Hybrid multimedia-filter prototype (HMP) for the degradation of trihalomethanes precursors and pathogens control from raw waters

By

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Abstract

The need for affordable and resource conserving water purification methods has only increased over the years. Alongside that, the occurrence and discovery of emerging contaminants demand the research and development of new technologies to properly address the destruction/removal of such contaminants. One of those emerging contaminants is trihalomethane. Trihalomethanes (THMs) are disinfection by-products that form when chlorine reacts with naturally occurring organic matter (such as humic acids). With that in mind, a hybrid system was developed, combining two known methods of water purification: filtration and oxidation. The system was comprised of a lab-scale biosand filter (LSBF); as well as a nanocomposite substrate embedded with titanium dioxide (TiO_2) nanoparticles. The LSBF was used to eliminate pathogens, while the TiO_2 embedded nanocomposites was used to degrade suspended solids. The project also aimed to study the impact of the filter's sand bed depth in the removal of pathogens by reducing it 26.67 cm. The LSBF was operated in batch mode allowing an idle time of 24 hours between filtration to promote the establishment of a biolayer on top of the sand bed. The water source was the "Oro Creek" located in Mayaguez, Puerto Rico. The LSBF effluent is then exposed to the TiO_2 nanocomposite for 8 hours under UV light. The water is analyzed for pathogen population and organic matter quantified as total organic carbon (TOC) content, in order to observe the reduction of both parameters. Results revealed that a reduction in the sand bed depth showed no significant difference in the removal efficiency in turbidity and pathogen when compared against a standard sand bed depth. This indicated that bio filters can be constructed

with fewer materials without losing the pathogen removal quality. Furthermore, the hybrid system showed slightly more pathogen removal to a near complete removal in the water. In terms of organic matter, the LSBF was capable of halving the amount of TOC in the water, while the hybrid system improved the reduction up to 75%. Ultimately, the hybrid system proved effective in eradicating the pathogen content in the water while also removing the vast amount of TOC, reducing the potential formation of THMs.

Resumen

La necesidad de métodos de purificación de agua que sean costo efectivo y conservadores de recursos ha aumentado a través de los años. Además, la ocurrencia y descubrimiento de contaminantes emergentes demanda la creación de nuevas tecnologías para remover esos contaminantes. Uno de estos contaminantes es trihalometano. Trihalometanos (THMs) son productos de desinfección que se forman cuando cloro entra en contacto con materiales orgánicos (como los ácidos húmicos). Con esto en mente, se desarrolló un sistema híbrido que combina dos métodos de purificación de agua anteriormente conocidos; filtración y oxidación. El sistema desarrollado está compuesto por un filtro biológico lento de arena; además de un sustrato nanocompuesto incrustado con nano partículas de dióxido de titanio (TiO_2). El filtro biológico lento de arena fue usado para eliminar patógenos, mientras que el sustrato nanocompuesto se utilizó para para degradar solidos suspendidos. Este proyecto a su vez se pretende estudiar el impacto del filtro de arena en la remoción de patógenos reduciendo la profundidad del filtro por 26.67 cm. El filtro biológico lento de arena se llenaba de agua por tandas permitiendo un tiempo de reposo de 24 horas entre cada filtración para promover el establecimiento de una biocapa encima del lecho de arena. La fuente de agua fue la Quebrada de Oro, ubicada en Mayagüez, Puerto Rico. Luego, el efluente se expuso al nano compuesto por 8 horas bajo luz ultravioleta. El contenido de patógenos y carbono orgánico total (COT) del agua fue analizado en todas las etapas, para así observar la reducción de ambos parámetros. Las pruebas que involucran las alturas de los biofiltros revelaron que no hubo diferencias significativas en la eficiencia de purificación al reducir la profundidad de los filtros,

cuando comparados a la profundidad estándar. Esto nos indica que los biofiltros pueden construirse con menos materiales sin perder la calidad de eliminación de patógenos. Por otra parte, el sistema híbrido mostró una eliminación de patógenos ligeramente más cercana a una eliminación casi completa de todos los patógenos en el agua. En términos de materia orgánica, los biofiltros fueron capaces de reducir a la mitad la cantidad de COT en el agua, mientras que el sistema híbrido aumenta esa reducción a un 75%. Finalmente, el sistema híbrido demostró ser eficaz en erradicar el contenido de patógenos en el agua y al mismo tiempo eliminar una gran cantidad del COT, reduciendo la posible formación de trihalometanos.

“For whatever we lose (like a you or a me),
It's always our self we find in the sea.”
— E.E. Cummings, 100 Selected Poems

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To Carmen and Ali, parents who push me forward

To Mariam, a sister I trust to listen when have doubts

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List of Symbols and Abbreviations

TiO_2	Titanium Dioxide
UV	Ultraviolet
CWA	Clean Water Act
EPA	Environmental Protection Agency
TOC	Total Organic Content
HA	Humic Acid
LSBF	Lab Scale Biosand filter
DOC	Dissolved Oxygen Content
pH	Range of acidity from 0 to 14
Cl_2	Chlorine
THM	Trihalomethanes
ANOVA	Analysis of Variance
GTC	Glass Titanium Composite

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1. Introduction

Water contamination and how we treat it has become more and more complicated as our understanding of how different chemical and contaminate react grows. One such relationship lays in one of the most used pathogen removal agents, chlorine. This compound is one of the cheapest and easiest to use disinfectant in water treatments, and its presence can be felt worldwide [1]. However, the problem with its common use lies in its interactions with humic acid. This acid is the result of the natural organic matter degradation in the water, from leaves and smaller organisms that decompose over time. When humic acid comes in contact with chlorine, it results in the formation of trihalomethanes (THMs), compounds that are carcinogenic or as it is more commonly known, cancerous [1][2].

An attractive method for organic matter destruction lies in advanced oxidation processes comprising the use of semiconductors to promote a photodegradation reaction. One of those appealing semiconductors is titanium dioxide (TiO_2), which is an extremely effective photo-activated semiconductor that is safe for human contact, making its usage far more viable than much more dangerous chemicals [3]. The challenge is how to expose the TiO_2 to the water in a safe and efficient way that does not allow it to become entrenched in the water. By embedding TiO_2 in a solid matrix instead of suspending it, we allow it to treat the water without necessitating the usage of additional filters for its final removal from water.

Another complication in water treatment relates to its cost and maintenance. The reduction of construction costs and space used for treatment methods can be extremely

useful for communities that do not have the economic resources to provide a high end treatment plant. One such avenue is reducing pathogens from the water supply through easy to build and maintain methods such as filtration. Filtration with biofilters is a system that sets itself up through the formation of the biolayer, removing the need for chemical usage. One such method of reducing costs is to examine how much the heights of bio filters can be reduced and still provide efficient and acceptable pathogen removal.

1.1 Scope

The scope of this research is to create a hybrid system composed of a biofilter and a nanocomposite with embedded TiO_2 particles. With this system, the aim is to reduce the amount of pathogens and organic matter in the water and reduce the chances that chlorine could come in contact with potential reactants and form THMs. The ultimate goal is to create and affordable system for water treatment and purification.

1.2 Objectives

The project can be divided into two phases:

- Phase 1: Evaluating the pathogen reduction capacity of a standard depth filter vs. a reduced depth filter. The specific objectives of Phase I are:

1. Design and develop two sets of lab scale biosand filters (LSBF) to resemble a standard and a reduced sand bed depth.

2. Test the filters for pathogens removal using *E.coli* and *Enterococci* as indicators.

- Phase 2: Evaluate a hybrid system composed of the LSBF and a TiO_2 nanocomposite for the reduction of both pathogens and organic matter. Specific objectives for Phase 2 are:

    1. Evaluate a glass/ TiO_2 nanocomposite on an individual level to test effectiveness for organic matter reduction.

    2. Combine both methods (LSBF + TiO_2 nanocomposite) to create the hybrid system and test for both pathogens and organic matter content in water, and the system's effectiveness to reduce both contaminants.

2. Literature Review

Water is the most important and essential resource on the planet. Its presence is tantamount for life, and it is consumed by every living being. The need for safe, clean water for human consumption has encouraged the development and establishment of treatment processes. In most forms of treatment, the most common used disinfectant agent is chlorine. Its usage in disinfecting water is common worldwide and its low cost contributes to its affordability.

This does not only impact locations with enough money to support a full treatment system. In places that are unable to provide adequate monetary resources (such as war zones, economically stagnant regions and other such impacted locations) alternative forms of treatment are available. One method is the usage of chlorine tablets, which provide a quick and easy way of disinfecting the water for small families that acquire their water directly from point sources such as rivers and lake [4].

Despite all its benefits, an unpleasant interaction puts its usage in jeopardy. While for bacteriological issues chlorine possesses much efficiency, a unique reaction occurs when it comes in contact with naturally organic and inorganic matter in water [5]. This reaction results in a group of chemicals called Trihalomethanes. This is a subgroup of disinfection byproducts or DBP's. In this group of chemicals, we find chloroform; bromodichloromethane, dibromochloromethane, and bromoform (see Table 1 and Figure 1). The official EPA maximum annual allowable average is an estimated 80 ppb [1].

Table 1 Trihalomethanes Varieties and Chemical Formula

Trihalomethane	**Chemical Formula**
Trichloromethane(chloroform)	$CHCl_3$
Dibromochloromethane	$CHClBr_2$
Bromodichloromethane	$CHCl_2Br$
Tribromomethane	$CHBr_3$

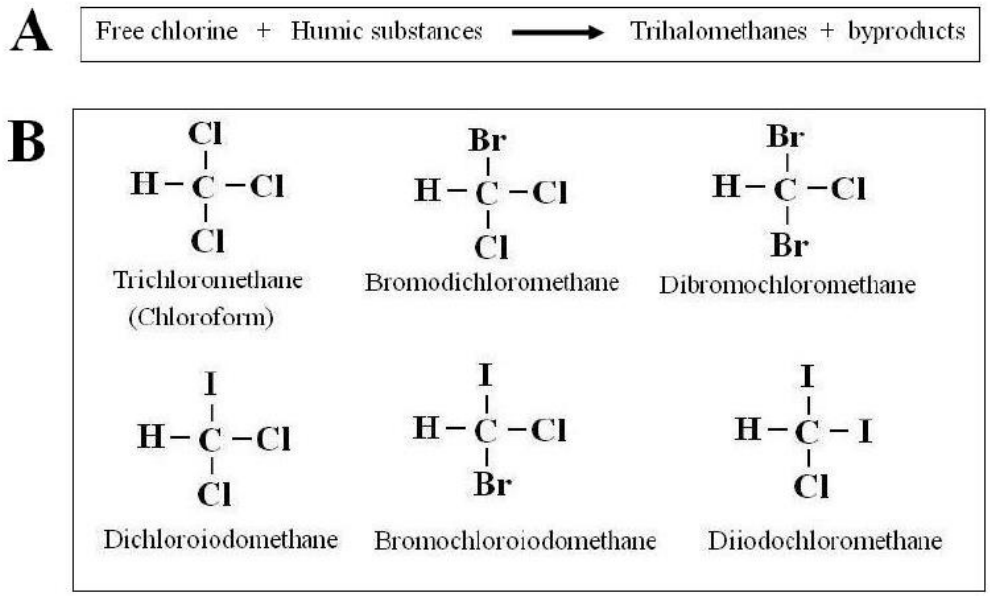

Figure 1 Common Trihalomethane Chemicals. A Refers to the Chemical Reaction, B Refers to the Chemical Equations. [6]

The issue with THM's, aside from the fact that they may occur in water that is properly treated, is that they are carcinogenic, as proven in controlled laboratory settings [5]. The most common and well known is chloroform, the most commonly found in water systems and is not the most dangerous. On the other hand, dibromochloromethane presents the highest cancer risk with the smallest exposure required at 0.6 mg/l, with the other chemical (Bromoform and Chloroform) following

quickly after. Bromodichloromethane has been associated with birth defects at exposure levels of 20 ug/l [7][8]. In fact, chloroform requires quantities of over 6 ug/l before it provides any threat to the human body. The current regulatory amount for the 4 chemicals combined is a scant 80 ug/l (or 80 ppb), with each having an individual requirement. Table 2 provides maximum allowed levels in drinking water as defined by EPA [9]. The World Health Organization (WHO) has its own standards and limits, but are somewhat more lenient, due to the economic disparity between nations, making it difficult to be as aggressive as the EPA. These standards are noted in Table 3. In spite of these standards, THMs are common in both the United States and Puerto Rico water sources. While their concentration varies from state to state, the mere fact that they are detectable is cause for concern. Refer to Figure 2 for THM detection within the US.

Table 2 Maximum Quantities of Allowed Trihalomethanes in Drinking Water, as Defined by the EPA. [9][1]

Trihalomethane	**Allowed quantity in water**	**Total allowed**
Bromodichloromethane	0-0.6 ppb	
Bromoform	5 ppb	0.080 mg/l or 80 ppb per year
Dibromochloromethane	60 ppb	
Chloroform	70 ppb	

Table 3 WHO Maximum Quantities for Trihalomethanes in Drinking Water [2].

Trihalomethane	**Allowed quantities in water**
Bromodichloromethane	$6x10^{7}$ ppb
Bromoform	100 ppb
Dibromochloromethane	100 ppb
chloroform	300 ppb

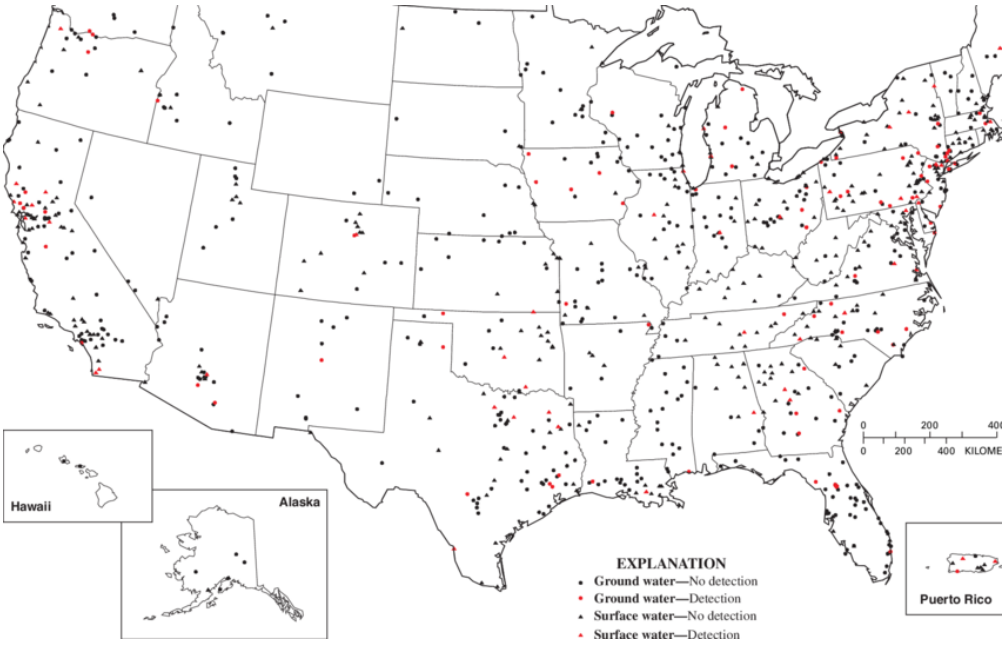

Figure 2 Map of Trihalomethane Detection in the United States [10]

THMs are affected heavily by factors such as pH, temperature, and presence of organic materials that can react with chlorine to form them. This is noted in a 2010 study on the significant influence that these factors can have on the formation of such chemicals, as noted in Table 4 [11][12][13]. These factors are summarized in the Equation 2.1 [12]

$$THMs = \beta_0 + \beta_1 * DOC + \beta_2 * Cl_2 + \beta_3 * pH + \beta_4 * T + \beta_5 * t + \beta_6 * (Cl_2 - 4.47)(T - 15.03) \quad (2.1)$$

Where:

THM+ THMs in water (µg/L),

DOC+ DOC (mg/L),

Cl_2= chlorine does (mg/l),

T= reaction temperature (Celsius),

t= reaction time (hours), and

β= model parameters (regression coefficients).

To reduce the formation of these compounds one can reduce the presence of organic materials before they reach the chlorination stages, the earliest one being pre-filtration. In the pre-chlorination, alternative compounds that do not react with organic materials can be substituted; this may not be possible depending on the standards of the region. If that is not an option, then an improvement of filtering methods can serve as a reducing factor, alongside the application of buffers to control the pH levels, which can mitigate the formation factor even further. In the United States current methods do in fact reduce many of these organic materials, although their aim may be for other health hazards such as pathogens.

One must always strive for improvement of these high-impact technologies. Accordingly, using a filtration method and its reduction capabilities are a large part of this research. By studying the sand filtration methods and its effect on the amount of organic matter, we can assess its capability in reducing the formation of THMs. The other factor depends on the reaction of organic matter with other compounds, such as TiO_2, the second branch of our research. THM's are not only field of study or concern,

as we also wish to understand the efficiency of these treatment systems on pathogens, specifically *E.coli* and *Enterococci*

Table 4 Screening Effects of the Factors for THM's formation [12]

Factor	**Estimate**	**Standard error**	**t-Ratio**	**Prob>[t]**	**Comments**
DOC (mg/L)	8.2765113	0.660098	12.54	<.0001	Significant
Cl2dose (mg/L)	13.5204	0.778209	17.37	<.0001	Significant
pH	3.1344643	1.128998	2.78	.0063	Significant
Temperature (Celsius)	0.8275548	0.145827	5.67	<.0001	Significant
Time (hours)	0.4979956	0.069532	7.16	<.0001	Significant
(DOC-4.98)*(Cl2dose-4.47)	0.1338685	0.18607	0.72	0.4731	
DOC-4.98)*(pH-7.21)	0.7191256	0.585068	1.23	0.2212	
DOC-4.98)*(Temp-15.03)	-0.035973	0.071869	-0.50	0.6175	
DOC-4.98)*(Time-25.94)	0.0290981	0.034955	0.83	0.4067	
(Cl_2dose-4.47)*(pH-7.21)	-0.384541	0.729288	-0/53	0.5989	Significant
(Cl_2dose-4.47)*(Temp-15.03)	0.1844682	0.087763	2.10	0.0375	
(Cl_2dose-4.47)*(Time-25.94)	-0.020419	0.042293	-0.48	0.6300	
(pH-7.21)*(Temp-15.03)	0.0924586	0.116099	0.80	0.4272	
(pH-7.21)*(Time-25.94)	-0.042656	0.057219	-0.75	0.4573	
(Temp-15.03)*(Time-25.94)	-0.014185	0.007341	-1.21	0.2206	

2.1 *Coliforms* and *Enterococci* as Indicators of Fecal Contamination

Inevitably water carries bacteriological organisms as the precious liquid comes in contact with the outside world. Thus, since water is exposed to other factors, such as animals, plant life and waste, the chances of pathogens presence in water bodies increases [14]. This is a large part why we disinfect water, and why chlorine is paramount in water treatment.

Table 5 Waterborne Pathogens, Associated Illnesses, and Source of Wastes [15]

Pathogenic Agent	**Acute Effects/Chronic or Ultimate Effects**	**Wastes**
Bacteria:		
Campylobacter jejuni	Gastroenteritis/death from Guillain-Barre syndrome	Human/animal feces
Escheria coli (pathogenic strains)	Gastroenteritis/*E.coli 0157:H7*	Domestic sewage
Leptospira	Leptospirosis	Animal urine
Salmonella typhi	Typhoid fever/reactive arthritis	Domestic Sewage
Shigella dysenterriae	Bacillary dysentery	Human feces, domestic sewage
Vibrio cholera	Cholera/death	Domestic sewage, shellfish, saltwater
Yersinia spp.	Acute gastroenteritis/diarrhea, abdominal pain, arthritis	Water, milk, mammalian alimentary canal
Viruses		
Adenovirus	Respiratory and gastrointestinal infections	Domestic sewage
Calicivirus	Gastroenteritis	Domestic sewage
Coxsackievirus (some strains)	Includes severe respiratory diseases, fever, rashes, paralysis, meningitis	Domestic sewage
Echovirus	Similar to Coxsackievirus	Domestic sewage
Hepatitis A	Includes hepatitis (liver); kidney and spleen	Domestic sewage

Many pathogens cause a variety of illnesses and maladies when present in the human body. While viruses can have a presence in the water, the most common and easily detected pathogens are usually bacteria, as noted in Table 5 [15][14][16]. In the case of parasites, which are also easily detected, their adults forms are usually removed

in filtering phases due to their size. With bacteria being so prevalent in our water supplies, either naturally or accidentally, detection standards become mandatory [17] in order to properly prepare the pertinent treatment process for the region of interest. One such method is to use an indicator, both easily identified and quantified in order to better understand the presence of other bacteria in the water.

One of the most effective methods to assess water quality is monitoring the presence of coliforms. Coliforms are generally classified as Total Coliforms, and then divided further into fecal coliforms, which are the main point of contention (Figures 3 and 4). Fecal coliforms exist within the fecal matter of humans and warm blooded animals, which contain a staggering amount of microbes, viruses, protozoa and other contaminants that can find their way into water sources [18]. It is this commonality that makes coliforms so attractive to study, as their presence is common within nearly all warm-blooded animals, and it also serves as an indicator of more dangerous pathogens. It should be noted that coliforms can be harmful on their own, as many are responsible for diarrhea and other intestinal illnesses. One of the most well-known coliforms is *Escherichia coli* or *E. coli* [19]. Alongside *E.coli* is the observation of Enterococcus. The presence of these two in water is a clear indicator of some foreign pathogens being introduced into a given water body [20]. The difference between the two has less to do with their composition, but rather with their habitats. *Enterococci* are present in both marine and fresh waters, while *E.coli* is exclusive to fresh waters [20][21]. The EPA recommended mean levels for these pathogens in natural water bodies over a 30 day are 126 CFU/100ml for *E.coli* and 35 CFU/100ml for *Enterococci* [22]. Both have a presence in fecal matter, but *E.coli* can occur in other sources, which

makes *Enterococci* a good backup indicator to the presence of fecal contamination as well as an additional quantifying method in the event of a cultivation error with *E.coli* [23][24]. However, the absence of these bacteria does not eliminate the possibility of other pathogens in the water; it is simply a useful indicator, not a definitive one.

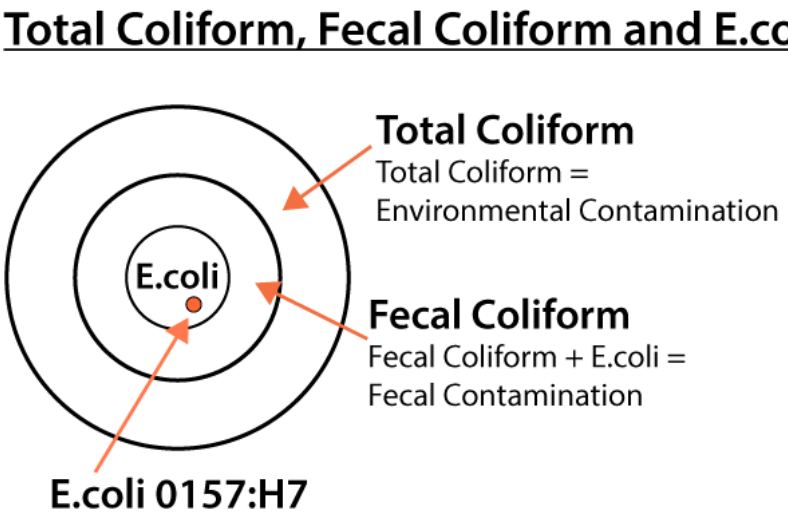

Figure 3 Coliform Group Divisions, Including Total, Fecal *Coliforms* and *E.coli* [16]

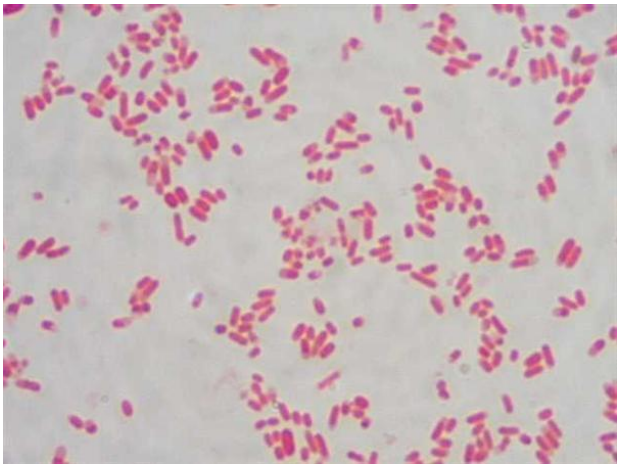

Figure 4 Microscopic View of *E.coli, 10µm scale* [25]

A 1992 study on Puerto Rico and its watersheds argued against using *E.coli* as an indicator, noting that the high rainfall and the abundance of certain types of flora, led to

a higher than recommended *E.coli* amount [25]. This calls into question its validity as a good indicator for tropical waters. We will concede on the abundance of *E.coli* and *Enterococcus* in Puerto Rican water sources. Yet, its prevalence is not the focus of this thesis, and as such is not the main concern and will not prevent us from using it as an indicator. In a more recent study a far more positive outlook on *E.coli* as indicator was given, provided that this is not the only one being used. The study, done in Singapore, examined *E.coli* as well as alternative indicators such as human specific markers (for example *M. smithii*) to assess how each method rendered an estimate of the bacteriological quality of the tropical waters [21]. Notably, the article mentioned that *E.coli* did serve as a good indicator "for predicting pathogens in tropical surface waters". However, it also underscored the importance of using multiple indicators to assist in providing a clearer picture of the quality of the body of water being tested. For example, while *Salmonella* is positively correlated with *E.coli*, certain pathogens like Norovirus are much more accurately detected through the use of *M. smithii*. This leads to the idea that using both traditional and human markers can provide a far more accurate reading of the water sample. There is a greater emphasis on combining methods and integrating other procedures such as dissolved oxygen content and turbidity analysis.

Improving these methods is important, as many locations with little to no purification methods are heavily affected, and are often poorly financed [14]. These locations have difficulty affording and implementing water purification systems, so to provide a widespread method to whole communities is a complicated endeavor. Under the blanket term of household water treatment technologies or HWTT, there are various methods to deal with this situation. Their usage is to eliminate turbidity and pathogens in

water at a small-scale level that is easily mass produced and used. One simple method is to boil the water, as the heat serves to eliminate the pathogens from the water [27][28]. However, its efficiency is debatable and its effect on turbidity is negligible at best. Another well-known method, which is the cornerstone of this proposal, is water filtration.

As a final observation regarding the indicators chosen for the study, we proceeded with the traditional indicators. Thus, rather than an analysis of the water source, this work is an analysis on the efficiency of the filtration methods being used. While there could be an issue with the number of pathogens detected, the nature of the sand filter biolayer requires that any pathogens detected or not, are integrated into the biolayer. As such, their detectability is not what is being examined, but the ability of the filter to manage bacteriological contamination in general. Furthermore, the second stage of the hybrid system is designed to eliminate pathogens with UV light, and relies on Total Organic Carbon (TOC) as its main indicator, providing a secondary source of information. That being said, future projects could add or consider additional indicators to improve the analysis of the filter.

2.2 Filtration, Slow Sand Filtration, Bio Sand Filtration

Filtration is a process by which water is passed through a granular media, wherein any pathogens encounters mechanisms such as sedimentation, interception and flocculation [17][29][30]. Often, sand is used due to its small particle size, which removes turbidity by impeding the flow of minerals and other compounds that cause physical effects on the water [30]. There are two main types of sand filtration: rapid-

sand and slow-sand filtration [29]. For the sake of expediency and to limit the scope of the project, the focus will be on slow sand filtration.

The technique was developed in 1804 and consists of water passing through a sand layer with grains ranging from 0.2 to 0.4 mm [31]. However, not only the physical mechanism demonstrates the usefulness of the filtration method. The biofilters are run in batch mode, and in the case of our project are run over an idle time of 24 hours. As the raw water passes through the sand, a biolayer forms on the top surface of the sand, also known as a Schmutzdecke, represented in Figure 5 [32][33]. This causes the filter to have a biological mechanism, which allows the biodegradation of pathogens like the aforementioned coliforms. The Schmutzdecke, from here on referred to as the biolayer, is caused when the pores in the surface sand clog, allowing the bacteria to grow and interact with one another. Its composition reflects the water that was used to feed the filter, as a high level of protozoa means the biolayer bears similar pathogen levels [34]. The biolayer works by combining several mechanisms such as predation and a lack of resources. The small exposed area and its lack of nutrients cause the amount of bacteria that can survive within the biolayer to remain relatively low [35]. By combining this with the physical mechanism provided by the sand, the amount of pathogens in the effluent produced by the filter is reduced. The easiest to use and least time consuming filter is the intermittent biosand one, which works in a batch system, allowing for leeway when water is introduced into the system, giving the user more control over water [36].

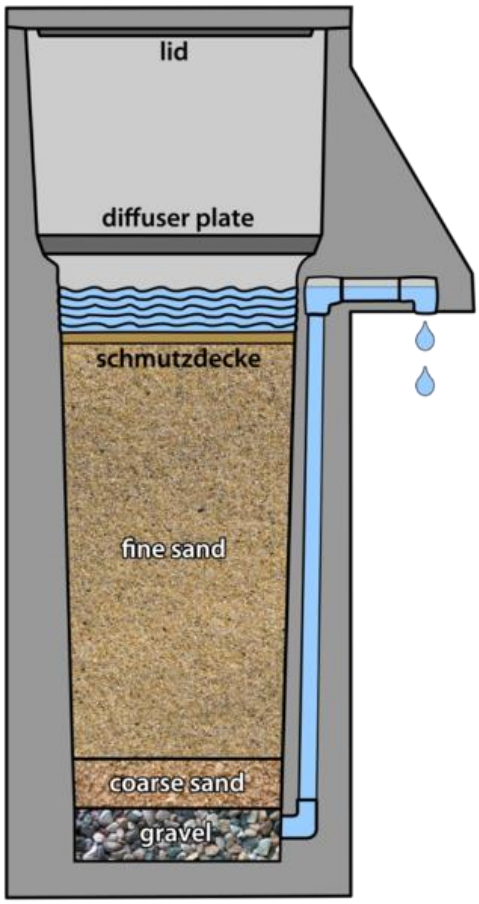

Figure 5 Diagram of a Traditional Biosand Filter [37]

We used the slow sand filter, as mentioned earlier, with a biolayer composed of traditional indicators and whatever pathogens might exist in the water [38][39]. Such biolayer permits the filter to remove pathogens effectively. Since the creek involved in this study is near a residential district, the fecal contamination is very probable, providing us with a hotbed of bacteriological activity. However, filtration is not the only method for improving water quality that was considered in this study. Another approach consisting on the photocatalytic effect of semiconductor compounds was evaluated for the reduction of natural organic matter.

2.3 Solar Disinfection and TiO_2

One method that forms the backbone of the other aspect of this proposal is reduction of pathogens and natural organic matter from water. By storing water in transparent containers, the pathogens in the water are exposed to UV light, which can impede cellular growth and stop the pathogens from growing [40]. However, the constant maintenance of the container itself, as well as the high time of usage to actually impact the water does not make this attractive [27]. Thus, this method needs improvement to become more efficient and expedient. Even more, the system can disinfect pathogens and oxidize organic matter, both chemically and biologically. As mentioned earlier, the interaction between chlorine and organic matter such as humic acid can cause the formation of THM's [41]. By combining the UV exposure with photocatalytic compounds, the better purification method can result. In this project, the method combines UV light with a glass / TiO_2 composite, where the dioxide is a potent photocatalytic compound with low cost and high stability compared to other semiconductors [40]. The benefits of TiO_2 have been proven in studies involving the slurry method, which has shown removal rates of over 90 percent. Removing TiO_2 from treated water is quite a task, hence the dioxide embedding [3][42]. However there are different polymorphs of TiO_2, and the one that allows for photocatalytic excitation is its anatase form. When exposed to UV light, anatase causes an oxidation reaction, which may degrade organic matter that survived or was ignored by other treatment methods. This produces water and carbon dioxide and removes much of the organic matter; as a consequence, THM formation is a non-issue as no reactant with chlorine would be

available, as noted in Figure 6. By selecting this method, which eliminates pathogens and organic carbon through chemical means, and combining it with sand filters, which use biological and physical mechanisms, we can establish a very efficient water purification system.

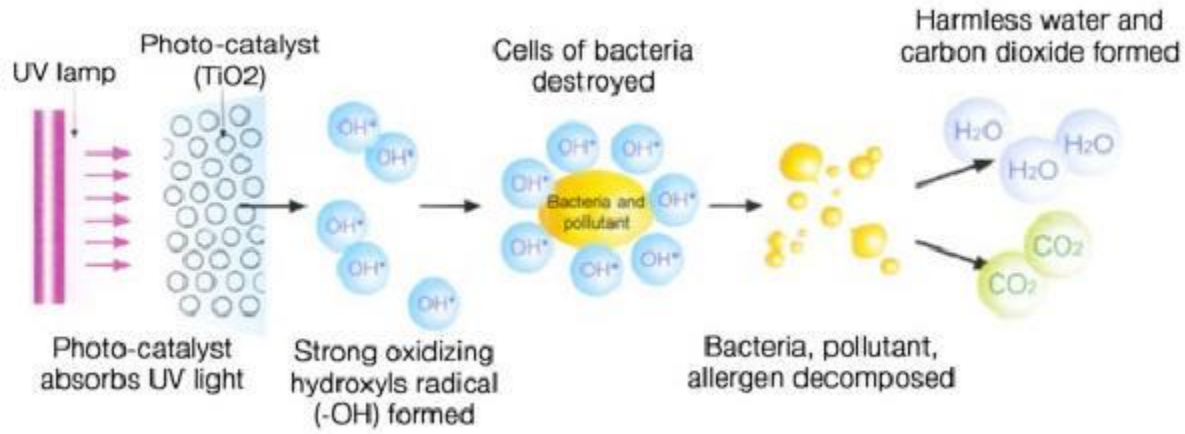

Figure 6 Principle of Photo-Catalytic Degradation [43]

3. Methodology

In order to properly evaluate the hybrid filtration system, it is important to set up each individual system and its components before combining them into one whole. The two systems evaluated hereby are the LSBF and the glass-TiO_2 composite (hereafter referred to as GTC). Both systems have different procedures and methods of evaluation that will be discussed in the following sections.

3.1 Materials and Equipment

The LSBFs are made of PVC pipes with different heights depending on the filter design. Set #1 is composed of three LSBF with a height of 96.52 cm (38 inches) (hereby referred to as standard height), while set #2 is composed of three LSBF at 69.85 cm (27.5 inches) (referred to as Reduced Height). Both filters have the same diameter of 2.86 cm (1.125 inches). To create a head for the water to flow, plastic tubing was used to transport the water. The LSBF are packed with rock, sand with a layer of gravel at the bottom serving as its base. The GTC were fabricated in a prior project [42]. The GTC is a composite made out of crushed recycled glass embedded with TiO_2 nanoparticles, having an average particle size of 32 nm. Alongside both systems there is low range total organic carbon (TOC) vials, spectrometry equipment, and specialized agar for bacteria culturing, which have their own dedicated sections below.

3.2 Lab-Scale Biosand Filters (LSBFs)

The LSBFs are designed to keep a filtration rate of 400 L/h/m^2 or 0.258 L/h/in^2, which is the typical filtration rate on a conventional intermittent biosand filter (IBSF). The filters were designed to receive 200 mL of raw water, which require a surface area of 7.94 cm^2 (i.e. 3.18 cm in diameter) to keep the desired hydraulic loading. This cross sectional area is smaller than the typical area in an actual IBSF in order to provide convenience in the experimental procedure by reducing the water volume needed to feed the filter in a 1:1 pore volume (including the volume of the standing water zone). The filters were built of PVC tube. Two filter sets, comprised of 3 filters per set for a total of six filters, were arranged to have two different heights per set. Filters in the Standard Height Set are 96.52 cm (38 inches) in height and were packed with 54.34 cm (21.4 inches) of sand while filters in the Reduced Height Set will be 69.85 cm (27.5 inches) in height and packed with 27.94 cm (11 inches) of sand (Figure 7). Both filter sets had 10.16 cm (4 inches) of coarse and fine gravel to support the sand. The purpose of having two different heights is to evaluate the filters efficacy by reducing the filtration medium depth. Each filter effluent was handled by a plastic tubing that, when placed at a specific height, provides a standing zone in the filters surface that promotes and keeps the biolayer. The filters were fed from a surface water source (Oro Creek) discussed in section 3.2.1. The filters were operated in batch mode. The water sat within the filter for 24 hours, whereupon a new sample of water was poured into the filter, draining the filter of the previous day's water. Said water was collected in a beaker for further study. The first thirty days was essential in the establishment of the biolayer

on the surface of the sand. The biolayer provides an additional filtration element to the filter, and its usage is essential in the project. The effluent of these filters is to be analyzed for bacteriological and UV spectrophotometry testing, which will be discussed in the following sections.

Figure 7 Side View of the LSBF (Standard Height used for Reference)

3.2.1 Water Collection

The water was collected from Oro Creek, a creek located nearby the Civil Engineering Building (Figure 8). The creek runs through the entire university, and its outward appearance indicates high levels of sediments and contamination, as the water is brown and cloudy. The water was collected every day, with samples from the previous day saved in case of emergencies or need of repeating prior testing. The water

was collected by placing a sterilized beaker into the creek without touching the creek bed so as not to disturb the ground. It was then transferred to a 1 gallon plastic jug, which was then transported immediately for testing and use in the biofilters.

Figure 8 Sampling Point used in the Oro Creek

3.3 Glass Composite Embedded with TiO_2

3.3.1 Preparation of Water Sample

The GTC were used along with water collected from both the creek and the effluent of the LSBF. The water was poured into a small beaker, whereupon a small magnetic bar was placed inside to stir the water. Afterward a metal basket was placed partially within the water (so as to not come in contact with the water) and the GTC is submerged half an inch below the water in the basket.

3.3.2 Setting up Treatability Studies for Organic Matter Degradation

Photoreactor boxes made out of wood were set up. They had holes cut in the top of the box to accommodate UV lamps (UVL-21 Compact UV Lamp, 4 watts) that provided the necessary UV exposure. The box had the entire interior surface lined with aluminum paper to make certain that the GTC is exposed to UV for the activation of the TiO_2. Inside the box a magnetic stirrer along with the magnet bar in the sample (described in Section 3.3.1) stirred the water causing it to pass around and through the GTC. The sample from 3.3.1 was placed on the stirrer and the stirring speed was turned down. The box was then sealed and the lamps, turned on. The box was left closed for eight hours, based on prior testing [42]. After 8 hours, the water was then collected in amber vials to protect it from exposure to external UV light sources and analyzed for total organic carbon content.

3.4 Bacteriological Analysis

To quantify pathogen concentration present in the water, we used *Escherichia coli* and *Enterococcus* . For the *E. coli* quantification, the EPA Method 1604 with MI medium was performed, while the *Enterococcus* concentration was quantified by the EPA Method 1600 with Enterococcus Indoxyl-β-D-Glucoside Agar (mEI). Both methods of quantification used the membrane filtration technique. The water collected from the creek and the LSBF effluent was diluted in a 10:90 dilution for use in filtration. This method was also applied to the GTC effluent in section 4.3. The water was then poured into the filtration rig and drained through a 0.45 µm membrane filter. Then said

membranes were removed from the rig and placed in petri dishes prepared with agar, with each agar being made for different bacteria, as discussed in the following subsection.

3.4.1 Agar Preparation and Usage

The MI agar allowed examining the *E.coli*, while *Enterococcus* required MeI agar. Both agars have nearly identical preparation methods, relying on correct ratios of water and agar, and the use of an autoclave to heat the mix. The main difference is the component added after heating: For MI the reagent was cefsulodin, and for MeI, nalxidic acid. Both served as stabilizing buffer agents that are usually added upon usage as the agar is being poured in the petri dishes.

3.4.2 Agar Storage and Bacteria Counting

The petri dishes were stored in incubators, which are designed for different types of agar. One incubator is at 37ºC, made for MI agar, while the other, at 42ºC, is perfect for MeI agar. After 24 hours, we evaluated the petri dishes. Due to the 10:90 ratios, the number of colonies counted had to be multiplied by ten to acquire the true value of the bacteria in the water. This entire procedure must be done in duplicate to avoid any false readings.

3.5 Total Organic Carbon Analysis

The natural organic matter levels in any water sample were quantified by means of total organic carbon (TOC) via a UV/Vis spectrometry. This method measures the sample absorbance as a function of a specific wavelength. To properly correlate the absorbance with the organic matter content, a calibration curve was first constructed by plotting absorbance readings (at λ=254 nm) of samples with known TOC concentrations against their TOC concentrations. The samples were first tested using the HACH vial testing method (low range).

3.6 Hybrid System Testing

Once the TOC comparison graph was completed, we combined the LSBF and GTC methods in sections 3.2 and 3.3 to construct the hybrid system. To test the effectiveness of the hybrid multimedia-filter prototype (HMP) for pathogens and organic matter reduction, a series of processes were developed and tested, as indicated in Figure 9.

The main method consisted of collecting raw water samples from Oro Creek, which were then passed through an LSBF. To also test the effectiveness of the filter height alongside the HMP, two filters were used, a 96.52 cm (38 inches) one and a 69.85 cm (27.5 inches). Once the raw water was filtered through one of the LSBF, the effluent was then placed in contact with the GTC suspended in a beaker, to be placed inside a closed-box photoreactor. Under UV light, photoreaction occurred as the water was stirred for 8 hours.

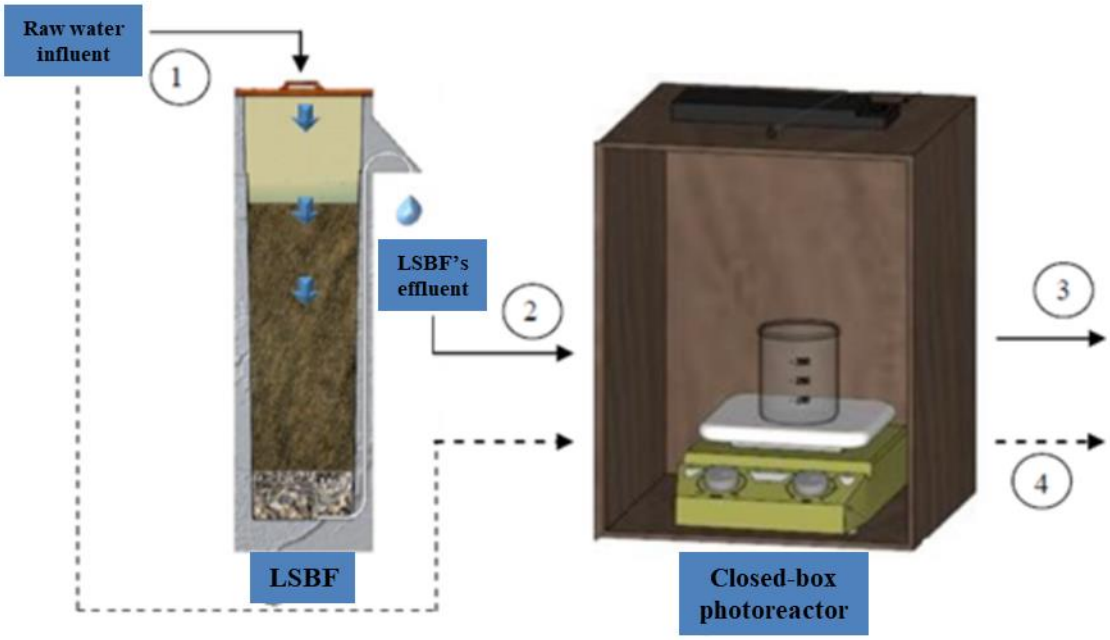

Figure 9 HMP Array for Treatability Studies and their Sampling Points as Denoted by the Numbered Sections

Other tests included relates to the type of water used and the type of test. These correspond to the numbered points highlighted in Figure 9. Point 1 corresponded to raw water while Point 2 refers to the LSBF effluent, which is then used as influent for the photoreactor process. Point 3 is the effluent water treated in the photoreactor, and Point 4 is an effluent from the photoreactor pertaining to raw water treated only with the photoreactor (bypassing the LSBF). However, in order to observe the effects as accurately as possible, four control specimens were used. Control 1 refers to raw water set aside for 24 hours. Control 2 consists of water taken from the LSBF effluent and set aside for 8 hours. In the case of Control 2, because there are two LSBF used, the 96.52

cm (38 inch) filter is denoted 2a and the 69.85 cm (27.5 inch) filter is denoted 2b. Control 3 refers to raw water placed in contact with the photoreactor, but with no UV light. Control 4 refers to LSBF effluent in contact with the photoreactor with no UV light. This will be for 8 hours.

4. Results and Discussion

4.1 Oro Creek Bacteriological Profile

The first step was to get a biological picture of the Oro Creek, in order to understand the pathogen load to which the filters would be subjected during the experiment. For a period of two months in 2016, water was collected at 3 different time periods (9am, 1pm, and 4pm) in order to examine how weather and temperature affected the biological quality of the water and when would be the appropriate time to identify environmental conditions for consistent bacteriological quality (see Appendix B). The amount of *E.coli* and *Enterococci* in each water sample was quantified as seen in Table 6. Each sample was taken once a day for two months to judge the best time. While the resultant analysis did not reveal a trend for the pathogen content in the water, we ultimately decided to take our samples at 9 am in the morning, partially for convenience, but also because we observed higher quantities of debris in the water in the mornings. This debris would theoretically decompose into humic acid, which would be necessary for the hybrid system testing.

Table 6 Oro Creek Bacteriological Profile for June and July, 2016 in Terms of *E.coli* and *Enterococci* Population Averages

Time	E.coli (CFU/100ml) effluent	Enterococci (CFU/100ml) effluent
9am	530	1325
1pm	550	1470
4pm	720	1290

4.2 *E. coli* and *Enterococci* Reduction within the LSBF: Standard Height vs Reduced Height

One aspect of the project was to test the efficiency of a reduced sand bed depth. Two LSBF with different sand bed depths (53.34 cm vs 27.94 cm) were evaluated for pathogens removal. Each evaluation was done in triplicate to verify consistency and reproducibility. Hence, the study was carried out in two filter sets, each set consisting of 3 filters, for a total of 6 filters. Both sets were started at the same time and ran for 30 days in order to form the biolayer. The results of the first 30 days and ensuing two months are presented in Table 7, Figure 10 and Figure 11 (for E.coli), Figure 12 and Figure 13 (for Enterococcus). The table and the figures indicated a marked improvement in the filters efficiency. The first day showed minimal bacteriological reduction, compared to the near complete removal at the 30-day mark. With such a marked improvement, we can assume that the reduction can be attributed to the formation of the biolayer. After 30 days, the biolayer had formed and was working at maximum capacity. At this point, the actual experiment could begin, as biolayer was the most time consuming aspect of the project due to the establishment period.

Table 7 E.coli Quantification over the First 30 Days for Both Filter Sets.

	E. coli population (CFU/100 ml)		
Time (day)	Influent	Reduced LSBF effluent	Standard LSBF effluent
1	460	700	340
2	180	140	100
30	1300	1300	135

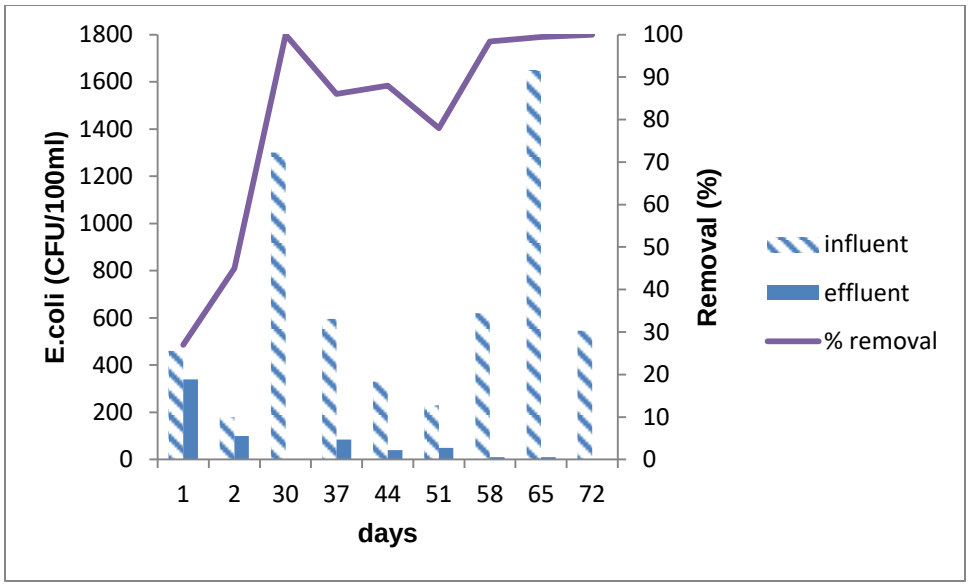

Figure 10 Standard LSBF Influent and Effluent *E. coli* Levels for the First Two Months of Operation

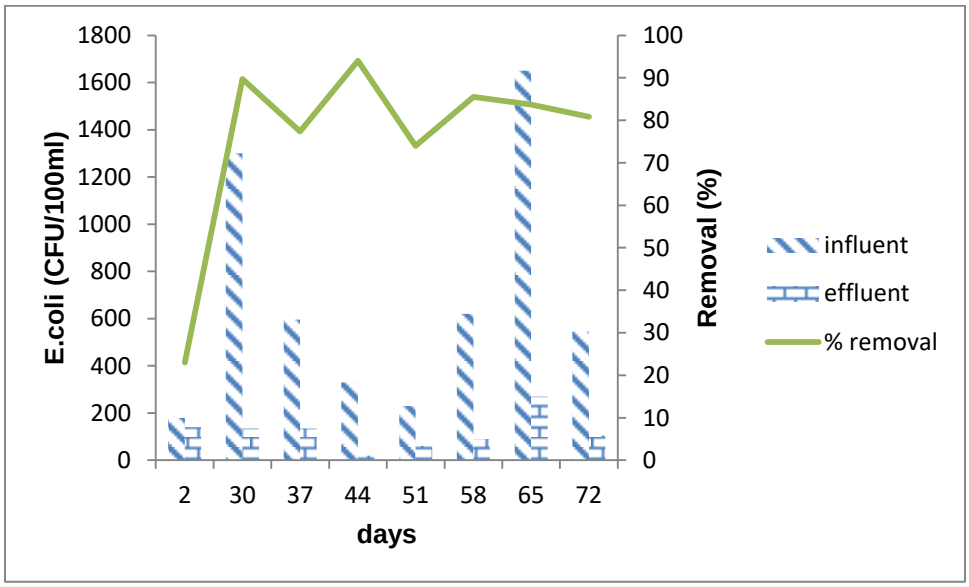

Figure 11 Reduced LSBF Influent and Effluent *E. coli* Levels for the First Two Months of Operation

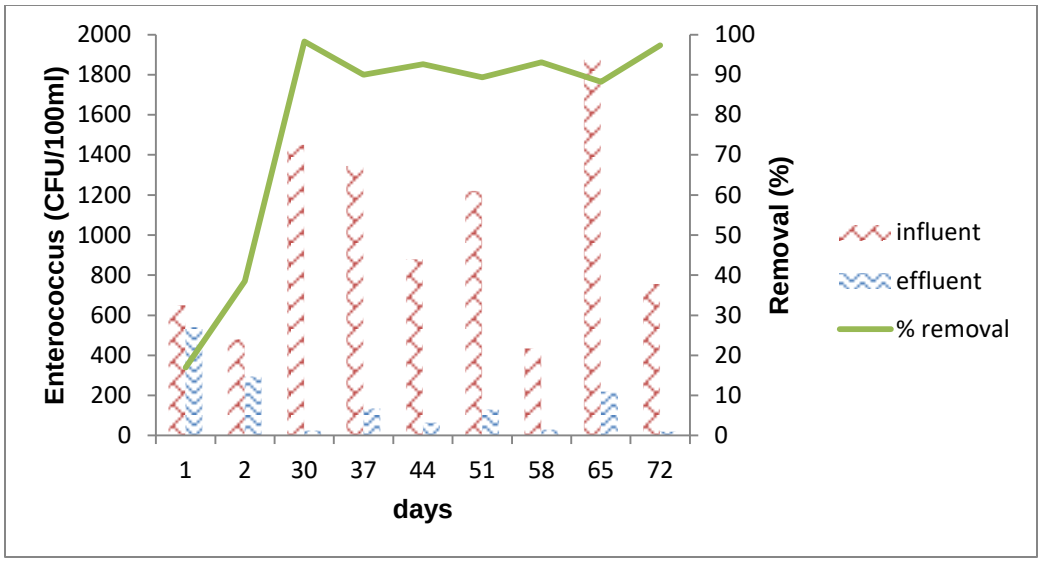

Figure 12 Standard LSBF Influent and Effluent Enterococcus Levels for the First Two Months of Operation

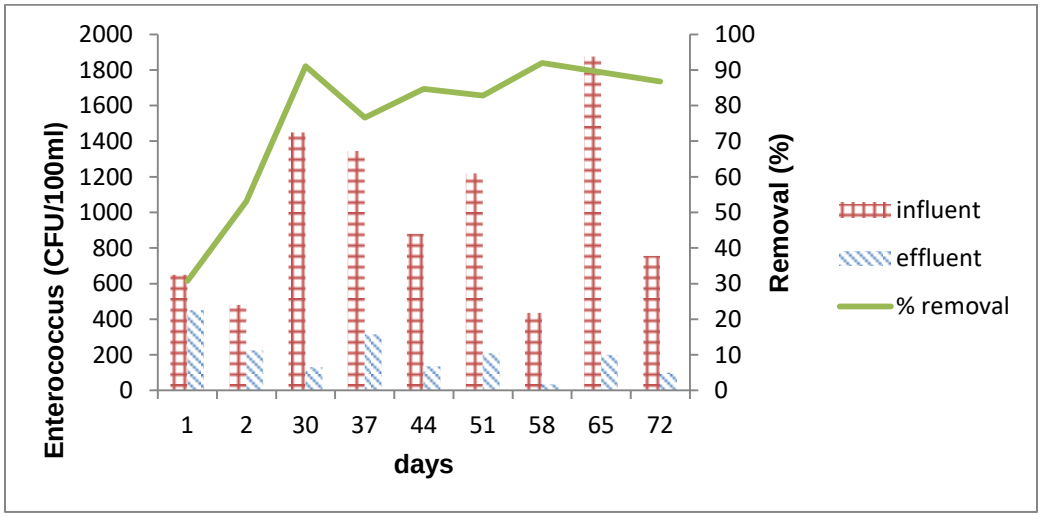

Figure 13 Reduced LSBF Influent and Effluent Enterococcus Levels for the First Two Months of Operation

Once the biolayer had established, we continued the operation of the filters feeding a new batch of water every 24 hour. The actual testing was done weekly, with membrane filtration being used to prepare each sample for analysis and bacteria cultivation. Figures 14 and 15 show random *E.coli* levels in the filter's influent and effluent after the

first 6 weeks continuous operation. Figure 16 and 17 do the same for *Enterococci*. All the figures show the removal efficiency when compared against the *E. coli* and *Enterococcus* levels in the raw water (influent). After the biolayer had been established, *E.coli* and *Enterococcus* removal rates remained for the most part in the 90-100% removal range. This is notable, as *Enterococcus* levels are substantially higher than *E. coli* in the influent in most of our tests, and the reduction levels still remain at a 95% range. All the data pertaining to Figures 11-18 can be found in Appendix D.

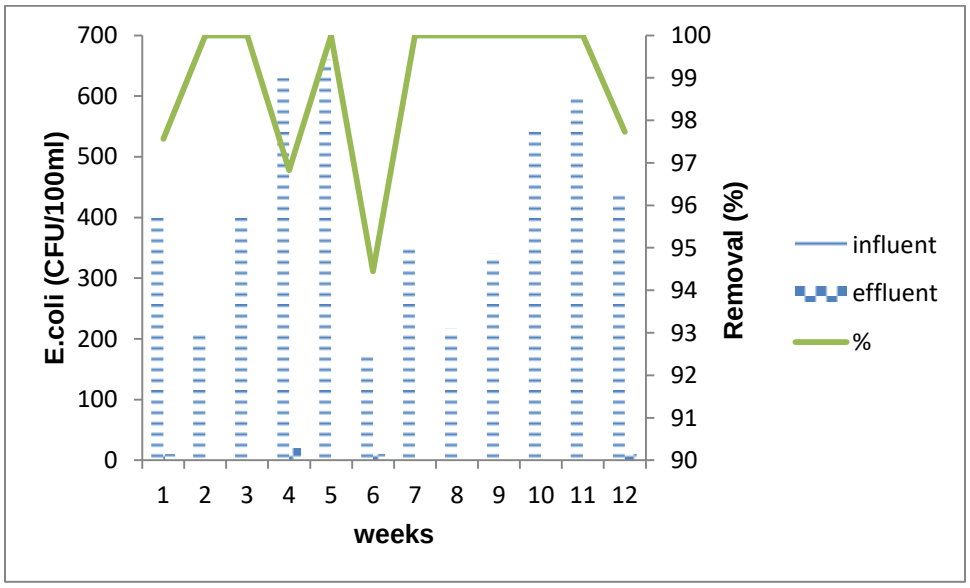

Figure 14 *E. coli* Levels in the Filter's Influent and Effluent and Percent Reduction for the Standard Height LSBF

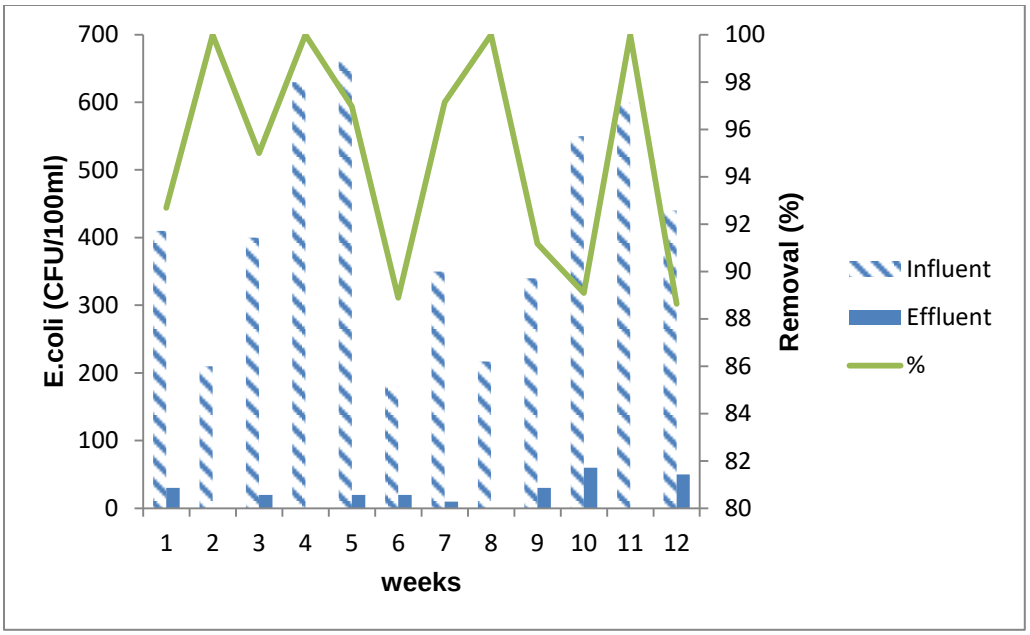

Figure 15 *E. coli* Levels in the Filter's Influent and Effluent and Percent Reduction for the Reduced LSBF

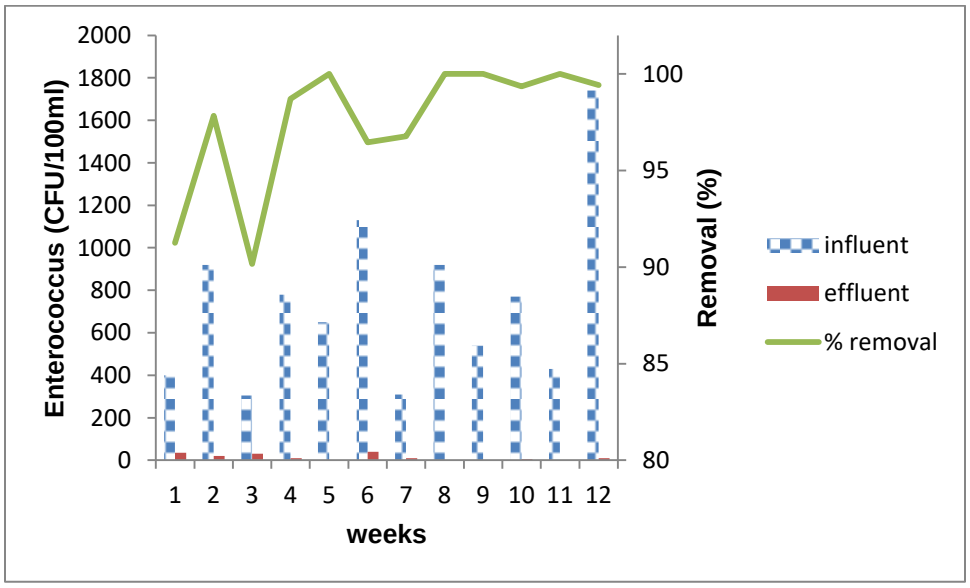

Figure 16 *Enterococcus* Levels in the Filter's Influent and Effluent and Percent Reduction for the Standard LSBF

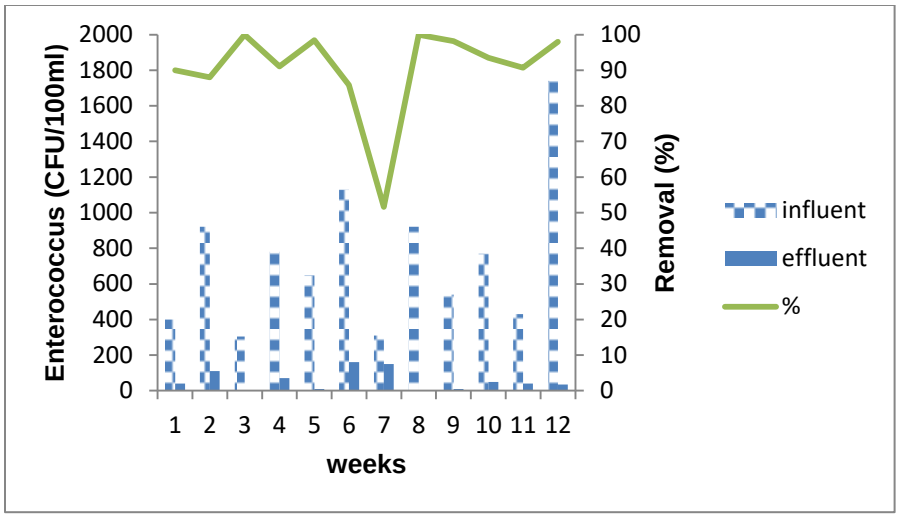

Figure 17 *Enterococcus* Levels in the Filter's Influent and Effluent for the Reduced LSBF

A statistical analysis allowed comparing the performance of both filters (i.e. standard vs. reduced). A t-test with a 95 confidence interval proved that no significant difference existed between the filters removal rate. Table 8 shows the results from this comparison. The means and variances between the filters are nearly identical, with the standard height being somewhat smaller, but not to an affecting degree. The null hypothesis in this case is defined as no difference between the filters efficiency.

Table 8 t-test Data for Comparing the Standard and Reduced LSBF Performance on E. coli and Enterococcus Removal

	Reduced	***Standard***
Mean	5	4.545455
Variance	55	47.27273
Observations	11	11
Pooled Variance	51.13636	
Hypothesized Mean Difference	0	
Df	20	
t Stat	0.149071	
P(T≤t) one-tail	0.441495	
t Critical one-tail	1.724718	
P(T≤t) two-tails	0.88299	
t Critical two-tails	2.085963	

The differences between the filters variances are fairly small, but the real proof is in the p-value which, due to being less than the t value, does not disprove the null hypothesis. This allows saying with certainty, that there is not significant difference between either filter. To further hammer this point home, an ANOVA test was performed. Data is presented in Table 9.

We ran an ANOVA test against both control and the reduced and standard heights. Any difference in there mean would disprove the null hypothesis. Based on the ANOVA test we reject the null hypothesis (fcrit<F, p-values<α). The control has far more bacteria than the reduced and standard heights, which were proven earlier to have no statistical significant differences between them. Thus, it is safe to say that the filters have a positive removal effect on the pathogen levels in water, and that the height of the filter does not pose a negative impact on the efficiency.

Table 9 ANOVA Test Between Control Water, Reduced and Standard LSBF.

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Control	11	6780	616.36	21105.45
Reduced	11	55	5	55
Standard	11	50	4.55	47.27

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2742986	2	1371493	194.01	6.9×10^{-18}	3.32
Within Groups	212077.3	30	7069.24			
Total	2955064	32				

Bio filters must receive a slight “refresher” once they are run for several months, and ours were no exception. Naturally, we did extra tests to verify if the filters had lost their efficiency, and found that they maintained their bacteria removal quality. The filter ran for almost two years, and in all that time the reduced filter kept up with the standard filters in the removal of both pathogen indicators.

This reduction rate proves that in this lab scale experiment, the reduced height filter performed at the same level as the standard height filter. For this stage of the experiment, we can conclude that the reduced height is as efficient as its standard height competitor, and theoretically under realistic parameters, it should provide the same pathogen removal at lower costs. For the hybrid system, we used a smaller number of filters, i.e. from 3 per height to one per height. All the filters operated at the same level, with only slight differences spread out over large stretches of time. For the final hybrid system test we chose the reduced height filter in order to provide the optimal version of our hybrid system.

4.3 TOC Linear Correlation

One major issue in the testing of our hybrid system was the quantification of humic acid. This difficulty led us to quantify TOC instead, as this is much easier to analyze. However, while it is easier, the method we have, Low Range TOC Vials, is far too costly to operate for the amount we needed. A cheaper method, UV spectrophotometry, is easy to use and less expensive than the vials, but needs conversion in order to acquire the correct value of TOC. This led us to linearly correlate the TOC vial results to our UV spectrophotometry results, in order to make it easier to analyze our results. The results

of this analysis can be found in Figure 18. By comparing the spectrophotometer results to the TOC vials, we were able to acquire a linear equation (a=157.58*b) to calculate the estimated TOC content in our samples without using more costly methods. The variable “a” is the TOC content and the variable “b” is the absorbance detected by the spectrophotometer. Due to the highly variable conditions found in the tested water, the correlation coefficient is high enough (R^2 = 0.762), as it provides a good guideline for our investigation. We used it for the remainder of our experiment.

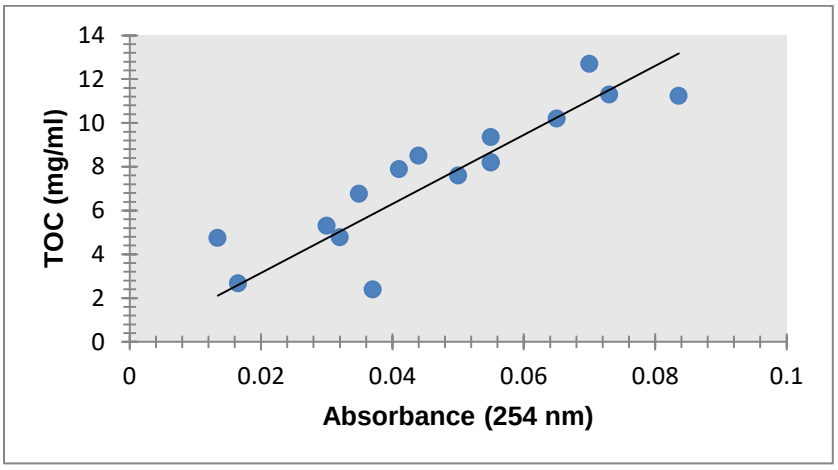

Figure 18 Linear Correlation between TOC Vials and UV Spectrophotometry

4.4 Nanocomposite Substrate Analysis

The final element of the hybrid system that needed to be tested was the nanocomposite, i.e. glass-TiO_2 composite or GTC. As this technology is fairly new compared to the bio filters, the water exposure was not established. For our project, the nanocomposite was made from recycled glass that had been sintered with embedded titanium dioxide particles [3]. These disc-shaped specimens were placed in metal baskets. Said metal baskets were submerged in the sample water, where they were

exposed to UV light for 8 hours. These also served as a good test of our linear regression equation in Figure 18. However, we were also curious as to whether or not the UV light was actually what was causing the TOC reduction. As such, we ran tests involving the creek water being in contact with the nanocomposite without the UV light exposure (dark conditions). The reason for this is that potential contaminant could adhere to the substrate itself, which would make identifying the hybrid systems effectiveness more difficult. The results of the nanocomposites with and without UV light can be seen in Table 10. However, we also tested the pathogen removal of the substrates, as illustrated by Table 10.

Table 10. TOC, E. coli and Enterococcus Levels in Water Samples Being Treated with the GTC under UV Light and Dark Conditions

Water sample	**TOC level**	**E.coli (CFU/100ml)**	**Enterococcus (CFU/100ml)**
Raw water	7.53444	750	1400
Nanocomposite +UV light	3.331	635	1125
Nanocomposite (no UV light)	6.747	720	1380

The results show significant difference when UV light is used in terms of TOC reduction (around 45%). However, the pathogen removal is fairly similar in this case, although there is a slightly more significant decrease within the UV light exposed group. This difference between parameters is broken down in Table 11.

Table 11. t-test between UV Light and no UV Light Exposure with the GTC Treatability Study

	UV light	***No UV light***
Mean	3.3	6.32
Variance	0.055	1.996
Observations	6	6
Pooled Variance	1.03	
Hypothesized Mean Difference	0	
df	10	
t Stat	-5.16	
P(T<=t) one-tail	0.000212	
t Critical one-tail	1.812461	
P(T<=t) two-tail	0.000424	
t Critical two-tail	2.228139	

From the outset, we see a large variance in efficiency when UV light is absent. This can be attributed to potential porosity in the substrate being used, or adhesion potential of the glass varying per experiment run. In the removal rate of TOC, the t-test proves a significant difference between the use of UV light and the lack of it,.

While we used a linear relationship, the nature of the spectrophotometry results allowed acquiring a fair understanding of how the TOC reduction occurs at each treatment level, as indicated in Figure 8. The nanocomposite discs were not completely identical, which could cause variations in the results. As such, in order to avoid a large variability in the results, the available discs were tested individually to find the ones that had the highest removal rates (Table 12). Furthermore, the adhesion of the titanium dioxide to the glass is not perfect. The magnetic spinning caused by the stir plate produced what appeared to be small debris in the water. However, this was temporary and after several uses, no more debris was visible or detectable in the analysis. We can attribute this to excess material that was not well-attached to the glass. The 8-hour time period was decided after a series of tests at various periods ranging from 1-24 hours in

order to find the optimal range for the maximum amount of TOC removal (Figure 19). This testing period was shorter than the filter one, due to the simplicity of running the glass nanocomposite method and ease of use. As such, after running the finalized method, we proceeded to the hybrid method, which as established previously, combines both methods of removal into one system.

The amount of nanocomposite substrates ready for major use was decided by a percentage removal higher than 50%. Note that this is the bare minimum acceptable number, and this removal rate is not constant, but the average of several runs. Four main GTC samples were chosen due to the fact that maximum number of photo reactive containers available was four. The remaining nanocomposites were kept as backups in case of damage or disrepair.

Table 12 GTC TOC Removal Efficiency Comparison

Nanocomposite Substrate	**TOC removal rate**
Disc-1A	50%
Disc-1b	45%
Disc-1c	58%
Disc-1d	57%
Disc-1e	60%
Disc-1f	40%
Disc-1f	30%
Disc-1g	55%
Disc-1h	38%

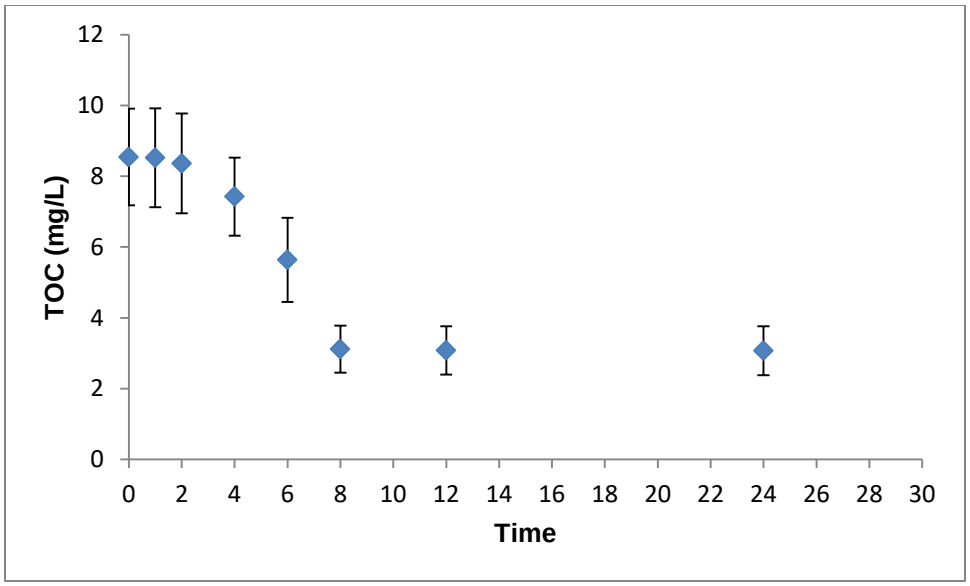

Figure 19 Residual TOC levels After Exposure to the GTC under UV light (n=4)

The data shown in Figure 19 refer to four different samples run over 24 hours. The trend is one that is common within the nanocomposite removal rate. In the initial hours, little or no change in TOC level occurs within the water sample, as the contact time is too limited to have any meaningful effect on the TOC content in the water. A decline does begin to occur at the four-hour mark, which continues to get smaller and smaller until the 8-hour mark, where it slows down and stabilizes. This 50-60% removal rate is one that is present in practically every test involving the GTC, including the hybrid system, which improves upon this rate, in a significant way. Figure 20 shows the decline in terms of absorbance for a 24-hour run. There is a decrease in the TOC of the system as every treatment procedure gets added. The hybrid system nearly reaches 80% reduction, but it never fully eliminates all the TOC in the system.

The pathogen removal rate of the nanocomposite was from 20-30%, but the TOC reduction rate is over 60%. The pathogen removal rate can be attributed to the UV light

itself rather than the GTC, but the TOC removal is well within the expected parameters. The experiment was conducted for longer periods of time to see if this would improve the removal rate, but after 8 hours, the efficiency of the nanocomposite did not improve in any meaningful way. As such, the minimum time required for the hybrid system to work at full efficiency is 33 hours (24 for the bio filter, 8 for the nanocomposite, and 1 for the collection of the effluent).

4.5 Hybrid System

The hybrid system consists of combining the prior two purification systems, transferring the effluent from the LSBF to the photoreactor box housing the GTC and UV lights. As mentioned, the approximate detention time for the whole process is around 33 hours, during which the water is passed through the bio filter, which upon exiting it, is collected and placed in contact with the GTC, which is then exposed to UV light for 8 hours. Table 13 presents the average data gathered from the whole process for 6 runs.

Table 13. Enterococcus, E. coli and TOC Residual Levels in Water Samples Treated in the Hybrid System Based on an Average Collected from Six Runs

Sample	Enterococcus (CFU/100ml)	E.coli (CFU/100ml)	TOC (mg/l)
Point 1	880	630	8.53
Point 2a (reduced height)	0	15	4.71
Point 3a (reduced height)	15	10	2.9
Point 2b (standard height)	0	0	3.06
Point 3b (standard height)	10	0	2.15
Control 1	870	580	9.32
Control 2	0	10	3.04
Control 3	650	430	6.43
Control 4	0	20	3.25

Having confirmed that both filter heights behaved similarly, we opted to report only the reduced height in order to summarize and speed up the performance of the HMP. We performed statistical tests, comparing each component against the hybrid system, as well as a comparison to the control with all the methods as a final test. The results of the statistical analysis are tabulated in Tables 14, 15 and 16. Alongside these tests, Figure 20 shows the percentage reduction of TOC across each method of treatment including the controls. The maximum reduction rate for TOC was 75% with the hybrid system, whereas the GTC yielded a reduction rate from 50 to 64%, which is deemed significant. As such the GTC alone is a valid option in reducing TOC contamination in a water sample.

Table 14. Data Obtained for t-test Analysis between the GTC and the Hybrid System (Filter + GTC) (Reduced)

	nanocomposite	**hybrid**
Mean	3.297983	2.6724
Variance	0.055328	0.106699
Observations	6	6
Pooled Variance	0.081013	
Hypothesized Mean Difference	0	
df	10	
t Stat	3.806866	
P(T<=t) one-tail	0.001723	
t Critical one-tail	1.812461	
P(T<=t) two-tail	0.003447	
t Critical two-tail	2.228139	

Table 15. t-test between Reduced Depth and Hybrid System (Reduced)

	Reduced	***hybrid***
Mean	4.2447	2.6724
Variance	0.483266	0.106699
Observations	6	6
Pooled Variance	0.294982	
Hypothesized Mean Difference	0	
df	10	
t Stat	5.014157	
P(T<=t) one-tail	0.000263	
t Critical one-tail	1.812461	
P(T<=t) two-tail	0.000526	
t Critical two-tail	2.228139	

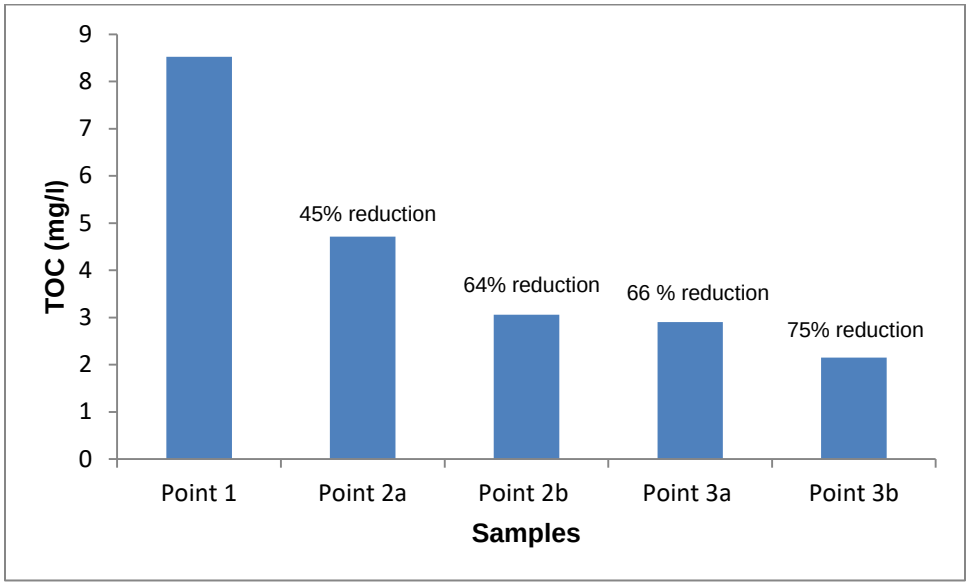

Figure 20 TOC Removal Percentage Comparison

The statistical tests both showed a significant difference between each individual method (filter and nanocomposite) and the hybrid system. The hybrid system in each individual test showed a significant improvement in the TOC removal from the spate components, indicating how the combination of both methods results in a system that can have the best impact on both pathogen and TOC removal. Table 13 shows a complete eradication of bacterial contamination in the water taken from the creek once

exposed to the hybrid system. However, to remove all doubt, one last ANOVA test was performed to prove that there is a significant difference between all methods compared to the raw water taken from the creek, using TOC as the testing parameter.

Table 16 ANOVA Test between Control, Reduced Depth, Nanocomposite and Hybrid Systems

Null: $\mu_{control}=\mu_{reduced}=\mu_{nano=}\mu_{hybrid}$

Alternate: $\mu_{control\neq}\mu_{reduced}\neq\mu_{nano=}\mu_{hybrid}$

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Control	6	46.39	7.73	2.45
Reduced	6	25.46	4.24	0.48
Nanocomposite	6	19.78	3.29	0.05
Hybrid	6	16.03	2.67	0.10

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	91.78329	3	30.59443	39.49745	$1.36x10^{-8}$	3.098391
Within Groups	15.49185	20	0.774592			
Total	107.2751	23				

Based on this, we reject the null hypothesis (fcrit<F, p-values<α). This tells us that there is a significant difference between the TOC levels of each method, and due to the prior tests, we already know that the hybrid system is significantly superior to its individual components, and this test proves that it is the superior method in TOC removal. Table 16 shows that the hybrid system is nearly completely equal in pathogen removal to the

reduced depth. Any small bacteria colonies that are counted can be attributed to human error during the cultivation method or can be attributed as an outlier. As such, based on data and the tests performed, one can state that the hybrid system is the overall superior method for the removal of both TOC and pathogens. While the filter on its own has similar pathogenic removal rates, its TOC removal is rather inadequate. The reverse applies to the nanocomposite substrate, as while it can remove TOC nearly as good as the hybrid, its pathogen removal is almost nil. Ultimately, the hybrid system has value as a disinfecting method for water treatment and further testing in both lab and live scale environments is needed.

5. Conclusions

The formation of Trihalomethanes is a serious predicament that affects any community that uses traditional disinfection techniques. To counteract this, while also providing additional disinfection methods, a hybrid system was developed to eliminate both pathogens and total organic carbon. The system is a compound of a slow sand bio filter and a TiO_2 nanocomposite. Both were tested individually and then as a combined system.

The bio filters were tested for the effectiveness at reduced heights and performed very well. There was no statistical difference between the effectiveness of the filters regardless their standard or reduced height under an idle time of 24 hours. Overall both filter sets showed pathogen removal above 95%, with a TOC removal between 50-60%. The benefits of this become obvious when considering the real world applications. By reducing the filter depth but not the filtration rate, the cost of construction in a real world scenario decreases substantially, making such methods far more accessible to communities that may not be able to afford them.

The GTC performed very well at removing TOC, reaching levels of 65%, while also showing great resilience in being used multiple times. Its pathogen removal capabilities were not nearly as absolute as the filters but did have an impact. Furthermore, when tested on its effectiveness without UV light vs UV light, there was a slight decrease in TOC without UV light, however this was attributed to the adsorption properties of the GTC. When combined as a hybrid system, the pathogen removal rate neared 99%, with both reduced and standard matching each other's performance. The TOC removal increased further leading nigh 75% removal rate.

A complete eradication of both bacteria and TOC with only 2 methods is unlikely (and impossible, as TOC measurements encompass all organic carbon material), but considering the ease of construction and maintenance, one can safely state that the hybrid system does have merit and deserves to be tested in the field, with standards beyond lab scale specifications.

6. Follow up Work

Additional research following this work may include:

- Study the height reduction of the bio filters in real life conditions.
- Test the GTC's in real life situations and improve the production process.
- Test the hybrid system in a large-scale design to verify its efficiency in a community environment.

7. Recommendations

E.coli, *Enterococci*, and TOC are extremely common contaminants in water, and any method that can reduce them is a method worth investigating. Since nearly all raw water treatment plants use chlorine as its main disinfectant, any means of reducing the possibility of THM formation is in need of research, and the hybrid system developed provides one such method.

The reduction in sand bed depth (i.e. filter height) showed significantly similar results to standard heights when done at an idle time of 24 hours, reducing the need for larger scale constructions. The test of the GTC's showed significant reduction in TOC levels, however it can be further improved. For instance, the method of creating the GTC can be refined, and the hours of exposure can be fine-tuned. Additionally, all the GTC used were relatively small constructs and were not tested in a larger scale, so creating a community scale version of the GTC would not only prove its effectiveness in treating GTC it would also show its viability in providing for communities lacking a water treatment plant.

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Appendix A. Alternative Water Source Analysis

While our primary water source was the Oro Creek, we did in fact expose the filters briefly to alternative water sources to verify the effectiveness of the filters when exposed to other water sources. The ones we tested were well water, bottled water and tap water. Due to the nature of the source, one would assume them to be free of all pathogenic contamination. The individual analysis revealed bacterial growth, however in the case of the bottled water, the contamination could be attributed to contamination during testing (Table 18). The well was a local well within the Civil Engineering department, and while the well water looked clean, its tubing was maintained out in the open, providing a breeding ground for bacteria (Table 17).

Table 17 Pathogenic Analysis of Well Water in Regards to E.coli and Enterococcus

sample	Well CFU/100ml	Standard CFU/100ml	Reduced CFU/100ml
E.coli Sample 1	130	0	0
E.coli Sample 2	90	10	0
Enterococcus Sample 1	220	25	20
Enterococcus Sample 2	375	10	0

Table 18 Pathogenic Analysis of Bottled Water in Regards to E.coli and Enterococcus

sample	Bottled CFU/100ml	Standard CFU/100ml	Reduced CFU/100ml
E.coli Sample 1	10	0	0
E.coli Sample 2	0	0	0
Enterococcus Sample 1	20	5	0
Enterococcus Sample 2	15	0	0

Table 19 Pathogenic Analysis of Tap Water in Regards to E.coli and Enterococcus

sample	Tap CFU/100ml	Standard CFU/100ml	Reduced CFU/100ml
E.coli Sample 1	30	0	15
E.coli Sample 2	15	0	0
Enterococcus Sample 1	20	5	0
Enterococcus Sample 2	55	0	0

The filters continued operating within the previously established parameters, and had above 90% removal rates. That being said, the study did show how even location deemed “clean” might still have contamination due to human error, location or due other issues, such the cultivation the bacteria itself. It also gives greater appreciation to the disinfection techniques already in place, especially when compared to the results of an out in the open creek.

Appendix B. Full Week Analysis of TOC and Pathogens in Creek Water

In order to understand how weather impacts the pathogenic and toc content of raw water, two full week creek analysis were performed. Each day, water samples were tested for both bacterial and TOC content, with collection periods coinciding with periods of high rainfall, and a period with a severe lack of. The results of the first week detailed in Table 20, show a high volume of bacteria. Since the location is near urbanization, the high rainfall may bring additional contaminants that normally don't reach during more normal periods. The rain also leaves behind high humidity, which also impacts the growth of not only bacteria but also larger organisms such as parasites. The Dry and Hot weather (Table 20) is less straightforward, as the highly hot weather, not humid, just hot, does not seem to be a positive influence on the bacteria's growth. However its content does not stray away too far from regular samples. Notably, the creek bed is extremely low during high heat/low rain periods, and a lot of debris is acquired while sampling, even in areas that are deeper than others. Ultimately, while the creek analysis did not provide a new perspective on the creek, the TOC results proved invaluable in the establishing of our linear regression graph and the equation produced by it.

Table 20 Pathogenic Analysis of Raw Water in Regards to E.coli and Enterococcus

Weather	E.coli	Enterococcus	TOC
Heavy rain	865	1220	6.54
Dry and Hot	770	1450	9.75
Regular Sample	745	900	7.21

Appendix C. Filter Design Parameters

As established prior, the filtration rate for a biofilter is 400 L/hr/m^2. However additional data was required for the design. Initially, the area of an actual intermittent biosand filter was calculated (A=10in x 10in= 100in^2) as 100 in^2 with a known volume of 20 L. Using this data and the relation Q=FR x A, Q was found to be 25.8 L/hr. This value was then used to derive the filtration time to be 46.51 minutes. These pieces of data can be used to calculate the area of the lab scale version through the relationship V=FR x A x t. The complete design parameters can be found below in Tables 21 and 22:

Table 21 Design Parameter for Standard Height Biofilter

Design Parameter	Value
Filtration Rate	400 L/hr/m^2
Volume of water	200 ml
Flow rate	258 ml/hr
Filtration time	46.51 min
Area of filter	16.54 cm^2
Diameter of filter	2.86 cm
Gravel Height	10 cm
Sand Height	54.3 cm
Empty Space Height	31.19 cm
Total Height	96.52 cm
Residence Time	24 hr

Table 22 Design Parameters for Reduced Height Biofilters

Design Parameter	Value
Filtration Rate	400 L/hr/m^2
Volume of water	200 ml
Flow rate	258 ml/hr
Filtration time	46.51 min
Area of filter	16.54 cm^2
Diameter of filter	2.86 cm
Gravel Height	10 cm
Sand Height	27.94 cm
Empty Space Height	31.19 cm
Total Height	69.85 cm
Residence Time	24 hr

Appendix D. Raw Data for Filter Experiments

Table 23 Data for Figure 11

E. coli	Influent CFU/100ml	Effluent CFU/100ml	% removal
1	460	340	27
2	180	100	45
30	1300	0	100
37	595	85	86
44	330	40	88
51	230	50	78
58	620	10	98.4
65	1650	10	99.4
72	545	0	100

Table 24 Data for Figure 12

E. coli	Influent CFU/100ml	Effluent CFU/100ml	% removal
2	460	140	23
30	1300	135	89.7
37	595	135	77.4
44	330	20	94
51	230	60	74
58	620	90	85.5
65	1650	270	83.7
72	545	105	80.8

Table 25 Data for Figure 13

Enterococcus	Influent CFU/100ml	Effluent CFU/100ml	% removal
1	650	540	16.92
2	480	295	38.54
30	1450	25	98.27
37	1345	135	89.96
44	880	65	92.61
51	1220	130	89.34
58	435	30	93.10
65	1875	220	88.26
72	755	20	97.35

Table 26 Data for Figure 14

Enterococcus	Influent CFU/100ml	Effluent CFU/100ml	% removal
1	650	450	30.76
2	480	225	53.1
30	1450	130	91.03
37	1345	315	76.57
44	880	135	84.65
51	1220	210	82.78
58	435	35	91.95
65	1875	200	89.33
72	755	100	86.75

Table 27 Data for Figure 15

Standard LSBF	Influent CFU/100ml	Effluent CFU/100ml	% removal
1	410	10	97.56
2	210	0	100
3	400	0	100
4	630	20	96.82
5	660	0	100
6	180	10	94.44
7	350	0	100
8	217	0	100
9	340	0	100
10	550	0	100
11	600	0	100
12	440	10	97.72

Table 28 Data for Figure 16

Reduced LSBF	Influent CFU/100ml	Effluent CFU/100ml	% removal
1	410	30	92.68
2	210	0	100
3	400	20	95
4	630	0	100
5	660	20	96.96
6	180	20	88.89
7	350	10	97.14
8	217	0	100
9	340	30	91.18
10	550	60	89.09
11	600	0	100
12	440	50	88.64

Table 29 Data for Figure 17

Standard LSBF	Influent CFU/100ml	Effluent CFU/100ml	% removal
1	400	35	91.25
2	920	20	97.82
3	305	30	90.16
4	780	10	98.72
5	650	0	100
6	1130	40	96.46
7	310	10	96.77
8	920	0	100
9	540	0	100
10	770	5	99.35
11	430	0	100
12	1740	10	99.43

Table 30 Data for Figure 18

Reduced LSBF	Influent CFU/100ml	Effluent CFU/100ml	% removal
1	400	40	90
2	920	110	88.04
3	305	0	100
4	780	70	91.02
5	650	10	98.46
6	1130	160	85.84
7	310	150	51.61
8	920	0	100
9	540	10	98.15
10	770	50	93.51
11	430	40	90.7
12	1740	35	97.99

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