought, this was restricted to 488MLD). The City of Cape Town (2017) estimates that two-thirds of its demand (consumption) ends up at its wastewater treatment plants. This equates to roughly about 592MLD that is lost to the ocean. The city identified 13 of its 20 wastewater treatment plants as having a potential for reuse and is providing 50MLD of non-potable final effluent to indirect reuse users across the city (City of Cape Town, 2018). Considering the allocated non-potable reuse volumes from the City of Cape Town (2018) and the water use licences of the 13 identified treatment plants, the City has a theoretical potential of 500MLD available for new reuse projects. This potential is roughly about 56% (500MLD/888MLD) of the normal unconstrained daily demand (888MLD) of the City of Cape Town. With the New Water Programme, the City is planning to utilize 110MLD of the 500MLD, i.e. 40MLD at Cape Flats WWTW for the Cape Flats MAR scheme and 70MLD at Zandvliet WWTW for direct potable reuse (Department of Water and Sanitation, 2018).

The Cape Flats MAR Water Reclamation Plant (WRP) forms part of the Cape Flats Aquifer Potable Reuse Scheme. It is an indirect potable reuse scheme, which will inject treated secondary effluent into the Cape Flats Aquifer. The injected water will then be required to travel at least two months through the aquifer before being abstracted. After abstraction, it will be further treated before being distributed into the potable network. One of the most critical treatment processes in the Cape Flats MAR WRP is the O_3/Biological-Active-Carbon (O_3/BAC) filtration process (Smuts & Marais, 2018). The use of advanced water treatment processes like O_3/BAC filtration is motivated by the need for alternative water resources and the risk of organic micropollutants and pathogens when reusing wastewater. The O_3/BAC filtration process is an essential step in this reuse scheme to remove pathogens and micro-organics if applied and operated correctly. The O_3/BAC process is expensive to build and operate and has many variables that affect the costs and removal efficiencies.

The recent drought in South Africa, the estimated 56% of Cape Town unconstrained demand flowing from wastewater treatment works into the sea and the initiative by the City of Cape Town to find alternative water sources makes investigating the O_3/BAC process and its application to filtered final effluent of Cape Flats WWTW relevant. The O_3/BAC process can help to mitigate the risks associated with organic micropollutants and pathogens to produce safe water for the City of Cape Town. Additionally, investigating it can help optimize the O_3/BAC process treatment costs.

1.2 Research problem

At the centre of the problem is the millennium development goal of provision of water and sanitation, which draws from goals around climate change, the education of society about the value of water, water-wise habits, and water conservation. Additionally, new sources of water must be identified, which must comply with public health standards that in return influence the costs of water. Figure 1.1 below shows a schematic of the contextual problem our society is facing today.

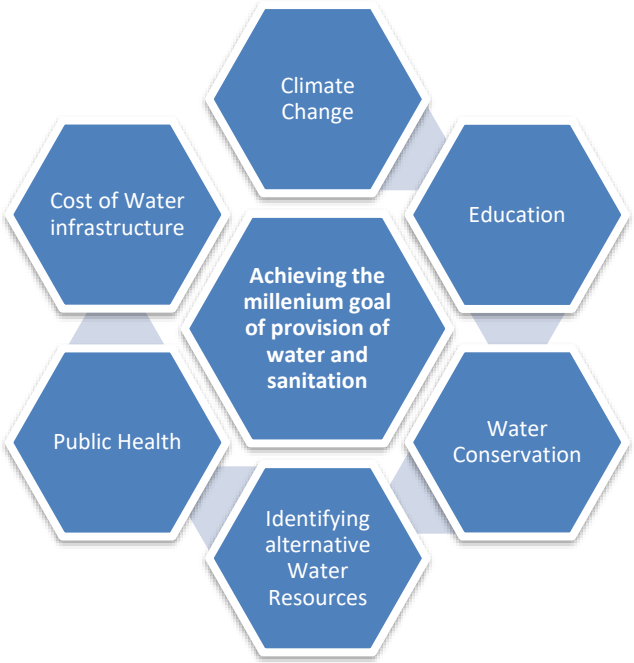


Figure 1.1 – Schematic of the contextual problem of water provision globally.

Various processes can reduce pathogens and organic micropollutants and usually, a multi-barrier approach is used to ensure that the water is safe to drink. One of the most effective processes to deal with the above two groups of contaminants is the combination of dosing O_3 into water and then biologically filtering the water.

For the Cape Flats MAR WRP, the O_3/BAC process step is the main Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC) and organic micropollutant removal step, which doubles up as a disinfection step that kills pathogens (Smuts & Marais, 2018). The O_3/BAC step is the heart of the Cape Flats pre-injection Water Reclamation Plant. The O_3/BAC process is also the most cost-intensive process (for both energy costs and liquid oxygen costs) in the Cape Flats MAR WRP treatment train. This process is thus critical but also costly and therefore raises the concern of how the O_3/BAC process can be customised—with regard to treatment objectives—and optimised—with regard to cost—towards generating safe drinking water.

Hence, the hypothesis of the current research is whether the treatment of filtered final effluent by the O_3/BAC process can be tailored and optimized for specific treatment objectives in a process train that aims to produce safe drinking water. In light of these optimisation concerns, the following research questions were identified:

i) How does the performance validation of the O_3/BAC process influence the number of O_3/BAC treatment objectives that can be achieved?

ii) How do the costs of different O_3/BAC treatment objectives relate to one another?

   a. Costs of 3-log Cryptosporidium O_3 inactivation;
   b. Costs of 2-log Cryptosporidium O_3 inactivation;
   c. Costs of 1-log Cryptosporidium O_3 inactivation;
   d. Costs of 3-log Giardia O_3 inactivation;
   e. Costs of 2-log Giardia O_3 inactivation;
   f. Costs of 1-log Giardia O_3 inactivation;
   g. Costs of 4-log Virus O_3 inactivation;
   h. Costs of 3-log Virus O_3 inactivation;
   i. Costs of 2-log Virus O_3 inactivation;
   j. Costs of Group 1 organic micropollutant O_3 oxidation;
   k. Costs of Group 2 organic micropollutant O_3 oxidation;
   l. Costs of Group 3 organic micropollutant O_3 oxidation;
   m. Costs of Group 4 organic micropollutant O_3 oxidation;
   n. Costs of Group 5 organic micropollutant O_3 oxidation;
   o. BAC filtration with an EBCT of 10 minutes;
   p. BAC filtration with an EBCT of 15 minutes; and
   q. BAC filtration with an EBCT of 20 minutes.

iii) How do international costing models relate to the capital cost and operation and maintenance (O&M) costs of the O_3/BAC process in Southern Africa (Namibia and South Africa)?

iv) Is there an optimum O_3 contact time in terms of capital and operation and maintenance (O&M) costs for the O_3 disinfection process?

v) How effectively can the O_3/BAC process remove the organic micropollutants found in the Cape Flats WWTW final effluent?

1.3 Research objectives

The general aim of the current study is to evaluate the costs and performance of the O_3/BAC process in the context of the Cape Flats MAR WRP. The objectives of the research are to study the interdependencies between different O_3/BAC treatment objectives, optimum operational conditions for the O_3/BAC process and the efficiency of the O_3/BAC process to deactivate pathogens and remove organic micropollutants (which include contaminants of emerging concerns) in the Cape Flats wastewater reuse context. This will be done by focusing on:

i) A literature study on the latest technological advancements and state of the art alternatives available within the O_3/BAC process, including an analysis of the process' removal efficiency and how sensitive it is to variables such as O_3 dosage, type of contaminants, biological diversity, filter bed depth and empty bed contact time (EBCT);

ii) An identification of the O_3/BAC treatment objectives;

iii) A cost comparison of the treatment alternatives for different process assessment/validation methods using pre-existing costing models;

iv) A comparing of international costing models to assess actual O_3/BAC process costs in Southern Africa;

v) An investigating of whether an optimum O_3 contact time exits and where the 20-year cash flow present value (discounted cash flow) cost of the O_3 system is at its lowest;

vi) A grouping of the organic micropollutants based on their O_3 and hydroxyl radical ($OH\cdot$) reaction rates; and

vii) A study of the presence of organic micropollutants in the final effluent of Cape Flats wastewater treatment works (WWTW), before and after treatment with the O_3 process. Organic micropollutants removal are estimated with removal prediction models and the safety of the water are rated with a water quality risk analysis.

1.4 Research scope and limitations

1.4.1 Type of research

The current thesis is for the fulfilment of a 120 credits dissertation and the following mixed-methods are applied to this research:

i) Design Research: a comparison of different treatment alternatives by evaluating their costs and process performance. This will also be used to investigate O_3 cost optimisation and how the international costing models fit within the Southern African (South Africa and Namibia) context; and

ii) Case Study: an evaluation of the removal of organic micropollutants with the O_3/BAC process, from the Cape Flats WWTW filtered final effluent.

The design research method is chosen because, at the time of writing, the project in question is in the design phase and there are insufficient funds and time to build pilot plants or conduct bench-scale tests to do experimental research. Therefore, state of the art research findings can be applied to the O_3/BAC filtration process for Cape Flats MAR WRP. By establishing clear links between the current research and design aspects, the aim is to produce safe water at much lower costs.

In addition, the current research will implement a descriptive case study on available raw water quality data to predict the level of treated water quality that can be expected based on the contaminant removals achieved, as predicted by regression models and contaminant reaction rates. Although regression models come with inaccuracies, the aim of the case study is to provide more information on some of the expected outcomes of the O_3/BAC process.

1.4.2 Key outputs of research

The key outputs identified are:

i) Finding the optimum O_3 dosage and contact time point in terms of costs, based on the CT-value concept, by doing a life cycle cost analysis of the process, specifically looking at capital and operational costs;

ii) Comparing the O_3/BAC process evaluation methods and investigating their influence on the treatment objectives;

iii) Comparing costing models; and

iv) Showing the removal efficiency of the O_3/BAC process for some groups of organic micropollutants in the Cape Flats MAR WRP context.

1.4.3 Research assumptions

The following research assumptions were made:

i) The filtered water entering the O_3/BAC process has a turbidity of <0.3mg/l NTU 95% of the time and < 1mg/l NTU 100% of the time (US EPA, 2010);

ii) Liquid oxygen is the source of oxygen for O_3 generation at 10% dose concentration (this was a decision made for the Cape Flats MAR WRP [Smuts and Marais, 2018]);

iii) Changes in bulk organic matter are found to be quite similar between different wastewater matrices, even with considerable differences in water qualities (Snyder *et al.*, 2014). Removal efficiencies and regression models of other similar treatment plants are applied to the O_3/BAC process at Cape Flats filtered final effluent. Care has been taken to assure that the different treatment plants used in the current research are also tertiary filtered (either by rapid gravity sand or membrane) effluent; and

iv) O_3 decay-characteristics (k-factor) and instantaneous O_3 demand (IOD), as shown in Table 2-14, are used for all calculations. The k-factor and IOD's of Table 2-14 are determined for wastewater with similar water quality parameters as those expected at Cape Flats WWTW given that there are no O_3 decay tests results available for the Cape Flats WWTW final effluent.

1.5 Overview of dissertation

1.5.1 Conceptual framework

In Figure 1.2 the conceptual framework of the current research is presented. It shows the interconnectivity between water quality, water safety, the treatment costs of the O_3/BAC process in the water reuse context and the importance of treatment efficiency and process optimization in relation to treatment costs. At the centre of the framework are water scarcity and alternative water resources that drive water reuse as an alternative water resource.

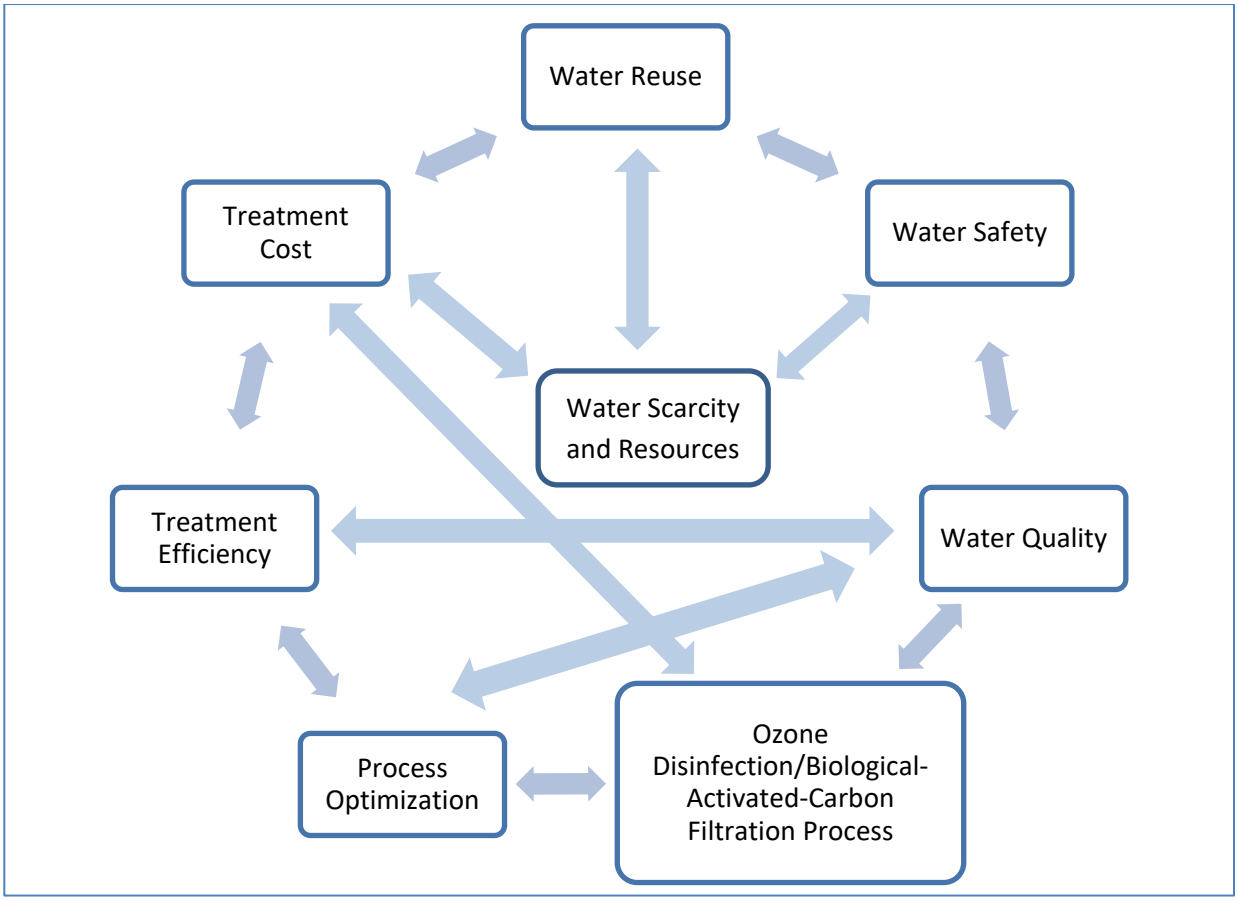


Figure 1.2 – Schematic of the Conceptual Framework of the current study.

1.5.2 Research framework

Figure 1.3 shows the research framework for the current study. Chapter 1, the introduction, gives a background of the project and identifies the research problem, research objectives, assumptions, and outputs. Chapter 2, the literature study, covers the literature of the O_3 process and the BAC filtration process by looking at treatment variables within each process and aspects affecting its removal efficiency and costs. The variables include among others the effects of O_3 decay, O_3 transfer efficiency, O_3 injection types, micro-organic contaminant removal, impact of empty bed contact time and filtration bed depth on the O_3/BAC filtration process. Chapter 3 describes the research methods. Besides, it gives background on the research site, grouping of organic micropollutants, calculation of removal efficiencies and costing models that will be used for comparisons and investigations. Chapter 4 shows and discusses the results of the study, and lastly, Chapter 5 concludes with a summary of all the main findings, shortcomings, and future research.

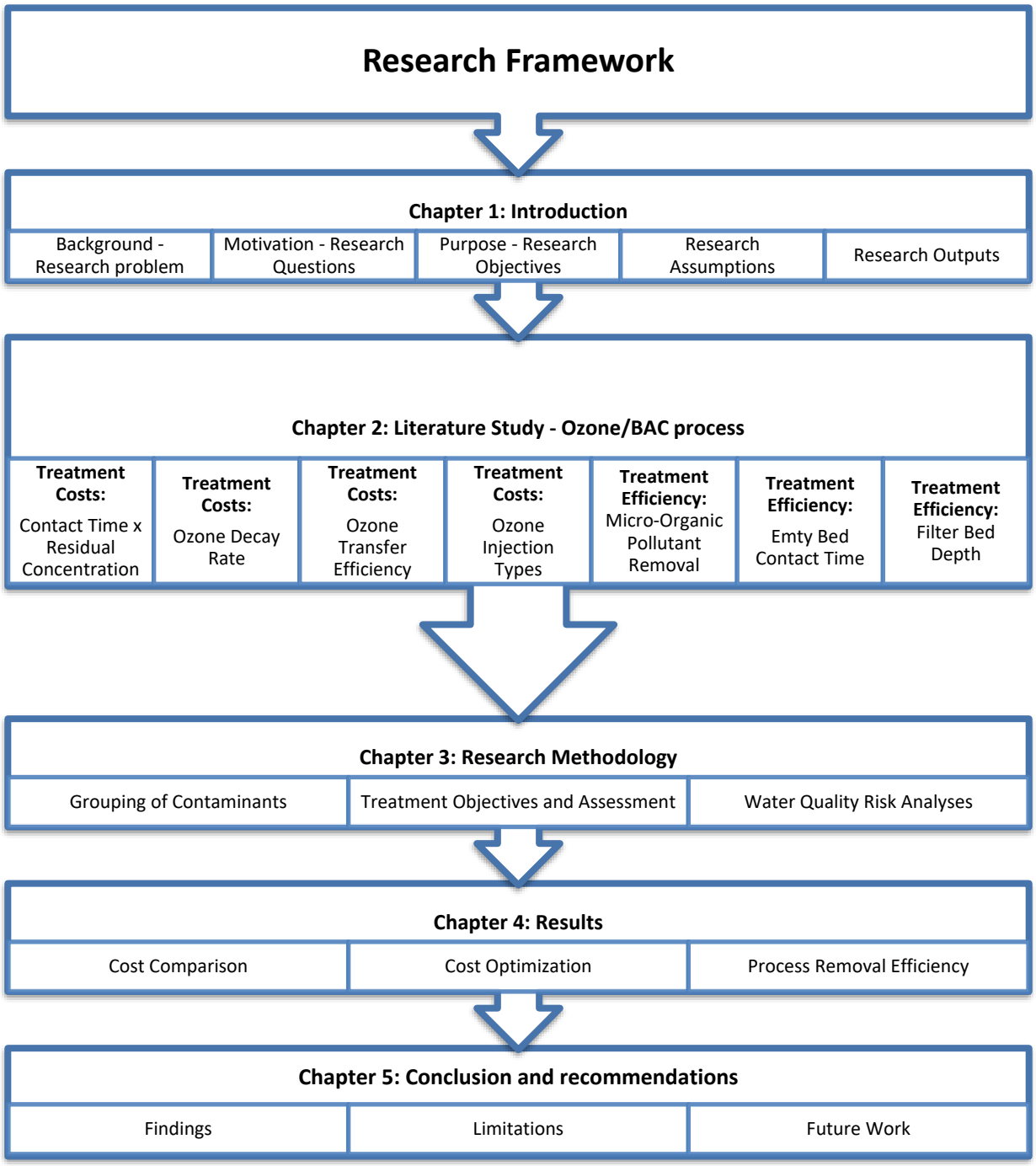


Figure 1.3 – Research Framework Diagram.

For clarity, Figure 1.4 below shows the main concepts of the study and their interrelationship.

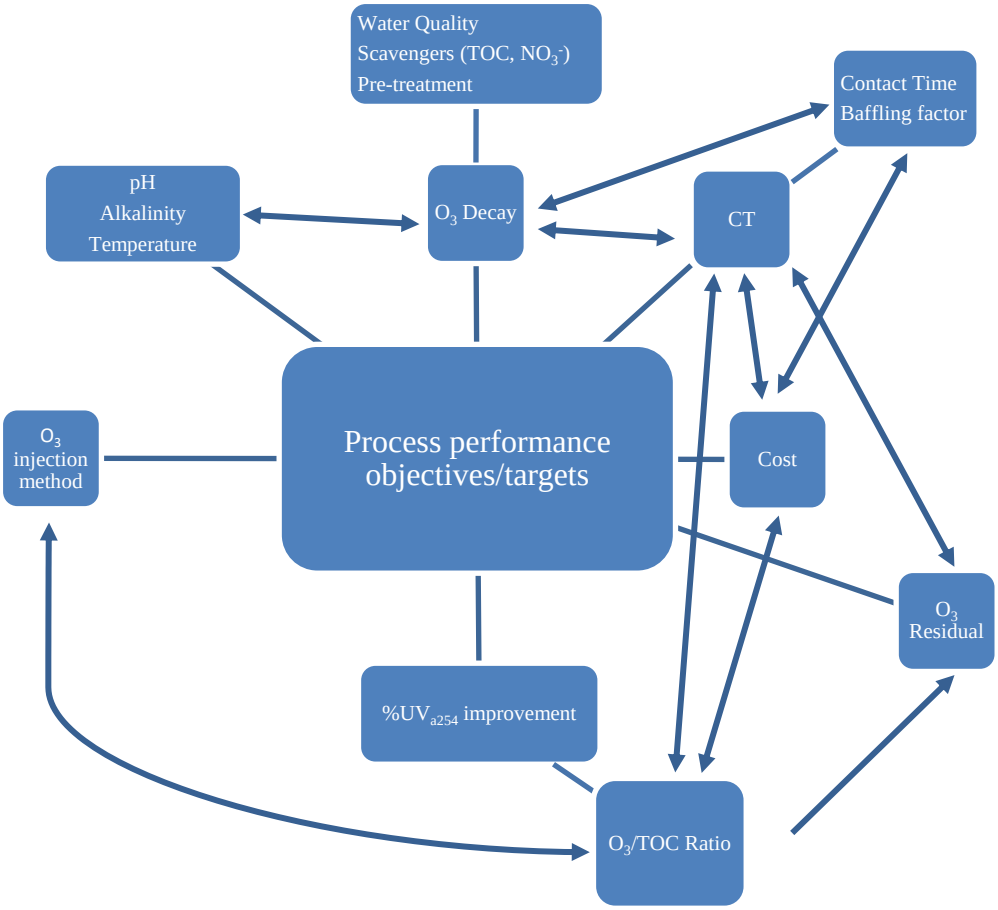


Figure 1.4 – Mind map of the main concepts in the study and their interrelationship.

At the centre of Figure 1.4 is the process performance objectives. The objectives are influenced by the water quality (pH, alkalinity, temperature, scavengers, and pre-treatment), O_3 decay rate, UV_{a254} improvement and injection method. In turn, the process performance objectives influence the required CT-value that affects the costs. The CT- value is also impacted by the O_3 decay rate, effective contact time, O_3/TOC dose ratio and O_3-residue in the contact tank. The costs are moreover determined by the O_3/TOC dose ratio and CT-value.

Chapter 2 : Literature Review

The main focus of the literature review is on the factors influencing the O_3/BAC process efficiency, validation and cost. The literature review begins in sections 2.1 and 2.2 with information on the two main contaminants i.e. pathogens and organic micropollutants, that drive the implementation of the O_3/BAC. Section 2.3 describes why it is so important and beneficial to combine the O_3 and BAC filtration processes. Section 2.4 is dedicated to the O_3 process and Section 2.5 looks at the BAC filtration process.

2.1 Pathogens

Although there are various approaches to policy and planning of water reuse schemes, research seems to focus on the costs and benefits of potable reuse, public acceptance of reuse schemes, consumer safety in terms of human health (pathogens) and monitoring and assessing contaminants of emerging concerns (Burgess *et al.*, 2015). While there are significant numbers of microorganisms, parasites and viruses in wastewater including bacteria and parasites, only a small percentage of these microorganisms cause diseases, i.e. are pathogenic (Snyder *et al.*, 2014). Municipal wastewater systems collect pathogens transmitted by humans with the intention of separating them from drinking water sources. The pathogens that are found in wastewater have diverse behaviours and characteristics and will most commonly lead to a gastrointestinal diseases if ingested (World Health Organisation, 2017). Table 2-1 below shows examples of pathogen groups (bacteria, viruses, protozoa, and helminths), their species and associated illnesses.

Table 2-1 – Wastewater borne enteric pathogens (World Health Organisation, 2017).

Pathogen	Species Type	Illness
Bacteria		
Burkholderia	*B. pseudomallei*	Melioidosis
Campylobacter	*C. coli, C. jejuni*	Gastroenteritis, Guillain–Barré syndrome
Escherichia coli - diarrhoeagenic		Gastroenteritis
Escherichia coli - enterohaemorrhagic	*E. coli*	Gastroenteritis, haemolytic uremic syndrome
Legionella spp.	*L. pneumophila*	Respiratory illness (pneumonia, Pontiac fever)
Mycobacteria (non-tuberculous)	*M. avium complex*	Respiratory illness (hypersensitivity pneumonitis), skin infections
Salmonella Typhi		Typhoid
Other Salmonella	*S. enterica, S. bongori*	Gastroenteritis, reactive arthritis
Shigella	*S. dysenteriae*	Dysentery
Vibrio cholerae	*V. cholerae*	Cholera

Table 2-1 continued.

Pathogen	Species Type	Illness
Viruses		
Adenoviridae	Adenoviruses	Gastroenteritis, respiratory illness, eye infections
Astroviridae	Astroviruses	Gastroenteritis
Caliciviridae	Noroviruses, sapovirsus	Gastroenteritis
Hepeviridae	Hepatitis-E virus	Infectious hepatitis
Picornaviridae	Enteroviruses	Gastroenteritis, respiratory illness, nervous disorders, myocarditis
	Parechoviruses	Gastroenteritis, respiratory illness
	Hepatitis-A virus	Infectious hepatitis
Reoviridae	Rotavirus	Gastroenteritis
Protozoa		
Acanthamoeba	A. culbertsoni	Granulomatous amoebic encephalitis
Cryptosporidium	C. hominis/parvum	Gastroenteritis
Cyclospora	C. cayetanensis	Gastroenteritis
Entamoeba histolytica	E. histolytica	Amoebic dysentery
Giardia	G. intestinalis	Gastroenteritis
Naegleria fowleri	N. fowleri	Amoebic meningitis
Helminths		
Ascaris	A. lumbricoides (roundworm)	Abdominal pain, intestinal blockage
Taenia	T. saginata (tapeworm)	Abdominal pain
Trichuris	T. trichura (whipworm)	Abdominal pain, diarrhoea

Water reuse aims to close the gap between drinking water and wastewater systems (World Health Organisation, 2017). A series of additional treatment steps after secondary wastewater treatment (i.e. activated sludge reactor, secondary settling and disinfection [US EPA - Office of Water, 1998]) lead to what is called, tertiary treated wastewater that improves effluent quality beyond standard effluent discharge limits (Environmental Protection Agency Ireland, 1997). Wastewater is tertiary treated to remove pathogens, organics, turbidity, nitrogen, phosphorus and metals (Gerba, Pepper & Brusseau, 2019), which helps reduce the O_3 demand and possible pathogen particle shielding (Lazarova *et al.*, 2014). Reuse treatment trains are dictated by pathogen removal and a small list of indicator trace organic compounds, which require multi-barrier tertiary treatment trains (Gerrity *et al.*, 2014). Multi barrier treatment trains that deal with

pathogens and organics are used at most full-scale reuse facilities. However, the specific treatment processes used vary according to local regulations and site-specific conditions.

Table 2-2 below shows the performance of various treatment processes in log removals of pathogens. Log removal quantifies the success of pathogen removal and is "*[d]etermined by taking the logarithm of the ratio of pathogen concentration in the influent and effluent water of a treatment process.*" (Water Research Australia, 2014:1). For the purposes of the current study 1 log = 90% removal, 2 log = 99% removal, 3 log = 99.9% removal and 4 log = 99.99% removal.

Table 2-2 – Potential log reduction of pathogens by various processes (Mosher et al., 2016).

	Pathogen and Total Coliform Log Reduction							
Process/Technology	**Cryptosporidium**		**Giardia**		**Virus**		**Total Coliform**	
	TCEQ	UER	TCEQ	UER	TCEQ	UER	TCEQ	UER
Microfiltration or ultrafiltration	4	4	4	4	0	0	N/A	3
Membrane bioreactor	0	4	0	4	0	0	N/A	3
Reverse osmosis	0	2	0	2	0	2	N/A	4
Nanofiltration	0	---	0	---	0	---	N/A	---
Chlorine	0	0	1	1	3	3	N/A	3
Ultraviolet irradiation disinfection	4	4	4	4	4	4	N/A	5
Ultraviolet/photolysis	4	≥4	4	≥4	4	≥4	N/A	≥5
Advanced oxidation processes	4	6	4	6	4	6	N/A	6
Ozone	3	3	3	3	5	5	N/A	3
Ozone/biological activated carbon	3	3	3	4	5	5	N/A	4
Stabilization	---	---	---	---	---	---	N/A	---
Engineered storage	---	---	---	---	---	---	N/A	---
TCEQ = Texas Commission on Environmental Quality. UER = Upper End Reduction. N/A = Not applicable.								

Pathogen reduction and chlorinated disinfection by-product removal have put the focus on the O_3/BAC process and removal of biodegradable organic matter (BOM) (Emelko *et al.*, 2006). Shown below is the log reduction requirements for pathogens in reuse treatment trains in Texas (Table 2-3), California (Table 2-4) and as prescribed by the National Water Research Institute (NWRI) (Table 2-5).

Table 2-3 – Pathogen Log reduction requirements in Texas (Mosher et al., 2016).

Microbial Group	Criterion[a] (Minimum Log Reduction)
Enteric viruses	8
Cryptosporidium	5.5
Giardia	6
[a] Reduction between treated wastewater and finished drinking water.	

Table 2-4 – Pathogen log reduction requirements in California (Mosher et al., 2016).

Item	Enteric Virus	Giardia	Cryptosporidium
Untreated wastewater maximum concentration	10^5 virus/L	10^5 cysts/L	10^4 oocysts/L
Tolerable drinking water concentration (TDWC)	2.2×10^{-7} virus/L	6.8×10^{-6} cysts /L	1.7×10^{-6} oocysts /L
Ratio of TDWC to wastewater concentration	2.2×10^{-12}	6.8×10^{-11}	1.7×10^{-10}
Required log reduction value	12	10	10

Table 2-5 – Pathogen Log reduction requirements by the NWRI (Mosher et al., 2016).

Microbial Group	Criterion[a] (Minimum Log Reduction)	Possible Surrogates
Enteric viruses	12	MS2 bacteriophage
Cryptosporidium[b]	10	Latex microspheres, AC fine dust, inactivated Cryptosporidium oocysts, aerobic spores
Total coliform bacteria[c]	9	Not applicable
[a] Reduction is between raw wastewater and finished drinking water. [b] Also documented to provide 10-log or greater reduction of Giardia cysts. [c] Also, protective for enteric pathogenic bacteria.		

2.2 Organic micropollutants

Michael-kordatou *et al*. (2015) noted that one of the most important ways to achieve sustainable water management is the reuse of wastewater. For direct potable reuse (DPR) and indirect potable reuse (IPR), Zhu *et al*. (2015) identified the following contaminants of eco-toxicological and epidemiological concerns:

i) Total organic carbon (TOC);

ii) Pharmaceutical and personal care products (PPCPs);

iii) Endocrine-disrupting compounds (EDCs); and

iv) Organic micropollutants.

The dissolved component of organic matter in the final effluent is a diverse mixture of the following compounds:

i) EDCs;

ii) PPCPs;

iii) Disinfection by-product precursors;

iv) Natural organic matter; and

v) Soluble microbial products.

Natural organic matter originates from all-natural material present in ground- or surface water. Soluble microbial products are formed in the biological processes of wastewater treatment and consist mainly of humic substances, carbohydrates, and proteins. Disinfection by-products are known to be carcinogenic. The low molecular weight dissolved organic matter in the effluent plays a significant role in DBP formation. Endocrine-disrupting compounds, pesticides, industrial chemicals, residues of personal care products, pharmaceuticals, etc. are called chemicals of emerging concern (CECs) and form part of dissolved organic matter. They are present in water in the micrograms per liter (µg/l) and nanograms per liter (ng/l) range (Michael-Kordatou *et al*. 2015)**.** The United States Environmental Protection Agency (USEPA) defines EDC's as compounds that affect the natural processes of the body that relate to reproduction, homeostasis, development and behaviour (Sayles, 2002). Furthermore, Zhu *et al*. (2015) found adverse effects of EDC's on animals, leads to concerns that there may be high risks to human health.

2.3 Combining O_3 and BAC filters

The combination of ozonation and biological activated carbon filtration is the most promising combination between a chemical- and biological process, and it has received much attention given that the combined operation has overcome many of the economic and technological challenges (Wu *et al.*, 2018). The O_3/Biological-Activated-Carbon (O_3/BAC) process can produce a significantly high quality water compared to reverse osmosis (RO) with the added benefit of not producing brine (Vatankhah *et al*., 2019 and Song *et al*., 2015). Song *et al*. (2015) also remarked that the de-facto reuse had forced some water utilities around the world to revert to the O_3/BAC process to remove contaminants.

Putting a biological activated filter (BAF) after O_3 increases TOC removal due to the biodegradation of organic matter in the filters, mostly formed in the O_3 process (Zhu *et al.*, 2015 and Lage Filho 2010). Ross *et al.* (2019) and Singer, (1990) found that if the O_3 process is added prior to the BAC filter, it can remove an additional 15–20% of organic carbon (TOC). In addition, Urfer *et al.* (2019) indicated that ozonation and biofiltration must be considered a combined process given that without biological filtration, biological regrowth will occur in downstream systems. Other benefits of combining O_3 and BAC are:

i) The extension of the granular activated carbon (GAC) life (Sundaram & Pagilla, 2019); and

ii) The reduction of dissolved organic carbon (DOC) and oxidation by-products (Gerrity *et al.*, 2015) (Chiang & Pan, 2016).

iii) Reduction of toxicity caused by ozonation by-products with biological filtration (Li *et al.*, 2015)

2.4 Ozone gas for water treatment

O_3 gas is produced in an O_3 generator when oxygen is passed by an electrical current, where O_2 is converted to O_3 (Arn *et al.*, 2011). O_3 formation requires high amounts of energy and oxygen, thus the process is costly. The O_3 generator produces a gas stream that is a combination of oxygen and O_3. O_3 ranges between 1–14% (by weight) of the combined gas stream (Arn *et al.*, 2011). The percentage is a result of the amount of energy applied to the oxygen stream and cooling water temperature in the generator.

O_3 gas is a powerful oxidant and disinfectant. Hence, its primary goal is to disinfect water (Emelko *et al.*, 2019). The most critical impact of O_3 oxidation in water is the inactivation of pathogens, i.e. contaminants are attacked by O_3 directly by oxidation and indirectly by hydroxyl radicals formed during O_3 decomposition (Lage Filho, 2010).

2.4.1 Product of O_3 residual concentration and contact time (CT-value)

O_3 is the second strongest oxidant after the hydroxyl radical - $OH\cdot$ in water treatment (Letterman, 1999). However, without a measurable CT-value very little inactivation of bacteria and viruses are achieved and no inactivation of spore-forming bacteria can be attained (Snyder *et al.*, 2014). Disinfection by chemicals does not remove pathogens but inactivates them. The level of inactivation is quantified by the term *log inactivation* that is a measure of the number of pathogens that are inactivated during disinfection (US EPA - Office of Water, 1999b). O_3 is becoming more popular for disinfection purposes given its effectiveness in eliminating nearly all microorganisms, including Giardia and Cryptosporidium (Snyder *et al.*, 2014).

As O_3 is injected into water, there is commonly a high initial uptake (initial demand) of O_3 as it reacts with scavengers and readily reactive constituents in the water. Gerrity *et al.* (2014) referred to this initial demand as the instantaneous O_3 demand (IOD). As O_3 further auto decomposes into the water and the initial demand is met, a dissolved O_3 concentration starts to form. The point where an increase in O_3 dosage results in an increase in residual O_3 is defined as the O_3 demand. The residual O_3 present in the water becomes a highly effective disinfectant over time. For disinfection, the residual O_3 is the most critical parameter given that the direct pathway of O_3 oxidation is the primary pathway of the inactivation of pathogens (Lage Filho, 2010). In contrast, hydroxyl radicals play a small role in the inactivation of resistant pathogens (Von Gunten, 2002).

The CT framework (residual disinfectant concentration times exposure time) is the foundation of oxidation-based disinfection processes in the United States (US) (Snyder *et al.*, 2014). The product of residual O_3 concentration (C) and contact time (T) concept, called CT-value, developed by the US EPA requires, for a specific log removal, a stipulated CT-value to be maintained in the O_3 system. This means that some residual dissolved O_3 (C) must be kept for a specific time (T), and the product of the two must comply with the requirements of the US EPA log inactivation tables. The CT-values for Giardia, Cryptosporidium and viruses are also shown in Table 2-6 to Table 2-8 below. Temperature affects the ozone decay rate, which indirectly affect the residual O_3 concentration in the CT-value. The effects of temperature are further discussed in Section 2.4.3.

Table 2-6 – Ozone CT table for Giardia (Van Der Walt, Krüger & Van Der Walt, 2009).

Log Inactivation	**Giardia CT at Temperature (°C)**		
	1°C	**13°C**	**22°C**
0.5	0.48	0.19	0.1
1	0.97	0.38	0.21
1.5	1.5	0.58	0.31
2	1.9	0.76	0.42
2.5	2.4	0.95	0.52
3	2.9	1.14	0.62

Table 2-7 – Ozone CT table for Cryptosporidium (from Equation 2.1).

Log inactivation	**Cryptosporidium CT at 13°C**
1-log	7.5
2-log	15.0
3-log	22.5

Table 2-8 – Ozone CT table for viruses (US EPA - Office of Water, 1999b).

Log Inactivation	Temperature (°C)														
	10	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**
2	0.5	0.46	0.42	0.38	0.34	0.3	0.29	0.28	0.27	0.26	0.25	0.23	0.21	0.19	0.17
3	0.8	0.74	0.68	0.62	0.56	0.5	0.48	0.46	0.44	0.42	0.40	0.37	0.34	0.31	0.28
4	1	0.92	0.84	0.76	0.68	0.6	0.58	0.56	0.54	0.52	0.5	0.46	0.42	0.38	0.34

The Long Term 2 Enhanced Surface Water Treatment Rule (US EPA, 2010) developed equations to determine the log credit for Cryptosporidium, Giardia and viruses. Equation 2.1 gives the Cryptosporidium log-removal achieved for a specific CT-value and at a particular temperature (US EPA, 2010).

$$Cryptosporidium\ Log\ Credit = 0.0397 \times (1.09757)^{Temp} \times CT \qquad \textbf{Equation 2.1}$$

Equation 2.2 gives the Giardia log-removal achieved for a specific CT-value and at a particular temperature (US EPA, 2010).

$$Giardia\ Log\ Credit = 1.038 \times (1.0741)^{Temp} \times CT \qquad \textbf{Equation 2.2}$$

Equation 2.3 gives the Virus log-removal achieved for a specific CT-value and at a particular temperature (US EPA, 2010).

$$Virus\ Log\ Credit = 2.1744 \times (1.0726)^{Temp} \times CT \qquad \textbf{Equation 2.3}$$

The US EPA states that the CT-value is (US EPA - Office of Water, 1999a: 2-25):

"*[o]ne of the most important factors for determining or predicting the germicidal efficiency of any disinfectant is the CT factor, a version of the Chick-Watson law. The CT factor is defined as the product of the residual disinfectant concentration, C, in mg/l, and the contact time, T, in minutes, that residual disinfectant is in contact with the water.*"

Schulz *et al.* (2019) supplement this by noting that the CT-value is to be determined by the O_3 residual values of the outlet of the O_3 contact tank. The T-value in the CT concept is further

defined to be "*the time it takes for 10% of particular concentration to pass through a contact basin*" otherwise called T_{10} (US EPA, 2010:11-7). The T_{10} -value is described by Schulz, Davis, Bonacquisti, and Navratil (2005) as the hydraulic retention time multiplied by the baffling factor, which accounts for flow short-circuiting. According to Van Der Walt, Krüger and Van Der Walt (2009), the C in the CT-value refers to the minimum required disinfectant concentration. Guidelines for selecting baffling factors are provided below in Table 2-9.

Table 2-9 – Guidelines for selecting baffling factors (US EPA, 1991).

Baffling Condition	T_{10}/T	Baffling Description
Unbaffled (mixed flow)	0.1	None, agitated basin, very low length to width ratio, high inlet and outlet flow velocities
Poor	0.3	Single or multiple unbaffled inlets and outlets, no intra-basin baffles
Average	0.5	Baffled inlet or outlet with some intra-basin baffles
Superior	0.7	Perforated inlet baffle, serpentine or perforated intra-basin baffles, outlet weir or perforated launders
Perfect (plug flow)	1	Very high length to width ratio (pipeline flow), perforated inlet, outlet, and intra-basin baffles

With each increasing log-removal, the O_3 dose has to increase to achieve inactivation but it can also be influenced by the O_3 disinfection contact time (T) selected. As the exposure time (T) increases, the residual O_3 concentration (C) decreases to achieve the same CT-value. However, the residual O_3 concentration decay across the O_3 contact tank has to be accounted for.

A study by Kaiser et al. (2013) showed that maintaining a constant O_3 residual at the end of the O_3 contact tank resulted in varying pathogen disinfection results. They noted, however, that the variation is covered in the CT concept. More importantly, the current study found that it takes a significant amount of time to notice a change in O_3 concentration due to a change in O_3 dose or change in water quality, if measured at the end of the contact tank. This can cause inefficiently disinfected lumps of water to go through. Their proposal to measure residual O_3 after the initial O_3 demand phase reduced the time required to adapt to the changes in flows and prevented lumps of inefficiently disinfected water to escape.

According to the long term 2 enhanced surface water treatment rule (LT2ESWTR) from the US EPA (2010), O_3 contact tanks can be divided into theoretical or physical sections or chambers for the determination of the CT-value. Furthermore, the chambers (partitions) are distinguished by two types, i.e. a reactive chamber, where O_3 can react with the water and a dissolution chamber where O_3 is dosed into the water. Dissolution chambers are further divided into a co-current O_3 contact chamber, where the water and the gas bubbles flow in the same direction (both upwards),

and into a counter-current contact chamber, where the O_3 bubbles flow upwards and the water downwards. Figure 2.1 below is a graphic demonstration of the different types of O_3 contact chambers.

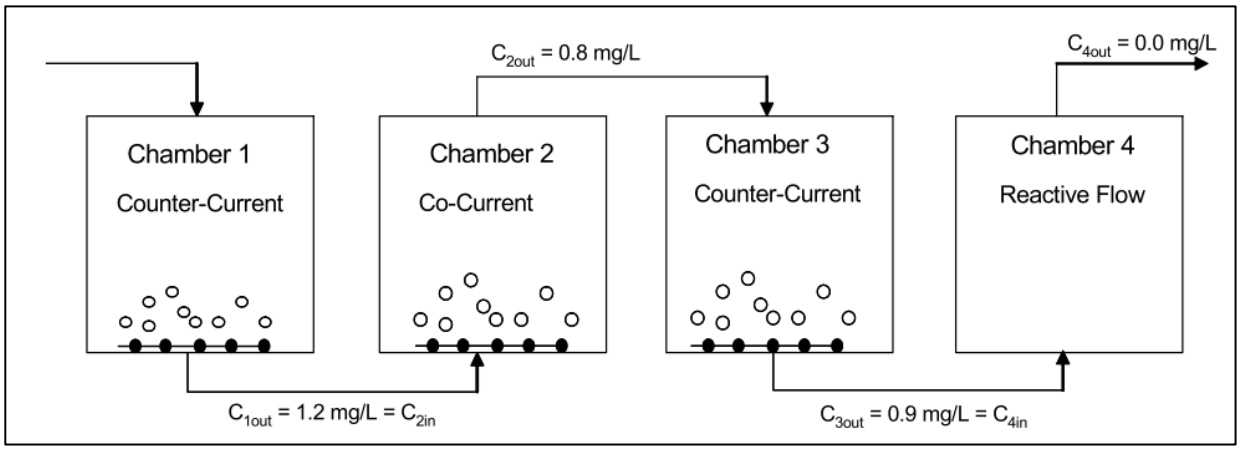


Figure 2.1 – O_3 contact tanks chamber types (US EPA, 2010)**.**

The LT2ESWTR describes four ways to determine the CT-value (US EPA, 2010). The four methods and their requirements are shown below in Table 2-10.

Table 2-10 – CT-value calculation methods requirements (compiled from US EPA, 2010).

Method	Comments
T_{10} method	• No inactivation credit is given for the first dissolution chamber. • CT-value can be calculated for the entire contact tank or for individual segments of the contact tank summed together. • A decay test is recommended to determine T_{10}; otherwise, a baffling factor must be assumed.
CSTR method	• Should be applied to each individual type of segment/chamber. • Ideal to use when no tracer tests are available or when the contact tank has significant back-mixing, i.e. T_{10}/HDT < 5.
Extended T_{10} method	• Requires that the residual O_3 concentration be measured at no less than 3 points in the contact tank. • Can only be applied to reactive chambers and not O_3 dissolution chambers.

Method	Comments
	• A decay test is recommended to determine T_{10}; otherwise, a baffling factor must be assumed.
Extended CSTR method	• Requires that the residual O_3 concentration be measured at no less than 3 points in the contact tank. • Can only be applied to reactive chambers and not O_3 dissolution chambers.

The CT-value calculation method selected depends on whether tracer test (hydraulic flow characterisation of the contact tank according to the US EPA, (2010) LT2ESWTR) results are available, the configuration of the contact tank and the amount of process monitoring and analysis that a system plans to undertake. The use of the CSTR or extended CSTR methods is recommended when no tracer studies are available. A combination of the CT-value calculation methods can be used. Generally, the USEPA deems the extended methods more complex to use but they can be programmed into a spreadsheet. According to the LT2ESWTR, for the T_{10}-method, the dissolved O_3 concentration, i.e. C, in the CT-value can be measured directly at the outlet of each contact chamber/segment or determined indirectly by predicting the C value at the outlet of each contact chamber/segment using the dissolved O_3 concentration at the outlet of the contact tank. The T_{10} method, as a general rule, underestimates the CT-value obtained. LT2ESWTR found T_{10}/HDT or baffling factor to be 0.65, even in well-baffled O_3 contact tanks.

Table 2-11 below describes the methods used in different segments when no tracer study is available, i.e. the CSTR method. Note that no inactivation credit is given for the first dissolution chamber. Measurements of O_3 residual concentration are required at the end of each dissolution chamber. For more than three consecutive reactive chambers, the extended CSTR method is recommended.

Table 2-11 – Recommended methods to calculate the log inactivation of pathogens without tracer data (US EPA, 2010).

	Section Description	Terminology	Method for Calculating Log-Inactivation	Recommended Restrictions
Without Tracer Data	**Chambers where ozone is added**			
	First chamber	First Dissolution Chamber	No Cryptosporidium log-inactivation credit is recommended	The SWTR criteria for 1st chamber credit should still be used if calculating inactivation of Giardia and virus
	Other chambers	Co-Current or Counter-Current Dissolution Chambers	CSTR method in each chamber with a measured effluent ozone residual concentration	No credit should be given to a dissolution chamber unless a detectable ozone residual has been measured upstream of this chamber

	Section Description	Terminology	Method for Calculating Log-Inactivation	Recommended Restrictions
	Reactive Chambers			
	≥ 3 consecutive chambers	Extended Reactive Zone	Extended CSTR method in each chamber	Detectable ozone residual should be present in at least 3 chambers in this zone, measured via in-situ sample ports. Otherwise, the CSTR method should be applied individually to each chamber having a measured ozone residual
	< 3 consecutive chambers	Reactive Chamber(s)	CSTR method in each chamber	The SWTR criteria for 1st chamber credit should still be used if calculating inactivation of Giardia and virus

In most cases, unless a pilot plant is built, the tracer study data on a specific tank will not be available. Therefore, using the CSTR method for determination of the CT-value is useful given that it does not require the contact tank baffling factor and reduces the effective contact time used in the CT concept. The CSTR method for determining CT is shown below in Equation 2.4 (US EPA, 2010).

$$-Log\left(I/I_0\right) = \log(1 + 2.303 \times k_{10} \times C \times HDT) \qquad \textbf{Equation 2.4}$$

Where:

$-\log(I/I_0)$ = the log inactivation

k_{10} = log base 10 inactivation coefficient (L/mg-min)

C = concentration from Table 2-12

HDT = Hydraulic detention time (minutes)

The methods used to determine the residual O_3 concentration, C, for Equation 2.4 above are shown below in Table 2-12.

Table 2-12 – Guidelines to calculate the O3 residual concentration using the T10 or CSTR method (US EPA, 2010).

Method	Turbine	Dissolution Chamber Co-Current Flow	Dissolution Chamber Counter-Current Flow	Reactive Chamber
T_{10}	C_{out}	C_{out} or $(C_{in}+C_{out})/2$	$C_{out}/2$	C_{out}
CSTR	C_{out}	C_{out} or $(C_{in}+C_{out})/2$	$C_{out}/2$	C_{out}

The formulas to determine the log base 10 inactivation coefficient (k_{10}) for Cryptosporidium, Giardia, and viruses (Rakness *et al.*, 2005) in Equation 2.4 is given by Equation 2.5 below.

$$k_{10,C} = 0.0397 \times (1.09757)^{Temp} \quad \textbf{Equation 2.5}$$

$$k_{10,G} = 1.038 \times (1.07401)^{Temp}$$

$$k_{10,v} = 2.174 \times (1.07262)^{Temp}$$

When the long term 2 enhanced surface water treatment rule was first proposed in 2003, Schulz *et al*. (2005) proposed the use of the geometric mean method for CT-value validation, which is similar to the CSTR method, to reduce the higher O_3 dose required for the CT-values of the proposed Cryptosporidium. The geometric mean method calculates the average residual O_3 concentration under the decay curve (Schulz *et al*., 2005) and is described by Equation 2.6. The study suggested that the calculated average residual O_3 should be used in the CT concept to integrate and give credit to the whole residual O_3 under the decay curve.

$$C_{avg} = \frac{C_0(1 - e^{-K_d t})}{K_d t} \quad \textbf{Equation 2.6}$$

Where:

$C_0 = initial\ ozone\ residual\ (^{mg}/_{l})$

$K_d = decay\ rate\ (min^{-1})$

$t = time\ (min)$

$C_{avg} = \frac{CT}{T_{10}})$

Gerrity *et al.* (2014) found that for tertiary filtered effluent, the CT-value targets were achieved after 5 minutes and for the standard secondary effluent, they were only achieved after a full 15 minutes. The wastewater characteristics of the study mentioned above are shown below in Table 2-13.

Table 2-13 – Secondary and tertiary wastewater characteristics as found in the Gerrity *et al.* (2014).

Parameter	Secondary effluent	Tertiary Effluent
Free Chlorine (mg/l)	<0.02	<0.02
Total Chlorine (mg/l)	<0.02	2.3

Parameter	Secondary effluent	Tertiary Effluent
pH	7	7.3
Alkalinity (mg/l as $CaCO_3$)	143	166
TOC (mg/l)	8.65	8.2
$UV_{254\ absorbance}$ (cm-1)	0.142	0.13
SUVA (L/mg-m)	1.64	1.59
Total Nitrogen (mg-N/l)	17	10
Total Kjeldahl N (mg-N/l)	2.1	2.7
Total organic N (mg-N/l)	1.29	1.7
NH_3 (mg-N/l)	0.81	1
NO_3 (mg-N/l)	15	6.8
NO_2 (mg-N/l)	<0.25	<0.25
Bromide (µg/l)	130	25
Bromate (µg/l)	<5	<5

Equation 2.7 below gives the CT-value as a function of time, TOC, IOD and O_3 dose as defined by Gerrity *et al.* (2014). The constant k describes the dissolved residual O_3 decay rate in Equation 2.7. Typical values of these constants, k and IOD, for the wastewater characteristics shown in Table 2-13 are shown in Table 2-14.

$$O_3 - CT\ (mg - min/l) = \frac{\frac{O_3}{TOC} \times TOC - IOD}{k} \times (1 - e^{-kt}) \qquad \textbf{Equation 2.7}$$

Table 2-14 – Typical values of variables in Equation 2.7 and Equation 2.11 (Gerrity *et al.*, 2014).

	Secondary Effluent			Tertiary Effluent		
O_3/TOC ratio	**k (min^{-1})**	**IOD (mg/l)**	**R^2**	**k (min^{-1})**	**IOD (mg/l)**	**R^2**
0.3	n/a*	2.2	n/a*	n/a*	1.9	n/a*
0.5	n/a*	4.2	n/a*	0.5131	3	0.99
1.1	0.2351	5.6	1	0.1278	4.9	0.99
1.7	0.0769	8.2	0.97	0.0673	6.4	0.97
*No measurable dissolved ozone residual						

Table 2-15 shows the CT targets of the O_3 process in the study by Gerrity *et al.* (2014). The table also shows, for four pathogens, the health targets of the system, the log credit shortfall

after ozone treatment, the minimum O_3 CT-value required, and the minimum O_3/TOC dosage ratio needed.

Table 2-15 – Ozone CT-value targets of the study by Gerrity *et al*. (2014).

Indicator/Surrogate/pathogen	Health Criteria (logs)	Ozone target (logs)	Log credit shortfall after ozone (logs)	Minimum O_3 CT-value (mg-min/l)	Minimum O_3/TOC ratio
Total Coliform	9	3	6	1	0.8
Virus	12	6	6	0.2 – 0.9	0.8 - 1
Giardia	10	3	7	0.95	N/a
Cryptosporidium	10	2	8	8.9 - 12	N/a

2.4.2 Link between O_3 disinfection and organic micropollutant oxidation

There is a correlation between the O_3 dose required for disinfection and the O_3 dose required for organic micropollutant oxidation, and it is influenced by the incoming TOC concentration. Gamage *et al.* (2013) proposed a regression formula, Equation 2.8 below, that relates ozone CT to the O_3/TOC ratio with bench-scale experiments on filtered effluent (through a 10µm and then 0.5µm cartridge filters) from 5 wastewater facilities in the United States (US). This equation was determined by integrating the residual O_3 over its decay time.

$$Ozone\ CT\ (mg-min/l) = 10 \times O_3/TOC - 3.3\ ;R^2 = 0.86 \qquad \textbf{Equation 2.8}$$

Snyder et al. (2014) also proposed a general regression equation, Equation 2.9 below for O_3 exposure (CT) in relation to the O_3/TOC ratio. This equation was based on literature they reviewed, and the O_3-exposure determined by integrating the residual O_3 over its decay time.

$$Ozone\ exposure\ (mg-min/l) = 12.5 \times (O_3/TOC\ or\ O_3/DOC) - 4.47 \qquad \textbf{Equation 2.9}$$

From the results of the bench-scale experiments of Snyder et al. (2014) (which used secondary and tertiary effluent from 10 wastewater treatment sites, five in the US and five in Europe and Australia), a regression formula, Equation 2.10 below, was extracted to predict the amount of exposure that can be obtained at various O_3 dosage ratios. The equation was obtained by integrating the residual O_3 concentration over its decay time.

$$Ozone\ CT\ (mg-min/l) = 6.403 \times (O_3/TOC)^{2.506}\ ;R^2 = 0.89 \qquad \textbf{Equation 2.10}$$

These simplified general equations for the prediction of O_3 exposure do not account for water quality parameters like pH, alkalinity, and concentration of organic matter (TOC or DOC). Only at O_3 dosage ratios of > 0.35 O_3/TOC or O_3/DOC can O_3 exposure (CT) be quantified with these equations due to the instantaneous O_3 demand using all the O_3 (i.e. without residual O3) forming below this value. Comparable levels of oxidation were observed at the same O_3/TOC dosage ratio using the final effluent from the 10 wastewater treatment plants mentioned above, despite them having significant differences in water quality and O_3 exposure (CT).

2.4.3 Impact of influent water quality on the O_3 process

Elovitz, Von Gunten, and Kaiser (2000) investigated the influence of pH, alkalinity, temperature, type and concentration of organic matter on the decay of O_3 and O_3 exposure. For a constant dose of O_3, varying O_3 exposure was found in different waters. Previously they found that when O_3 exposure and concentration are known, one can predict the hydroxyl radical concentration and exposure. This is useful to predict the O_3 micropollutant oxidation. Their experiments were conducted in a laboratory using distilled ozonated water on water samples from various treatment plants across Switzerland. Their main findings are given below:

i) In the second phase of O_3 depletion, after a first rapid depletion phase, O_3 followed a first-order rate decomposition.

ii) As temperature increased, the O_3 decomposition rate also increased. Temperature increases between 5–35°C decreased the O_3 exposure by a factor of 10 without changing the hydroxyl radical exposure.

iii) As pH increased, the O_3 decomposition rate also increased. This was expected as the hydroxide ion initiates O_3 depletion. The observations from the pH experiments were that O_3 decomposition increased with a factor of 3 for every unit change in pH. Furthermore, the study found that as pH increased, the O_3 exposure decreased, but the hydroxyl radical exposure remained unchanged. Varying the pH between 6–9 reduced the O_3-exposure by a factor of 40 while the hydroxyl radical exposure remained constant.

iv) O_3 decomposition is inhibited by alkalinity in the water given that bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) react with hydroxyl radicals in water, which reduces the formation of superoxide ($O_2^{-}\cdot$), which in turn react with O_3 and increase its decay. On the other hand, alkalinity increases $OH\cdot$ decay and exposure. The results showed a double decrease in O_3 decomposition as the alkalinity increased from 0 to 1.5mM. Alkalinity increases from 0 to 2.5mM increased the O_3 exposure by a factor of 4 and the hydroxyl radical decreased.

v) A wide variety of O_3 and hydroxyl radical exposure values existed, which indicated that the nature of the organic matter played a significant role in exposure rates.

vi) O_3 decomposition was more rapid in the source waters with higher DOC concentrations and lower alkalinity than in waters with high alkalinity and low DOC concentrations.

vii) Residual O_3 is primarily influenced by the O_3 decay rate, which is affected by the pH, temperature, and alkalinity and is subsequently influenced by the hydraulic retention time and the O_3 dose.

Inorganic compounds like nitrates, iron, manganese, and hydrogen sulphide are usually oxidized quickly by O_3, except for ammonia, which is slowly oxidised by both O_3 and hydroxyl radicals (von Gunten, 2003). Fortunately, ammonia does not influence the O_3 disinfection efficiency.

The organic water quality parameters influencing the O_3 demand include turbidity, colour and TOC. Tests by Lage Filho (2010) confirmed this when a much higher CT was achieved with water that had a lower TOC concentration, but with the same or lower O_3 doses. The other water quality parameters that influence the process are pH, alkalinity, temperature, and some inorganic compounds as highlighted above. However, the nature of the water treated by an O_3 process, did not affect the CT-value increasing linearly with an increase in O_3 dose (Lage Filho, 2010).

2.4.4 O_3 Dose concentration

O_3 dose concentration is defined as the O_3 weight as a percentage of the total gas dosed. Schulz *et al.* (2019) noted that fine bubble diffusion works best at low O_3 concentrations of 1 to 4%. Lage Filho (2010) found that one of the most significant factors influencing the CT-value is the O_3 dose concentration. His study shows that CT-values increased with an increase in O_3 dose concentration.

2.4.5 O_3 Dose

O_3 dose can be defined as the ratio of O_3 concentration dosed per concentration of TOC or DOC present. Singer, (1990) identified the O_3/TOC ratio as the focal point for maximizing O_3 treatment. Also, Reungoat *et al.* (2012) concluded that DOC removal is increased when the O_3 dose is increased.

Fast reacting compounds with O_3 require about 0.47mg O_3/ mg DOC (Hollender *et al*., 2009 in Hu *et al.,* 2012). Studies by Zhu *et al.* (2015) showed that contaminants with lower O_3 rate constants require higher O_3 doses to be removed efficiently. Optimum biodegradable dissolved organic carbon (BDOC) formation occurs better over a short contact time and a high O_3 dose as opposed to a long contact time and a low O_3 dose (Volk et al., 1993 in Khan *et al.,* 2019).

Table 2-16 shows the effects of various O_3 dosage ratios on ultraviolet-absorbance (UV_a) and ultraviolet-transmittance (UVT). At a O_3 dose of 1.5mgO_3/mgTOC, the UVT improved from

77% to 91% for the tertiary treated effluent and from 75% to 91% for the secondary effluent (secondary effluent treated by granular media filtration and chlorine disinfection).

Table 2-16 – O_3 dose ratio with UVT improvement for secondary and tertiary effluents (Gerrity *et al.*, 2014).

Matrix	O_3/TOC ratio	Actual UVa (cm^{-1})	Actual ΔUV_a	Predicted ΔUV_a	Actual UVT
Secondary Effluent	0	0.126	-	-	75%
	0.26	0.092	23%	23%	81%
	0.5	0.086	32%	34%	82%
	1	0.048	62%	51%	90%
	1.5	0.043	66%	65%	91%
Chlorinated Tertiary Effluent	0	0.113	-	-	77%
	0.25	0.07	38%	22%	85%
	0.5	0.056	50%	34%	88%
	1	0.039	65%	51%	91%
	1.5	Not available	Not available	65%	Not available

Results from Gerrity *et al.* (2014) in Table 2-17 gave O_3 dose requirements for specific target compounds. Musk Ketone required significantly high O_3 doses of 9.2mg O_3/mgTOC for 0.3log reduction and TCEP required an O_3 dose ratio of 3.1mgO_3/mgTOC. Except for 1,4 dioxane at 1.1mg O_3/mgTOC, the rest of the compounds in Table 2-17 shows lower O_3 dose ratio requirements. Moreover, Gerrity *et al.* (2014) observed that O_3 provided particularly good trace organic compound oxidation at the O_3 dose to TOC ratio of 1.5.

Table 2-17 – O_3 dose to TOC ratios for specific target compounds (Gerrity *et al.*, 2014).

Target Compound	Treatment Goal	Required O_3/TOC
Triclosan	0.5 Log	>0.26
Sulfamethoxazole	0.5 Log	>0.26
Carbamazepine	0.5 Log	>0.26
Trimethoprim	0.5 Log	>0.26
Naproxen	0.5 Log	>1
Gemfibrozil	0.5 Log	>0.26
Phenytoin	0.5 Log	>1
Meprobamate	0.5 Log	>1
Musk Ketone	0.5 Log	>9.2

Target Compound	Treatment Goal	Required O_3/TOC
1,4-Dioxane	0.5 Log	>1.1
TCEP	0.3 Log	>3.1

2.4.6 O_3 Decay rate

A pseudo-first-order expression can represent the decomposition process of O_3 in most waters after the initial uptake demand. This first-order expression is a combination of the n^{th} order kinetic reactions which, when combined, becomes a first-order reaction (Hermanowicz, Bellamy & Fung, 1999). Research by Neumann *et al.* (2007) show that O_3 decay is time dependant and that it slows down as time progresses.

The effect of O_3 decay constants and source water quality on the CT-value was studied by Lage Filho, (2010). Tests in that study were done on four contactor columns with 20.6 minutes of empty bed contact time (EBCT). O_3 decay rates were determined for various contact times, feed gas concentrations and dosing points. The author found that the O_3 demand increased proportionately with the TOC concentration. Other water quality parameters influencing O_3 demand are turbidity and colour. Alkalinity, much less so than TOC, acts as an inhibitor off O_3 to react with water and results in slower O_3 decay rates. O_3 dosed in water with high TOC concentration resulted in high O_3 decay rates. Furthermore, the author found that O_3 decay is slower at higher O_3 doses as the first order O_3 decay constant decreased with an increase in O_3 dose. This effect of various initial dosing concentrations on O_3 decay is shown in Figure 2.2. The water source in Figure 2.2a had a low alkalinity (±6.5 mg $CaCO_3$/l) and TOC (±1.7 mg/l) concentration, while the water source in Figure 2.2b had high alkalinity (±110 mg $CaCO_3$/l) and TOC (±4.9mg/l) concentration. Increasing the O_3 dose in water having low TOC concentration and alkalinity resulted in decreasing O_3 decay rates. For water with high TOC concentration and alkalinity, the O_3 decay rate increased given the increased demand TOC had on O_3.

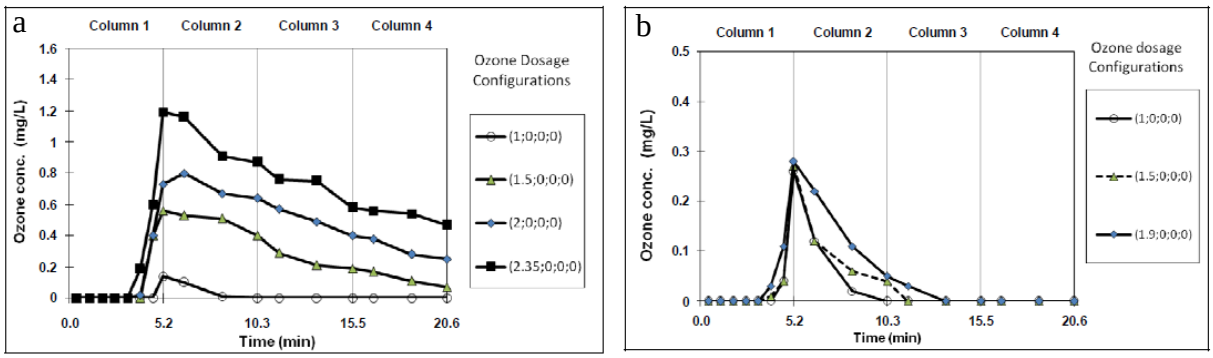


Figure 2.2 – Effect of O_3 dose-ratios at the start of the contact-column for two water sources (Lage Filho, 2010)**.**

O_3 decay in secondary effluent or water with high dissolved organic matter is categorised by two energetically different stages (Snyder *et al.*, 2014). The first stage is a short, typically 30s, O_3 demand phase when O_3 is quickly consumed, caused by an instantaneous O_3 demand (IOD). The IOD that is mainly influenced by organic matter and it can be predicted by a second-order equation (Wert *et al.*, 2007). After this initial period, the decay rate resembles a first-order equation (Buffle *et al.*, 2006). Gerrity *et al.* (2014) also found that during the second stage, the rate constant of the dissolved residual O_3 decay decreased with a higher O_3 dose.

To illustrate this, a model was developed by Gerrity *et al.* (2014) to predict residual O_3 concentrations in secondary and tertiary wastewater effluent. The model is given in Equation 2.11 as a function of O_3 dose concentration, TOC concentration, IOD, time and decay constant (k). Table 2-14 shows typical values for these constants.

$$Ozone\ residual\ (mg/l) = (O_3/TOC \times TOC - IOD) \times e^{-kt} \qquad \textbf{Equation 2.11}$$

2.4.7 O_3 Injection methods

O_3 injection can be done by various methods Schulz *et al.* (2019)**,** i.e.: (i) direct side stream venturi injection, (ii) in-line static mixing tanks, (iii) fine bubble diffusion, and (iv) mechanical mixing. Most often O_3 dosing is done by fine bubble diffusers to transfer gas to water in a counter-current contact tank, which provides time for O_3 to react with the compounds in the water. Smaller bubble size from diffusers results in a larger area to gas-volume ratio, which results in a higher transfer rate (Lage Filho, 2010; Zhou and Smith, 2000). This may be due to the enormous impact gas flow rate has on the specific surface area of gas bubbles. Table 2-18 shows a comparison of the two most commonly used methods.

Table 2-18 – Comparison of the two most commonly used O_3 injection methods (summarised from Schulz *et al.* 2019 and Rajagopaul, Mbongwa, & Nadan, 2008).

Considerations:	Fine Bubble Diffusion	Side Stream Injectors
Clogging	Can clog and must be replaced every 2 – 5 years	Less susceptible to plugging
Contact tank	Deep contact tank required	Shallower contact tank required
By-products	More susceptible to the formation of bromate at flows lower than design flows (Wert, Lew & Rakness, 2017)	Can also cause bromate to form from bromide. Bromate formation can be managed by keeping the O_3 contact time in the side stream less then 5seconds (Wert, Lew & Rakness, 2017).
Medium required	No side stream water is needed	Clean water is needed for side stream injection

Considerations:	Fine Bubble Diffusion	Side Stream Injectors
Optimum O_3 concentration and flow	Works best at high gas flow rates and low O_3 concentrations of between 1 -4%. Requires adequate gas-liquid mixing.	Most efficient at low gas flow rates and high O_3 concentrations (6-12%)
Costs	No pumping costs	Higher head losses and pumping costs Lower maintenance cost compared to diffusers
Gas-liquid separation	Only gas piping required	Horizontal piping causes gas-liquid separation
O_3 transfer	85-95% O_3 transfer	Up to 95% O_3 transfer
Uses	Colour removal, primary disinfection, odour and taste removal	Odour and taste removal, colour removal and manganese and iron oxidation
Process control		Limited turndown capability

2.4.8 O_3 Chemistry

During O_3 treatment Lage Filho, (2010) recognised that the following processes occur as O_3 gas mixes with water:

i) O_3 mass transfer process;

ii) O_3 auto decomposition; and

iii) Competitive reaction of dissolved O_3 with constituents in water.

The author also noted that O_3 treatment efficiency is affected by:

i) Water quality;

ii) O_3 contactor configuration; and

iii) Operating conditions

O_3 oxidation works through two processes to oxidise organic components like aromatic functional groups, aromatic rings and double bond compounds. Firstly, by O_3 oxidation directly, called ozonolysis, and secondly by indirect oxidation by hydroxyl radical - OH· (Michael-Kordatou *et al*., 2015). This indirect process is described by Singer (2019) as fast, nonselective and having constants of the second order. He also found that basic pH values (>7) favour the indirect process while an acidic pH with hydroxyl radical scavengers like carbonate and bicarbonate favour the direct pathway.

O_3 does not remove DOC but reduces $UV_{a254,}$ which represents aromaticity. The aromatic character of high molecular weight compounds like fulvic, protein-like and humic substances, possesses more reaction sites that can be oxidised (Michael-Kordatou *et al*., 2015).

Contaminants with lower O_3 rate constants require higher O_3 doses so they can be removed efficiently. Table 2-19 show some direct and indirect O_3 kinetic rates of some micropollutants (Zhu *et al*., 2015)**.**

Table 2-19 – Direct and indirect rate constants of some chemicals (Zhu *et al*., 2015).

Micropollutant	**k_{O3} (mol/l/s)** **Molecular ozone rate constant**	**$k_{OH\cdot}$ (mol/l/s)** **Hydroxyl radical rate constant**
Carbamazepine	3×10^5	8.8×10^9
Diclofenac	13×10^6	7.5×10^9
Ibuprofen	9.6	7.4×10^9
Benzoltriazole	$1.86\text{-}2.7 \times 10^2$	$7.1\text{-}8.1 \times 10^9$
Atenolol	$1.2\text{-}2.1 \times 10^3$	$7.5\text{-}8.5 \times 10^9$
Sulfamethoxazole	4.7×10^4	5.5×10^9
Metoprolol	2×10^3	7.3×10^9

2.4.9 O_3 Contact Tanks

An O_3 contact tank provides time for O_3 to react with the compounds in the water. Deeper contactors result in higher transfer efficiency (Lage Filho, 2010).

O_3 contact tanks can be configured in many ways depending on the application and injection method. The two most significant parameters that can be adapted in a contact tank are the amount and positions of injection points as well as the contact time.

Earlier studies by Filho and Filho (1999), as reported in Lage Filho (2010), suggest that O_3 dose application can be optimised by dosing different O_3 amounts at various points along the contact tank. In addition, a study by Filho (2010) found that if the same total O_3 dose was dosed at different points along the contact tank, other O_3 decay profiles were generated. To maximize the CT-value, the study recommended a marginally higher O_3 dose than required for the initial demand such that the initial dose complements the second O_3 dose and so forth. By contrast for example, Schulz *et al*. (2019) determined the CT-value by the residual O_3 concentration at the contact tank outlet.

Furthermore, the study by Lage Filho (2010) ascertained that the CT-value was influenced far more by the contact time than the O_3 decay rate. Splitting the O_3 dose into various points did not impact the CT-value as much as the O_3 weight percentage and concentration dose did. However, as the O_3 dose increased, the benefit of dosing at two points in the O_3 contact tank became more apparent (Lage Filho, 2010). Figure 2.3 shows the advantage of splitting the O_3 dose for two water sources, each graph representing a water source. This is evident by looking at the differences between the dark bars and the light bars of the charts. At some split ratio the same CT-value can be achieved at a lower O_3 dose ratio.

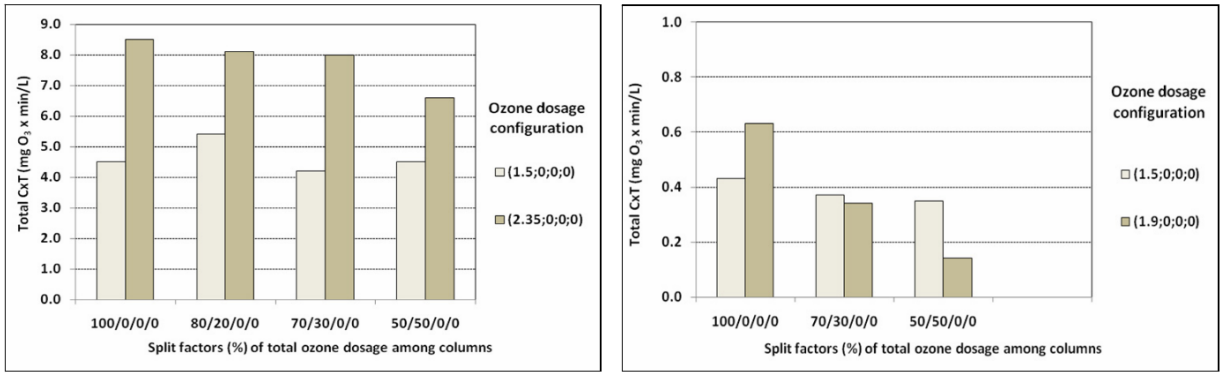


Figure 2.3 – Effect of splitting the O_3 dose on CT-value (Lage Filho, 2010).

A study by Snyder *et al*. (2014) presented bench-scale experiments of the O_3 process treating various tertiary treated final effluents. The results in Figure 2.4 show that the quality of the source water plays a significant role in the time it takes until O_3 depletion. This has a large effect on the optimal O_3 contact time, which, in turn, influences the size of the O_3 contact tank.

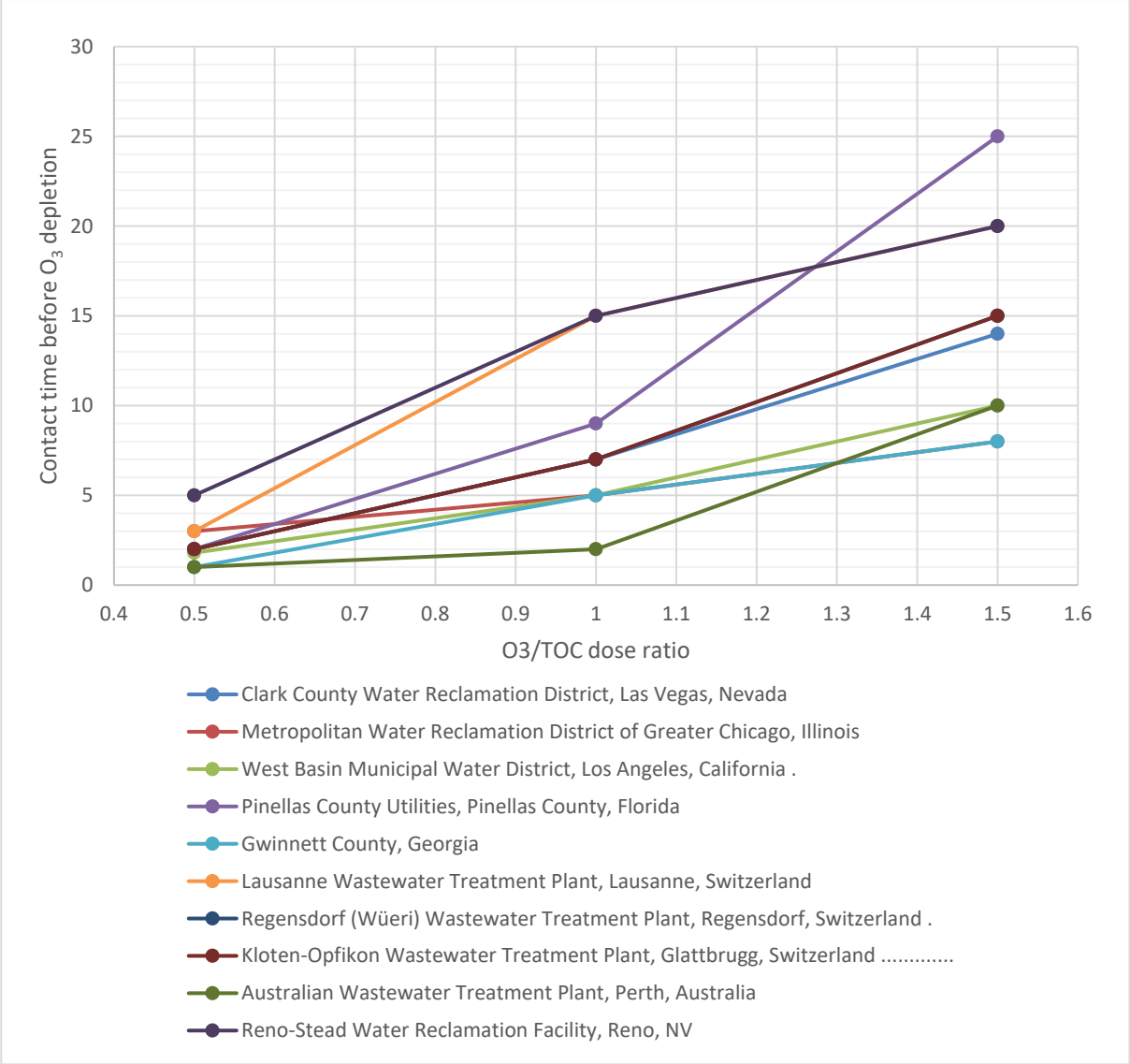


Figure 2.4 – O_3 contact time until residual O_3 depletion for tertiary treated final effluent from various wastewater treatment plants (adapted from Snyder *et al.* 2014).

2.4.10 LOX and PSA oxygen supply

Feed gas, i.e. O_2 to the O_3 generators can be supplied by among others, with either liquid oxygen (LOX) or pressure swing adsorption (PSA). The two methods are mainly differentiated by onsite generation (PSA) or off site generation (LOX) of O_2 (Rajagopaul, Mbongwa & Nadan, 2008). Table 2-20 shows a comparison of the two O_2 feed systems.

Table 2-20 – Comparison of LOX and PSA oxygen supply systems (adapted from Rajagopaul, Mbongwa and Nadan, 2008).

Parameter	LOX	PSA
Complexity	Simplest system.	Simple system. Alternative to LOX in small to medium ozone systems.
Capital Cost	Lowest capital cost.	High capital cost.
Operational Cost	Lowest specific energy (kWh/kg-O_3), but high LOX purchase cost which varies with the location of the site. Most cost competitive with high efficiency generators. High	High level of maintenance required. Energy and maintenance cost high.
Storage requirements	LOX storage required. Defrosting required. Tanks are insulated to reduce liquid boil off which roughly occurs at about 0.3-0.5% of the tank capacity per day.	No storage required.

The current study considers LOX in the cost functions given that it applies to the Cape Flats advanced treatment facility where LOX will be used to feed the ozone generators to produce O_3 gas.

2.4.11 Effect of O_3 dose on organic matter

The concern with natural organic matter (NOM) in drinking water is that it causes odour-, taste- and colour-related problems, in addition to microbial regrowth concerns and issues with processes in treatment plants (Korotta-Gamage & Sathasivan, 2017). Korotta-Gamage and Sathasivan, (2017) described NOM as made up of two types of matter i.e. a large hydrophobic type with high molecular weight called humic substances, and a small type with low molecular weight such as amino acids, sugars, carbohydrates and carboxylic acids. The authors further divided them into refractory (non-biodegradable) and biodegradable organic matters. The biodegradable matter is associated with the low molecular weight and hydrophilic nature. The non-biodegradable matter can form disinfection by-products, yet it does not cause biological regrowth.

Coagulation mainly removes the hydrophobic and higher molecular weight compounds (Sharp *et al.*, 2006) and consequently does not affect the assimilable biodegradable organic matter required for biological degradation (Volk *et al*., 2000).

O_3 is very efficient in the transformation of bulk organic matter into assimilable organic carbon and biodegradable organic carbon. The performance of this transformation process by O_3 can be observed by the change in UV_{a254} (Gerrity *et al.,* 2014). O_3 treatment reduces apparent weight fraction, colour, taste, and odour in UV_{a254} by causing a loss in aromaticity and depolymerization. Aromatic compounds and unsaturated carbon bonds in water are unbiodegradable and their concentration is linked to the concentration of UV_{a254}. Therefore, the reduction of UV_{a254} by O_3 treatment also results in the improved biodegradability of water. In this process, dissolved organic carbon is transformed from large molecules into small molecules that are more biodegradable by O_3 treatment (e.g. from humic substances to organic acids) (Ibn Abdul Hamid *et al.,* 2019; Mccreary *et al.,* 2019). This is substantiated by Urfer *et al.* (2019), who found that ozonation increases the fraction of biodegradable natural organic matter in water. According to Urfer *et al*. (1997), the eight effects of ozonation on natural organic matter are:

i) Hydroxyl formation;

ii) Carbonyl formation;

iii) Carboxyl group formation;

iv) Polarity increase;

v) Hydrophilicity Increase;

vi) Double bonds loss;

vii) Aromaticity loss; and

viii) Distribution, into lower molecular weight compounds, shift.

Zhu *et al.* (2015) states that the O_3 process selectively oxidises activated aromatic systems, double bonds, and non-protonated amines in water. Then, the formation of hydroxyl radicals during the auto decomposition of O_3 further reacts with inorganic and organic compounds. A pilot study by Zhu *et al.* (2015) found that the UVT improved from an average 53.9% in the influent water to 77.9% after O_3/BAC filtration.

While O_3 alone does not have an impact on TOC or DOC removal (Gerrity *et al*., 2014), Hübner et al. (2012) showed in a pilot plant experiment that O_3 improved DOC removal from 22% to 34% when the effluent is treated in a slow sand filter.

Organic micropollutants contribute to the toxicity of water and are typically not removed by wastewater treatment works and conventional water treatment processes. Therefore, advanced processes, such as ozonation, are required to remove organic micropollutants, such as ozonation. Ozonation also has the added advantage of producing the low amounts of residue (waste) and

costs (Bui *et al*., 2016). O_3 can successfully oxidise the organic micropollutants carbamazepine, primidone, phenytoin, and sucralose that are typically considered biologically recalcitrant and not removable by soil aquifer treatment. Organic micropollutants carbamazepine and naproxen are susceptible to treatment by both O_3 and OH·. Meprobamate is susceptible to treatment by OH· while TCPP and musk ketone are resistant to treatment by O_3 and OH· (Gerrity *et al*., 2014).

A case study by Gerrity *et al.* (2014) found that musk ketone required impractically high O_3 doses of 9.2 mgO_3/mgTOC for 0.3log reduction and TCEP needed an O_3 dose ratio of 3.1 mgO_3/mgTOC. Except for 1,4 dioxane at 1.1 mgO_3/mgTOC, the rest of the organic micropollutants showed lower O_3 dose ratio requirements.

2.4.12 Formation and effect of Hydroxyl Radical

Ozonation of treated effluent is considered an advanced oxidation process given the high yield of OH· when O_3 reacts with organic wastewater constituents. The yield and thus the OH· exposure, linearly varies with the O_3 dose ratio (Gerrity *et al*., 2014). Furthermore, Snyder *et al.*, (2013) noted that OH· exposure is expensive and complicated to measure given that there is no direct method so measure OH· exposure. Hence, they highlighted the need for cheaper alternatives, like UV_{a254} and fluorescence spectra, to measure the performance of the process. The Hydroxyl radical OH· is very ineffective to eliminate spore-forming microorganisms like giardia cysts, cryptosporidium oocysts and bacillus spores and is therefore not recommended for processes that require the inactivation of these contaminants (Snyder *et al.,* 2014).

2.4.13 O_3 organic micropollutants removal efficiency

An O_3/BAC pilot study by Zhu *et al.* (2015) was conducted from 10 March to 13 April 2014. In their study the authors varied the O_3 dose between 0.6 - 1.2mg O_3/mg TOC and used an EBCT of 15minutes. The biological active filter (BAF) no. 2, in their study, was a dual media filter with 610mm of spent GAC (effective size between 1-1.2mm and uniformity coefficient of 1.7) on top of 300mm of sand (0.5 mm of effective size and uniformity coefficient of 1.4). O_3 was injected with ceramic diffusers into two in-series O_3 contact columns. One column was operated in an upstream mode and the other in a downstream mode. The O_3 dose averaged out to be 0.8mg-O_3/mg-TOC. Secondary effluent was fed to the pilot plant and had the following average key concentrations, TOC of 12mg/l, UVT of 53.9% and TSS of 7.9mg/l. Results from the same study showed that COD removal plateaued at an O_3 dose of 0.8mg O_3/mgTOC (Zhu *et al*., 2015). Table 2-21 shows the removal efficiencies of some organic micropollutants:

Table 2-21 – Removal efficiencies for some organic micropollutants (Zhu *et al.*, 2015).

Compound	Before O_3 ng/l	After O_3 ng/l	After BAF 1 ng/l	After BAF 2 ng/l	O_3 removal %	BAF 1 Removal %	BAF 2 Removal %
Atenolol	315 ±89	54 ±50	42 ±40	15 ±4	39 ±4	2 ±3	6 ±7
Carbamazepine	265 ±57	15 ±0	15 ±0	15 ±0	94 ±1	0 ±0	0 ±0
Diclofenac	7 ±218	25 ±0	25 ±0	25 ±0	69 ±8	0 ±0	0 ±0
Ibuprofen	366 ±415	42 ±4	40 ±0	40 ±0	7 ±7	0 ±0	0 ±0
Sulfamethoxazole	53 ±28	15 ±0	15 ±0	15 ±1	16 ±9	0 ±0	0 ±0
Citalopram	364±53	32 ±33	26 ±28	3 ±1	68 ±41	2 ±3	8 ±10
Ciprofloxacin	1269 ±426	30 ±23	44 ±54	20 ±0	21 ±8	0 ±1	0 ±0
Metoprolol	1590 ±448	225 ±214	202 ±198	43 ±12	73 ±36	2 ±0	12 ±15
Propranolol	103.5 ±30	3 ±0	3 ±0	3 ±0	97 ±1	0 ±0	0 ±0
Benzotriazole	2180 ±680	565 ±420	560 ±462	103 ±57	57 ±26	1 ±3	24 ±19
BAF 1 = Anthracite and sand dual media biological active filter BAF 2 = GAC and sand dual media biological active filter							

In a pilot study by Hübner *et al.* (2012), O_3 of 0.8 mg O_3/mg DOC was dosed into filtered final effluent. The O_3 treatment removed various trace organic compounds, as can be seen in Table 2-22.

Table 2-22 – Removal of organic micropollutants by ozonation (Hübner *et al.*, 2012).

Substances	Surface water [µg/L]			Removal via ozonation
	Average	**Min**	**Max**	
ETBE	0.44	0.1	1	≈50%
MTBE	0.10	<0.03	0.21	Not calculated
1-Acetyl-1methyl-2-dimethyl-oxamoyl1-2-phenylhydrazid (AMDOPH)	0.14	0.09	0.17	≈50%
Carbamazepine	1.09	0.63	1.3	>98%
Phenazon	0.12	0.08	0.21	> 0%
Acetylaminoantipyrin (AAA)	0.34	0.22	0.41	>90%
Formylaminoantipyrin (FAA)	0.49	0.34	0.59	>90%

Substances	Surface water [µg/L]			Removal via ozonation
	Average	Min	Max	
Primidone	0.13	0.08	0.16	≈70%
para-Toluensulfonamid (p-TSA)	0.13	0.09	0.22	>50%
Benzensulfonamid (BSA)	0.08	0.04	0.11	>50%
Sulfamethoxazole	0.17	0.09	0.25	>80%
Metoprolol	0.23	0.12	0.38	>90%
Benzotriazol	2.2	1.7	3.2	≈85%
Tolyltriazol	0.95	0.71	1.4	>94%

Levine *et al.* (1999) did research on the removal efficiency of organic and trace organic compounds in a multi-barrier pilot reuse facility treating final effluent at Lake Arrowhead. One of the barriers was an O_3/BAC filtration process. The full treatment train consisted of coagulation→sedimentation→filtration→ozonation→BAC-filtration→UF→RO→post-ozonation. Organic micropollutant removal was tested by measuring the base neutral acids, which included all semi-volatile trace organic contaminants. The pilot plant consisted of an O_3 contact tank with 20 to 40 minutes of contact time in which O_3 was dosed in a counter-current configuration. The O_3 dose was approximately 15mg/l (±5). The EBCT for the BAC filters was 15 minutes, the media in the filters were 1.2m deep, and the media was active carbon called filtrasorb F-400 (Calgon corporation). The treatment efficiency of both processes was measured by DOC removal. DOC and $UV_{absorbance-254}$ (UV_{a254}) tests were started 50 days after filtration through the BAC. The UVT results after filtration were in the range of 50–79%, after ozonation they were in the range of 63–89% and after BAC filtration they were in the range of 76–98%. This corresponds to a UVT improvement of between 18–26%. The DOC results after filtration were 5 to 15mg/l; after ozonation 5 to 15mg/l and after BAC filtration 1 to 10mg/l. These results indicate a 26% average improvement of the DOC concentration from 7.85 to 5.75mg/l (Levine *et al.*, 1999).

Snyder *et al.* (2014) grouped TOrCs into five classes based on their oxidation potential. The five groups are defined in Table 2-23.

Table 2-23 – Definitions of trace organic compound groups (Snyder *et al.*, 2014).

	Hydroxyl Radical Reaction rate constant - k_{O3} ($M^{-1}s^{-1}$)	**Hydroxyl Radical Reaction rate constant - $k_{OH\cdot}$ ($M^{-1}s^{-1}$)**	**Example TorCs**
Group 1	$> 10^5$	$> 5 \times 10^9$	bisphenol A, carbamazepine, estrone
Group 2	$10 < k_{O3} < 10$	$> 5 \times 10^9$	atenolol, amikacin, benzotriazole
Group 3	$k_{O3} \leq 10$	$> 5 \times 10^9$	ibuprofen, phenytoin, TCEP
Group 4	$k_{O3} < 10$	$1 \times 10^9 < k_{\cdot OH} < 5 \times 10^9$	atrazine, iopromide, meprobamate
Group 5	$k_{O3} < 1$	$\leq 1 \times 10^9$	TCEP, NDMA

Table 2-24 below shows the effects of increasing O_3 dose on TOrC removal in its various groups.

Table 2-24 – The average removal of TorC groups at various O_3 doses (Snyder *et al.*, 2014).

O_3 Dose	**1.5mg/L**	**3mg/L**	**6mg/L**	**9mg/L**
O_3:TOC Ratio	**0.25**	**0.5**	**1**	**1.5**
	Average percent destruction of target compounds in the O_3 unit process			
Group 1	>90%	>90%	>90%	>90%
Group 2	>60%	>90%	>90%	>90%
Group 3	>30%	>60%	>90%	>90%
Group 4	>15%	>30%	>60%	>80%
Group 5	<5%	>5%	>15%	>20%

2.4.14 O_3 treatment costs

The removal of organic microcontaminants is done with advanced treatment processes that result in higher energy costs. Quantifying these costs can help compare treatment alternatives and infrastructures' planning (Plumlee *et al.*, 2014).

When it comes to wastewater reuse, Zhu *et al*. (2015) described RO as the most common process, with the drawbacks of being expensive and producing a brine that must be disposed of. In comparison with other treatment trains, they noted that the O_3/BAC process is attractive given its high treatment performance, minimum residue, and lower operating costs.

Plumlee *et al.* (2014) developed a conceptual O&M and capital cost model to enable the comparison of various treatment train combinations. Their cost estimates are still at a conceptual

level, specifically for feasibility and planning evaluations where less than 1% of the design is done. The level of the cost estimate is accurate within a -30%–50% band. The costing models assume the following: 30% contingencies, 30% installation costs and 15% profit. Cost curves are applicable to wastewater volumes in the range of 1–80 Million Gallons per day (MGD). O_3 costs were based on 6mg/l influent TOC and O_3 dose ratio of 0.5mg O_3/mg TOC. The O_3 cost estimates were based a configuration having the O_3 step before RO. Table 2-25 shows the cost equations developed in the current study.

Table 2-25 – O_3 Cost estimate equations at a conceptual level (Plumlee *et al.*, 2014).

Process	Capital Cost ($M/MGD)	Annual O&M Cost ($M/MGD)
O_3	$2.26 \times (\text{Plant Capacity, in MGD})^{-0.54}$	$0.0068 \times (\text{Plant Capacity, in MGD})^{-0.051}$

Plumlee *et al.* (2014) further developed equations for O_3 doses higher than 0.5mg O_3/mg TOC. The equations in Table 2-25 were based on an O_3 dose of 0.5mg O_3/mg TOC. Equation 2.12 and Equation 2.13 give the capital and O&M costs estimation equations for an O_3 system with a dose higher than 3mg/l O_3, where r = O_3 dose/3.

$$\Delta Capital\ (\$M) = 0.0156 \times Design\ Capacity\ (in\ MGD) \times (r - 1) \qquad \textbf{Equation 2.12}$$

$$\Delta O\&M\ (\$M) = 0.005 \times Design\ Capacity\ (in\ MGD) \times (r - 1) \qquad \textbf{Equation 2.13}$$

Table 2-26 below shows the effect of increasing the O_3 dose on cost based on the equations in Table 2-25 for a O_3/BAC filtration process of 50MGD that is treating 6mg/l TOC and has an EBCT of 10 minutes.

Table 2-26 – The cost and average removal of TorC groups at various O_3 doses (Plumlee *et al.*, 2014).

O_3 Dose	**1.5mg/L**	**3mg/L**	**6mg/L**	**9mg/L**
O_3:TOC Ratio	**0.25**	**0.5**	**1**	**1.5**
Conceptual-level cost estimate				
Capital Costs	$49M	$50M	$52M	$53M
Annual O&M	$2.7M	$2.8M	$3.1M	$3.3M

2.4.15 Grouping of organic micropollutants based on their O_3 reaction rate

Snyder *et al.* (2014) found that the ability of O_3 compared to hydroxyl radical (OH·) to oxidise contaminants varies depending on the contaminant in consideration. These distinctions motivated Snyder *et al.* (2014) to group organic micropollutants based on their mode of oxidation. They noticed that some contaminants are very susceptible to both O_3 and OH· oxidation; others only to O_3 oxidation or to OH· oxidation, and some neither to O_3 nor OH· oxidation (Snyder *et al.*, 2014). If all the groups are to be oxidised, the process has to provide either for moderate OH· exposure or very high O_3 dosages.

Snyder *et al.* (2014) further commented that the combination of O_3 and H_2O_2 is more relevant to water with low organic matter given that OH· formation is relatively good in water with higher organic matter. They found that for secondary effluent type water with higher organic matter concentrations, OH· forms rapidly from the reaction between O_3 and organic matter and the OH· exposure is similar whether H_2O_2 is combined with O_3 or not.

Table 2-27 below elaborates on Table 2-23 and shows the O_3 and OH· reaction rates applicable to each group, including the O_3 dosage ratio required for removal, the removal efficiency achievable and the method of removal. Table 2-28 below gives examples of organic micropollutants in each group.

Table 2-27 – Organic micropollutant grouping based on O_3 and OH· reaction rates (Snyder *et al.*, 2014).

Group	k_{O3} value ($M^{-1}.s^{-1}$)	$k_{OH\cdot}$ value ($M^{-1}.s^{-1}$)	O_3 dose ratio required to remove (O_3/TOC)	Oxidation efficiency / removal (%)	Method of removal
Group 1	$> 10^5$	$> 5 \times 10^9$	0.25	>90%	Very susceptible to both O_3 and ·OH
Group 2	$10 < k_{O3} < 10^5$	$> 5 \times 10^9$	0.5	>90%	Moderately susceptible to O_3 / highly susceptible to ·OH
Group 3	< 10	$> 5 \times 10^9$	1	>90%	Very resistant to O_3 / highly susceptible to ·OH
Group 4	< 10	$1 \times 10^9 < k_{OH} < 5 \times 10^9$	> 1.5	>90%	Very resistant to O_3 / moderately susceptible to ·OH
Group 5	<1	$< 1 \times 10^9$	1.5	<50%	Very resistant to both O_3 and ·OH

Table 2-28 – Organic micropollutants in each group (Snyder *et al.*, 2014).

Group	Applicable organic contaminants
Group 1	Phenolic (Bisphenol A, estrone, nonylphenol, triclosan), aniline (sulfamethoxazole, diclofenac), double bond (carbamazepine), amine (ciprofloxacin, roxithromycin) and activated-aromatic-containing compounds (naproxen, propranolol)
Group 2	Primary/secondary amines (amikacin, atenolol), weakly activated aromatic systems (benzotriazole and bezafibrate)
Group 3	Benzene rings (ibuprofen, phenytoin), long alkyl chains
Group 4	Deactivated benzene (atrazine, iopromide), short aliphatic carbon chains (meprobamate)
Group 5	Short aliphatic carbon chains with electronegative halogens or nitro parts (Tris-(2-chloroethyl)-phosphate) (TCEP), NDMA)

It should, however, be mentioned that Sonntag and Von Gunten (2012), as reported by Park *et al.* (2017) stated that grouping elements in order to predict their removal could be inaccurate given the significant variations in the oxidation rate constants of elements.

2.4.16 Assessment of the O_3 process performance

Snyder *et al.* (2014) proposed the use of indicator compounds to determine the success of oxidation of organic compounds. The main goal of using indicator compounds is to provide a low-cost and simple tool to measure the performance of advanced oxidation processes. The authors further advocated that using indicator compounds is an efficient way to monitor process performance and reduce the number of contaminants that must be tested for. They recommended that the selection of indicator compounds be made based on three factors viz., their relatively high concentrations, their suitability to represent a range of reaction rate k-values / O_3 reactivity, and lastly the compounds limits regulations concerning public health.

Snyder *et al.* (2014) found that the same O_3/TOC dosage ratio produces similar results, even with different CT-values and high variations in water quality. This makes the O_3/TOC dose ratio a particularly useful measure of organic micropollutant oxidation. Similarly, relative $UV_{absorbance254}$ (UV_{a254}) changes occurred at the same O_3 dose ratio in different wastewater effluents.

The report by Snyder *et al.* (2014) further explained that O_3 is highly effective in improving the visible colour of water measured by $UV_{absorbance}$. However, in some cases, they found that regardless of the O_3 dose, the relative improvement in the visible light spectrum is the same. $UV_{absorbance}$ can be measured in the visible light range of 436nm or the invisible light range of 254nm. Organic matter that is aromatic and unbonded contributes to the invisible $UV_{absorbance}$ range. Bonded aromatic organic matter contributes to the visible $UV_{absorbance}$ range. While the improvement of $UV_{absorbance}$ across the O_3 process appears satisfactory in the visible light range, the actual improvement measured in the invisible light range, UV_{a254}, is significantly less than it

would appear in the to the visible eye given that it picks up more compounds in the invisible light range.

Snyder *et al.* (2014) concluded that the relative improvement in UV absorbance at 254nm over an O_3 process remains the preferred way to assess the process efficacy and to determine the optimum O_3 dose.

Snyder *et al.* (2013) proposed Equation 2.14 to describe the % ΔUV_{a254} improvement (ΔUV_{a254}) across an O_3 process based on the O_3/TOC dose ratio applied to the filtered final effluent.

$$\Delta UV_{254}(\%) = 100 \times 0.5077 \times (O_3/TOC)^{\,0.5968} \quad R^2 = 0.92 \qquad \textbf{Equation 2.14}$$

Similarly, Selvy (2015) derived Equation 2.15 that is a regression formula predicting UV_{a254} removal using data obtained from a pilot study treating membrane bioreactor (MBR) effluent by an O_3/BAC process with exhausted GAC media.

$$\Delta UV_{254} = 0.1863 \ln(x) + 0.5066 \quad R^2 = 0.99328 \qquad \textbf{Equation 2.15}$$

The link between ΔUV_{a254} and the removal of specific organic micropollutants is described by Equation 2.16 (Snyder *et al*., 2013).

$$\left(1 - \frac{C}{C_0}\right) \times 100(\%) = Slope \times \left[\left(1 - \frac{UV}{UV_0}\right) \times 100(\%)\right] + intercept \qquad \textbf{Equation 2.16}$$

C_0 = organic micropollutant concentration before treatment

C = organic micropollutant concentration after treatment

UV_0 = UV_{a254} before treatment

UV = UV_{a254} after treatment

Slope – obtained from Table 2-29

Intercept – obtained from Table 2-29

The link between ΔUV_{a254} and the removal of specific pathogens or microorganisms is described by Equation 2.17 (Snyder et al., 2013).

$$\left(1-\frac{N}{N_0}\right)\times 100(\%) = Slope \times \left[\left(1-\frac{UV}{UV_0}\right)\times 100(\%)\right] + intercept \qquad \textbf{Equation 2.17}$$

N_0 = Pathogen concentration before treatment

N = Pathogen concentration after treatment

UV_0 = UV_{a254} before treatment

UV = UV_{a254} after treatment

Slope – obtained from Table 2-29

Intercept – obtained from Table 2-29

Table 2-29 below gives the slope, intercept, and correlation coefficient of surrogate pathogens and some contaminants in each group for their removal calculation in Equation 2.16 and Equation 2.17. The surrogates/indicators selected by Snyder *et al.* (2014) to test the efficacy of O_3 disinfection were the bacillus subtilis to represent spore-forming pathogens, Escherichia coli for coliform bacteria and the f-specific coliphage, MS2 bacteriophage, for human-specific viruses like poliovirus, echovirus and coxsackievirus. Bacillus subtilis spores are a bacterium highly resistant to oxidation and are a surrogate for Giardia and Cryptosporidium. For organic micropollutants in group 1 to 4, as can be seen in Table 2-29, there is also an indicator compound for the removal of compounds in the group.

Table 2-29 – Table with slope and intercept coefficients for Equation 2.16 and Equation 2.17 (Snyder *et al.*, 2013).

Contaminant	Slope	Intercept	R^2
Group 1			
Bisphenol	N/a	N/a	N/a
Carbamazepine	N/a	N/a	N/a
Diclofenac	N/a	N/a	N/a
Naproxen	N/a	N/a	N/a
Sulfamethoxazole	N/a	N/a	N/a
Triclosan	N/a	N/a	N/a
Trimethoprim	N/a	N/a	N/a
Indicator	N/a	N/a	N/a
≈100% Removal	>30% ΔUV_{254} absorbance		
Group 2			
Atenolol	2.34	-2	0.77
Gemfibrozil	1.72	34	0.56
Indicator	2.03	16	0.57
≈100% Removal	>50% ΔUV_{254} absorbance		

Contaminant	Slope	Intercept	R^2
Group 3			
DEET	1.53	0	0.63
Ibuprofen	1.56	7	0.59
pCBA	1.31	3	0.48
Phenytoin	1.68	3	0.56
Primidone	1.44	4	0.61
Indicator	1.5	3	0.54
≈100% Removal	>70% ΔUV_{254} absorbance		
Group 4			
1,4 Dioxane	1.57	-18	0.69
Atrazine	1.79	-19	0.72
Meprobamate	1.87	-15	0.73
Indicator	1.78	-17	0.69
≈100% Removal	>70-90% ΔUV_{254} absorbance		
Group 5			
TCEP	0.52	-7	0.45
≈100% Removal	N/a		
Microbial Inactivation			
Bacillus spores	N/a	N/a	
E.coli	0.13	-1.1	0.5
MS2	0.14	0	0.69

From Table 2-29 above, it can be seen that for group 1 organic micropollutants, the UV_{a254} must be improved by >30% for ±100% of their removal. For group 2 organic micropollutants, the UV_{a254} must be improved by >50% for ±100% removal. For group 3 organic micropollutants, the UV_{a254} must be improved by >70% for ±100% removal. For group 4 organic micropollutants, the UV_{a254} must be improved by >70-90% for ±100% removal.

In contrast, it should further be noted that predicting O_3 oxidation of organic micropollutants is difficult when treating wastewater given of the quantification of O_3 and hydroxyl radical exposure during the rapid initial phase (Park *et al.*, 2017). The effectiveness of the removal of organic compounds with O_3 significantly depends on the time and concentration of O_3 and OH· exposure called CT-value (Snyder *et al*., 2014).

2.5 Biological activated carbon filtration

Converting existing filters to a biological active filter (BAF) is an effective way to remove emerging contaminants (Zhang *et al*., 2017). Granular activated carbon (GAC) filters, typically operating on the principle of adsorption of organic micropollutants, are converted to biological activated carbon filters when an oxidation step is put in place before the GAC filter. This oxidation step enhances the biological activity in the water by converting large organic molecules into low molecular weight molecules. The ability of biological activated carbon (BAC) filters to remove natural organic matter (NOM) and disinfectant by-products precursors have been the focus of several research studies to improve the performance of the related processes (Ross *et al.*, 2019).

Findings by Kalkan *et al.* (2011) indicate that the removal of dissolved organic carbon (DOC) depends on the type of carbon used, empty bed contact time (EBCT), biodegradability of the water, microbial diversity of BAC columns and temperature.

Urfer *et al.* (1997) found that biofiltration has the following benefits viz., less potential for regrowth of bacteria, a reduction in the potential formation of chlorine disinfection by-products, a removal of taste- and odour-causing compounds, a removal of concerning organic contaminants, and a decrease in corrosion potential.

Future research on BAC filtration should focus on the impact of EBCT, temperature, total suspended solids (TSS), and nutrients such as phosphorous on BAC filtration performance (Zhu *et al*., 2015).

2.5.1 BAC filters contaminant removal mechanisms

The GAC in the BAC filter primarily works on the principle of adsorption (Levine *et al*., 1999), and subsequently gradually converts to a BAC as bacteria colonize the surface of the GAC and metabolize the influent organic matter. The usable organic matter by the bacteria is increased during the ozonation step when high molecular weight compounds are converted to more biodegradable compounds. Compounds that are most likely to be found in the aqueous phase are more likely to be biodegraded. One explanation for this is the bacteria's preference to metabolize free-flowing contaminants instead of contaminants that are already adsorbed and have a bond with the GAC, hence resisting biodegradation (Levine *et al*., 1999).

When bacteria are colonized on the filter media, biofiltration removes organic micropollutants in two ways, firstly, by the metabolism of bacteria that harvest organic carbon substrates during

growth (Benner *et al*., 2013), and secondly by co-metabolism, where the enzymes produced during primary substrate utilization biodegrade organic matter (Zearley & Summers, 2012).

Tests on unozonized and untreated surface water found that when adsorption capacity is finished in GAC filters, DOC can still be biologically removed by up to 15 to 20% in BAC filters. After the depletion of the adsorption capacity, BAC filters can only remove the BDOC portion of the DOC and nothing more (Korotta-Gamage & Sathasivan, 2017).

2.5.2 Impacts of influent water on the BAC filtration process

A study of the response of BAC filters to changes in source water quality was conducted by Ross *et al.* (2019). They tested the influence of pre-treatment and water qualities on BAC performance. The study reported that it is not essential to change feed quality given the BAC filters adaptable biomass activity or adsorption capability.

2.5.3 Impacts of EBCT on organic micropollutant removal

For granular activated carbon (GAC) media, Zhang *et al*. (2017) found that EBCT have a significant impact on dissolved organic carbon removal (DOC). The authors found that dropping the EBCT from 18 to 10 minutes resulted in 50% less DOC removal. Moreover, that BAF filters operated at high EBCTs showed good emerging contaminants removal even without pre-ozonation.

Research by Khan *et al. (*2019) concluded that biodegradable dissolved organic carbon (BDOC) removal in BAC filters is a function of EBCT. A laboratory-scale study by Hozalski *et al. (*2019) indicated that BDOC removal increased with greater EBCT but plateaued at an EBCT of 25 minutes. The study also observed that for up to 90% removal in BAC filters, assimilable organic carbon (AOC) requires 2 minutes EBCT and BDOC between 10–20 minutes. With an O_3 dose of 0.5 to 1 mgO_3/mgTOC applied to river water, Lechevallier *et al.* (1992) found TOC was removed as follows:

i) EBCT 5min - TOC removal of 29%;

ii) EBCT 10min - TOC removal of 33%; and

iii) EBCT 20min - TOC removal of 51%.

Figure 2.5 further illustrates the little benefit of increasing the EBCT beyond 20 minutes. The results are from an experimental pilot study on final effluent from a membrane bioreactor and dosing 1 mgO_3/mgDOC (Vatankhah *et al*., 2019).

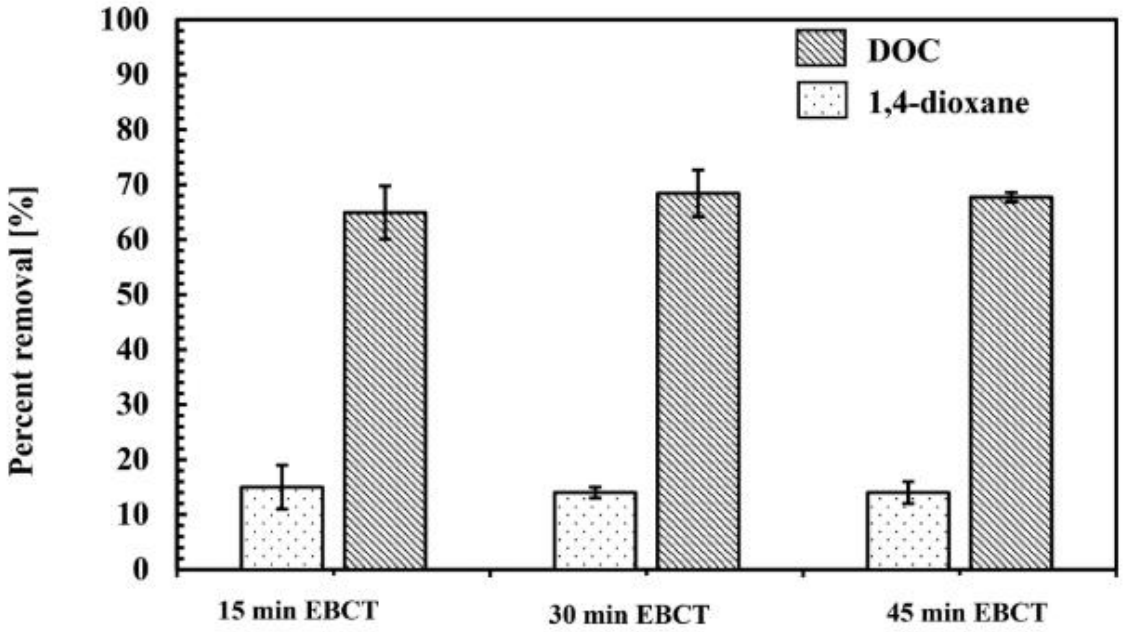


Figure 2.5 – Effect of EBCT on removal percentage in a BAC filter (Vatankhah *et al*., 2019).

At higher EBCT, filters have more media and therefore, more area is available as attachment sites for biofilm to grow and utilize constituents in the water. A study by Sundaram et al. (2020) concluded that if the O_3/BAC filtration process is the main organic micropollutant removal step, higher EBCT, of approximately 20 minutes, is required. Figure 2.6 shows the relationship between biomass utilization and EBCT. However, Wang *et al*. (1995) found that biomass does not increase with increasing filter depth. There is a point where other factors, like available biodegradable matter or dissolved oxygen, become the limiting factor for treatment efficiency and an increase in EBCT has the reverse effect on organic micropollutant removal. Experiments by Kalkan *et al*. (2011) on secondary effluent showed that for a BAC filter with an EBCT of 18 minutes and a media depth of 500mm, most of DOC removal happened in the top 250mm of the column, which equates to an EBCT of 9 minutes.

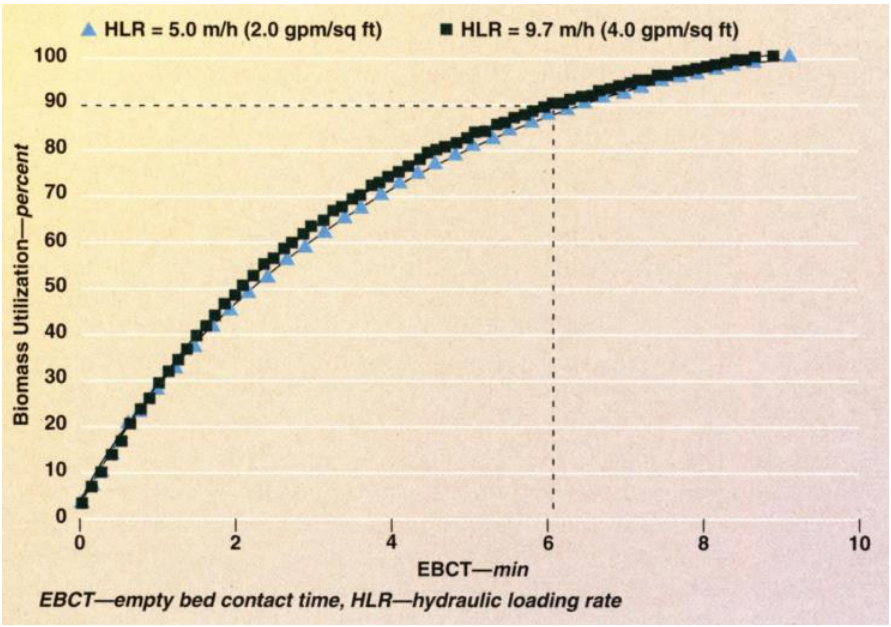


Figure 2.6 – Biomass utilization as a function of EBCT (Carlson & Amy, 1998).

In general, Reungoat *et al.* (2012) found that DOC removal increases when EBCT and O_3 dose are increased.

2.5.4 Impact of filter media type on biofilter performance

Biofilter media can be categorised into adsorptive, of which granular activated carbon (GAC) is a prominent example and non-adsorptive of which sand and anthracite are the most common. The specific surface area (unit surface area per unit volume of filter) of sand is higher than GAC. Little biological growth occurs in GAC micropores, but GAC adsorbs micropollutants, which increases their time in the filter bed. This provides sufficient retention time for the slowly biodegradable constituents to be degraded (DiGiano *et al*., 1981). More suitable bacterial attachment sites are provided by the irregular surface and macro-porous structure of GAC. These sites provide high protection to shear stress for the biofilm (Urfer *et al*., 1997).

Converting existing filters to a biologically active filters (BAF) are an effective way to remove emerging contaminants (Zhang et al., 2017). Typical filter media include sand, anthracite, and GAC. Research by Wang *et al.* (1995) stated that GAC filter media can host three to eight times more biomass than other media like anthracite or sand, thus removing more biodegradable organic matter (BOM). This was substantiated by Zhang *et al*. (2017), who showed GAC media have better emerging contaminants removal efficiencies compared to dual media filters. Research done by Urfer *et al.* (1997) found that a GAC-Sand filter removes aldehyde better in colder temperatures, forms a biofilm quicker, has better DOC and TOC removal capability, establish

itself quicker on GAC-Sand media after operating failure and has better resistance to oxidant residuals compared with an anthracite-sand filter.

Kalkan *et al.* (2011) studied the effects of different carbon types on BAC performance, treating secondary effluent. The study found that activated carbon that is thermally activated is more reactive to oxygen given that its activation occurred in the absence of oxygen. Thermally activated carbon can chemisorb (hold by chemical force) oxygen onto its surface and change the surface chemistry. This makes it challenging to use DO, which is an indication of biomass activity, within the depth of the reactor. Chemically activated carbon is not affected by the interaction of oxygen that much given that it contains a significantly high number of oxidised sites. Properties of activated carbon grades used in the study by Kalkan *et al.* (2011) are shown in Table 2-30, and the influent and effluent DOC concentrations for various carbon types are shown in Figure 2.7. The average influent DOC concentration was 9.23mg/l, average effluent DOC concentration 5.02mg/l for the PK1-3 carbon and average effluent DOC concentration 5.67mg/l for the CAgran carbon (See Table 2-30 below for details of the respective carbon media). During the first 83 days, DOC removal was 81% for PK1-3 and 64.5% for CAgran. During the subsequent 55 days, the removal dropped to 74% and subsequently to 58% when the influent DOC was high. From day 140, the DOC removal dropped to 45.9% for PK1-3 and to 37.8% for CAgran (Kalkan *et al*., 2011).

Table 2-30 – Properties of GAC (Kalkan *et al*., 2011).

Activated Carbon	**PK 1-3**	**BACF 30**	**GAC 830 W**	**CAgran**
Origin	Peat	Coal	Coal	Wood
Physical Form	Granular	Granular	Granular	Granular
Activation method	Thermal	Thermal	Thermal	Thermal
Sotal Surface Area (m^2/g)	875	1050	1100	1400
Micro pore volume (cm^3/g)	0.3	0.42	0.42	0.26
Meso pore volume (cm^3/g)	0.19	0.12	0.1	0.6
Macro pre volume (cm^3/g)	0.74	0.32	0.3	0.89

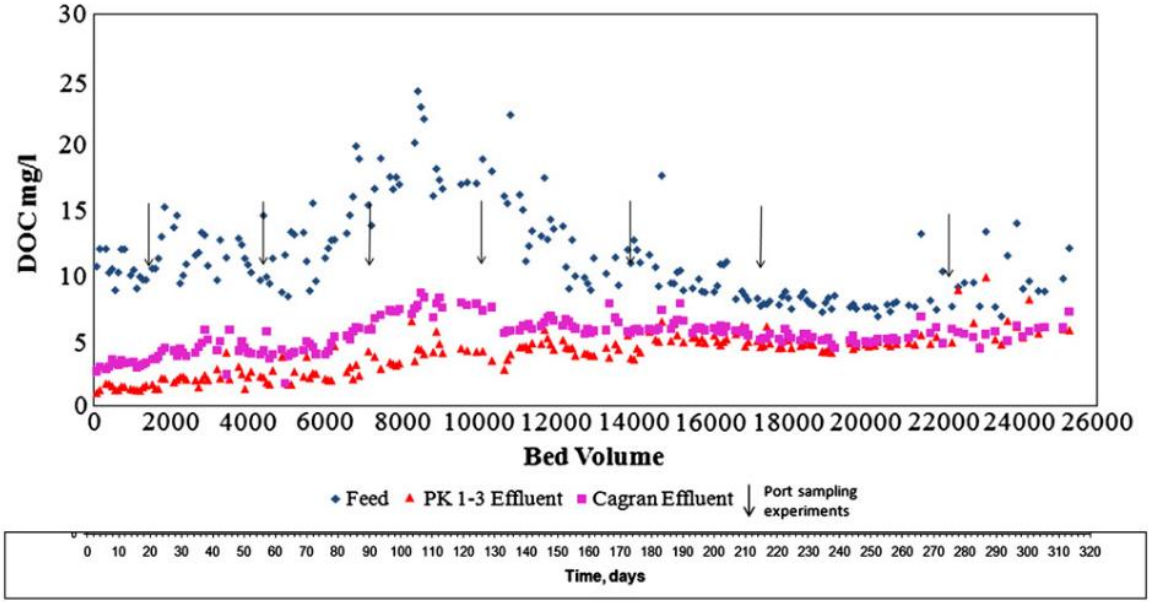


Figure 2.7 – Influent and effluent DOC concentrations (Kalkan *et al.*, 2011).

2.5.5 Impact of BAC filter media depth on filter performance

Carpenter and Helbling (2017) observed better removal of micro-organic contaminants in biofilters with deeper media beds. In their filters, five organic micropollutants (valsartan, naproxen, trimethoprim, ibuprofen, and acetaminophen) showed higher second-order rate constants as the filter depth increased. This indicated that at deeper media levels, biofilters have better biotransformation ability for some organic micropollutants, even when the biological community is small and low amounts of nutrients are available. Figure 2.8 illustrates the relationship between filter depth and biomass concentration (Carpenter & Helbling, 2017). From the figure it is evident that the biomass concentration decreased with increasing filter media depth.

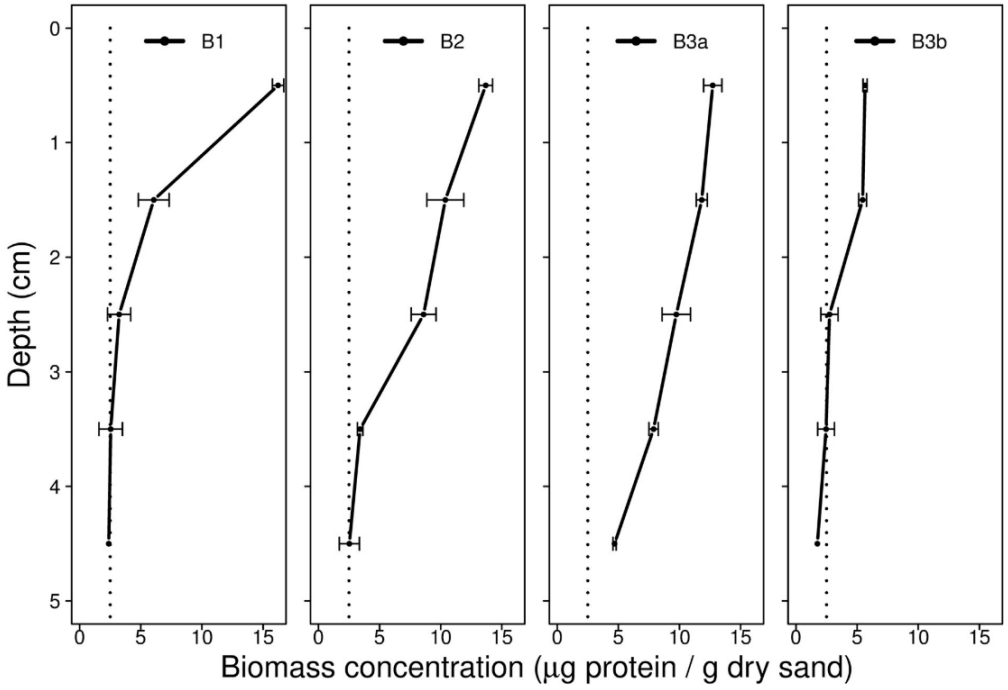


Figure 2.8 – Relationship between biomass concentration and filter depth for four filters (Carpenter & Helbling, 2017).

Research on the dynamics and organization of bacterial communities in biofilters by Boon *et al*. (2011) revealed that an increase in filter depth resulted in more microbial variety. The results also showed that nutrients were filtered through and reached the lower portions of a filter bed feeding oligotrophic organisms, which led to a biological community at deeper depths with more lushness, variety, and diversity.

A study by Kalkan et al. (2011) sampled DOC, ammonium (NH_4-N), and dissolved oxygen (DO) at various bed depths within the filter bed to investigate changes in concentrations. They found the DO decreased with increasing depth in the filter media as it was utilized to biodegrade organic carbon. Most of the NH_4-N removal occurred within the first 250mm of the BAC columns. For the filter containing PK 1-3 carbon (See Table 2-30 for details of the PK 1-3 and CArgran carbon), the NH_4-N was removed at 58%, of which 40% occurred within the top 250mm of the 500mm deep filter bed. For the filter containing CAgran carbon, the NH_4-N was removed at 44%, of which 29% occurred within the top 250mm. This was confirmed by Zhu *et al*. (2015) who found that the amount of ammonia-oxidizing bacteria decreased deeper in the media bed. Most of the DOC removal occurred within the top 250mm of the column, which equates to an EBCT of 9 minutes (Kalkan *et al*., 2011). Khan *et al*. (2019) also observed BDOC removal within the top 40% of the filter depth.

2.5.6 Impact of BAC filter filtration rate on filter performance

Filtration rates between 1.5–15m/h did not impact substrate removal in tests on biological sand filters (Wang & Summers, 1996). This was later confirmed by Wert *et al.* (2008) who found that filtration rates between 4.8–14.6m/h did not have an impact on BOM removal. However, when the filtration rate was increased to 14.6m/h it did reduce the oxidation of ammonia to nitrite by 60%. Urfer *et al.* (1997) attributed the low impact of typical hydraulic loading rates on biodegradable organic matter removal to the low shear stress at these filtration rates, which is favourable for the growth of thick biofilm. Khan *et al.* (1998) however, found BDOC removal dropped from 70% at 6m/h to 30% at 12m/h and again to 20% at 18m/h.

2.5.7 Impact of BAC bed life on contaminant removal

Reungoat *et al.* (2011) categorised the bed life of biofilters in three phases:

i) Phase 1: removal by adsorption phase;

ii) Phase 2: removal by a combination of adsorption, biodegradation and a drop in organic compound removal; and

iii) Phase 3: removal by biodegradation that continues for years, while only accompanied by lower removal as observed in Phase 1.

Studies by Zhang *et al.* (2010) showed good removal of DOC by BAC filtration even beyond five months of running the filters after depletion of adsorbability of the carbon.

Research by Kalkan *et al.* (2011) studied the effect of different types of activated carbon on DOC removal and found DO uptake and DOC removal started to correlate from the number of bed volumes 13,840 and upwards. The results indicated that after 13,840 number of bed volumes or 173 days, biodegradation became the most prominent DOC removal mechanism. Subsequently, DOC removal dropped from 81% to 46%.

Levine *et al*. (1999) tested the effectiveness of removing organic contaminants from the final secondary effluent in the Lake Arrowhead water reuse facility by adsorption and biodegradation using the O_3/BAC process. They found that it took 50 to 100 days for the process to reach a steady-state DOC and $UV_{absorbance-254}$ removal and only after 200 days did the organic micropollutants start breaking through.

2.5.8 Effect of dissolved oxygen on the removal of organics

The O_3 process increases the amount of dissolved oxygen (DO) in the water, thereby allowing aerobic bacteria like planctomycetes, a-Proteobacteria, b-Proteobacteria and d-Proteobacteria to dominate (Zhu *et al*., 2015). Accordingly, experiments by Greenstein *et al.* (2018) found that the ozonation of river water increases the DO from 7.4(±1.2)mg/l to 17.6 (±3.2) mg/l.

When the DO profile drops over a biofilter, it is an indication of biological activity (Reungoat *et al*., 2012). Experiments on secondary effluent treatment by BAC filters confirmed that DOC biodegradation and nitrification occur as the DO profile drops through the bed of the BAC filter (Kalkan *et al*., 2011).

Kalkan *et al*. (2011) found the following stoichiometric uptake/release of oxygen occurs in a BAC filter:

i) Nitrification: -4.33mg O_2/mg NH_4-N;

ii) Carbon consumption: -2.66mg O_2/mg DOC; and

iii) Denitrification: +2.86g O_2/g NO_3-N.

2.5.9 Biological activity in a BAC filter

Biological activity occurs in filters when the filters are fed with biodegradable organic carbon. GAC filters primarily operate on the principle of adsorption of organic micropollutants and then are converted to BAC filters when an oxidation step is put in place before the GAC filter. This oxidation step enhances the biological activity in the water by converting large organic molecules into low molecular weight molecules. This biological activity attaches itself to the GAC grains. Carbon in the form of BDOC is regularly believed to be the limiting factor for heterotrophic microorganisms that require nutrients in the typical ratio of C:N:P of 100:10:1 (Van Der Kooij, Visser & Hijnen, 1982). However, some studies found phosphorous to be the limiting factor (Lehtola *et al.*, 2002). To this day, no correlation has been found between assimilable organic carbon (AOC), the readily available carbon for cell growth, and biomass growth (Ross *et al*., 2019).

The formation of biofilm on GAC is aided by the presence of adsorbed organic constituents that create a suitable environment for the growth of microorganisms (De Waters & DiGiano, 1990). This process of biofilm growth is further facilitated by biodegradable matter and DO in the water, that creates the right conditions for bacteria to live on filter media (Song *et al*., 2015).

In filters that are biologically active, heterotrophic bacteria, as biofilm attached to the filter medium, can oxidize BOM by using it as a carbon energy source. Better understanding between the amount of biomass and the degradation of BOM is required, and so also is the understanding on community structure in biofilter depth (Urfer *et al*., 1997). This is further substantiated by findings by Emelko *et al.* (2006) who found higher biomass in anthracite filters with the same removal capabilities than GAC filters with less biomass. This indicated that BOM removal is not directly related to the biomass in the filter.

A study by Greenstein *et al.* (2018) focussed on the removal of trace organic compounds (TOrCs) added to Colorado river water by a dual GAC-sand filter and an anthracite-sand filter. The BAC filters removal mechanism showed a shift from adsorption to biodegradation after 140 days of filtration. At the end of the study, the BAC filter had a more diverse microbial mass (examined with 16S rRNA sequencing), even though the anthracite filter and the BAC filter biomass amounts were the same. The micro-organism, burkholderailes, was the most abundant in the filter media, while acidobacterium (not found on anthracite) was the second most abundant. Other microorganisms on the BAC media included bacteria from the phyla bacteroidetes, acidobacteria, actinobacteria, planctomycetes, and proteobacteria. In turn, Zhu *et al.* (2015) found that after the amount of DO in the water increased due to ozone treatment, aerobic bacteria like planctomycetes, a-Proteobacteria, b-Proteobacteria and d-Proteobacteria started to dominate.

2.5.10 BAC filters removal efficiency

A pilot plant study by Greenstein *et al*, (2018) used a 12-chamber O_3 contact tank and 200mm-deep spent (10-year-old) GAC media on top of 300mm of sand. The spent GAC had an effective size (ES) of 0.9mm and a 1.5 uniformity coefficient (UC). Raw water characteristics at the plant were Alkalinity of 138mg/l as $CaCO_3$, DOC of 2.4mg/l and pH of 8. The O_3 dose ratio used was 0.8 mgO_3/ mg-DOC, and the EBCT of the filters was 10.2 minutes. After ozonation, trace organic compounds (TOrC) increased. The BAC removed 74% (±8) of AOC compared with 42% (±23%) of anthracite. The consumption of AOC consisted of a small mass, 5 to 10% of DOC, and did not influence the overall removal of DOC. The current study used exhausted GAC media and attributed all removal to biodegradation. Removal percentages of organic micro contaminants are shown in Figure 2.9 below. The results also show that an increase in TOrC resulted in more biodegradation.

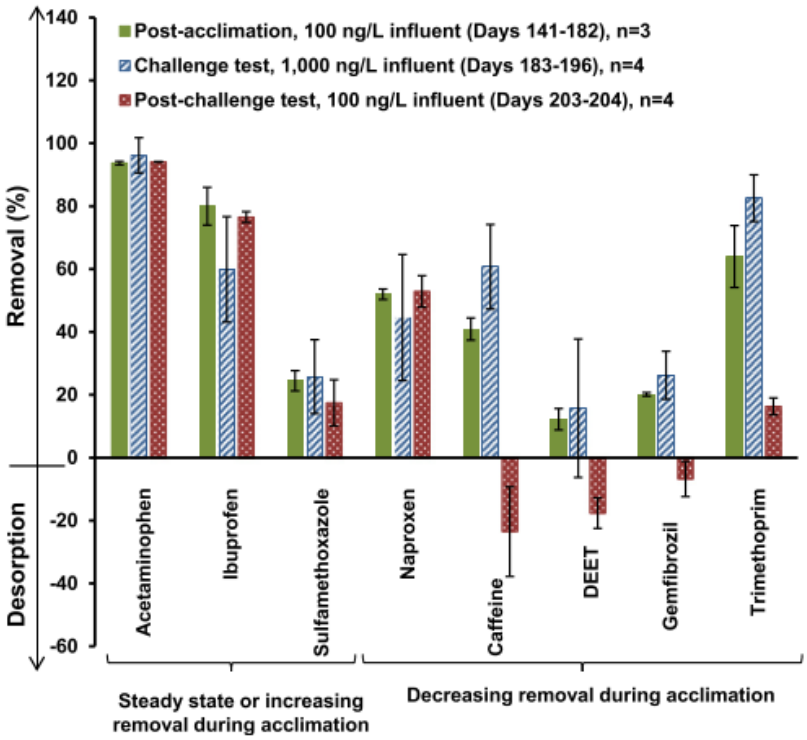


Figure 2.9 – Removal of some micropollutants at various stages of BAC filtration (Greenstein *et al.*, 2018).

Similarly, Urfer *et al.* (1997) found higher BOM removal in influent with higher BOM concentrations. Over time, more ibuprofen was removed from the BAC filters. Moreover, the filters consistently removed 24% of sulfamethoxazole and 93% of acetaminophen (Greenstein *et al.*, 2018).

The results of an O_3/BAC study by Zhu *et al*. (2015), details previously described in Section 2.4.13, showed UVT improvement from 53.9% to 77.9% on average after O_3 and BAC treatment.

In a study by Kalkan *et al.* (2011), secondary effluent was fed to different types of GAC to investigate the effects of GAC on biodegradation. EBCT was 18 minutes, and the media depth used was 500mm. The BAC influent water quality is shown in Table 2-31.

Table 2-31 – Secondary effluent and BAC filter influent water quality (Kalkan *et al*., 2011).

Constituent	Average (S.D.)	Minimum Value	Maximum Value
NH_4-N (mg/l)	0.44 (0.68)	0.01	5
NO_3-N (mg/l)	4.33 (1.73)	0.5	10
NO_2-N (mg/l)	0.07 (0.11)	<0.01	0.69
DOC (mg/l)	11.42 (3.58)	6.67	24.91
BDOC/DOC	0.23 (0.23)	<0.01	1.09
UV_{254} (cm^{-1})	0.22 (0.12)	0.1	1.24
pH	7.79 (0.37)	6.43	8.8

For new BAC media, the adsorption of contaminants is high, although the biodegradation also helps with removal. During the first 83 days, DOC removal was 81% for PK1-3 and 64.5% for CAgran. During the subsequent 55days, removal with higher influent DOC dropped to 74% and 58%, respectively for PK1-3 and CAgran carbon. From Day 140, the DOC removal dropped to 45.9% with PK1-3 and to 37.8% for CAgran. The average influent DOC concentration was 9.23mg/l, and the average effluent DOC concentration was 5.02mg/l for PK1-3 and 5.67mg/l for the CAgran carbon. The BDOC/DOC ratio in the influent of the BAC filters was 0.23 (Kalkan *et al*., 2011). The above results show the influence of BAC filter media type and the gradual change from adsorption to biological degradation of DOC. In addition, Reungoat *et al.* (2012) found that when DOC was removed by up to 50% trace organic compounds (TrOCs) were removed by 90%.

2.5.11 BAC filter treatment cost

For TOC reduction, O_3/BAC is a more cost-effective removal process than GAC, yet the cost of O_3/BAC treatment can double that of a conventional treatment plant (Neukrug *et al*., 1984). BAC filtration is more cost-effective than GAC filtration given that the biological activity in the BAC filters causes less pore clogging by organic matter (Ross *et al*., 2019). A reclamation plant in El Paso, Texas, replaced the BAC carbon twice during its 27 years of operation (Zhu *et al*., 2015). Zhang *et al*. (2017) estimated that the most cost-effective point of sufficient emerging contaminant removals is reached by operating dual media biologically active filters, in combination with pre-ozonation, at an EBCT of 10 minutes.

Table 2-32 below shows conceptual level costs estimate equations for BAC filters with various EBCTs. Capital cost estimates for BACs were done for an EBCT of both 10 minutes and 20 minutes, and they include the cost of filter media, backwash pumping, yard piping, filter structure, intermediate lift pumping, set work and electrical control systems.

Table 2-32 – BAC cost estimate equations at a conceptual level (Plumlee *et al.*, 2014).

Process	Capital Cost ($M/MGD)	Annual O&M Cost ($M/MGD)
BAC		
10 min EBCT, 1–10 MGD	$2.92 \times (\text{Plant Capacity, in MGD})^{-0.52}$	$0.074 \times (\text{Plant Capacity, in MGD})^{-0.19}$
20 min EBCT, 1–10 MGD	$3.03 \times (\text{Plant Capacity, in MGD})^{-0.48}$	$0.085 \times (\text{Plant Capacity, in MGD})^{-0.16}$
10 min EBCT, 10–80 MGD	$1.43 \times (\text{Plant Capacity, in MGD})^{-0.17}$	$0.059 \times (\text{Plant Capacity, in MGD})^{-0.044}$
20 min EBCT, 10–80 MGD	$1.52 \times (\text{Plant Capacity, in MGD})^{-0.15}$	$0.07 \times (\text{Plant Capacity, in MGD})^{-0.036}$

2.5.12 Assessment of the BAC filtration process performance

TOC removal is a performance indicator of BAC filters (Neukrug *et al.*, 1984). Singer *et al.* (1985) noted the trend of using $UV_{254\text{-absorbance}}$ before and after O_3 to optimize the O_3 dose when disinfection is not required before the BAC filters.

In many studies, the assessment of the BAC filtration process is with UV_{a254} or TOC removal across the process (Zhang and Shao, 2008; Selvy, 2015; Gifford, Selvy and Gerrity, 2018; Sundaram and Pagilla, 2019; Arnold *et al.*, 2018). However, no correlation was found between UV_{a254}, or TOC removal, and the removal of organic micropollutants in their groups by a BAC filter. The results of Sundaram and Pagilla's (2019) study on the O_3/BAC process showed significant improvement in removal efficiency with increasing EBCT, even after 32,000 number of bed volumes. They grouped organic micropollutants into the following three groups:

i) Organic micropollutants readily oxidised by O_3;

ii) Organic micropollutants moderately oxidised by O_3; and

iii) Organic micropollutants marginally oxidised by O_3.

Their results show that the removal of organic micropollutants marginally oxidized by O_3 increased approximately 20% to more than 90% when the EBCT was increased from 10 minutes to 20 minutes. The improvement in removal was mainly attributed to adsorption, even after 32,000 bed volumes. They also observed that smaller hydrophilic material with a high

biodegradability but a low adsorbability formed as a result of the ozonation. This leaves fewer competitors for adsorption sites, which increases the adsorption life of the GAC.

Selvy (2015) and Gifford *et al*. (2018) both studied the effects of the O_3/TOC dose ratio and EBCT on TOC removal. Both studies used MBR effluent and exhausted GAC media, deriving Equation 2.18 to Equation 2.21, to determine the optimum EBCT for TOC removal at a specific O_3/TOC ratio. They subsequently used the same O_3/TOC dose ratio to determine the TOC removal percentage. Their optimum EBCT results were determined at the level where TOC removal started to plateau.

$$Optimum\ EBCT\ (min) = 50.3 \times \left(\frac{O_3}{TOC}\right) + 1.98 \quad R^2 = 0.988$$

Equation 2.18

(Gifford *et al*., 2018)

$$Optimum\ EBCT\ (min) = 3.4192 \ln\left(\frac{O_3}{TOC}\right) + 9.96 \quad R^2 = 0.91482$$

Equation 2.19

(Selvy, 2015)

$$BAC\ TOC\ removal\ (\%) = 14.3 \times \left(\frac{O_3}{TOC}\right) + 10.1 \quad R^2 = 1$$

Equation 2.20

(Gifford *et al*., 2018)

$$\Delta TOC_{max}\ at\ optimum\ EBCT = 14 \times \left(\frac{O_3}{TOC}\right) + 14.6 \quad R^2 = 0.986$$

Equation 2.21

(Gifford *et al*., 2018)

There was no predictable correlation between UV_{a254} and the EBCT of tertiary treated wastewater effluent. Nonetheless, Zhang and Shao (2008) derived Equation 2.22, that relates UV_{a254} improvement to EBCT using river water at a constant O_3 dose ration of 0.75mgO_3/mgCOD. It should however be noted that when Equation 2.22 is used on filtered final effluent it can represent a major simplification, given the differences between river water and final effluent. Other factors, including the O_3 dose and BAC filter media, also impact the UV_{a254} across a BAC filter.

$$\Delta UV_{254}(\%) = 5.842 \ln(EBCT) + 0.046 \quad R^2 = 0.8226$$

Equation 2.22

2.6 Literature review summary

The literature study discusses the factors and parameters influencing the performance and costs of the O_3/BAC filtration process. The two groups of contaminants that the O_3/BAC filtration process handles are pathogens and organic micropollutants. These two groups of contaminants pose risks to humans if ingested, depending on their concentrations, and hence they must be removed, up to certain levels, from wastewater sources (See Section 2.1 and 2.2). The combination of the O_3 process and BAC filtration process is also critical (see Section 2.3).

Section 2.4.1 to 2.4.13 discuss various factors that influence the O_3 process, i.e. water quality parameters, O_3 injection methods, O_3 concentration, and O_3 dose. The key factors further investigated in the current study are:

i) The CT factor equals to the residual concentration multiplied by the effective contact time;

ii) The link between organic micropollutant oxidation and pathogen inactivation;

iii) The consequence of O_3 decay on the process performance and costs;

iv) The role of the O_3 contact tank on the O_3 process and costs; and

v) The success of the O_3 process to remove organic micropollutants.

Section 2.4.14 to 2.4.16 discuss the O_3 costing models, background of the grouping of organic micropollutants and the O_3 process assessment methods used in the current study.

Section 2.5.2 to 2.5.10 discuss various factors that influence the BAC filtration process, i.e. water quality parameters, filter media type, filter media depth, filtration rate, bed life and biological activity. However, the key factor further investigated in the current study is the impact of EBCT on process performance and cost;

Section2.5.11 to 2.5.12 discuss the BAC filtration process costing models and the BAC filtration process assessment methods used in the current study.

Chapter 3 : Research methodology

The current chapter describes how the research was conducted. The current research focusses on the ozone/biological activated carbon filtration (O_3/BAC) process and its application to the filtered final effluent of the Cape Flats Wastewater Treatment Works (WWTW).

The study scope is limited to the filtered secondary effluent from the Cape Flats WWTW. This water is intended to be injected into the Cape Flats Aquifer as part of an indirect reuse scheme and one of the City of Cape Town's potable water augmentation sources. Hence, the relevance of the current research given that it is an existing project which, at the time of writing, is approaching the construction phase in which the O_3/BAC process will be implemented. Also, water quality data of the Cape Flats WWTW secondary effluent are available. The current research is also timely given the severe drought that Cape Town experienced recently (Department of Water and Sanitation, 2018) after which investigations suggested that the reclamation of final effluent can promote the future water resilience of Cape Town.

The research consists of two parts. The first part is the *design research* that studies the costs of the O_3/BAC process and ways to optimize the process based on the selected treatment objective (see Sections 3.8 to 3.9). The second part is the *case study* that assesses the efficiency of the O_3/BAC process for the removal of organic micropollutants and pathogens in the context of the Cape Flats WRP (See Section 3.9 to 3.10). Table 3-1 shows how the research methodology sections are categorised.

Table 3-1 – Category breakdown of research methodology sections.

Category	Section
Site and Sampling details (materials and methods)	**3.1 Cape Flats Managed Aquifer Potable Reuse Scheme** *This section gives context to the bigger picture into which the research fits.*
	3.2 The Cape Flats WWTW location and process *This section provides the details of the research site and the WWTW process.*
	3.3 Sampling points and sampling methods *This section gives the location of the sampling points and the water quality test methods used.*
Design Approach	**3.4 O3/BAC filtration treatment objectives** *This section identifies the treatment objectives of the O_3/BAC process.*
	3.5 The O3/BAC process assessment methods *This section looks at the methods used to assess the performance of the O_3/BAC process.*

Category	Section
	3.6 O3/BAC costing models *This section lays out the costing models used in the study.*
	3.7 Comparison of US concept costing models to Southern African project costs *This section describes the method of comparison used to compare international costing models with Southern African costing models and actual costs.*
	3.8 O3 cost optimization *This section gives the procedure that was followed to investigate if there is an optimum contact time for the O_3 process.*
Case Study	**3.9 Grouping of organic micropollutants** *This section defines how the organic micropollutants found in the Cape Flats WWTW final effluent are grouped based on their second order reaction rates.*
	3.10 Organic micropollutant water quality risk assessment *This section provides the methods followed to conduct a water quality risk assessment on the organic micropollutants of Cape Flats WWTW before and after O_3 treatment.*

Section 3.1 starts by giving an overview of the Cape Flats MAR scheme. Section 3.2 gives an overview of the Cape Flats WWTW system and configuration while Section 3.3 gives an overview of the experimental procedure. Section 3.4 identifies the treatment objectives of the O_3/BAC process considered in the current research, and Section 3.5 explains how the identified treatment objectives can be assessed or validated. Section 3.6 looks at the selection of costing models, and Section 3.7 describes how the selected international costing models can be compared with South African costs. Section 3.8 describes how the optimization of the O_3 costs will be investigated. Then, Section 3.9 describes how the organic micropollutants identified in the final effluent of the Cape Flats WWTW are grouped based on their reaction rates. Finally, Section 3.10 explains how to conduct a water quality risk analysis of the water before and after the O_3/BAC process.

3.1 Cape Flats Managed Aquifer Potable Reuse Scheme

The Cape Flats Water Reclamation Plant (WRP) forms part of the *Cape Flats Aquifer Potable Reuse Scheme*. It is an indirect potable reuse scheme, which aims to inject high quality advanced treated secondary effluent into the Cape Flats Aquifer. The injected water will then be required to travel at least two months through the aquifer before being abstracted. After abstraction, it will further be treated before being distributed into the potable network.

The WRP plant will supply treated water to the aquifer by a pipeline that splits to two areas, i.e. the southern and northern areas. The ring main nearest to the beach includes a saltwater intrusion barrier (SWI). This barrier will prevent saltwater ingress into the aquifer.

The proposed injection points will be located to prevent the existing contaminated plume from spreading into the aquifer. Figure 3.1 shows a layout of the proposed ring mains. The scheme includes the following components:

i) Water reclamation plants at two WWTWs:

   a. Cape Flats WWTW (White)
   b. Borcherds Quarry WWTW (Future. Not shown)

ii) Injection pipelines and injection wells (red);

iii) Abstraction pipelines and boreholes (green); and

iv) Post aquifer tank farms and water treatment sites (yellow).

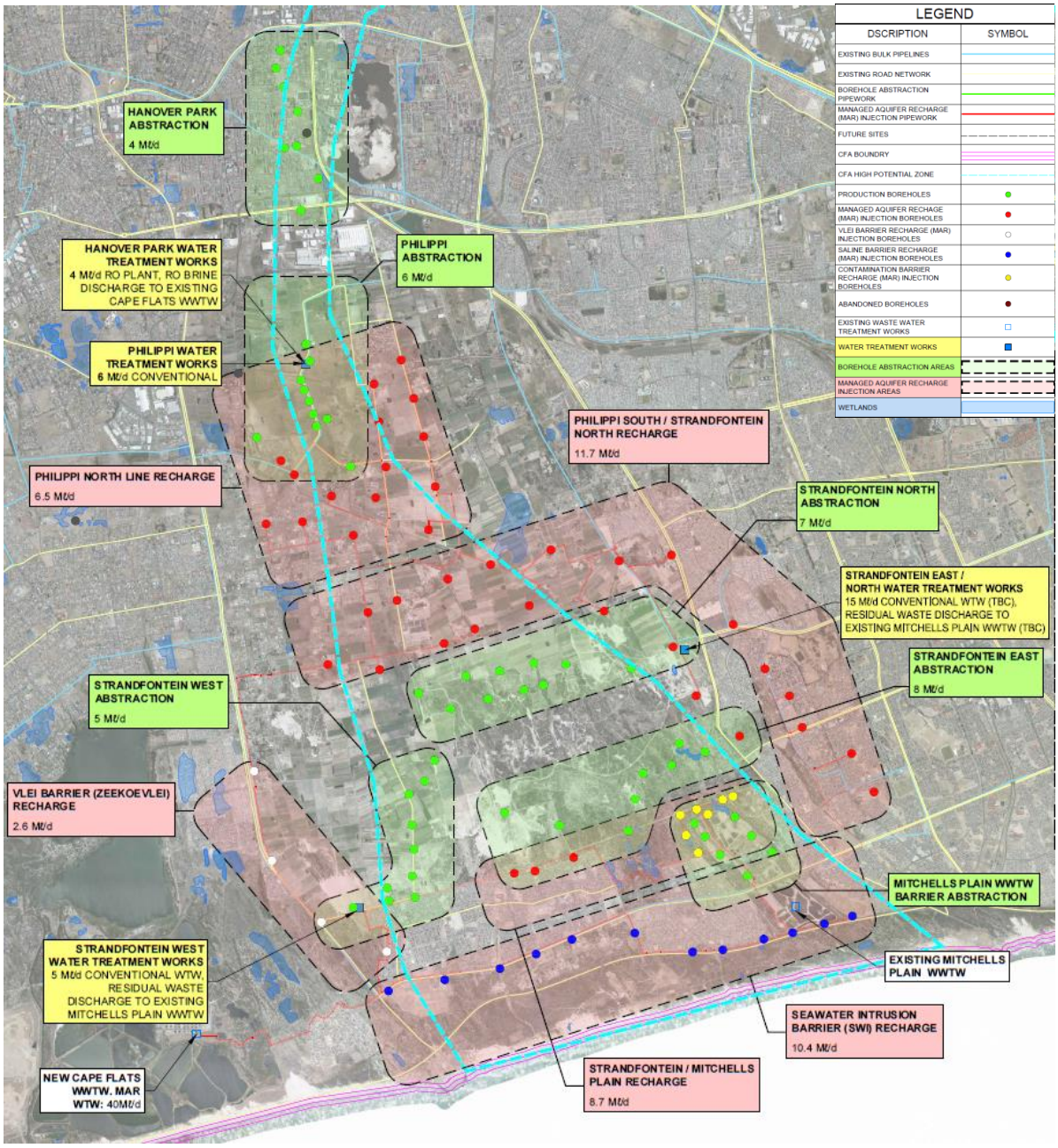


Figure 3.1 – Layout of the Cape Flats Managed Aquifer Potable Reuse Scheme.

3.1.1 The Cape Flats water reclamation plant

The overall process treatment train of the Cape Flats WRP is made up of the following components:

i) Ferric chloride dosing between the reactor and secondary settling tanks. This step is added to improve the phosphate removal in the activated sludge plant (i.e. to augment the

biological phosphate removal with chemical phosphate precipitation – iron phosphates precipitates are formed in the process);

ii) Coagulation and flocculation with ferric chloride and pH adjustment. This step also assists with binding and precipitation of remaining phosphates in addition to conventional coagulation and flocculation;

iii) Dual media filtration with anthracite and sand. It is a step for the removal of turbidity, TOC and colour. It also assists the downstream processes of O_3 disinfection and UV disinfection;

iv) O_3 (see Section 2.4) and BAC filtration (see Section 2.5). This is a pathogen and TOC removal step. It also assists with the removal of contaminants of emerging concern (CEC). This step offers the flexibility to dose acetic acid before the BAC filters, which will serve as a carbon source for the organisms in the filter; the organisms can use the carbon source to denitrify the nitrate remaining in the water;

v) Space and hydraulic allowance for GAC filters. This step offers the flexibility to upgrade the plant to include GAC filters, should it be necessary in the future.

vi) Hydrogen peroxide (H_2O_2) and UV disinfection. It's a disinfection and advanced oxidation process step;

vii) Stabilization with Caustic Soda (NaOH); and

viii) H_2O_2 dosing as an additional post disinfectant.

Figure 3.2 below shows the Process treatment train schematic of the Cape Flats MAR WRP.

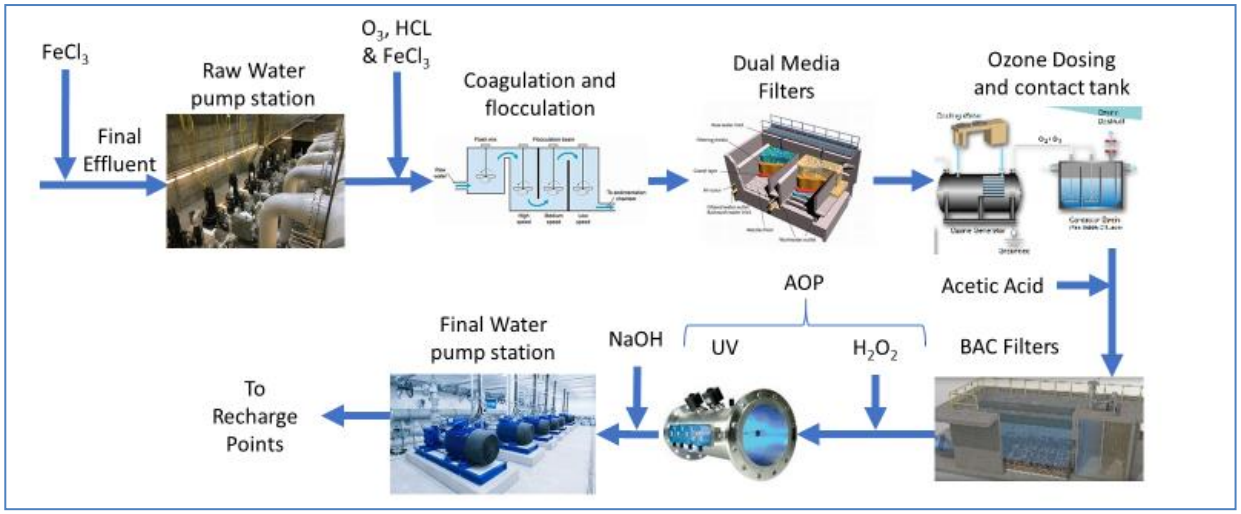


Figure 3.2 – Process treatment train schematic of the Cape Flats WRP.

The process train does not remove Total Dissolved Solids (TDS). The TDS in the treated water is dependent on what the water treatment plant receives from the wastewater treatment works.

Water quality tests on the final effluent indicated an average TDS concentration of 500 to 1000mg/l, which is within the requirements of the injection water quality standard.

When nitrate and nitrite are above their required concentrations, a carbon source (acetic acid in the case of the Cape Flats WRP) can be dosed before the BAC filters to provide the electron donor for the facultative heterotrophic organisms to denitrify the nitrate and nitrite to nitrogen gas. Alternatively, the flow to the PSTs can be manipulated to lower the TKN/COD ratio. This will improve denitrification and phosphate uptake.

For the treatment process to meet the required TOC injection water quality standard (<10mg/l), the incoming TOC level must be below 16.7mg/l. Additional sampling shows an average TOC value of 8.4mg/l in the final effluent of the Cape Flats WWTW. The proposed process train is dependent on the quality of secondary effluent it receives, that which is nitrified and denitrified and adequately settled in the Secondary Settling Tanks. The plant will have critical control points that measures certain specific parameters online to ensure that the water quality from the wastewater treatment works and throughout the plant remains within a set range. Table 3-2 below shows the considered water quality parameters and their associated injection water quality standard.

Table 3-2 – Injection water quality standard.

Water Quality Parameter	Unit	Pre-injection quality Standard	Treatment Step
Colour	mg/l Pt	50#	Will reduce the colour through the media filters and O_3/BAC process.
Total Dissolved Solids (TDS)	mg/L	≤ 1200*	Effluent quality varies between 500 to 1000 mg/l. The treatment plant will not affect TDS.
Turbidity	NTU	0.3+	Removed with media filtration. Might be slight variances in NTU due to biomass washout/colouration from the BAC filters.
Total Suspended Solids (TSS)	mg/l	1#	Removed with media filtration. Might be slight variances in TSS due to biomass washout from the BAC filters.
Total Organic Carbon (TOC)	mg/L	<10*	Removed with media filtration and O_3/BAC. When TOC > 16.7mg/l, the treatment plant will not be able to reach the water quality standard and the risk of micropollutants ending up in the aquifer is high. The operational rule will be that if effluent TOC is > 16.7mg/l, the MAR WRP will not take effluent.
Dissolved Organic Carbon (DOC)	mg/L	<10*	Removed with dual media filtration and O_3/BAC process.

Table 3-2 continued.

Water Quality Parameter	Unit	Pre-injection quality Standard	Treatment Step
Biochemical oxygen demand (BOD)	mg/L	<5[#]	BOD is removed in the O_3/BAC treatment step.
Ammonia as N (NH_4-N)	mg/L	≤ 1.5[#]	It should be reduced in the activated sludge process and further oxidized in the O_3 step. If the biological process is not nitrifying/denitrifying, then no treatment at the MAR WRP.
Nitrate plus Nitrite as N (NO_3+NO_2-N)	mg/L	<10[#]	After Cape Flats diffuser refurbishment, the expected nitrate is 9mg/l. Provision is made to dose acetic acid before the BAC filters to denitrify with the bacteria in the BAC filters.
Ortho Phosphate as P (PO_4-P)	mg/L	<1[#]	After Cape Flats diffuser refurbishment expected phosphate after biological reactor is 2 to 6 mg/l. Treated with Ferric Chloride in activated sludge plant to reduce effluent phosphates.
Iron as Fe	mg/L	<0.3*	Will be oxidised in the O_3 process and filtered out in the BAC filters.
* (SANS, 2015) [+](US EPA, 2010) [#] Adopted design standard			

3.2 The Cape Flats WWTW location and process

The proposed site for the new Cape Flats WRP is situated within the boundaries of the existing Cape Flats WWTW. Figure 3.3 shows the layout. The location of the site is on the old sludge drying beds, which are intended to be demolished. The WRP site has the following advantages:

i) Close access to the wastewater treatment plant, from where the secondary effluent can be collected;

ii) One stage pumping through a relatively short pipeline to the head of the new WRP; and

iii) Gravity flow into the new WRP.

The Cape Flats WWTW treats settled sewage through 4 process trains, each train consisting of a combination of biological reactors and secondary settling tanks. The oldest of the reactors being Reactors A and B and the newest being Reactors G and H. Tenders are out to replace the fine bubble diffusers for all the reactors. This will significantly improve the final effluent quality.

Figure 3.3 – Proposed Site Layout of the Cape Flats WRP.

The Cape Flats WWTW consists of a 5-Stage Modified Bardenpho activated sludge process. The capacity of the works is linked to the incoming flow and COD concentration, as shown in Figure 3.4 below. The capacity was determined as the point where there is no sludge carry-over from the secondary settling tanks at peak wet weather flow, and where there is sufficient sludge age for nitrification in the winter. The WWTW can be operated with or without primary settling tanks.

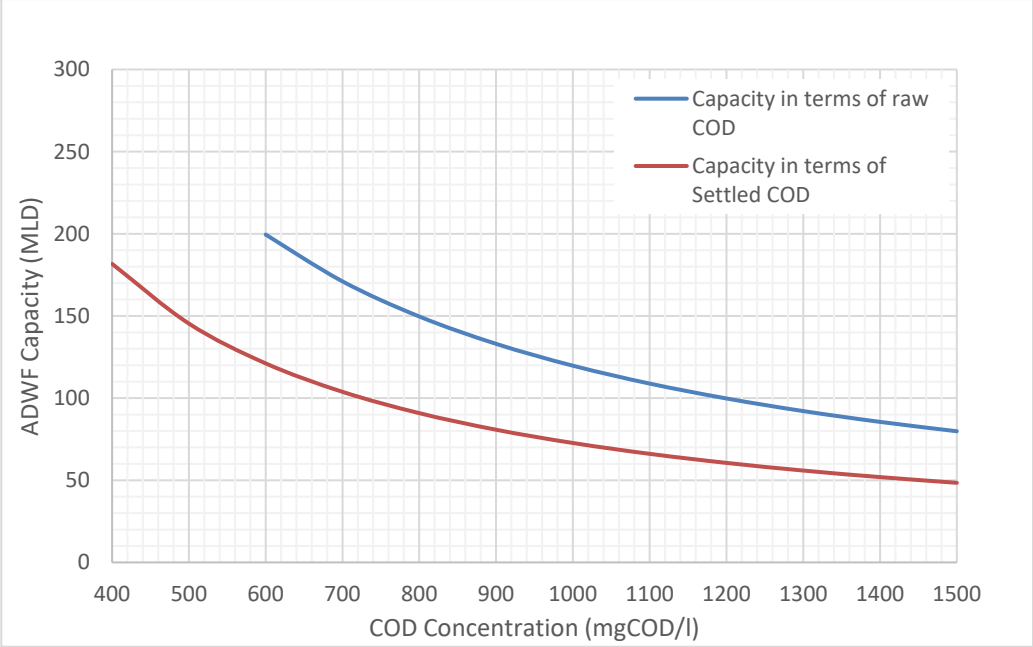


Figure 3.4 – Capacity of Cape Flats WWTW.

For the calculation of the capacity, the following assumptions and operating parameters were selected:

i) Influent data from weekly sampling by Scientific Services. The data set dates from July 2014 to October 2017 (a period of 3.25 years). Based on this data, the Cape Flats received an average of 112 tCOD/d of unsettled raw sewage.

ii) Minimum Temperature of 14 °C;

iii) Sludge Age of 17 days;

iv) PWWF/ADWF ratio of 3.0;

v) DSVI for Sludge settleability of 125 ml/g;

vi) Raw UPO COD Fraction of 13%;

vii) Raw USO COD Fraction of 5%;

viii) Settled UPO Fraction of 5%; and

ix) VFA in influent of 50 mg COD/l.

Apart from the capacity, the 5-stage Modified Bardenpho process (like the one at the Cape Flats WWTW) is not ideal for higher TKN/COD ratios. The data indicated a high settled wastewater TKN/COD ratio of 0.116, which is not ideal for the 5-stage Modified Bardenpho process (Henze *et al.*, 2008). This causes high nitrate concentrations to be recycled from the SST underflow to

the anaerobic tank, thereby inhibiting the phosphate removal. A steady-state nitrification, denitrification and biological excess phosphorous removal activated sludge model, by Henze et al. (2008), indicates an effluent nitrate concentration of 9mg N/l, which is recycled to the anaerobic zone. Hence, the unstable effluent phosphate concentrations between 2 mg-P/l and 6 mg-P/l after the biological reactor. Nonetheless, these phosphate concentrations can be reduced to 1 mg-P/l by dosing ferric chloride after the SSTs.

3.3 Sampling points and sampling methods

Water quality sampling is planned 1-2 times a year to build a baseline dataset of the expected water quality from the Cape Flats WWTW. In the current study, two samples were taken that included organic micropollutants. The first round consisted of effluent from a maturation pond (pond S4), which occurred when the reclamation plant planned to extract final effluent from the ponds. The second round consisted of SST effluent from Reactors C and D.

This research considers the following water quality datasets:

i) Organic micropollutant grab sampling by A.L. Abbott and Associates. Testing of the final effluent from Pond S4 on 24 February 2018 was done by Eurofins (see Figure 3.5 for the sampling location); and

ii) Organic micropollutant two-hourly flow weighted sampling by A.L. Abbott and Associates. Testing of the effluent from the SSTs of Reactors C and D on 1 December 2019 was done by Eurofins (see Figure 3.3 for sampling location).

Table 3-3 shows the list of organic micropollutant groups Eurofins Laboratory measured including their corresponding testing method. For the water quality tests, Eurofins Laboratory used a combination of their internal standards, normal calibration standards, and surrogate standards or isotopic-labelled standards, depending on the organic micropollutants tested.

Table 3-3 – Groups of organic micropollutants measured including their testing method.

Contaminant Group	Testing Method as reported by Eurofins laboratory report
1,2-dibromoethane (EDB), 1,2-dibromo-3-chloropropane (DBCP)	EPA 504.1
Chlorinated Acids	EPA 555
Endocrine-disrupting chemical (EDC) & pharmaceuticals and personal-care products (PPCP)	Liquid Chromatography tandem Mass Spectrometry (LC-MS/MS).
Flame Retardants	EPA 527
Volatile Organics EPA	EPA Method 524.3
Semi-Volatile Organics	EPA Method 525.2 Extended with TIC's
Herbicides	EPA Method 515.3
Pesticides	EPA Method 505
Trihalomethanes	Method 524
Haloacetic Acids	SM6251B

The list of organic micropollutants measured can be found in **Appendix A** while the water quality data results are listed in **Appendix B**.

The water quality, i.e. the organic micropollutants, was assessed using the quality standards as prescribed by the California State Water Resources Control Board (Anderson *et al.*, 2010).

Figure 3.5 – Position of Pond S4.

3.4 O_3/BAC filtration treatment objectives

The O_3/BAC filtration process can have different treatment objectives depending on its application and targeted contaminants.

3.4.1 O_3 treatment objectives

The main objective of ozonation is usually disinfection, but it can also serve as a strong oxidant that removes organic micropollutants.

For disinfection, the objective can be to target viruses, Giardia or Cryptosporidium, separately, or as a combination of them. For the current research, the disinfection objectives are a combination of any of the log removals listed in Table 3-4. The O_3 dose, for disinfection, in turn, will be determined as the product of the highest residual O_3 concentration and the effective contact time (CT-value), as required to achieve the log-removal selected in Table 3-4.

Table 3-4 – O_3 disinfection treatment objectives (CT-values sourced from Table 2-6 to Table 2-8).

	1 Log removal	2 Log removal	3 Log removal	4 Log removal
Giardia	● (CT = 0.38 @ 13°C)	● (CT = 0.76 @ 13°C)	● (CT = 1.14 @ 13°C)	
Cryptosporidium	● (CT = 7.5 @ 13°C)	● (CT = 15 @ 13°C)	● (CT = 22.5 @ 13°C)	
Viruses		● (CT = 0.38 @ 13°C)	● (CT = 0.62 @ 13°C)	● (CT = 0.76 @ 13°C)

For O_3 organic micropollutant oxidation, the O_3 dose ratio determines the treatment objective to be reached. Table 3-5 below shows the appropriate O_3 dose ratio based on the group of organic micropollutants targeted (see Table 2-27 showing organic micropollutant groups definition).

Table 3-5 – O_3 oxidation treatment objectives (Adapted from Snyder *et al*. 2014).

O_3/TOC ratio	Group1	Group2	Group 3	Group 4	Group5
0.25	●				
0.5	●	●			
1	●	●	●		
1.5	●	●	●		●
>1.5 (1.6 used in calculations)	●	●	●	●	●

To summarize, there are nine possible disinfection objectives (as identified in Table 3-4) and five possible oxidation objectives (as identified in Table 3-5) for O_3 treatment. They are:

i) 3-log Cryptosporidium O_3 inactivation;

ii) 2-log Cryptosporidium O_3 inactivation;

iii) 1-log Cryptosporidium O_3 inactivation;

iv) 3-log Giardia O_3 inactivation;

v) 2-log Giardia O_3 inactivation;

vi) 1-log Giardia O_3 inactivation;

vii) 4-log Virus O_3 inactivation;

viii) 3-log Virus O_3 inactivation;

ix) 2-log Virus O_3 inactivation;

x) Group 1 organic micropollutant O_3 oxidation;

xi) Group 2 organic micropollutant O_3 oxidation;

xii) Group 3 organic micropollutant O_3 oxidation;

xiii) Group 4 organic micropollutant O_3 oxidation; and

xiv) Group 5 organic micropollutant O_3 oxidation;

The O_3 disinfection and oxidation treatment objectives are compared by using the following equations:

i) Equation 2.7 (Section 2.4.1) that gives the CT-value as a function of time, TOC, IOD, and O_3 dose;

ii) Equation 2.8 (Section 2.4.2) that relates the ozone CT to the O_3/TOC ratio with bench-scale experiments on filtered effluent;

iii) Equation 2.10 (Section 2.4.2) that gives the amount of O_3 exposure (CT-value) that can be obtained at various O_3 dose ratios; and

iv) Equation 2.11 (Section 2.4.6) that estimate the residual O_3 concentrations in secondary and tertiary wastewater effluents as a function of O_3 dose concentration, TOC concentration, IOD, time, and decay constant - k.

3.4.2 BAC filtration treatment objectives

BAC filter organic micropollutants and TOC removal are linked to the BAC empty bed contact time (EBCT) and also to the O_3/total-organic-carbon (O_3/TOC) dose ratio (Sundaram & Pagilla, 2019). In the current study, only EBCT is used as a variable to select a treatment objective for the BAC filters. Figure 3.6 shows a chart of the TOC removal efficiency, for various EBCTs, and the influent TOC concentration for a BAC filter. The chart can be used as an additional guideline for the selection of EBCT when TOC removal is the target. The chart is based on 0.2-0.3kgTOC/d/carbon-m^3 removed in a BAC filter after its adsorption capacity has been depleted, as determined by Sundaram and Pagilla (2019). The error bars at the top of each bar represent the difference between 0.2 and 0.3kgTOC/d/ carbon-m^3.

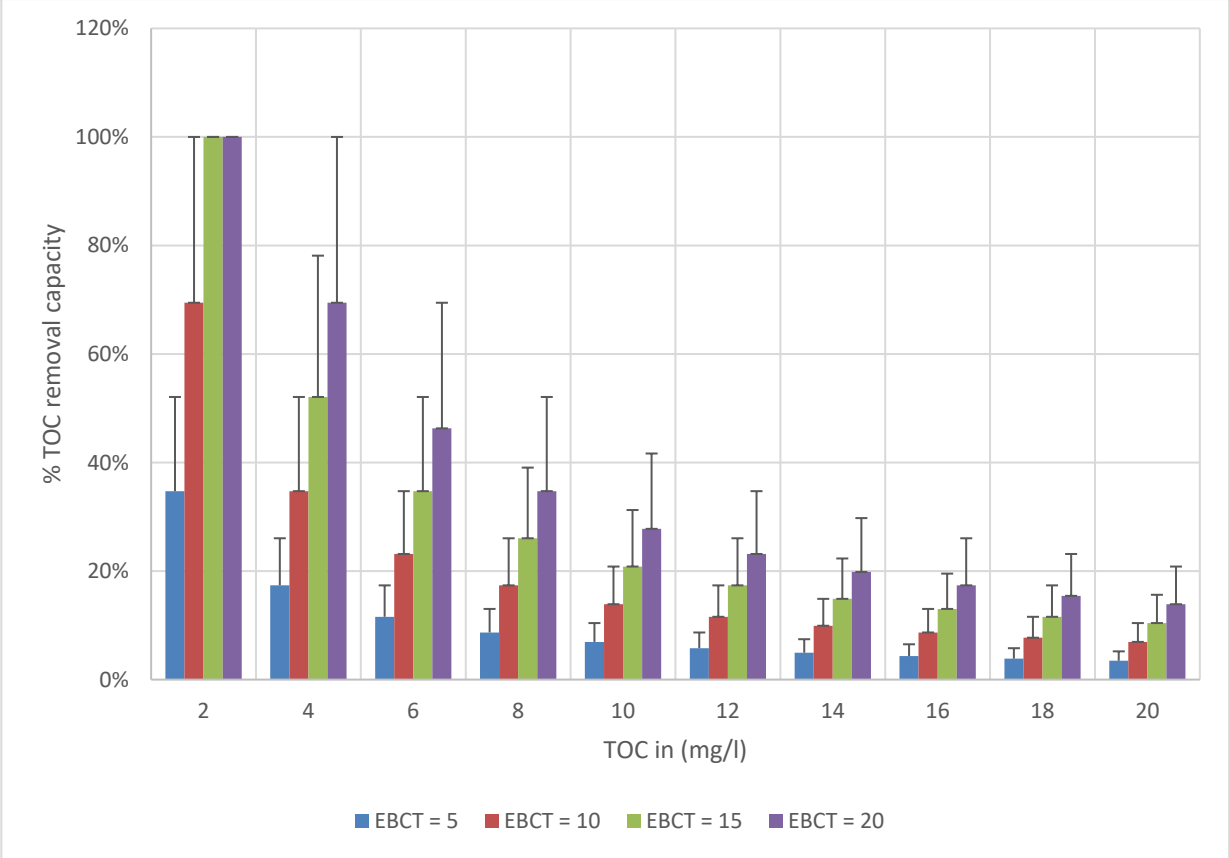


Figure 3.6 – BAC filtration TOC removal as a function of TOC_{in} and EBCT.

Figure 3.6 above is a different presentation of the finding of Sundaram and Pagilla, (2019) which shows that removal of TOC in a BAC filter is not only dependant on the EBCT but also the influent TOC concentration. TOC removal drop as the influent TOC concentration increase. These findings will be used to interpret the results of the current study.

As shown in Table 3-6, the current research has identified three treatment objectives for BAC filtration, including targeting readily oxidizable (group 1-2), moderately oxidizable (group 1-3) or marginally oxidizable (group 1-5) organic micropollutants. The table also shows that when the O_3/BAC process is the main organic micropollutant removal step, an EBCT of approximately 20 minutes is more efficient to remove organic micropollutants (Sundaram & Pagilla, 2019).

Table 3-6 – BAC Filtration treatment objectives (adapted from Sundaram and Pagilla [2019]).

EBCT (minutes)	Organic micropollutants readily oxidised by O_3	Organic micropollutants moderately oxidised by O_3	Organic micropollutants marginally oxidised by O_3
10	●		
15	●	●	
20	●	●	●
Example of organic micropollutants	Naproxen, triclosan, Gemfibrozil, carbamazepine (Group 1-2)	Sucralose, DEET, Atenolol, Sulfamethoxazole (Group 1-3)	TDCPP, TCEP, TCPP (Group 1 – 5)

When selecting a BAC filtration treatment objective, the complete process train must be considered. In a multi-barrier treatment plant, the treatment objective of BAC filtration is usually a low selection of micropollutant groups, groups 1 to 2 or 1 to 3 for example, leaving the rest of micropollutants to be removed by another process in the train.

3.5 The O_3/BAC process assessment methods

From the literature summary in Section 2.4.16 and Section 2.5.12, the parameters in Table 3-7 were identified and used to assess the treatment objectives of the O_3/BAC process.

Table 3-7 – Assessment parameters of the O_3/BAC process for the two main objectives.

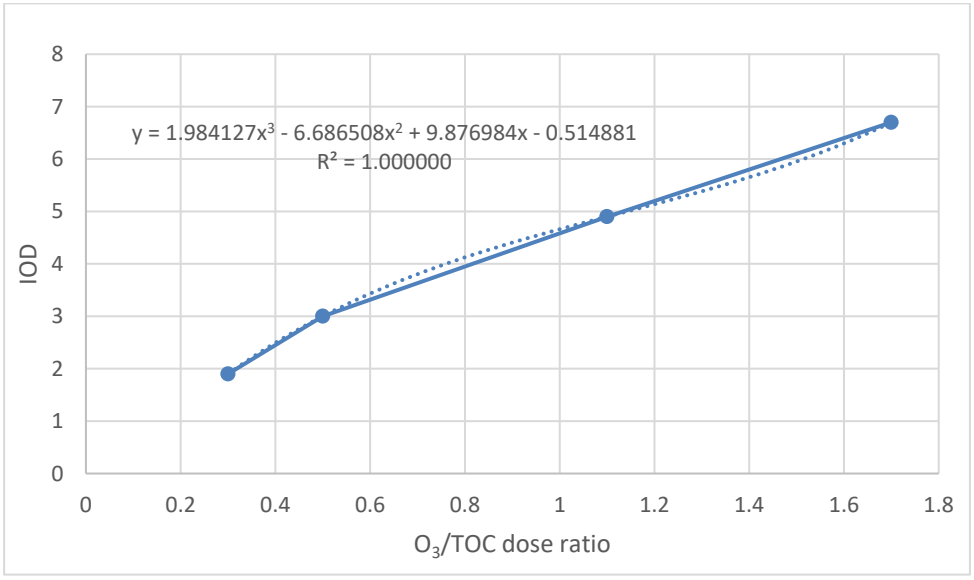
Objective	O_3	BAC filtration
Organic micropollutants	UV_{a254}	EBCT and UV_{a254} or TOC
Pathogens	CT - Value	-

UV_{a254}, as measured by a spectrophotometer or equivalent apparatus, is practical to measure and relates to various target compounds. It is therefore identified as the most suitable primary measurement of process performance for the O_3/BAC process in this study.

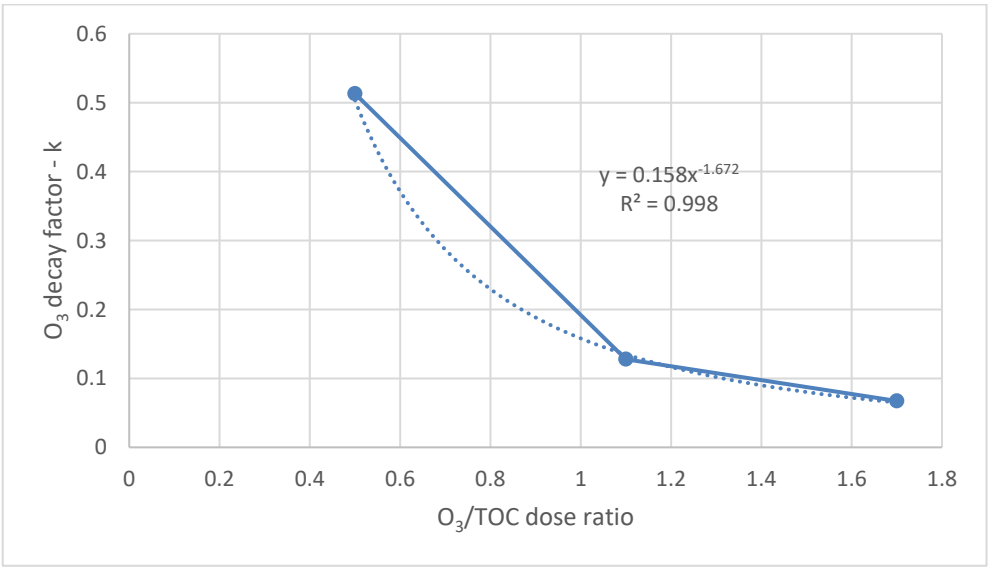
3.5.1 O_3 process assessment

As discussed in Section 2.4, various factors influence the O_3 process. Nonetheless, the factors that the current research focuses on are the instantaneous O_3 demand (IOD) and the O_3 decay rate (k). The O_3 decay rate (k) is influenced by the O_3 dose ratio (O_3/TOC) as is evident from the respective k-values at the three ozone dose ratios 0.5, 1.1 and 1.7-O_3/TOC in Table 2-14.

In order to assess the performance of the O_3/BAC treatment process, the IOD and O_3 decay factors (k-factors) presented in Table 2-14 were used. These factors were selected given that the water quality for which they were determined (See Table 2-13 as per Gerrity *et al*. [2014]) closely matches the water quality of the filtered Cape Flats final effluent (refer to Section 3.2). There is a relationship between the IOD and k-factors and their corresponding O_3/TOC dose ratio (See Table 2-14). Equation 3.1 gives the adopted third-order polynomial regression function and also the relationship between the O_3/TOC dose ratio and the IOD (adapted from Gerrity *et al*. 2014). Equation 3.2 gives the selected power-function regression and also the relationship between the O_3/TOC dose ratio and the O_3 decay factor (k) (adapted from Gerrity *et al*. 2014).



Equation 3.1



Equation 3.2

The O_3 contact tank baffling factor also plays a role in the CT-value credited to the O_3 disinfection process. For the current study, a baffling factor of 0.67 was used, which implies "superior" flow distribution (baffling) according to Table 2-9.

Various CT-value regression formulas that relate the O_3/TOC dose ratio to the achieved CT-value are presented in Section 2.4.1. The various existing methods to validate CT-values achieved in a system are discussed in Section 2.4.1. The current research focuses on the *CSTR method* and the *T_{10} method*. The CSTR method is also described as an integrated approach. It is implemented by dividing the O_3 contact tank into segments and then measuring the residual O_3 for each segment. Then, the residual O_3 is multiplied by the time it takes for the water to flow between segments (Δt). The blue columns in Figure 3.7 represent the segments of the O_3 contact tank, when using the CSTR method. The T_{10} method determines the CT-value as the product of the total effective contact time and the residual O_3 at the end of the contact tank, for the entire contact tank (depicted by the orange block in Figure 3.7). Alternatively, the T_{10} method sums up the CT products of the individual segments of the contact tank, similarly to the CSTR method. In the current research, however, the T_{10} method is implemented for the entire contact tank.

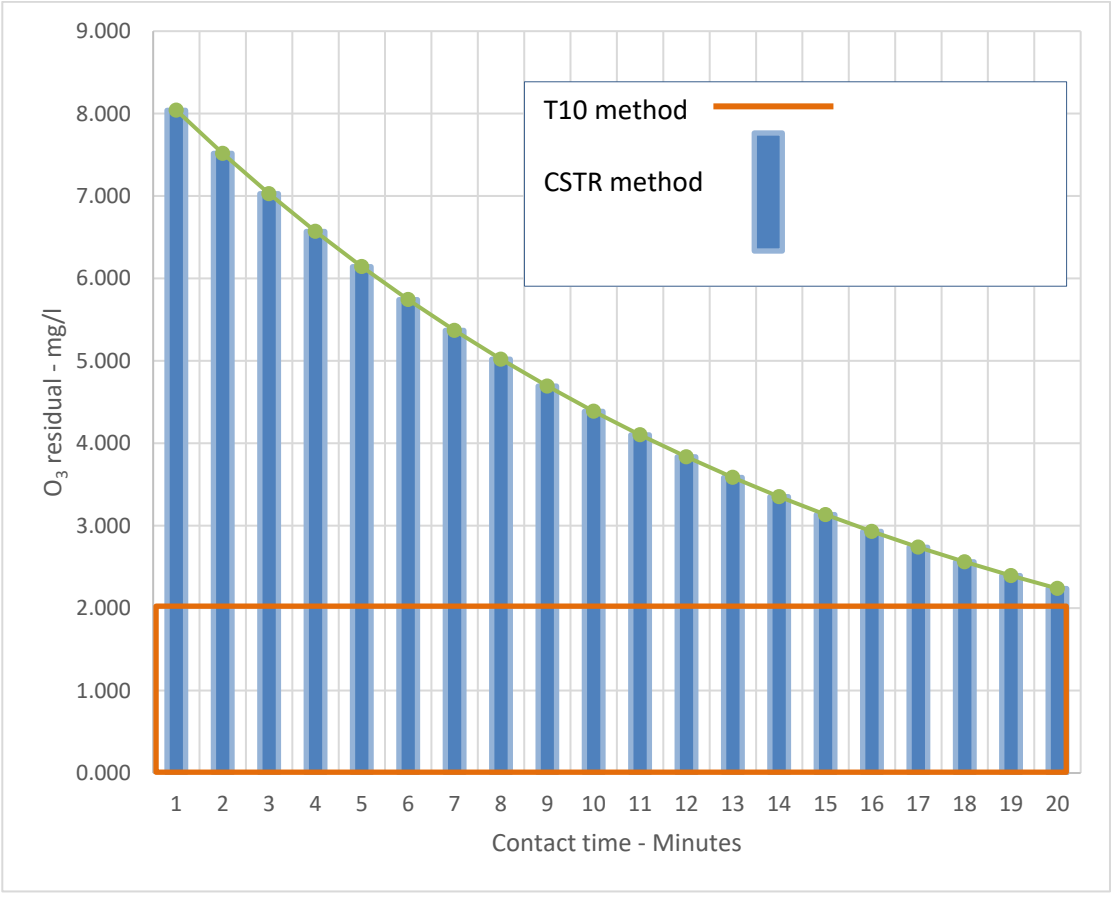


Figure 3.7 – Explaining the CSTR method and the T_{10} method.

In the current research, the O_3/TOC dose ratios required for the O_3 process, as determined by the three process performance validation methods are compared. The equations of the performance validation methods are listed in Table 3-8 below. The results of this comparison are given in Section 4.1.1.

Table 3-8 – O_3 process performance assessment methods and corresponding equations.

Method	**Conservative regression**	**CSTR method (Integration method)**	**T_{10} method with one residual O_3 reading**
Equation	Equation 2.8	Equation 2.7	Equation 2.11 later adapted to Equation 3.8 in Section 3.8

Equation 2.8 gives the lowest CT-value credit when compared to the others and is used to represent the conservative case in the comparison. Equation 2.7 represents the integrated approach (or the CSTR method) to the O_3 process assessment/validation and Equation 2.11 the T_{10} method.

3.5.2 BAC filtration assessment

Section 2.5 describes the various factors influencing the BAC filtration process. The BAC filtration process requirements for each of its treatment objectives (as identified in Section 3.4) are compared in Section 4.1.3 by using Equation 2.18 to Equation 2.22 as follows:

i) Equation 2.18 and Equation 2.19 for optimum EBCT;

ii) Equation 2.20 and Equation 2.21 for TOC removal estimation; and

iii) Equation 2.22 for UV_{a254} removal.

3.6 O_3/BAC costing models

The costing models that are used are discussed in Section 2.4.14 and Section 2.5.11 of the literature review. They are conceptual level costing models (defined by the American Association of Cost Estimation as class 4 - planning level), designed to be used as a basis for comparison, and they yield accuracies between -30–50%. The cost curves were developed on a per-unit-flow basis and bench-scale projects were used to determine the annual operation and maintenance (O&M) costs. All cost curves are in 2011 United States Dollar and adjusted to the September 2011 Engineering New-Record construction cost index.

The O_3 capital cost equations shown in Table 2-25 (for the O_3 dose of 3mg-O_3/l) and Equation 2.12 (for the O_3 dose > 3mg-O_3/l) are used in this study. According to Snyder *et al*. (2014), the O_3 capital cost consists of the components listed in Table 3-9.

Table 3-9 – Components of O_3 capital cost (Snyder et al., 2014).

Reference Number	Description	Detail
1.	O_3 contact tank cost	For a contact tank with retention time of 5 minutes.
2.	O_3 equipment capital cost	O_3 duty generators and 1standby generator, LOX system, nitrogen gas system, O_3 injection, O_3 destruction, monitors, and a control system.
3.	Installation cost	30% of 2
4.	O_3 system cost	1+2+3
5.	Yard piping	10% of 4
6.	Sitework and landscaping	5% of 4
7.	Site electrical and control construction cost	20% of 4
8.	All trades subtotal	4+5+6+7
9.	Contractor overhead and profit	15% of 8
10.	Contingency	30% of 8
11.	Total construction cost	8+9+10
12.	Engineering, legal and administrative cost	35% of 11

The O_3 annual O&M cost can be estimated by the equation in Table 2-25 (for O_3 a dose of 3mg-O_3/l) and Equation 2.13 (for O_3 doses greater than 3mg-O_3/l). Both equations are used in this study. O_3 O&M cost consists of the following components (Snyder *et al*., 2014):

i) O_3 generation energy cost \$0.0988/kWh in 2011 \$; and

ii) O_3 destruction energy cost \$0.0988/kWh in 2011 \$.

The annual O&M cost calculated above by Equation 2.13 does not include liquid oxygen (LOX) consumables. For the purpose of the current study, LOX is used for O&M costing purposes at an O_3 dose concentration of 10%. From Figure 3.8, it can be seen that the LOX cost per pound (lb) of O_3 generated is \$0.5/lb-O_3 or \$1.1/kg-O_3.

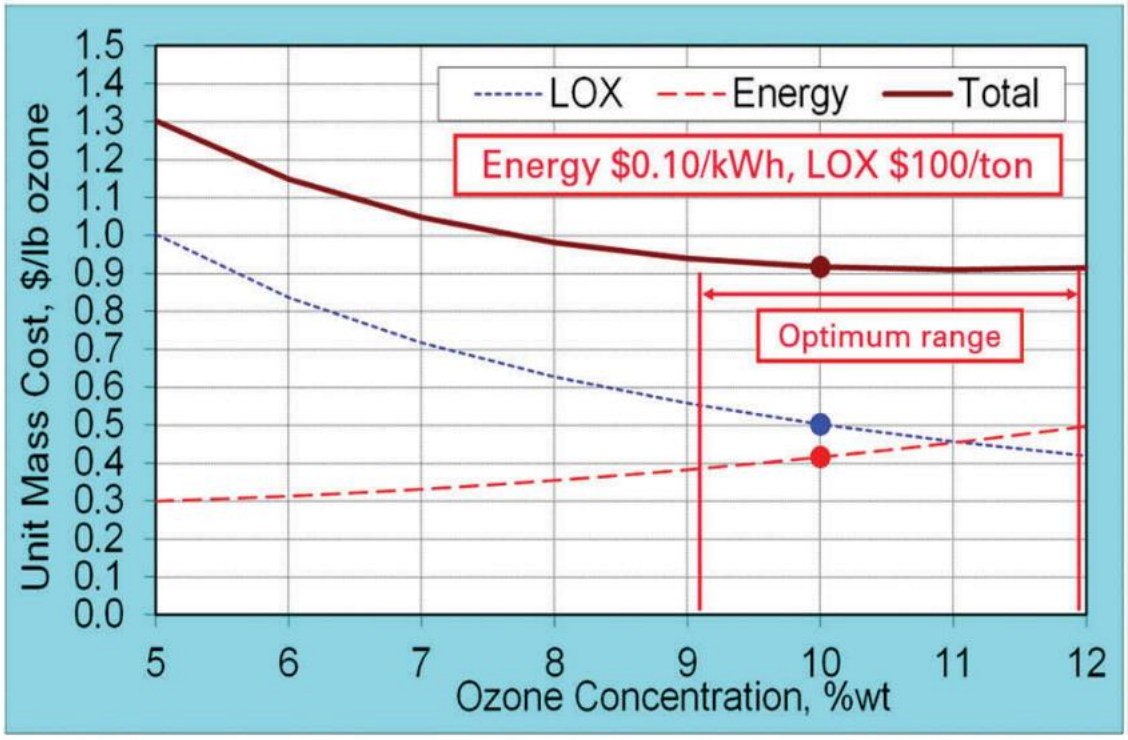


Figure 3.8 – O_3 Energy cost and LOX consumption cost (Mundy *et al*., 2018).

The published costs of Figure 3.8 are compared to LOX costs obtained from a local South African supplier in 2018 (at R2.85/kg) and inflated to a 2020 price (R3.2/kg). It should, however, be noted that LOX costs are lower if higher volumes are used, and the above LOX price is for a 310t/month user. A comparison of the annual LOX costs over a range of O_3 production doses (kg/d) are shown in Figure 3.9 below.

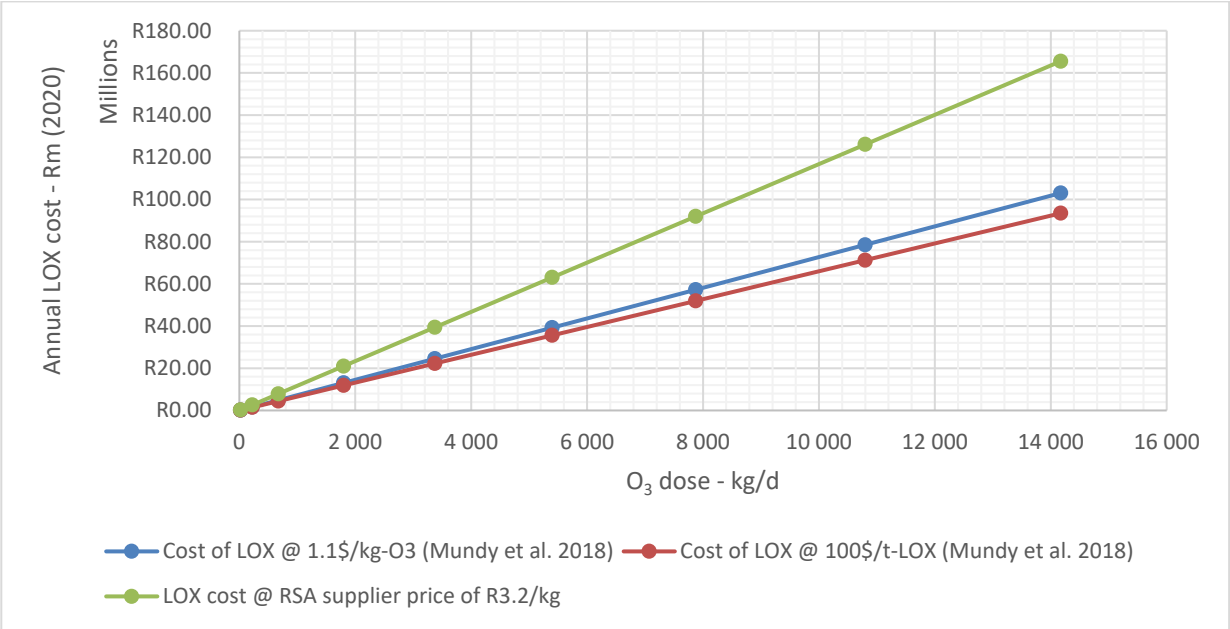


Figure 3.9 – Comparison of literature LOX cost with South African supplier LOX cost at various O_3 doses.

From Figure 3.9 above, it can be seen that the South African LOX costs that are used in the costing models are considerably higher than those published by Mundy *et al*. (2018). The South African LOX cost are used in the costing models.

The BAC filters capital cost equations shown in Table 2-32 are used in the current study. The BAC filters capital cost consists of the components Table 3-10.

Table 3-10 – Components of BAC filtration cost (Snyder et al., 2014).

Reference Number	Description	Detail
1.	BAC filter structure	
2.	GAC media	0.45g/cm^3 @ $1.65/lb and installation 30% of media cost.
3.	Backwash pumping	
4.	Intermediate pumping	
5.	Total process capital cost	1+2+3+4+5
6.	Yard piping	10% of 5
7.	Sitework and landscaping	5% of 5

Reference Number	Description	Detail
8.	Site electrical and control construction cost	20% of 5
9.	All trades subtotal	5+6+7+8
10.	Contractor overhead and profit	15% of 9
11.	Contingency	30% of 9
12.	Total construction cost	9+10+11
13.	Engineering, legal and administrative cost	35% of 12

The BAC filters O&M cost equations shown in Table 2-32 are used in this study. The BAC filtration O&M cost consists of the following components (Snyder *et al*., 2014):

i) GAC replacement every eight years;

ii) Energy (1kWh/1000gal @ $0.0988/kWh [U.S. Energy Information Administration, 2010]); and

iii) Labour ($20.27/hr for water/wastewater treatment plant operators (U.S. Bureau of Labor Statistics, 2011) x 1.85 for overhead costs).

The cost estimate equations presented above are used to determine the total cost (annualised capital and annual O&M) of the O_3/BAC process for each of the treatment objectives identified in Section 3.4 and for the three assessment/validation methods of Table 3-8, over a 20-year project lifetime. All costs are in 2011-US-dollar terms.

The first step of this part of the current study is to bring the cost functions to 2020-US-dollar terms using an average annual inflation rate of 1.74%, as calculated using data from COINNEWS MEDIA GROUP, (2020) between 2011 and 2020.

The second step is to convert the 2020-US-dollar costs to South African Rands using the average monthly rand-dollar exchange rate of R17.16/$ for June 2020, as reported by Nedbank (2020).

Capital costs are presented as current (year 2020) costs and O&M costs are presented as current (year 2020) annual costs. Life cycle costs (LCC) are calculated as current present value (PV) costs (year 2020 Rand) using the discounted cash flow method over the project lifetime of 20-years, as presented by Dijk, (2006). The PV LCC calculations are done in Microsoft Excel using

the excel functions as described in Sections 4.2 and 4.6 of Blank and Tarquin (2008:84-97) for "*present worth analysis of equal life alternatives for two or more alternatives*". The method accounts for the capital cost in the first year, which is annualised, and then added to the annual O&M cost for the rest of the 20 years. Furthermore a discount rate of 6% is used and so also is the average annual South African inflation (since 2009) of 5.35% (Macrotrends, 2020) to compare different treatment alternatives for a 40MLD treatment plant. A summary of the PV LCC input parameters is given in Table 3-11. The results are shown in Section 4.2.

Table 3-11 – PV LCC input parameters

Parameter	Value
Evaluation method	Discounted cash flow method over the project lifetime of 20-years.
Discount rate	6%
Annual inflation rate – United States	1.74% (COINNEWS MEDIA GROUP, 2020)
Annual inflation rate – South Africa	5.35% (Macrotrends, 2020)
Evaluation period	20-years
Rand dollar exchange rate	R17.16/$ (Nedbank, 2020)
Treatment base case	40MLD O_3 process that receives 9mg/l of TOC with a treatment objective is 3-log Cryptosporidium removal, i.e. a CT-value of 22.5mg-min/l

3.7 Comparison of US concept costing models to Southern African project costs

The costing models that are used in this section of the study are conceptual level costs with a significant degree of inaccuracy, as discussed above in Section 3.6. Nonetheless, they are appropriate for use in comparing different treatment options based on cost. This Section of the study aims to apply the international costing models to actual projects in Southern Africa (Cape Flats MAR WRP in South Africa and Goreangab WRP in Namibia) and then compare their actual costs to that predicted by the models. In order to compare the costs of similar systems the costing models must be adjusted to the conditions of the actual projects. In this adjustment, the O_3 dose, O_3 dose ratio, EBCT, filtration rate and contact time aforementioned are considered. To make this comparison, the costs are brought to 2020 South African Rands (SAR) as described in Section 3.6.

The following comparisons are made:

i) US concept level O_3 capital cost estimates vs. actual Southern African O_3 costs;

ii) South African published O_3 capital cost estimates vs. actual Southern African O_3 costs;

iii) US concept level O_3 O&M cost estimates vs. South African O_3 O&M cost estimates; and

iv) US concept level BAC capital cost estimates vs. actual Southern African BAC costs;

For the O_3 system, the SAR cost functions are compared and adjusted to the O_3 capital and O&M cost functions, as presented by Van Der Walt *et al.* (2009). They noted that after the consideration of all the factors for the O_3 production, the production cost is R30/kgO_3 (O&M costs in 2009 Rands), which is adjusted to 2020 SAR for comparison purposes. The capital cost curve of the current study is shown in Figure 3.10. This cost curve includes the contact tank, storage buildings for the O_3 equipment and all associated civil work. The O_3 equipment includes the O_3 generators, air preparation equipment, pipework, O_3 dosing equipment, O_3 destructors, and all instrumentation and control systems associated with the O_3 system, which are similar to the items considered in the cost functions presented in Section 3.6.

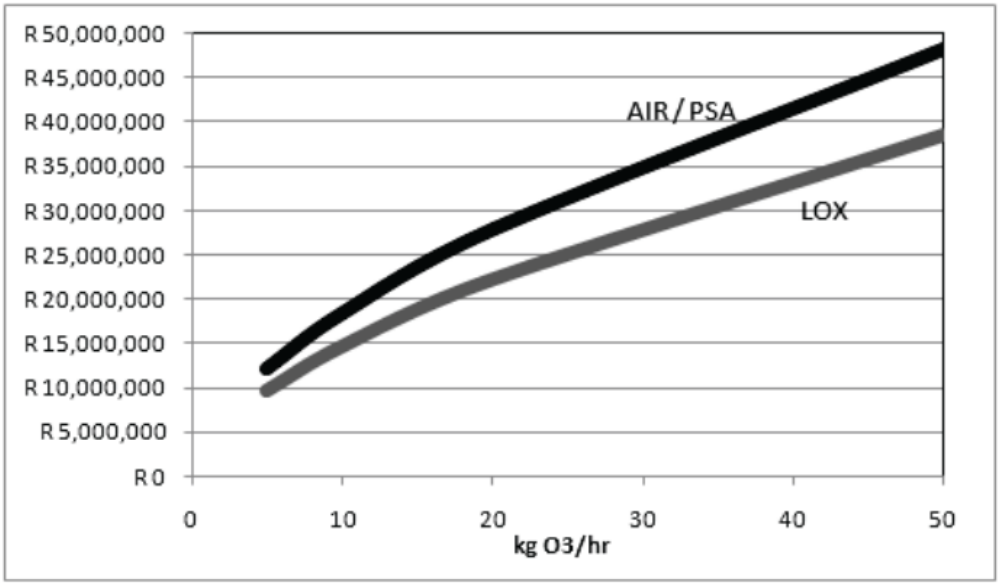


Figure 3.10 – O_3 system capital cost function per kgO_3/hr produced in 2009-Rand as reported by Van Der Walt *et al.* (2009).

The O_3 and BAC SAR-cost functions are compared to the actual capital and O&M costs of two known projects in Southern Africa. The first project is the New 21MLD Goreangab water reuse plant, as provided by Turner *et al.* (2015), and the second project is the Cape Flats O_3/BAC system (40MLD), as provided by tenders received for the project. The details of the plants in the

above projects are shown in Table 3-12. The costs of the projects are adjusted to include 15% for contractors overheads and profit, 30% for contingencies, and 35% for engineering, legal and admin costs, as provided by Snyder *et al*. (2014). For the comparisons of the costs of the two projects, refer to Section 4.3.

Table 3-12 – Details of the O_3/BAC process at Cape Flats WRP and New Goreangab WRP (Turner *et al*., 2015).

Parameter	Goreangab O_3/BAC process (FMG Goreangab Joint Venture, 2006)	Cape Flats O_3/BAC process (Smuts & Marais, 2018)
Flow (MLD)	21	40
O_3/TOC ratio	1.37	2
O_3 dose – kgO_3/hr (max)	18	52
O_3 contact time (minutes)	18	24
No. of O_3 generators	3 (2+1)	3 (2+1)
EBCT (minutes - max)	10	18
mg-O_3/l dosed	20.57	31.20
Design mg-TOC/l incoming	15.00	15.60

3.8 O_3 cost optimization

The current section aims to investigate the lowest-cost point (optimal in terms of cost) between residual O_3 concentration (C) and O_3 contact time (T) in the CT concept. The longer the contact time (T), the higher the cost of the contact tank. In contrast, the larger the residual O_3 concentration (C), the higher the O_3 capital and O&M costs.

The cost functions presented in Section 3.6 are used for the O_3 system capital and O&M costs and to investigate the existence of an optimum point. The capital cost functions of Section 3.6 are for a contact time of 5 minutes. A cost function for varying O_3 contact tank volumes is derived using Table 3-13 below.

Table 3-13 – O_3 contact tank capital cost per unit volume of tank (Snyder *et al*., 2014).

System Capacity (MGD)[a]	Total Volume (Gal)[b]	No. of Contactors	Contactor Volume (gal)	No. of Cells	Contactor Width (ft)[c]	Contactor Cost ($)
10	34 700	2	17 300	2	15.2	$ 98 400.00
16	55 500	2	27 700	2	24.4	$ 133 000.00

Table 3-13 continued.

System Capacity (MGD)[a]	Total Volume (Gal)[b]	No. of Contactors	Contactor Volume (gal)	No. of Cells	Contactor Width (ft)[c]	Contactor Cost ($)
21	74 000	2	37 000	3	21.7	$ 161 000.00
41	141 000	2	70 700	6	20.7	$ 244 000.00
52	180 000	2	90 100	8	19.8	$ 285 000.00
200	693 000	6	116 000	10	20.3	$ 1 000 000.00
288	999 000	8	125 000	10	22.0	$ 1 400 000.00
389	1 350 000	12	113 000	10	19.8	$ 1 970 000.00
535	1 860 000	16	116 000	10	20.4	$ 2 680 000.00

[a]Based on an ozone dose of 3mg/l

[b]Based on a contactor HRT of 5 min

[c]Based on a depth of 24 ft (including 5 ft freeboard), length of 4 ft/cell, not to exceed 10 cells

The cost function derived from Table 3-13 is given in Figure 3.11. This is used to adapt the cost functions for various contact times other than 5 minutes, since the cost O_3 cost functions were derived for a contact tank of 5 minutes.

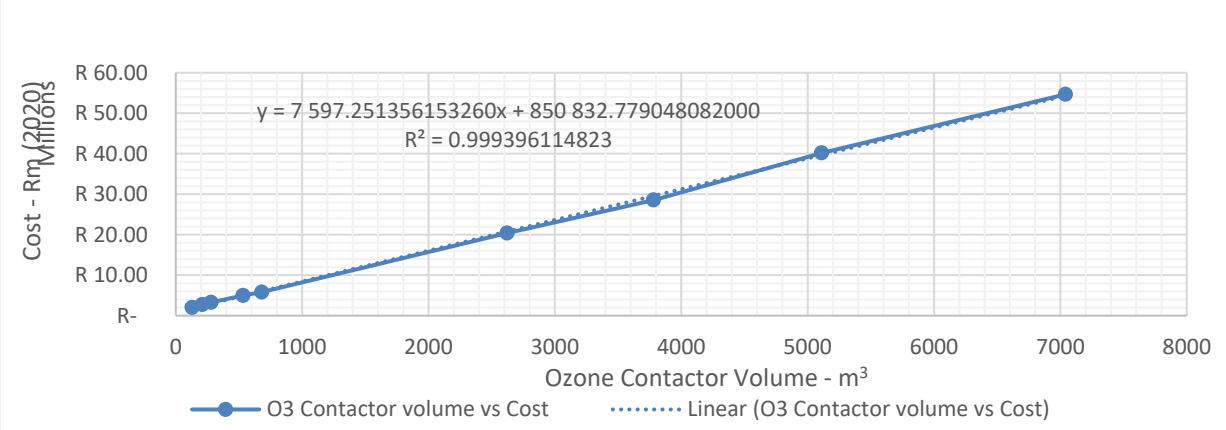


Figure 3.11 – O_3 contact tank volume vs cost with the corresponding cost function.

In order to determine the lowest-cost point, the IOD and O_3 decay factors (k-factors) presented in Table 2-14 and the adopted O_3/TOC dose ratio relationships presented by Equation 3.1 and Equation 3.2 are used.

Furthermore, the O_3 dose ratio at the beginning of the O_3 contact tank is determined by Equation 3.3 below that gives the O_3/TOC dose ratio that corresponds to the incoming TOC ratio and O_3 dosed (i.e. $O_{3\text{-dosed}}$).

$$\frac{O_3}{TOC} = \frac{\frac{O_{3-dosed}}{TOC_{in}}}{O_3 transfer_{efficiency}} \qquad \textbf{Equation 3.3}$$

Rewriting Equation 3.3 in terms of $O_{3\text{-dosed}}$ yields Equation 3.4. Equation 3.4 gives the $O_{3\text{-dosed}}$ in terms of the O_3/TOC dose ratio, O_3 $transfer_{efficiency}$ and TOC_{in}.

$$O_{3-dosed} = \frac{O_3}{TOC} * O_3 transfer_{efficiency} * TOC_{in} \qquad \textbf{Equation 3.4}$$

Rewriting Equation 2.11, which takes account of the O_3 decay, in terms of $O_{3\text{-dosed}}$ or O_3/TOC*TOC yields Equation 3.5. Equation 3.5 gives O_3-dosed in terms of the residual O_3, i.e. $O_{3\text{-residual}}$, at the end of the contact tank and IOD (adapted from Gerrity *et al*. 2014).

$$O_{3-dosed} = \frac{O_{3-residual}}{e^{-kt}} + IOD \qquad \textbf{Equation 3.5}$$

When $O_{3\text{-residual}}$ is replaced by CT/t from the CT concept, Equation 3.6 is obtained that gives $O_{3\text{-dosed}}$ in terms of *CT*, O_3 decay factor (*k*), contact time (*t*) at the end of the contact tank and *IOD* (adapted from Gerrity *et al*. 2014).

$$O_{3-dosed} = \frac{\frac{CT}{HDT * f_{baffling}}}{e^{-kt}} + IOD \qquad \textbf{Equation 3.6}$$

When the IOD term in Equation 3.6 is replaced by Equation 3.1, and the decay factor (*k*) in Equation 3.6 is replaced by Equation 3.2, then Equation 3.7 is obtained that gives $O_{3\text{-dosed}}$ in terms of the O_3/TOC dose ratio and contact time (*t*) at the end of the contact tank.

$$O_{3-dosed} = \frac{\frac{CT}{HDT * f_{baffling}}}{e^{-\left(0{,}158\left(\frac{O_3}{TOC}\right)^{-1{,}672}\right)t}} + 1{,}984127\left(\frac{O_3}{TOC}\right)^3 - 6{,}686508\left(\frac{O_3}{TOC}\right)^2 + 9{,}876984\left(\frac{O_3}{TOC}\right) - 0{,}514881$$

Equation 3.7

When Equation 3.4 and Equation 3.7 are combined, Equation 3.8 is obtained that yields the derived expression to determine the O_3/TOC dose ratio when *CT*, contact time (*t*) O_3 $transfer_{efficiency}$, and TOC_{in} are known.

$$\frac{O_3}{TOC} * O_3 transfer_{efficiency} * TOC_{in} = \frac{\frac{CT}{HDT * f_{baffling}}}{e^{-\left(0{,}158\left(\frac{O_3}{TOC}\right)^{-1{,}672}\right)t}} + 1{,}984127\left(\frac{O_3}{TOC}\right)^3 - 6{,}686508\left(\frac{O_3}{TOC}\right)^2 + 9{,}876984\left(\frac{O_3}{TOC}\right) - 0{,}514881$$

Equation 3.8

Equation 3.8 is used to determine the O_3/TOC dose ratio for a specific contact time – t while still meeting the treatment objective CT-value. Equation 3.8 represents the T_{10} method of Table 3-8 while Equation 2.7 represents the CSTR method, i.e. the integrated method. The above two equations are used to investigate the lowest cost points for the respective methods.

To investigate the existence of a lowest cost point at a specific contact time, the following parameters are used viz., a 40MLD O_3 process that receives 9mg/l of TOC with a treatment objective is 3-log Cryptosporidium removal, i.e. a CT-value of 22.5mg-min/l. With the O_3/TOC dose ratio determined from Equation 3.8 or Equation 2.7 and the known flow of the treatment plant, the present value (PV) life cycle cost (LCC) of the system total cost over 20 years is determined. This PV LCC of the total cost is used to investigate the existence of a lowest cost point (in terms of both capital and operating costs) at a specific contact time – t (using the parameters of Table 3-11).

The lowest cost point is also evaluated for the other disinfection treatment objectives of Table 3-4 using the CSTR method and the T_{10} method of Table 3-8. The results of this cost optimization exercise, (i.e. low cost) are presented in Section 4.4.

3.9 Grouping of organic micropollutants

For the current study, the organic micropollutants (see Table 2-27 in Section 2.4.15) measured in the Cape Flats WWTW final effluent are grouped as per Snyder *et al.* (2014) (see Table 2-27) based on their O_3 and OH· reaction rates. The results of the grouping process are shown in Section 4.5.

3.10 Organic micropollutant water quality risk assessment

This study plans to do a water quality risk assessment of the organic micropollutants in the Cape Flats WWTW final effluent. With the organic micropollutants O_3 and OH· second-order reaction rates (k-values) known, they can be grouped as described in Section 3.9. To predict the removal of contaminants with the O_3 process the current study implements the method proposed by Snyder *et al.* (2013) (see Equation 2.14 to Equation 2.17). The steps of the above process are described by Equation 3.9 for organic micropollutants.

$$Organic\ micropollutant\ target\ group \xrightarrow{yields} {}^{O_3}/_{TOC}\ \text{(Table 2-27)} \xrightarrow{yields} \Delta UV_{a254}\ \text{(Equation 2.14)} \xrightarrow{yields} Indication\ of\ \%\ removed\ \text{(Equation 2.16)} \qquad \textbf{Equation 3.9}$$

The risk assessment is done on the organic micropollutants that are above the water quality standards, as described in Section 3.3, including the pre- and post-treated water. Post-treated water includes the concentration of residual organic micropollutants, i.e. after predicted removals have been allocated to the constituents in the Cape Flats WWTW effluent.

The water quality of the Cape Flats WWTW is evaluated against two things firstly, the likelihood (λ) of a contaminant being above their standard, and secondly the resulting consequence (μ) of consuming water containing levels of the contaminant above or below the standard (see Section 3.3 for the water quality standards used). When a contaminant is below the standard it is deemed to have a moderate impact, i.e. minor impact for a large population (Table 3-14). The evaluation is done by rating an organic micropollutant according to the definitions of Table 3-14 which gives λ and μ a score according to the score column. The risk profile score is then obtained with the multiplication-product of the λ and μ score. The risk profile score categorises the risk rating on a risk profile according to Table 3-15. The categories are no-risk ($\lambda \times \mu < 1$), low-risk ($1 > \lambda \times \mu < 19$), medium-risk ($19 > \lambda \times \mu < 60$) or high-risk ($\lambda \times \mu > 60$). Possible combination outcomes of the λ and μ multiplication-product and the associated risk profile are shown in Table 3-16.

When the concentration of an organic micropollutant is over its standard (see Section 3.3), the λ is scored "almost certain" and the μ "moderate", giving it a medium risk profile. When the μ of the organic micropollutant is still over its standard after treatment, then it is scored as above, i.e. λ = "almost certain" and μ = "moderate". When the concentration of the organic micropollutant is below its standard after treatment, the λ is scored "unlikely" and μ "moderate", giving it a low-risk profile.

The treatment parameters that are used in the risk assessment to predict the removal of the organic micropollutants in the Cape Flats filtered final effluent are the same as those presented in Table 3-12 for the Cape Flats WRP.

The results of the water quality risk analysis pertaining to the organic micropollutants are presented in Section 4.6.

Table 3-14 – Contaminant λ and μ score rating table (Adapted from Walker *et al*. 2016).

Likelihood (λ)	Score	Consequence (μ)	Score
Almost certain (Is expected to occur with a probability of multiple occurrences within a year)	1	**Catastrophic** (Major impact for large population, i.e. widespread acute health impact expected, resulting in hospitalization, decreased life expectancy, or both)	100
Likely (Will probably occur within a 1- to 5-year period)	0.8	**Major** (Major impact for a small population, i.e. potential acute health impact affecting a limited number of the community)	70
Moderately likely/possible (Might occur or should be expected to occur within a 5- to 10-year period)	0.5	**Moderate** (Minor impact for a large population, i.e. repeated breach of a chronic health parameter, long-term or lifetime exposure required, or potential widespread aesthetic impact)	20
Unlikely (Could occur within 20 years or in unusual circumstances)	0.2	**Minor** (Minor impact for small population, i.e. elevated levels of a chronic health parameter, no health impact expected, or potential local aesthetic impact)	2
Rare (May occur only in exceptional circumstances. May occur once in 100 years)	0.1	**Insignificant** (Insignificant impact or not detectable, i.e. no expected health impacts or an isolated exceedance of an aesthetic parameter)	1
Not Applicable	0	**Not Applicable**	0

Table 3-15 – Water Risk Profile.

Range	Risk Profile
Risk ≤ 1	No-Risk
1 > Risk ≤ 19	Low
19 < Risk ≤ 60	Medium
Risk > 60	High

Table 3-16 – Risk Matrix (likelihood × consequence).

Likelihood	Consequence				
	Insignificant	**Minor**	**Moderate**	**Major**	**Catastrophic**
Almost Certain	1	2	20	70	100
Likely	0.8	1.6	16	56	80
Moderately likely	0.5	1	10	35	50
Unlikely	0.2	0.4	4	14	20
Rare	0.1	0.2	2	7	10

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Chapter 4 : Results

The current chapter discusses the results and findings obtained following the research methodology described in Chapter 3. Throughout the chapter the main insights from the results are presented in textboxes to highlight the most significant findings.

4.1 Comparison of the O_3/BAC process assessment methods

This investigation involves comparing the O_3/TOC ratios required for each treatment objective as determined by the three assessment/validation methods described below.

The CT-value (see Section 2.4.1) assesses the O_3 process performance for disinfection and the O_3/TOC dose ratio for organic micropollutant oxidation. Various methods exist to validate the CT-value achieved, i.e. the performance assessment. Three of these methods used in assessing the performance of the O_3 disinfection process (taken from Table 3-8) were selected and used in the current study. The methods are:

i) The conservative method using Equation 2.8 (see Section 2.4.2 and Section 3.5);

ii) The CSTR/integrated method using Equation 2.7 (see Section 2.4.1 and Section 3.5); and

iii) The T_{10} method with residual O_3 measurement at the end of the O_3 contact tank using Equation 3.8 (see Section 2.4.1, Section 3.5 and Section 3.8).

4.1.1 Comparison of the O_3/TOC dose ratio for the O_3 process

Table 4-1 below shows the O_3/TOC ratio required to achieve each treatment objective (as per Section 3.4) presented according to the three methods of Table 3-8, namely, the conservative method, the CSTR/integrated method, and the T_{10} method. Specifically, the values for the T_{10} method in Table 4-1 below were determined using Equation 3.8, a TOC_{in} concentration of 9mg/l, and an O_3 hydraulic contact time of 15 minutes, which represent the base case for the current study.

Table 4-1 – Comparison of O_3/TOC dose ratios required for treatment objectives.

Method			**Conservative**	**CSTR/integra-ted method**	**T_{10} method**
Disinfection	**Objective**	**CT required @ 13°C (mg-min/l) from Table 3-4**	**O_3/TOC ratio using Equation 2.8**	**O_3/TOC ratio using Equation 2.7**	**O_3/TOC ratio using Equation 3.8**
Virus	2-log	0.38	0.368	0.219	0.71
	3-log	0.62	0.392	0.247	0.76
	4-log	0.76	0.406	0.261	0.78
Giardia	1-log	0.38	0.368	0.219	0.71
	2-log	0.76	0.406	0.261	0.78
	3-log	1.14	0.444	0.292	0.82
Cryptosporidium	1-log	7.5	1.081	0.524	1.14
	2-log	15.0	1.83	0.663	1.34
	3-log	22.5	2.58	0.767	1.51
Oxidization					
	Group 1		0.25*		
	Group 2		0.5*		
	Group 3		1*		
	Group 4		>1.5*		
	Group 5		1.5*		
*From Table 2-27					

The O_3/TOC dose ratio relates the given treatment objectives to the various assessment/validation methods and provides a method of comparison. In Figure 4.1 below, the O_3/TOC dose ratio requirements for each treatment objective are compared graphically for different assessment/validation methods.

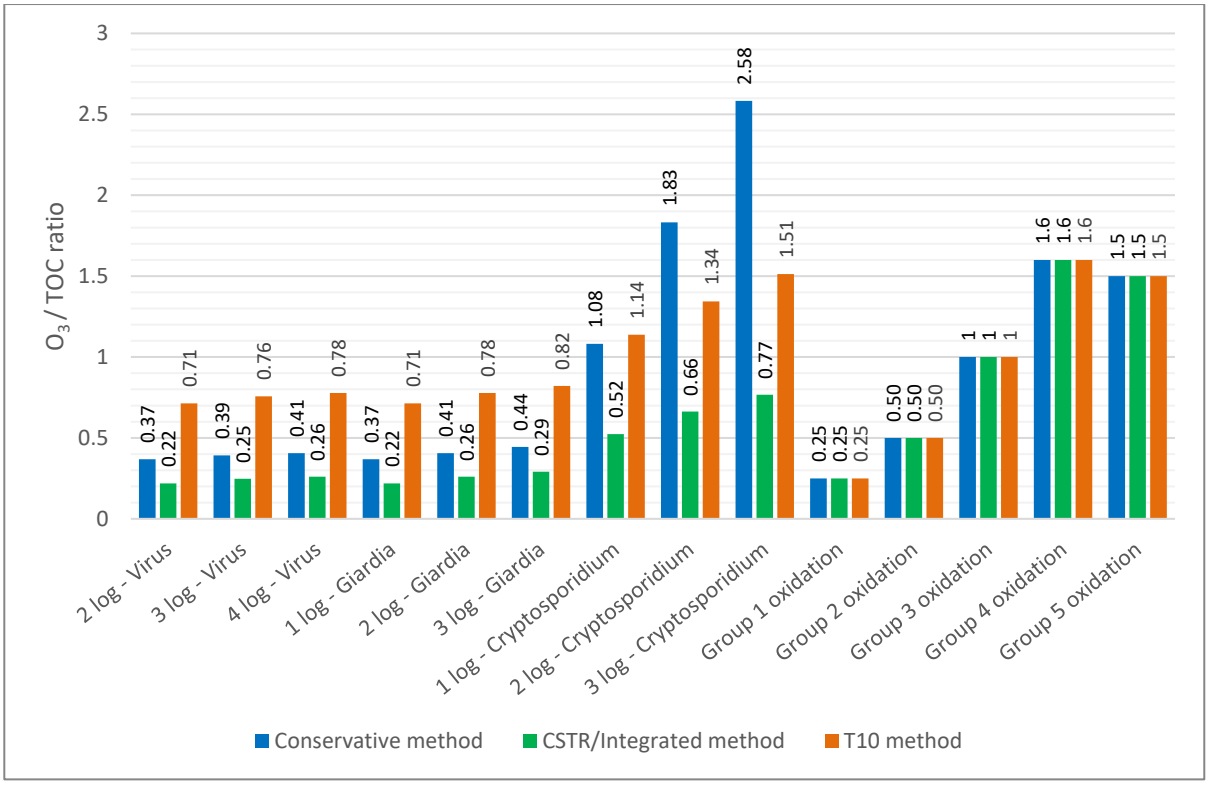

Figure 4.1 – Graphical comparison of O_3/TOC dose ratio for all three assessment methods.

The O_3/TOC dose ratio, as determined by the conservative method for 3-log Cryptosporidium inactivation, requires the highest O_3 dose ratio of 2.58mgO_3/TOC. Generally, on the one hand the CSTR/integrated method gives the lowest O_3/TOC ratio. On the other hand, the T_{10} method yields the highest O_3/TOC ratio, except for 2-log- and 3-log Cryptosporidium inactivation.

Insight 1: For a multi treatment objective use of the O_3 process (i.e. multiple disinfection objectives and organic micropollutants oxidation objectives) it is better to validate the process with the T_{10} method given that more treatment objectives are validated with this method. For custom treatment objective applications (i.e. one or two disinfection objectives) it is more optimal to use the CSTR method for validation which will result in the lowest O_3/TOC dose ratio.

Table 4-2 below shows how the treatment objectives relate to one another depending on the selected validation/assessment method. The above is true for an O_3 treatment step receiving 9mg/l TOC and a hydraulic retention time (HDT) of 15 minutes. Hence, the observations from Table 4-2 as follows:

i) More groups of organic micropollutants are oxidised when using the T_{10} method;

ii) More disinfection inactivation can be validated using the CSTR/integrated method, when selecting the O_3/TOC dose ratio for organic micropollutant oxidation; and

iii) More oxidation groups can be covered, when Cryptosporidium disinfection is the treatment objective, when using the conservative method of validation/assessment.

Furthermore, from Table 4-2, it is clear that the selection of a treatment objective and the method for the assessment of the treatment performance affect each other. For example, when the T_{10} method is used for the validation of the 3-log Cryptosporidium inactivation treatment objective, all but one of the other treatment objectives are also achieved, except for the group 4 organic micropollutant oxidation. When the O_3 process is explicitly implemented, for the 2-log virus inactivation, it can be optimized by using the CSTR method for validation/assessment, which results in the lowest O_3/TOC dose ratio required.

Also, for an O_3 process multi-treatment objective scenario, the selection of the performance assessment/validation methods plays a significant role in the requirement for monitoring and validation, i.e. the CSTR/integrated method requires much more residual O_3 meters.

Table 4-2 – Treatment objectives inter-relationship for all three assessment methods.

	Treatment objectives achieved based on treatment objective selected (first column)													
Treatment objective selected ↓	**2 log Virus**	**3 log Virus**	**4 log Virus**	**1 log Giardia**	**2 log Giardia**	**3 log Giardia**	**1 log Crypto-***	**2 log Crypto-***	**3 log Crypto-***	**Group 1 oxidation**	**Group 2 oxidation**	**Group 3 oxidation**	**Group 4 oxidation**	**Group 5 oxidation**
2 log - Virus	●#+			●#+						●+	+			
3 log - Virus	●#+	●#+		●#+						●+	+			
4 log - Virus	●#+	●#+	●#+	●#+	●#+					●#+	+			
1 log - Giardia	●#+			●#+						●+	+			
2 log - Giardia	●#+	●#+	●#+	●#+	●#+					●#+	+			
3 log - Giardia	●#+	●#+	●#+	●#+	●#+	●#+				●#+	+			
1 log – Crypto-	●#+	●#+	●#+	●#+	●#+	●#+	●#+			●#+	●#+	+		
2 log –Crypto-	●#+	●#+	●#+	●#+	●#+	●#+	●#+	●#+		●#+	●#+	●+	●	
3 log – Crypto-	●#+	●#+	●#+	●#+	●#+	●#+	●#+	●#+	●#+	●#+	●#+	●+	●+	●+
Group 1 oxidation	●#	#		#						●#+				
Group 2 oxidation	●#	●#	●#	●#	●#	●#				●#+	●#+			
Group 3 oxidation	●#+	●#+	●#+	●#+	●#+	●#+	●#	#	#	●#+	●#+	●#+		
Group 4 oxidation	●#+	●#+	●#+	●#+	●#+	●#+	●#+	#+	#+	●#+	●#+	●#+	●#+	●#+
Group 5 oxidation	●#+	●#+	●#+	●#+	●#+	●#+	●#+	●#+	#	●#+	●#+	●#+		●#+

***** Cryptosporidium
● Conservative method
CSTR/integrated method
+ T_{10} method

4.1.2 Assessment of the O_3 process performance

Figure 4.2 below shows the CT-values that can theoretically be obtained when using the CSTR/integrated method for process validation (Equation 2.7) at various O_3 contact times and O_3 dose ratios (i.e. O_3/TOC dose ratios of 0.5, 1.1, and 1.7). The results are valid for water with a decay rate represented by Equation 3.2 and an instantaneous O_3 demand represented by Equation 3.1. From Figure 4.2 it is evident that CT-values between 3–95 mg-min/l can be obtained with the CSTR method depending on the O_3/TOC dose ratio. The CT-value is higher at higher O_3/TOC dose ratios because at a constant incoming TOC concentration (9mg/l in this case), increasing the O_3/TOC dose ratio would mean increasing the O_3 dose which results in a higher O_3 residual. It is also evident that the benefit of increasing the CT-value by increasing the contact time starts to plateau as the contact time is increased between 5–20 minutes. The plateau effect is more evident at a low O_3/TOC dose ratio (O_3/TOC = 0.5) than at a high O_3/TOC dose ratio (O_3/TOC = 1.7).

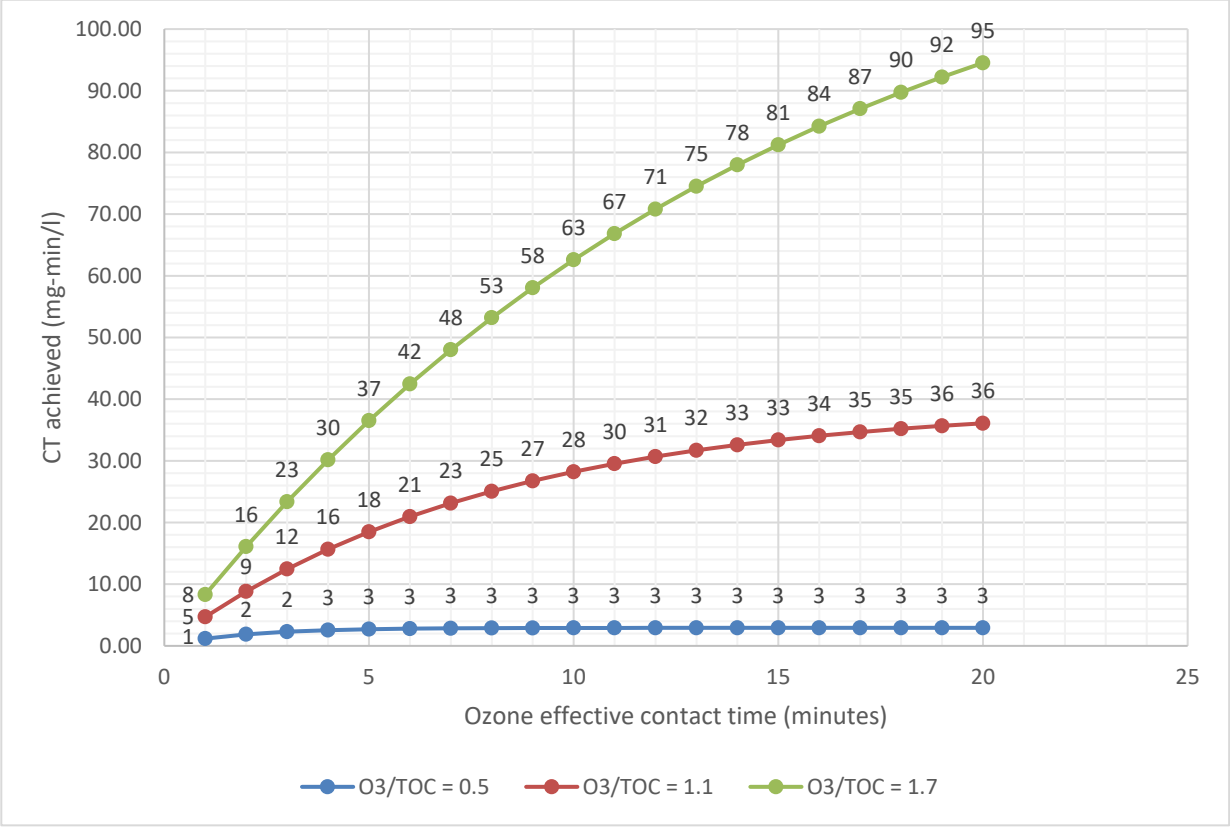

Figure 4.2 – CT-values achieved using the CSTR method (Equation 2.7) at various O_3/TOC dose ratios and contact times.

Furthermore, Figure 4.3 below shows the CT-values that can be obtained when using the T_{10} method for process validation (Equation 3.8 and a TOC_{in} concentration of 9mg/l) at various O_3 contact times and O_3 dose ratios (i.e. O_3/TOC ratios of 0.5, 1.1, and 1.7). The results are valid

for water with a decay rate represented by Equation 3.2 and an instantaneous O_3 demand shown by Equation 3.1. From Figure 4.3 it is evident that, depending on the O_3/TOC dose ratio, CT-values between 0.7–31.4 mg-min/l can be obtained with the T_{10} method. The CT-values obtainable with the T_{10} method is much lower (±67% less) than those obtainable with the CSTR method (Figure 4.2). The lower CT-values of the T_{10} method are attributed to the residual O_3 decay across the contact tank, which is only measured at the end of the contact tank for the T_{10} method, i.e. no credit is given for the residual O_3 concentration that existed in the tank above which is measured at the end of the contact tank. At an O_3/TOC dose ratio of 1.7, the highest CT-value is achieved with 15–16 minutes contact time and at an O_3/TOC dose ratio of 1.1, the highest CT-value is achieved with 7–8 minutes contact time. At the lowest O_3/TOC dose ratio of 0.5 very low CT-values are obtained, due to most of the dose being absorbed by the IOD before a residual O_3 can be formed. Beyond the points where the highest CT-values are achieved the CT-values starts to drop. The decrease in CT-values is again attributed to the effect of O_3 decay.

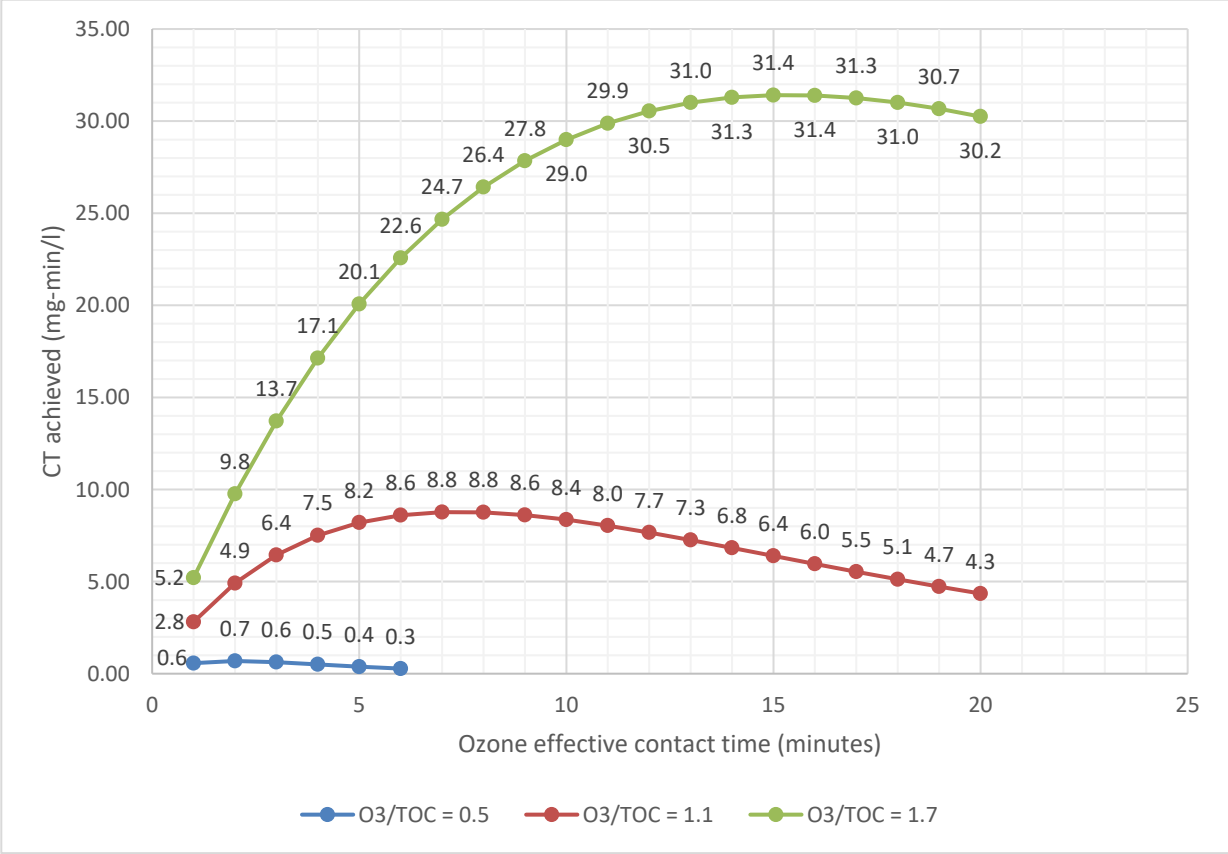

Figure 4.3 – CT-values obtained using the T_{10} method (Equation 3.8) at various O_3/TOC dose ratios and contact times.

From Figure 4.2 and Figure 4.3, it can be seen that when using the T_{10} method with one residual O_3 meter, much lower CT-values are predicted compared with using the CSTR/integrated method. For the same CT-values of the CSTR method, much higher O_3/TOC dose ratios would

be required, which result in higher cost requirements. Given the higher O_3/TOC dose ratios required for the same CT-value, more of the other treatment objectives, such as higher groups of organic micropollutants oxidation, can be achieved by using the T_{10} method as is evident from Table 4-1.

4.1.3 Comparison of the BAC filtration process performance

The most critical process parameter for the BAC filtration process is the empty bed contact time (EBCT) (Letterman, 1999; Arn et al., 2011). The EBCT must be selected based on the target groups of organic micropollutants, as shown in Table 3-6, despite it also being influenced by the O3/TOC implemented before the BAC filters. To relate the O_3/TOC dose ratio to EBCT, Equation 2.18 and Equation 2.19 are used and compared. They give the optimum EBCT for a specific O_3/TOC ratio. The BAC filtration performance can be assessed either by TOC or UV_{a254} removed. To predict the TOC removal (ΔTOC) capacity, Equation 2.20 and Equation 2.21 are adopted and compared. To predict the UV_{a254} removal (ΔUV_{a254}), Equation 2.22 is adopted, and the predictions are shown below.

Figure 4.4 below shows the optimum EBCT at various O_3/TOC dose ratios. The EBCT values of 15 to 20 minutes are much lower than those required for high removal efficiencies of organic micropollutants that are marginally oxidised by O_3 (Table 3-6). The discrepancy between the optimum EBCT of the two methods (see Equation 2.18 and Equation 2.19) is high (64% difference) at lower O_3/TOC dose ratios and significantly correlates at high O_3/TOC ratios (2% difference). Nevertheless, Equation 2.19 is a more conservative approach. The ΔTOC prediction models show a higher correlation, of 10%, at a greater O_3/TOC ratio of 2, in contrast to a 30% correlation at the lowest O_3/TOC ratio of 0.5. The models predict TOC removals between 17-43%, depending on the O_3/TOC ratio. The incoming TOC concentration also influences the TOC removal capacity of a BAC filter (see Figure 3.6). When the results of Figure 4.4 are compared with Figure 3.6, it appears that the results of the former correspond to a TOC concentration of between 2–8mg/l.

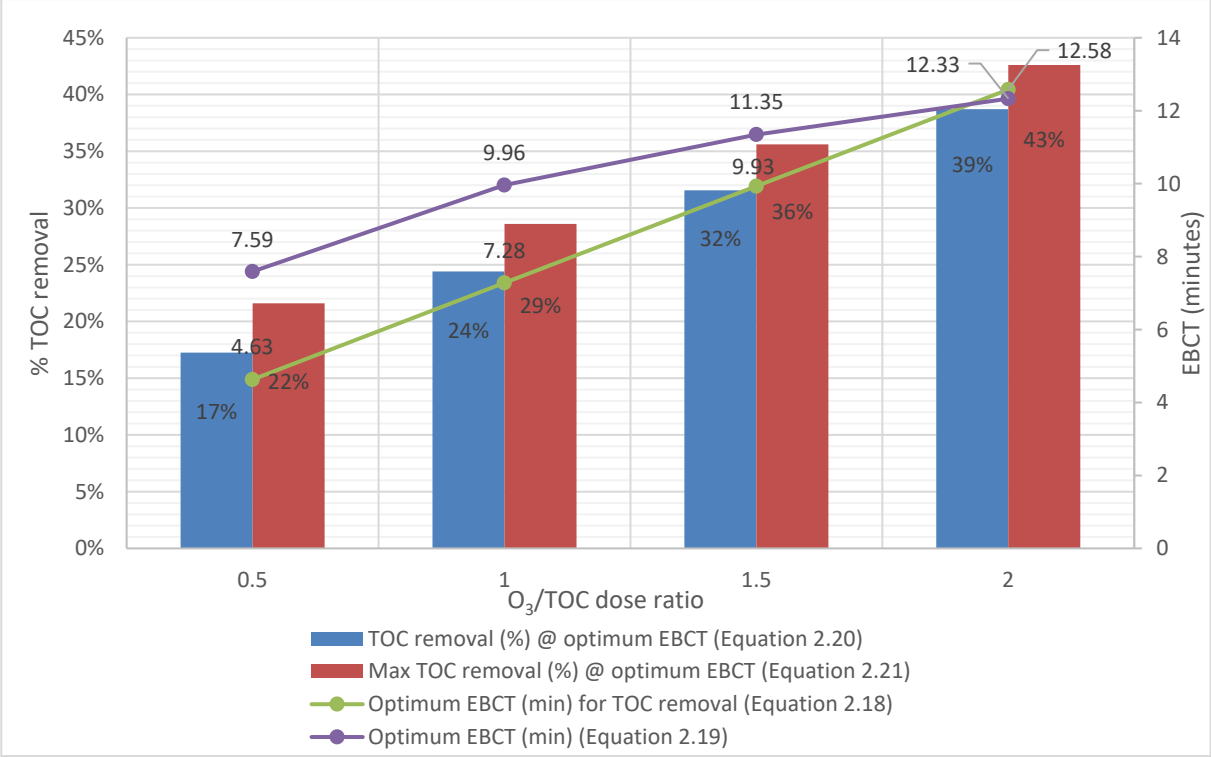

Figure 4.4 – Optimum EBCT and predicted TOC removals at various O_3/TOC ratios.

When comparing Figure 4.4 with the treatment objective outlined in Table 3-6, it appears that the optimum EBCT for TOC removal does not correlate with the EBCT required for the removal of organic micropollutants that have been either moderately or marginally oxidised by O_3. The optimum EBCT required for TOC removal only caters for organic micropollutants readily oxidised by O_3.

Insight 2: The optimum EBCT prediction models are not suitable for the removal of organic micropollutants moderately or marginally oxidised by O_3, since they require EBCT greater than 20 minutes according to Table 3-6. Based on the findings by Sundaram and Pagilla (2019) the BAC filtration TOC removal models (Equation 2.20 and Equation 2.21) are applicable to BAC filters receiving between 2–8mgTOC/l.

Figure 4.5 below shows the ΔUV_{a254} at various EBCT values and varies between 9–18% from 5–20 minutes EBCT. The values in the graph were generated from Equation 2.22 and the methodology described in Section 3.5.

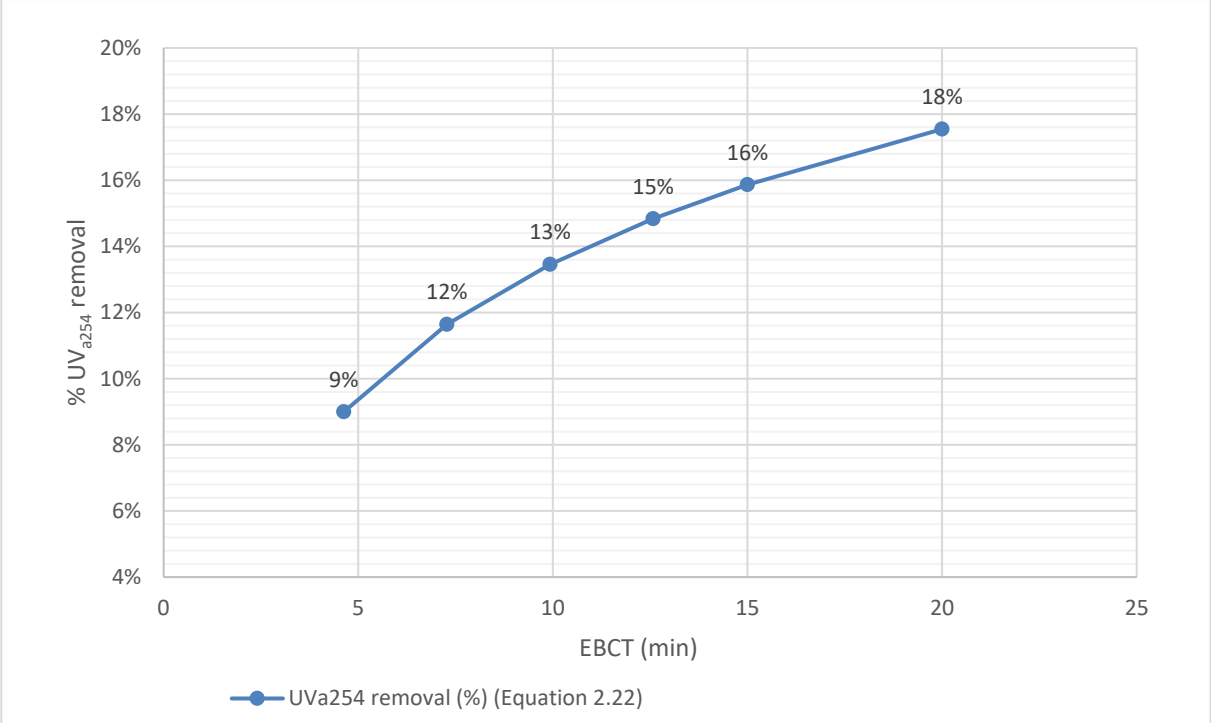

Figure 4.5 – Predicted UV_{a254} removals at various EBCT values.

The results presented in the current section show that for each process performance assessment used, different O_3/TOC dose ratios are required, which in turn results in the achievement of different treatment objectives. For example, if a multi treatment objective is desired, then it is preferable to use the T_{10} assessment method given that more treatment objectives can be validated henceforth. Besides, when the O_3 system is implemented for a specific treatment objective, then the CSTR/Integrated method results in the lowest O_3/TOC dose ratio required. Furthermore, the optimum EBCT required for the removal of TOC is much lower than the EBCT required for the removal of organic micropollutants that are moderately or marginally oxidised by O_3.

4.2 Relative cost comparison of treatment objectives

The current section investigates the relations between the cost of different O_3/BAC treatment objectives (see section 3.6 for further details). Concept level cost estimate models were used to evaluate the cost associated with each treatment objective (as identified in Section 3.4). This cost comparison was made to demonstrate how each treatment objective and process assessment/validation method (Table 3-8) can influence cost, including capital cost, annual operation and maintenance (O&M) cost, and the 20-year present value (PV) life cycle cost (LCC). The LCC include capital cost in the first year and O&M costs for the rest of the years the years, escalated with inflation. Throughout the cost calculations, an O_3/TOC dose ratio of 1.6 is used, specifically for group 4 organic micropollutants oxidation. Group 4 organic micropollutants require a O_3/TOC dose ratio of greater than 1.5.

For all the O_3/BAC treatment objectives and process assessment/validation methods, the cost estimates are presented as follows for the base case as shown in Table 3-11:

i) Figure 4.6 for capital cost estimates. One can observe that the predicted capital costs vary from R133-million for 2-log virus inactivation to a maximum of R156-million for 3-log Cryptosporidium inactivation.

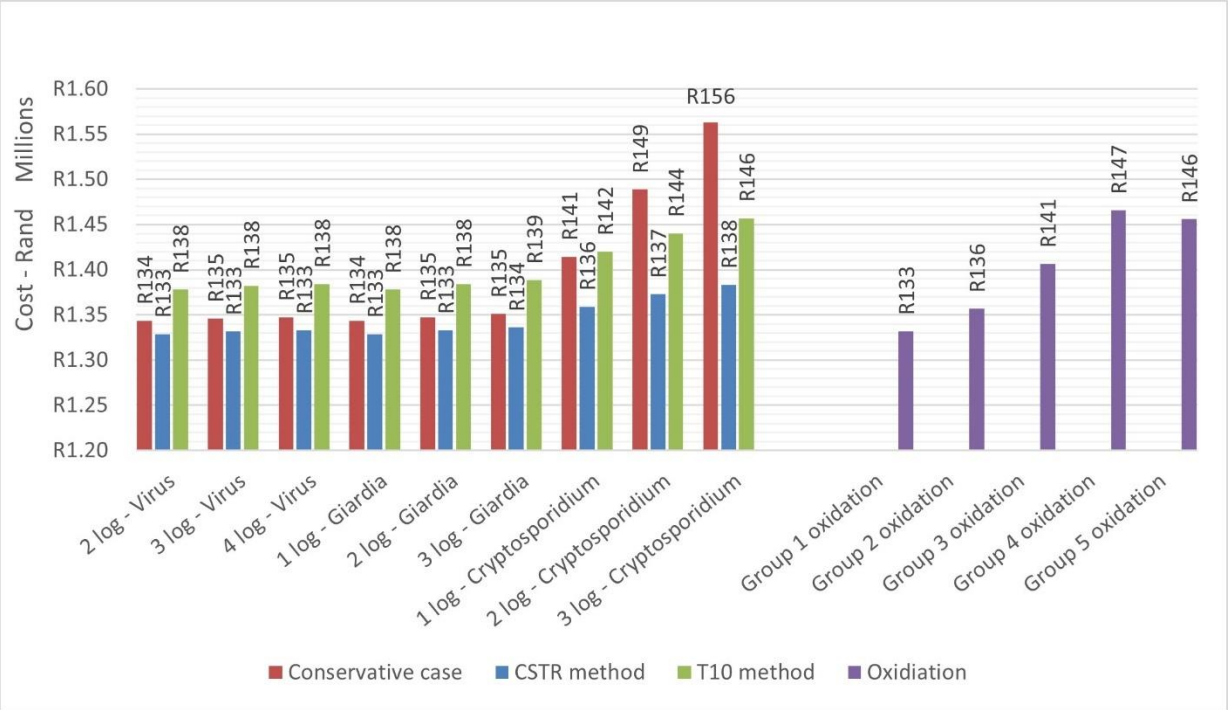

Figure 4.6 – Comparison of concept level capital cost estimates for three assessment methods.

ii) Figure 4.7 for annual O&M cost estimates. The figure shows that the predicted O&M costs vary from R2-million for 2-log virus inactivation to a maximum of R19-million for 3-log Cryptosporidium inactivation, depending on the validation method and treatment objective.

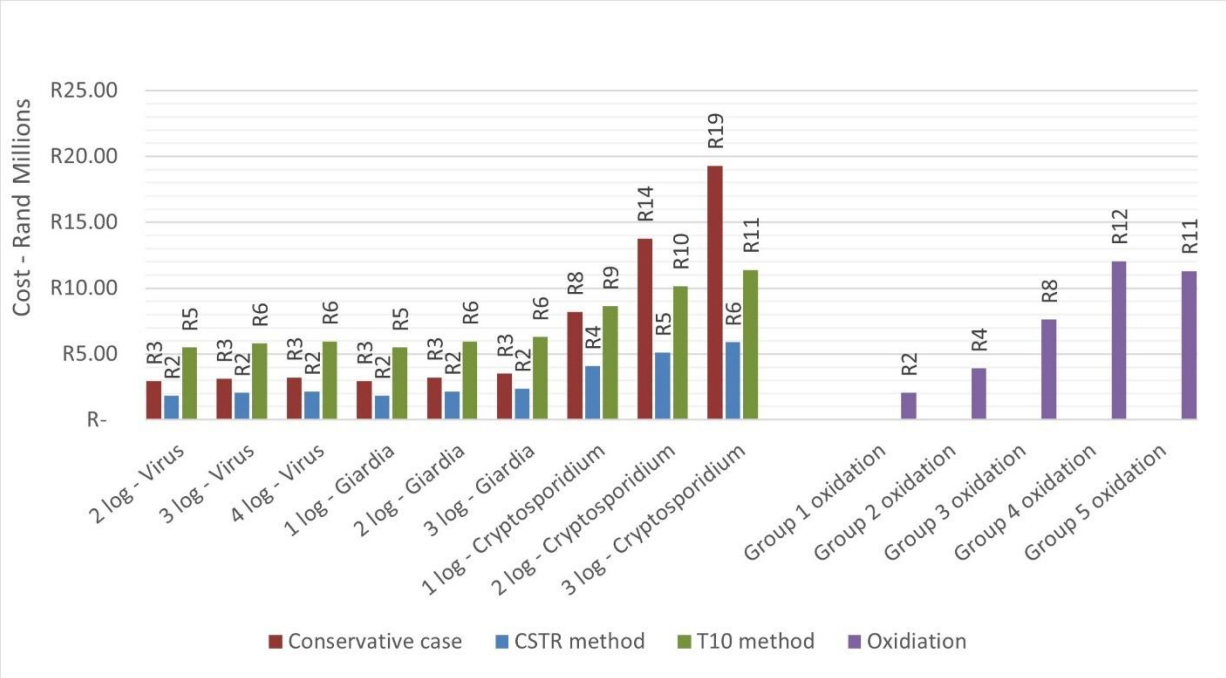

Figure 4.7 – Comparison of concept level annual O&M cost estimates for all treatment objectives using three disinfection assessment methods.

iii) Table 4-3 for the difference in capital and annual O&M costs between the T_{10} method and the CSTR method of a 40MLD O_3 process receiving 9 mgTOC/l. The table compares the difference in costs determined with the T_{10} method and the CSTR method. On average the capital costs differ by R 5.62-million, and the O&M costs differ by R 4,18-million.

Table 4-3 – Comparison of the difference between O_3 costs for the T_{10} and CSTR method.

Treatment objective	T_{10} Method Capital cost - CSTR Method capital cost	T_{10} method annual O&M cost - CSTR method annual O&M cost
2 log - Virus	R 4 902 125.04	R 3 650 393.34
3 log - Virus	R 5 056 617.50	R 3 765 436.97
4 log - Virus	R 5 121 070.72	R 3 813 432.40
1 log - Giardia	R 4 902 125.04	R 3 650 393.34
2 log - Giardia	R 5 121 070.72	R 3 813 432.40
3 log - Giardia	R 5 251 644.01	R 3 910 664.49
1 log - Cryptosporidium	R 6 088 664.26	R 4 533 956.05
2 log - Cryptosporidium	R 6 743 112.40	R 5 021 294.32
3 log - Cryptosporidium	R 7 390 832.63	R 5 503 622.62
Average	R 5 619 695.81	R 4 184 736.21
Minimum	R 4 902 125.04	R 3 650 393.34
Maximum	R 7 390 832.63	R 5 503 622.62

Insight 3: For a 40MLD O_3 process, receiving 9mgTOC/l, and having a 15-minute contact time, the average predicted differences for capital costs and annual O&M costs between the T_{10} method and the CSTR method are R5.6-million (capital) and R4.2-million (O&M), respectively. Hence, favouring the CSTR method. An O&M difference of R4.2-million is significant if considered over a lifespan of 20 years.

iv) Figure 4.8 for 20-year PV LCC cost estimates. The figure reveals that the predicted PV LCC vary from R156-million for 2-log virus inactivation to a maximum of R472-million for 3-log Cryptosporidium inactivation.

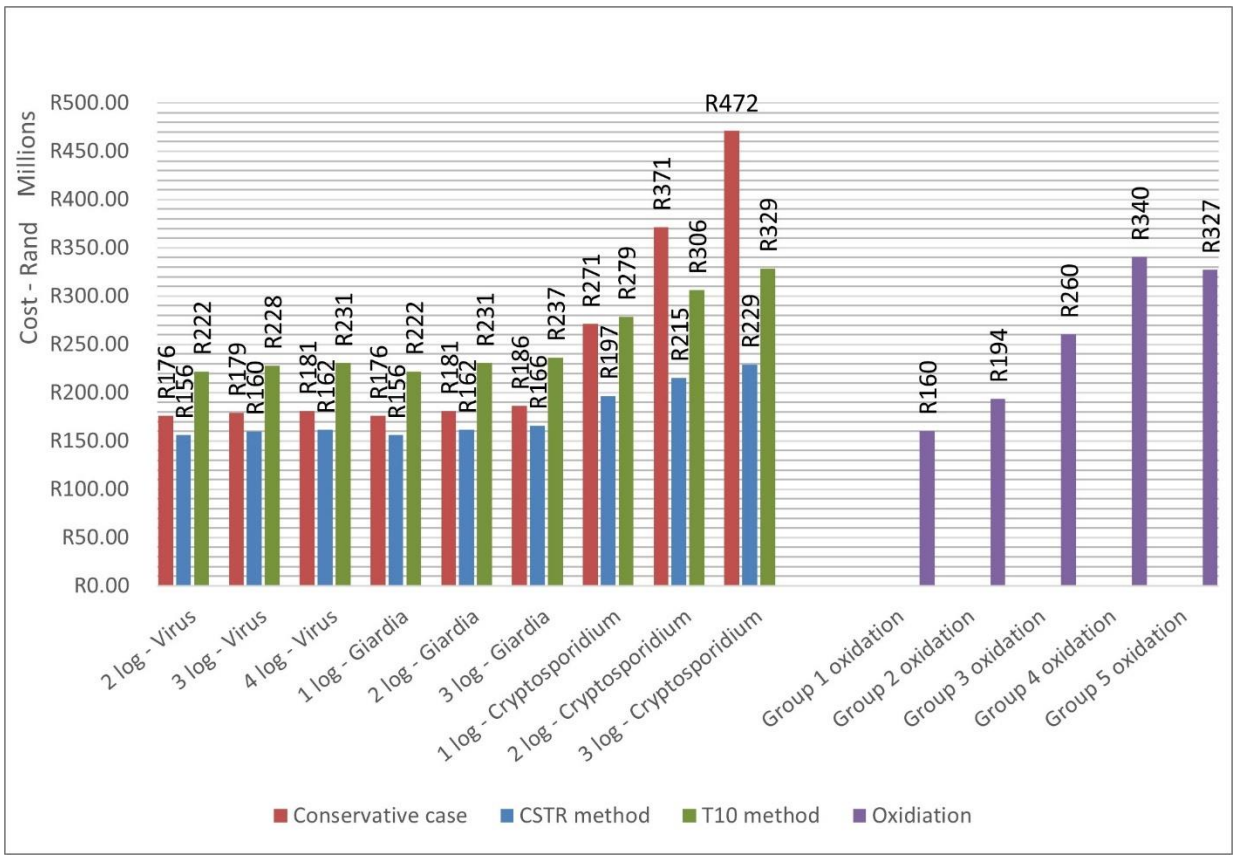

Figure 4.8 – Comparison of concept level 20-years PV LCC cost estimates for three assessment methods.

v) Figure 4.9 for capital, annual O&M, and LCC cost estimates for BAC filtration objectives. The figure shows that there is no significant difference in cost (20-year LCC, capital or annual O&M cost) between 10–20 minutes EBCT. The annual O&M cost estimates vary from R1-million between 10–15 minutes EBCT to R2-million between 15–20 minutes EBCT. The capital cost estimates vary, being R11-million between 10 minutes and 15

minutes EBCT, and R12-million between 15 minutes and 20 minutes EBCT. It is to be noted that there is only a 16% increase in the 20-year PV LCC, going from 10 to 20 minutes EBCT, which is highly cost effective considering the benefits of the added process performance that comes with a longer EBCT (see Table 3-6).

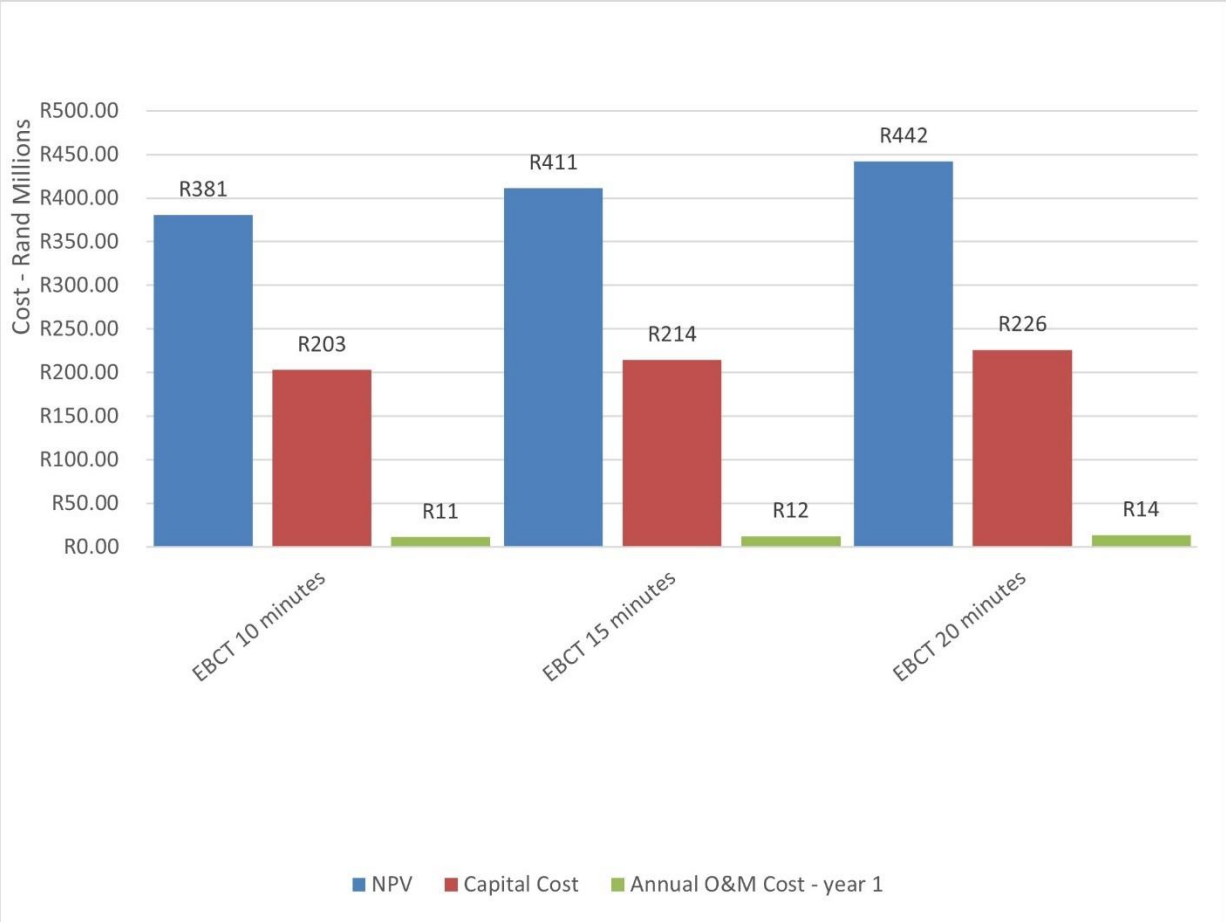

Figure 4.9 – BAC filtration concept 20-year PV LCC, capital and O&M costs estimates.

Insight 4: The BAC filtration costing models predict a 11% increase (R23-million) in capital cost between a 10 to 20 minutes EBCT for a 40MLD BAC filtration process. The costing models predict a 28% increase (R3-million) in annual O&M costs between a 10 to 20 minutes EBCT. The combined effect of the above increases is a 16% increase (R61-million) in the 20-year PV LCC between a 10 to 20 minutes EBCT.

Figure 4.6 to Figure 4.8 show that the T_{10} method of process assessment/validation results in the highest capital costs, O&M costs, and PV LCC, with the exception of the Cryptosporidium inactivation objective, where the conservative method is more expensive. In comparison, the CSTR/integrated method yields the lowest capital costs, O&M costs, and PV LCC. However,

this CSTR/integrated method also results in the lowest oxidation amounts of the different organic micropollutant groups (refer to Section 4.1.1).

In summary, the current section shows that the CSTR/integrated method yields the lowest capital costs, O&M costs and PV LCC.

4.3 Applying US concept costing models to the Southern African context

The current section investigates the relevance of the international costing models with regard to the capital and O&M costs of the O_3/BAC process in Southern Africa. All costs, i.e. capital and O&M, are converted to current SAR values using the average monthly SAR-USD exchange rate and the average annual inflation rate between 2011 and 2020 as on June 2020 (see Section 3.6 for detailed information on inflation and exchange rate). The methodology for this cost conversion is described in Section 3.7. Various sources were used to gather the costs for comparison; firstly, US concept level capital- and O_3-O&M cost estimate models (as referenced in Section 3.6); secondly, published South African capital and O_3-O&M cost estimate models (details in Section 3.7); and thirdly, actual Southern African O_3/BAC process project costs (the Cape Flats MAR WRP in South Africa and the Goreangab WRP in Namibia) Similar operating conditions (see Table 3-12) and flows as those of the actual Southern African projects are used in the costing models. This section makes the following comparisons:

i) Figure 4.10 compares the US concept level O_3-capital cost estimates and South African O_3-capital cost estimates with their respective actual Southern African O_3-costs. From Figure 4.10 below, it is clear that the published South African O_3-capital cost estimates underestimate the actual O_3-capital costs (from known projects). Whereas the US-based concept-level cost model (purple line) overestimates the capital cost of the Goreangab O_3-process (blue dot) but underestimates the capital cost of the Cape Flats O_3-process (red dot). The latter observation can be attributed to unique features of the O_3-process at Cape Flats MAR WRP (i.e. the O_3 contact tank, the O_3 dosing room, pipework, etc.) that is sized for 64MLD (Smuts & Marais, 2018). Besides, the 35% engineering, legal and admin costs, the 30% contingency costs and the 30% installation costs of the US model are higher than the typical professional costs in South Africa. Hence, there is no clear correlation between the costing models and the actual costs.

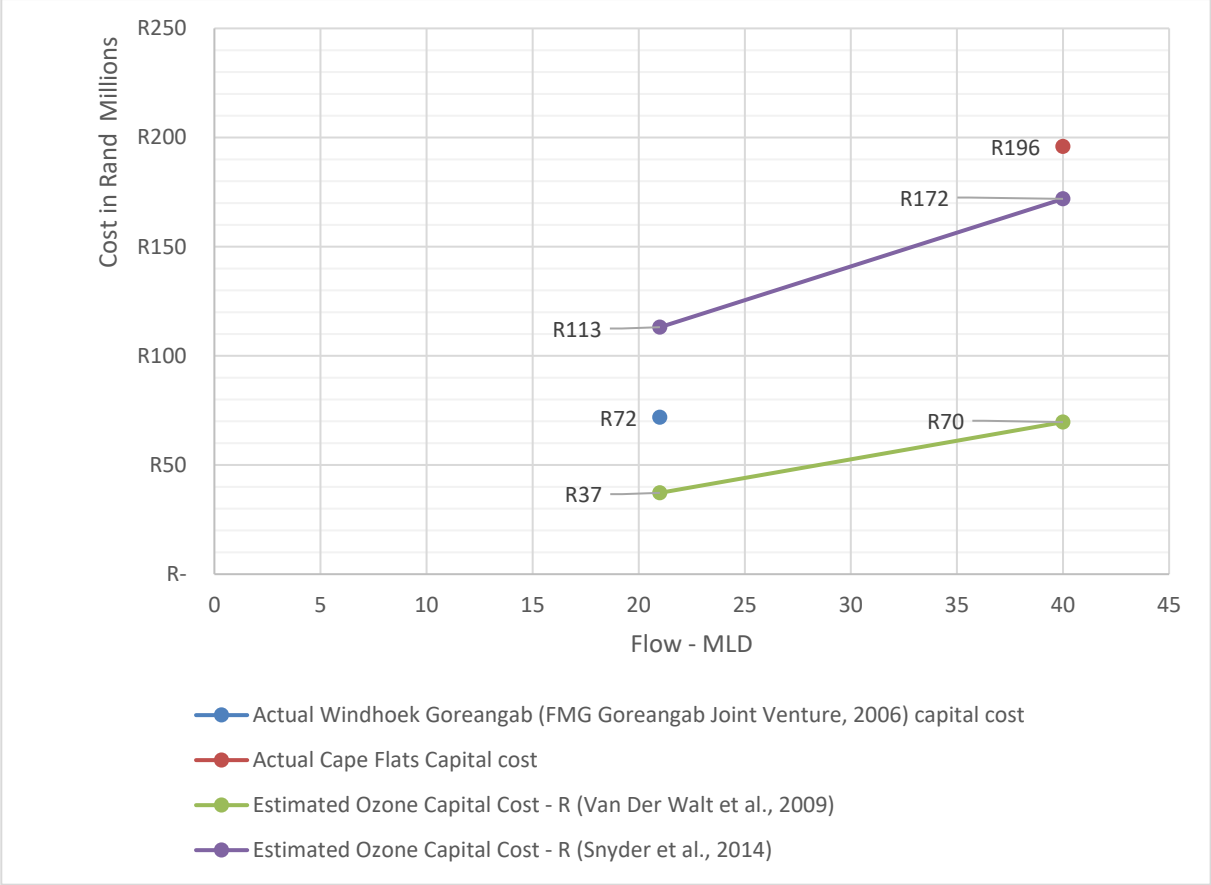

Figure 4.10 – O_3 capital cost comparison to Southern African projects costs.

Insight 5: US based costing models overestimate the actual capital costs in Southern Africa and the South African costing models underestimate the actual capital costs in Southern Africa. For both costing models significantly good correlations, between 6–7% in annual O_3 O&M costs, are observed.

ii) Figure 4.11 compares the US concept level annual O_3-O&M cost estimates with published South African annual O_3-O&M cost estimates. Good correlations are observed in Figure 4.11 below between the published South African O_3-O&M annual cost model and the US O_3-O&M annual cost model. The South African O_3-O&M annual cost model predicts slightly lower O&M costs or alternatively the US O_3-O&M annual costs are merely 6–7% higher.

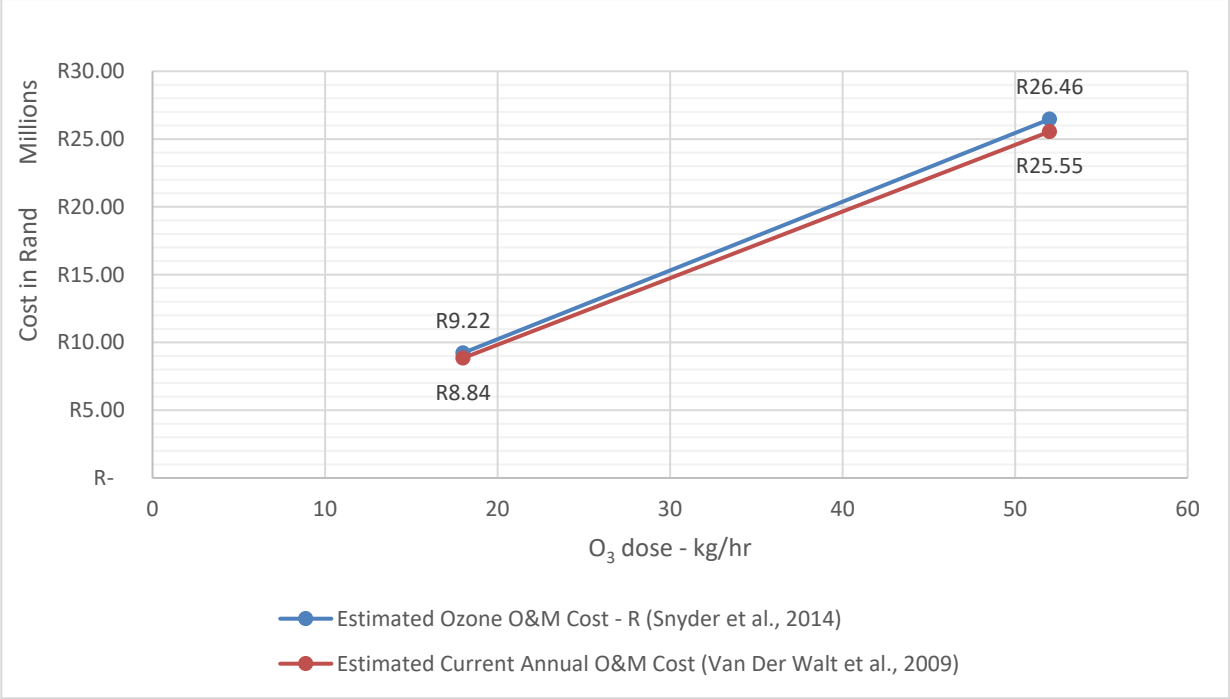

Figure 4.11 – O_3 annual O&M cost estimate comparison.

iii) Figure 4.12 compares the US concept level BAC-capital cost estimates with the actual Southern African BAC costs. From this figure, it is clear that the US-based concept-level cost model overestimates the actual capital cost of both the Goreangab WRP BAC-process and the Cape Flats MAR WRP BAC-process. In the case of the Goreangab WRP, the US-based concept-level cost model generates a result that is 112% more expensive than the actual cost. In the case of the Cape Flats MAR WRP, the US-based concept-level cost model generates a result that is 38% more expensive than the actual cost. These discrepancies do not bring any meaningful correlation to the fore.

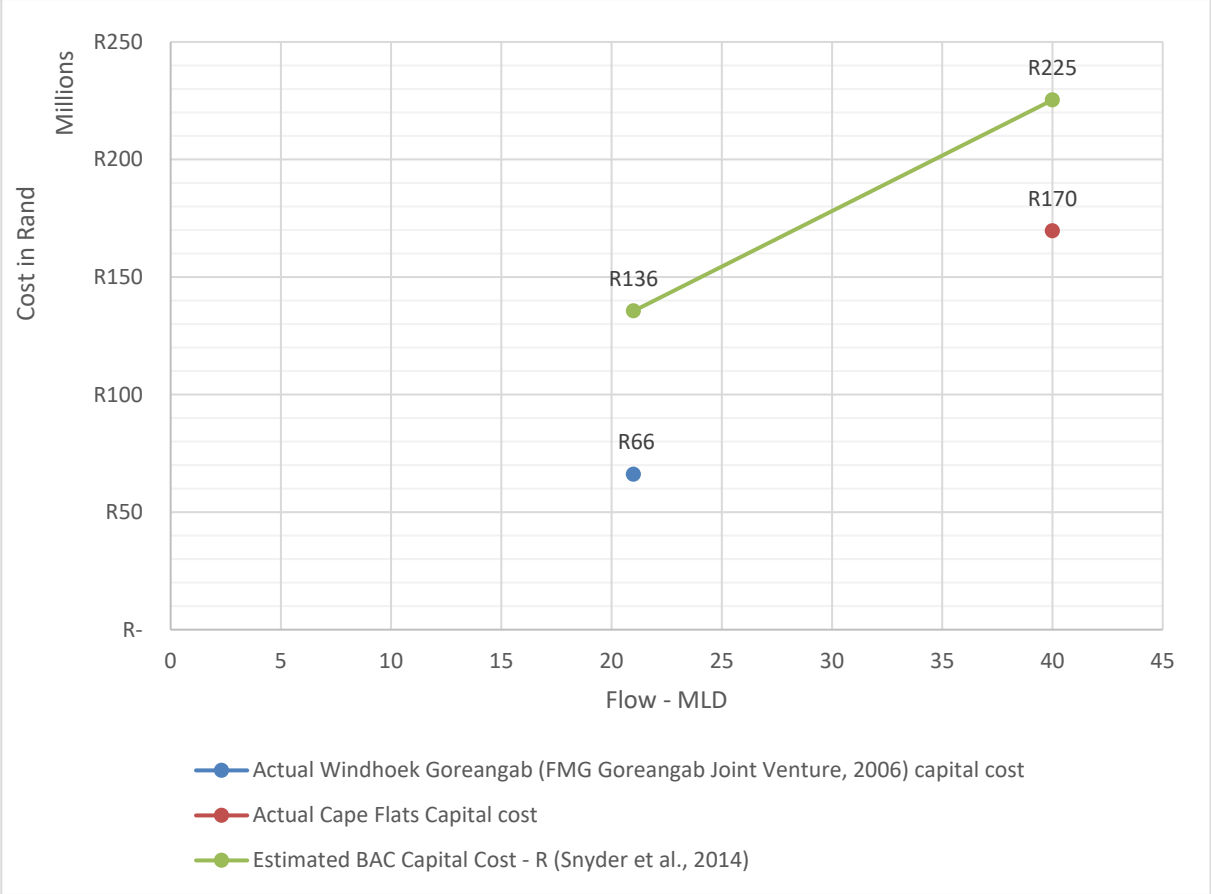

Figure 4.12 – BAC filtration capital cost comparison.

There were no meaningful correlations between the international capital costing models and the actual Southern African costs. For the O&M costs, however, good correlations were found, i.e. with merely a 6–7% difference between the South African O_3-O&M annual cost model and the US O_3-O&M annual cost model.

4.4 O_3 cost optimization

The following question was posed in Section 1.2, i.e. If there is an optimum O_3 contact time in terms of capital and O&M costs for the O_3 disinfection process, what is it? The current section attempts to answer this question. In particular, the focus is on investigating the CSTR/integrated method (Equation 2.7) and the T_{10} method (Equation 3.8). The instantaneous O_3 demand (IOD) and O_3 decay rate, regression equations as described in Section 3.5, were used as inputs for Equation 2.7. Firstly, the O_3/TOC dose ratio was determined for a treatment plant receiving 9mg/l of TOC and a treatment objective of 3-log Cryptosporidium inactivation (CT-value of 22.5 mg-min/l). Secondly, the O_3/TOC ratio, as determined by the equation mentioned above, was used to determine the capital and O&M costs using the US concept-level cost estimate models for a 40MLD treatment plant and an O_3 contact tank baffling factor ($f_{baffling}$) of 0.67. The optimum

contact time was then determined by taking the lowest 20-year PV LCC point over a range of contact times. The results are shown for a O_3-transfer efficiency of 98% and 90% on all the graphs. The same procedure is also followed for other disinfection objectives to determine their optimum contact time and cost point.

For the CSTR method, Figure 4.13 below gives the O_3/TOC ratio at various O_3 contact times, all required to achieve 3-log Cryptosporidium inactivation. Figure 4.14, in turn, gives the 20-year PV LCC associated with achieving 3-log Cryptosporidium inactivation by using the CSTR method.

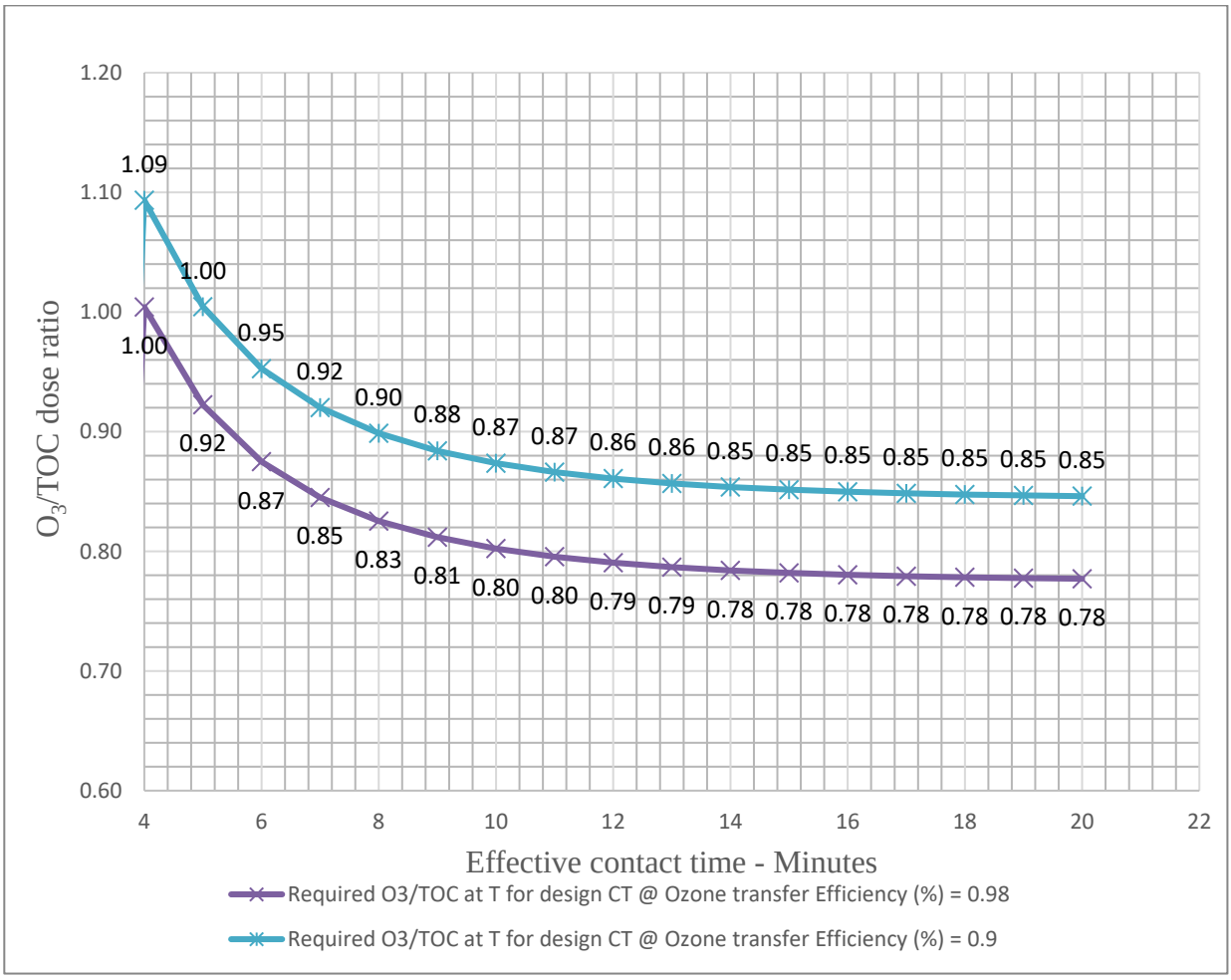

Figure 4.13 – O_3/TOC dose ratio required as determined by the CSTR method at various O_3 contact times to achieve design CT of 22.5 mg-min/l.

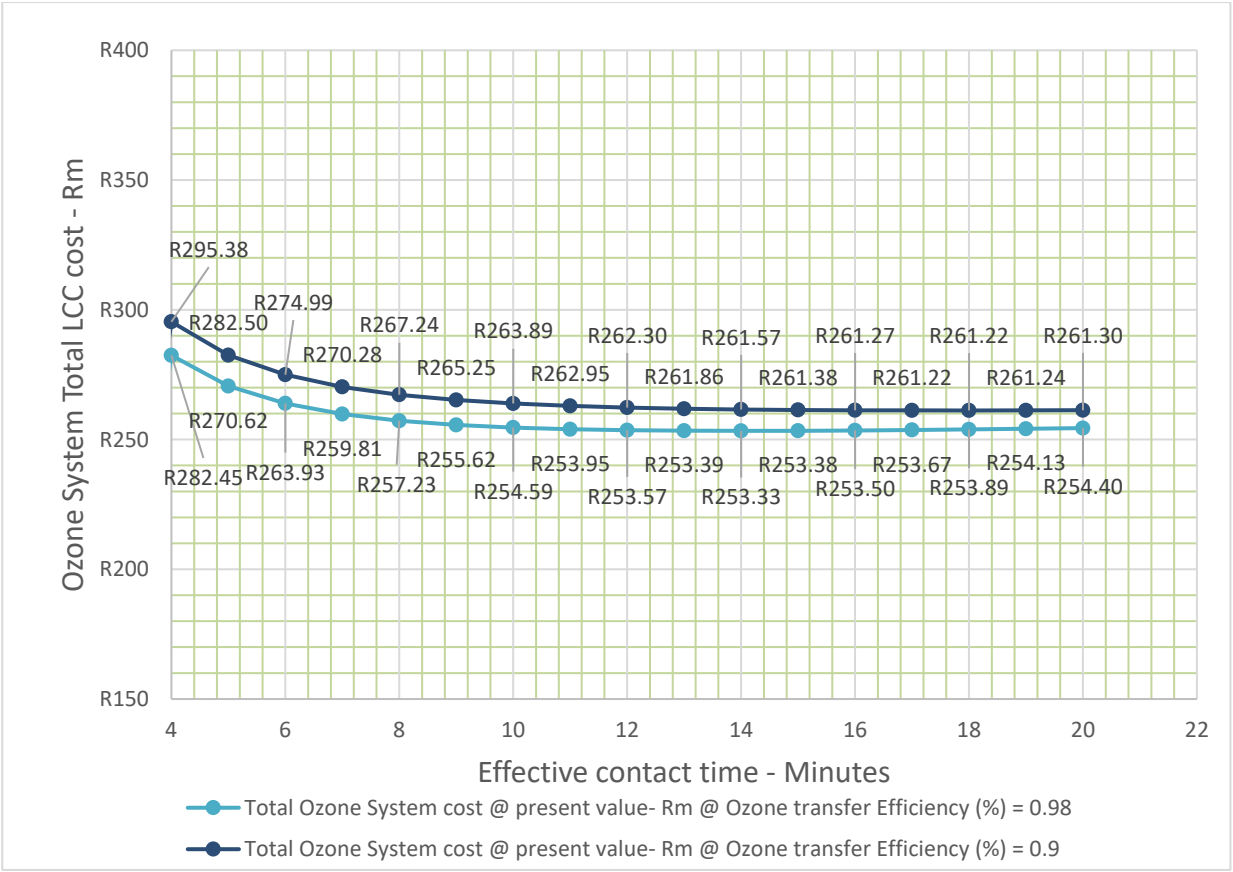

Figure 4.14 – The 20-year present value LCC using the CSTR method for 3-log Cryptosporidium inactivation (CT of 22.5 mg-min/l).

For the CSTR method, Figure 4.13 shows that the benefit of increasing the O_3 contact time plateaus after 14 minutes of contact time. Figure 4.14, furthermore, reveals that the optimum contact time to achieve 3-log Cryptosporidium inactivation with the CSTR method is also 14 minutes and there is only a negligible drop in cost after 14 minutes of contact time after which the cost starts to pick up again.

For the T_{10} method, Figure 4.15 gives the O_3/TOC ratio at various O_3 contact times required to achieve 3-log Cryptosporidium inactivation. Figure 4.16, in turn shows the 20-year PV LCC associated with achieving 3-log Cryptosporidium inactivation.

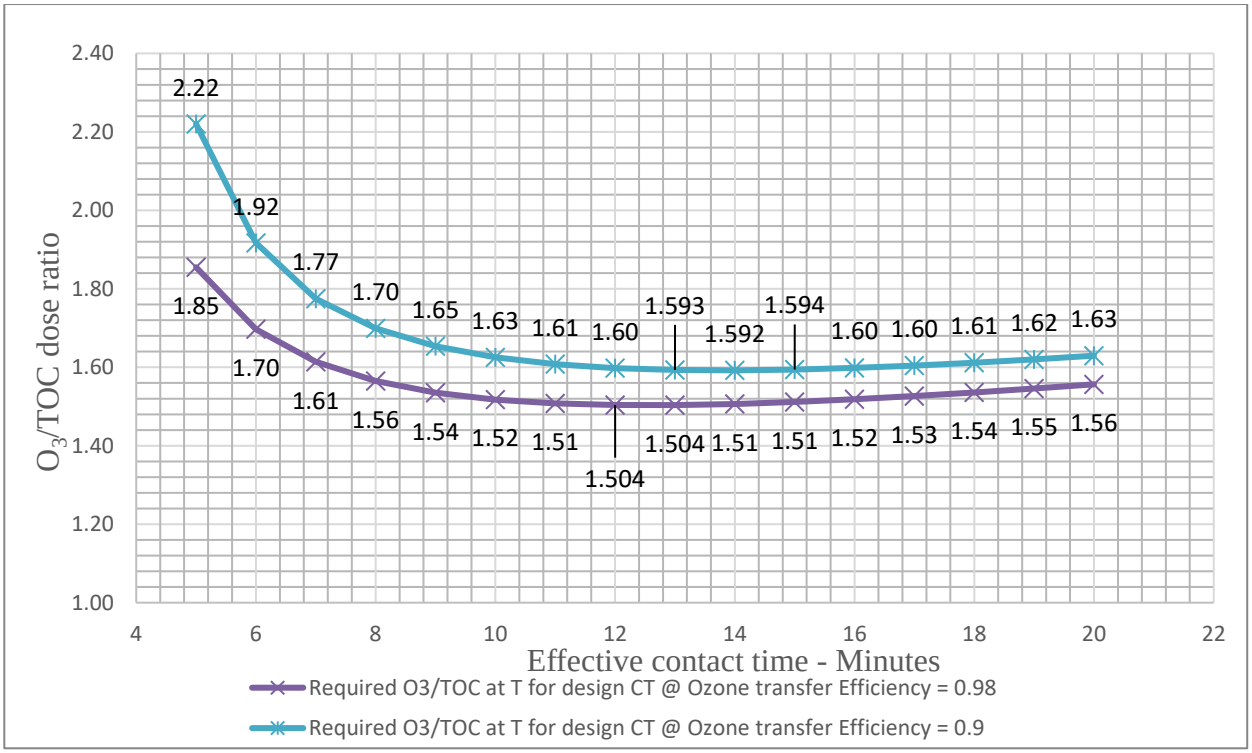

Figure 4.15 – O_3/TOC dose ratio required as determined by using the T_{10} method at various O_3 contact times to achieve design CT of 22.5 mg-min/l.

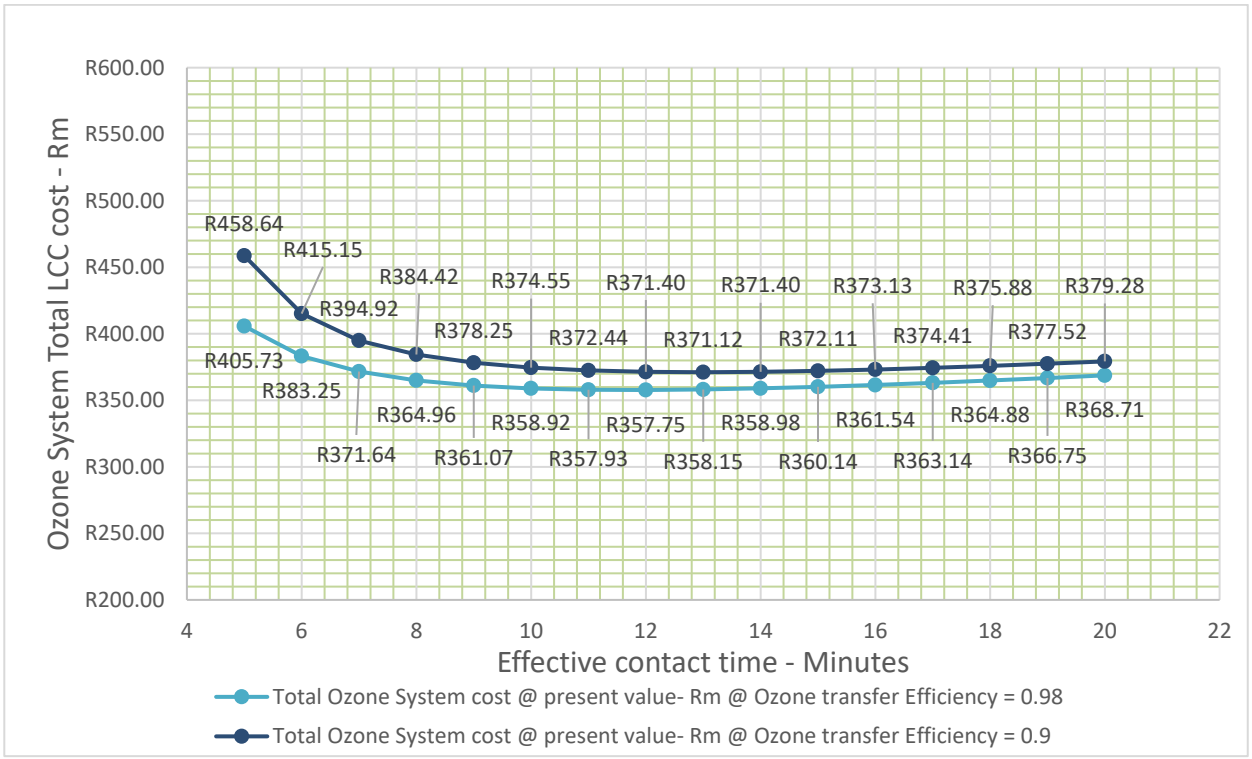

Figure 4.16 – The 20-year PV LCC using the T_{10} method for 3-log Cryptosporidium inactivation (CT of 22.5 mg-min/l).

It is observed from Figure 4.15 that for the T_{10} method, the lowest O_3/TOC dose ratios are between 12–16 minutes O_3 contact time. Figure 4.16 further reveals that the optimal 20-year PV LCC point to achieve 3-log Cryptosporidium inactivation is 12 minutes of contact time.

Insight 6: The most optimum contact time (i.e. the one producing the lowest 20-year PV LCC) for 3-log Cryptosporidium inactivation with O_3 for the CSTR method was found to be 14 minutes, after which, the PV LCC cost plateaued. The most optimum contact time (i.e. the one producing the lowest 20-year PV LCC) for 3-log Cryptosporidium inactivation with O_3 was found to be 12 minutes for the T_{10} method. The results are applicable for a 40MLD plant and feedwater with the characteristics of Table 2-14.

In terms of the other treatment objectives, the optimum contact times in terms of the lowest 20-year PV LCC are shown in Figure 4.17 (as determined by using the CSTR method) and Figure 4.18 (as determined by using the T_{10} method). To clarify, contact times below 5 minutes were not considered, and the results are valid for the different conditions outlined in Section 3.8., i.e. a 40MLD O_3 process that receives 9mg/l of TOC, discount rate of 6% and an average annual South African inflation since 2009 of 5.35% (Macrotrends, 2020).

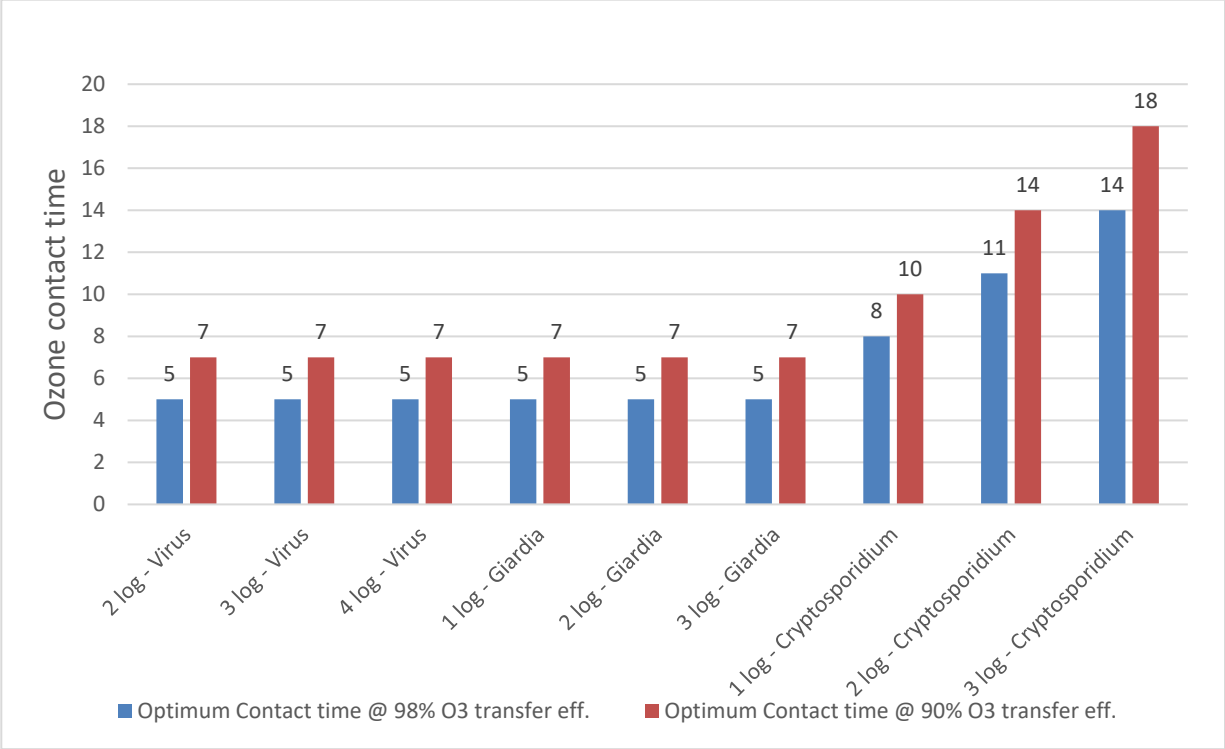

Figure 4.17 – Optimum contact time for lowest 20-year PV LCC cost determined by the CSTR method for various disinfection treatment objectives.

Figure 4.17 reveals that the optimum contact time for 2 to 4 log virus inactivation by O_3, including 1 to 3 log Giardia inactivation by O_3, lies between 5–7 minutes, as determined by using the CSTR method. In contrast, the optimum contact time for 1 to 3 log inactivation of Cryptosporidium lies between 8–18 minutes, depending on the O_3 transfer efficiency.

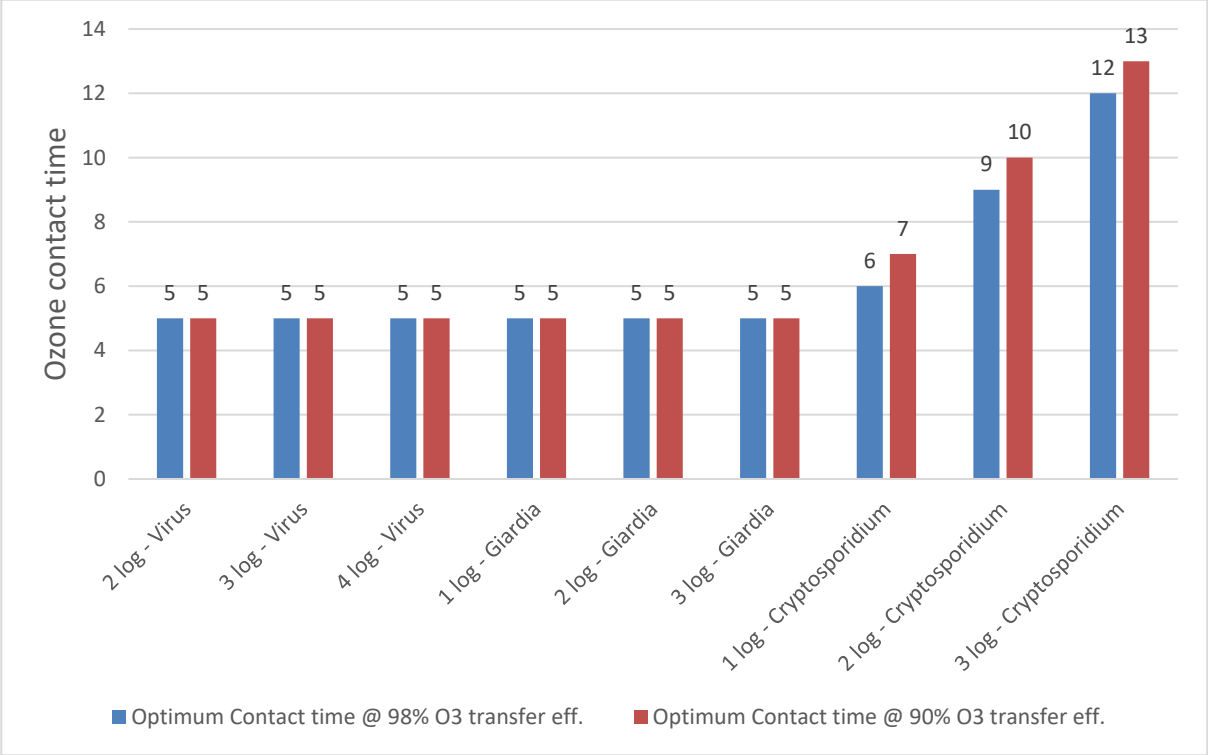

Figure 4.18 – Optimum contact time for lowest 20-year PV LCC determined by using the T_{10} method for various disinfection treatment objectives.

Figure 4.18 presents the optimum contact times as determined by the T_{10} method. It shows that for 2 to 4 log virus inactivation and 1 to 3 log Giardia inactivation, the optimum contact time lies at 5 minutes. Besides, the optimum contact time for 1 to 3 log Cryptosporidium inactivation lies between 6–13 minutes, depending on the O_3 transfer efficiency.

Generally, the CSTR method requires longer O_3 contact times and lower O_3/TOC dose ratios than the T_{10} method that requires shorter O_3 contact times and higher O_3/TOC dose ratios. It is important to note that the optimum contact times observed in the results are only applicable to the O_3 decay rates, the IOD, and the parameters used for the evaluation in the current section of the study.

4.5 Grouping of Cape Flats WWTW filtered final effluent key organic micropollutants

The current section investigates the extent to which the O_3/BAC process can remove the organic micropollutants found in the Cape Flats WWTW final effluent. The first step involves determining the second-order reaction rates associated with O_3 and hydroxyl radical (OH·) for each organic micropollutant removal. The second step groups the micropollutants based on their reaction rates. This section goes on to group the micropollutants found at the Cape Flats WWTW.

The first step of identifying organic micropollutants in the Cape Flats WWTW final effluent included conducting water quality tests that can detect more than 400 organic micropollutants. Specifically, the number of organic micropollutants that were detected in the final effluent of the Cape Flats WWTW was 112. See **Appendix B** for a summary of the organic micropollutants water quality test results. The second step consisted in searching for the O_3 and hydroxyl radical second-order reaction rates O_3 (k_{O3} and $K_{OH\cdot}$) for each organic micropollutants found in the Cape Flats WWTW SST final effluent. Values were found for 63 of the organic micropollutants that were arranged into five groups. The respective reaction rates are summarised in Table 4-4. However, it should be noted that not all reaction rate pH values were considered as it were outside of the scope of the current study. The reaction rate of organic micropollutants change with pH. The following number of organic micropollutants were found in each group (see Table 2-27 showing organic micropollutant groups definition):

i) 19 organic micropollutants in group 1;

ii) 11 organic micropollutants in group 2;

iii) 13 organic micropollutants in group 3;

iv) 15 organic micropollutants in group 4; and

v) 5 organic micropollutants in group 5.

Table 4-4 – Grouping of organic micropollutants in Cape Flats WWTW final effluent.

Group	Organic micro-pollutant	k_{O3} ($M^{-1}s^{-1}$)	Source	$k_{OH\cdot}$ ($M^{-1}s^{-1}$)	Source
1	Triclosan (anti-septic)	4.00E+07	(Gerrity *et al.*, 2012)	1.00E+10	(Gerrity *et al.*, 2012)
	17α-ethinyl estradiol	3.00E+06	(Gomes *et al.*, 2017)	9.80E+09	(Gomes *et al.*, 2017)
	Sulfamethoxazole	2.60E+06	(Gerrity *et al.*, 2012)	5.50E+09	(Jin, Peldszus & Huck, 2012)
	Estrone	1.82E+06	(Jin, Peldszus & Sparkes, 2014)		
	estradiol	1.70E+06	(Jin, Peldszus & Sparkes, 2014)	1.41E+10	(Wols & Hofman-Caris, 2012)
	estriol	1.66E+06	(Jin, Peldszus & Sparkes, 2014)		
	Amoxicillin	1.51E+06	(Jin, Peldszus & Sparkes, 2014)	5.43E+09	(Wols & Hofman-Caris, 2012)
	4-Nonylphenol	1.41E+06	(Jin, Peldszus & Sparkes, 2014)		
	Diclofenac	1.00E+06	(von Gunten, 2003)	7.50E+09	(von Gunten, 2003)
	Bisphenol A	7.00E+05	(Gomes *et al.*, 2017)	1.00E+10	(Gomes *et al.*, 2017)
	Lincomycin	6.76E+05	(Jin, Peldszus & Sparkes, 2014)		
	Butylparaben	4.40E+05	(Gomes *et al.*, 2017)	9.20E+09	(Gomes *et al.*, 2017)
	Propylparaben	4.10E+05	(Gomes *et al.*, 2017)	8.60E+09	(Gomes *et al.*, 2017)
	Ethylparaben	3.40E+05	(Gomes *et al.*, 2017)	7.70E+09	(Gomes *et al.*, 2017)
	Trimethoprim	3.00E+05	(Gomes *et al.*, 2017)	8.92E+09	(Gomes *et al.*, 2017)
	Carbamazepine	3.00E+05	(Gomes *et al.*, 2017)	8.80E+09	(Gomes *et al.*, 2017)
	Methylparaben	2.50E+05	(Gomes *et al.*, 2017)	6.80E+09	(Gomes *et al.*, 2017)
	Naproxen	2.00E+05	(Gomes *et al.*, 2017)	9.60E+09	(Gomes *et al.*, 2017)
	testosterone	1.00E+05	(Gerrity *et al.*, 2011)		
2	Lidocaine (anesthetic agent)	7.30E+04	(Gomes *et al.*, 2017)	1.00E+10	(Gomes *et al.*, 2017)
	Gemfibrozil	5.00E+04	(Gomes *et al.*, 2017)	1.00E+10	(Gomes *et al.*, 2017)

Group	Organic micro-pollutant	k_{O3} ($M^{-1}s^{-1}$)	Source	$k_{OH\cdot}$ ($M^{-1}s^{-1}$)	Source
	Mycrocystin-LR	3.40E+04	(von Gunten, 2003)		
	Triclocarban	5.00E+03	(Park *et al.*, 2017)		
	Atenolol	1.70E+03	(Gomes *et al.*, 2017)	7.05E+09	(Gomes *et al.*, 2017)
	Caffeine (stimulant)	650	(Farley, 2018)	5.90E+09	(Farley, 2018)
	Bezafibrate	590	(Gomes *et al.*, 2017)	7.40E+09	(Gomes *et al.*, 2017)
	progesterone	5.00E+02	(Gerrity *et al.*, 2011)		
	Acesulfame (sweetener)	88	(Gomes *et al.*, 2017)	5.44E+09	(Gomes *et al.*, 2017)
	Quinoline	51	(Parker, 2014)	7.00E+09	(Parker, 2014)
	Clofibric Acid	5.00E+03	(Jin, Peldszus & Huck, 2012)	5.03E+09	(Wols & Hofman-Caris, 2012)
3	Ibuprofen	9.1	(Gomes *et al.*, 2017)	7.40E+09	(Gomes *et al.*, 2017)
	Phenytoin	<10	(Gomes *et al.*, 2017)	5.00E+09	(Gomes *et al.*, 2017)
	Primidone	1	(Gomes *et al.*, 2017)	7.00E+09	(Gomes *et al.*, 2017)
	Benzene	2.00	(von Gunten, 2003)	7.90E+09	(von Gunten, 2003)
	Diazepam	0.75	(Gomes *et al.*, 2017)	7.20E+09	(Gomes *et al.*, 2017)
	Fluoxetine	--	--	8.40E+09	(Park *et al.*, 2017)
	Diltiazem	--	--	8.30E+09	(Park *et al.*, 2017)
	Metolachlor	1.10	(Jin, Peldszus & Sparkes, 2014)	6.96E+09	(Wols & Hofman-Caris, 2012)
	Phenol			1.03E+10	(Park *et al.*, 2017)
	Paracetamol – reported as acetaminophen			5.85E+09	(Wols & Hofman-Caris, 2012)
	Diazinon			8.75E+09	(Wols & Hofman-Caris, 2012)
	Ketoprofen	0.4	(Rosal *et al.*, 2010)	6.89E+09	(Wols & Hofman-Caris, 2012)

Group	Organic micro-pollutant	k_{O3} ($M^{-1}s^{-1}$)	Source	$k_{OH\cdot}$ ($M^{-1}s^{-1}$)	Source
	Phenazone			7.93E+09	(Wols & Hofman-Caris, 2012)
4	DEET (insecticide)	<10	(Gomes *et al.*, 2017)	4.95E+09	(Gomes *et al.*, 2017)
	Atrazine	6	(Gomes *et al.*, 2017)	3.00E+09	(Gomes *et al.*, 2017)
	Meprobamate	<1	(Gomes *et al.*, 2017)	4.00E+09	(Gomes *et al.*, 2017)
	Iopromide	<0.8	(Gomes *et al.*, 2017)	3.30E+09	(Gomes *et al.*, 2017)
	Erytromycin	--	--	3.00E+09	(Gomes *et al.*, 2017)
	Iohexol	--	--	3.21E+09	(Gomes *et al.*, 2017)
	Octylphenol	--	--	4.00E+09	(Gerrity *et al.*, 2011)
	2,4-D (2,4-dichlorophenoxy	2.29	(Jin, Peldszus & Sparkes, 2014)	3.24E+09	(Wols & Hofman-Caris, 2012)
	Simazine	4.79	(Jin, Peldszus & Sparkes, 2014)	2.90E+09	(Wols & Hofman-Caris, 2012)
	1,4-Dioxane	0.3	(Parker, 2014)	2.50E+09	(Parker, 2014)
	Diuron	14.7	(Rosal *et al.*, 2010)	4.60E+09	(Wols & Hofman-Caris, 2012)
	Propazine			1.65E+09	(Wols & Hofman-Caris, 2012)
	Linuron			4.30E+09	(Wols & Hofman-Caris, 2012)
	Cyanazine	7.41	(Jin, Peldszus & Sparkes, 2014)	1.90E+09	(Broséus *et al.*, 2009)
	Metformin	1.2	(Jin, Peldszus & Huck, 2012)	1.00E+07	(Khouri *et al.*, 2004)
5	TCEP (flame retardant)	<1	(Gomes *et al.*, 2017)	6.00E+08	(Gomes *et al.*, 2017)
	TCPP	<1	(von Sonntag & von Gunten, 2015)	7.00E+08	(von Sonntag & von Gunten, 2015)
	Bromoform	<0.2	(von Gunten, 2003)	1.30E+08	(von Gunten, 2003)
	NDMA	0.05	(von Sonntag & von Gunten, 2015)	4.50E+08	(von Sonntag & von Gunten, 2015)
	Chloroform		(von Gunten, 2003)	5.00E+07	(von Gunten, 2003)

When compared with their respective standard, nine organic micropollutants were above their limit. The results are summarised in Table 4-5 below that further summarises the maximum value of each organic micropollutant, the standard/limit, the minimum reduction required to get it within the water quality standard as well as the group to which each belongs. For 1,7 - Dimethylxanthine, no reaction rate was found, and thus no group is attached to this micropollutant. The organic micropollutants found to be above their standard in the Cape Flats WWTW final effluent ranged from group 1 to group 3 and also group 5, but no group 4 micropollutants were found to be above their standard.

Table 4-5 – Organic micropollutants above their standard.

Compound	Use	Maximum Value Detected (ng/l)	California State Water Resources Control Board (ng/l)	Minimum Reduction Required	Group
Carbamazepine	Antiepileptic (*Carbamazepine*, 2020)	2000	1000	50%	1
Ethinyl Estradiol - 17 Alpha	Birth control (*Ethinyl Estradiol*, 2020)	290	280	3%	1
Amoxicillin	Antibiotic (*Amoxicillin*, 2020)	15000	1500	90%	1
4-nonylphenol	Detergent (*4-Nonylphenol*, 2020)	170000	110000	35%	1
Caffeine	Central nervous system stimulant (*Caffeine*, 2020)	3200	350	89%	2
Quinoline	Used in dyes, resins etc. (*Quinoline*, 2020)	3100	10	99.99%	2
Fluoxetine	Antidepressant (*Fluoxetine*, 2020)	37000	10000	73%	3
N-Nitroso dimethylamine (NDMA)	Disinfectant byproduct (DBP), pesticide, rocket fuel (*N-Nitroso dimethylamine*, 2020)	4.1	1	76%	5
1,7-Dimethylxanthine	Psychoactive central nervous system stimulant. Like caffeine. (*1,7-Dimethylxanthine*, 2020)	3000	70	98%	

4.6 Organic micropollutant water quality risk analysis

The current section is the second part that investigates the extent to which the O_3/BAC process can remove the organic micropollutants found in the Cape Flats WWTW final effluent. The focus is on the organic micropollutants that were found to be above the recommended standard (Table 4-5). The first step involves determining the O_3/TOC dose ratio required to reduce the organic micropollutants to below their standard and then to calculate the predicted removal. The second step includes conducting a water quality risk profile on the identified organic micropollutants to indicate the water quality risk before and after removal treatment.

Insight 7: A risk analysis of the organic micropollutants in the Cape Flats WWTW secondary effluent predicts that the O_3 process can reduce the risk of more than 87% of the pollutants that are above the recommended standards before O_3 treatment.

Based on the grouping of the organic micropollutants, as shown in Table 4-5, the required O_3/TOC dose ratio was obtained from Table 2-27. Subsequently, the O_3/TOC dose ratio was used to determine the ΔUV_{a254} by using Equation 2.14. Then, by using the ΔUV_{a254}, the predicted removal of each organic micropollutant in Table 4-5 was determined with Equation 2.16.

Table 4-6 indicates the O_3/TOC dose required to reduce the organic micropollutants to within their standard (based on the group indicator removal). The highest O_3/TOC dose required was 1.5mgO_3/TOC for N-Nitroso dimethylamine (NDMA).

Table 4-6 – O_3/TOC dose ratio required to achieve the minimum reduction.

Compound	Minimum reduction required (Table 4-5)	Group	O_3/TOC dose ratio required to achieve minimum reduction (Equation 2.14 & Equation 2.16)	ΔUV_{a254} (Equation 2.14)	Organic micropollutant group removal indication (Equation 2.16)
Carbamazepine	50%	1	0.25	22%	90%
Ethinyl Estradiol - 17 Alpha	3%	1	0.25	22%	90%
Amoxicillin	90%	1	0.25	22%	90%
4-nonylphenol	35%	1	0.25	22%	90%
Caffeine	89%	2	0.56	36%	89%
Quinoline	99.99%	2	0.71	41%	99.99%

Table 4-6 continued.

Compound	Minimum reduction required (Table 4-5)	Group	O_3/TOC dose ratio required to achieve minimum reduction (Equation 2.14 & Equation 2.16)	ΔUV_{a254} (Equation 2.14)	Organic micropollutant group removal indication (Equation 2.16)
Fluoxetine	73%	3	1.00	51%	79%
N-Nitroso dimethylamine (NDMA)	76%	5	1.50	65%	23%
1,7-Dimethylxanthine	98%				

Table 4-7 below shows the organic micropollutant water quality risk analysis and profile before treatment, as described in Section 3.10. All organic micropollutants have a medium risk profile. No O_3 or hydroxyl radical reaction rates were found for 1,7 - Dimethylxanthine, and thus no pre- or post-treatment rating is provided.

Table 4-7 – Organic micropollutant risk rating before treatment.

Potential hazards	Concentration after treatment (ng/l)	Likelihood (λ)	Rating	Consequence (μ)	Rating	Risk rating (λ×μ)	Risk profile
4-nonylphenol	170 000	Almost certain	1	Moderate	20	20	Medium
Caffeine	3 200	Almost certain	1	Moderate	20	20	Medium
17 Alpha Ethinyl Estradiol	290	Almost certain	1	Moderate	20	20	Medium
Carbamazepine	2 000	Almost certain	1	Moderate	20	20	Medium
Quinoline	3 100	Almost certain	1	Moderate	20	20	Medium
Amoxicillin	15 000	Almost certain	1	Moderate	20	20	Medium
N-Nitroso dimethylamine (NDMA)	4.1	Almost certain	1	Moderate	20	20	Medium
Fluoxetine	37 000	Almost certain	1	Moderate	20	20	Medium
1,7-Dimethylxanthine	3 000	Almost certain	1	Moderate	20	20	Medium

Table 4-8 below shows the organic micropollutant water quality risk analysis and profile after treatment with an O_3/TOC dose ratio of 1.5 and using Equation 3.9 as described in Section 3.10. The O_3 process at the Cape Flats MAR WRP can dose a O_3/TOC ratio of more than

1.5mgO_3/mgTOC which is sufficient to reduce most of the organic micropollutants to within their standard. As can be observed from Table 4-8, all the organic micropollutants have a low-risk profile after treatment, except NDMA. Hence, it can be concluded that the O_3/BAC process at the Cape Flats MAR WRP can theoretically lower the risk of more than 87% (7 out of 8) of the organic micropollutants in the Cape Flats WWTW final effluent that are found to be above their standard, i.e. from medium risk, to low risk and to within the standard. This finding proves the hypothesis that the O_3/BAC process can help to produce safe drinking water with regards to organic micropollutants. This risk assessment does not consider O_3 oxidation organic micropollutant transformation products. No consideration was given to the additional biological removal of organic micropollutants by the BAC filtration process given that no removal prediction models were found. Li *et al.* (2015) however, found that BAC filtration reduced the toxicity caused by ozonation transformation products. As an extra precaution, the treatment train at Cape Flats MAR WRP has allowed for another step, namely the UV advanced oxidation, to reduce NDMA within its standard.

Table 4-8 – Organic micropollutant risk rating after treatment.

Potential hazards	Concentration after treatment (ng/l)	Likelihood (λ)	Rating	Consequence (μ)	Rating	Risk Rating (λ×μ)	Risk Profile
4-nonylphenol	3400	Unlikely	0.2	Moderate	20	4	Low
Caffeine	0	Unlikely	0.2	Moderate	20	4	Low
17 Alpha Ethinyl Estradiol	5.80	Unlikely	0.2	Moderate	20	4	Low
Carbamazepine	40	Unlikely	0.2	Moderate	20	4	Low
Quinoline	0	Unlikely	0.2	Moderate	20	4	Low
Amoxicillin	300	Unlikely	0.2	Moderate	20	4	Low
N-Nitroso dimethylamine (NDMA)	3.16	Almost certain	1	Moderate	20	20	Medium
Fluoxetine	0	Unlikely	0.2	Moderate	20	4	Low
1,7-Dimethylxanthine							

The main finding of Sections 4.5 to 4.6 is that the O_3 process can reduce more than 87% of the organic micropollutants initially found to be above their standard in the Cape Flats WWTW final effluent to acceptable standard, i.e. within their standard.

4.7 Summary of findings

A detailed discussion of the main findings of the current study are presented in Section 4.1 to 4.6. The current section provides only a summary of the seven key insights from the findings in Chapter 4. More specifically, Table 4-9 below gives a summary of the research questions and findings, i.e. the methodologies and their associated results herein presented as insights. Also presented in the current section, after Table 4-9, is a more detailed summary of the main findings.

Table 4-9 – Summary of research questions and their associated methodology and results.

No.	Research question	Methodology followed towards results	Results
1.	How does the performance assessment of the O_3/BAC process influence the number of O_3/BAC treatment objectives achieved?	The required O_3/TOC ratio for all the treatment objectives identified in Table 3-4 and Table 3-5, was determined with the following methods: 1. CSTR method - Equation 2.7 2. Conservative method - Equation 2.8 3. T_{10} method - Equation 3.8	**Insight 1:** For a multi treatment objective use of the O3 process (i.e. multiple disinfection objectives and organic micropollutants oxidation objectives) it is better to validate the process with the T10 method given that more treatment objectives are validated with this method. For custom treatment objective applications (i.e. one or two disinfection objectives) it is more optimal to use the CSTR method for validation which will result in the lowest O3/TOC dose ratio. (See Page No. 4-100) **Insight 2:** The optimum EBCT prediction models are not suitable for the removal of organic micropollutants moderately or marginally oxidised by O3, since they require EBCT greater than 20 minutes according to Table 3-6. Based on the findings by Sundaram and Pagilla (2019) the BAC filtration TOC removal models (Equation 2.20 and Equation 2.21) are applicable to BAC filters receiving between 2–8mgTOC/l. (See Page No. 4-100)
2.	How do the costs of different O_3/BAC treatment objectives relate to one another?	The costs of the treatment objectives are identified in Table 3-4, Table 3-5, and Table 3-6 and were investigated by using the cost functions of Section 2.4.14 and Section 2.5.11 for a 40MLD O_3/BAC process receiving 9mgTOC/l. The costs were determined for each of the O_3/TOC ratios determined in research question 1 above.	**Insight 3:** For a 40MLD O3 process, receiving 9mgTOC/l, and having a 15-minute contact time, the average predicted differences for capital costs and annual O&M costs between the T10 method and the CSTR method are R5.6-million (capital) and R4.2-million (O&M), respectively (See Page No. 4-106)

No.	Research question	Methodology followed towards results	Results
			Insight 4: The BAC filtration costing models predict a 11% increase (R23-million) in capital cost between a 10 to 20 minutes EBCT for a 40MLD BAC filtration process. The costing models predict a 28% increase (R3-million) in annual O&M costs between a 10 to 20 minutes EBCT. The combined effect of the above increases is a 16% increase (R61-million) in the 20-year PV LCC between a 10 to 20 minutes EBCT. (Page No. 4-110)
3.	How do international costing models relate to the capital cost and O&M costs of the O_3/BAC process in Southern Africa?	The following comparisons were done: 1. US concept level O_3-capital cost estimates (see Section 2.4.14 for costing models) vs. actual Southern African O_3-costs (for project details see Table 3-12); 2. South African published O_3-capital cost estimates (see Figure 3.10) vs. actual Southern African O_3-costs; 3. US concept level O_3-O&M cost estimates (see Section 2.4.14 for costing models) vs. South African O_3-O&M cost estimates (see Figure 3.9); and 4. US concept level BAC-capital cost estimates (see Section 2.5.11 for costing models) vs. actual Southern African BAC-costs (for project details see Table 3-12);	**Insight 5:** US based costing models overestimate the actual capital costs in Southern Africa and the South African costing models underestimate the actual capital costs in Southern Africa. For both costing models significantly good correlations, between 6–7% in annual O3 O&M costs, are observed. (See Page No. 4-113)
4.	Is there an optimum O_3 contact time in terms of capital and O&M cost for the O_3 disinfection process?	This investigation was done for a 40MLD O_3 process receiving 9mgTOC/l. The optimum contact time was determined for all the treatment objectives of Table 3-4 by using Equation 2.7 for the CSTR method and Equation 3.8 for the T_{10} method.	**Insight 6:** The most optimum contact time (i.e. the one producing the lowest 20-year PV LCC) for 3-log Cryptosporidium inactivation with O3 for the CSTR method was found to be 14 minutes, after which, the PV LCC cost plateaued. The most optimum contact time (i.e. the one producing the lowest 20-year PV LCC) for 3-log Cryptosporidium inactivation with O3 was found to be 12 minutes for the T10 method. The results are applicable for a 40MLD plant and feedwater with the characteristics of Table 2-14. (See Page No. 4-119)

No.	Research question	Methodology followed towards results	Results
5.	How effectively can the O_3/BAC process remove the organic micropollutants found in the Cape Flats WWTW final effluent?	The organic micropollutants with known O_3 and OH· reaction rates were grouped based on Table 2-27. Their removal was then predicted using the methodology outlined by Equation 3.9.	**Insight 7:** A risk analysis of the organic micropollutants in the Cape Flats WWTW secondary effluent predicts that the O3 process can reduce the risk of more than 87% of the pollutants that are above the recommended standards before O3 treatment. (See Page No. 4-126)

In section 4.1.1, the current study investigates how the O_3/TOC dose ratios for the various treatment objectives compared with one another, using the three process validation methods, i.e. the T_{10} method, the CSTR method and the conservative method. It was found that, generally, the CSTR method gives the lowest O_3/TOC ratio while the T_{10} method produces the highest ratio, except for 2-log- and 3-log Cryptosporidium inactivation for which the conservative method gives the highest ratio. The above findings correspond to the LT2ESWTR (US EPA, 2010) that states that the T_{10} method, as a general rule, underestimates the CT-value obtained. From section 4.1.1, the following points were identified as the main findings:

i) The oxidation of more groups of organic micropollutants are achieved when using the T_{10} method;

ii) The CSTR method validates higher levels of disinfection inactivation (CT-values) when the O_3/TOC dose ratio is selected for organic micropollutant oxidation;

iii) The conservative method of validation covers more oxidation groups when the Cryptosporidium disinfection is selected as a treatment objective;

iv) The O_3 process can be optimised by using the CSTR method to tailor it to a small number of treatment objectives. For instance, when the O_3 process is explicitly implemented for 2-log virus inactivation, it can be optimised by using the CSTR method for validation, which will result in the lowest required O_3/TOC dose ratio; and

v) The T_{10} method of validation can be used to achieve more treatment objectives in the case of a multibarrier treatment train. For instance, when the T_{10} method is used for validation of a treatment objective of 3-log Cryptosporidium inactivation, all but the treatment objectives of group 4 organic micropollutants oxidation are achieved.

The CT-values obtained with the validation methods for varying O_3/TOC dose ratios are investigated in Section 4.1.2. The section showed that using the T_{10} method with one residual O_3 meter at the end of the contact tank, lower CT-values are validated as opposed to using the CSTR

method. To achieve the same CT-values of the CSTR method, much higher O_3/TOC dose ratios would be required with the T_{10} method, which would result in higher cost requirements, but on the positive side more groups of organic micropollutants can be oxidised. The CT-values determined by the CSTR value plateaued between 0-20 minutes contact time. For the T_{10} method the CT-value reached a maximum after which is started to reduce between 0-20 minutes contact time.

In Section 4.1.3, there is a comparison of the BAC filtration performance assessment models. The results show that better correlations between TOC removal and optimum EBCT prediction models are achieved at high O_3/TOC dose ratios, O_3/TOC = 2 as compared to O_3/TOC = 0.5. The optimum EBCT value does, however, not correlate with the EBCT required for the removal of organic micropollutants marginally oxidised by O_3. It is concluded that the TOC removal prediction models (17–43% TOC removal depending on the O_3/TOC ratio and the EBCT) seems to be only valid for incoming TOC concentrations of between 2–8mg/l.

In Section 4.2 the costs of different O_3/BAC treatment objectives are compared with one another. Generally, the T_{10} method yields the highest capital cost, O&M cost, and 20-year PV LCC, except when Cryptosporidium inactivation is the objective. Otherwise, the conservative method is most expensive of all the methods. In turn, the CSTR method yields the lowest capital cost, O&M costs and 20-year PV LCC, but also the lowest number of organic micropollutant groups being oxidised (refer to Section 4.1.1). For the O_3 process considered (40MLD), the costs compare as follows:

i) The predicted capital costs vary from R133-million, for 2-log virus inactivation, to a maximum of R156-million, for 3-log Cryptosporidium inactivation;

ii) The predicted O&M costs vary from R2-million, for 2-log virus inactivation, to a maximum R19-million, for 3-log Cryptosporidium inactivation; and

iii) The predicted 20-year PV LCC costs vary from R156-million, for 2-log virus inactivation, to a maximum R472-million, for 3-log Cryptosporidium inactivation.

Besides, for the BAC filtration process considered (40MLD), the differences in costs (20-year PV LCC, capital, and O&M costs) between the 10- , 15- and 20-minute EBCTs were found to be relatively small. The costs compare as follows:

i) The annual O&M cost estimates vary, being R1-million on average between 10- and 15-minute EBCT;

ii) The annual O&M cost estimates vary, being R2-million on average between 15- and 20-minute EBCT;

iii) The capital cost estimates vary, being R11-million on average between 10- and 15-minute EBCT; and

iv) The capital cost estimates vary, being R12-million on average between 15-minute and 20-minute EBCT.

The 16% increase in the BAC 20-year PV LCC from 10- to 20-minute EBCT is small considering the added process performance benefits at a higher EBCT, i.e. more TOC removal and organic micropollutant removal.

Section 4.3 compared international, i.e. US costing models, to South African costing models and Southern African actual costs of the O_3/BAC filtration process (Cape Flats MAR WRP in South Africa and Goreangab WRP in Namibia). The findings shown that the South African O_3-capital cost models underestimate the actual O_3-capital costs. In turn, the US-based concept-level cost models overestimate the capital cost of the Goreangab O_3-process but underestimate the capital cost of the Cape Flats O_3-process. The above observation can be attributed to selected distinct features of the O_3 process at the Cape Flats MAR WRP (i.e. the O_3 contact tank, the O_3 dosing room, pipework, etc.), that is sized for the future (64 MLD) processing capacity of the plant (Smuts & Marais, 2018). Also, the comparison adds 35% to the capital cost of the O_3 process at the Cape Flats MAR WRP, particularly for engineering, legal and administration costs. 35% is high when compared with typical professional costs in South Africa. Lastly, no clear correlation between the costing models and the actual costs was observed. Similarly, no meaningful correlations were found between the international (US) capital costing models and the actual Southern African costs were observed for the BAC filtration process.

For the annual O_3-O&M costs, statistically significant correlations were observed between the published South African O_3-O&M annual cost model and the US O_3-O&M annual cost model. The South African O_3-O&M annual cost model predicts slightly lower O&M costs, while the US O_3-O&M annual cost model predicts 6–7% higher costs.

For the O_3 decay rates and the instantaneous O_3 demands used in the current study, Section 4.4 derived the optimum cost contact time for each disinfection treatment objective identified in Table 3-4 for the T_{10} method and the CSTR method. For the CSTR method, the benefit of increasing the O_3 contact time beyond 14 minutes, for 3 log inactivation, plateaued. For the T_{10} method, a low-cost point exists between 5–20 minutes of contact time, depending on the treatment objective.

Moreover, it was found, for the CSTR method, that the optimum contact time, for 2 to 4 Log virus inactivation by O_3 and 1 to 3 Log Giardia inactivation by O_3, lies between 5–7minutes. The optimum contact time for 1 to 3 log inactivation of Cryptosporidium lies between 8–18 minutes for the CSTR method, depending on the exact treatment objective and O_3 transfer efficiency.

For the T_{10} method, the optimum contact time was found to be 5 minutes, specifically for 2 to 4 log virus inactivation and 1 to 3 Log Giardia inactivation. The optimum contact time for 1 to 3 log inactivation of Cryptosporidium was found to be between 6–13 minutes for the T_{10} method, depending on the exact treatment objective and O_3 transfer efficiency.

In Sections 4.5 to 4.6 a water quality risk analysis was done on the micropollutants in the Cape Flats final effluent. The study found that the O_3 process can reduce more than 87% of the organic micropollutants in the Cape Flats WWTW final effluent to within acceptable standards, i.e. below their standards and with a low risk profile. Notwithstanding the findings of Li *et al.* (2015) that BAC filtration can reduce the toxicity caused by ozonation transformation products, no consideration was given to the additional biological removal of organic micropollutants by the BAC filtration process. The current study could find no BAC filtration organic micropollutant removal prediction models.

The research hypothesis was confirmed given that the O_3/BAC process can be optimised by carefully selecting the desired treatment objectives (displayed in Table 3-4 to Table 3-6) and then the validation method yielding the lowest O_3/TOC dose ratio (see Table 4-2 and Figure 4.1) at the most optimum O_3-contact time (see Figure 4.17 and Figure 4.18).

Chapter 5 : Conclusion and recommendations

5.1 Summary of study

Treated final WWTP effluent is a large water source that usually ends up in the ocean, especially in the Cape Town context, where the City has a theoretical potential of 500MLD available for new reuse projects. The Cape Flats MAR WRP forms part of the Cape Flats Aquifer Potable Reuse Scheme and aims to harness this potential. One of the most critical treatment processes in the Cape Flats MAR WRP is the O_3/Biological-Active-Carbon (O_3/BAC) filtration process given that it inactivates pathogens and reduces organic micropollutants.

When final effluent of WWTP systems is considered for reuse, the health risk associated with organic micropollutants (chronic health risk) and pathogens (acute health risk) in the effluent has to be considered, given its source and content. Advanced treatment processes like adsorption onto activated carbon or oxidation by ozonation are required to reduce the chronic and acute health risks.

The combination of O_3 and BAC filtration is attractive because it inactivates pathogens an oxidises organic micropollutants and it can produce a high-quality water compared to RO. Other benefits of combining O_3 and BAC filtration is extended activated carbon life, increased TOC removal and the reduction of ozonation by-products. However, O_3 disinfection in wastewater reuse treatment trains, puts a high demand on energy usage and can increase the costs associated with water production. Nevertheless, when designing treatment facilities, treatment objectives are the first priority and the optimisation of costs, the second priority.

The recent drought in South Africa, the potential for reuse in Cape Town and the initiative by the City of Cape Town to find alternative water sources makes investigating the O_3/BAC process and its application to filtered final effluent of Cape Flats WWTW relevant.

Given its relevance, its high costs and its critical role in the Cape Flats MAR WRP treatment train the question is raised of how the O_3/BAC process can be customised—with regard to treatment objectives—and optimised—with regard to cost—towards generating safe drinking water.

To summarise, the current study set out to answer the five research questions as follows:

i) How does the performance validation of the O_3/BAC process influence the number of O_3/BAC treatment objectives that can be achieved? It was found that, generally, the CSTR method gives the lowest O_3/TOC ratio while the T_{10} method produces the highest ratio, except for 2-log- and 3-log Cryptosporidium inactivation's for which the conservative method gives the highest ratio. However, more groups of organic micropollutant can be oxidised when using the T_{10} method if multiple treatment objectives are the aim, i.e. disinfection and oxidation. For BAC filtration it was found that at high O_3/TOC dose ratios (O_3/TOC = 2) better correlations between two prediction models of TOC removal (10% difference) and two prediction models of optimum EBCT (2% difference) are achieved when compared to low O_3/TOC dose ratios (O_3/TOC = 0.5). Furthermore, it was found that the predicted optimum EBCT values (maximum 12.58 minutes) at all O_3/TOC dose ratios do not correlate with the EBCT required for the removal of organic micropollutants marginally oxidised by O_3 (EBCT required are 20 minutes). It was concluded that the TOC removal prediction models, which predicted 17–43% TOC removal depending on the O_3/TOC ratio, are only valid for incoming TOC concentration of between 2–8mg/l;

ii) How do the costs of different O_3/BAC treatment objectives relate to one another? Generally, the T_{10} method yields the highest capital cost, O&M costs, and 20-year PV LCC, except when Cryptosporidium inactivation is the objective. Otherwise, the conservative method is the most expensive of all methods. In turn, the CSTR method yields the lowest capital cost, O&M costs and 20-year PV LCC, but also the lowest number of organic micropollutant groups being oxidised;

iii) How do international costing models relate to actual capital cost and O&M costs of the O_3/BAC process in Southern Africa? No clear correlation between the costing models and the actual costs was observed. Also, for the BAC filtration, no meaningful correlations between the international (US) capital costing models and the actual Southern African costs were observed. For the annual O_3-O&M costs, statistically significant correlations were observed between the published South African O_3-O&M annual cost model and the US O_3-O&M annual cost model. The South African O_3-O&M annual cost model predicts slightly lower O&M costs, while the US O_3-O&M annual cost model predicts 6–7% higher costs;

iv) Is there a O_3 contact time that minimises the 20-year present value (PV) Life Cycle Cost (LCC), including the capital and operation and maintenance (O&M) cost for the O_3 disinfection process? An O_3 contact time that resulted in the lowest PV LCC was found for the T_{10}- and CSTR- methods and each treatment objective for a 40MLD O_3 process that receives 9mg/l of TOC. For the CSTR method, the optimum contact time, for 2 to 4 Log virus inactivation by O_3 and 1 to 3 Log Giardia inactivation by O_3, was found to lie between 5–7 minutes. The optimum contact time for 1 to 3 log inactivation of Cryptosporidium lies between 8–18 minutes for the CSTR method. For the T_{10} method and specifically for 2 to

4 log virus inactivation and 1 to 3 Log Giardia inactivation the optimum contact time was found to be 5 minutes. The optimum contact time for 1 to 3 log inactivation of Cryptosporidium was found to be between 6–13 minutes for the T_{10} method;

v) How effectively can the O_3/BAC process remove the organic micropollutants found in the Cape Flats WWTW final effluent? It was found that the O_3/BAC process can theoretically reduce the risk of more than 87% of the organic micropollutants with concentrations above their standard. After O_3 treatment 7 of the 9 organic micropollutants (9 having concentrations above their standard) were rated as low risk. When organic micropollutants are considered, the results proved that the O_3/BAC process can help to produce safe drinking water.

By answering the above five questions, the current study proved that the O_3/BAC filtration process can be optimised to meet specific treatment objectives. Firstly, by selecting the best performance validation method (CSTR or T_{10} method) for the treatment objective. Secondly, by determining the most optimum O_3 contact time for the treatment objective yielding the lowest 20-year PV LCC. Furthermore, by ensuring that the CT-value is maintained in an O_3 process with the CSTR or T_{10} method, the inactivation of pathogens is validated and that contributes to the aim of producing safe water. The results of the water quality risk analysis on organic micropollutants together with the CT-value validation proves that the combination of O_3 and BAC filtration can be an effective process to eliminate pathogens and organic micropollutants.

The main insights of the study are:

i) Insight 1: For a multi treatment objective use of the O_3 process (i.e. multiple disinfection objectives and organic micropollutants oxidation objectives) it is better to validate the process with the T_{10} method given that more treatment objectives are validated with this method. For custom treatment objective applications (i.e. one or two disinfection objectives) it is more optimal to use the CSTR method for validation which will result in the lowest O_3/TOC dose ratio.

ii) Insight 2: The optimum EBCT prediction models are not suitable for the removal of organic micropollutants moderately or marginally oxidised by O_3, since they require EBCT greater than 20 minutes according to Table 3-6. Based on the findings by Sundaram and Pagilla (2019) the BAC filtration TOC removal models (Equation 2.20 and Equation 2.21) are applicable to BAC filters receiving between 2–8mgTOC/l.

iii) Insight 3: For a 40MLD O_3 process, receiving 9mgTOC/l, and having a 15-minute contact time, the average predicted differences for capital costs and annual O&M costs between the T_{10} method and the CSTR method are R5.6-million (capital) and R4.2-million (O&M),

respectively. Hence, favouring the CSTR method. An O&M difference of R4.2-million is significant if considered over a lifespan of 20 years.

iv) Insight 4: The BAC filtration costing models predict a 11% increase (R23-million) in capital cost between a 10 to 20 minutes EBCT for a 40MLD BAC filtration process. The costing models predict a 28% increase (R3-million) in annual O&M costs between a 10 to 20 minutes EBCT. The combined effect of the above increases is a 16% increase (R61-million) in the 20-year PV LCC between a 10 to 20 minutes EBCT.

v) Insight 5: US based costing models overestimate the actual capital costs in Southern Africa and the South African costing models underestimate the actual capital costs in Southern Africa. For both costing models significantly good correlations, between 6–7% in annual O_3 O&M costs, are observed.

vi) Insight 6: The most optimum contact time (i.e. the one producing the lowest 20-year PV LCC) for 3-log Cryptosporidium inactivation with O_3 for the CSTR method was found to be 14 minutes, after which, the PV LCC cost plateaued. The most optimum contact time (i.e. the one producing the lowest 20-year PV LCC) for 3-log Cryptosporidium inactivation with O_3 was found to be 12 minutes for the T_{10} method. The results are applicable for a 40MLD plant and feedwater with the characteristics of Table 2-14.

vii) Insight 7: A risk analysis of the organic micropollutants in the Cape Flats WWTW secondary effluent predicts that the O_3 process can reduce the risk of more than 87% of the pollutants that are above the recommended standards before O_3 treatment.

5.2 Conclusions

The main conclusions of the study are as follows:

i) The results of the comparison of the O_3/TOC dose ratio required by the T_{10} method and the CSTR method showed that the treatment objectives of the O_3/BAC filtration process determine which assessment is best suited for the system (see Section 4.1). Using the best suited method reduces the O_3/TOC dose ratio required and therefore the cost associated with constructing and operating the system.

ii) The comparisons of international (US) costing models, firstly with South African costing models, and secondly to actual costs in Southern Africa, give context to the international costing models regarding their accuracy in the Southern African context. Many variables including, the inflation rates, discount rates, exchange rates, etc., and the nature of the international costing models namely, the conceptual level costing models, imply that no clear correlation can be found besides the close correlation of the O_3-O&M costs.

iii) The current study derived a method to determine the most cost effective O_3 contact time when the O_3 decay rate and IOD of a O_3 process feed water are available (see Section 4.4).

This finding can help to determine the optimum contact time that results in lower O&M and capital costs of O_3 systems. Table 5-1 summarises the optimum O_3 contact times identified in the current study.

iv) The current study showed how efficiently the O_3 process can oxidise organic micropollutants in the Cape Flats WWTW final effluent. The study found that the O_3 process can reduce more than 87% of the organic micropollutants to within acceptable standards, i.e. below each micropollutants standard and within a low risk profile (see Sections 4.5 and 4.6).

Table 5-1 – Summary of the optimum O_3 contact times identified.

	Treatment Objectives optimum contact time (minutes)								
Process validation method	**2-log Virus**	**3-log Virus**	**4-log Virus**	**1-log Giardia**	**2-log Giardia**	**3-log Giardia**	**1-log Crypto***	**2-log Crypto***	**3-log Crypto***
T_{10}	5	5	5	5	5	5	6–7	9–10	12–13
CSTR	5–7	5–7	5–7	5–7	5–7	5–7	8–10	11–14	14–18
* Short for Cryptosporidium									

The increasing stress on existing conventional water sources like dams and rivers creates the need for alternative water sources. One such alternative water source is secondary effluent like in the case of Cape Flats MAR WRP. The use of secondary effluent holds high risk given the pathogens and organic micropollutants found in them. Furthermore, the increase in electricity costs and the rising cost of water treatment amplifies the necessity for process optimisation. The current study has shown that the O_3/BAC process is theoretically effective in reducing the organic micropollutants found in the Cape Flats WWTW secondary effluent. Ensuring that the CT-value of a selected treatment objective is maintained with either the CSTR or T_{10} method can ensure that pathogens are inactivated. Furthermore, the findings provide new ways to optimise the O_3/BAC filtration process to best suit specific treatment objectives (combination of points i) and iii) above). The O_3/BAC filtration objectives should be selected based on the intended purpose of the process in the bigger picture of a treatment train, i.e. disinfection or oxidation. The ways in which the process can be optimised are by:

i) The selection of the best suited validation method for the treatment objectives at hand as illustrated by the use of Table 4-2; and

ii) The selection of the most cost-efficient contact time based on Equation 3.8 (T_{10} method) or Equation 2.7 (CSTR method) depending on the validation method.

5.3 Shortcomings

The limitations of the current study are:

i) Not all the organic micropollutants O_3 and hydroxyl radicals second order reaction rates could be found;

ii) Risk assessments are conducted only on organic micropollutants found in the water quality results of two samples (see Section 3.3). Further expansion of the baseline water quality dataset on the Cape Flats WWTW final effluent can reveal the presence of additional organic micropollutants;

iii) Specific aspects of water quality (pH, alkalinity, temperature, etc.) are not taken into account in this study;

iv) The specific effects of the different types of GAC media are not considered;

v) Findings are only valid for a final effluent with the decay and IOD characteristics as highlighted below in Table 5-2;

Table 5-2 – Final effluent characteristics for which results are valid.

	Tertiary Effluent		
O_3/TOC ratio	**k (min^{-1})**	**IOD (mg/l)**	**R^2**
0.3	n/a*	1.9	n/a*
0.5	0.5131	3	0.99
1.1	0.1278	4.9	0.99
1.7	0.0673	6.4	0.97
*No measurable dissolved ozone residual			

vi) The grouping of elements, to predict their removal, can be inaccurate given the significant variations in the second order reaction rates of organic micropollutants (Sonntag and Von Gunten, [2012] and Park et al., [2017]); and

vii) The presence of organic micropollutant transformation products after treatment with O_3 are not considered.

5.4 Future research

The future research that can be conducted should focus on:

i) The existence of the most cost efficient O_3 contact times for other O_3 decay rates and IOD values;

ii) The possibility of checking and comparing the actual O_3 decay rate and IOD of the filtered Cape Flats WWTW final effluent with the respective values used in the current study, when the O_3/BAC filtration process of the Cape Flats MAR WRP is in operation;

iii) The possibility of comparing the actual removal of organic micropollutants with values predicted in the current study when the O_3/BAC filtration process of the Cape Flats MAR WRP is operational;

iv) The possibility of comparing the actual removal of TOC at various EBCT with values predicted in the current study when the O_3/BAC filtration process of the Cape Flats MAR WRP is operational; and

v) The sensitivity and influence that the inflation rate and the USD exchange rate has on the international costing models to predict O_3/BAC filtration costs in Southern Africa.

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Appendices

Appendix A

Organic micropollutants tested

	Parameter	Reporting Limit	Unit
	EDB & DBCP (EPA 504.1 - Monrovia)		
1	1,2,3-Trichloropropane	0.02	ug/L
2	1,2-Dibromo-3-chloropropane (DBCP)	0.01	ug/L
3	1,2-Dibromoethane (EDB)	0.01	ug/L
	Chlorinated Acids (EPA 555)		
4	2,4,5-TP (Silvex)	0.1	ug/L
5	2,4-D	0.1	ug/L
6	Dalapon	1	ug/L
7	Dicamba	0.1	ug/L
8	Dinoseb	0.1	ug/L
9	Pentachlorophenol	0.04	ug/L
10	Picloram	0.1	ug/L
	EDC & PPCP (Method LC MS MS)		
11	1,7-Dimethylxanthine	10.0 ng/L	
12	17alpha-Ethynyl estradiol	5	ng/L
13	17beta-Estradiol	5	ng/L
14	2,4-D	5	ng/L
15	4-Androstene-3,17-dione	5	ng/L
16	4-Nonylphenol	100	ng/L
17	4-tert-Octylphenol	50	ng/L
18	Acesulfame-K	20	ng/L
19	Acetaminophen	5	ng/L
20	Albuterol	5	ng/L
21	Amoxicillin	20	ng/L
22	Antipyrine	5	ng/L
23	Atenolol	5	ng/L
24	Atrazine	5	ng/L
25	Azithromycin	20	ng/L
26	Bendroflumethiazide	5	ng/L
27	Bezafibrate	5	ng/L
28	Bisphenol A	10	ng/L
29	Bromacil	5	ng/L
30	Butalbital	5	ng/L
31	Butylparaben	5	ng/L
32	Caffeine	5	ng/L

	Parameter	Reporting Limit	Unit
33	Carbadox	5	ng/L
34	Carbamazepine	5	ng/L
35	Carisoprodol	5	ng/L
36	Chloramphenicol	10	ng/L
37	Chloridazon	5	ng/L
38	Chlorotoluron	5	ng/L
39	Cimetidine	5	ng/L
40	Clofibric acid	5	ng/L
41	Cotinine	10	ng/L
42	Cyanazine	5	ng/L
43	DEET	10	ng/L
44	Dehydronifedipine	5	ng/L
45	Desethylatrazine	5	ng/L
46	Desisopropylatrazine	5	ng/L
47	Diaminochlorotriazine	5	ng/L
48	Diazepam	5	ng/L
49	Diclofenac	5	ng/L
50	Dilantin	20	ng/L
51	Diltiazem	5	ng/L
52	Diuron	5	ng/L
53	Erythromycin	10	ng/L
54	Estriol	5	ng/L
55	Estrone	5	ng/L
56	Ethylparaben	20	ng/L
57	Flumequine	10	ng/L
58	Fluoxetine (Prozac)	10	ng/L
59	Gemfibrozil	5	ng/L
60	Ibuprofen	10	ng/L
61	Iohexal	10	ng/L
62	Iopromide	5	ng/L
63	Isobutylparaben	5	ng/L
64	Isoproturon	100	ng/L
65	Ketoprofen	5	ng/L
66	Ketorolac	5	ng/L
67	Lidocaine	5	ng/L
68	Lincomycin	10	ng/L
69	Linuron	5	ng/L
70	Lopressor	20	ng/L
71	Meclofenamic acid	5	ng/L

	Parameter	Reporting Limit	Unit
72	Meprobamate	5	ng/L
73	Metazochlor	5	ng/L
74	Methylparaben	20	ng/L
75	Metolachlor	5	ng/L
76	Naproxen	10	ng/L
77	Nifedipine	20	ng/L
78	Norethisterone	5	ng/L
79	Oxolinic acid	10	ng/L
80	Pentoxifylline	5	ng/L
81	Primidone	5	ng/L
82	Progesterone	5	ng/L
83	Propazine	5	ng/L
84	Propylparaben	5	ng/L
85	Quinoline	5	ng/L
86	Salicylic acid	100	ng/L
87	Simazine	5	ng/L
88	Sucralose	100	ng/L
89	Sulfachloropyridazine	5	ng/L
90	Sulfadiazine	5	ng/L
91	Sulfadimethoxine	5	ng/L
92	Sulfamerazine	5	ng/L
93	Sulfamethazine	5	ng/L
94	Sulfamethizole	5	ng/L
95	Sulfamethoxazole	5	ng/L
96	Sulfathiazole	5	ng/L
97	Sulfometuron Methyl	5	ng/L
98	Testosterone	5	ng/L
99	Theobromine	10	ng/L
100	Theophylline	20	ng/L
101	Thiabendazole	5	ng/L
102	Triclocarban	5	ng/L
103	Triclosan	10	ng/L
104	Trimethoprim	5	ng/L
105	Tris(1,3-dichloro-2-propyl) phosphate	100	ng/L
106	Tris(2-carboxyethyl)phosphine hydrochloride	10	ng/L
107	Warfarin	5	ng/L
	EDB/DBCP (by Method EPA 504.1)		
108	1,2-Dibromo-3-chloropropane (DBCP)	0.01	ug/L
109	1,2-Dibromoethane (EDB)	0.01	ug/L

	Parameter	Reporting Limit	Unit
	Flame Retardants (EPA 527)		
110	2,2',4,4',5,5'-Hexabromobiphenyl (HBB)	0.7	ug/L
111	2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	0.8	ug/L
112	2,2',4,4',5-Pentabromodiphenyl ether (BDE-99)	0.9	ug/L
113	2,2',4,4',6-Pentabromodiphenyl ether (BDE-100)	0.5	ug/L
114	2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	0.3	ug/L
115	Atrazine	0.5	ug/L
116	Bifenthrin	0.5	ug/L
117	Bromacil	0.5	ug/L
118	Chlorpyrifos	0.5	ug/L
119	Dimethoate	0.7	ug/L
120	Esbiol	0.5	ug/L
121	Esfenvalerate	0.5	ug/L
122	Esfenvalerate	0.5	ug/L
123	Hexazinone	0.5	ug/L
124	Kepone	0.5	ug/L
125	Malathion	0.5	ug/L
126	Mirex	0.5	ug/L
127	Nitrofen	0.5	ug/L
128	Norflurazon	0.5	ug/L
129	Oxychlordane	0.5	ug/L
130	Parathion	0.5	ug/L
131	Prometryn	0.5	ug/L
132	Propazine	0.5	ug/L
133	Terbufos-sulfone	0.4	ug/L
134	Thiobencarb	0.5	ug/L
135	Vinclozolin	0.5	ug/L
	Volatile Organics EPA (EPA Method 524.3)		
136	1,1,1,2-Tetrachloroethane	0.5	ug/L
137	1,1,1-Trichloroethane	0.5	ug/L
138	1,1,2,2-Tetrachloroethane	0.5	ug/L
139	1,1,2-Trichloroethane	0.5	ug/L
140	1,1-Dichloroethane	0.5	ug/L
141	1,1-Dichloroethylene	0.5	ug/L
142	1,1-Dichloropropylene	0.5	ug/L
143	1,2,3-Trichlorobenzene	0.5	ug/L
144	1,2,3-Trichloropropane	0.5	ug/L
145	1,2,4-Trichlorobenzene	0.5	ug/L
146	1,2,4-Trimethylbenzene	0.5	ug/L

	Parameter	Reporting Limit	Unit
147	1,2-Dibromo-3-chloropropane (DBCP)	0.2	ug/L
148	1,2-Dibromoethane (EDB)	0.2	ug/L
149	1,2-Dichlorobenzene	0.5	ug/L
150	1,2-Dichloroethane	0.5	ug/L
151	1,2-Dichloropropane	0.5	ug/L
152	1,2-Xylene	0.5	ug/L
153	1,3 + 1,4-Xylene	0.5	ug/L
154	1,3,5-Trimethylbenzene	0.5	ug/L
155	1,3-Dichlorobenzene	0.5	ug/L
156	1,3-Dichloropropane	0.5	ug/L
157	1,4-Dichlorobenzene	0.5	ug/L
158	2,2-Dichloropropane	0.5	ug/L
159	2-Chlorotoluene	0.5	ug/L
160	4-Chlorotoluene	0.5	ug/L
161	4-Isopropyltoluene	0.5	ug/L
162	Benzene	0.5	ug/L
163	Bromobenzene	0.5	ug/L
164	Bromochloromethane	0.5	ug/L
165	Bromodichloromethane	0.5	ug/L
166	Bromoform	0.5	ug/L
167	Bromomethane	0.5	ug/L
168	Carbon tetrachloride	0.5	ug/L
169	Chlorobenzene	0.5	ug/L
170	Chloroethane	0.5	ug/L
171	Chloroform	0.5	ug/L
172	Chloromethane	0.5	ug/L
173	cis-1,2-Dichloroethylene	0.5	ug/L
174	cis-1,3-Dichloropropylene	0.5	ug/L
175	Dibromochloromethane	0.5	ug/L
176	Dibromomethane	0.5	ug/L
177	Dichlorodifluoromethane	0.5	ug/L
178	Dichloromethane	0.5	ug/L
179	Ethylbenzene	0.5	ug/L
180	Hexachlorobutadiene	0.5	ug/L
181	Isopropylbenzene	0.5	ug/L
182	Methyl-t-butyl ether (MTBE)	0.5	ug/L
183	n-Butylbenzene	0.5	ug/L
184	n-Propylbenzene	0.5	ug/L
185	Naphthalene	0.5	ug/L

	Parameter	Reporting Limit	Unit
186	sec-Butylbenzene	0.5	ug/L
187	Styrene	0.5	ug/L
188	tert-Butylbenzene	0.5	ug/L
189	Tetrachloroethylene	0.5	ug/L
190	Toluene	0.5	ug/L
191	trans-1,2-Dichloroethylene	0.5	ug/L
192	trans-1,3-Dichloropropylene	0.5	ug/L
193	Trichloroethylene	0.5	ug/L
194	Trichlorofluoromethane	0.5	ug/L
195	Vinyl chloride	0.2	ug/L
	Semi Volatile Organics (EPA Method 525.2 Extended with TIC's)		
196	1,2,4,5-Tetrachlorobenzene	0.5	ug/L
197	1-Methylnaphthalene	0.1	ug/L
198	2,2',3',4,6-Pentachlorobiphenyl	0.1	ug/L
199	2,2',3,3',4,4',6-Heptachlorobiphenyl	0.5	ug/L
200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	0.5	ug/L
201	2,2',4,4',5,6'-Hexachlorobiphenyl	0.1	ug/L
202	2,2',4,4'-Tetrachlorobiphenyl	0.1	ug/L
203	2,3-Dichlorobiphenyl	0.1	ug/L
204	2,4,5-Trichlorobiphenyl	0.1	ug/L
205	2,4-Dinitrotoluene	0.5	ug/L
206	2,6-Dinitrotoluene	0.5	ug/L
207	2-Chlorobiphenyl	0.1	ug/L
208	2-Methylnaphthalene	0.1	ug/L
209	4,4'-DDD	0.1	ug/L
210	4,4'-DDE	0.1	ug/L
211	4,4'-DDT	0.1	ug/L
212	Acenaphthene	0.1	ug/L
213	Acenaphthylene	0.1	ug/L
214	Acetochlor	0.1	ug/L
215	Alachlor	0.1	ug/L
216	Aldrin	0.1	ug/L
217	alpha-Chlordane	0.1	ug/L
218	alpha-Hexachlorocyclohexane	0.1	ug/L
219	Ametryn	0.1	ug/L
220	Anilazine	1	ug/L
221	Anthracene	0.1	ug/L
222	Aspon	0.1	ug/L
223	Atraton	0.1	ug/L

	Parameter	Reporting Limit	Unit
224	Atrazine	0.1	ug/L
225	Azinphos-ethyl	0.5	ug/L
226	Azinphos-methyl	0.5	ug/L
227	Bendiocarb	0.5	ug/L
228	Benfluralin	0.1	ug/L
229	Benzo(a)anthracene	0.1	ug/L
230	Benzo(a)pyrene	0.02	ug/L
231	Benzo(b)fluoranthene	0.1	ug/L
232	Benzo(g,h,i)perylene	0.1	ug/L
233	Benzo(k)fluoranthene	0.1	ug/L
234	beta-BHC	0.1	ug/L
235	Bolstar	0.1	ug/L
236	Bromacil	0.1	ug/L
237	Butachlor	0.1	ug/L
238	Butylate	0.1	ug/L
239	Butylbenzylphthalate	1	ug/L
240	Carbophenothion	0.5	ug/L
241	Carboxin	0.1	ug/L
242	Chlorfenvinphos	5	ug/L
243	Chlorobenzilate	0.1	ug/L
244	Chloroneb	0.1	ug/L
245	Chloropropylate	0.1	ug/L
246	Chlorothalonil	0.1	ug/L
247	Chlorpropham	0.1	ug/L
248	Chlorpyrifos	0.1	ug/L
249	Chlorpyrifos methyl	0.5	ug/L
250	Chrysene	0.1	ug/L
251	cis-Nonachlor	0.1	ug/L
252	cis-Permethrin	0.1	ug/L
253	Clomazone	0.1	ug/L
254	Clopyralid	10	ug/L
255	Coumaphos	0.1	ug/L
256	Crotoxyphos	0.5	ug/L
257	Cyanazine	0.1	ug/L
258	Cycloate	0.1	ug/L
259	DCPA	0.1	ug/L
260	delta-BHC	0.1	ug/L
261	Demeton O	0.5	ug/L
262	Demeton S	0.5	ug/L

	Parameter	Reporting Limit	Unit
263	Desethylatrazine	1	ug/L
264	Desisopropylatrazine	1	ug/L
265	Di(2-ethylhexyl)adipate	0.6	ug/L
266	Di(2-ethylhexyl)phthalate	0.6	ug/L
267	Di-n-butylphthalate	2	ug/L
268	Di-n-octylphthalate	2	ug/L
269	Diazinon	0.1	ug/L
270	Dibenzo(a,h)anthracene	0.1	ug/L
271	Dichlobenil	0.1	ug/L
272	Dichlofenthion	0.1	ug/L
273	Dichloran	0.5	ug/L
274	Dichlorvos	0.1	ug/L
275	Dicrotophos	0.5	ug/L
276	Dieldrin	0.1	ug/L
277	Diethylphthalate	1	ug/L
278	Dimethoate	0.5	ug/L
279	Dimethylphthalate	1	ug/L
280	Dioxathion	0.5	ug/L
281	Dioxathion A	0.5	ug/L
282	Dioxathion B	0.5	ug/L
283	Diphenamid	0.1	ug/L
284	Disulfoton	0.1	ug/L
285	Disulfoton sulfone	0.1	ug/L
286	Disulfoton sulfoxide	10	ug/L
287	E-Phosphamidon	0.5	ug/L
288	Endosulfan I	0.1	ug/L
289	Endosulfan II	0.1	ug/L
290	Endosulfan sulfate	0.1	ug/L
291	Endrin	0.01	ug/L
292	Endrin aldehyde	0.5	ug/L
293	EPN	0.5	ug/L
294	EPTC	0.1	ug/L
295	Erucylamide	5	ug/L
296	Esfenvalerate	0.5	ug/L
297	Ethalfluralin	0.1	ug/L
298	Ethion	5	ug/L
299	Ethofumesate	0.5	ug/L
300	Ethoprop	0.1	ug/L
301	Etridiazole	0.1	ug/L

	Parameter	Reporting Limit	Unit
302	Famphur	0.1	ug/L
303	Fenamiphos	0.1	ug/L
304	Fenarimol	1	ug/L
305	Fenitrothion	0.5	ug/L
306	Fenoxaprop-ethyl	1	ug/L
307	Fensulfothion	0.5	ug/L
308	Fenthion	0.1	ug/L
309	Fluazifop-butyl	0.1	ug/L
310	Fluchloralin	0.1	ug/L
311	Fluometuron	0.5	ug/L
312	Fluoranthene	0.1	ug/L
313	Fluorene	0.1	ug/L
314	Fluridone	1	ug/L
315	Fonofos	0.1	ug/L
316	gamma-BHC (Lindane)	0.02	ug/L
317	gamma-Chlordane	0.1	ug/L
318	Heptachlor	0.04	ug/L
319	Heptachlor epoxide	0.02	ug/L
320	Hexachlorobenzene	0.1	ug/L
321	Hexachlorocyclopentadiene	0.1	ug/L
322	Hexazinone	0.1	ug/L
323	Indeno(1,2,3-cd)pyrene	0.1	ug/L
324	Iprodione	0.5	ug/L
325	Isofenphos	0.5	ug/L
326	Isophorone	0.1	ug/L
327	Leptophos	0.5	ug/L
328	Malathion	0.1	ug/L
329	Metalaxyl	0.5	ug/L
330	Methoxychlor	0.1	ug/L
331	Methyl paraoxon	0.5	ug/L
332	Methyl parathion	0.5	ug/L
333	Metolachlor	0.1	ug/L
334	Metribuzin	0.1	ug/L
335	Metsulfuron-methyl	10	ug/L
336	Mevinphos	0.1	ug/L
337	MGK 264 isomer a	0.1	ug/L
338	MGK 264 isomer b	0.1	ug/L
339	MGK 326	0.1	ug/L
340	Mirex	0.5	ug/L

	Parameter	Reporting Limit	Unit
341	Molinate	0.1	ug/L
342	Monocrotophos	0.5	ug/L
343	Naled	0.5	ug/L
344	Naphthalene	0.1	ug/L
345	Napropamide	0.1	ug/L
346	Norflurazon	1	ug/L
347	Oryzalin	10	ug/L
348	Oxadiazon	0.1	ug/L
349	Oxychlordane	0.1	ug/L
350	Oxyfluorfen	0.5	ug/L
351	Parathion	0.5	ug/L
352	Pebulate	0.1	ug/L
353	Pendimethalin	0.1	ug/L
354	Pentachlorobenzene	0.5	ug/L
355	Pentachloronitrobenzene	0.5	ug/L
356	Pentachlorophenol	1	ug/L
357	Phenanthrene	0.1	ug/L
358	Phorate	0.1	ug/L
359	Phosmet	0.5	ug/L
360	Profluralin	0.1	ug/L
361	Prometon	1	ug/L
362	Prometryn	0.1	ug/L
363	Pronamide	0.1	ug/L
364	Propachlor	0.1	ug/L
365	Propanil	0.5	ug/L
366	Propazine	0.1	ug/L
367	Propiconazole isomer a	5	ug/L
368	Propiconazole isomer b	5	ug/L
369	Prothiofos	0.5	ug/L
370	Pyrene	0.1	ug/L
371	Simazine	0.07	ug/L
372	Simetryn	0.1	ug/L
373	Stirofos	0.1	ug/L
374	Sulfotep	0.5	ug/L
375	Tebuthiuron	10	ug/L
376	TEPP	1	ug/L
377	Terbacil	0.1	ug/L
378	Terbufos	0.5	ug/L
379	Terbutryn	0.1	ug/L

	Parameter	Reporting Limit	Unit
380	Thiabendazole	10	ug/L
381	Thiobencarb	0.1	ug/L
382	Thionazin	0.5	ug/L
383	trans-Nonachlor	0.1	ug/L
384	trans-Permethrin	0.1	ug/L
385	Triadimefon	0.5	ug/L
386	Tribufos	0.1	ug/L
387	Trichloronate	0.5	ug/L
388	Tricyclazole	1	ug/L
389	Trifluralin	0.1	ug/L
390	Vernolate	0.1	ug/L
391	Vinclozolin	0.5	ug/L
392	Z-Phosphamidon	0.5	ug/L
	Herbicides (EPA Method 515.3)		
393	2,4,5-T	0.5	ug/L
394	2,4,5-TP (Silvex)	0.1	ug/L
395	2,4-D	0.1	ug/L
396	2,4-DB	2	ug/L
397	3,5-Dichlorobenzoic acid	0.5	ug/L
398	Acifluorfen	1	ug/L
399	Bentazon	0.5	ug/L
400	Chloramben	2	ug/L
401	Dalapon	1	ug/L
402	DCPA acid metabolites	0.5	ug/L
403	Dicamba	0.1	ug/L
404	Dichlorprop	2	ug/L
405	Dinoseb	0.1	ug/L
406	MCPA	0.5	ug/L
407	Mecoprop	0.5	ug/L
408	Pentachlorophenol	0.04	ug/L
409	Picloram	0.1	ug/L
410	Triclopyr	0.5	ug/L
	Pesticides (EPA Method 505)		
411	Aroclor 1016	0.08	ug/L
412	Aroclor 1221	0.19	ug/L
413	Aroclor 1232	0.23	ug/L
414	Aroclor 1242	0.26	ug/L
415	Aroclor 1248	0.1	ug/L
416	Aroclor 1254	0.1	ug/L

	Parameter	Reporting Limit	Unit
417	Aroclor 1260	0.2	ug/L
418	Chlordane	0.1	ug/L
419	Dieldrin	0.1	ug/L
420	Endrin	0.2	ug/L
421	gamma-BHC (Lindane)	0.1	ug/L
422	Heptachlor	0.1	ug/L
423	Heptachlor epoxide	0.02	ug/L
424	Methoxychlor	1	ug/L
425	PCBs, Total	0.26	ug/L
426	Toxaphene	1	ug/L
	Pesticides		
427	Alachlor	0.1	ug/L
428	Aldrin	0.1	ug/L
429	Atrazine	0.1	ug/L
430	Benzo(a)pyrene	0.02	ug/L
431	Bromacil	0.1	ug/L
432	Butachlor	0.1	ug/L
433	Di(2-ethylhexyl)adipate	0.6	ug/L
434	Di(2-ethylhexyl)phthalate	0.6	ug/L
435	Endrin	0.01	ug/L
436	Fluorene	0.1	ug/L
437	gamma-BHC (Lindane)	0.02	ug/L
438	Heptachlor	0.04	ug/L
439	Heptachlor epoxide	0.02	ug/L
440	Hexachlorobenzene	0.1	ug/L
441	Hexachlorocyclopentadiene	0.1	ug/L
442	Methoxychlor	0.1	ug/L
443	Metolachlor	0.1	ug/L
444	Metribuzin	0.1	ug/L
445	Propachlor	0.1	ug/L
446	Simazine	0.07	ug/L
	Trihalomethanes (by Method 524)		
447	Bromodichloromethane	0.5	ug/L
448	Bromoform	0.5	ug/L
449	Chloroform	0.5	ug/L
450	Dibromochloromethane	0.5	ug/L
	Haloacetic Acids (SM6251B)		
451	2,4,6-Trichlorophenol(88-06-2)	0.03	ug/L
452	Bromochloroacetic acid(5589-96-3)	0.04	ug/L

	Parameter	Reporting Limit	Unit
453	Dibromoacetic acid(631-64-1)	0.06	ug/L
454	Dichloroacetic acid(79-43-6)	0.05	ug/L
455	Monobromoacetic acid(79-08-3)	0.08	ug/L
456	Monochloroacetic acid(79-11-8)	0.08	ug/L
457	Organics, semivolatile(E-12884)	N/A	
458	Organochlorine pesticides(E-12851)	N/A	
459	Trichloroacetic acid(76-03-9)	0.05	ug/L
	Other		
460	1,4 Dioxane		
461	Bromate		
462	Chlorite		
463	Gross Alpha		
464	Gross Beta		
465	NDMA		
466	Perchlorate		
467	Chlorodibromomethane		
	Anabolics (progesterone and testosterone)		
468	andorostenedione		
469	Dactinomycin (DACT)		
470	flumeqine		
471	lidocaine		
472	phenazone		
473	Metformin		
474	Iohexol		
	Flame retardants		
475	Tris(1,3-dichloroisopropyl)phosphate (TDCPP)		
	Other		
476	Diethanolamine (DEA)		
477	**Herbicides/Pesticides**		
478	metazachlor		
479	OUST (sulfameturon, methyl)		

Appendix B

Organic micropollutants found in Cape Flats WWTW effluent

	AL Abbot & Eurofins	AL Abbot & Eurofins	
	Pond S4	C&D	
Parameter	**2018/02/24**	**2019/12/01**	
Pharmaceuticals			
Antibiotics (erythromycin, sulfamethoxazole, triclosan, trimethoprim)			
erythromycin	98	200	ng/ℓ
sulfamethoxazole	3200	7000	ng/ℓ
triclosan	240	70	ng/ℓ
trimethoprim	44	870	ng/ℓ
Atenolol	100	440	ng/ℓ
Diazepam	0	0	ng/ℓ
Carbamazepine	2000	980	ng/ℓ
Cotinine	900	130	ng/ℓ
Diclofenac	350	590	ng/ℓ
Ibuprofen	1000	0	ng/ℓ
Gemfibrozil	0	0	ng/ℓ
Iopamidol	0	0	ng/ℓ
Iopromide	76	340	ng/l
Meprobamate	300	1000	ng/ℓ
Primidone	0	24	ng/ℓ
Phenyltoin - reported as Dilantin	210	0	ng/ℓ
Sulfamethoxazole	3200	7000	ng/ℓ
Paracetamol - reported as acetaminophen	140	0	ng/ℓ
Steroids (ethynylestradiol, estrone, estradiol, estriol)			
ethynylestradiol	290	0	ng/ℓ
estrone	11	0	ng/ℓ
estradiol	0	0	ng/ℓ
estriol	0	0	ng/ℓ
Anabolics (progesterone and testosterone)			
progesterone	6.7	0	ng/ℓ

	AL Abbot & Eurofins	AL Abbot & Eurofins	
	Pond S4	C&D	
Parameter	**2018/02/24**	**2019/12/01**	
testosterone	0	0	ng/ℓ
Metformin	960	0	ng/ℓ
Sulfamethazine	0	0	ng/ℓ
Trimethoprim	44	870	ng/ℓ
Bezafibrate	180	540	ng/ℓ
Fluoxetine	44	0	ng/ℓ
Iohexol	7800	10000	ng/ℓ
Naproxen	0	260	ng/ℓ
Bendroflumethiazide	0	0	ng/ℓ
Butalbital	0	0	ng/ℓ
chloramphenicol	0	0	ng/ℓ
Warfarin	31	23	ng/ℓ
salicylic acid	0	150	ng/ℓ
albuterol	53	46	ng/ℓ
amoxicillin	15000	4900	ng/ℓ
androstenedione	92	0	ng/ℓ
carbadox	0	0	ng/ℓ
carisoprodol	140	38	ng/ℓ
cimetidine	3000	630	ng/ℓ
Dactinomycin (DACT)	0	0	ng/ℓ
dehydronifedipine	0	0	ng/ℓ
diltiazem	0	12	ng/ℓ
flumeqine	0	0	ng/ℓ
ketoprofen	0	0	ng/ℓ
ketorolac	0	0	ng/ℓ
lidocaine	180	99	ng/ℓ
lincomycin	0	0	ng/ℓ
lopressor	0	0	ng/ℓ
meclofenamic acid	230	0	ng/ℓ
norethisterone	31	0	ng/ℓ
nifedipine	0	0	ng/ℓ
oxolinic	0	0	ng/ℓ

	AL Abbot & Eurofins	AL Abbot & Eurofins	
	Pond S4	C&D	
Parameter	**2018/02/24**	**2019/12/01**	
pentoxifulline	0	0	ng/ℓ
phenazone	50	14	ng/ℓ
sulfachloropyridazine	0	0	ng/ℓ
sulfadiazine	0	90	ng/ℓ
sulfadimethoxine	0	0	ng/ℓ
sulfamerazine	0	0	ng/ℓ
sulfamethizole	0	0	ng/ℓ
sulfathiazole	0	0	ng/ℓ
theophylline	0	6000	ng/ℓ
Radionuclides			
Gross alpha	0	0	Bq/ℓ
Gross beta	0	0	Bq/ℓ
Herbicides/Pesticides			
Azinphos-methyl	0	0	ng/ℓ
Diazinon	0	0	ng/ℓ
Dichlorvos	0	0	ng/ℓ
Ethion	0	0	ng/ℓ
Ethoprophos (Mocap)	0	0	ng/ℓ
Fenthion	0	0	ng/ℓ
4,4-DDT	0	0	ng/ℓ
Chlordane	0	0	ng/ℓ
Thiophanate	0	0	ng/ℓ
1,2-Dibromo-3-chloropropane	0	0	ng/ℓ
Imidacloprid	0	0	ng/ℓ
Propoxur	0	0	ng/ℓ
Carbendazime	0	0	ng/ℓ
Atrazine	0	0	ng/ℓ
Clofibric Acid	0	0	ng/ℓ
Simazine	69	150	ng/ℓ
2,4 D (2,4-dichlorophenoxy acetic acid)	54	0	ng/ℓ
bromacil	0	0	ng/ℓ

	AL Abbot & Eurofins	AL Abbot & Eurofins	
	Pond S4	C&D	
Parameter	**2018/02/24**	**2019/12/01**	
chlorindazon	0	0	ng/ℓ
chlorotoluron	0	0	ng/ℓ
cyanazine	0	0	ng/ℓ
diuron	180	320	ng/ℓ
isoproturon	0	0	ng/ℓ
linuron	0	0	ng/ℓ
metazachlor	0	0	ng/ℓ
metolachlor	0	5.2	ng/ℓ
OUST (sulfameturon, methyl)	0	0	ng/ℓ
propazine	25	0	ng/ℓ
thiabendazole	17	49	ng/ℓ
Volatile organics			
Benzene	0	0	ng/ℓ
Dichloromethane	0	1500	ng/ℓ
Trihalomethane (Bromodichloromethane)	0	0.001	ng/ℓ
Trihalomethane (Dibromochloromethane)	0	0.001	ng/ℓ
Ethylbenzene	0	0	ng/ℓ
Monochlorobenzene	0	0	ng/ℓ
Styrene	0	0	ng/ℓ
Perchlorate	0	0	ng/ℓ
1,4-Dioxane	0	380	ng/ℓ
Sucralose (EPA reference compound)	0	46000	ng/ℓ
Tris(2-Carboxyethyl phosphine) hydrochloride (EPA reference compound)	0	0	ng/ℓ
Triclosan (EPA reference compound)	0	70	ng/ℓ
N,N-diethyl-meta-toluamide (EPA reference compound)	0	0	ng/ℓ
Monochloramine	0	0	ng/ℓ
Phenol	0	0	ng/ℓ
Other			
Acesulfame	23000	84	ng/ℓ
Bisphenol A (BPA)	240	160	ng/ℓ
Caffeine	3200	1400	ng/ℓ

	AL Abbot & Eurofins	AL Abbot & Eurofins	
	Pond S4	C&D	
Parameter	**2018/02/24**	**2019/12/01**	
DEET	1400	470	ng/ℓ
Propylparaben	0	0	ng/ℓ
Triclocarban	730	110	ng/ℓ
4-nonylphenol	50000	0	ng/ℓ
4-tert-octylphenol	0	0	ng/ℓ
butylparaben	0	0	ng/ℓ
ethylparaben	0	0	ng/ℓ
isobutylparaben	0	0	ng/ℓ
methylparaben	0	0	ng/ℓ
1,7-dimethylxanthine	870	3000	ng/ℓ
Diethanolamine (DEA)	0	0	ng/ℓ
quinoline	30	0	ng/ℓ
theobromine	1200	1600	ng/ℓ
Flame retardants			
TCEP (Tris(2-chloroethyl)phosphate)	72	53	ng/ℓ
TCPP (Tris (chloroisopropyl) phosphate)	790	2500	ng/ℓ
TDCPP	0	210	ng/ℓ