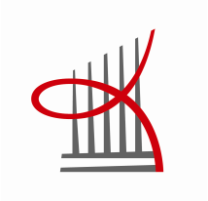

DISINFECTION OF WASTEWATER USING TiO_2 SEMICONDUCTOR PHOTOCHEMISTRY

Sarmad Ismail

Bachelor's thesis

May 2013

Degree Programme in Environmental Engineering

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ABSTRACT

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Disinfection of wastewater using TiO_2 semiconductor photochemistry

Bachelor's thesis 32 pages
May 2013

There is a raise in concern as shown in recent studies, that when it comes to the traditional wastewater disinfection methods such as chlorination and ozonation, there is a formation of health related disinfection by-products such as trihalomethanes and haloacetic acids that can have carcinogenic tendencies. One of the alternative methods available for commercialization in the near future are advanced oxidation processes, which use semiconductor photochemistry in disinfection. The most effective photo catalyst for these disinfection purposes is TiO_2, which is a non-toxic substance that is widely used in products like toothpastes and cosmetics. Traditionally these methods are added as a tertiary or final stage of wastewater treatment, which renders them an additional cost to wastewater systems. In this research, heterogeneous photo catalysis of TiO_2 is combined with a pressure driven nanofiltration system, in order to integrate disinfection into a water quality solution and avoid the separation step of methods in order to design a continuous water treatment plan. The objective of the research was to test the inactivation of E. coli bacteria trough photocatalytic disinfection in synthetic wastewater, to determine if the integrated filtration system can be viable in photocatalytic disinfection.

Keywords: Wastewater, disinfection, Titanium Dioxide.

Scope of the research

To study the effects of semiconductor photocatalysis using E. coli, experiments were conducted from April trough July 2012. A reactor was built in the laboratory of URJC in order to streamline the testing process. Bacteria in synthetic water were pumped in a constant flow up to a reactor membrane that was previously coated with varied amounts of TiO_2 suspension, and exposed to UV-light from the inside. The TiO_2 was tested with diffraction methods to determine its quality before testing commenced. Samples were collected during timed intervals, and diluted to make the bacteria countable. Before each experiment, formaldehyde tests were conducted and bacteria prepared in a broth from set cultivation. First samples were then taken to enumerate the starting concentration of the bacteria, kept at a constant 10^6 CFU/ml concentration for the start of every test. During each sampling time, samples were taken from both the tank and the permeate of the steel membrane reactor. Diluted samples were then applied to the Agar dishes in different volumes and dried overnight to allow the bacteria to cultivate. The inactivation of E. coli was calculated the following day from the dishes, and total concentration determined. The experiments were done in room temperature, and the overnight drying process of the agar dishes was done in a constant 37 °C oven.

Overview of the report

The second chapter discusses characteristics of advanced oxidation processes and disinfection methods, and then TiO_2 photocatalytic disinfection. The third chapter is about methodology used and experimental design, including variables tested during the research, such as testing procedures and disinfection of the tank between tests. This chapter also includes the methodology of the preparation of the tests and the reactor itself. Chapter 4 is about the results and conclusions that can be made from them.

Acknowledgements

This research is a continuation of the work of Rafael van Grieken, Javier Marugan and Cristina Pablos from URJC in Madrid, Spain. I would like to thank the University of Rey Juan Carlos in Madrid, Spain for allowing me to participate in their on-going research in developing advanced oxidation processes and methods for disinfecting wastewater.

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Abbreviations and table of figures

UV – Ultraviolet

DPBs – Disinfection By Products

WHO – World Health Organization

AOP – Advanced Oxidation Process

OH – Hydroxyl

TiO_2 – Titanium Dioxide

XRD – X-Ray Diffraction

eV – Electronic Volt

E.coli – Escherichia Coli

CFU – Colony Forming Units

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1. Introduction

There are many forms of the inactivation of health related microorganisms in water disinfection, mainly focused on chemicals, methods such as in chlorination that have been traditionally used for disinfection of drinking water and treatment for wastewater effluents. These methods are considered extremely effective against a multitude of pathogenic microorganisms such as Escherichia Coli, but require adding a chemical into the process that can leave harmful residue, therefore disinfection options of wastewater have recently been in need of reform; since research has shown that these traditional methods such as chlorine-based technologies have been discovered to lead to the formation of chloro-organic disinfection by-products known as DBPs. These DPBs can have carcinogenic and mutagenic effects on mammals and for that reason new disinfection technologies are being developed, in order to overcome the current drawbacks of water treatment and meet the WHO guidelines on drinking water quality.

A relatively new alternatives to standard chlorination are Advanced Oxidation Processes (AOPs), which are chemical processes designed to remove organic and inorganic material from contaminated water. These alternatives use the oxidation of highly reactive hydroxyl (OH) radicals, but may require variable operation conditions such as temperature, pressure and pH. In this regard, as an AOP, heterogeneous photo catalysis using TiO_2 and irradiation of UV-light is the best alternative since it requires little to none operational conditioning. Further more, AOP treatment methods do not remove all contaminants without pre treatment and are thus usually deployed as a final stage of the treatment process. This coupled with usual high costs of AOP chemicals has rendered these methods impractical today. *(Cho et. al, 2004, Marugan et. al, 2010, Pablos et. al, 2011, Richardson, 2003, World Health Organization, 2008)*

1.1 Basic principles of photocatalysis

Common oxidation technologies such as chlorination and ozonation have long been used for the purposes of disinfecting water. However effective they are, several concerns have been raised regarding these wastewater treatment methods, with the main concerns being due to the formation of potentially harmful disinfection by-products such as trihalomethanes and haloacetic acids. These by-products form when the chemicals react with the naturally occurring organic matter and halide ions. One of the alternative methods of disinfection is photocatalysis, which is the photocatalytic destruction of organic compounds that is based on basic semiconductor photochemistry. In this instance, the light absorbing qualities of semiconductors allows these species that usually have the highest available band full of electrons, to produce electron hole pairs that react with the surface absorbed species.

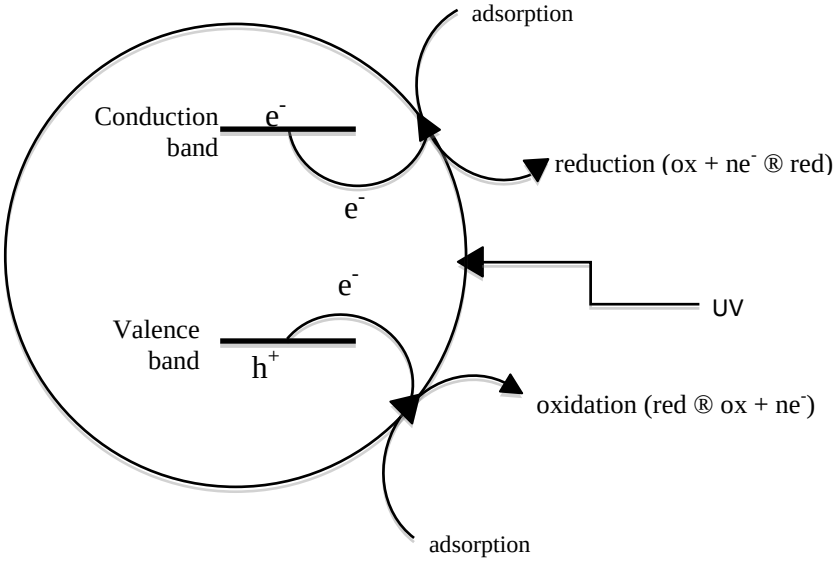


Figure 1. Illustration of the principles of photocatalysis showing the energy band gap diagram of a TiO2 spherical particle.

With the basic photochemistry and the photocatalytic properties of the semiconductor, where the UV-illuminated catalyst displaces electrons under sufficient wavelength from the valence band of the catalyst; for many catalysts this wavelength is below 400 nm. Thus, an electron/hole pair is produced on the semiconductor surface as *figure 1* illustrates. Photocatalytic oxidation of an organic species often proceeds via adsorption of the pollutant on the surface of the catalyst, followed by direct subtraction of the pollutant's electrons by positively charged holes. There is also another possible way,

which is oxidation with OH radicals, generated from water of the aqueous environment that takes place at the catalyst surface or in its vicinity. Both of these unique reactions may happen simultaneously and which of these two mechanisms dominates depends solely on the chemical and adsorption properties of the pollutant.

These methods are commonly referred to as Advanced Oxidation Processes, or AOP's, which are aqueous phase oxidation methods, that are based on highly reactive species, primarily OH radicals. Key AOP's are the heterogeneous and homogeneous photocatalysis that are based on ultraviolet (UV) radiation. (Van Grieken et. al, 2009, Mills, et. al, 2003, Comninellis et. al, 2008)

1.2 TiO_2 as a catalyst

1.2.1 Introduction

Advanced Oxidation Process (AOP) heterogeneous photocatalysis is based on the possible generation of hydroxyl radicals that are highly reactive, in this case when UV light irradiation contacts the TiO_2 semiconductor particle surface. Nano crystalline Titanium Oxide (TiO_2, *titania*) has been extensively studied for its outstanding physical and chemical properties in applications utilizing its photocatalytic potential. It is by far the most effective photocatalyst for this purpose, and it is an abundant non-toxic material that is commonly used commercially in toothpastes and many different cosmetics. The potency of TiO_2 as a catalyst in photocatalytic applications comes from its crystal structure and structural properties. Catalyst morphology affects the transport of reactants and products to and from the catalytic active sites, as well as the UV absorbance for the photo-excitation of the catalyst, which enhances the generation of electron-holes pairs. The most common type of setup of this catalyst is a discontinuous photoreactor operating with TiO_2 particles in suspension. Due to the economical and practical restrictions however, many research efforts have been dedicated to the development of immobilized systems. While these systems can show lower oxidation activities when compared with powder TiO2 in a slurry system, mainly due to the decrease in the surface area available

and in restrictions for mass transfer, the immobilization procedure is designed in order to guarantee the long-term stability of the TiO_2. (H. Choi et al. 2006, Van Grieken et al. 2009, Bing Ye et. al, 2010)

1.2.2 Physical and chemical characteristics of used TiO_2 particles

The X-Ray Diffraction (XRD) measurements conducted on the Titania used in this research show that the TiO_2 particles belong mainly to *Anatase* and somewhat to *Rutile* crystallographic systems. TiO_2 is an n-type semiconductor and the band gap of Anatase is 3.2eV, and when the particles are radiated by a source of light whose energy is equal or greater than the band gap of that phase, the electrons of the valence band are transitioned to the conduction band, thus resulting in the production of the corresponding holes. These photo-generated holes are very strong oxidizers, and can easily obtain electrons, and more importantly seize the electrons of different organic compounds adsorbed on the surface of semiconductor particles. By means of this process, a substance that does not have initial photon absorbsion capabilities, and cannot be directly oxidized would be activated and oxidized by a photocatalyzer, in this case TiO_2. (Bing Ye et. al, 2010)

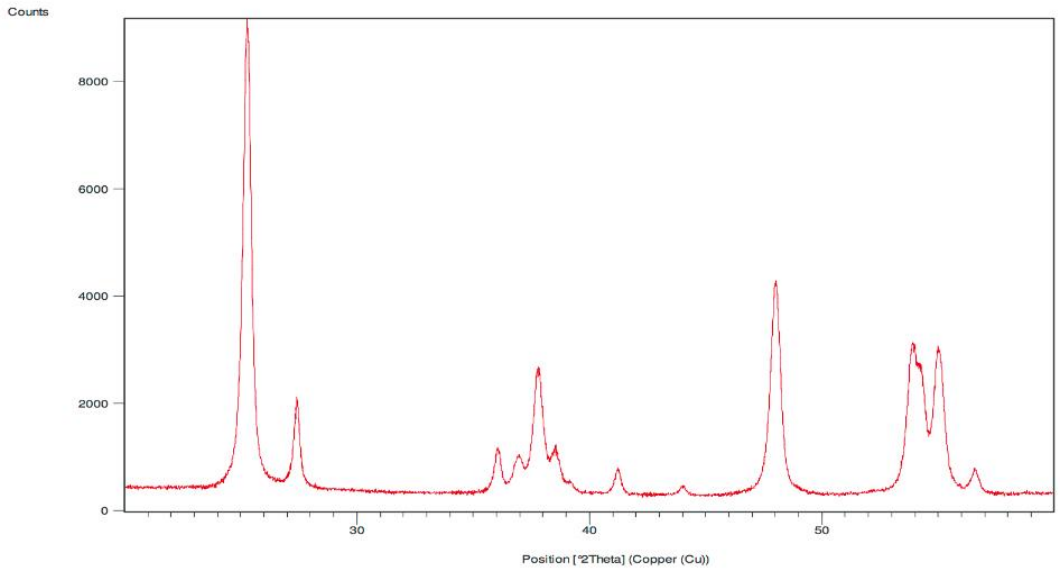


Figure 2. Results of XRD test on TiO_2^{P25} used as a catalyst, showing counts of particles compared to the position.

No.	Pos. [°2Th.]	d-spacing [Å]	Rel. Int. [...	FWHM [°2Th.]	Area [cts*°2Th.]	Backgr.[cts]	Height [cts]
1	25.2683	3.52468	100.00	0.2952	2519.96	421.00	8653.71
2	27.4265	3.25204	19.21	0.2362	387.17	402.00	1661.97
3	36.0396	2.49216	9.60	0.2165	177.40	317.00	830.74
4	36.9633	2.43197	8.18	0.3149	219.96	314.00	708.15
5	37.7085	2.38363	24.88	0.1440	413.35	311.00	2152.86
6	37.8697	2.37582	25.11	0.1181	253.12	311.00	2173.05
7	38.5405	2.33600	9.97	0.0984	83.76	308.00	862.90
8	39.1924	2.29863	2.56	0.1574	34.46	306.00	221.87
9	41.2634	2.18793	5.17	0.0984	43.45	298.00	447.65
10	44.0042	2.05780	1.71	0.2362	34.41	288.00	147.69
11	48.0564	1.89333	44.86	0.2362	904.33	300.00	3881.91
12	53.8049	1.70383	29.09	0.0984	244.36	318.00	2517.43
13	54.2839	1.68992	27.17	0.1181	273.89	317.00	2351.38
14	54.9851	1.66864	31.02	0.2400	859.13	316.00	2684.78
15	55.1630	1.66781	25.98	0.1440	431.67	315.00	2248.30
16	56.5939	1.62496	5.23	0.3360	202.75	313.00	452.57

Figure 3. Results of XRD test on TiO_2^{P25} used as a catalyst.

1.3 Bacteria type

E. Coli was selected as model microorganism in determining the effectiveness of photo catalysis in this research because of its wide use as fecal contamination indicator. Additionally, research conducted before this one observed the differences of photocatalytic inactivation between gram-negative and gram-positive bacteria (Van Grieken, 2010). Consequently, it was concluded that despite their differences in cell wall structure both E. coli and E. faecalis show very similar interaction with the catalyst, where the OH radical attack on the cell wall is quite effective for both. The main influence of this variable is essentially related to the absorption of UV- radiation, in this case the higher relative sensibility of mechano-osmotic stress observed for E. coli, therefore it was selected as the model organism. The Colección Española de Cultivos Tipo provided E. Coli K12 strain for the purposes of this research.

2. Methods and materials

2.1 Design

2.1.1 Experimental design

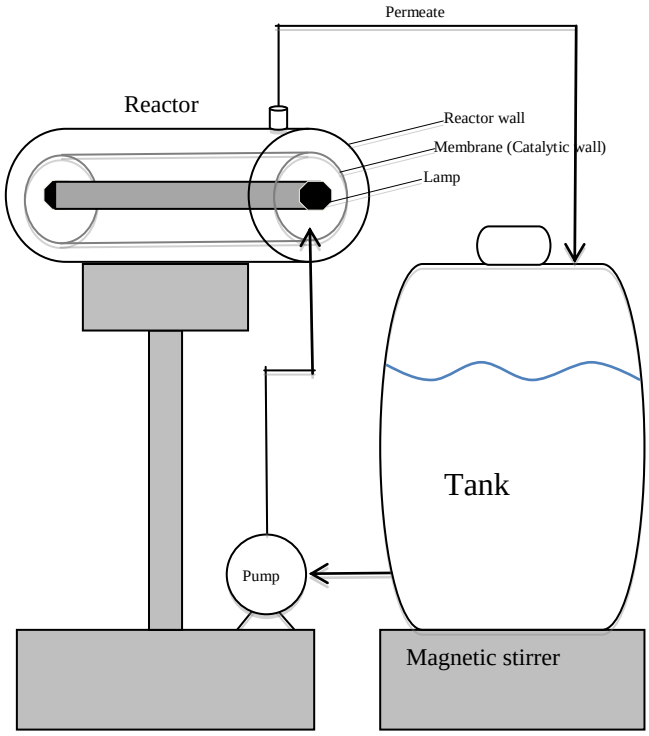


Figure 4. Basic reactor system

This research was based on bringing this Advanced Oxidation Process to a state where it can be considered more beneficial to traditional chemical processes that are the dominating disinfection methods. To try and prove this, the target was to incorporate a membrane system within the chemical process in order to maximize efficiency of disinfection. The basic experimental setup is an annular photoreactor operating in recirculation with a stirred reservoir tank where the bacteria was added. While attempting to avoid separation between chemical and mechanical disinfection, it is notable that different reactor configurations such as ones where the catalyst is inside the reactor can ultimately change the interaction between the catalyst and the bacteria. This alteration in interaction can yield different activities in the photocatalytic inactivation effectiveness over a longer period of irradiation time. The most common types of experimental setups perform photocatalytic experiments where Titania is usually used in form of nanoparticles in suspension for enhanced surface area and activity in catalysis, however it has proven that in these slurry systems, nanosize TiO_2 particles are difficult to handle and remove from suspension after their intended application in water treatment. It was however important to place the Nano sized TiO_2 particles within the reactor itself while simplifying the post-test handling and removal of the catalyst. Therefore, the wastewater from the tank is pumped straight to the area between the lamp and the membrane. This way, the effectiveness of the catalyst in surface area and activity is sustained, while a closed loop system provided easy means to cleanse

the reactor afterwards. The reactor design allowed for the catalyst to be fixed on the inner wall of the steel membrane inside the reactor, the catalytic wall, and trough pressure created by the closed valve system. A pump drives the solution from the stirred reservoir tank to the inside of the photocatalytic membrane reactor consisting of an annular reactor of 15 cm long, 3 cm inner-tube diameter and 6 cm external-tube diameter and the photocatalytic membrane is placed between the inner and external glass tubes. The experimental setup is also equipped with sensors for monitoring the temperature, pressure and the flow of the different streams individually. The system was also provided also with a control panel that allowed maintaining the operation under constant pressure and flow conditions. The catalyst is added into the reservoir tank, and system started and tested with formaldehyde experiments in order to determine the absence of TiO_2 suspension in the tank before the addition of bacteria. The illumination inside the reactor membrane was provided by a Philips TL 6W black lamp, which was placed in the axis of the reactor. (Marugan, et al. 2011, C. Pablos et al. 2011, R. van Grieken et al. 2009, Marugan et al. 2012, Choi et al. 2006)

2.1.2 Membranes

Traditionally a membrane process can be defined as splitting the intake stream by a membrane into a concentrate and a permeate fraction. Pressure driven porous membrane processes use the pressure difference between the feed and permeate side as the driving force to transport the wastewater solvent through the membrane at a desired rate. These processes are powerful techniques that allow the separation of a wide range of components and solvents, in an aqueous state. This leads to a number of available applications in this case in separation of wastewater effluents and further advancing our oxidation process. This particular study required photocatalytic degradation of organic molecules and simultaneous filtration power of the membrane system, in order to combine the two methods and simplify the water disinfection procedures. The photocatalytic

Figure 5. Membranes used in study

membrane reactor that was developed permitted different situational and operational configurations that allowed the continuous treatment of wastewater, but also the possible partial or total recirculation of both the concentrate and permeate. Membranes are usually used for filtration processes in many different applications and are usually constructed from organic and ceramic materials, however a there has been a growing interest in metallic membranes used as porous micro- and nano-filters. The 316L stainless steel membranes used had a tube-like configuration, with 15 cm long and 5 cm diameter and had a pore size of 0.20 and 0.50 μm. They were supplied by Shijiazhuang Beot Inorganic Membrane Separation Equipment Co. Ltd. stationed in China. In addition to morphing two stages of water treatment together, using these membranes solved two problems that were present in most photocatalytic disinfection systems; Firstly issue being the removal of the catalyst for cleaning purposes, as a traditional slurry system doesn't allow simple cleaning and maintenance, and secondly the continuous system allowed to minimize biofouling that can lead to negative operational problems such as rising energy demand, chemical cleaning agents cost and finally, a shortened membrane lifetime.

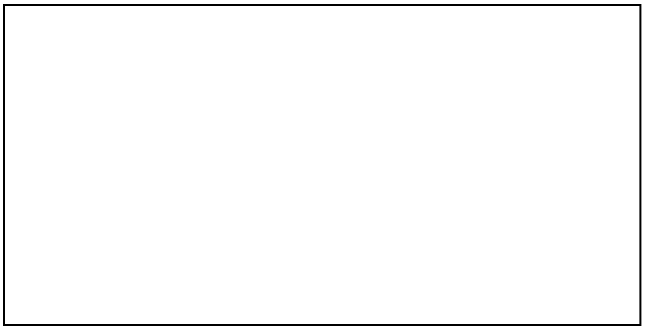


Figure 6. Detailed schematic of the photocatalytic membrane reactor. Confidential figure

The system designed for the purposes of this research, allowed periodic cleaning of the membranes, simply by replacing the reservoir tank wastewater with Methanol (CH_3OH). Several tests proved that a single methanol pumping run coupled with 3 ultrapure water runs at 10min each, provided us with a clean tank and pumping system. From there, the removal of the membrane and replacing it with another one was simple, and efficient. The Titania coated membrane is then placed in a methanol bath in an ultrasonic cleaner for the removal of rest of the TiO_2 particles from the inner catalytic wall. (Marugan et al. 2012, Van de Bruggen et al. 2003)

2.1.3 Main pumping system

The experimental setup was designed to allow constant pressure and flow throughout the system, in order to un-hinder bacterial growth. Pre-experiment testing was conducted to measure the best available pressure consistency using a set frequency and pumping volume. A Pumping frequency of 20 over 60s was set, because it provided the most constant pressure during the test-runs. Additionally, the system was set to pump at 50%volume. In order to maintain and monitor the efficiency and consistency of the pumping system, various instruments had to be added to the structure. Most important for this experiment, the flow meter was placed at the beginning of the pumping cycle, to monitor constant flow. The flow was also measured in the concentrate for recording purposes to determine the amount of water passing trough the membrane, as was the temperature and pressure. All of the experiments were conducted in room temperature. This configuration provided also with a control system that allow the operation under constant pressure and flow conditions.

2.1.4 Closed/open valve system

The design of the reactor system allowed for easy cleaning trough the open and closed valve configuration design. The individual outlet streams of the reactor, concentrate and permeate, can be driven to external storage tanks or re-circulated back into the main reservoir as in this case. This allowed for the easy methanol cleaning method to be carried out after every test run, in order to clear the pumping system and reservoir of bacteria. In the beginning stages of the initial experimenting, test runs with the open valve were conducted, to determine if bacteria were stuck on the membrane or dying from pressure post closed valve testing. It was later determined that the closed valve system had no infraction with killing bacteria due to stress. For the principal tests however, the valve was closed to force the bacteria to pass trough the membrane and keep the TiO_2 attached to the catalytic wall. (Marugan et al. 2012)

2.2 Test preparation & procedures

2.2.1 Synthetic wastewater

In order to successfully evaluate the manner of which this method can be effective, the water used in the reaction process must be wastewater in order to allow the bacteria to have ample living conditions throughout the reaction period, as opposed to using aquapure water, where there are no nutrients. In order to simulate a good environment for the bacteria to live in, wastewater effluent from the University of Rey Juan Carlos was evaluated to determine its composition. These substances were then added mixed with aquapure water to create the concentrated synthetic wastewater used in the experiments. The synthetic wastewater concentrate was prepared in batches of 1L, from which 150ml per litre of aquapure water were added to the reservoir tank prior to testing. The total organic carbon value for this mixture was 100ppm.

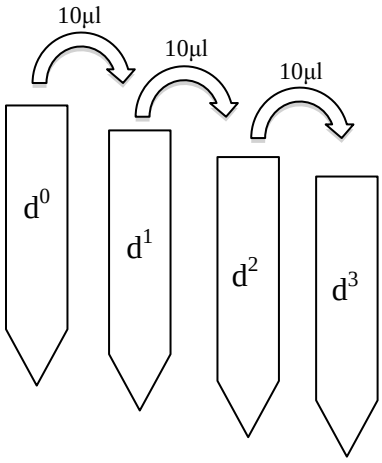
Substance	Amount per litre
Calcium Chloride ($CaCl_2$)	4mg
Sodium Chloride ($NaCl_2$)	7mg
Potassium hydrogen Phosphate (K_2hPO_4)	28mg
Magnesium Sulphate ($MgSO_4$)	110mg
Beef extract	30mg
Urea	2mg
Meat peptone	160mg

2.2.2 E-coli preparation

The K-12 strain E-coli bacteria obtained from Colección Española de Cultivos Tipo were frozen at -20°C until usage period. Prior to experiments, normally in the beginning of the week to save time, the bacteria culture for one week's tests was prepared in a sterile environment, by adding the 10^9 CFU mL^{-1} bacteria to a Millers LB Broth (Scharlab) liquid nutrient medium for a total of 100ml of culture to be used during the week. This solution is then placed into a rotary shaker to be stirred for at least 24h in order to incubate and evenly distribute the bacteria within the culture. After at least 24h incubation period and before each experiment, 5ml of the bacteria culture is centrifuged for 15 minutes at 3000rpm, after which the excess water is decanted. The remaining bacteria

concentration is then resurfaced with 5ml of aquapure water (MilliQ, 18.2 Ω) and a dilution procedure is performed with the removal of 1ml from the bacterial suspension, leaving 4ml to obtain the bacterial concentration of 10^6 CFU mL^{-1} for the 4l reservoir. The bacterial concentration is then discharged to the reservoir 10 minutes prior to commencing the test to the stirred reservoir tank containing synthetic wastewater in order to ensure the bacteria is distributed evenly within the tank before the start of the experiment. The concentration of viable bacteria along the reaction was followed through a standard serial dilution procedure and then placed on the Agar dishes.

2.2.3 Agar dish preparation & sample dilution



For the agar dishes, LB nutrient agar was used to follow the total inactivation and to simplify the bacterial counting. The E. coli was grown in LB nutrient agar (Miller's LB Agar, Scharlab) as a solid culture media following the normal operational procedure stated on the packaging. After the samples were taken from the reservoir tank and permeate individually, the bacteria is diluted trough a series dilution of d^0 (1/1), d^1 (1/10),d^2 (1/100) and d^3(1/1000). First dilution was done by removing 10µL of the original sample and adding it to 90µL of Milli-Q water, followed by similar dilutions for d^{1-3}, while stirring the samples between all dilutions in order to distribute the bacteria and the synthetic wastewater. This series dilution was done to be able to count the bacteria in 10^x Colony-Forming Units (CFU), with the original d^0 having a 10^6 CFU concentration. Therefore, assumptions could me made by counting the bacteria in the dishes according to this CFU dilution model, with d^1, d^2 and d^3 having 10^5, 10^4 and 10^3 CFU respectively. Additionally, d^{-1} and d^{-2} agar dishes were made with concentrations of 10^2 and 10 CFU if the dilutions do not have countable bacteria. Each of the decimal dilutions were spotted eight times on nutrient agar plates in amounts of 10µL each and incubated at 37 ° C for 24 h before counting. The d^{-1} agar plates had five spots of 100µL and d^{-2} had one drop of 1mL distributed on the plate.

2.2.4 TiO_2 Coating methods

In the primary stages, the method used for the immobilization of TiO_2 was a simple dip-coating procedure where a machine was designed to mechanically lower the membrane into a tank of TiO_2 solution. Before the coating procedure, the membranes were sonicated in ethanol for 30mins to clean the surface of the membrane from impurities. The coating tank was filled with a suspension of Degussa P25-TiO_2 powder employed as a photocatalyst in deionized water, which was kept at an acidic pH of 1.5 with HNO_3. The dip coating procedure was assisted by Bungard Elektronik RDC-15 equipment, which would lower the membrane at a controlled speed of 0.65 mm s^{-1}. After a single coating cycle, the membrane was dried at 110 ºC for 24h and calcinated at 500 ºC for 2h with a heating rate of 5 degrees centigrade from room temperature per minute. Prior to the testing procedures, the membrane was mounted on the reactor and cleaned with water for a period of 30mins, to remove any possible impurities that may have been poorly attached to the metal surfaces. This coating method, while effective, created some pressure problems with the reactor, and had to be discarded in order to conduct multiple bacteria tests in a week, since one coating would consume upwards of 2 days a week. For testing purposes, the coating method used was a simple suspension system, where the closed valve system would ensure that the TiO_2 would adhere to the inside of the membrane and create a catalytic wall. Permeate and tank water were tested after every adhering run with formaldehyde tests, to ensure that the TiO_2 wasn't passing through the membrane. Using this method, the variance of pressure was significantly lower, since the nano-crystalline structure of the TiO_2 was not hardened on the inside surface, possibly covering the pores. The variable TiO_2 amounts could be added directly to the tank in this system, thus eliminating an arduous step of calcinating the membrane.

2.2.5 Pre-test Sterilization

Prior to bacterial tests, sterilization had to be undertaken in order to rid the system and materials from all bacteria. The tank and pumping system had a simple method of pumping methanol (CH_3OH) into the system for duration of 10 minutes. Using this method, the bacteria that could have been in the system or in the tank would die and be set

in the tank. Following this 10-minute period, the system was rinsed with distilled Aquapure water (MilliQ, 8Ω) 3 times, each for duration of 10 minutes. Because of the nature of bacteria, and its ability to stem from rather small concentrations, additional samples were taken in each of the distilled water cycles to determine that the bacteria is in fact decreasing to an insignificant, and if possible, an inexistent concentration. This method was deemed successful in previous testing done with a similar setting, and was used throughout this research. The material used, as well as the dilution water, was also sterilized in 120°C for 180 minutes using a sterilizing machine, and then placed in a sterile environment, where it would remain until the testing phase. Every dilution and test related action was done under the hood par from the sample taking using portable sealable eppendorf liquid tubes. These methods were highly important to refrain from any outside contamination, which would be seen on the Agar plates.

2.3 Formaldehyde as an oxidation by-product

Formaldehyde (HCHO), also known as *Methanal,* is an aldehyde commonly formed as a by-product of Methanol oxidation. Much like the hydroxyl radicals formed in the advanced oxidation methods used in this research, it also has anti-bacterial effects, and can cause additional bacteria termination in the reactor as a by-product oxidizer trough a heterogeneous reaction on the surface of the TiO_2 particles. The HCHO adsorbs on the surface of TiO2, and first oxidizes to dioxymethylene before it further oxidizes to formate. This is explained by the phenomena that in photo-irradiation in which the wavelength is less than the band gap excitation wavelength, in this case 3.2eV for Anatase, the photo generated electron and hole pairs are first exited on the TiO_2 particle surface. On the particle surface, the hydroxyl groups capture the created h+ electron holes, and produce hydroxyl radicals that are extremely oxidizing to organic matter. In spite of formate usually being created using infrared radiation, previous studies have shown that ultraviolet radiation can accelerate

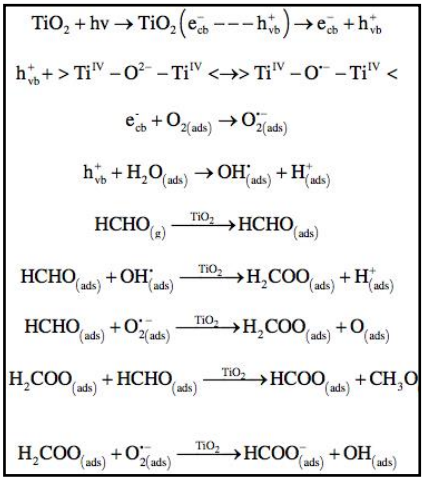


Figure 7. Common reactions in formaldehyde reaction with TiO_2. (Bing Ye et. al, 2010)

this reaction and the formation of formaldehyde in TiO_2. In addition to determination of the amount of formaldehyde adsorbed in the TiO_2 and bacteria tests, it was also a target for this particular test to show the threshold of which concentration of titanium dioxide and methanol in the photocatalytic reactor would produce the most consistent amounts of formaldehyde, and therefore affect the test results strongest, thus presenting the maximum amount of formaldehyde to Titania ratio. The tested TiO_2 amounts were 0.1, 0.2, 0.3, 0.4, of P25, with methanol in concentrations of 30-, 100-, 500- and 1000mM. The reservoir tank had 4L of synthetic wastewater during the tests. The UV-radiation was provided by a Philips 6W black light. (Bing Ye et. al, 2010)

2.3.1 Test Preparation

These tests were carried out separate to the testing phase with bacteria as an artificial way of creating formaldehyde. The determination of formaldehyde in this research was carried out in the form of spectral analysis using a basic reaction of methanol (CH_3OH) with an Ammonium phosphate $(NH_4)_3PO_4$ buffer and an acetone (37%) indicator. The ammonium phosphate buffer used was measured to the concentration of 20 grams per liter, and the pH was regulated to be at 6,0 using ammonia (NH_3). The solution tested in the spectrometer at 412nm consisted of 1,5ml of sample from the reactor, 30µl of acetic acetone and 1,5ml of ammonium phosphate buffer. The measurements were taken in 20-minute intervals for a total of 120 minutes and absorbance recorded and compared with different concentrations of methanol in the wastewater. Before every absorption measurement, a sample was used to zero the spectrometer, consisting of 1,5ml buffer, 30µl of acetone and 1,5ml of aquapure water instead of the reactor sample.

$$\mathbf{CH_3OH + O_2 = CH_2O + H_2O}$$

Oxidation of methanol creating formaldehyde and water

3. Results

3.1 Results and discussion of formaldehyde test

During the cross testing it was discovered, as seen in *graph 2*, using 0,1g of TiO_2 per 4 liters of wastewater and a concentration of 100mM of methanol yielded the highest concentration of formaldehyde. After determining the optimum concentration of methanol, the TiO_2 variables were repeated twice in 100mM and the results are seen in *table 1*, and presented in *graph 3*. During these tests, it was noticed that the original 0,1g concentrations produced the largest amounts of formaldehyde, while the 0,3g tests provided the most consistent results. One possible explanation for this is that under these conditions where the difference between light intensity and reactant concentration was variably high, it is possible that the reaction reached a point where the mass transport of the organic compounds is hindered, therefore resulting in a lower formation of formaldehyde (Fujushima, 2000). It should be noted that formaldehyde adsorbs strongly on the TiO_2 particle surface, which in turn means that TiO_2 can be effective even at a low formaldehyde concentration and not necessarily affected by small concentrations of additional formaldehyde that may be formed due to disinfection procedures. Therefore, it was determined that the disinfection procedure between the bacterial tests would not falsify the results greatly, as long as the methanol concentration is kept to a minimal.

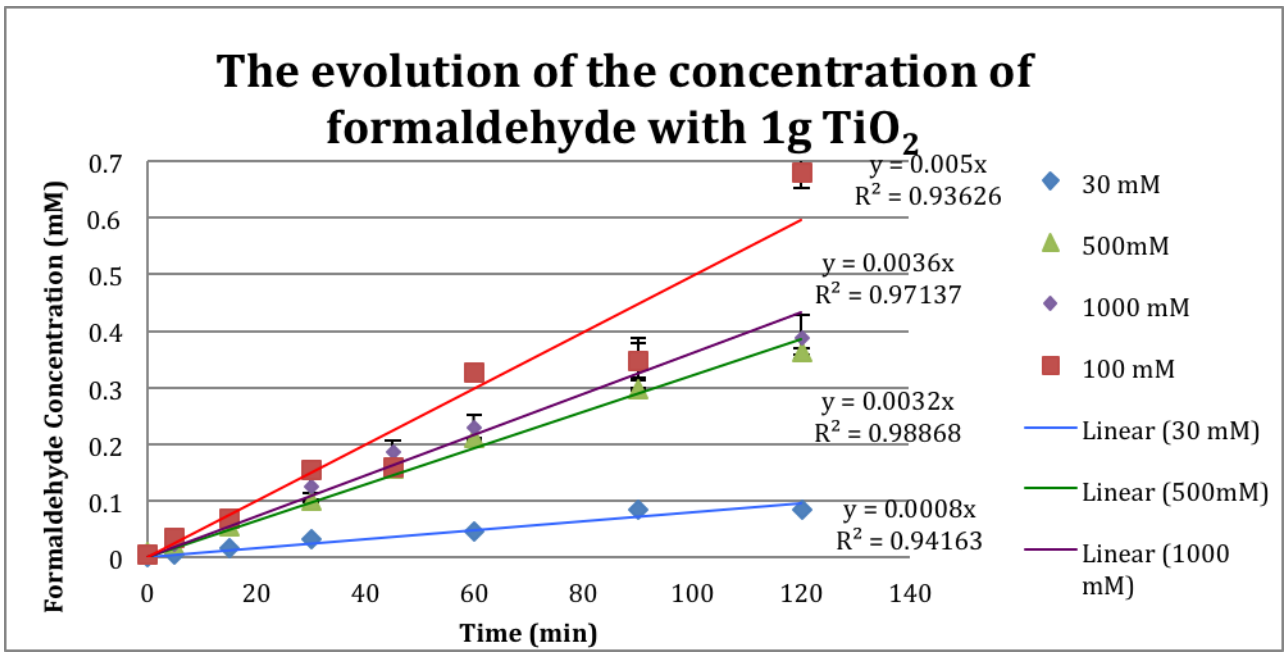


Figure 8. Evolution formaldehyde concentration

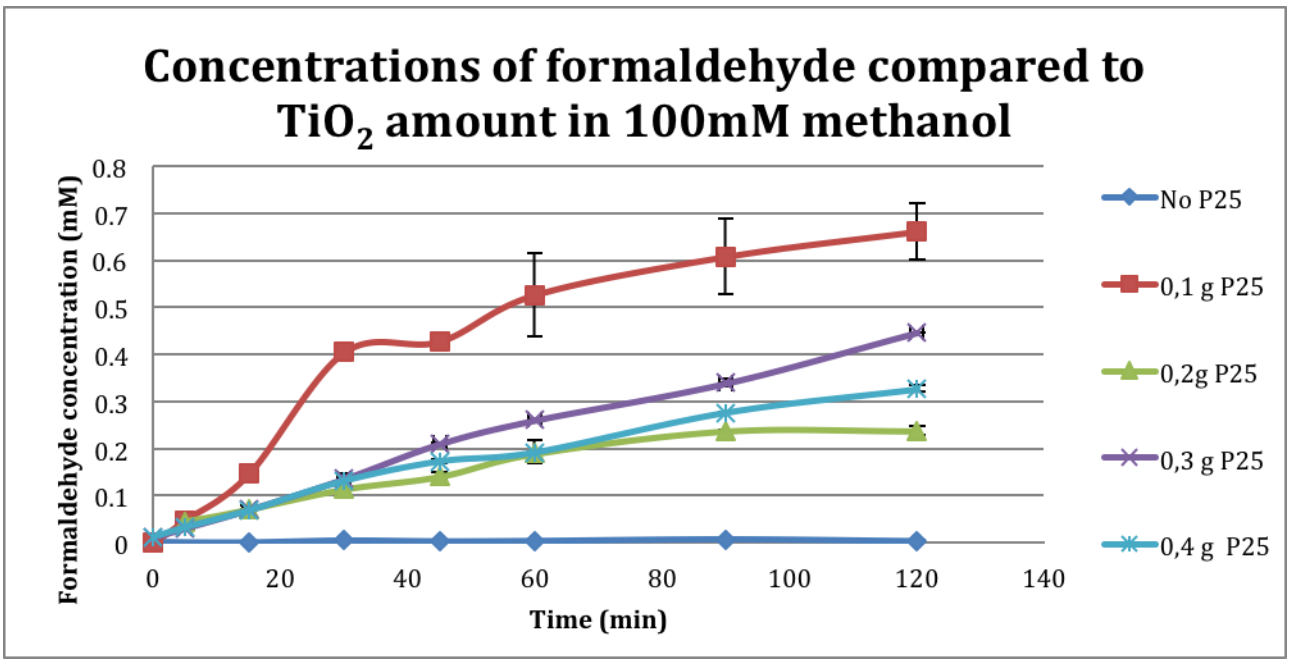


Figure 9. Comparison in concentrations of formaldehyde in respect to TiO_2 and Methanol

Photolysis, methanol concentration = 100mM. Membrane 0,5 μm. 0g of TiO_2.						
Time (min)	**Absorbance**		**Formaldehyde concentration (mM)**			**Error**
0	0	0.003	0	0.002603037	0.001301518	0.001840625
15	0	0.003	0	0.002603037	0.001301518	0.001840625
30	0.005	0.007	0.004338395	0.006073753	0.005206074	0.001227083
45	0.005	0.003	0.004338395	0.002603037	0.003470716	0.001227083
60	0.005	0.005	0.004338395	0.004338395	0.004338395	0
90	0.008	0.01	0.006941432	0.00867679	0.007809111	0.001227083
120	0.005	0.004	0.004338395	0.003470716	0.003904555	0.000613542
Photolysis, methanol concentration = 100mM. Membrane 0,5 μm. 0,1g of TiO_2.						
Time (min)	**Absorbance**		**Formaldehyde concentration (mM)**			**Error**
0	0.216	0.222	0.187418655	0.192624729	2.1692E-05	0.00368125
5	0.272	0.277	0.236008677	0.240347072	0.048177874	0.003067708
15	0.385	0.391	0.334056399	0.339262473	0.146659436	0.00368125
30	0.68	0.692	0.590021692	0.600433839	0.405227766	0.0073625
45	0.705	0.72	0.611713666	0.62472885	0.428221258	0.009203125
60	0.755	0.898	0.655097614	0.779175705	0.527136659	0.08773646
90	0.855	0.985	0.74186551	0.854663774	0.608264642	0.079760418
120	1.03	0.933	0.893709328	0.809544469	0.661626898	0.059513543
Photolysis, methanol concentration = 100mM. Membrane 0,5 μm. 0,2 g of TiO_2.						
Time (min)	**Absorbance**		**Formaldehyde concentration (mM)**			**Error**
0	0.237	0.153	0.205639913	0.132754881	0.169197397	0.051537501
5	0.097	0.1	0.084164859	0.086767896	0.045466377	0.001840625
15	0.124	0.136	0.107592191	0.118004338	0.072798265	0.0073625
30	0.181	0.177	0.157049892	0.153579176	0.115314534	0.002454167
45	0.203	0.217	0.176138829	0.188286334	0.142212581	0.008589583
60	0.263	0.269	0.228199566	0.23340564	0.190802603	0.00368125
90	0.319	0.323	0.276789588	0.280260304	0.238524946	0.002454167
120	0.313	0.33	0.271583514	0.286334056	0.238958785	0.010430208
Photolysis, methanol concentration = 100mM. Membrane 0,5 μm. 0,3 g of TiO_2.						
Time (min)	**Absorbance**		**Formaldehyde concentration (mM)**			**Error**
0	0.013	0.015	0.011279826	0.013015184	0.012147505	0.001227083
5	0.033	0.041	0.028633406	0.035574837	0.032104121	0.004908333
15	0.076	0.088	0.065943601	0.076355748	0.071149675	0.0073625
30	0.149	0.166	0.129284165	0.144034707	0.136659436	0.010430208
45	0.241	0.245	0.209110629	0.212581345	0.210845987	0.002454167
60	0.3	0.302	0.260303688	0.262039046	0.261171367	0.001227083
90	0.385	0.398	0.334056399	0.345336226	0.339696312	0.007976042
120	0.515	0.516	0.446854664	0.447722343	0.447288503	0.000613542
Photolysis, methanol concentration = 100mM. Membrane 0,5 μm. 0, 4g of TiO_2.						
Time (min)	**Absorbance**		**Formaldehyde concentration (mM)**			**Error**
0	0.019	0.01	0.0164859	0.00867679	0.012581345	0.005521875
5	0.036	0.042	0.031236443	0.036442516	0.033839479	0.00368125
15	0.079	0.081	0.068546638	0.070281996	0.069414317	0.001227083
30	0.146	0.159	0.126681128	0.137960954	0.132321041	0.007976042
45	0.196	0.204	0.170065076	0.177006508	0.173535792	0.004908333
60	0.242	0.202	0.209978308	0.17527115	0.192624729	0.024541667

90	0.318	0.32	0.275921909	0.277657267	0.276789588	0.001227083
120	0.369	0.383	0.320173536	0.332321041	0.326247289	0.008589583
Photolysis, methanol concentration = 100mM. Membrane 0,5 µm. 0,5g of TiO_2.						
Time (min)	**Absorbance**		**Formaldehyde concentration (mM)**			**Error**
0	0.035	0.022	0.030368764	0.026350337	0.02835955	0.002841457
5	0.055	0.038	0.047722343	0.041407673	0.044565008	0.004465146
15	0.098	0.071	0.085032538	0.073780944	0.079406741	0.007956078
30	0.166	0.133	0.144034707	0.124975885	0.134505296	0.013476623
45	0.309	0.269	0.268112798	0.232635834	0.250374316	0.025086002
60	0.317	0.286	0.27505423	0.238658768	0.256856499	0.025735478
90	0.326	0.289	0.282863341	0.245434569	0.264148955	0.026466138
120	0.346	0.324	0.30021692	0.260491904	0.280354412	0.028089828

Figure 10. Results of the formaldehyde experiment.

3.2 Experiments with aquapure water

Before the experiments containing any Titania or UV-radiation, it was decided to primarily test if the permeability of bacteria is indeed not feasible with aquapure water even in an open loop system where the concentrate was discharged and recycled back to the tank. Due to a phenomenon known as *osmotic stress*, the stress that the bacteria cells are strongly influenced by the purity of the water and therefore the lack of ions present in

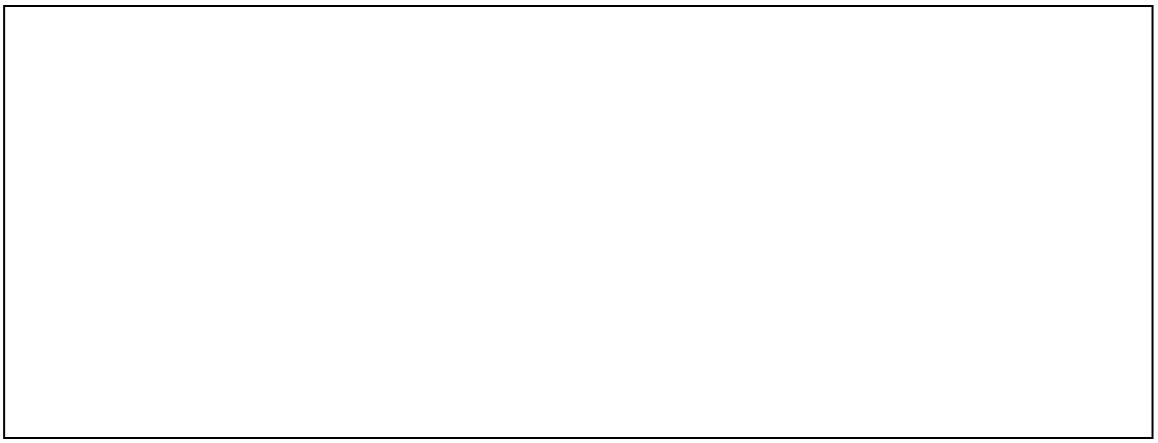


Figure 11. Comparison of osmotic stress using a 0,5 µm membrane. Confidential figure

the aquapure water. This suggests that When osmotic stress is removed by synthesizing the wastewater and adding some organic matter, it should be considered that these anions and organic matter present in the water serve as nutrients for the bacteria, therefore helping to maintain their viability. Consequently, this should not apply to the photocatalytic degradation of said organic compounds, as they depend on the radiation absorption of the molecules. These are not influenced on by the osmotic and nutrient exposure of the substances present in the wastewater.

Further examination at a microbiological scale further explains the phenomenon causes magnesium and calcium leakage in the cell walls is caused by the lack of ions in deionized water, and leads to the loss of bacterial permeability. Therefore, when the cells are more stable in an actual wastewater or wastewater simulating solution, they require a more damaging effect in order to be inactivated, which in turn should result in longer reaction times. It was suggested trough these results, that the for the organic/inorganic mixture of the simulated wastewater plant effluent would enhance the positive effects and

cancel out the inhibitory effects of the lack of anions in aquapure water. In conclusion, these primary tests, while failed in their own accord, clearly showed that the effect of the lack of external compounds present in the pure water changed the efficiency inactivation, even without the presence of any catalyst or radiation. Therefore this particular advanced oxidation process cannot be generalized to any process which contains inactivation of microorganisms, as the microbiological aspects make photocatalytic disinfection processes much more sensitive to the water composition. (Marugan et al. 2010)

3.3 UV-only experiment

Prior to the addition of Titanium dioxide in the process, it should be determined if the presence UV-radiation in itself has germicidal effects. Previous studies have been conducted where different comparisons have been made at the effect of using different wavelengths in order to disinfect bacterial sources. Normally, these UV-radiation experiments have consisted of exposing the disinfectant to a lamp generating a wavelength of approximately 250nm, which is in the middle of the germicidal band, and causes damage in the DNA of the bacteria. While this method has been proved working (Burch & Thomas, 1998), the method was only found effective at low turbidity and low quantity water, and would require some pre treatment such as filtration. While the system built for this research does fit the characteristics of pre filtration, in this case filtration is simultaneous with irradiation due to the structure of the reactor, the irradiation time would be very small in every cycle to be considered viable. It should also be noted that the radiation source used in this experiment was between 315nm and 400nm. This region of wavelength has been experimented with (Acra et al. 1984) and was proven to be the most germicidal range for bacteria in water. In this experiment a 600W Philips black light lamp. In order to stabilize its emission power and spectrum of 375nm, the lamp was switched on 15 min before the reaction. Using this wavelength and the membrane with a pore size of 0,5μm, it was found out trough testing that while turning on the UV-radiation lamp in a closed valve system did have some disinfecting properties even in a span of just 60 minutes, it was not effective enough to be recommended for use at 10^6 CFU

concentration, as the concentration did not drop significantly enough to be passed as a successful method of disinfecting wastewater.

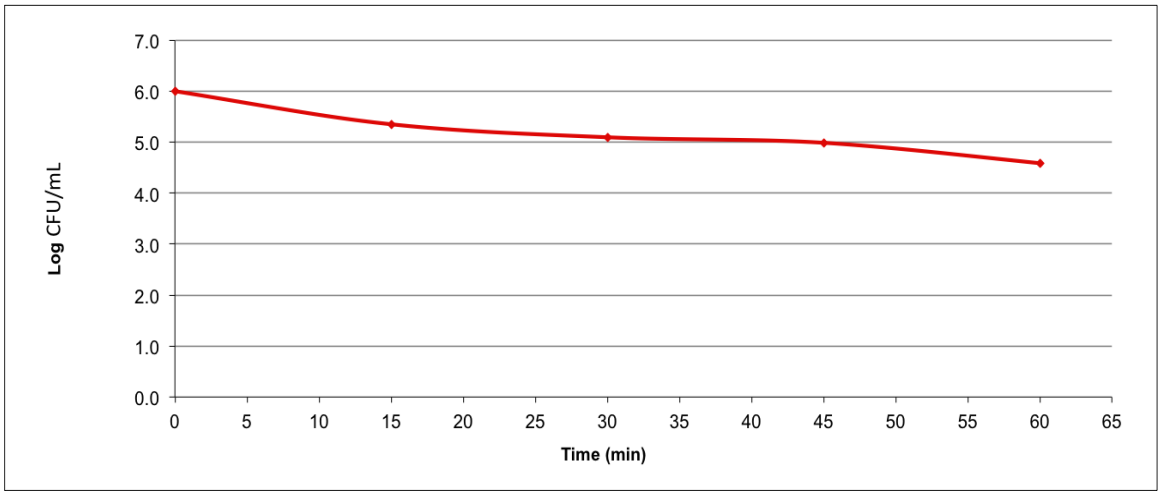


Figure 12. UV only experiment results

3.4 TiO_2 + UV experiments

3.4.1 Introduction

The final testing phase in this research was conducted in phases of five different amounts of TiO_2 suspensions. TiO_2 was added 15 minutes before the start of the test in order to make sure the particles adhered to the inner surface of the membrane thus creating a catalytic wall. After all of the titanium dioxide was adhered to the wall, the bacteria were added as described in previous chapters and sampling begun. The testing times were 60minutes in order to repeat tests for maximum accuracy.

3.4.2 Results

While all concentrations of TiO_2 provided bacterial inactivation, the results were very mixed. Starting with the lowest concentrations of 0.1g/4l and 0.2g/4l, the Titania and UV-light combination managed to lower the bacterial concentration below the UV only experiment of approx. $10^{4,6}$CFU/ml, as presented below.

Time(min)	CFU/mL	Log CFU/mL
0	2100000.0000	6.322219
5	514285.7143	5.711204
15	41250.0000	4.615424
30	712.5000	2.852785
45	1075.0000	3.031408
60	1485.7143	3.171935

Table 2. 0.1g

Time(min)	CFU/mL	Log CFU/mL
0	2100000.0000	6.322219
5	514285.7143	5.711204
15	3962.5000	3.597969
30	2325.0000	3.366423
45	2412.5000	3.382467
60	2242.8571	3.350802

Table 3. 0.2g

While the two different concentrations reached a very similar inactivation level, it should be noted that the suspension with 0,2g reached its final point much faster at around 15minutes. After this point, the amount of Titania was the limiting factor, and it could not manufacture any additional hydroxyl radicals in order to further disinfect the wastewater. It can be therefore assumed, that even if the reaction period was much longer, the bacteria would not inactivate, but instead reactivate and raise the concentration if kept in the closed cycle. With the higher concentrations, like the previous two tests, these three concentrations also were very close in terms of inactivation power, and even though the patterns are different, the results are basically in distinguishable. While 0,5g/4L had the best E-Coli inactivation result, it seems that 0,4g/4L has a faster inactivation rate, as it reached 10^2 CFU/ml much faster. This can be explained due to the pressure difference that was created in the membrane inner wall, that might have caused a smaller irradiation time per cycle by pushing the bacteria trough the pores faster. This can be further explained by the slower inactivation rate of the 0,55g/4L concentration, as in terms of disinfection in this reactor design and system, 0,4g/4L seemed to produce the best result with a 0,5μm

steel membrane. As seen in *graph 6*, the initial inactivation rate was faster with 0,1g/4L and 0,2g/4L than the higher concentration in the photoreactor simply because of the available surface area on the TiO_2 particles within the membrane.

Time (min)	CFU/mL	Log CFU/mL
0	1837500.0000	6.264227
5	337500.0000	5.528274
15	12714.2857	4.104292
30	262.5000	2.419129
45	100.0000	2.000000
60	74.0000	1.869232

Table 1. 0.4g

Time (min)	CFU/mL	Log CFU/mL
0	2350000.0000	6.371068
15	110000.0000	5.041393
30	3500.0000	3.544068
45	200.0000	2.301030
60	50.0000	1.698970

Table 2. 0.5g

Time (min)	CFU/mL	Log CFU/mL
0	3612500.0000	6.557808
15	135000.0000	5.130334
30	13750.0000	4.138303
45	178.7500	2.252246
60	136.2500	2.134337

Table 3. 0.55g

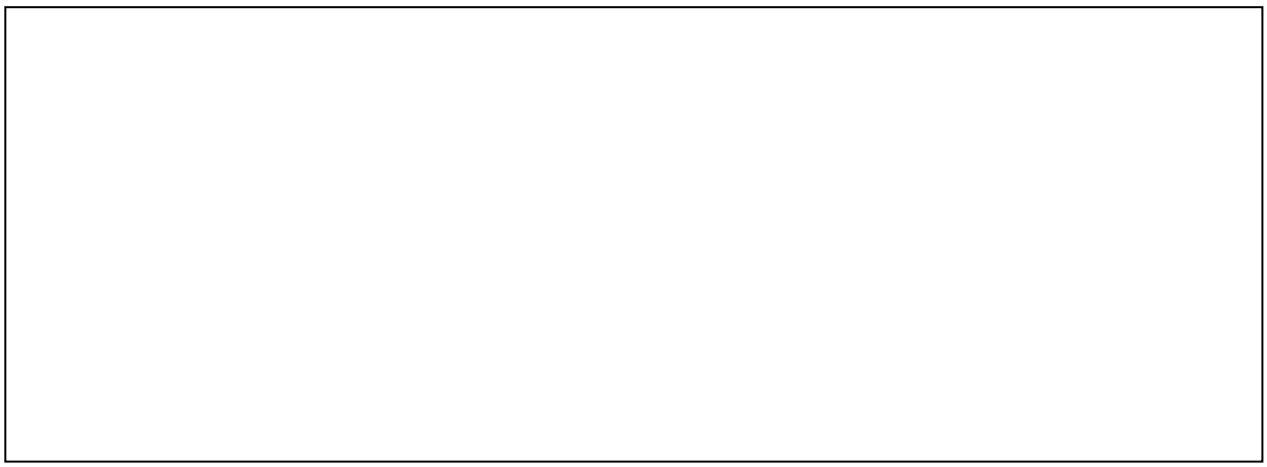


Figure 13. Full comparison of all conducted TiO_2 tests. Confidential figure.

4. Discussion

4.1 Reactor design

Pressure-driven membrane processes are powerful techniques that can allow a wide range of separation of components. With a micro filter consisting of pores as small as the 0,5μm membranes used in this study, it would remove more than one component at a time thus streamlining the water purification process. Combining the photocatalytic properties of TiO_2 and UV radiation is a powerful method to enhance the bacterial inactivation in wastewater. These factors provide a large advantage over the more traditional chemical processes not only in restructuring to fit many needs, but over the lack of harmful carcinogenic compounds that are created in processes such as ozonation and chlorination. While the primary function at the moment is the production of clean drinking water made simpler by the wide availability of Titania and simplicity of the process, it can be expected that the applications of this advanced oxidation process will increase rapidly. In principle, we found this method of disinfecting water to be feasible, at least on this small scale. Whether the problems solved with this design, such as membrane fouling, carry over on a larger scale and pose problems remains to be seen and tested. The design of this particular reactor can be implemented on a larger scale, and the optimal concentrations found trough testing. The advantage of this system showed in the ability of the fixed bed reactor in damaging cells from the very beginning of the reactions, and even with a lower radiation and radical hydroxyl generation rates the immobilized system produces damage over a sufficient irradiation time. The effect could be even greater if the pore size is 0,2μm, but we found that our reactor design could not handle the pressure levels the smaller pores created. (Pablos et al. 2011, Van Grieken et al. 2009)

4.2 Inactivation process

The reactor design in this provides a enhancement over traditional multi stage processes of chemical and bacterial separation, as it has been shown before trough research of differences of photocatalytic oxidation of chemical compounds and bacterial inactivation (Marugan et al. 2010), these two processes are quite different from one another. However, as proven by this particular research, the adsorption of molecules on the surface of the TiO_2 particle itself should not be different in both types of catalytic applications, as the oxidation of the molecule itself is the result of the chemical reaction with the radicals that modify the molecular structure of the harmful compound. A further explanation why an immobilized system is more beneficial is that the most effective form of bacterial inactivation is produced when the cell wall is weakened to a point that it is not acting as a barrier between the cell and its surroundings. This form of attack on the cell wall is more effective when there is a concentrated attack on a small region on the external surface of the bacteria, rather than distributed on the entire surface evenly. Additionally, the auto-recovery mechanisms of microorganisms can be an issue for dead bacteria, for instance in a water reservoir or dark water transport pipes. These repair mechanisms lack efficiency when there is a large damage on a specific area of the cell in comparison to small distributed damage, which is another aspect to consider in the post reaction difference in slurry and fixed bed reactors. (Pablos et al. 2011, Marugan et al. 2010)

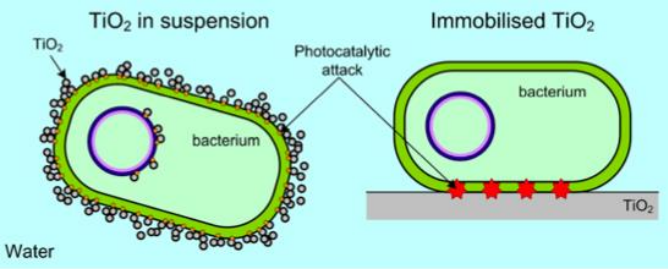


Figure 14 Schematic representation of the differences in the bacteria–TiO2 interaction and membrane distribution of the photocatalytic attacks for slurry and fixed-bed systems. (Pablos et al. 2011)

5. Conclusions

This research was conducted to study the effects of integrating a porous membrane into an advanced oxidation process, in order to attempt to remove the separation of methods in wastewater disinfection. The variables tested were water composition, disinfection methods and Titania amount. All experiments were conducted in the laboratory to refrain from contamination and insure the tests were done in a controlled environment.

1. Using 4-5g/4L concentration of Titania allowed a 5-log deactivation of bacteria in synthetic wastewater during a short period of 60 minutes. This required the use of a porous steel membrane with a pore size of 0,2μm and a UV-lamp operating at 375nm.

2. Although the total inactivation of bacteria was not achieved, the research provided us with positive results that point toward a possibly successful method of disinfection. This optimism is caused by the fact that only 4-5g/4L is a very small concentration, one that could be very much higher if the reactor is structured better.

3. The reactor design provides a much more effective bacteria deactivation due to the concentrated attack on a small region on the external surface of the bacteria, rather than distributed on the entire surface evenly.

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