Contents

1. Introduction and Motivation

Groundwater is a vital source of drinking water across the world. The demand for fresh water has steadily increased as the world population grows, and in the United States, it is the source of nearly a quarter of the drinking water consumed [1]. Unfortunately, it is also easily polluted and difficult to clean up due to its relative inaccessibility.

While many pollutants are found in groundwater, one of the most common is known as methyl tertiary butyl ether (MTBE). It is a fuel oxygenate that was commonly added to petrol in the 1990s and early 2000s in order to improve the fuel efficiency of car engines and hence reduce air pollution. However, MTBE has a very unpleasant taste even at concentrations as small as 5 – 15 µg/l (15 parts per billion), and small amounts can render large volumes of groundwater non-potable [2]. It is most commonly introduced into the environment through leaking underground storage tanks and spilled petrol. A relatively high solubility in water and persistence in the environment allows MTBE pollution to spread far beyond the source of contamination, and widespread use has resulted in large levels of contamination present in groundwater sources. Increasing use of MTBE in Asia due to its low cost indicates that MTBE pollution will remain a problem for some time to come.

There are many methods available that remove MTBE from groundwater sources. However, most of these methods are costly, disruptive or difficult to control, and hence are not ideal when considering a sustainable option. Pump and treat systems need to draw water out of the ground before treating it, and this is costly as it requires large amounts of energy. Bioremediation uses bacteria to break down pollutants, but requires space and a controlled environment, and these can be difficult to implement in urban areas. Chemical oxidation is yet another alternative. However it requires the release of chemicals into the groundwater and these cannot be easily controlled once released. Ex situ methods of remediation face further obstacles in the form of legislation. The Water Framework Directive [3,4] does not allow for the removal, partial treatment and subsequent recharging back into the ground of water. As such, there is a real and pressing need for an inexpensive and non disruptive method of MTBE remediation.

Photocatalysis is a remediation technique that can fulfill these conditions. Simply put, it involves the use of a regenerating catalyst to break down unwanted contaminants into harmless end products in the presence of UV light. This can be carried out in situ by placing the immobilised catalyst in the pathway of contaminated groundwater, and activating it via a UV light source. As there is no need to remove water from the ground, this technique avoids the costs and legal restrictions associated with ex situ treatments. The process is also easily controlled as catalysts and chemicals are not released into the groundwater plume, and the reaction can be stopped by removing the UV source [5]. Finally, as the catalyst is unchanged [6] at the end of the reaction, the incorporating device can be left in place for the duration of the remediation exercise. This technique is therefore well suited to urban areas where underground storage tanks containing MTBE laden fuels are often found.

Photocatalysis, however, has some notable problems. Firstly, the time taken for the degradation of contaminants is notably longer than with other methods of remediation. While this is a problem in applications involving fast moving water, the technique is well suited for slow moving groundwater plumes. Secondly, as Chan (2005) demonstrated, it is difficult to reliably immobilise the P25 titanium dioxide catalyst commonly used in photocatalytic reactors [5]. Prior studies on the subject have managed to coat a mesh with the titanium dioxide catalyst and successfully use the coated mesh to break down contaminants. However, the catalyst layer is not robust and can be removed with the wipe of a gloved thumb.

Pilkington Activ™ is a commercially available self-cleaning window glass. It is ordinary glass coated with a 15nm thick layer of titanium dioxide that enables it to break down a variety of organic contaminants, thus making it self-cleaning. Previous studies have shown that it is effective that breaking down methylene blue dye; a dye commonly used in research as a proxy for organic contaminants in groundwater [7]. Furthermore, the catalyst film is robust and is designed to withstand years of outdoor use in buildings. The low cost and robust nature of Activ™ makes it ideal for use in a photocatalytic reactor. However, there is little literature relating the effect of Activ™ on the breakdown of MTBE and this needs to be investigated before a prototype reactor can be developed.

2. Project Aims

The overall aim of this project, and that of the past work done in the department, is to eventually use photocatalysis as an effective and sustainable method of cleaning up organic pollutants in groundwater. For the reasons outlined in section 1, this project will specifically focus on the cleanup of MTBE. It is hoped that the development of this technology will eventually be extended to a whole host of organic contaminants.

The primary aims of this project are:

- To investigate the feasibility of Pilkington Activ™ glass as a catalyst in the cleanup of MTBE in groundwater.
- To understand the effect of variables such as light intensity, rate of aeration, groundwater flow rate, mixing and pollutant concentration on the rate of breakdown of MTBE by Pilkington Activ™.
- To optimise the above variables for use in an in situ groundwater treatment photocatalytic reactor.

3. Theory and Literature Review

3.1 Photocatalytic Mechanism

Photocatalysis is the degradation of compounds in the presence of a photocatalyst, oxygen and sufficient light energy. While this process comprises multiple detailed steps and various pathways, it can be simplified into the following 3 steps.

1. Activation of photocatalyst
2. Generation of hydroxyl radicals
3. Degradation of contaminants

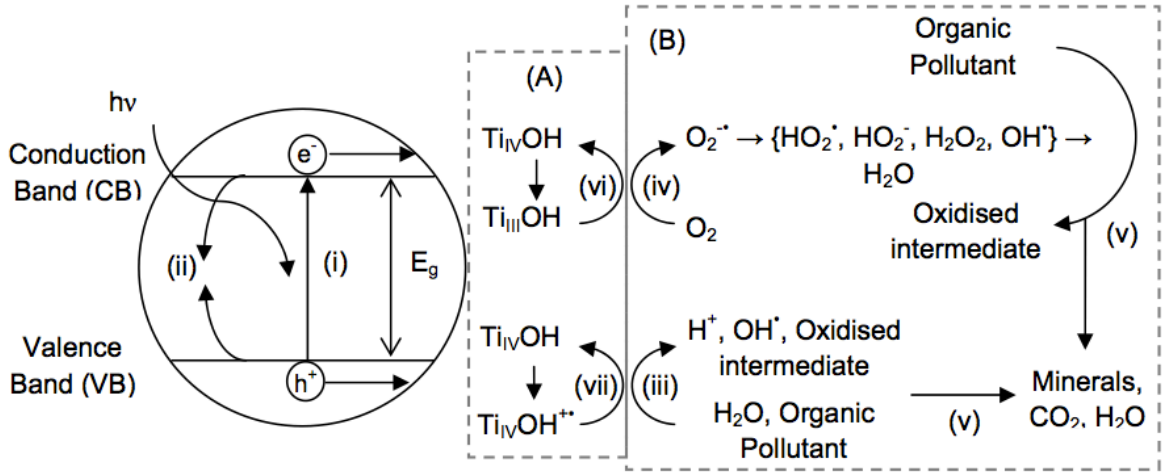

Figure 1: Photocatalytic mechanism [6]

Activation of photocatalyst

The photocatalyst is activated by the irradiation of light energy. Incoming photons of a sufficient energy excite an electron e_{CB}^- in the photocatalyst from the valence band to the conductance band. This generates a hole h_{VB}^+ in the valence band, and both the valence band and conductance band become highly reactive. This is shown in (i) in Fig. 1 above.

The catalysts commonly used in this technique are semiconductors such as TiO_2, Fe_2O_3 and ZnO, and are characterised by their distinctive band gap energies E_g [8]. In order for the promotion of the electron from the valence band to the conductance band, the energy of the photon E_p must exceed E_g. The energy, and thus the required wavelength of irradiated light can be determined using Planck's relation for a photon:

$$E_p = hc/\lambda$$

Here, h is the Planck's constant, c is the speed of light and λ is the wavelength of the light. The band gap energy E_g for the most commonly used photocatalyst TiO_2 is 3.1 eV. Thus, the photon energy E_p must exceed 3.1 eV. Using Planck's relation, this translates to a maximum wavelength λ_{max} of 400nm.

Generation of hydroxyl radicals

There are 2 main pathways by which hydroxyl radicals are generated. First, the water molecules adsorbed onto the catalyst surface react with valence band holes to form OH^- hydroxyl radicals and H^+ hydrogen ions. This is shown in (iii) in Fig. 1. The second pathway is through the conductance band electron. Dissolved oxygen molecules capture the conductance band electron and form oxygen radicals O_2^-, which go on to form more hydroxyl radicals. This is shown in (iv).

Degradation of contaminants

There are 3 main pathways by which pollutant molecules *R* are degraded [5]; direct oxidation via the valence band hole h_{VB}^+, direct reduction via the conductance band electron e_{CB}^- or by indirect oxidation via hydroxyl radicals OH^-.

Direct oxidation: $h_{VB}^+ + R \rightarrow CO_2 + H_2O + R''$

Indirect oxidation: $OH^- + R \rightarrow CO_2 + H_2O + R''$

Direct reduction: $e_{CB}^- + R \rightarrow CO_2 + H_2O + R''$

The end products for the full degradation via the photocatalytic mechanism for all pathways are carbon dioxide, water and mineral acids [5]. For MTBE ($C_4H_9OCH_3$) specifically, the degradation can be summarised in the following equation [6].

$$C_4H_9OCH_3 + 7.5O_2 \rightarrow 5CO_2 + 6H_2O$$

3.2 TiO_2 photocatalyst

Out of the commonly used semiconductors mentioned in section 3.1, TiO_2 is the most common choice for photocatalysis. The reasons for this are that it is inexpensive, commercially available, non-toxic, photostable and catalytically efficient [9]. Furthermore, TiO_2 shows a greater activity in catalysing the breakdown of organic compounds when compared with other photocatalysts [10]. The use of TiO_2 is particularly relevant in groundwater treatment as it is non-toxic and biologically inert, eliminating the need for safety procedures, which can raise the cost of the process.

3.3 Previous work

Previous research in the field as well as in the department has traditionally used Degussa P25 TiO_2. This is a commercially available form of TiO_2 that provides good performance as a photocatalyst, and is available as an opaque white powder. Extensive research has been conducted on the subject of photocatalysis using P25 TiO_2. In particular, Lim [6] used P25 TiO_2 to attempt the cleanup of MTBE in groundwater, and Stewart [7] briefly compared the performance of P25 TiO_2 and Pilkington Activ™ using the proxy methylene blue dye.

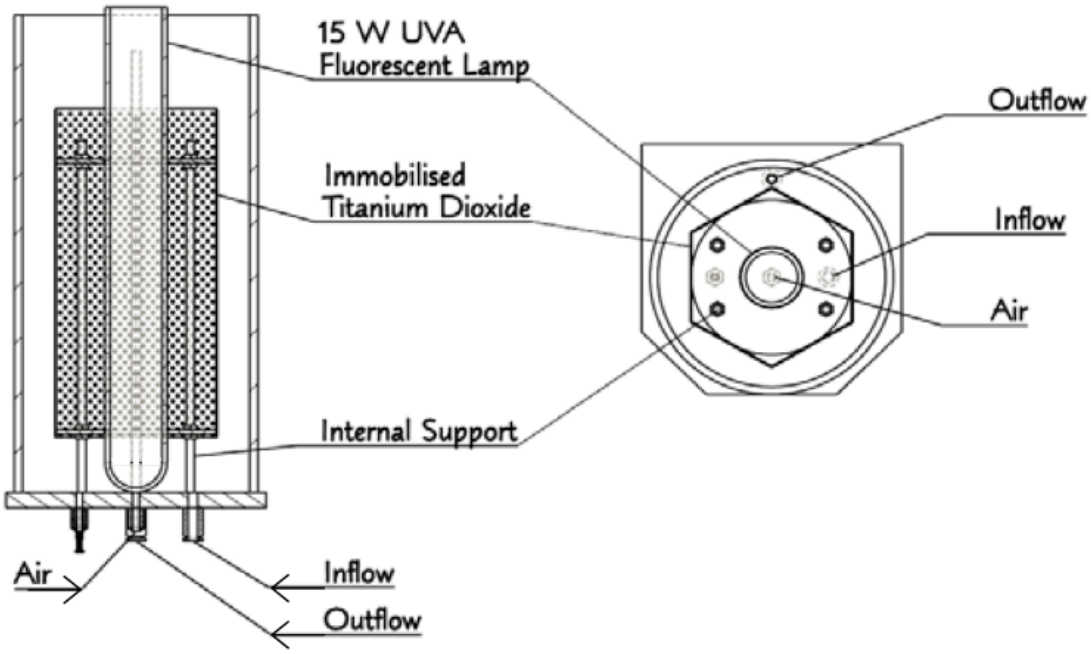

Figure 2: Honeycomb photocatalytic reactor (left: cross section, right: top view) [6]

Lim investigated the photocatalytic breakdown of MTBE through the use of a honeycomb shaped reactor as shown in Fig 2. P25 TiO_2 powder was immobilised onto a mesh through the use of heat treatment, and these meshes were then arranged in a hexagonal honeycomb shape. The UV light source required for the activation of the process was encased in a waterproof casing and placed in centre of the honeycomb. Air was bubbled upwards in the centre of the reactor while MTBE solution was passed through it before collection and testing.

Lim's research provides some useful insight into the development of TiO_2 photocatalytic reactors. Firstly, TiO_2 that is immobilised onto a mesh is a difficult material to work with as the coated mesh is not robust. It is easily removed with the wipe of a thumb, and some TiO_2 was noted to flake off during the experiments. This is not ideal for use in the field as groundwater contains suspended particles that can potentially cause further flaking of the TiO_2 coating. Moreover, the goal is to create an in situ reactor that requires only periodic maintenance, and having to replace TiO_2 meshes frequently is not ideal.

Secondly, Lim showed that larger amounts of MTBE are degraded when the velocity of the flowing contaminated water is slower. That is, the amount of MTBE degraded is a function of the hydraulic residence time, and that the critical hydraulic residence time is likely to be 1 day. This is shown in Fig 3. This is important in determining the efficient flow rates in a future reactor.

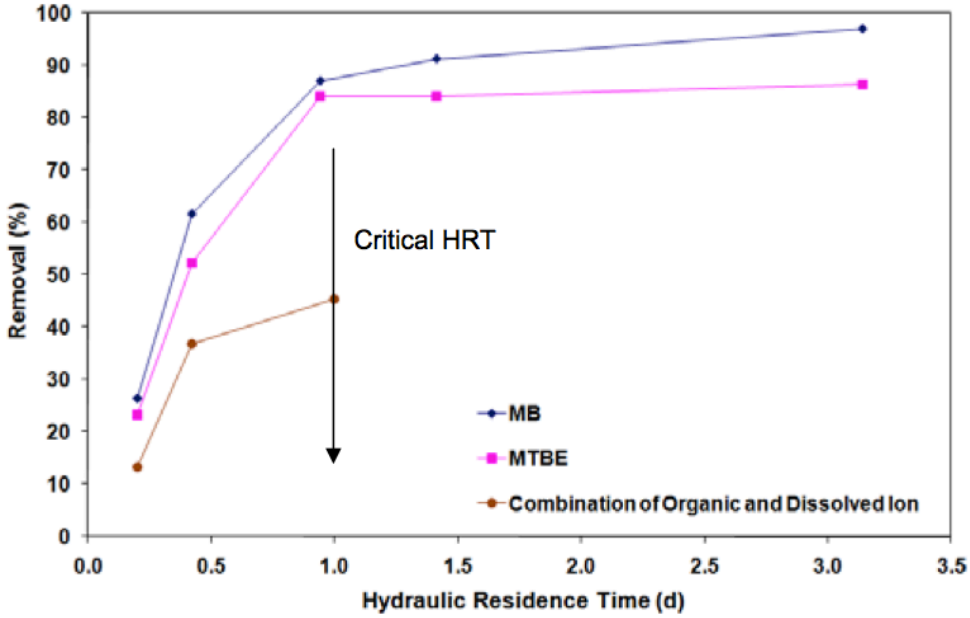

Figure 3: Percentage removal for varying hydraulic residence time [6]

Thirdly, we can use Lim's results from the honeycomb reactor to approximately quantify the rate of breakdown of MTBE by P25 TiO_2. Using the results for 1 day HRT (hydraulic residence time),

Catalyst area (cm^2)	Initial MTBE concentration (mg/l)	Volume treated (l)	MTBE removal (%)
720	80	8	84

Table 1: Honeycomb reactor selected results [6]

Hence, the clean up rate is 0.76 mg MTBE/cm^2 catalyst for a HRT of 1 day and 365nm light intensity of 1mw/cm^2. This is a useful result that will be used in the design of a reactor in section 4.

Stewart's [7] research provides insight into the relative performance of P25 TiO_2 and Pilkington Activ™ by using MB dye as a proxy for MTBE. Stewart used the same P25 TiO_2 mesh used by Lim, and tested it against Activ™ under the similar light intensity conditions used to obtain Table 1. As can be seen from Fig 4, the mesh is approximately 5.3 times as efficient as Activ™ at breaking down MB dye. As Lim [6] showed that MB dye and MTBE have a very similar response to photocatalytic degradation, we can make the preliminary assumption that Activ™ is approximately 5 times less efficient than Degussa P25 TiO_2. Thus, we can expect a clean up rate of 0.14 mg MTBE/cm^2 of Activ™ glass under the conditions of 1 day HRT and 1 mW/cm^2 light intensity of wavelength 365nm.

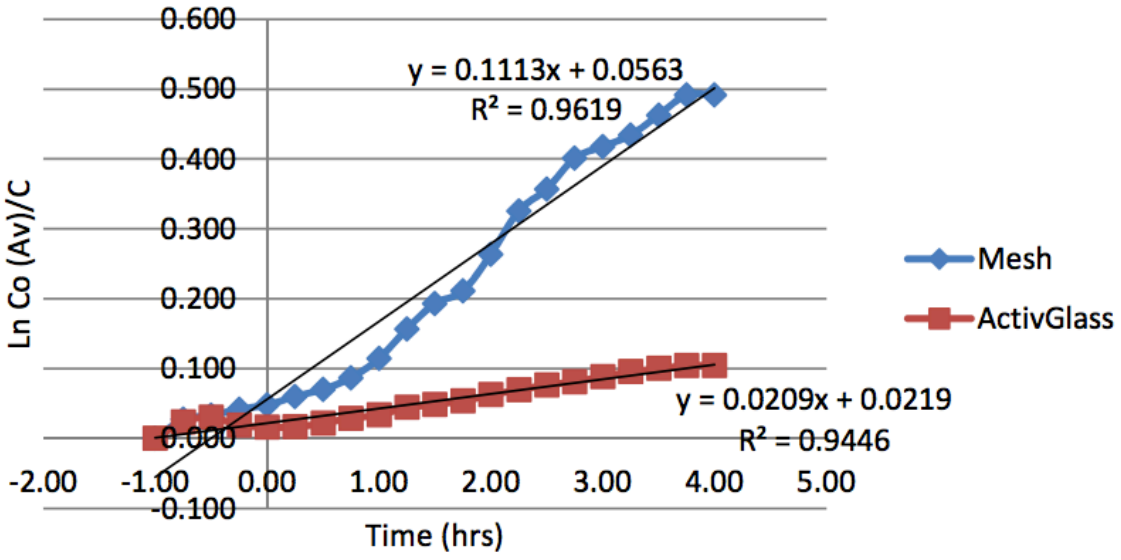

Figure 4: P25 TiO_2 comparison with Activ™ [7]

4. Project and Experiment Design

4.1 Project Design

As briefly mentioned in section 2, the purpose of this project is to use photocatalysis as a remediation technique in the cleanup of groundwater contaminated by MTBE. In order to achieve this in a simple, cost effective manner, it is best to use a funnel and gate system similar to one used in permeable reactive barriers. A funnel is created through sheet piling, and a pit is dug into which a reactive gate is placed. The contaminant plume is directed into the gate and remediated groundwater flows out.

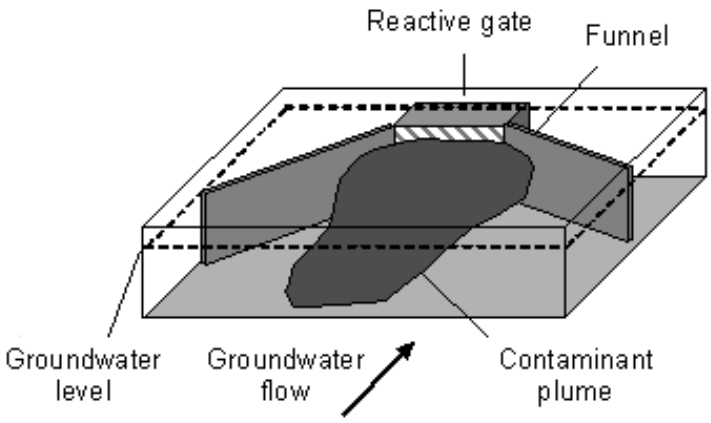

Figure 5: Funnel and gate system [11]

This system is quick and simple to implement in a variety of conditions, easily modified and easy to maintain. Mass balance calculations are sufficient to determine the length and width of the gate required in order to achieve critical HRT conditions, and the remediation process does not require extensive groundwork, unlike the case when excavation and soil washing techniques are employed.

4.2 Theoretical Approach to Gate Design

An initial theoretical approach was used to try and define experimental parameters, as well as the processes to be experimentally understood, as theoretical values may be inaccurate. A flowchart of the experimental sub-processes is shown in Fig 1 below.

While some quantities such as the intensity and wavelength of incident light can be reliably quantified and controlled, others such as drop back rate from valence band to conductance band can only be roughly approximated. Instead, it is better to determine the overall performance of Pilkington Activ™ by varying the reliably quantifiable inputs and measuring the effect on the rate of breakdown of MTBE.

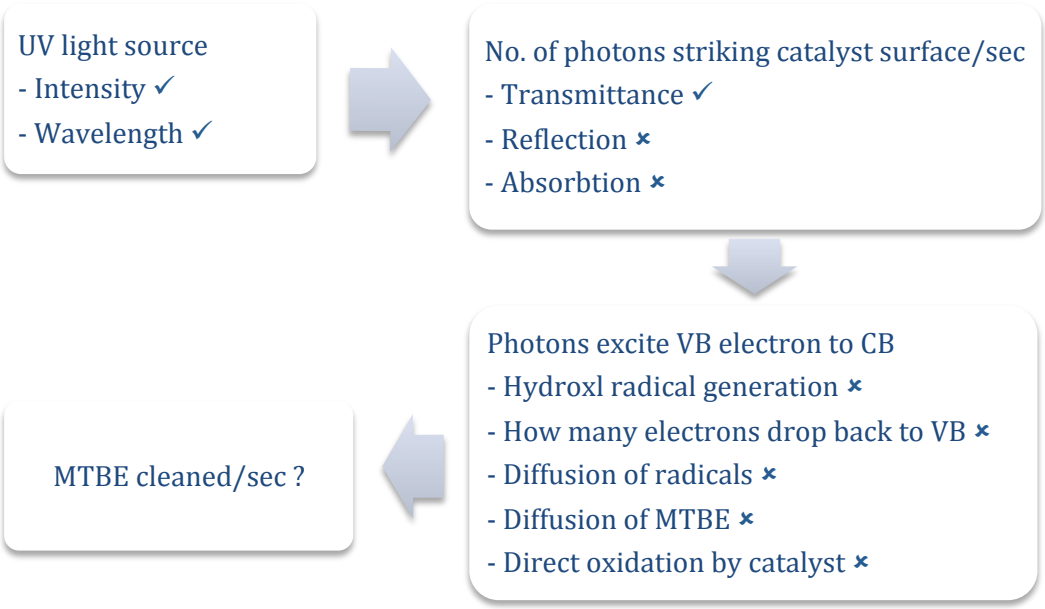

Figure 6: Flowchart of experimental sub-processes

4.3 Experiment Design

This sub-section will explain the principles and reasoning behind the chosen experimental design and introduce the reactor cell design as it is highly influenced by the experimental aims and objectives. Section 5 will progress into the details of the experimental techniques, equipment and error analysis.

In order to create an effective gate using Activ™, it is important to understand its effect on the breakdown of MTBE. To reiterate the project aims, the first step is to show that Activ™ can catalyse the breakdown of MTBE. Secondly, it is important to understand the effect of the following variables on the rate of breakdown of MTBE.

- Light intensity
- Rate of aeration
- Mixing
- Pollutant concentration

A prototype reactor can only be designed after these variables are well understood, as it has to make efficient use of available resources.

4.3.1 Light Source

As discussed in section 3, in order to activate the photocatalyst and excite an electron from the valence band to the conductance band, the light source must have a wavelength of less than 400nm. Moreover, Activ™ glass's transparency drops of rapidly at wavelengths below 400nm [7]. This has a detrimental effect if multiple sheets of Activ™ are to be stacked and activated by a single light source as sheets further away from the light source receive a smaller proportion of the light energy. As that light intensity is a factor in determining the rate of breakdown of MTBE, successive layers of Activ™ glass will be less efficiently utilised. Thus it is beneficial to use a light source that has a wavelength of less than 400nm, but higher than 350nm.

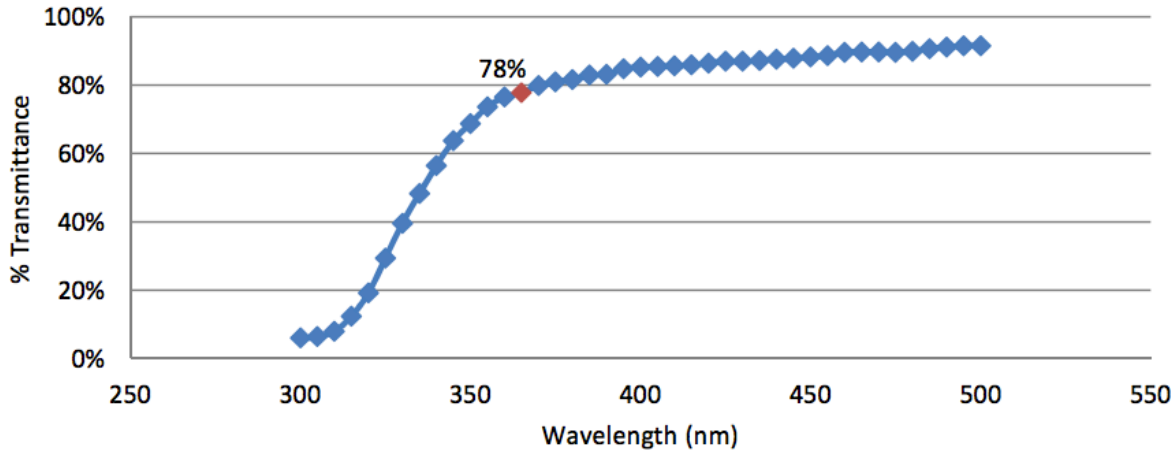

Figure 7: Activ™ transparency for UV-visible spectrum [7]

4.3.2 Reactor Cell Layout

Figures 8 and 9 show the proposed reactor cell design. It comprises a central aluminium frame sandwiched between a sheet of Activ™ glass and a sheet of ordinary 4mm window glass. The TiO_2 layer on the Activ™ glass is oriented toward the inside of the cell where the MTBE contaminated solution will be placed. The aluminium frame has 4 holes of diameter 5mm drilled into its sides to allow experiments to simulate groundwater flow and aeration using external pumps, and the 4 legs allow the cell to be used in a horizontal and vertical orientation. The holes also serve as access point from which samples can be taken at regular intervals. The internal sides of the frame are also angled to allow bubbled air to be directed to the exit holes. A wooden frame holds up the cell, and the cell may be used in a vertical or horizontal orientation.

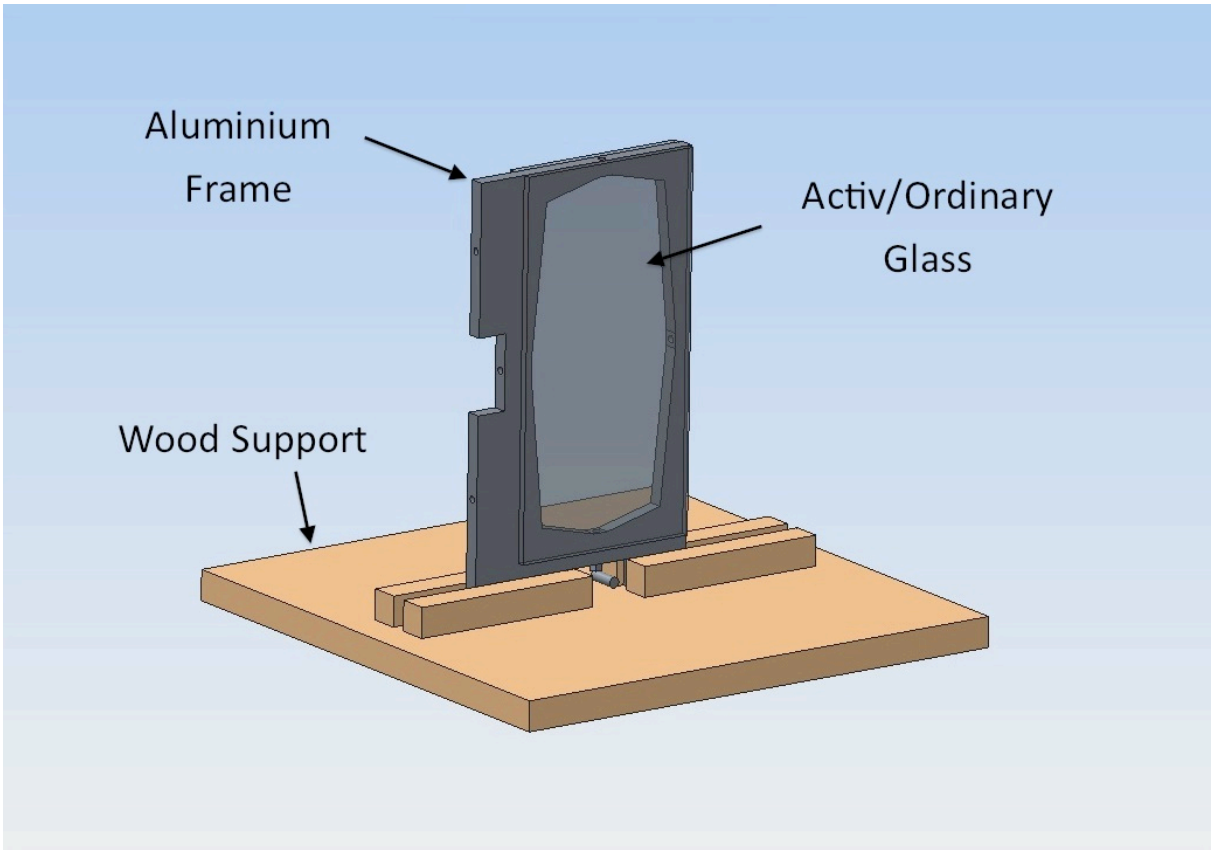

Figure 8: CAD rendering of reactor cell design shown in vertical orientation

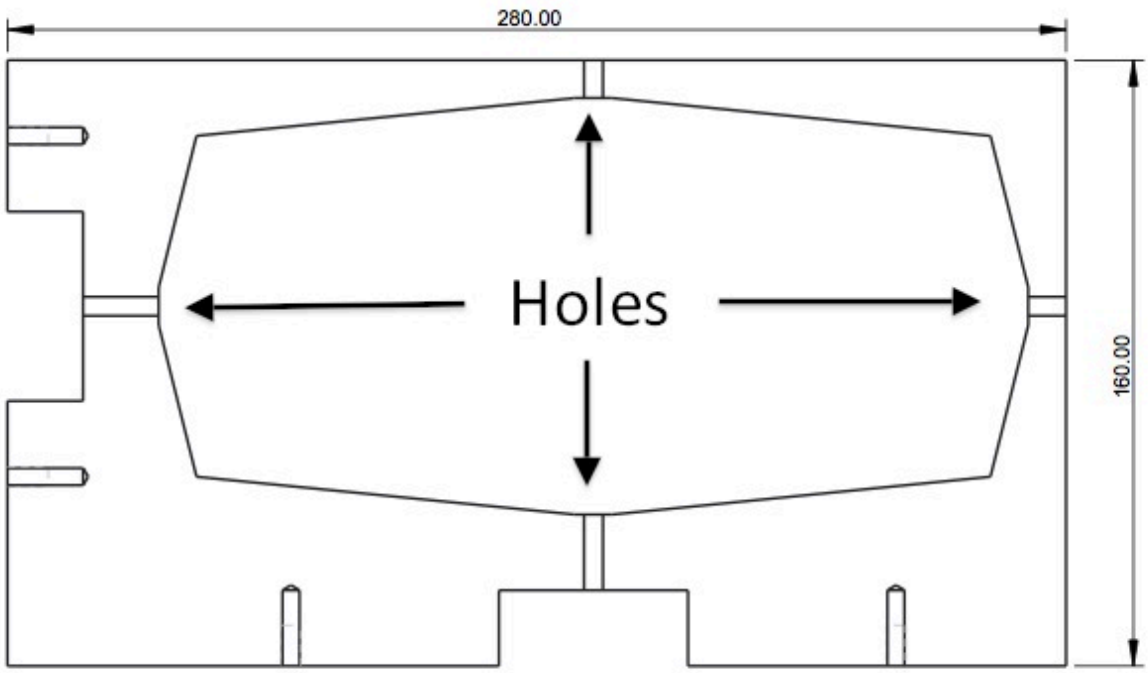

Figure 9: Cross section of aluminium frame shown in horizontal orientation

4.3.3 Reactor Cell Dimensions

As the proposed critical HRT is 1 day, and nominal groundwater flow rates in the field are on the order of 30cm/day, the cell was designed to have a length of 30cm to ensure sufficient time for MTBE breakdown to take place. As the available Activ™ glass size was restricted to 250mm by 250mm squares, the length of the cell was fixed at 250mm.

From section 3, the rate of MTBE breakdown is taken to be 0.14 mg MTBE/cm^2 of Activ™ glass under the conditions of 1 day HRT and a light intensity of 1 mW/cm^2 at a wavelength of 365nm. If nominal MTBE field pollution levels of 100 mg/l are taken as the initial concentration for the experiments, this requires 715cm^2 of Activ™ glass to fully break down the MTBE. Thus, a catalyst surface area of approximately 350cm^2 will be sufficient to fully catalyse the breakdown of 0.2 l of 100mg/l MTBE solution in 9 hours. Using this figure and working within the restrictions of available materials, the final internal dimensions of the cell were 240mm by 120mm by 10mm.

4.3.4 Experiment Layout

Figure 10 shows the experiment layout. The light source is mounted on a separate wooden frame, which allows the light intensity to be adjusted by varying its distance.

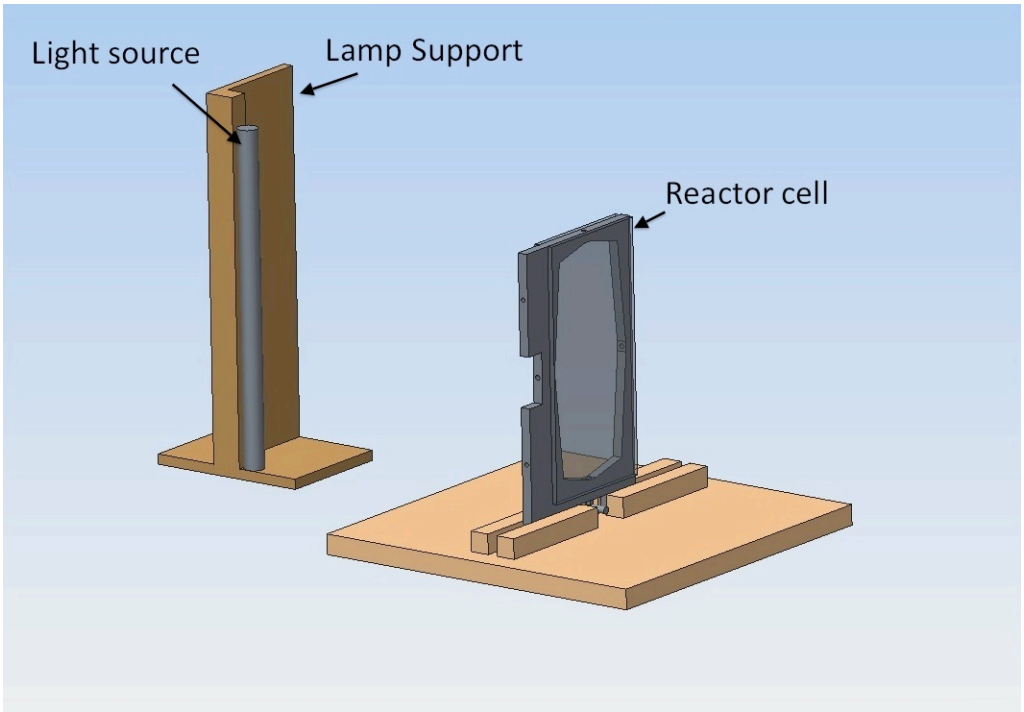

Figure 10: Experimental layout with cell in vertical orientation

5. Experimental Methods and Materials

This section builds on the principles of section 4 and considers the details of experimentation, including error analysis and proposition of experiments.

5.1 Experimental Method

5.1.1 Light Source

The light source used in this project is a 15W, 365nm Philips Cleo UVA lamp as shown in Figure 11. This is the same lamp used by Lim [6] and Stewart [7], allowing for easier comparison of results between projects. It satisfies the requirement that a suitable light source must emit UV light of wavelengths smaller than 400nm. Furthermore, as the wavelength is greater than 350nm, Activ™ remains relatively transparent, allowing 78% of 365nm light to pass through [7]. A wooden frame supports the lamp, allowing it to be used in a vertical and horizontal orientation.

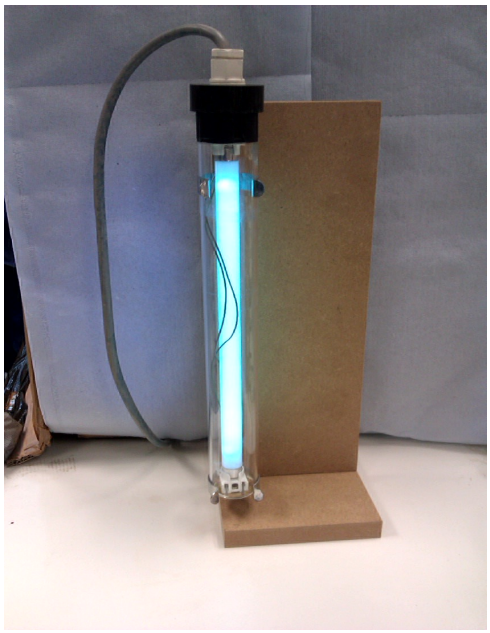

Figure 11: 15W Philips Cleo UVA lamp

5.1.2 Light Intensity Measurement

The light intensity was measured using an in house 365nm UV sensor combined with a standard voltmeter. The sensor was calibrated using a Thorlabs S120UV sensor and a Thorlabs PM100 light meter, and obeys a linear relationship between voltmeter reading and light intensity. The sensor was then used to measure the light intensity at varying distances from the Philips lamp, giving a useful relationship between distance and light intensity that is shown in Figure 12.

At distances smaller than 100mm, the sensor is unable to detect the true light intensity due to limitations in battery voltage. However, this can be reliably estimated from the available data.

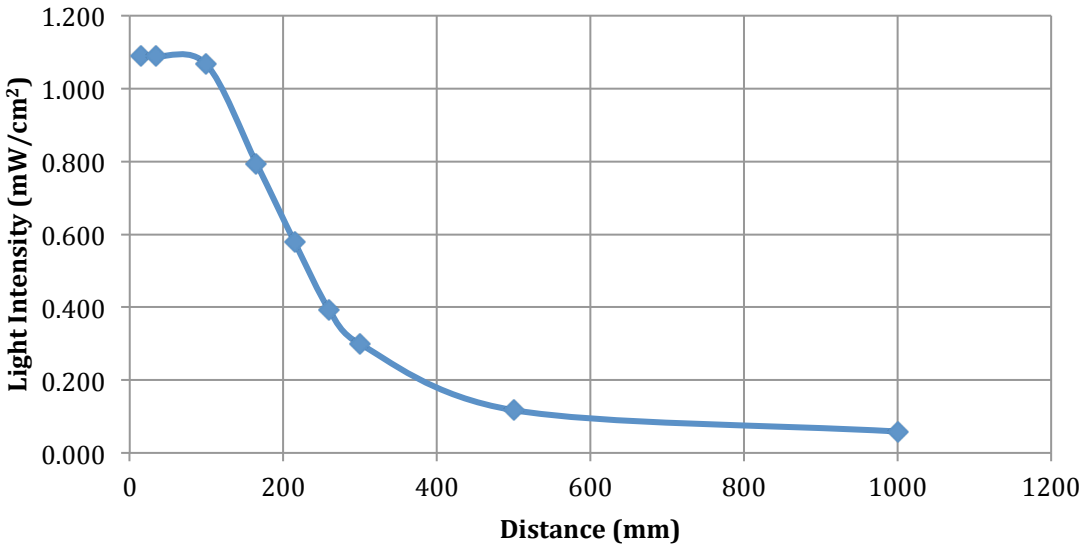

Figure 12: Light intensity variation with distance

5.1.3 Aeration

Aeration was achieved via a Hagen A-807 Optima air pump directed into the reactor cell via flexible 5mm tubing and fittings. The rate of airflow was adjusted using generic flow valves and was maintained at a constant 0.35ml/s flow rate throughout the project, unless otherwise specified.

5.1.4 Mixing

Mixing is provided through the use of a magnetic mixer. A 20mm long magnetic mixer is placed in the reactor cell and driven by a magnet attached to a Lego Mindstorms RCX 1.0 programmable motor. The motor can be programmed to turn on and off for specific durations, thus providing mixing while conserving energy by not running at full power for the entire duration of the experiment. The mixing program used for this project was a loop of 15 seconds at 240 rpm followed by 45 seconds at 0 rpm. The mixer is placed in the centre of the cell as shown in Figure 13.

Figure 13: Magnetic mixer

5.1.5 MTBE Stock Solution

The MTBE stock solutions used to calibrate the gas chromatograph (GC) were prepared by measuring out 500mg of analytical grade MTBE on a Mettler AE160 digital balance, and mixing this with 500ml of deionised water to create a stock solution of 1000mg/l. This was then diluted to obtain solutions of 100mg/l, 70mg/l, 50mg/l, 30mg/l, 10mg/l and 5mg/l, which were then sampled in a GC.

The 100mg/l MTBE stock solutions used for the experiments were prepared using by spiking 70µl of analytical grade MTBE using an Eppendorf 100µl pipette into a 500ml of deionised water in conical flask. While in theory this exceeds the 100mg/l concentration, in practice it was found that the resulting solution was reliably at a 100mg/l concentration with an error of less than 3%. 100mg/l concentrations were used to simulate approximate field concentrations near sources of MTBE contamination, as the device will be used under similar conditions. Fresh solutions were prepared immediately before experiment runs as MTBE is volatile.

5.1.6 Measurement of MTBE Levels Using Gas Chromatography

An Agilent 6850 Series gas chromatograph with flame ionisation detector was used in this project, using the same ambient headspace technique at 20°C used by Lim [6].

1ml samples of the MTBE solutions are placed in 2ml sealed vials and allowed to equilibrate. As MTBE is volatile, it vapourises and the air space in the vial (known as headspace) becomes contaminated with the MTBE. Given sufficient time to equilibrate, the concentration of MTBE in the headspace is proportional to the concentration of MTBE in the solution. This headspace volume can then be sampled in the GC by injecting a volume of 50µl into the column and obtaining a graphical readout of current (pA) vs time(s). The area under the peaks is then taken to be proportional to the concentration of MTBE in the solution, and is measured in pAs.

In practice, this method was found to be excellent for measuring volatile organics such as MTBE. The results obtained were repeatable, and the GC output graphs showed sharp, distinct peaks indicating accurate measurements. MTBE concentration and peak area were found to follow a linear relationship as shown in Figure 14. The GC was calibrated using stock solutions of concentration 100mg/l, 70mg/l, 50mg/l, 30mg/l, 10mg/l and 5mg/l. Storing the sample vials at 20°C for a period of 48 hours before sampling shows a distinct drop in concentration of MTBE in the vials. This drop is larger as the concentration of MTBE increases, justifying the fresh preparation of stock solutions before experiment runs.

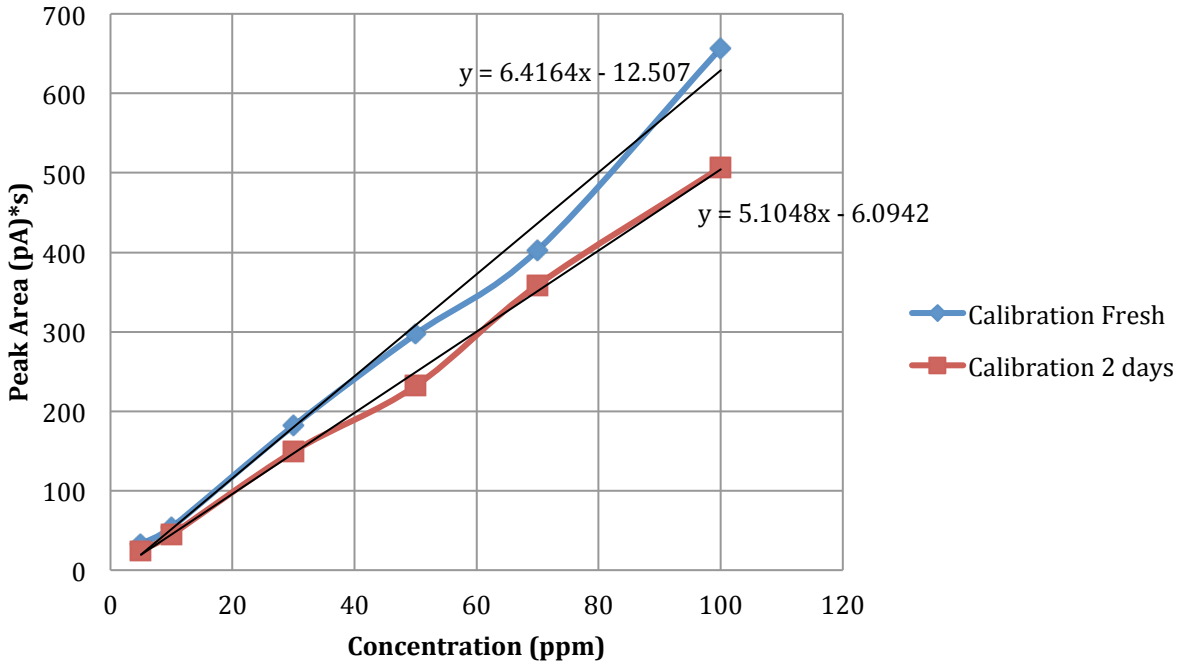

Figure 14: GC calibration of MTBE

5.1.7 Experimental Procedure

1. Reactor cell is prepared for particular experimental run. This includes connection/disconnection of aeration system, adjustment of distance between Activ™ catalyst surface and surface of Philips lamp and orientation of reactor cell.
2. MTBE stock solutions of 100mg/l were freshly prepared prior to each experimental run as described in subsection 5.1.4.
3. MTBE solution was transferred to reactor cell via holes in aluminium frame.
4. UV lamp was switched on at time 0 hours.
5. UV lamp was switched off at time 5 hours.

Notes

- Samples were taken every hour on the hour mark, beginning at 0 hours and ending at 5 hours. A calibration sample was also taken directly from the stock solution prior to the commencement of the experiment.
- Samples were taken using a glass syringe with a 12cm long hypodermic needle via the access holes in the aluminium frame.
- Samples are immediately stored in the lab refrigerator and kept under 5°C for the duration of the experiment. They are then removed together and left to calibrate at 20°C for the duration of 1 hour before being tested in the GC. This prevents loss of MTBE from the vial samples taken earlier in the experiment.
- Access holes were sealed using nylon screws during experiments without aeration to prevent loss of MTBE via vapourisation.
- Control experiments are run with all conditions identical with the exception of switching off UV lamp.

5.2 Error Analysis

There are multiple ways in which to establish the error inherent in the experimental procedure. The most common is to evaluate the error present in each step of the experiment, and to then obtain the overall error using the root-mean-squared method. While this is suitable for certain steps of the experimental method used in this project such as the error inherent in the Mettler digital balance and the error in volume of the conical flask, it is unsuitable to determine the overall error. This is because the major source of the error arises from the volatility of the MTBE. MTBE is lost when the stock solution is mixed to ensure homogeneity, when it is transferred from the conical flask to the reactor cell as well as during the course of the experiment due to its volatile nature. This nature cannot be effectively quantified using the root-mean-squared method.

As such, it is better to obtain the overall error directly such that it encompasses the accumulation of errors at each individual stage of the experiment. This is done by repeating certain sections of the overall experimental method to obtain multiple readings, and then conducting a statistical analysis.

The error analysis method used is as follows. As the stock solutions are benchmarked to a concentration of 100 mg/l and multiple stock solutions were created at this concentration over the course of the project, it is possible to obtain the overall standard error present at the beginning of the experiment runs. In order to then obtain the standard error present in the GC, multiple sample vials were run through the GC at concentrations of 100mg/l, 50mg/l, 10mg/l and 5mg/l. The standard error can then be used to evaluate the experimental results. The mean, standard deviation and final standard error are tabulated in the following section.

5.2.1 Standard Error

Concentration (mg/l)	Sample value mean μ (pAs)	Sample standard deviation (pAs)	Sample standard error (%)
100 (Stock solution error)	113.5	2.65	2.3
100 (GC error)	112.1	1.21	1.1
50	56.3	0.95	1.7
10	11.4	0.52	4.5
5	5.62	0.18	3.2

Table 2: Tabulated standard error

Error due to Mettler Balance

Accuracy of balance = ±0.1mg

Weight of MTBE measured = 500mg

Error = 0.02%

Error due to conical flask

Accuracy of flask = ± 1ml

Volume measured in flask = 500ml

Error = 0.2%

Error due to Eppendorf 100μl pipette

Error = 0.8% [12]

As expected, the standard error increases as the concentration of MTBE decreases. This is due to the error inherent in the GC having a greater effect at lower concentrations of MTBE. The overall error due to the making of the stock solution is also low at 2.3%. It is, however, substantially higher than the accumulated error from the lab equipment; the root-mean-squared value of which is 0.58%. As such, the volatalisation of MTBE dominates the error value present at higher concentrations and at the start of the experiment. At lower concentrations of MTBE, the error from the GC rises to 4.5% at 10mg/l. At this stage, the error from the GC is the dominant source of error.

5.3 Proposed Experiments

This section introduces the details of the experiments to be carried out, as well as the rationale behind a particular experiment. The proposed experiments will be conducted using layout shown in Figure 15 below. The Activ™ glass will be facing the light source. This is referred to as the Standard Orientation. In one experiment run, the ordinary glass will be facing the light source and this is referred to as the Flipped Orientation. Control experiments will be run and are shown in section 6.

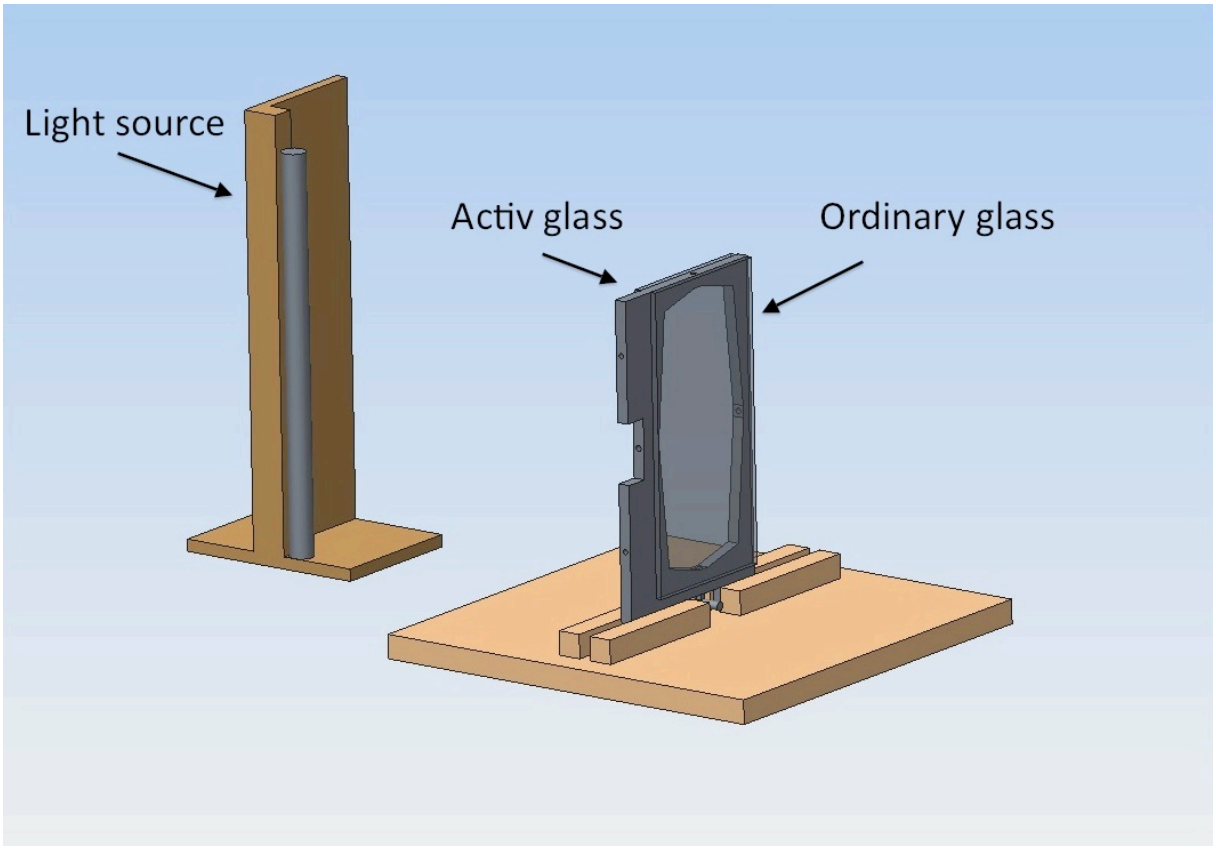

Figure 15: Standard orientation experiment layout

5.3.1 Feasibility of using Pilkington Activ™ to catalyse MTBE

Initial MTBE concentration:	100mg/l	Aeration:	0.35ml/s
Distance from light source:	5cm	Mixing:	Off
Orientation of Activ™:	Standard	Duration:	5 hours

This experiment is primarily concerned with 2 objectives. Firstly, it will determine if Pilkington Activ™ can catalyse the photocatalytic breakdown of MTBE when illuminated by UV light. Secondly, it will verify if this breakdown can occur quickly enough for it to be a viable cleanup technique. It will also verify if the calculations of breakdown rates approximated from previous work conducted on the subject are correct. 3 experiments are conducted. The first with the conditions as shown, the second with identical conditions with the exception of the UV light being turned off (control), and the third with the UV light on but with no aeration.

5.3.2 Separation of aeration and mixing

Initial MTBE concentration:	100mg/l	Aeration:	Off
Distance from light source:	5cm	Mixing:	240rpm
Orientation of Activ™:	Standard	Duration:	5 hours

The reactor cell is aerated from the bottom access hole. The bubbling is vigorous, and thus provides a mixing effect as well as adding oxygen to the MTBE solution. It is important to separate the effects of mixing from that of aeration. Multiple experiments were performed at this stage and are best explained in conjunction with the results in section 6.

5.3.3 Variation of light distance

Initial MTBE concentration:	100mg/l	Aeration:	0.35ml/s
Distance from light source:	Varies from 5 - 70 cm	Mixing:	Off
Orientation of Activ™:	Standard	Duration:	5 hours

This series of experiments was conducted to determine the effect of varying the light intensity on the breakdown of MTBE. Light input is the costliest operating expense of the cell, and minimising the light input required will satisfy the sustainability criterion.

5.3.4 Flipped orientation

Initial MTBE concentration:	100mg/l	Aeration:	0.35ml/s
Distance from light source:	5cm	Mixing:	Off
Orientation of Activ™:	Flipped	Duration:	5 hours

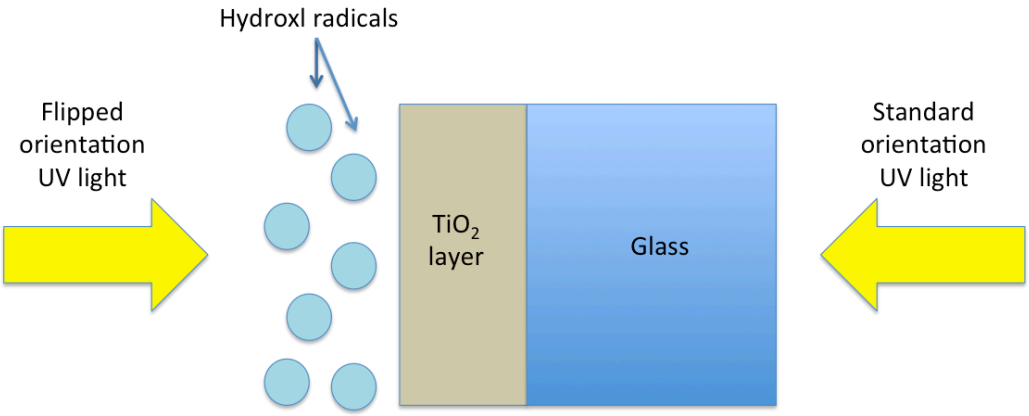

Figure 16: Expanded sketch of Activ™ glass

This experiment was conducted to investigate the effect of providing UV light in the standard and flipped orientations. In the standard orientation, UV light passes through 4mm of glass before striking the side of the 15nm thick TiO_2 layer closest to the glass surface. However, the holes and hydroxyl radical only have an effect on MTBE if they are generated on the side of the TiO_2 layer facing the solution. In the flipped orientation, the UV light passes through 4mm of glass and 10mm of MTBE solution before striking the TiO_2 layer. Thus it is prudent to check if the orientation has an effect on MTBE breakdown rates.

5.3.5 Low concentration of MTBE

Initial MTBE concentration:	10mg/l	Aeration:	Off
Distance from light source:	5cm	Mixing:	240 rpm
Orientation of Activ™:	Standard	Duration:	5 hours

As will be explained in section 6, it is shown that external aeration is required for MTBE breakdown at higher concentrations. However, at lower concentrations, there is sufficient oxygen present in the water to allow the MTBE to be degraded. As such, a low concentration run is conducted to investigate this hypothesis. Moreover, it is prudent to investigate if Activ™ has a catalysing effect at lower concentrations of MTBE.

6. Results and Discussion

6.1 Processing of results

Output values from the GC are converted to MTBE concentration values using Figure 14 in section 5.1.6. Calibration sample values taken from the MTBE stock solution are used as a benchmark and taken to be at a concentration of 100mg/l. The remainder of the sample values obtained from the GC are then calibrated against this and converted to MTBE concentration. These are then plotted on a graph of normalised concentration C/C_0 (concentration divided by calibration concentration) against time, as well as $\ln(C/C_0)$ against time. The results are expected to follow the trends shown in Figure 17[6].

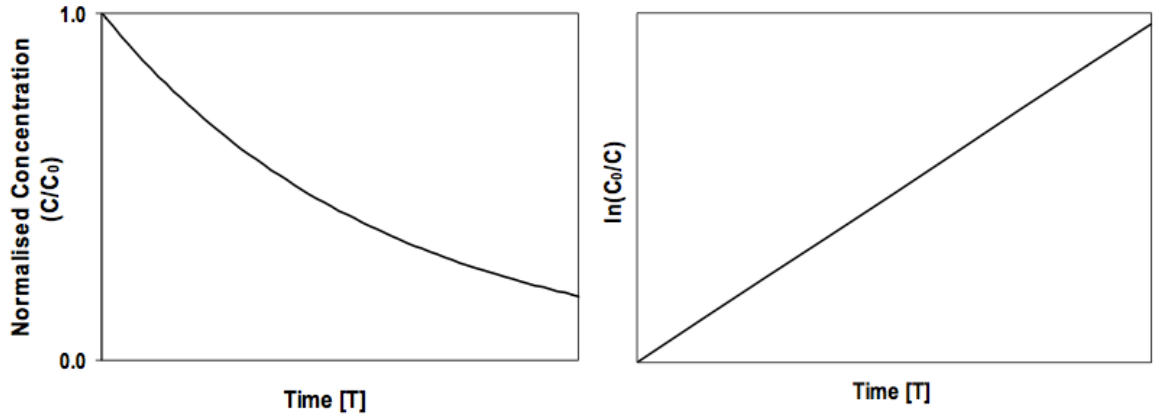

Figure 17: Experimental expected result trend [6]

The plot on the left demonstrates the expected exponential decay of MTBE over time. As the concentration of MTBE decreases, the rate of breakdown also decreases. The plot on the right demonstrates the method of obtaining the rate of reaction. The gradient of the line can be used when comparing the rate between multiple experimental runs.

6.2 Experimental Results

6.2.1 Feasibility of using Pilkington Activ™ to catalyse MTBE

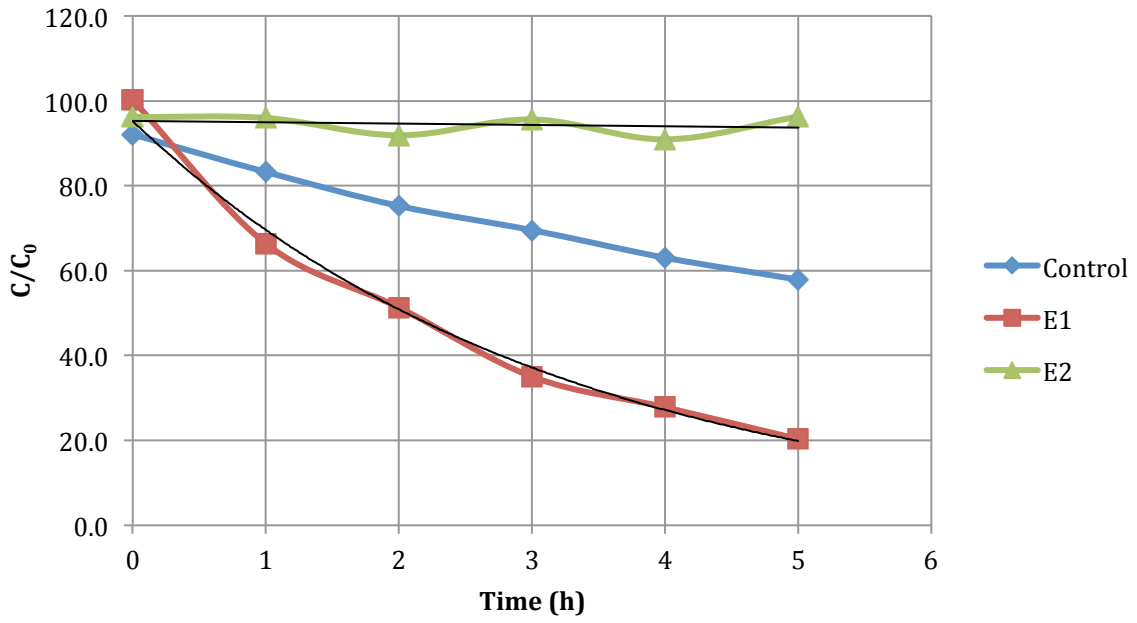

Figure 18: Feasibility experiment results

Experiment	UV light distance (cm)	Aeration (ml/s)
E1	5	0.35
E2	5	Off
Control	Off	0.35

Table 3: Summary of experimental conditions

The initial concentration of MTBE for all runs was 100mg/l.

A comparison of E1 and the control demonstrates that the UV light has a significant effect on the breakdown on MTBE. At the end of a period of 5 hours, the control experiment shows a drop in concentration of 34.2% while E1 shows a drop of 80.0%. A comparison of E1 and E2 shows that aeration is a necessary condition for the photocatalytic reaction, as E2 shows no appreciable drop in concentration despite the presence of UV light.

This confirms the 2 primary objectives for this experiment; Pilkington Activ™ is able to catalyse the breakdown of MTBE in the presence of sufficient UV light and oxygen, and that it is able to break down most of the MTBE in a short enough period of time to have a potential use in photocatalytic degradation of MTBE. This series of experiments also provides other insights.

Firstly, an aeration rate of 0.35ml/s is likely to be excessive. At this rate, 34.2% of the MTBE present was vapourised and lost. In a field scenario, this would mean that a substantial proportion of the MTBE present in groundwater would enter the atmosphere instead of being degraded by photocatalysis. This would result in either air pollution, or require the use of a separate treatment stage for the vapourised MTBE, both of which have negative consequences. Air pollution is unacceptable, while the use of a separate treatment stage greatly increases the complexity and cost of a future prototype design. This can be minimized by fine tuning the rate of aeration such that it provides sufficient oxygen to fuel the reaction while minimising the MTBE lost as vapour. A lower rate of aeration will decrease the amount of MTBE lost as it reduces the total surface area of uncontaminated air in contact with the contaminated MTBE solution.

Secondly, E1 shows a net degradation of 45.8mg/l in a period of 5 hours (removing the MTBE lost to the atmosphere in the control experiment). In section 4.2.3, full degradation is expected in a period of 9 hours. Hence E1 appears to be in line with the theoretical assumptions formed as a result of Lim's [6] and Stewart's [7] work.

Lastly, the aeration provides 2 separate functions. Firstly, it provides oxygen, which dissolves in the water and is used in the photocatalytic reaction. Secondly, the air bubbles travel the full length of the cell and provide a mixing effect as a result of the vortices generated. As such, it raises the question of weather the reaction requires external aeration, or if it requires only mixing. The former situation arises if it is a lack of oxygen in the water that limits the reaction, and the latter situation is the solution if slow diffusion is the limiting factor. As such, it is important to separate the effects of aeration and mixing. This is described in the next subsection.

6.2.2 Separation of aeration and mixing

A theoretical approach to determining the required amount of oxygen in the cell is as follows. From Lim's [6] work, we obtain the overall equation for the breakdown of MTBE as shown. 1 molecule of MTBE requires 7.5 molecules of oxygen to be fully decomposed into carbon dioxide and water.

$$C_4H_9OCH_3 + 7.5O_2 \rightarrow 5CO_2 + 6H_2O$$

The solubility of oxygen at 20°C is 8 mg/l. MTBE has a molecular weight of 88g/mol and oxygen has a molecular weight of 32g/mo. Amount of MTBE cleaned $= 8/(32\times7.5)\times 88 = 2.9$ mg/l. This is only a 3% drop in the initial concentration of MTBE and indicates that external aeration is likely to be critical.

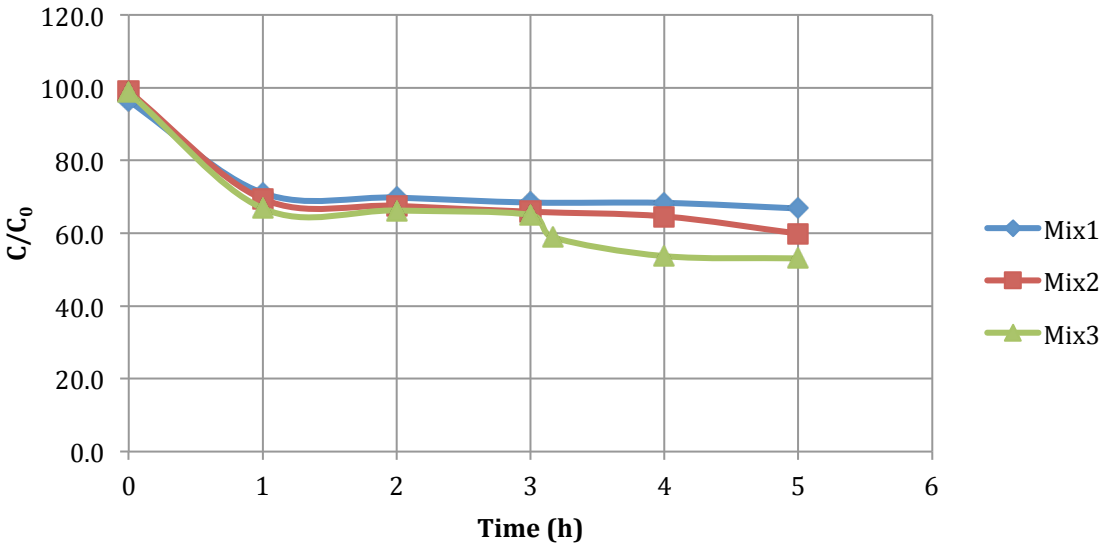

Figure 19: Mixing experimental results

Experiment	UV light distance (cm)	Aeration (ml/s)	Mixing (rpm)
Mix 1	5	Off	240
Mix 2	5	Off	240
Mix 3	5	Temporary	240

Table 4: Mixing experimental conditions

Mix 1 and 2 are repeats of the same experimental conditions, and show a drop in initial concentration of MTBE of 32% within the first hour and no substantial drop thereafter. Mix 3 is identical to mixes 1 and 2 in all aspects, with the exception of temporary aeration. The cell was aerated at 0.35ml/s for a period of 10min immediately after the 3 hour sample was taken.

Mix 1 and 2 demonstrate that mixing is likely to be a critical factor if the photocatalytic reaction is to occur within a period of 5 hours. While in theory this reaction would occur eventually without mechanical mixing due to diffusion, it shows that a prototype reactor requires mixing in order to achieve the photocatalytic breakdown of MTBE within a short frame of time.

Mixes 1 and 2 also show that there is sufficient oxygen present in the water to degrade 32 mg/l of MTBE. This is significantly larger than the theoretical maximum of 3 mg/l. A possible explanation for this is that the remaining concentration of MTBE in the vial is the indicator being measured, and not the carbon dioxide and water generated as a result of photocatalytic degradation.

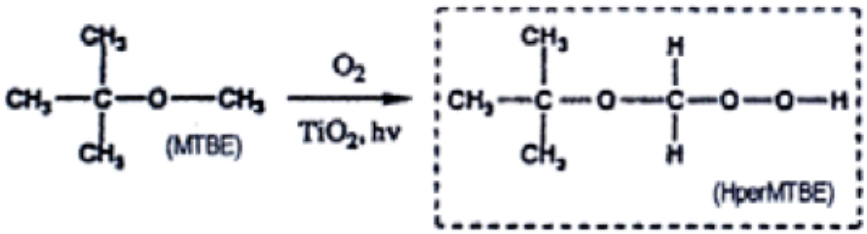

Figure 20: First stage of MTBE degradation [6]

The full breakdown of MTBE to carbon dioxide and water comprises multiple intermediate steps and intermediate products. These intermediate products cannot be measured in the GC available, and hence do not show up on output graphs. Figure 20 shows the first stage of MTBE degradation, which requires only 1 molecule of oxygen per molecule of MTBE degraded. If we assume that all the oxygen dissolved in the water was used up in the first stage of the MTBE degradation reaction, this brings the new theoretical maximum drop of MTBE to 22%. This is much closer to the experimental value of 32%, but the experimental value is still excessively large.

A possible explanation for the remaining 12% drop is due to bubbles of air stuck onto the surface of the ordinary glass (bubbles do not adhere to the Activ™ TiO_2 layer). An approximation of the volume of air present as a result of these bubbles is 880mm^3, which was generated by approximating the size of the bubbles present and multiplying this by the area and number of bubbles per cm^2. This provides an additional 3.4 mg/l of oxygen in the cell, which would react with 9.4 mg/l of MTBE. This brings the total theoretical amount of MTBE degraded to 31.4%, which agrees with the experimental result.

Mix 3 shows that oxygen is a limiting factor in the reaction. The reaction proceeds initially due to the presence of mechanical mixing, but stops within the first hour due to a lack of oxygen. After aerating the cell for 10min, some additional oxygen is introduced into the cell and the reaction continues and provides an additional drop 4.1% (disregarding the MTBE lost as vapour during aeration). This is not close to the 32% drop experienced in the first hour as it is likely that 10min of aeration is insufficient. Nonetheless, it shows that both mechanical mixing and additional aeration are critical to the reaction.

6.2.3 Variation of light distance

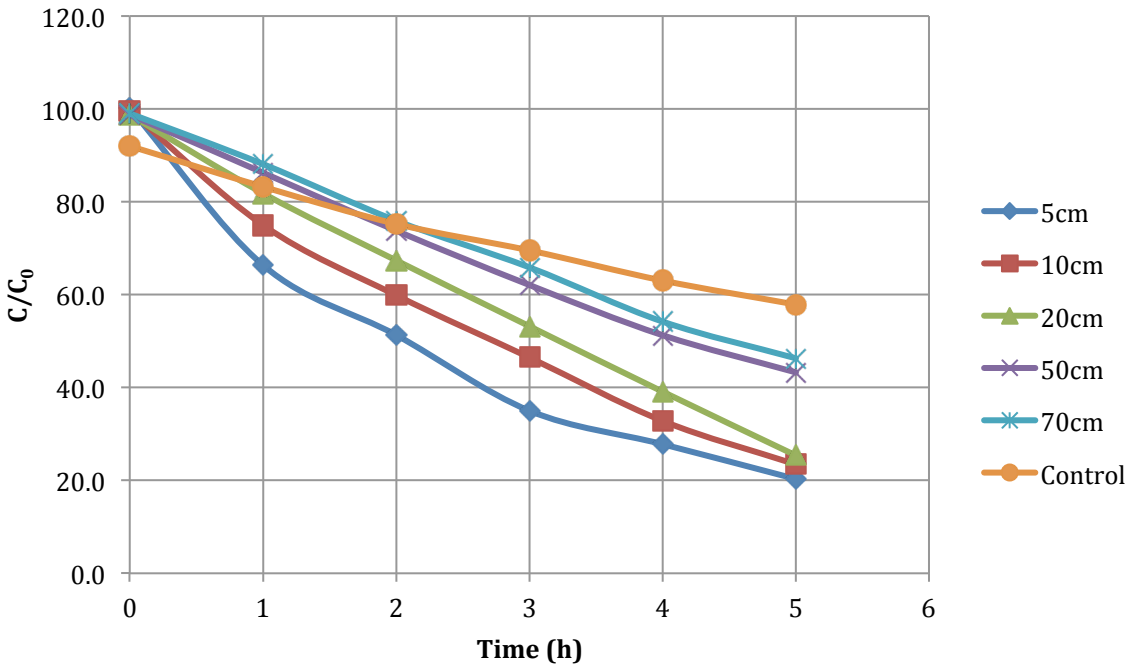

Figure 21: Light variation experimental results C/C_0 vs time

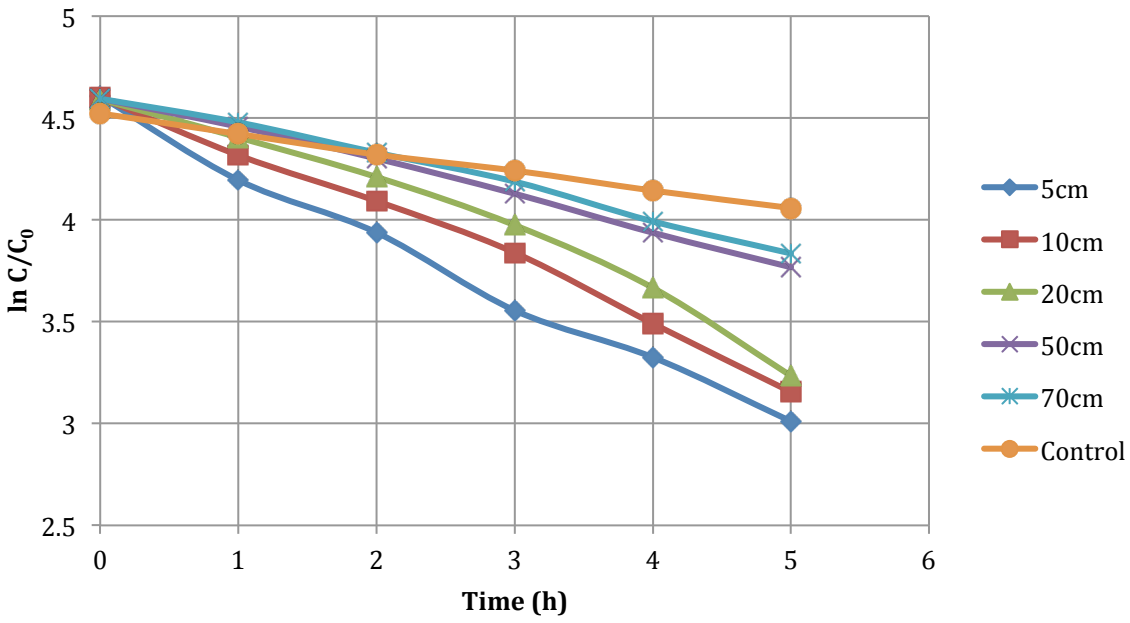

Figure 22: Light variation experimental results $\ln(C/C_0)$ vs time

The initial concentration of MTBE for all runs was 100mg/l. Aeration was provided at 0.35ml/s and there was no mechanical mixing.

UV light distance (cm)	Light intensity (mW/cm^2)	MTBE concentration at 5h (mg/l)	$\ln(C/C_0)$ Trendline gradient
5	1.52	20.3	0.313
10	1.09	23.5	0.285
20	0.63	25.4	0.264
50	0.12	43.3	0.166
70	0.09	46.3	0.154

Table 5: Tabulated experimental results

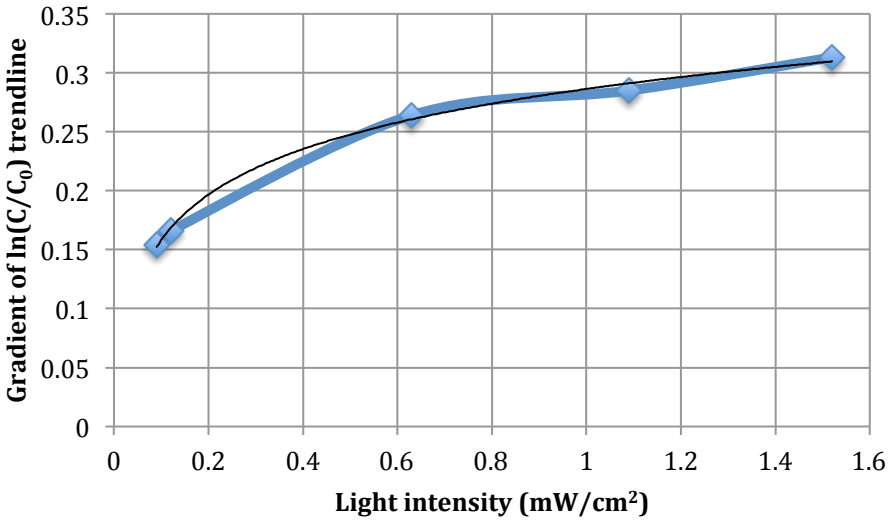

Figure 23: Plot of light intensity against gradient of ln(C/C0) trendline

Figure 21 shows a decrease in the concentration of MTBE for all runs. The experiments with UV light show a greater drop in concentration than the control. This confirms the results of section 6.2.1 by showing that UV light is required for photocatalysis, and that a drop in light intensity leads to a decrease in MTBE degraded.

Figure 22 shows a plot of $\ln(C/C_0)$ against time for varying light distances. The absolute value of the gradient decreases as the distance from the light source increases. This is in line with the theory that a lower light intensity will slow down the rate of photocatalysis of MTBE.

Figure 23 shows a plot of light intensity against gradient of $\ln(C/C_0)$ trend lines. This plot is close to logarithmic in shape. The rate of breakdown of MTBE, characterised by the gradient of the $\ln(C/C_0)$ trend lines, is shown to increase at a decreasing rate with an increase in light intensity. This suggests a decreasing rate of return with increasing light intensity, and the catalyst appears to become saturated with light as the light intensity increases.

6.2.4 Flipped orientation

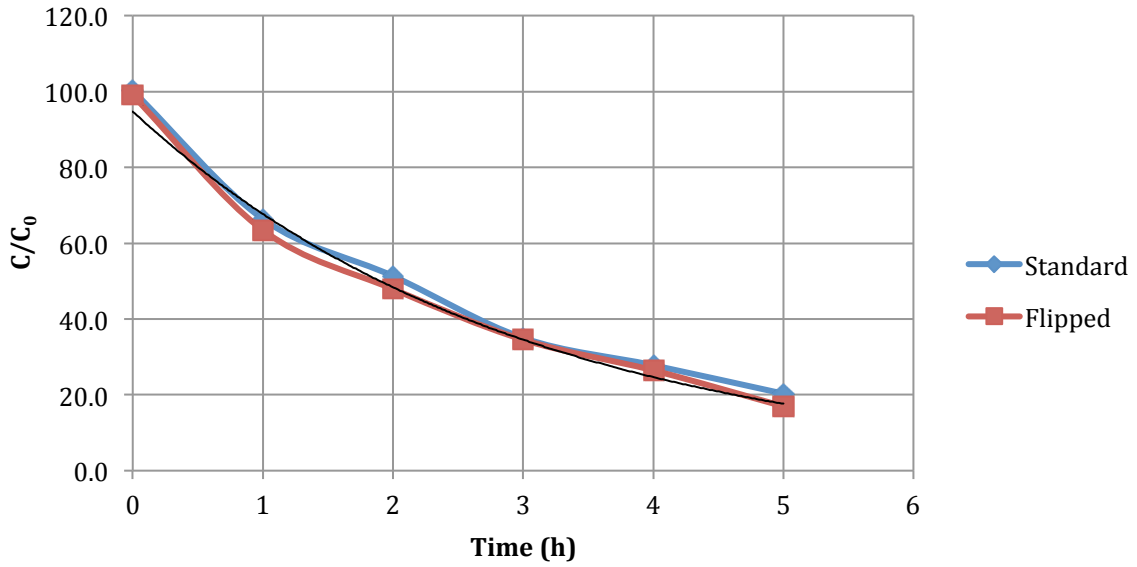

Figure 24: Flipped orientation experimental results

Figure 24 shows that there is little difference in results between the standard orientation and flipped orientation. This is likely due to the fact that in both cases, UV light has to pass through 4mm of glass, which is the main barrier to UV light. In the flipped orientation, the UV light has to pass through a further 10mm of MTBE solution, and the drop in light intensity as a result is negligible. The results also show that the results of illuminating the TiO_2 layer from the glass side and the solution side show no appreciable difference. In both cases, the plots follow the exponential decay expected.

This is a useful result as it shows that the direction of illumination does not matter in a prototype reactor, allowing a greater scope for the arrangement of the catalyst surfaces.

6.2.5 Low concentration of MTBE

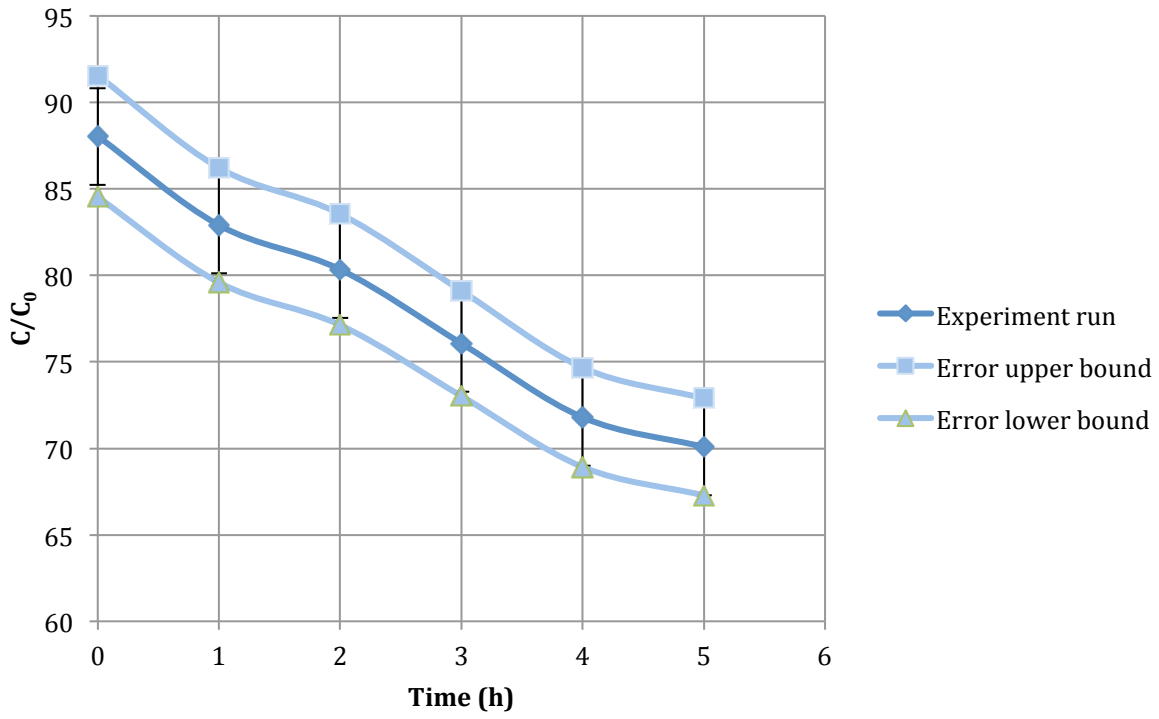

Figure 25: Initial concentration 10mg/l experiment results

Figure 25 shows an experiment run using an initial concentration of 10mg/l MTBE solution. The plot shows an overall decrease in concentration of 18% over 5 hours, or 1.8 mg/l of MTBE. This is within the theoretical maximum limit of MTBE degradation as described in section 6.2.2. With a low concentration of 10 mg/l, there is theoretically sufficient oxygen to deplete 5 mg/l or 50% of the MTBE present. It is likely that at low concentrations, the rate of reaction of MTBE degradation is slow enough to require a longer degradation time than 5 hours.

This has important implications for the prototype design. Firstly, even at such a low concentration, some external aeration is required to provide sufficient oxygen for full breakdown. Secondly, the rates of reaction are slow at concentrations on the order of magnitude of 10mg/l. As the desired concentration of MTBE in groundwater has to be below 5ppb, or 0.005 mg/l to be below the human taste threshold, Pilkington Activ™ will require substantial periods of time in order to catalyse the breakdown of MTBE.

7. Conclusions and Implications

This project has been able to investigate and understand some of the behaviour of Pilkington Activ™ regarding its use as a catalyst in the photocatalytic breakdown of MTBE in groundwater.

Firstly, it has been shown that Pilkington Activ™ is able to catalyse the breakdown of MTBE in the presence of sufficient oxygen and UV light at a rate that makes it suitable of use in groundwater treatment. This holds true for the range of initial concentrations of MTBE ranging from 10 mg/l to 100 mg/l. This is an important step as it confirms the validity of the project.

Secondly, it has been shown that UV light is a critical component in the photocatalysis of MTBE. Decreasing levels of light intensity yield lower rates of decomposition. Increasing the light intensity increases the rate of reaction, but at a decreasing rate, indicating a diminishing rate of return effect. This, again, is important as it sets a vital requirement for future use of Pilkington Activ™ in a photocatalytic reactor. Moreover, the effect of a diminishing rate of return with increasing light intensity has implications regarding the cost of a photocatalytic reactor. Too low a light intensity will not be sufficient to complete the breakdown quickly enough, while an excessive amount of light intensity will drive up cost, reducing the cost efficiency of the system.

Thirdly, it has been shown that aeration is a critical requirement as well. Water does not contain sufficient dissolved oxygen in order for the full breakdown 100 mg/l of MTBE. In theory, it only contains sufficient oxygen for the full breakdown of 3 mg/l of MTBE. As such, a means of aeration will be required in a future prototype design. Furthermore, excessive aeration causes a large proportion of MTBE to be lost to the atmosphere as vapour. This is unacceptable as it causes air pollution. Thus a secondary method of treatment must be employed in a prototype design in order to treat the escaping MTBE vapour. Additionally, the rate of aeration should be adjusted such that it provides sufficient oxygen to fuel the breakdown of MTBE while minimising the MTBE lost as vapour. A closed loop system that recycles air used for aeration can also be used to minimise the amount of MTBE lost from the groundwater.

Fourthly, it has been noted that mixing is a critical requirement as well. A lack of mixing results in a very slow rate of reaction as it is dependent on diffusion alone. This, combined with the slow rate of catalysis as a result of Pilkington Activ™ reduces the overall rate of reaction to unacceptable levels for groundwater treatment. In experiments where mechanical mixing was provided, the rate of reaction approached rates consistent with theoretical assumptions. It should be noted that mixing could be provided using aeration, as the bubble vortices are sufficient. A combination of aeration and mixing could be used to provide sufficient drivers for the reaction while limiting the energy input required.

Next, it has been demonstrated that the orientation of the TiO_2 layer on Pilkington Activ™ with regard to direction of illumination of UV light is inconsequential. The TiO_2 layer is possibly so thin at 15nm that the orientation has no effect. This is a useful result as it broadens the scope of design of a prototype reactor. UV light can be used to illuminate the catalyst surfaces in various arrangements in order to determine the most efficient design.

Lastly, it has been shown that breakdown of MTBE at low concentrations can be catalysed by Pilkington Activ™. However, the drawback is that the rates of reaction are slow, potentially making Activ™ unsuitable for use at low concentrations of MTBE. This, however, does not detract from the fact that Activ™ can be used efficiently at higher concentrations, making it useful as a first stage reactor in order to bring down the concentration of MTBE to a level where other techniques can be effectively utilised. Pilkington Activ™ is unlikely to be able to clean up MTBE to acceptable levels on its own as the human taste threshold for MTBE is 0.005 mg/l. At such low concentrations, it seems unlikely that Pilkington Activ™ can maintain reasonable rates of cleanup.

Pilkington Activ™ fulfills most of the requirements for the use as a catalyst in the photocatalytic cleanup of MTBE from groundwater. It is cheap, commercially available and robust, making it suitable for field use. It has been shown to be effective at decomposing MTBE under suitable conditions and at rates that enable it to be useful for cleaning groundwater. In this regard, it fits the bill in developing sustainable, low energy methods of remediating groundwater.

8. Future Work

As described in section 4, the long-term end purpose of this project is to develop a suitable prototype that is able to clean up MTBE in groundwater. In this regard, this project has provided insight into the behaviour of Pilkington Activ™ in response to the variables of light intensity, aeration, mixing, and low MTBE concentrations. It has also exposed a few areas that would be prime for bridging gaps in the knowledge required to build such a prototype.

Firstly, a series of experiments could be conducted to determine the response of Pilkington Activ™ to a series of groundwater flow rates. This would provide insight into the acceptable ratio of cross section areas of the groundwater plume and the prototype reactor. This would allow the cross sectional area of the prototype to be minimised, thus reducing the materials required to achieve clean up of MTBE.

Secondly, work could be done to determine the rates of MTBE cleanup by Pilkington Activ™ at very low concentrations of MTBE. This would conclusively show if Activ™ is sufficient on its own to catalyse the full breakdown of MTBE to levels below the human taste threshold. This seems unlikely, and as such, other techniques could be investigated for suitability of use in conjunction with Pilkington Activ™ in order to achieve a low energy, sustainable method of MTBE remediation.

9. Acknowledgements

I would like to thank my supervisor, Dr Rod Lynch, for his invaluable guidance and support throughout this project. I would also like to thank Dr Peter Long for his insightful advice and ingenious mechanical support. Dr Lynch and Dr Long were not only instrumental in the success of this project, but also in invoking in me a long forgotten feeling of enjoyment regarding the field of engineering. I am very much grateful for their help.

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Appendix A: Risk Assessment Retrospective

The Risk Assessment completed in Michaelmas term prior to the start of the experiment was found to be largely sufficient in ensuring a safe working environment during the course of the project. However, there is one notable aspect in which the safety can be further enhanced.

The process of the risk assessment can be modified to remind users that the chemicals used in the lab are not only the reagents directly used in the experiments. Various other chemicals are often used in order to effectively clean equipment and glassware prior to use and these are easily overlooked in the risk assessment. Perhaps a column reminding users to consider these cleaning chemicals would be helpful.