

**COMBINATION OF CARBON NANOTUBES AND
SOLAR PARABOLIC TROUGH COLLECTOR AS A
POLISHING UNIT FOR SAFE REUSE OF SECONDARY
TREATED WASTEWATER**



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APPROVAL SHEET

Certified that the contents and form of this thesis titled “Combination of carbon nanotubes and solar parabolic trough collector as a polishing unit for safe reuse of secondary treated wastewater” submitted by Ms. Sara Iqbal, Minha Hanif, Midhat Naveed and Haris Ali khan, have been found satisfactory for the requirement of the degree.

Supervisor: -----

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Sara Iqbal
Minha Hanif
Midhat Naveed
Haris Ali Khan

Dedication

We would like to dedicate this thesis to our parents whose constant love, support, guidance and prayers allowed us to be who we are today.

Abstract

Pakistan is on the verge of becoming a water-deficit country. The per-capita water availability has dramatically dropped from 5,600 m³ to 1,000 m³ over the period of few decades. Consequently, a paradigm shift is happening now towards the 3 R's: reuse, recycle or reclaim of wastewater. However, reclamation of wastewater should be at the levels that are safe and appropriate for reuse and recycle. Secondary wastewater treatment removes 85 to 95 % of BOD and TSS and minor portions of micro-pollutants. The purpose of tertiary treatment is to provide a final treatment stage to raise the effluent quality to such a level to make it suitable for intended reuse before it is discharged to the receiving environment such as sea, river, lake, ground, etc. As such, the idea of water reuse has been gaining momentum for quite some time and has recently found a more general context within the idea of the Circular Economy. This project proposes a polishing step with low energy and chemical footprint that would make the secondary treated wastewater, and harvested storm water safe and healthy for reuse in agriculture, and non-potable household use. The proposed project includes the evaluation of carbon nanotube (CNT)-based adsorption unit in tandem with parabolic trough collector (PTC)-based solar disinfectant. The CNT-based unit removal efficiency was around 90% for the organic and inorganic contaminants from the secondary effluent. The PTC-based disinfection unit was able to achieve higher log removal values around 3 at 6 hours exposure time. The effectiveness of our proposed technology was assessed by comparing it with conventional treatment process such as activated charcoal treatment. It was also observed that activated carbon can also be used as a cheap treatment as it also achieved reuse standards. In summary, we have designed a low-cost, low-tech, easily-scalable sustainable polishing step for secondary or tertiary treated wastewater which is also able to meet reuse standards of wastewater used for agriculture and horticulture purposes.

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1. Introduction

1.1 Background

Forty per cent of crop production comes from the 16% of agricultural land that is irrigated. These lands account for a substantial portion of increased yields obtained during the Green Revolution. Unless water-use efficiency is increased, greater agricultural production will require increased irrigation. However, globally irrigated area is declining, per capita irrigated area has declined by 5% since 1978, and new dam construction may allow only a 10% increase in water for irrigation over the next 30 years. Moreover, water is regionally scarce. Many countries in a band from China through India and Pakistan, and the Middle East to North Africa either currently or will soon fail to have adequate water to maintain per capita food production from irrigated land.

The disadvantages of untreated or partially treated wastewater include increased health risks and decreased environmental quality as water, soil, and crops become increasingly contaminated with pathogens, metals, etc. (Qadir et al 2007, Ensink et al 2008). Pathogens, e.g. bacteria, viruses, protozoa, and nematodes, can cause acute health affects (Ensink et al 2008).

Pakistan lack water and wastewater treatment facilities which are a growing concern for water reuse. The reuse of treated wastewater, especially in agriculture, is an appealing and practical solution for water scarcity that significantly relieves pressure on water resources.

As most of the post treatment is not being done in Pakistan and the secondary treated wastewater used for irrigation contains heavy metals, organic contaminants, micro pollutants and pathogens as well which are later transferred into the fruits and vegetables produced by untreated water. These vegetables and fruits pose health threat when consumed due to the possibility of the presence of a wide spectrum of pathogens, such as, coliforms as they have an adverse impact on human health.

This concern incentivized us to propose a final polishing unit currently for existing wastewater treatment plant such as membrane bioreactor at NUST. Furthermore, this technology can be used for raw water treatment, rain water harvesting and safe reuse of water in food processing, textile and other industries

1.2 Problem Statement

The issue of pathogens present in treated wastewater effluents has gained attention recently due

to an increased interest in reuse applications (Li et al. 2013; Zanetti et al. 2010).

Secondary biological treatment processes typically achieve less than 2-log reduction of viruses (Thebo, 2014) indicating that farmers where treated water is used for irrigation are at risk of contamination with enteric viruses (Pei-Ying Hong et al. 2018). (MaliheMoazeni et al. 2017) said that the local wastewater treatment process achieves 3.53 logs removal of heterotrophic bacteria while the fecal coliform bacteria were found at a high level exceeded the guideline limit for wastewater reuse in agriculture

(Hong et al. 2017) supported the findings of (Jong et al. 2010; Trinh et al. 2012; van den Akker et al. 2014) that the variability in microbial removal rates ($<10^4$ to $>10^6$ removal) poses an obstacle for reuse purposes, conferring that disinfection is necessary for post-MBR effluents.

Microbial assessment was done on MBR-NUST at IESE to assess the quality of effluent for its safe reuse. Microbial studies showed that the majority of the bacteria involved in MBR are Gram-negative in nature. The API results showed membrane bioreactor effluent was dominated by *Enterobacteriaceae*, followed by *Pseudomonadaceae* family. Therefore, MBR effluent needs final polishing unit for its safe reuse and to avoid substantial risks to humans (Sarah, 2015).

1.3 Health Effects

Human exposure to microbial hazards present in municipal wastewater can lead to acute gastrointestinal illness or more severe disease. (Kiley Daley et al. 2017)

Among the perceived health risks, skin problems were top-rated health risk while eye burn, sore feet and abdominal pains were rated low across the farming sites. (Desta Woldetsadik et al. 2018)

Antimicrobial resistance is a major concern as the excessive usage of antimicrobial drugs not only making the microorganisms resistant but also causing severe infections which are harder to treat (Ali Abdullah AM, 2017).

1.4 Objectives

Polishing units cannot be used as stand- alone so, to improve their efficiency they should be used in combination with other technologies.

Such combined system not only improves the efficiency of treatment but also helps in achieving the desired standards of drinking water. The main focus of the study was to design and develop a sustainable, low cost, low maintenance and low tech treatment system for the NUST MBR.

A system that is combination of carbon nanotubes and solar disinfection technologies would aim to reduce heavy metals, micro pollutants, excess nutrients and pathogens from the treated effluent for safe reuse in horticulture within NUST.

Main objectives of our study are following:

- To design and evaluate the performance of PTC solar disinfection unit.
- To design fixed bed column of carbon nanotubes.
- To evaluate the effectiveness in removing organic and inorganic, and biological contaminants of each unit first in isolation, then, by coupling for the effluent from the treated wastewater of MBR.

1.5 Scope

Scope of the study was defined as follows:

- To measure the optimum removal efficiency of PTC for pathogens by varying flow rates in different seasons
- To measure the optimum removal efficiency of organic and inorganic contamination by varying flow rates in adsorption column
- To compare the removal efficiencies of PTC as a storage tank and PTC along with acrylic tube
- To compare the removal efficiencies of activated carbon and carbon nanotube columns

2. Literature Review

2.1 Comparison of Existing Technologies:

Different materials and technologies were compared on the basis of cost, efficiency and many other parameters. Each technology has its own advantages and disadvantages

2.1.1 Membrane filtration

Membrane filtration is an efficient method but pathogens removal is based on averaged pore size of membrane (George et al., 2014)

2.1.2 Chlorination

Chlorination is basically a sodium hypochlorite solution which is used as a disinfectant. It reduces the hazards in handling and storing but hydrogen produced by electrolysis needs to be vented out because of its explosive nature. It also produces bio-accumulative & harmful DBPs that persist in the environment (Saqib et al. 2017)

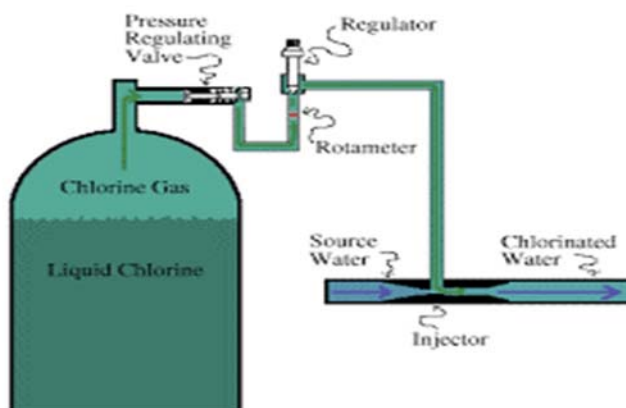


Figure 1: Chlorination

2.1.3 Ozonation

Ozone is an oxidizing agent whose disinfection efficiencies are higher than the disinfection with chlorine. It provides a reduction in UV absorbance and color but it is highly reactive and expensive technology (Alessandro Abbà, 2017)

2.1.4 Concentrating Systems

Systems that concentrate the incident light after passing through a reflective surface such as plastic, metallized glass and polished metal etc. are called concentrating systems. It has small reactor tube area, allowing the easier handling of wastewater. It is used in direct photo-catalysis for SODIS application. One disadvantage is the high cost and water overheating (Murillo et al. 2018).

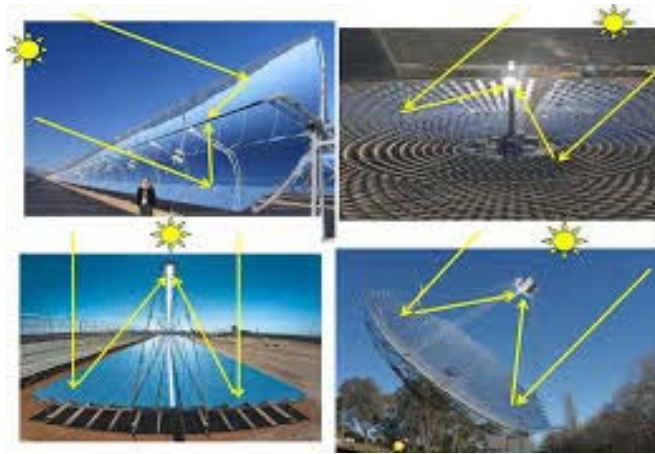


Figure 2: Concentrating Solar

2.1.5 Solar Disinfection

2.1.5.1 Parabolic Trough Collector

Parabolic reflective surfaces that concentrate the sun's radiation on a focal line; they are generally constructed by bending a sheet of reflective or highly polished material into a parabolic shape. Its application is different depending on aperture areas including solar water heating, desalination, and water disinfection

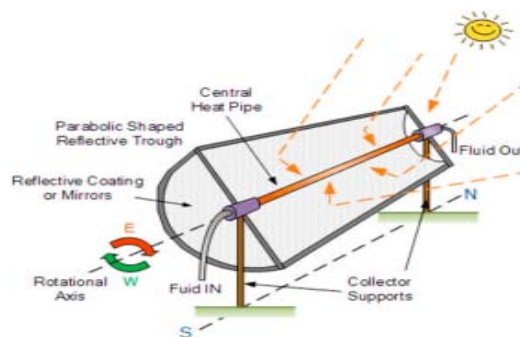


Figure 3: Solar parabolic trough collector

2.1.6 Carbon Nanotubes

Due to the unique porous structures and properties like tremendous flexibility, light weight, high strength and extremely high electrical and thermal conductivity can be used in many fields. Wastewater containing CNT can damage the aquatic life in water columns and sediment compartments as well as human health. CNT exposure affects cell viability and algal growth and CNTs can act as pesticide carriers affecting fish survival, metabolism, and behavior. It is used to remove inorganic pollutants

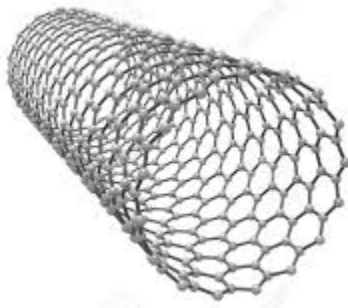


Figure 4: Structure of carbon nanotubes

2.1.7 Activated Carbon

The structure of activated carbon is similar to that of graphite. It has high porosity and has a high surface area of the order of 500 to 1500 m³ per kg of coal. It is used for the adsorption of solutes.



Figure 5: Activated carbon

2.1.8 Stainless steel

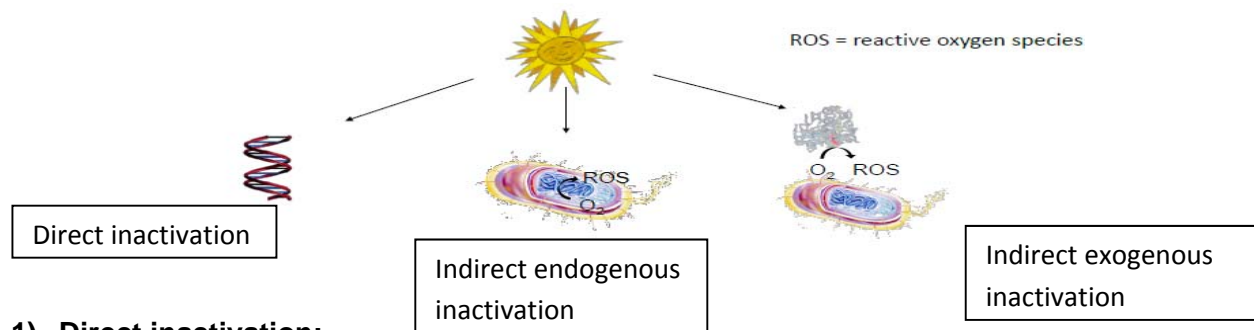
Stainless steel consists of carbon and iron compounds and a huge amount of chromium. Chromium is an alloy and its presence imparts famous corrosion resistance. It is cheap as compared to other materials. It is also durable and easy to clean.



Figure 6: Stainless steel

Mechanism of solar UV radiation:

Solar UV radiation work on three mechanisms



UVB light is absorbed by DNA/RNA which leads to genome damage. It is important for many organisms

2) Indirect endogenous inactivation:

In this, UVA, UVB, visible is absorbed by internal sensitizers which leads to the production of reactive oxygenated species resulting in genome and protein damage. It is important for for many bacteria and less relevant to viruses

3) Indirect exogenous inactivation

In this, UVA, UVB, visible is absorbed by external sanitizer which leads to the production of reactive oxygenated species resulting in genome and protein damage. It is important for viruses and few bacteria.

UV index in Islamabad:

Pakistan Meteorological Department

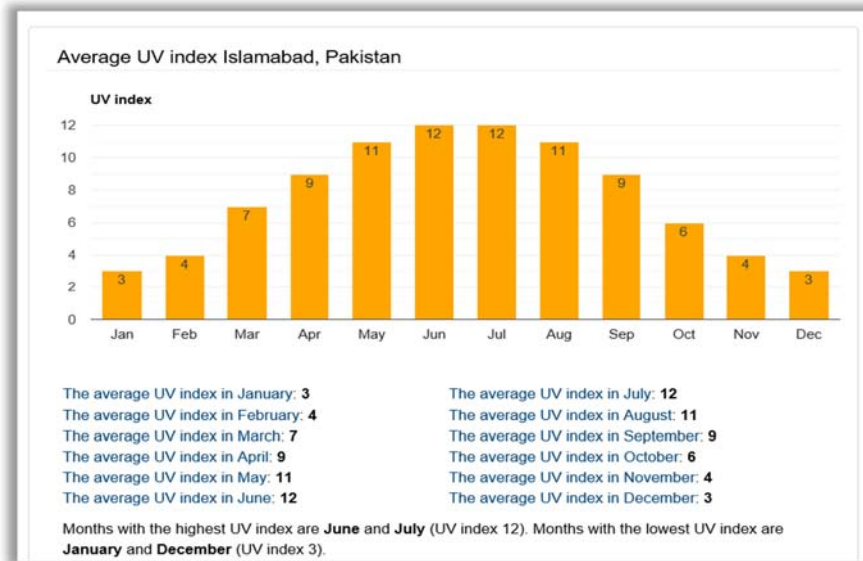


Figure 7 Average UV Index Islamabad, Pakistan

3. Materials and Methods

3.1 Materials and Design

3.1.1 Parabolic Trough Collector

With the help of literature, several materials were studied and compared on the basis of reflectivity and their respective costs. For an optimum choice, the reflectivity needed to be maximum while also being cost effective when incorporated into the constructed design. The materials studied are shown in the table below:

Table 1: Summary of Reflective Materials

Reflectivity Material	Reflectivity (Visible and Infrared Region)	Reflectance in Ultraviolet Range	Resistance to Weathering	Cost of Material
Silvered Glass Mirror	87-97 %	Very Low	Moderate	High
Aluminum Foil	55 %	Low	High	Very Low
Aluminum Plate	85-94%	Moderate	Low	Low
Galvanized Carbon Steel	---	Very High	Very High	High
Stainless Steel	> 35 %	High	High	Moderate

3.1.2 Stainless steel was chosen as an appropriate reflective material for the parabolic trough collector owing to its high reflectivity in the ultraviolet range while also being a locally available cheap option.

3..1.3 Collector Tube

The material selection of the collector tube was done after studying the ultraviolet transmissive properties and the cost of the materials.

The shortlisted options are summarized:

Table 2: Summary of Transmissive Materials

Material	UV Transmittance	Cost of Material	Limitations
Quartz	Very High (UVA, UVB and UVC)	Very High	Very Expensive
Acrylic Glass	High (UVA and UVB)	Moderate	Cheaply Available
Borosilicate Glass	High (UVA)	High	Transmits only UVA and Costly
Polyethylene Terephthalate (PET)	Moderate	Low	Produces Photoproducts

Acrylic (Poly Methyl Methacrylate) was preferred as an appropriate material for cylinder as it allows for transmission of UV-A, is light, less fragile while being available at a moderate cost.

3..2 Design of Parabolic Trough Collector and Collector Tube

The design criteria for the parabolic trough collector included the rim angle, focal point, aperture width etc.with their optimum ranges, as taken after studying the literature. The values chosen for each design criteria is given below in the table:

Table 3: Design Criteria

Collector parameters	Symbol	Design Criteria	Values
Rim Angle	ϕr (Degrees)	90-120	90
Focal Point	f (m)	0.25	0.25
Aperture Width	Wa (m)	0.5-2.0	1.00

Receiver Diameter	D (m)	0.1-0.3	0.187
Length	L (m)	2-5	1.20
Concentration Ratio	C (-)	1-15	2.1

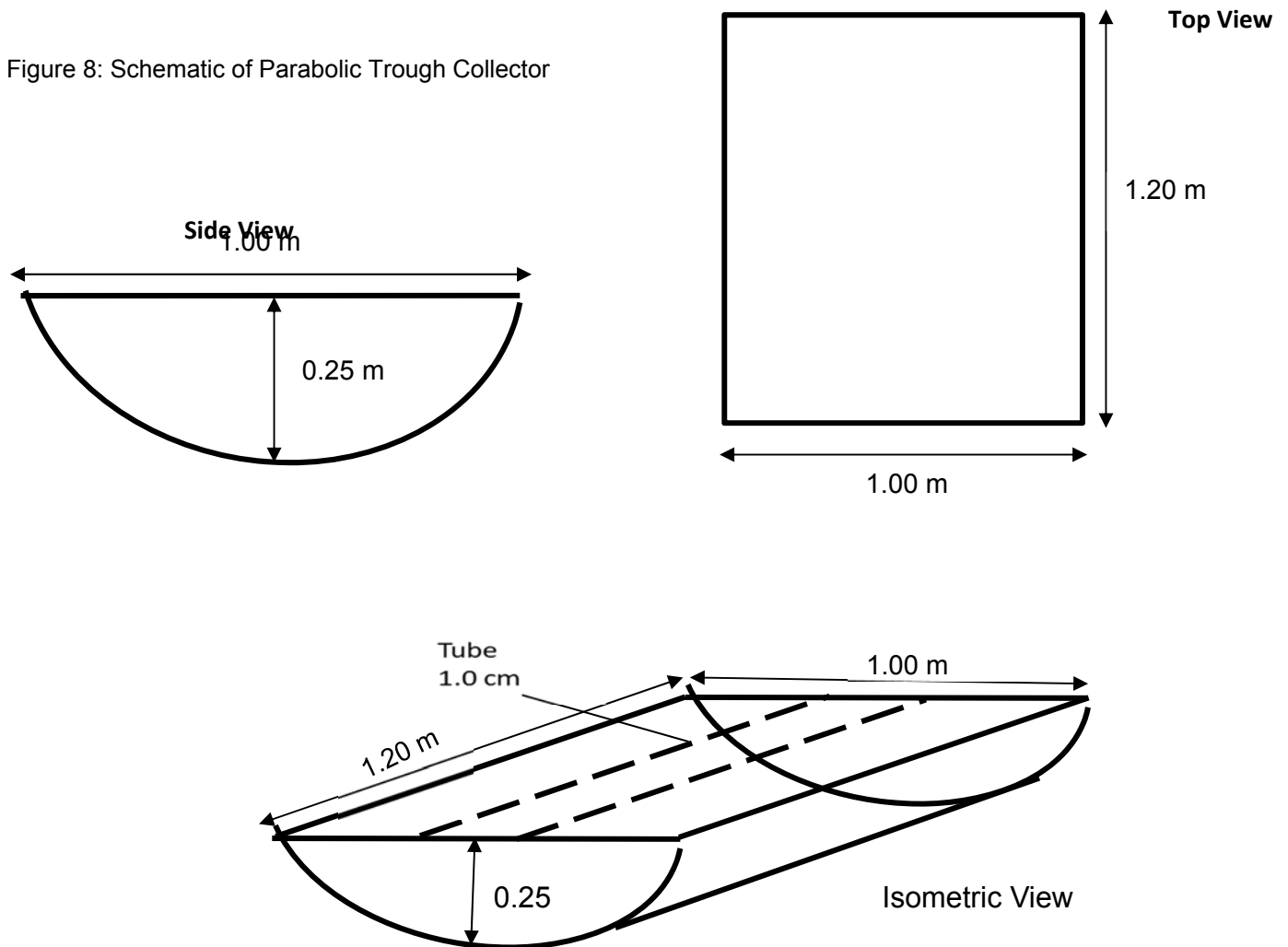
The stand was made adjustable to allow for manually changing angles for maximum solar irradiance directed to the tube.

The stand was placed in the North-South orientation facing the south in order for the SODIS units to receive maximum sunlight throughout the year

With the help of the design criteria, the drawing for the PTC and collector tube was done as shown below:

3.3 Schematic of Parabolic Trough Collector

Figure 8: Schematic of Parabolic Trough Collector



3.4.Design of Collector Tube

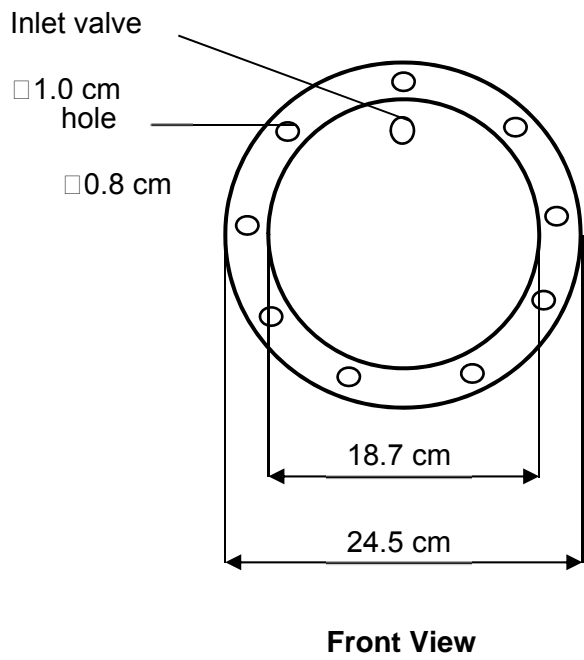
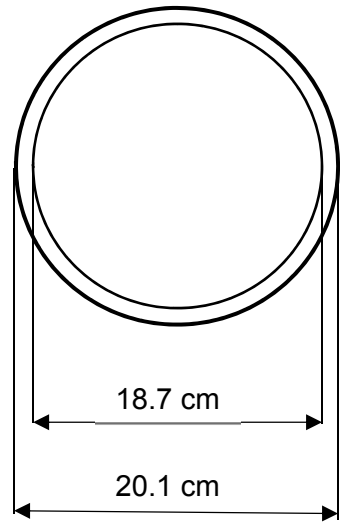
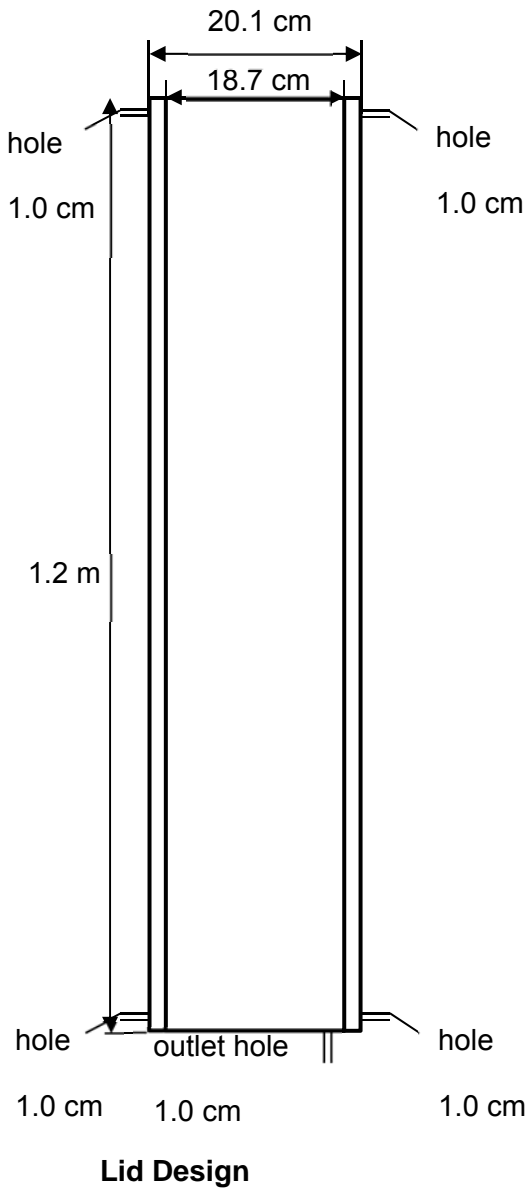







Figure 9: Schematic diagram of collector tube

3.5 Summary of Design Methodology

The steps followed in the design methodology are summarized below:

	<p>Design of Parabolic Trough Collector</p>
	<p>Design of Acrylic Cylinder</p>
	<p>Design of Adjustable Stand</p>
	<p>Design of Fixed Bed Column</p>
	<p>Integration of Adsorption and Disinfection Units</p>

3.6 Methodology Overview

The methodology followed comprised of the following steps in order:

1. MBR and wetlands effluents characterization:

Samples were taken from the MBR and wetlands effluent for characterization, against which the treatment efficiency would be measured.

2. Simulating PTC as a storage tank:

MBR effluent was treated using the PTC as a reflective storage tank. The disinfection took place owing to the reflective properties of the stainless-steel surface.

3. Sampling and testing from the PTC tank:

The treated effluent was then tested.

4. Disinfection using acrylic tube at the PTC focal line:

In the next step, acrylic tube placed at the focal line of the PTC contained the effluent. The solar irradiance concentrated on the effluent allowing an increased disinfection efficiency.

5. Sampling and testing from the acrylic tube in PTC:

The acrylic-tube treated effluent was sampled and tested on the same format as previous tests.

6. Comparing the efficiency of both units:

The results of both units were compared for the difference in efficiencies.

7. Evaluation of CNT column combined with disinfection unit:

The designed CNT column was used in combination with the PTC for further polishing of the effluent

8. Cost analysis:

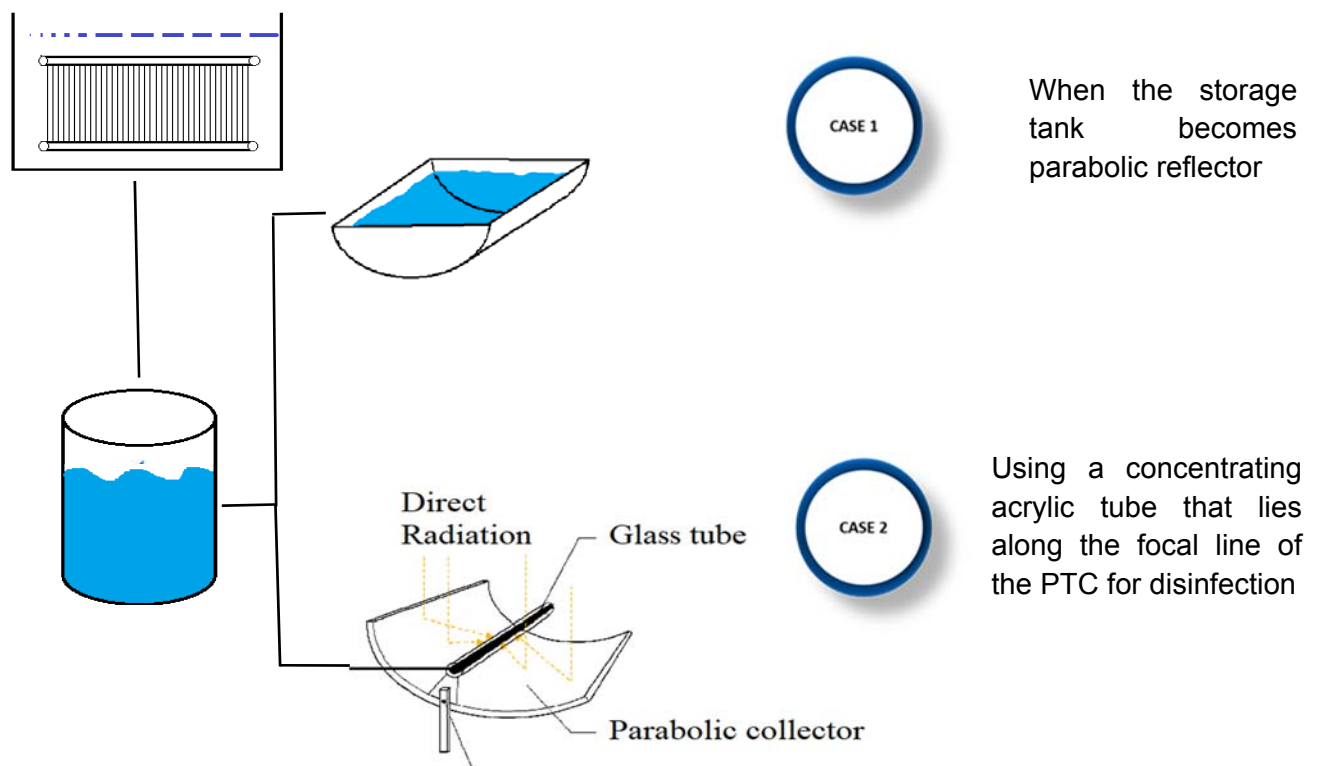
Cost analysis was done for full scale and operation scale for MBR, whereas the PTC was taken for cost evaluation for domestic disinfection as a single unit.

3.5.1 Sampling Methodology

1. 200 samples from solar disinfection units, 30 samples from activated carbon unit
2. Testing of collected samples and controls by following standard procedures
3. Analysis of samples within 24 hours

3.5.2 Schematics of the Methodology

Membrane Bioreactor



Membrane Bioreactor

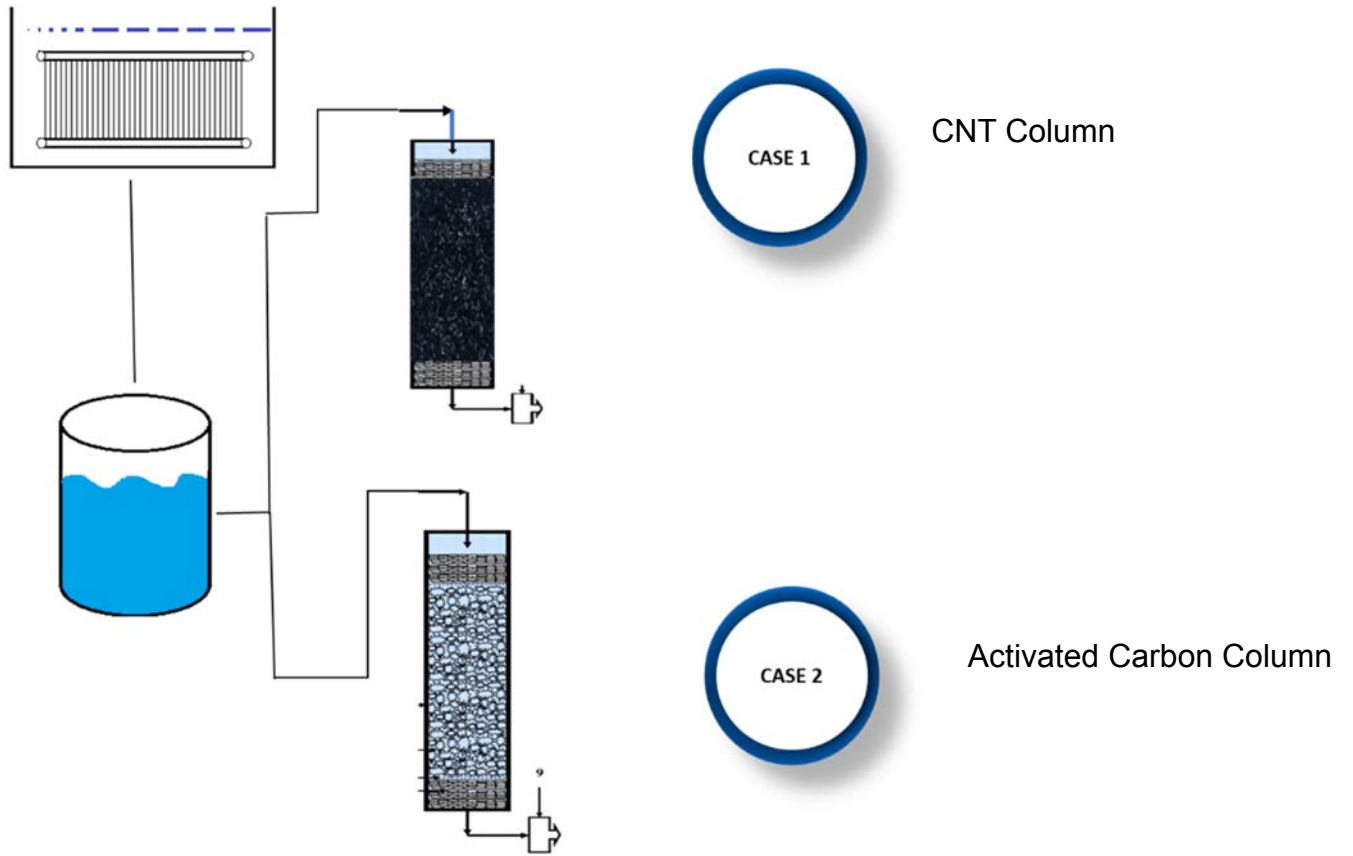


Figure 10: Schematic diagram of methodology

Overall Methodology

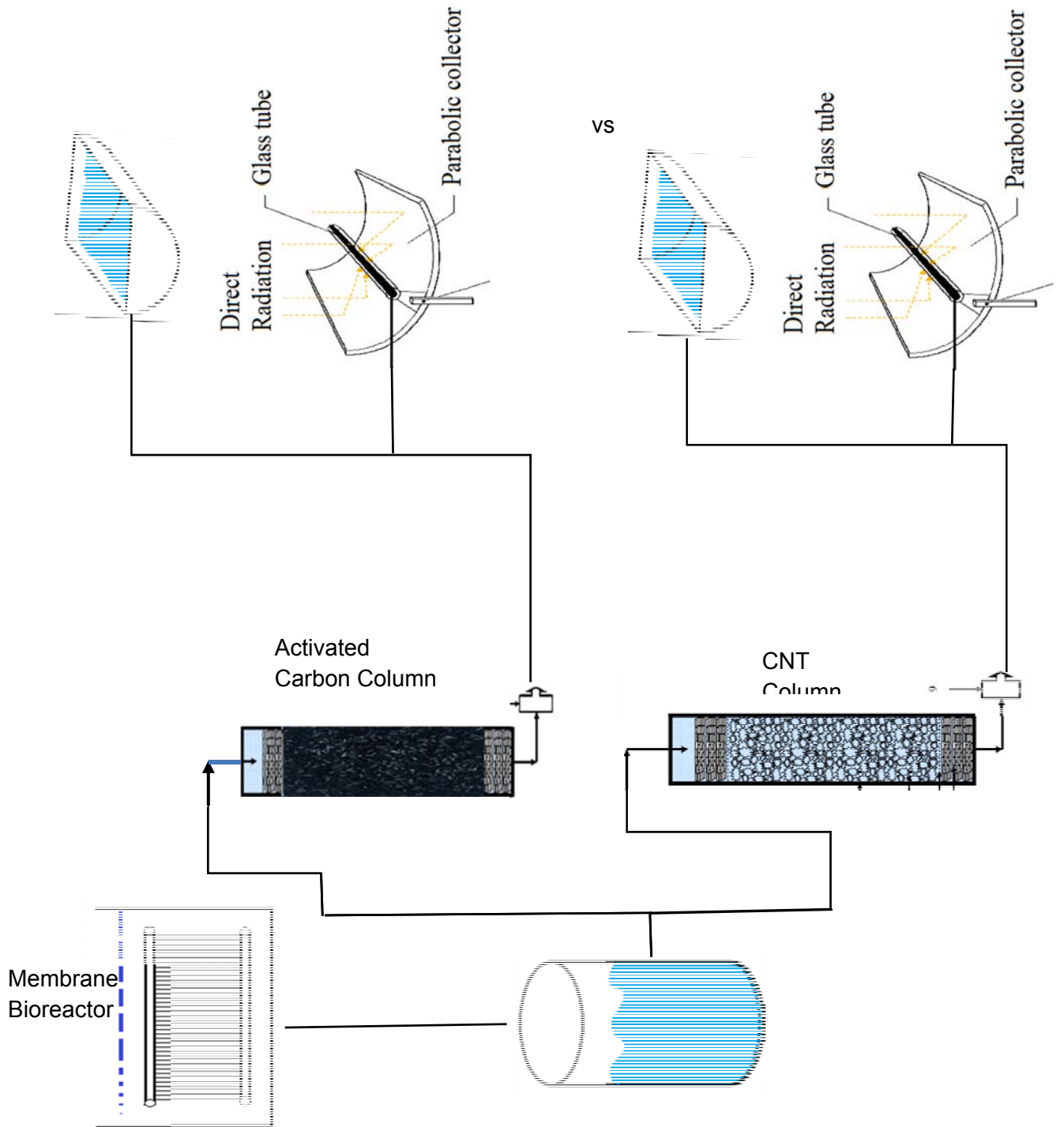


Figure 11: Overall Methodology

3.5.3 Testing Methodology

Effluent characterization was done by testing the following parameters:

- Physical:
 - pH
 - Temperature
 - Turbidity
 - Suspended solids
 - Conductivity
- Inorganic:
 - Nitrates
 - TKN
 - Sulfates
- Organic:
 - COD
 - Phosphates
- Microbiological:
 - Heterotrophic Bacteria
 - *E. Coli*
 - *Pseudomonas*

Reagents for COD, nitrates stock solution, nutrient agar (Plate count of heterotrophic bacteria), Eosin Methylene Blue (EMB) media (Microfiltration Technique for *E.coli*) and cetrimide agar (Plate count for *Pseudomonas*) were prepared in the labs.

3.5.4 Effluent Characterization

Physicochemical Parameters	MBR Results	Wetland Results	Reuse Standards*
pH	7.6 ± 0.36	6.7	6.5-8.4 (Portugal, 2000)
Conductivity (uS/cm)	938.67 ± 57.39	1258 ± 60.39	1000 (Portugal, 2006)
Turbidity (NTU)	0.87 ± 0.14	40.5	2 (US-EPA, 2012)
COD (mg/L)	60 ± 6.62	75.5 ± 5.46	60 (France, 2010)
Suspended Solids	4	53.3	10 (Italy, 2003)
TKN (mg/L)	5.04	--	15 (Italy, 2003)
Nitrates-N (mg/L)	18	22 ± 5	10 (Saudia, 2000)
Phosphates (mg/L)	3.129	13 ± 2	2 (Italy, 2003)
Sulfates (mg/L)	165	930	400 (Saudia, 2000)

Table 4: Physicochemical Parameters Characterization

Microbiological Parameters	MBR Results	Wetland Results	Reuse Standards*
E.Coli (CFU/100mL)	15320 ± 1560	29725 ± 2153	1000 (WHO, 2006)
Pseudomonas (CFU/mL)	6000 ± 550	16000 ± 1050	

Table 5: Microbiological Parameters Characterization

4. Results and Discussion

4.1 Evaluation Criteria for Microbiological Parameters

4.1.1 Samples

Samples taken were representative of following:

- Influent (MBR effluent in our case)
- Stainless steel PTC as a storage tank (SS Tank) effluent
- Acrylic tube placed at the focal line of PTC (Tube) effluent

4.1.2 Dependent Variables

Dependent variables are:

- Heterotrophic Bacteria
- *Pseudomonas*
- *E.Coli*

4.1.3 Independent Variables

Independent variables are:

- Exposure Time
- Solar Irradiance
- Type of Reactors
- Interspecies

4.2 Inactivation Graphs for Microbiological Parameters

The inactivation graphs for both the stainless steel PTC as a storage tank and acrylic tube placed at the focal line of PTC units were generated by taking replicates of samples at different time intervals (half hour interval from 2 to 8 hours) throughout a sunny day. Replicates were taken at 9:00 am, 11:00 am, 11:30 am, 12:00 pm, 12:30 pm, 01:00 pm, 01:30 pm, 02:00 pm, 02:30 pm, 03:00 pm, 03:30 pm, 04:00 pm, 04:30 pm, and 05:00 pm.

Bacterial count, exposure time and solar irradiation were noted and graphs were plotted for log removal values, colony forming units of heterotrophic bacteria, *E.coli* and *Pseudomonas* against

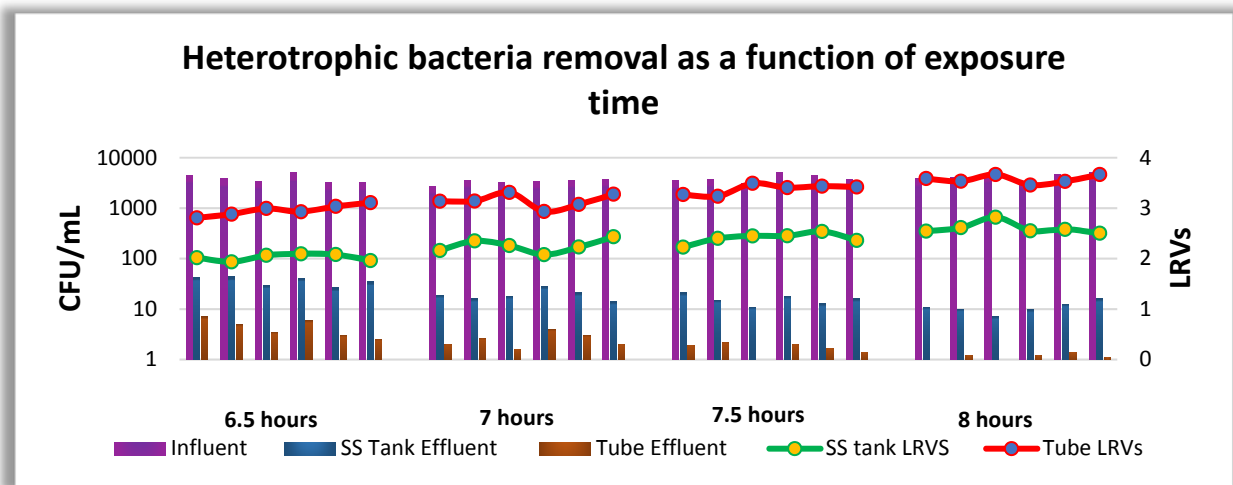
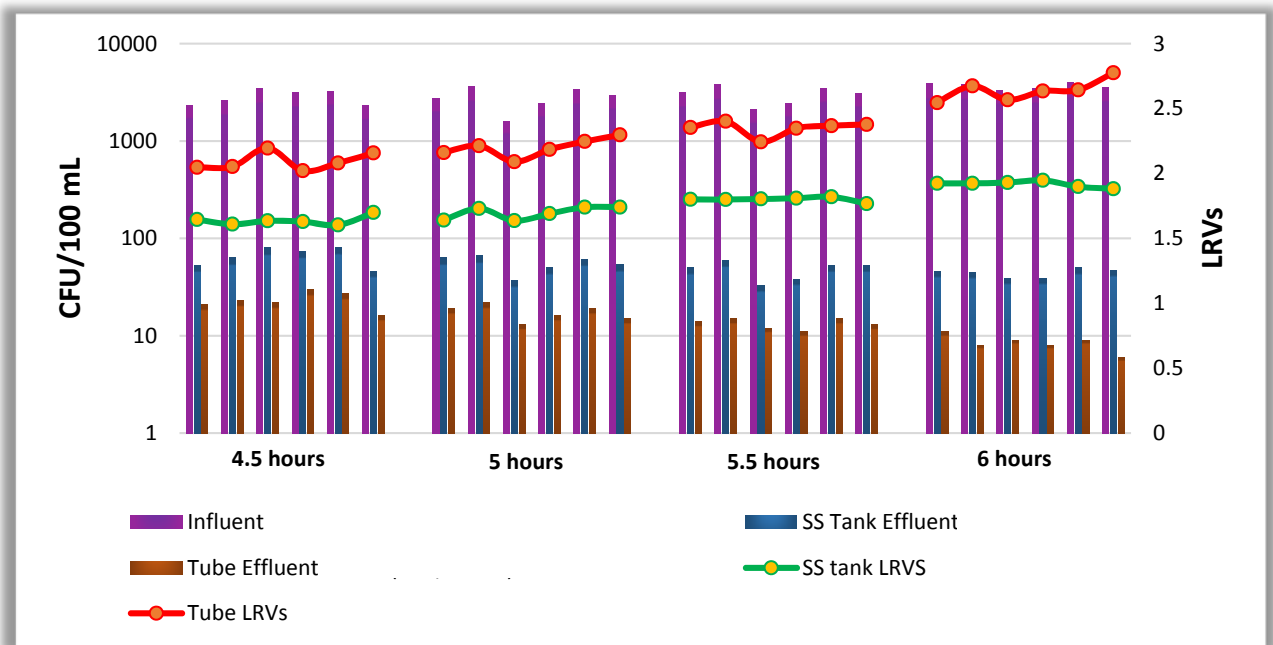
exposure time and solar irradiance respectively.

4.2.1 Graphs against Exposure Time

In the graphs below, the bars represent the colony forming units for influent which is MBR treated wastewater, compared against the colony forming units for effluents of both treatment units with respect to the exposure time. The lines show the log removal values of both treatment units.

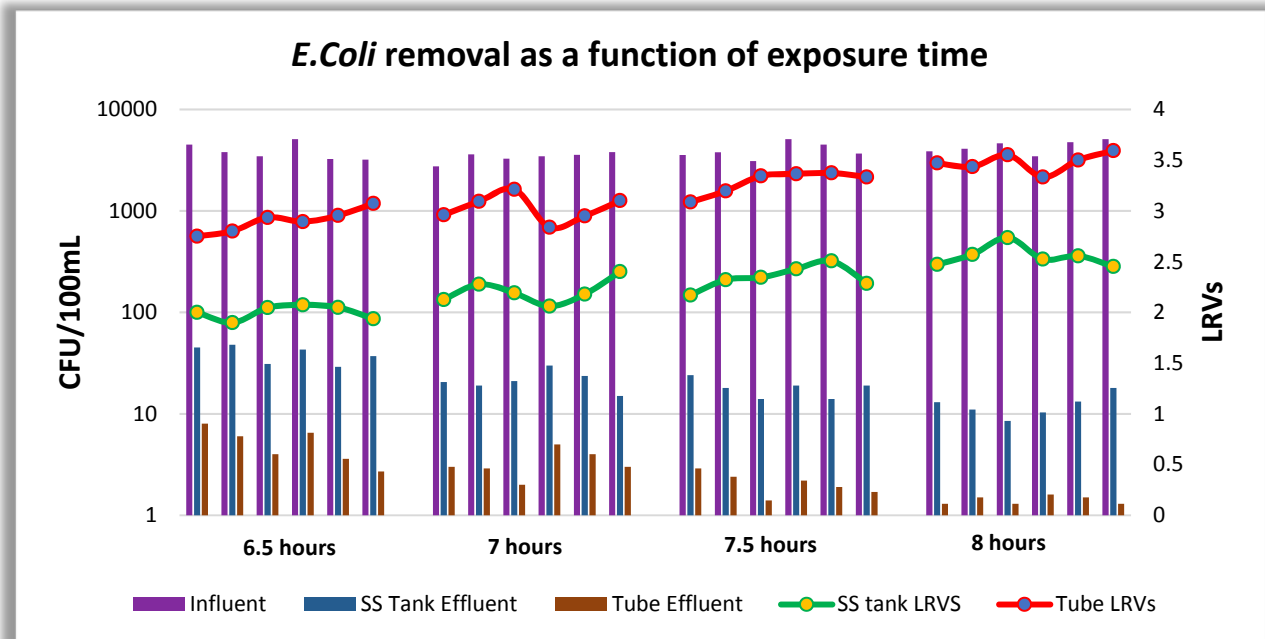
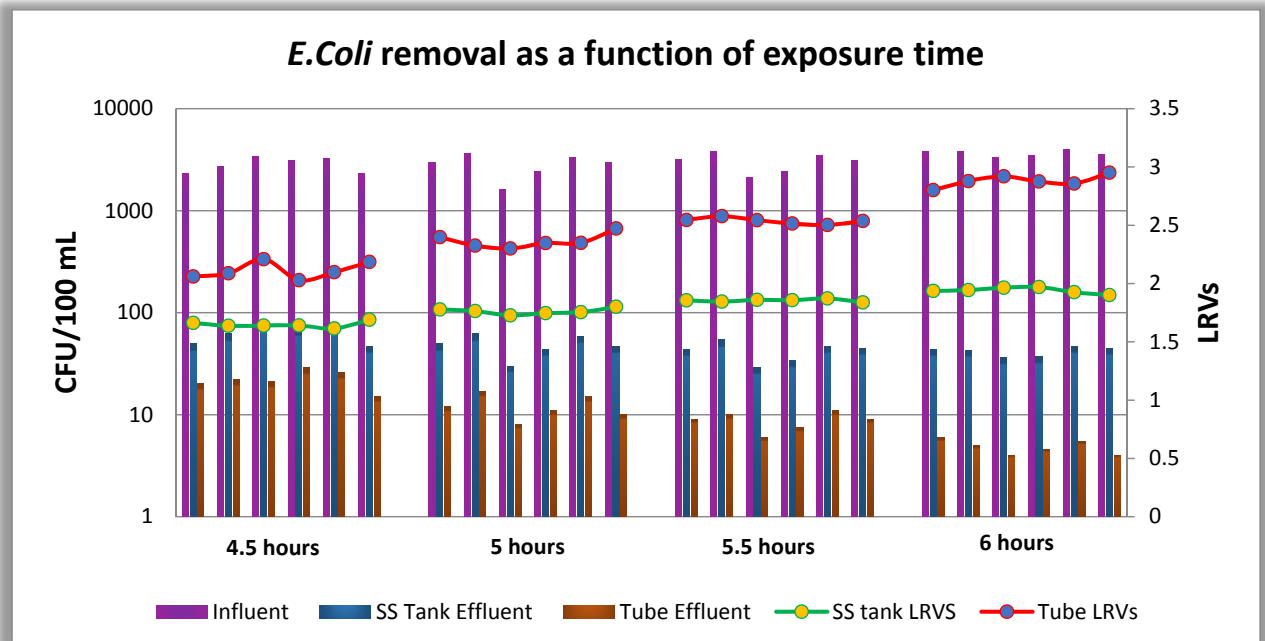
4.2.1.1 Heterotrophic Bacteria

Figure 12: Heterotrophic removal as a function of exposure time



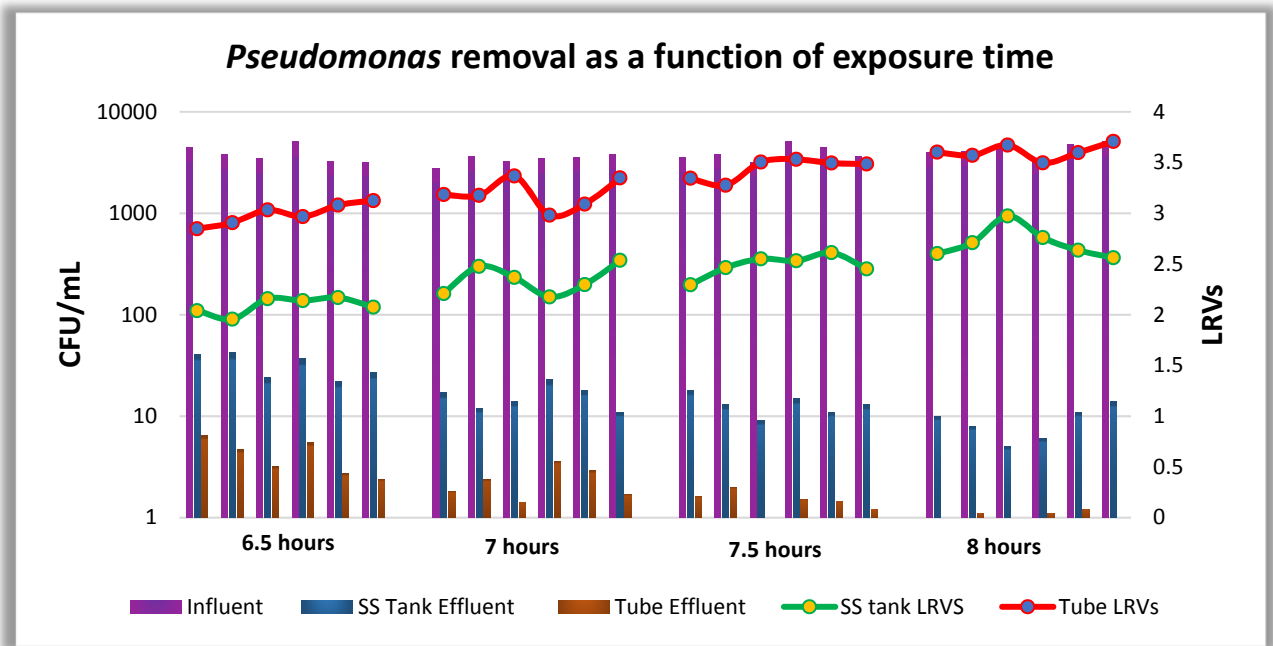
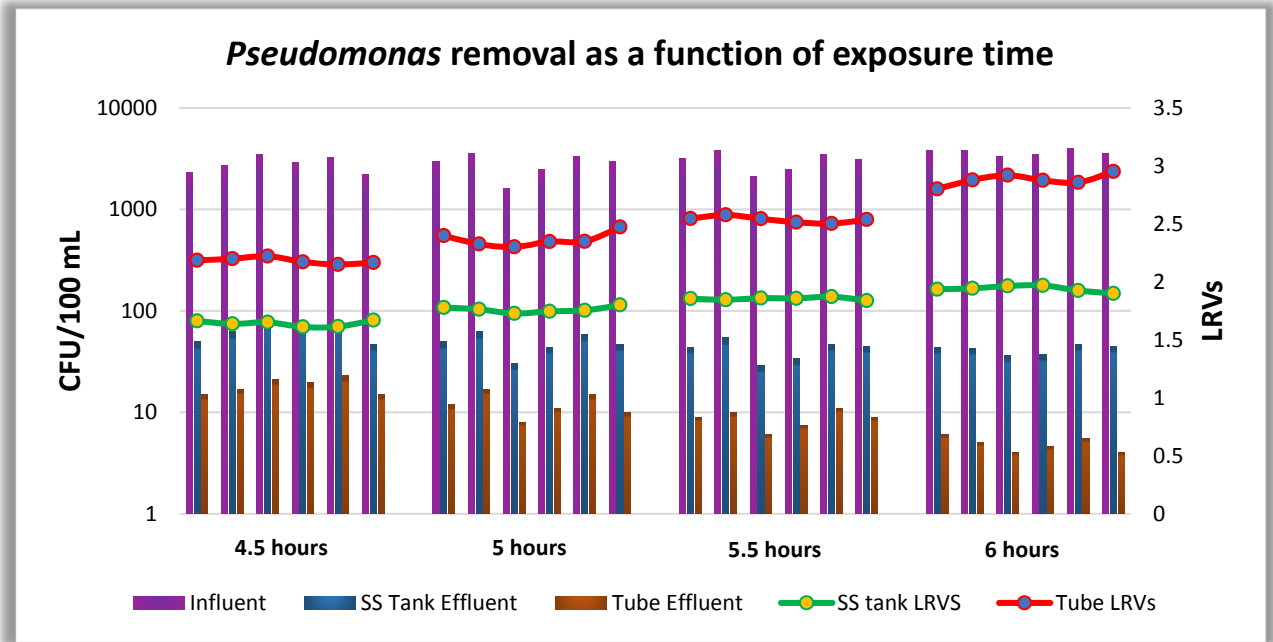
4.2.1.2 E.Coli

Figure 13: E.Coli removal as a function of exposure time



4.2.1.3 Pseudomonas

Figure 14: Pseudomonas removal as function of exposure time



From the graphs, it is clear that increase in exposure time results in increased log removal values as bacteria are exposed for a longer time so for more resistant bacteria UV gets enough time to penetrate to their DNA and destroy it.

Temperature observed was more than 40°C, which shows that pasteurization occurred. Hence, we interpreted that synergistic effect of both UV and temperature caused higher log removal values for bacterial species.

4.2.2 Graphs against Solar Irradiance

In the graphs below, the bars represent the influent which is MBR treated wastewater, compared against the effluents of both treatment units with respect to Solar Irradiance. The lines show the log removal values of both treatment units.

4.2.2.1 Heterotrophic Bacteria

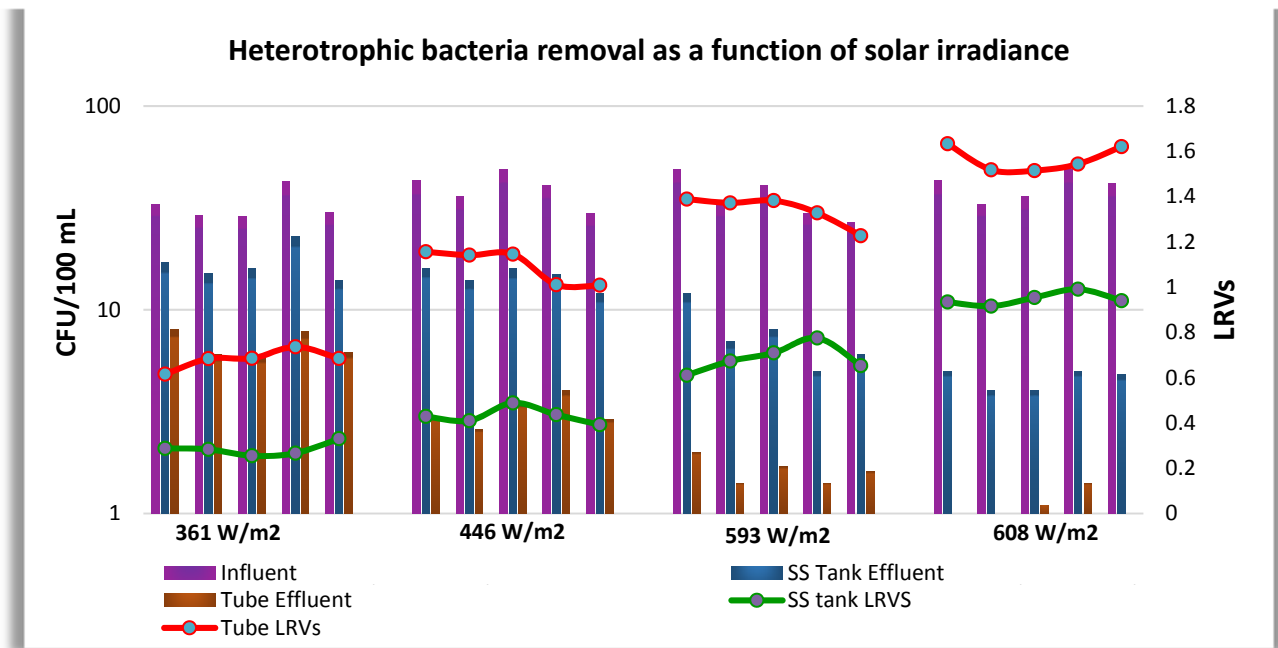


Figure 15: Heterotrophic bacteria as a function of solar irradiance

4.2.2.2 E.Coli

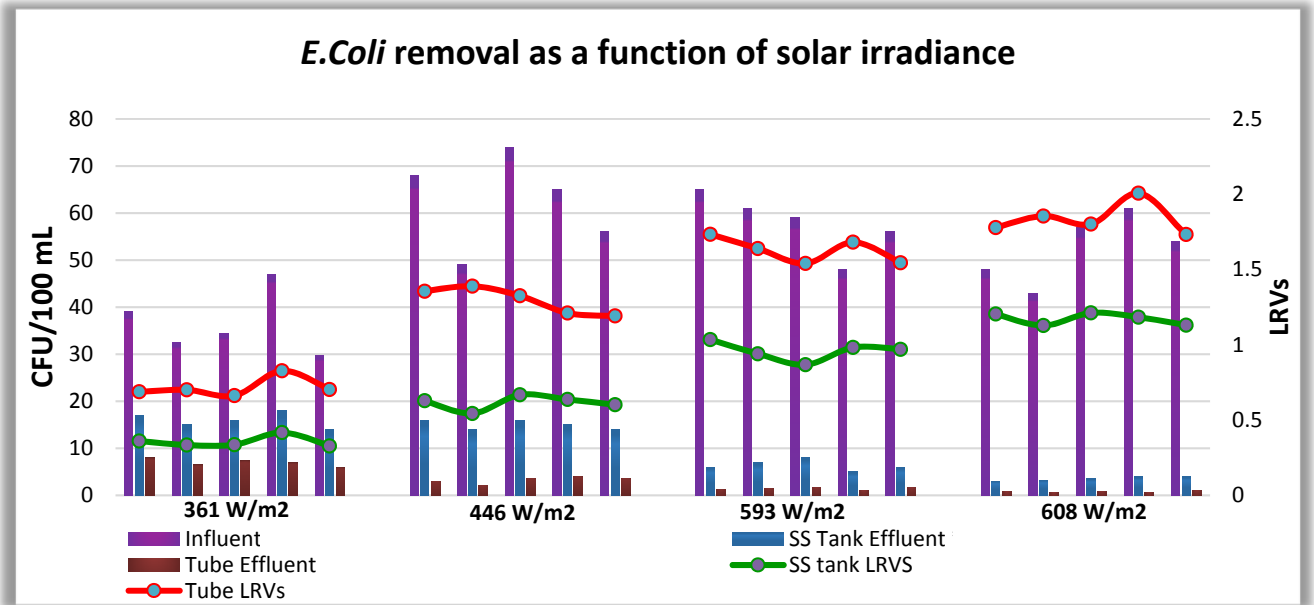


Figure 16: E.Coli removal as a function of solar irradiance

4.2.2.3 Pseudomonas

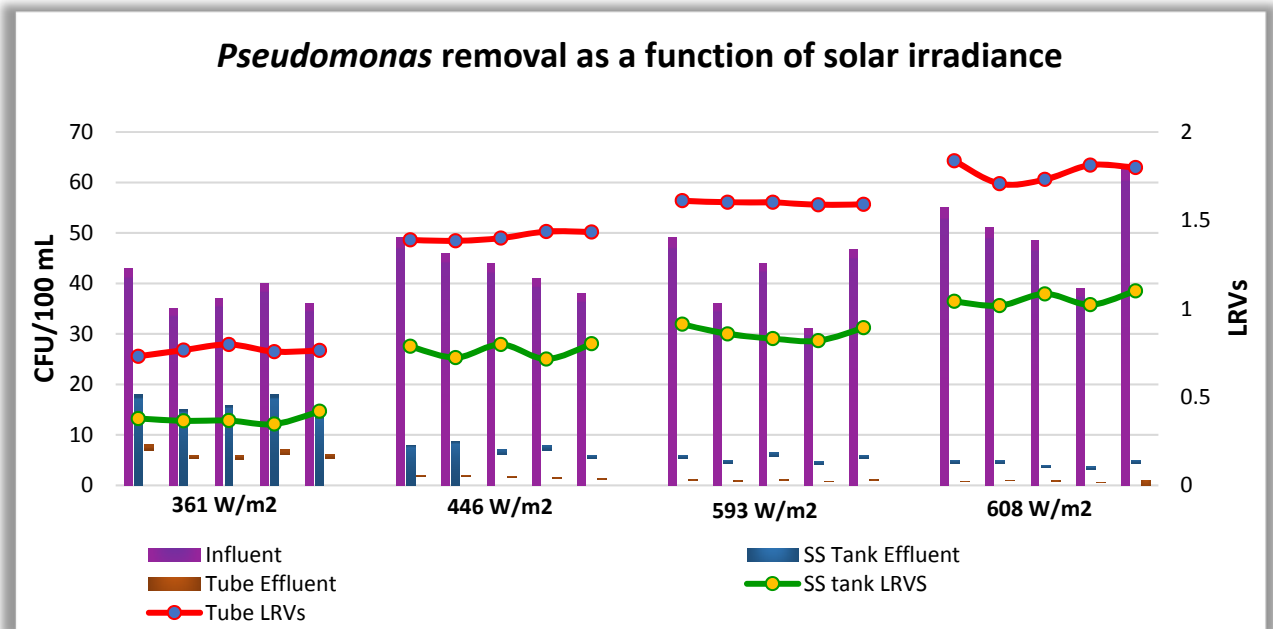


Figure 17: Pseudomonas removal as function of solar irradiance

These graphs (Heterotrophic bacteria, *E.Coli*, *Pseudomonas*) show higher log removal values for higher solar irradiance that clearly states that bacteria are more vulnerable to high intensity

radiations.

4.2.3 Interspecies Comparison

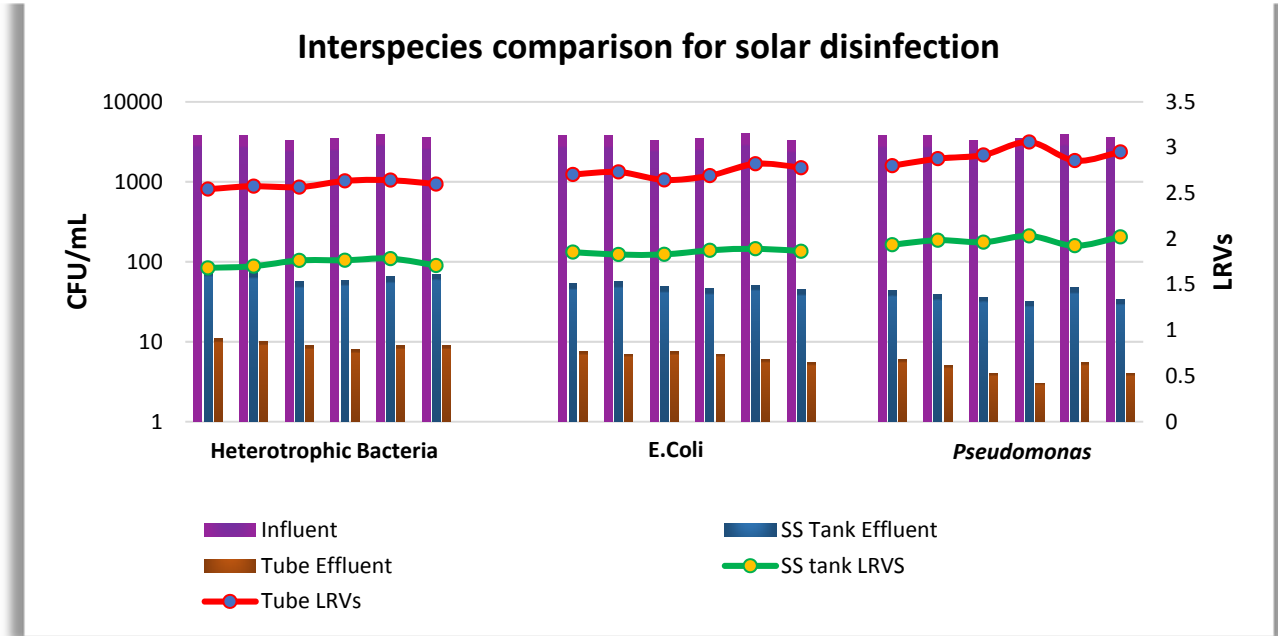
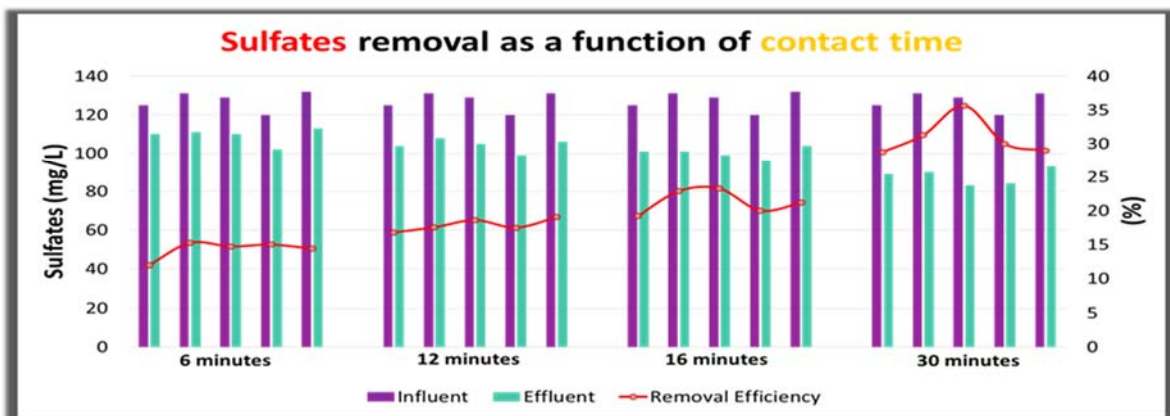


Figure 18: Interspecies comparison for solar disinfection

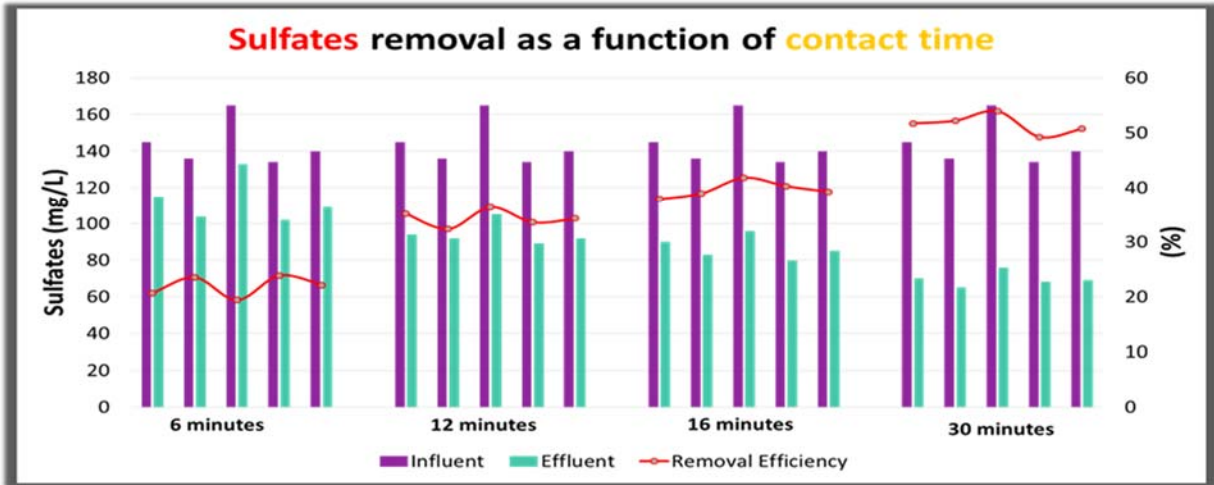
4.2.3 Graph of Sulfates and Phosphates

4.2.3.1 Sulphates

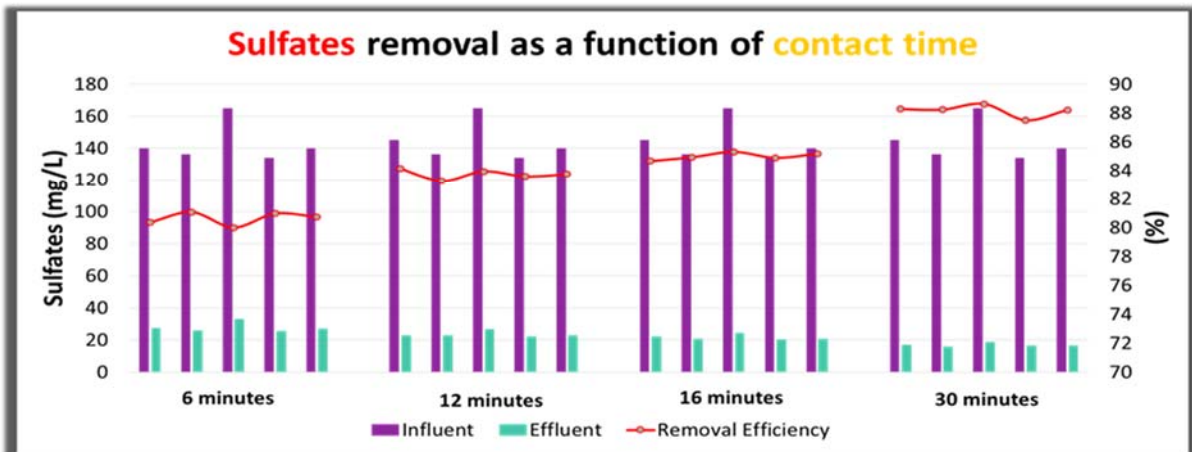
Activated carbon removal efficiency before solar treatment



Activated carbon removal efficiency after solar treatment



Carbon nanotubes removal efficiency before solar treatment



Carbon nanotubes removal efficiency after solar treatment

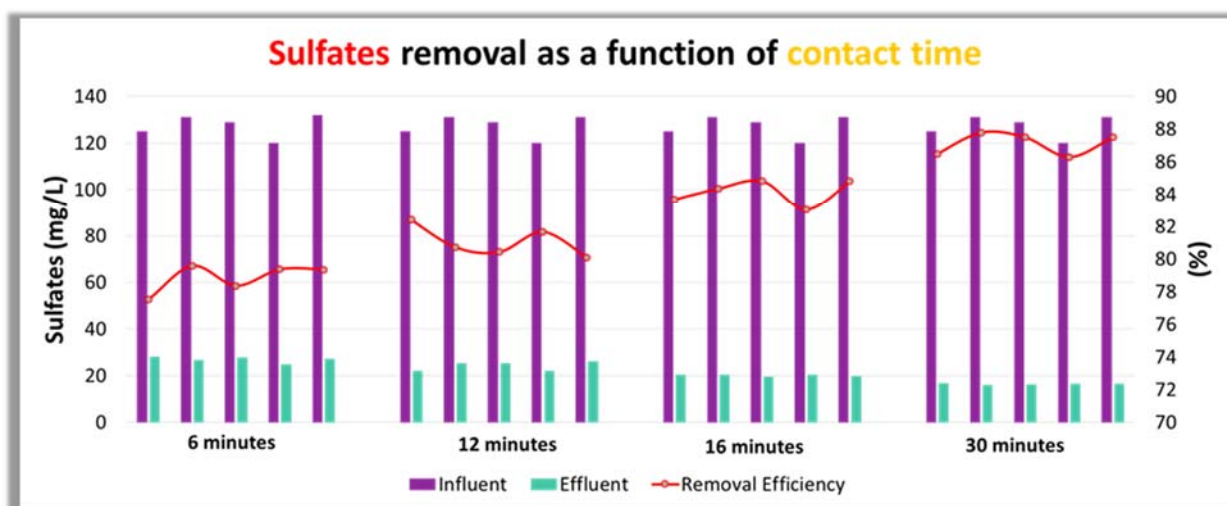


Figure 19: Sulphate removal from AC and CNTs as a function of contact time

4.2.3.2 Phosphates

Carbon nanotubes (CNTs) and activated carbon (AC) removal efficiency

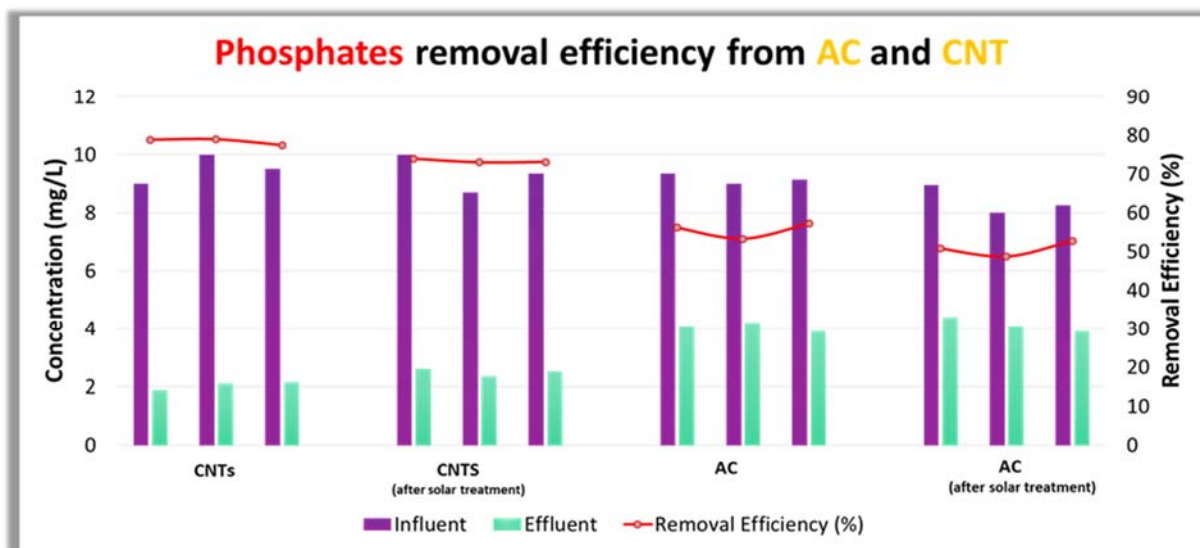


Figure 20: Phosphate removal from AC and CNTs

4.3 Activated Carbon Exhaustion Period

Activated Carbon Exhaustion Period

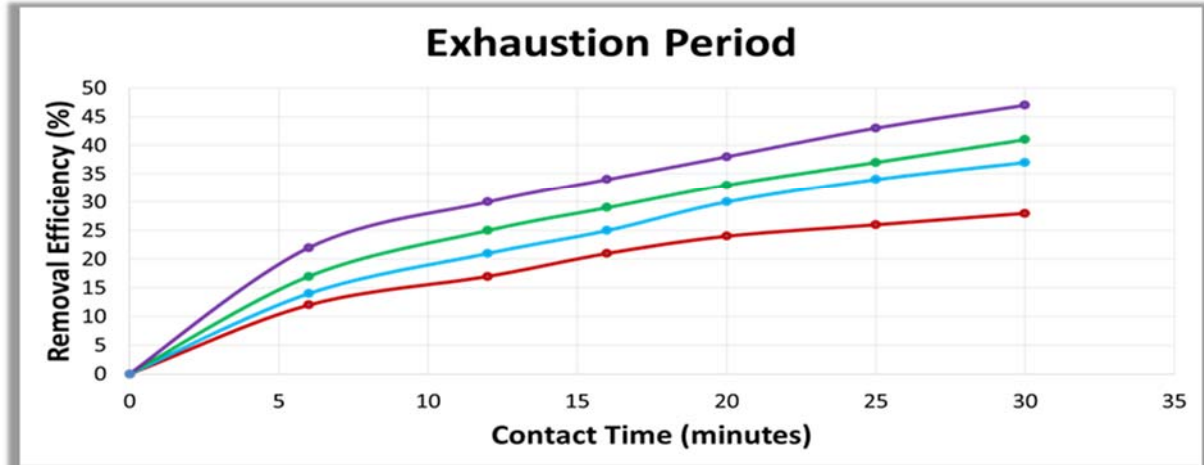


Figure 21: Activated carbon exhaustion period

4.4 Disinfect

All above graphs show that both carbon nanotubes and activated carbon were efficient in removing the organic and inorganic contaminants and bringing it below the reuse standards. By comparing removal efficiencies of both the columns carbon nanotubes were more efficient than activated carbon because of humongous surface area of CNTs. CNTs removal efficiency was around 90% and activated carbon removal efficiency was around 55%.

Exhaustion period of activated carbon was observed at one week interval for over one month. It is clear from the graph that removal efficiencies decreases with time, which states that adsorption is occurring on the activated carbon due to which it is exhausting and needs regeneration.

5. Conclusion and Recommendations

5.1 Conclusions:

The following conclusions were drawn, ensuing the end of the project experimentation:

1. Without a polishing unit, the MBR & phyto remediation effluent is unfit for agricultural reuse
2. Parabolic trough collector is an efficient design for disinfection
3. Carbon nanotubes are efficient for treating chemical pollution
4. Activated carbon performed well to meet reuse standards
5. Integration of carbon nanotubes and parabolic trough collector synergizes the treatability of wastewater
6. The designed polishing unit makes wastewater fit for reuse

5.2 Recommendations:

5.2.1 Limitations and prospects:

The limitations observed in the course of experimentations open new doors for up gradation and prospects. Some of these limitations are enlisted with their recommended solutions:

1. Dark conditions

- Upconversion – Infrared to UV conversion using advanced materials
- Full spectrum LED grow lights
- Solar powered UV lamps for night time

2. Solar nadir

- Use of digital solar tracking system so the optimum angle is achieved in real time

5.2.2 Applications

Some additional applications for the designed treatment unit of CNTs and PTC can be expected in the following cases:

➤ **Ecological Sanitation**

- Disinfection of urine to recover nutrients like nitrogen

➤ **Rainwater harvesting**

- Disinfection of harvested rainwater

➤ **Service station water recycling**

- Removal of detergents by CNTs and disinfection by PTC

➤ **Hydroponics**

- The polished water is fit for hydroponic applications

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