Greywater Treatment by Fenton, Photo-Fenton and UVC/H$_2$O$_2$ Processes

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

Wee Hong Chin

Bachelor of Engineering (Hons), University of Adelaide, Adelaide.

School of Civil, Environmental and Chemical Engineering RMIT University, Melbourne.

March 2009
In memory of my grandmother, Koe Fi Lan (1926-2006)
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party has been acknowledged; and ethics procedures and guidelines have been followed.

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(Wee Hong Chin)

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Last but not the least, the author thanks his family and friends for their unconditional support which sustained him throughout the entire candidature.
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<td>Absorbance at wavelength, $\lambda$</td>
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</tr>
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<td>KHP</td>
<td>Potassium hydrogen phthalate</td>
</tr>
<tr>
<td>LASs</td>
<td>Linear alkylbenzene sulphonates</td>
</tr>
<tr>
<td>LGW</td>
<td>Laundry greywater</td>
</tr>
<tr>
<td>LR GW</td>
<td>Low-range greywater</td>
</tr>
<tr>
<td>MBAS</td>
<td>Methylene Blue Active Substances</td>
</tr>
<tr>
<td>MBR</td>
<td>Membrane bioreactor</td>
</tr>
<tr>
<td>MCR</td>
<td>Membrane chemical reactor</td>
</tr>
<tr>
<td>MWCO</td>
<td>Molecular Weight Cutoff</td>
</tr>
<tr>
<td>MR GW</td>
<td>Mid-range greywater</td>
</tr>
<tr>
<td>NTU</td>
<td>Nephelometric turbidity unit</td>
</tr>
<tr>
<td>PAHs</td>
<td>Polycyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>PFS</td>
<td>Perfluorinated surfactant</td>
</tr>
<tr>
<td>PPCPs</td>
<td>Pharmaceutical and personal care products</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>QASs</td>
<td>Quaternary ammonium surfactants</td>
</tr>
<tr>
<td>QS</td>
<td>Quartz sleeve</td>
</tr>
<tr>
<td>RBCs</td>
<td>Rotary biological contactors</td>
</tr>
<tr>
<td>SA EPA</td>
<td>Environment Protection Authority of South Australia</td>
</tr>
<tr>
<td>SBR</td>
<td>Sequencing batch reactor</td>
</tr>
<tr>
<td>SGW</td>
<td>Shower greywater</td>
</tr>
<tr>
<td>SUWOX</td>
<td>Super-critical water oxidation</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>TGW</td>
<td>Teeth-brushing greywater</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organisation</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>XOCs</td>
<td>Xenobiotic organic compounds</td>
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</table>
Abstract

Greywater recycling for non-potable purposes has become an important means of reducing freshwater consumption. Although it has no input from toilets or industrial wastewater, robust treatment of greywater is required to ensure the safety of its reuse, especially for those applications with the potential for human exposure e.g., toilet flushing and garden irrigation.

Advanced oxidation processes (AOPs) have been used to treat drinking water and wastewater but their application to greywater is limited to photocatalysis (UV/TiO₂). Therefore, the aim of this project was to investigate three homogeneous AOPs, namely: Fenton, photo-Fenton, and UVC/H₂O₂ processes. Alum and ferrous sulphate coagulation were also compared, and their supernatants were treated by UVC/H₂O₂. The influence of pre-treatments (overnight settlement or coagulation), pH, dosage of reagents, reaction/irradiation time, concentration of contaminants and greywater type on these processes was examined, and their effectiveness was compared in terms of the removal of chemical oxygen demand (COD), type of treatment (physical separation versus chemical oxidation), sludge formation, complexity in operation, required pH condition, visual aesthetic of effluent and energy requirement.

The experimental plan comprised two stages. Stage 1 involved optimising the processes to treat greywaters collected by the researcher from home or in the laboratory. These included laundry greywater (LGW), teeth-brushing greywater (TGW) and shower greywater (SGW), and they were mixed and diluted with tap water to produce low-range greywater (LR GW), mid-range greywater (MR GW) and high-range greywater (HR GW). While LR GW (225 mg.L⁻¹ COD) was used in most experiments, the others were studied for the effects of initial COD level and greywater type. In Stage 2, the findings were tested on greywaters collected from a commercial accommodation (YHA) and two households (ATA-B and ATA-H).

It was found that alum coagulation removed 73% COD in LR GW and was more effective than ferrous sulphate coagulation (49%) and the Fenton process (45%). The photo-Fenton process achieved 83% COD removal, compared with 87% by overnight settlement and subsequent UVC/H₂O₂ treatment. Using ferrous sulphate and alum, sequential coagulation and UVC/H₂O₂ treatment removed 91% and 98% COD, respectively.

Overnight settlement generated little sludge and removed only 13% COD, and subsequent UVC/H₂O₂ treatment oxidised most organic contaminants with some being fully mineralised. All other processes removed substantial COD by coagulation and produced a large quantity of chemical sludge which may contain xenobiotic contaminants of unknown toxicity,
biodegradability or bioaccumulation characteristics and hence raises the issue of appropriate sludge disposal. Therefore, the selection of an appropriate process depends on the goal of treatment, i.e., whether destruction of the contaminants is required, and the issue of sludge disposal should be considered. In addition, for those processes using ferrous sulphate, the residual iron imparted a yellow tint to the treated water and was not aesthetically desirable.

The Fenton and photo-Fenton processes involved the optimisation of multiple parameters (pH, Fe\(^{2+}\):H\(_2\)O\(_2\), H\(_2\)O\(_2\):COD and reaction/irradiation time). For LR GW, Fe\(^{2+}\) dosage of 1 mM was adequate and the optimal Fe\(^{2+}\):H\(_2\)O\(_2\) for the Fenton and photo-Fenton processes was 1:5 and 1:10, respectively. Using the theoretical optimal ratio of 2.12 g H\(_2\)O\(_2\)/g COD, the COD removal by the photo-Fenton process was enhanced for LGW, TGW and HR GW. For SGW and TGW, floc formation was observed after pH neutralisation. For those with laundry input, flocs were formed during the oxidation stage of the processes; if not separated by settlement, the flocs re-dissolved in subsequent pH neutralisation and reduced the COD removal. The requirement for different procedures presents a major challenge to the design and operation of these processes. In addition to the selection or exclusion of particular type of greywater(s), a collection or mixing facility is needed and the application of these processes in larger scale recycling projects, where a larger population of users is involved and higher volumes of greywater are collected, may dampen such variation in the quality and type of greywater.

Due to the non-selectivity of the hydroxyl radicals (\(^*\)OH), the UVC/H\(_2\)O\(_2\) process was capable of treating all greywaters collected by the researcher, and its operation was moderate in complexity which involved optimising the H\(_2\)O\(_2\) dosage according to the COD level. The COD removal was modelled as a pseudo first-order reaction in terms of H\(_2\)O\(_2\) dosage. The rate constant (\(k'\)) increased linearly up to 10 mM H\(_2\)O\(_2\), above which the reaction was affected negatively due to the scavenging of \(^*\)OH by the excess H\(_2\)O\(_2\), and the COD removal followed a second-order equation of \(r = 0.0637 \times [\text{COD}][\text{H}_2\text{O}_2]\). At the optimal dosage of 10 mM H\(_2\)O\(_2\), similar COD removal was obtained at the initial pH of 3, 7 and 10. In contrast to the literature, operation of UV/H\(_2\)O\(_2\) in acidic conditions was not required and therefore avoided acidifying/neutralising large volumes of water and the associated concerns about the material of equipment and cost of chemicals. The COD removal was enhanced slightly when the initial pH was 10 and this was investigated by examining the change in pH during the UVC/H\(_2\)O\(_2\) treatment, the competition between CO\(_3^{2-}\)/HCO\(_3^-\) and Cl\(^-\) for the scavenging of \(^*\)OH and the dissociation of H\(_2\)O\(_2\) to O\(_2\)H\(^-\) at high pH. Despite the difference in the initial pH of 7 and 10, the formation of mineral acids, carbon dioxide and acidic intermediates reduces the solution pH to close to neutral, resulting in similar operating conditions. Although the scavenging of \(^*\)OH by CO\(_3^{2-}\)/HCO\(_3^-\) can be counteracted by the reduction in the reaction between \(^*\)OH and Cl\(^-\) at high pH, this did not adequately explain the slightly enhanced
performance of UVC/H$_2$O$_2$ at pH 10 since the ratio of chloride anions and total concentration of carbonate ([Cl$^-$]/cT) in the settled LR GW was 0.7, suggesting weak competition between the anions. In this case, both [Cl$^-$] and cT of the LR GW were higher than those of bathroom greywaters but comparable to laundry greywaters reported in the literature. The enhanced COD removal at the initial pH of 10 is attributed to the dissociation of H$_2$O$_2$ to O$_2$H$^-$ and the significantly higher molar absorption coefficient of O$_2$H$^-$ at 254 nm which would have led to the increased production of *OH from the photolysis of both H$_2$O$_2$ and O$_2$H$^-$. The benefits of operating at high initial pH diminished during the treatment due to the formation of acidic products which reduced solution pH. However, maintaining the pH at 10 or operating at a higher initial pH resulted in poorer COD removal, which was attributed to the increased decomposition rate of H$_2$O$_2$ to O$_2$ and H$_2$O under these pH conditions. Also, the performance of the UVC/H$_2$O$_2$ treatment was unaffected for initial pH 3 – 10 with the initial cT of at least 3 mM. For initial cT $\geq$ 10 mM, operating between pH 3 and 5 was essential.

After 3 hours of treatment (UV dose of 54,000 mJ.cm$^{-1}$), the effluent met the requirement of Class B reclaimed water specified by the Environment Protection Authority of Victoria, and less than 1 org/100 mL of *Escherichia coli* survived the treatment. A subsequent treatment such as filtration may be required to meet the requirements for Class A reclaimed water for biochemical oxygen demand (BOD$_5$), turbidity and total suspended solids. Since the biodegradability (as BOD$_5$/COD) of the settled LR GW was increased from 0.22 to 0.41 with 2 hours of UVC/H$_2$O$_2$ treatment, its integration with a subsequent biological treatment may be viable to reduce the costs and energy consumption associated with the UVC/H$_2$O$_2$ process.

The COD of the YHA greywater was mainly in the form of suspended solids which were readily removed by settling overnight and subsequent UVC/H$_2$O$_2$ treatment was not necessary. Coagulation using alum or ferrous sulphate, and the Fenton and photo-Fenton processes, only marginally improved the COD removal. For the ATA-B and ATA-H greywaters, coagulation alone was not effective, but with subsequent UVC/H$_2$O$_2$ treatment at least 95% COD removal was achieved. While a similar level of COD was removed by the Fenton and photo-Fenton processes, scum was formed during the oxidation stage, which prompted the need to use separation devices and/or frequent cleaning of the reactor. Perhaps due to its high level of COD and turbidity, and the presence of recalcitrant chemicals, the overnight settlement and subsequent UVC/H$_2$O$_2$ treatment did not result in satisfactory COD removal, but adding H$_2$O$_2$ in fed-batch mode reduced the irradiation time and H$_2$O$_2$ dosage. Due to the use of biodegradable products by the residents, ATA-B and ATA-H greywaters had high biodegradability and therefore a biological treatment would be more appropriate and UVC/H$_2$O$_2$ could be employed subsequently to improve the quality of the effluent.
Chapter 1. Introduction

Substantial effort has been devoted to research into and implementation of wastewater reuse. This world-wide effort has been prompted by the shortage of freshwater resources, increasing living standards and the increasing demand due to expanding population. Australia is the driest inhabited continent, and its problem of water shortage has been exacerbated by climate change and some projections suggest a bleak scenario for future supply, especially in southern and eastern Australia (Pittock, 2007). Thus, the potential of reusing wastewater to gain environmental and economic benefits is an attractive pathway for the sustainable management of water resources (Eriksson et al., 2002; Lazarova et al., 2003).

Conventional wastewater management adopts the “Mix-First-and-Separate-Later” approach. In essence, freshwater is used to transport waste to centralised wastewater treatment plants and the quality of the effluents from the plants is comparable with that of greywater (Günther, 2000). Therefore, Günther argued that the separation of greywater at source facilitates its reuse, and its potential for recycling has been widely discussed (for example, Christova-Boal et al., 1996; Jefferson et al., 2000; Jeffrey and Jefferson, 2001; Eriksson et al., 2002; Lazarova et al., 2003).

Greywater is defined as wastewater without any input from toilets or heavily polluted industrial process water (Eriksson et al., 2003). Due to the activities involved in its production, the quality and quantity of greywater vary significantly even within a property (Jefferson et al., 2000), and a wide range of values has been reported for parameters such as biochemical oxygen demand (BOD = 5 – 1460 mg.L⁻¹), chemical oxygen demand (COD = 13 – 8000 mg.L⁻¹), pH (5 – 10), turbidity (15 – 240 NTU) and suspended solids (17 – 330 mg.L⁻¹) (Eriksson et al., 2002).

Technologies that have been applied in greywater treatment vary from simple storage and diversion devices to sophisticated systems which are usually based on biological, physical separation and chemical/advanced oxidation processes. While advanced oxidation processes (AOPs) have been widely used in the treatment of drinking water and domestic or industrial wastewaters, its application in greywater treatment has been limited to photocatalysis.

Therefore, the aim of this laboratory-based study was to examine the applicability of three homogeneous AOPs in the treatment of greywater, namely: Fenton, photo-Fenton, and UVC/H₂O₂ processes. For comparison, the greywater was also treated by coagulation with alum or ferrous sulphate, and the supernatant was subjected to UVC/H₂O₂ treatment. The
effects of the following parameters were determined: the use of pre-treatments (overnight settlement or coagulation), pH, concentration of contaminant, type of greywater, dosage of reagents (alum, ferrous sulphate, and/or H₂O₂), and reaction/irradiation time.

Due to its accuracy, minimal analytical effort and short analysis time, COD was used as the main parameter to measure the effluent quality achieved by each process. Subsequently, the effluent from the optimised process was subjected to BOD₅ analysis since it is an important parameter specified by the Environment Protection Authority of Victoria (EPAV). Other parameters such as pH, turbidity, total suspended solids and the level of *Escherichia coli* were also evaluated but the main objective in this study was to reduce the COD in the greywater. While health risk is a major concern for the recycle of greywater, the risk can be minimised by providing multi-barrier protection and the disinfection of greywater can be achieved by treatments such as UVC irradiation and chlorination. The investigation for the effectiveness of these treatments and the potential problems can be found in the work of Gilboa and Friedler (2008) and Winward et al.(2008), and therefore not discussed in depth in this study.

Initially synthetic greywater was used for the experiments and it was prepared as per the recipe developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) (obtained through personal communication with Clare Diaper). However, some practical difficulties and concerns led to the use of real greywater collected from the researcher’s home, which had the advantage of being readily available and it was possible to control its quality. The greywater was collected from laundry, teeth brushing and shower, and they were mixed in various proportions to simulate greywater at different contaminant levels. The results were then validated with raw greywaters collected from external sources which included a commercial accommodation for backpackers and two residential houses.

The definition of greywater is elaborated in Chapter 2 which also discusses the selection of different types of greywater for reuse, its application, and the associated risks and hazards. International standards and guidelines for reclaimed water quality are summarised and synthetic greywater recipes found in the literature are compared. This is followed by a review of the technologies that have been applied in greywater treatment.

Chapter 3 describes the photo-reactor, along with the materials used in this project, the experimental procedures and the analytical methods. In Chapter 4, the options available for the source of greywater are examined: synthetic greywater prepared according to recipes from the literature, the collection and preparation of greywater from the researcher’s home, and greywaters collected from external sources.
Results for alum and ferrous sulphate coagulation, and the subsequent treatment of the supernatant by UVC/H$_2$O$_2$ are presented in Chapter 5. This is followed by the investigation of Fenton and photo-Fenton processes in Chapter 6. Chapter 7 discusses the UVC/H$_2$O$_2$ process by examining the effects of overnight settlement as a pre-treatment, H$_2$O$_2$ dosage, pH and the initial COD level and type of greywater.

The results of the various processes investigated in Chapters 5 – 7 are compared in Chapter 8 based on criteria such as the extent of COD removal, type of treatment (physical separation or chemical oxidation), sludge formation, complexity in operation, pH condition, visual aesthetic of effluent, and energy requirement. In Chapter 9, the optimised processes are applied to the greywaters collected from the external sources. Finally, Chapter 10 outlines the conclusions from this project along with some recommendations for future work.
Chapter 2. Literature Review

In this chapter, the definition of greywater is elaborated in Section 2.1, followed by discussion on its characteristics and the analytical parameters used to characterise its quality. In Sections 2.2 and 2.3, issues related to the selection of different types of greywater for reuse, their proposed application, and the associated risks and hazards are discussed. Various international standards and guidelines for reclaimed water quality are summarised in Section 2.4 and Section 2.5 compares the synthetic greywater recipes that are available in the literature. The technologies that have been applied in greywater treatment are reviewed in Section 2.6, and for ease of discussion, they are broadly classified as biological treatments, physical separation techniques, and chemical or advanced oxidation processes. When relevant, some examples for the application of these technologies in the treatment of drinking water and other wastewaters are also included. These are summarised in Section 2.7.

2.1 Greywater: Definition and Characteristics

Greywater is defined as any wastewater produced from private, public or commercial properties without any input from toilets, bidets, urinals or heavily polluted industrial process water (Eriksson et al., 2003). By this definition, any wastewater produced from bathtubs, spas, showers, hand basins, washing machines, laundry troughs, dishwashers and kitchen sinks is classified as greywater.

Due to the daily activities involved in its production, the quantity and quality of greywater vary significantly even within a property, and the following characteristics of greywater have been discussed by Jefferson et al. (2000):

- Large temporal variability in quantity which creates the need for storage,
- Large variation in quality and therefore a robust treatment system is required, and,
- Low levels of nutrients and biodegradable organic compounds compared with municipal wastewater.

Various parameters have been used to characterise the quality of greywater. Friedler (2004) measured 20 parameters in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA, 1998). These included pH, electrical conductivity, chloride, sodium, boron, ammonia, phosphate, total solids, volatile total solids, volatile and total suspended solids, dissolved and total chemical oxygen demand, dissolved and total biochemical oxygen demand, dissolved and total organic carbon, total oil, anionic detergents (measured as methylene blue active substances, MBAS) and faecal coliforms. In addition,
heavy metals such as Ag, Cr, Ni, Cd, Mn, Cu, Pb, and Zn were analysed. Other parameters such as nutrient content (N and P), temperature, colour, turbidity, alkalinity, hardness, and content of other heavy metals (e.g., Al, Fe, and Hg) were also considered as important (Eriksson et al., 2002).

Data available in the literature on greywater characteristics have been reviewed by, for example, Jefferson et al. (2000), Eriksson et al. (2002), Lazarova et al. (2003), and Friedler (2004). Some researchers adopted a relatively general approach which considered greywater produced in the bathroom as a whole regardless of whether the source was the bathtub, shower or hand basin. Others conducted detailed investigation to the extent of analysing each individual washing cycle of a dishwasher or washing machine. The inherent variability in greywater characteristics, however, leads to difficulties in quantitatively comparing the parameters mentioned above. Nevertheless, a wide range of values has been reported for parameters such as BOD (5 – 1460 mg.L⁻¹), COD (13 – 8000 mg.L⁻¹), pH (5 – 10), turbidity (15 – 240 NTU) and suspended solids (17 – 330 mg.L⁻¹) (Eriksson et al., 2002).

Despite the differences in data quality and the approach adopted to obtain them, a few general observations have been summarised (Eriksson et al., 2002; Friedler, 2004):

- Greywater streams generally had high temperature, which favours microbiological growth and the precipitation of some inorganic salts,
- Bathroom greywater had a relatively low content of suspended solids but had potentially high pathogen levels,
- Laundry greywater had the highest alkalinity,
- Kitchen greywater had the highest total solids content and BOD, and
- Both laundry and kitchen greywaters had high COD, nitrogen and phosphorus content.

In short, kitchen greywater (especially that from the kitchen sink) contained the highest level of most chemical pollutants, and these chemicals were also found at high levels in laundry greywater. In contrast, bathroom greywater was low in chemical pollutants but was the major source of faecal coliforms, and hence had potentially high pathogen levels (Friedler, 2004). Bathroom greywater has been described as “light grey” while laundry and kitchen greywaters have been known as “dark grey” (Lazarova et al., 2003). While these terms reflect the loadings of chemical pollutants in the respective greywater, they underplay the degree of microbial contamination in bathroom greywater.
2.2 Selection of Greywater for Recycle

The selection of different greywater streams to be included in a reuse project depends on the amount of each stream available and its level of contaminants (Jefferson et al., 2004). Since the production of domestic greywater in urban areas is usually higher than the demand for reuse, Friedler (2004) suggested a detailed analysis to compare the effects on pollutant loadings by excluding one or several greywater streams to maximise the amount of water available for recycle while maintaining a low level of contaminants.

In Australia, the Environment Protection Authority of Victoria (EPAV) tabulated the typical pollutants in each type of greywater and their associated risks for domestic reuse (EPAV, 2001). In the report, explicit guidelines and some comments on risk management were provided for the diversion of untreated greywater and for the installation of approved treatment systems. In addition, greywater produced from the kitchen was not recommended for domestic reuse due to its high level of contaminants. Christova-Boal et al. (1996) also discouraged the reuse of kitchen greywater and claimed that its exclusion incurred negligible loss to the volume of water available for recycling since it accounted for only about 5% of the average household water consumption in Melbourne (or 10% of the total greywater produced). This is consistent with the observation by Jefferson et al. (2004) that smaller scale reuse projects tend to exclude highly polluted kitchen and/or laundry greywaters.

2.3 Applications of Recycled Greywater, Associated Risks and Hazards

Some of the proposed applications for greywater reuse include garden and crop irrigation, toilet and urinal flushing, washing of vehicles and windows, fire protection, development and preservation of wetland, groundwater recharge, and industrial use such as boiler feedwater, cooling system make-up water and concrete production, as listed variously by Eriksson et al. (2002; 2003), EPAV (2003), Li et al. (2003) and Jefferson et al. (2004).

Greywater reuse is not a new concept and some traditional or conventional practices, especially those at domestic level, are not controlled and in some cases involve little or no treatment. An example is the manual diversion of untreated greywater for garden irrigation. Under the current statutory regime in Victoria, household greywater diversion systems are not controlled by any specific local or state government regulations. However, householders may be subject to legal liabilities should a public health hazard, an environmental hazard or nuisance be created (EPAV, 2001).
Many researchers such as Lechte et al. (1995), Christova-Boal et al. (1996), Jeppesen (1996), Dixon et al. (1999b) and Eriksson et al. (2002) have raised or reviewed the concerns regarding greywater reuse. These include:

- Risks to public health due to human contact with microorganisms,
- Clogging of distribution system by suspended solids,
- Offensive odour caused by the formation of sulphide, and,
- Pollution of soil, surface water and groundwater due to irrigation, infiltration, and groundwater recharge.

In their comparison of greywater characteristics in two households, Casanova et al. (2001) detected the presence of faecal coliforms, faecal streptococci and *Pseudomonas aeruginosa*, and they found that the overall microbial, chemical, and physical quality of untreated greywater was between that of raw wastewater and secondary effluent. While the levels of total coliforms were similar in both cases, a higher level of faecal coliforms was detected in the sample from the household which had a child occupant.

Eriksson et al. (2002) reviewed studies on the survival of pathogens in greywater such as *Salmonella typhosa*, *Shigella dysenteriae*, *Legionella pneumophila*, pathogenic enteric bacteria, poliovirus, echoviruses, and adenoviruses. Frequently, indicator organisms such as faecal coliforms are used to indicate the degree of bacteriological contamination and hence to infer the potential for viral contamination. Ottoson and Stenström (2003a), however, believed that the risks may have been over-estimated because thermo-tolerant (faecal) coliforms may survive on degradable organic material and grow in the system. Hence, they proposed a “quantitative microbial risk assessment” based on faecal enterococci. In addition, Ottoson and Stenström (2003b) suggested that pathogenic bacterial growth in nutrient-rich systems (such as greywater sediments) is suppressed due to competition with other microorganisms.

Dixon et al. (1999b) argued that the risk to public health posed by non-potable greywater reuse depends not only on the concentration of the pathogenic microorganisms, but also the degree of exposure, and the health and age of the affected individuals. They also suggested a risk assessment framework to consider the real hazards associated with fresh and stored greywater at various scales for different applications.

Due to their resistance to water treatment processes including chlorination, the exposure to *Legionella* sp. through inhalation of aerosols from toilet flushing is thought to pose the highest health risk (Jeffrey and Jefferson, 2001). However, these researchers found no evidence that *Legionella* is more likely to proliferate in a greywater treatment system than in a potable water distribution system.
Gross et al. (2005) studied the environmental impact and health risks associated with greywater irrigation. They concluded that faecal coliforms did not survive in soil irrigated with untreated greywater. However, treatment of greywater before irrigation was strongly recommended due to the possible accumulation of salts, surfactants and boron which are detrimental to soil properties and plant health.

Christova-Boal et al. (1996) were also concerned about the use of untreated laundry greywater for garden irrigation due to its high level of salts, alkalinity, and heavy metals (e.g., Zn and Al). By measuring the capillary rise and infiltration in sand, Wiel-Shafarman et al. (2006) concluded that the accumulation of surfactants from irrigation with untreated laundry greywater resulted in water-repellent soils with affected flow pattern and productivity. According to the EPAV (2001), untreated laundry greywater produced in the wash cycle should be diverted to sewer and not reused for irrigation; the condition of the plants should also be monitored and the use of greywater discontinued if the plants appeared unhealthy.

In most cases, storage of greywater is necessary for its reuse, but prolonged storage of untreated greywater leads to offensive odour caused by anaerobic degradation of organic contaminants and the formation of sulphide (Dixon et al., 1999a; Jefferson et al., 2000; Eriksson et al., 2002). However, it has been shown that storing untreated greywater for 24 hours (but not beyond 48 hours) improves its quality due to the settlement of suspended matter and reduction in COD, but the level of total coliforms was increased indicating an environment that supported microbial growth during the storage period (Dixon et al., 1999a). Using a computer simulation model, Dixon et al. (2000) showed that the optimal greywater storage capacity for a household of four occupants was 250 L, and about 1000 L for a multi-occupancy building and it was largely independent of occupancy level.

There are also issues such as the possibility of cross-connection between greywater and potable water piping or accidental consumption of greywater (Lehr, 1987). Clear identification of piping and outlets is therefore essential for the safe recycle of greywater, and Lehr (1987) suggested the addition of blue vegetable dye to greywater, not only for clear identification, but also to improve its aesthetics if there is minimal treatment of the water.

Since the introduction of recycled water in 2001, there have been four cross-connection events detected within the Rouse Hill Development Area (Sydney, Australia) despite using purple pipes for identification. However, no adverse effect on human health has been found due to the use of multi-barrier risk management. Nevertheless, Sydney Water was investigating the options for rapid detection of cross-connection by the use of anti-ingestants and colourants, and sensor-based technology to provide on-line warning (Storey et al.,
Xenobiotic organic compounds (XOCs) originating from pharmaceuticals and personal care products (PPCPs) and other household products are a major concern (Ledakowicz, 1998; Ying et al., 2004). In a survey of common Danish household products, Eriksson et al. (2002) found at least 900 organic compounds that have been listed in the content declaration on the product packaging, and they were categorised as amphoteric, anionic, cationic and non-ionic detergents, bleaches, dyes, emulsifiers, enzymes, fragrances and flavours, preservatives, softeners, solvents, UV filters, and miscellaneous group. The enormous and increasing variety of these compounds in these products impedes the full investigation of their toxicity, biodegradability and bioaccumulation properties, and researchers such as Eriksson et al. (2003) and Palmquist and Hanæus (2004) have commented on this limitation, and the endocrine disruptive property of some of these chemicals has been highlighted (Ying et al., 2004). In some cases, compounds such as 17β-estradiol have been detected in the effluent of sewage treatment plants at concentrations ranging from ng.L⁻¹ to µg.L⁻¹ (Nakashima et al., 2002; Ying et al., 2004; Tan et al., 2007).

For similar reasons, surfactants which are heavily used in many of these household products are also perceived as potential threats to human and environmental health. While most surfactants are fairly biodegradable, those with aryl and branched alkyl groups are more persistent and have been found in treated effluent, activated sludge and receiving waters along with their partially-degraded products (Ikehata and El-Din, 2004). These compounds are toxic to aquatic organisms and some possess estrogenic activities, and the concerns as reviewed by Ikehata and El-Din (2004) are summarised in Table 2-1.
Biodegradation Products

- No information regarding biodegradation pathway for QASs
- Biodegradation product: carboxylic acid and sulphophenyl carboxylates (more polar and less toxic than LASs, do not appear to have estrogenic activity but persistent in water)
- Biodegradation product: polyethoxylate chain decreases aquatic toxicity
- Nonethoxylated alkylphenols, the final product of biodegradation, are the most toxic and persistent and tend to build up in primary and activated sludge
- Estrogenic activities of nonylphenol, mono- and diethoxylated alkylphenols to aquatic organisms, human effects are unknown

Table 2-1. Surfactants, major biodegradation products and their properties (Ikehata and El-Din, 2004).

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Properties</th>
<th>Biodegradation Products</th>
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<td><strong>Cationic:</strong></td>
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| • Quaternary ammonium surfactants (QASs, e.g. alkyl trimethylammonium, dialkyl dimethylammonium, and alkyl benzyl dimethylammonium, esterquats, alkyl pyridinium, alkylimidazolium) | *Strongly adsorbed by particulate matter, found largely in primary and activated sludge, therefore, anaerobic biodegradation is more important*  
  *Biodegradability depends on molecular structure, aromatic QASs and petroleum derived cationic surfactants are not readily degradable*  
  *Alkyl QASs appear to be more toxic than LASs, and toxicity increases with increased length of alkyl chain* |                         |
| • Non-quaternary ammonium surfactants (e.g., alkyl dimethylamine oxides) |                                                                             |                         |
| **Anionic:**           |                                                                             |                         |
| • Alkylbenzene sulphonates (ABSs)  
  • Linear alkylbenzene sulphonates (LASs)  
  • Aliphatic sulphonates  
  • Fatty alcohol sulphates  
  • Alcohol ether sulphates | *LASs were introduced as alternative to less biodegradable ABSs, however, acute toxicity of LASs to various aquatic organisms has been reported which increases with increasing number of carbon atoms in the alkyl chain*  
  *LASs are readily biodegradable in aerobic conditions, but anaerobic conditions and high concentration inhibit their degradation*  
  *Accumulation in digested sewage sludge*  
  *Rapidly degrade in soil, minimal impact on soil organisms and plants* | Biodegradation product: carboxylic acid and sulphophenyl carboxylates (more polar and less toxic than LASs, do not appear to have estrogenic activity but persistent in water) |
| **Non-ionic:**         |                                                                             |                         |
| • Alkylphenol ethoxylates (APEs)  
  • Alcohol ethoxylates (AEs) | *APEs often contain highly branched alkyl chain*  
  *Decrease in the length of polyethoxylate chain increases its aquatic toxicity*  
  *Have been replaced with more biodegradable AEs*  
  *APEs appear to accumulate in anaerobically digested sludge*  
  *APEs and AEs degrade fairly quickly when applied to soil, without showing adverse effects to soil fertility* |                         |
### 2.4 Required Quality of Treated Water

In Victoria (Australia), guidelines for the use of reclaimed water at larger scale are specified in EPAV Publication 464.2. These guidelines target the use of reclaimed water from facilities which treat municipal wastewater, industrial process water, as well as sewage produced from individual commercial premises such as hotels, motels, schools and caravan parks. As shown in Table 2-2, each classification of reclaimed water, its intended use, and the appropriate treatment processes has been established by the authority (EPAV, 2003) and they have been used as a guideline in this project.

#### Table 2-2. Classes of reclaimed water and corresponding standards for biological treatment and pathogen reduction (EPAV, 2003).

<table>
<thead>
<tr>
<th>Class</th>
<th>Water quality objectives: medians unless specified</th>
<th>Treatment processes</th>
<th>Range of uses: uses include all lower class uses</th>
</tr>
</thead>
</table>
| A     | • < 10 E. coli orgs/100 mL  
• Turbidity < 2 NTU  
• < 10 mg.L\(^{-1}\) BOD  
• < 5 mg.L\(^{-1}\) suspended solids  
• pH 6 – 9  
• 1 mg.L\(^{-1}\) Cl\(_2\) residual (or equivalent disinfection) | Tertiary and pathogen reduction with sufficient log reductions to achieve:  
<10 E. coli per 100 mL;  
<1 helminth per litre;  
< 1 protozoa per 50 L; and  
< 1 virus per 50 L. | Urban (non-potable): with uncontrolled public access  
Agricultural: e.g. human food crops consumed raw  
Industrial: open systems with worker exposure potential |
| B     | • < 100 E. coli orgs/100 mL  
• < 20 mg.L\(^{-1}\) BOD  
• < 30 mg.L\(^{-1}\) suspended solids  
• pH 6 – 9 | Secondary and pathogen reduction (including helminth reduction for cattle grazing) reduction | Agricultural: e.g. dairy cattle grazing  
Industrial: e.g. washdown water |
| C     | • < 1000 E. coli orgs/100 mL  
• < 20 mg.L\(^{-1}\) BOD  
• < 30 mg.L\(^{-1}\) suspended solids  
• pH 6 – 9 | Secondary and pathogen reduction (including helminth reduction for cattle grazing use schemes) | Urban (non-potable) with controlled public access  
Agricultural: e.g. human food crops cooked/processed, grazing/fodder for livestock  
Industrial: systems with no potential worker exposure |
| D     | • < 10000 E. coli orgs/100 mL  
• < 20 mg.L\(^{-1}\) BOD  
• < 30 mg.L\(^{-1}\) suspended solids  
• pH 6 – 9 | Secondary | Agricultural: non-food crops including instant turf, woodlots, flowers |
The classifications of reclaimed water developed by individual state and territory governments in Australia vary in their approach. Therefore, a national guideline, “National Water Quality Management Strategy – Australian Guidelines for Water Recycling: Managing Health and Environmental Risks” (2006a), has been drafted based on a standard risk assessment and Hazard Analysis Critical Control Point system, and the concept of identifying and producing recycled water of a quality that is “fit-for-purpose” has been proposed to replace the Class A to D system, which is considered as lacking flexibility. While Phase 1 of the guidelines focused on both large-scale sewage/greywater and on-site greywater treatments to recycle water as a replacement of drinking water for non-potable use, Phase 2 dealt with planned augmentation of drinking water supply by treated stormwater or sewage. Microbial safety is defined in terms of Disability Adjusted Life Years, which measure health impacts in terms of illness and early death for the determination of pathogen reduction requirements; chemical safety is defined in terms of values set by other guidelines and a method was developed which involves a hierarchy of applying existing guidelines (e.g., Australian Drinking Water Guidelines), published toxicological information, a threshold of toxicological concern approach, therapeutic doses for human pharmaceuticals, and acceptable daily intake for veterinary and agricultural chemicals (Wiesner et al., 2007).

Surendran and Wheatley (1998) summarised various international guidelines or standards for the quality of reclaimed water suitable for toilet flushing and, in some cases, for other non-potable reuse. The list has been expanded or adapted from the work of other researchers (for example, Jefferson et al., 2000; Lazarova et al., 2003; Pidou et al., 2007) and is shown in Table 2-3.

The requirements for BOD level, turbidity and pH are generally similar in various international guidelines or standards; maximal allowable BOD in the reclaimed water is 20 mg.L⁻¹ in many cases, and the pH is generally in the range of 6 – 9. However, the acceptable levels of microbial contamination vary significantly. Two trends have been identified: Less stringent standards suggested by the World Health Organisation (WHO) took the view that reclaimed water of quality similar to that of bathwater water was acceptable since the level of risk to the user was about the same, while the more conservative standards did not consider greywater as much different from municipal or industrial wastewater and hence required a practically non-detectable level of the indicator organisms (Jefferson et al., 2000).
Table 2-3. Standards or guidelines for the quality of reclaimed water for toilet flushing and other non-potable reuse.

<table>
<thead>
<tr>
<th>Country/Organisation</th>
<th>Faecal coliforms (cfu/100ml)</th>
<th>Total coliforms (cfu/100ml)</th>
<th>BOD (mg.L⁻¹)</th>
<th>Turbidity (NTU)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia ²</td>
<td>&lt; 4</td>
<td>&lt; 1</td>
<td>20</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>Australia (Queensland) ⁵</td>
<td>–</td>
<td>100</td>
<td>20</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Australia (SA EPA) ³</td>
<td>–</td>
<td>&lt; 10 (E. coli)</td>
<td>&lt; 20</td>
<td>&lt; 2</td>
<td>–</td>
</tr>
<tr>
<td>Canada (British Columbia) ³</td>
<td>2.2 median m</td>
<td>14 for any sample m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>China (toilet flushing) ⁴</td>
<td>–</td>
<td>&lt; 3 cfu.L⁻¹ (E. coli)</td>
<td>&lt; 10</td>
<td>&lt; 10</td>
<td>6.5 – 9</td>
</tr>
<tr>
<td>European Commission (bathing water) ¹</td>
<td>100 g</td>
<td>500 g</td>
<td>–</td>
<td>2 f</td>
<td>6 – 9</td>
</tr>
<tr>
<td>Germany ¹</td>
<td>100 g</td>
<td>500 g</td>
<td>20 f</td>
<td>1 – 2 m</td>
<td>6 – 9 f</td>
</tr>
<tr>
<td>Israel ⁵</td>
<td>&lt; 1</td>
<td>–</td>
<td>10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Japan ¹</td>
<td>10 for any sample m</td>
<td>10 m</td>
<td>10 m</td>
<td>5 m</td>
<td>6 – 9 m</td>
</tr>
<tr>
<td>Japan Sewage Works Association (toilet flushing) ⁴</td>
<td>–</td>
<td>&lt; 1,000 (E. coli)</td>
<td></td>
<td></td>
<td>5.8 – 8.6 f</td>
</tr>
<tr>
<td>South Africa ¹</td>
<td>0 f</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Spain (Canary Islands) ⁵</td>
<td>–</td>
<td>2.2</td>
<td>10</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>Taiwan Architecture and Building Research Institute (toilet flushing) ⁴</td>
<td>–</td>
<td>&lt; 1,000 (E. coli)</td>
<td>&lt; 10</td>
<td>–</td>
<td>6.8 – 8.5</td>
</tr>
<tr>
<td>UK Building Services Research and Information Association (BSRIA) ¹</td>
<td>14 for any sample f</td>
<td>0 for 90% sample f</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UK (bathing water criteria for toilet flushing) ¹</td>
<td>100 g</td>
<td>500 g</td>
<td>–</td>
<td>2 f</td>
<td>6 – 9</td>
</tr>
<tr>
<td>US EPA ¹</td>
<td>14 for any sample f</td>
<td>0 for 90% sample f</td>
<td>–</td>
<td>10 f</td>
<td>6 – 9 g</td>
</tr>
<tr>
<td>USA (California) ⁵</td>
<td>–</td>
<td>Average 2.2, maximum 23</td>
<td>–</td>
<td>Average 2, maximum 5</td>
<td>–</td>
</tr>
<tr>
<td>USA (Florida) ⁵</td>
<td>&lt; 25</td>
<td>–</td>
<td>20</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>WHO (lawn irrigation) ¹</td>
<td>200 g</td>
<td>1,000 m</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>


2.5 Synthetic Greywater Recipes

For studies on the characteristics of greywater or technologies for its treatment, some researchers collected real greywater (e.g., Li et al. (2003), Wiel-Shafran et al. (2006), and Rivero et al. (2006)), while others chose to use synthetic greywater for their experiments (e.g., Jefferson et al. (2003), Oschmann et al. (2005) and Nghiem et al. (2006)).

Several synthetic greywater recipes have been found in the literature and they are summarised in Table 2-4. These include a recipe that has been published by the BSRIA in the United Kingdom as part of a protocol for the testing of greywater treatment facilities (Brown and Palmer, 2002).

A similar procedure has been established by the Smart Water Fund (2003). While the greywater used to test a technology has to fall within the range of specified parameters, no explicit greywater recipe was provided. The Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia has since been developing a synthetic greywater recipe (Diaper et al., 2005; Toifl et al., 2006) with financial support from the Smart Water Fund, and it was obtained from Clare Diaper of the CSIRO through personal communication (2007) (Table 2-4).

Table 2-4. Synthetic greywater recipes (for 10 L of synthetic greywater).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tertiary Effluent 250 mL</td>
<td>Secondary Effluent 200 mL</td>
<td>Soap 620 mg</td>
<td>Sodium dodecyl sulphate</td>
</tr>
<tr>
<td>Shampoo 8.6 mL</td>
<td>Shampoo 7.2 g</td>
<td>Shampoo 1.6 ml</td>
<td>Humic Acids</td>
</tr>
<tr>
<td>Sunflower Oil 0.1 mL</td>
<td>Vegetable Oil 70 mg</td>
<td>Oil 80 μl</td>
<td>Cellulose</td>
</tr>
<tr>
<td>Tap Water Balance</td>
<td>Deodorant 100 mg</td>
<td>Hair 20 mg</td>
<td>Kaolin</td>
</tr>
<tr>
<td></td>
<td>Moisturiser 100 mg</td>
<td>Tap Water Balance</td>
<td>NaCl</td>
</tr>
<tr>
<td></td>
<td>Toothpaste 325 mg</td>
<td></td>
<td>CaCl₂</td>
</tr>
<tr>
<td></td>
<td>Laundry Powder 1.5 g</td>
<td></td>
<td>NaHCO₃</td>
</tr>
<tr>
<td></td>
<td>Clay 0.5 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄ 350 mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaHCO₃ 250 mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na₂PO₄ 390 mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Boric acid 14 mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lactic acid 280 mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tap Water Balance</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Alternative recipes have been suggested by Jefferson et al. (2003) and Oschmann et al. (2005), as shown in Table 2-4. Interestingly, the recipe used by Oschmann et al. did not include any household products. Instead, various chemicals were used to represent surfactants, dissolved organics, organic and inorganic particulates, monovalent and multivalent salts, and natural buffer.

While most of these recipes include household products such as shampoo and oil, Brown and Palmer (2002) suggested the use of tertiary effluent from wastewater treatment plants to simulate the microbial content in greywater, in contrast to the secondary effluent used in the CSIRO recipe. No wastewater treatment plant effluent is included in the recipes of Jefferson et al. (2003) or Oschmann et al. (2005). Tertiary effluent usually refers to water treated by a series of polishing treatments, including disinfection. Therefore, there may not be sufficient viable micro-organisms to simulate those in raw greywater unless it has been collected before the disinfection treatment.

Other than adding effluent from wastewater treatment plants, Toifl et al. (2006) have recommended the use of some surrogates for bacteria, protozoa, viruses and helminths to test the effectiveness of a greywater treatment system in the removal of micro-organisms. These are shown in Table 2-5.

**Table 2-5. Proposed surrogates of micro-organisms in greywater (Toifl et al., 2006).**

<table>
<thead>
<tr>
<th>Micro-organism</th>
<th>Surrogate if applicable</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Escherichia coli</em></td>
<td><em>E. coli</em> K12</td>
</tr>
<tr>
<td>Faecal <em>Enterococci</em></td>
<td><em>Enterococcus hirae</em></td>
</tr>
<tr>
<td>Adenovirus</td>
<td>*Bacteriophage (male specific) MS-2</td>
</tr>
<tr>
<td>Hepatitis A</td>
<td><em>Somatic coliphage ØX174</em></td>
</tr>
<tr>
<td><em>Cryptosporidium</em> and <em>Gardia</em></td>
<td><em>Clostridium perfringens</em> spores or 5 µm beads</td>
</tr>
<tr>
<td>Helminth</td>
<td>90 µm beads</td>
</tr>
</tbody>
</table>
2.6 Greywater Reuse and Treatment Systems

In this section, the technologies that have been applied to the treatment of greywater are discussed. The complexity of a suitable greywater diversion, treatment, or reuse system usually depends on the scale of the project. Relatively simple diversion or a basic screening device coupled with chemical disinfection provides little, if any, treatment before reuse. Larger scale projects usually involve more advanced technologies such as filtration (using sand and/or membranes such as microfiltration, ultrafiltration, nanofiltration or reverse osmosis), coagulation, advanced oxidation processes (e.g., UV/TiO₂), bioreactors and final disinfection units (Jefferson et al., 2000; Jeffrey and Jefferson, 2001; Pidou et al., 2007).

The technologies applied in greywater treatment can be categorised broadly as biological treatments, physical separation techniques, and chemical or advanced oxidation processes (AOPs). In many instances, combinations of processes have been proposed to improve the efficiency in the removal of contaminants or to reduce the size of equipment and consumption of chemicals.

In their review of greywater treatments, Pidou et al. (2007) discussed the shift in direction from coarse filtration or membrane filtration coupled with disinfection in the 1970s to biological treatments in the 1980s and 1990s, followed by membrane bioreactors and cheaper alternatives such as reed beds and ponds in the late 1990s. They also highlighted that only three types of chemical treatments have been applied to greywater treatment in the literature, and these are conventional coagulation, electro-coagulation and photocatalysis.

The application of AOPs in greywater treatment is indeed limited and the focus seems to be on photocatalysis. Therefore, examples from drinking water and wastewater treatments have been included in this section. The following review focuses on the removal of pollutants as measured by parameters such as BOD, COD, dissolved or total organic carbon, and absorbance.
2.6.1 Biological Treatments

Biological treatments are generally cheap and reliable and some of the suggested biological systems for greywater treatment include plant-covered horizontal or vertical flow soil filters, trickling filters, fluidised bed reactors and rotary biological contactors (RBCs) (Nolde, 2000). In their review of many biologically based treatments, Pidou et al. (2007) found that the hydraulic retention time ranged from 0.8 hours to 2.8 days, depending on the strength of the greywater.

Gross et al. (2007) employed a recycled vertical flow constructed wetland to treat greywater (COD = 840 mg.L⁻¹). Approximately 80% COD reduction was obtained after 8 hours of treatment and the treated water was considered by the researchers to be suitable for landscape irrigation, though subsequent disinfection of the effluent was recommended. The unit was claimed to be simple, low cost, and could be operated and maintained by unskilled operators.

A biological system treating greywater produced from hand- and dish-washing in a student hostel (BOD₇ = 47 mg.L⁻¹) was investigated by Günther (2000). Based on the concept of a “wetpark”, pathogenic bacteria, BOD and nutrients were removed when the incoming greywater flowed through three successive ponds. The “wetpark” was claimed to remove BOD (98%), nutrients and bacteria effectively with additional benefits such as low costs (compared with a conventional wastewater treatment system), providing habitat for animals, increasing local biodiversity, and having recreational, aesthetic and psychological values. Nevertheless, it has also been acknowledged that the system required a long turnover time and a large area for construction (Günther, 2000).

Shin et al. (1998) studied a sequencing batch reactor (SBR) for the treatment of greywater (COD = 79 mg.L⁻¹). By operating in cyclic and step-feed mode, significant improvement was made for nitrification and denitrification when compared with conventional operation. A subsequent microfiltration module was recommended to reduce the risk of suspended solids and pathogens being carried over in the treated effluent. The treated effluent had a COD of 20 mg.L⁻¹.

Researchers such as Jefferson et al. (2000) have proposed the combination of biological treatment with membrane filtration technology. Such integration includes biologically aerated filters (BAF) and membrane bioreactors (MBR). The former employs depth filtration and fixed film biological reactors while the latter combines an activated sludge reactor with a submerged or side-stream microfiltration membrane. Among these, the hydraulically operated submerged-type MBRs have been demonstrated to produce consistently high quality
permeate (COD reduction from $120 \pm 74.4$ mg.L$^{-1}$ to $9.6 \pm 7.4$ mg.L$^{-1}$), although high capital cost was acknowledged (Jefferson et al., 2000).

Friedler et al. (2006) compared a sand filter, a combination of RBC and sand filter, and a MBR with ultrafiltration module to treat low-strength greywater (COD = 211 mg.L$^{-1}$). It was concluded that the performance of the widely used sand filter was poor, and high quality effluents (COD = 40 mg.L$^{-1}$, BOD = 1 – 2 mg.L$^{-1}$, and turbidity = 0.2 – 0.6 NTU) were obtained from the MBR and the combined RBC and sand-filtration system.

A disadvantage of biological treatment is the generation of biological sludge which requires further treatment and disposal (Breithaupt et al., 2003). In addition, biological treatment systems are susceptible to non-biodegradable, xenobiotic, or toxic substances present in wastewater (Rajeshwar and Ibanez, 1996; Marco et al., 1997). As described in Table 2-1, some surfactants and their biodegradation products are recalcitrant and appear to accumulate in digested sludge.

Jefferson et al. (2000) observed that greywater is often low in biodegradability (BOD:COD ratio) and nutrient levels. Compared with the BOD:COD of municipal wastewater of 0.4 – 0.8 (Marco et al., 1997; Ledakowicz, 1998; Al-Momani et al., 2002), the ratio can be as low as 0.25 for some greywater (Jefferson et al., 2000). This prompted their subsequent development of a nutrient-balancing method to improve the efficacy of biological treatment for greywater (Jefferson et al., 2001). The proposed method uses nitrogen/phosphorus balancing followed by the addition of trace metal supplements. While the nitrogen/phosphorus balancing method could be generally applied to biological treatment, the dosing of the micro-nutrients had to be customised for individual cases. Considering the large temporal variability of greywater quality, good control is crucial to prevent over-dosage and subsequent inhibitory effects on the microbial growth in the treatment systems.

Oliver et al. (2000) treated synthetic greywater by a biomass recycle reactor which was designed to treat greywater produced on passenger ships, and its resistance to the addition of sodium hypochlorite was tested. The reactor was essentially a MBR and consisted of an aerated batch bioreactor and an ultrafiltration unit with 100 kDa MWCO membrane to recycle 100% of the biomass. The synthetic greywater fed to the reactor included laundry detergent (such as LASs), starch, and various salts and nutrients. The dosages of sodium hypochlorite (50 – 1000 mg.L$^{-1}$) were sufficient to kill more than 99% of the bacteria, but in all cases, the bioreactor operation was re-established within 10 to 48 hours after chlorine became undetectable. The ability to recover from the perturbation was considered very useful, especially when continuous monitoring of the system was not practical (Oliver et al.,
The researchers did not measure the BOD or COD of the synthetic greywater. Instead, the effect of the perturbation was measured by the utilisation of starch. During the recovery period, the utilisation of substrate virtually halted due to significant reduction in the population of viable cells, and this resulted in a dramatic increase in the concentration of total carbohydrate in the collected effluent.

In contrast, Nolde (2000) did not encounter this problem during the operation of a multi-stage RBC to treat greywater for toilet flushing, and it was claimed that products used for personal hygiene preparations (including occasional use of medicinal baths) and household-cleaning chemicals did not cause a problem to the biological treatment system. However, it was also mentioned that the washing liquid used in some of the experiments appeared to be less readily biodegradable, but the extent of the problem was not discussed. Nevertheless, the process was capable of reducing BOD\(_7\) from 50 – 250 mg.L\(^{-1}\) to consistently less than 5 mg.L\(^{-1}\) (Nolde, 2000).

### 2.6.2 Physical Separation Techniques

Physical separation techniques include sand filtration, coagulation/sedimentation, and membrane filtration. These techniques simply transfer the pollutants from one medium to another, and they frequently create the need to dispose of the separated or concentrated pollutants (Rajeshwar and Ibanez, 1996; Marco et al., 1997).

Prathapar et al. (2006) designed “Wudhu Water Works” for the treatment of ablution water produced in mosques. The system was essentially sand/activated carbon filtration coupled with a disinfection unit using chlorine tablets. The simple and low-cost unit was able to treat the collected ablution water to the required standards in Oman since the initial COD level was low (COD = 51 mg.L\(^{-1}\)), whereas when greywater contains a higher level of contaminants, the performance of sand filtration units is poor (Friedler et al., 2006).

In their review, Pidou et al. (2007) also concluded that simple physical separation techniques such as coarse filtration, sand filtration (with or without activated carbon) and sedimentation provided limited removal of organics and solids, and they were mostly used for the treatment of low strength greywater at small scale such as in a single household. While membrane filtration achieved good solids removal, their performance in organics removal produced mixed results and this depended on the pore size of the membrane (Pidou et al., 2007).
Similarly, Nolde (2000) remarked that ultrafiltration, nanofiltration, and reverse osmosis are energy intensive; less energy demanding microfiltration does not remove BOD, and hence the permeate has the potential for microbial regrowth in the distribution system and the emission of offensive odour. This conclusion was also reached by Ramon et al. (2004) for the treatment of low strength greywater (COD = 170 mg.L\(^{-1}\)) with direct membrane filtration. The permeate from ultrafiltration membranes of MWCO of 30, 200 and 400 kDa exceeded 10 mg.L\(^{-1}\) BOD (i.e., beyond the limit required by many standards in Table 2-3) and therefore lower MWCO membranes such as 200 Da MWCO range were necessary. Despite the potential costs involved, such as the energy requirement for high operating pressure (1-2 bar for ultrafiltration and 6-10 bar transmembrane pressure for nanofiltration), and the cleaning and replacement of membranes due to fouling, it has been argued that direct membrane filtration treatments have the advantage of simplicity for in-situ reuse purposes.

The fouling of ultrafiltration membranes has been studied by Nghiem et al. (2006) using a synthetic greywater containing NaCl, NaHCO\(_3\), kaolin, cellulose, humic acid and CaCl\(_2\). The total organic carbon (TOC) retention was found to decrease from about 50% to 20% as the concentration of humic acid increased from 20 to 80 mg.L\(^{-1}\) (initial TOC value was not provided). The researchers concluded that a low molarity of calcium (< 3 mM) significantly enhanced membrane fouling, which increased linearly with the concentration of organic matter (for cellulose or humic acid in the presence of one another). A thicker cake layer was formed with increased concentration of particulate matter but its resistance depended on the interaction with other constituents in greywater such as calcium and organic matter.

To alleviate the problem of fouling and biofouling of membranes, Friedler et al. (2008) explored pre-treatment options such as chlorination (NaOCl) and coagulation (FeCl\(_3\)) with subsequent sedimentation. The bathroom greywater collected from 14 flats was subjected to the pre-treatments before subsequent treatment by cross-flow ultrafiltration (MWCO of 100 kDa) and reverse osmosis module (99% salt rejection). Coagulation alone reduced the fouling of the ultrafiltration membrane as a more porous filtration cake was formed by particles of larger sizes; chlorination alone also decreased the fouling rate but to a lesser extent. Combining the two pre-treatments, however, resulted in a similar extent of fouling as pre-treating the greywater with coagulation alone. The permeate after the pre-treatments and ultrafiltration was claimed to be suitable for toilet flushing and garden irrigation, although the organic contaminants in the treated water was reported in TOC, not BOD that has been used in most guidelines (Table 2-3). Interestingly, the combined chlorination and coagulation followed by ultrafiltration produced permeate that resulted in lower flux and lower permeability in the subsequent reverse osmosis. Friedler et al. (2008) attributed this fouling effect to the increase in ions such as Na\(^+\), Cl\(^-\), Fe\(^{3+}\) and SO\(_4\)\(^{2-}\), which originated from the
addition of NaOCl, FeCl₃ and Na₂S₂O₃ (de-chlorination prior to reverse osmosis). These ions augmented the concentration polarisation layer and enhanced the transportation rate of solute towards the membrane surface and hence increased the fouling rate.

Kim et al. (2007) used metal membranes (pore size 0.5, 1, and 5 µm) to treat greywater, rainwater and a mixture of these. The poor particle rejection of fibrous filter media and the high cost of polymeric membranes was the justification for the use of the stainless steel metal membranes. The source of the greywater used was not specified and its COD level was notably low (23 mg.L⁻¹). The researchers appeared to focus on the removal of particles, and the efficiencies of the membranes were compared mainly in terms of particle size rejection and their permeability. None of the three types of metal membranes reduced the turbidity of greywater to less than 2 NTU as required by most standards or guidelines (Table 2-3) although 70%, 45%, and 45% COD reduction was achieved by the 0.5, 1, and 5 µm membranes, respectively.

Lin et al. (2005) summarised the advantages of electrocoagulation over conventional coagulation in relation to hydraulic retention time, particle removal efficiency, coagulant dosage, sludge production, cost, and simplicity in operation and maintenance. The proposed unit for domestic greywater treatment consisted of a collection tank, an electrocoagulation reactor, a flotation unit and a disinfection/storage tank. Aluminium was used as the sacrificial anode instead of iron in the electrolysis cell to prevent the colouration of the treated water from the oxidation of ferrous ions. Hydrogen gas evolved at the cathode was used in the subsequent flotation unit to separate scum which could be skimmed from the surface of water, and the treated water was then disinfected with NaOCl and stored (Lin et al., 2005). The source of the greywater used in the study was not provided but its COD level was specified as between 27 and 102 mg.L⁻¹. Although the unit was claimed to have the advantages of low cost and minimal space requirement, the reported quality of the reclaimed water appeared to fluctuate significantly with the quality of the raw greywater. When the COD and turbidity levels were as high as 102 mg.L⁻¹ and 120 NTU respectively, 44 mg.L⁻¹ of COD and turbidity of 17 NTU remained in the treated water.

Interestingly, Widiastuti et al. (2008) reviewed the application of natural and modified zeolite in water and wastewater treatments and urged further investigation of this low-cost technology for the removal of cation and anion contaminants, as well as microorganisms in greywater. However, the potential of this treatment for the removal of organics is yet to be determined.
2.6.3 Chemical and Advanced Oxidation Processes (AOPs)

Chemical oxidation processes utilise chemical oxidants such as ozone (O$_3$), hydrogen peroxide (H$_2$O$_2$), chlorine and potassium permanganate to oxidise the contaminants in wastewater (Scott and Ollis, 1995; Ikehata and El-Din, 2004). Relatively recent developments in AOPs have created much interest in these technologies, which usually rely on the generation of highly reactive oxygen-containing intermediates such as hydroxyl radicals (*OH) to achieve mineralisation of toxic soluble pollutants (Oppenländer, 2003; Parsons and Williams, 2004). A vast variety of technologies fall into the category of AOPs and have been listed variously by Rajeshwar and Ibanez (1996), Kamat and Vinodgopal (1998), Oppenländer (2003), Gogate and Pandit (2004a), and Parsons and Williams (2004):

- **Homogeneous photolysis**
  Generation of *OH or active oxidising species by the photolysis of additives in solution, e.g., Vacuum-UV with water (VUV/H$_2$O), UV/H$_2$O$_2$, UV/O$_3$, and Photo-Fenton reaction (solar or UV irradiation with Fe$_{2+}$/H$_2$O$_2$).

- **Heterogeneous photolysis or photocatalysis**
  Using a semiconductor, e.g., titanium dioxide (TiO$_2$), and a radiation source to induce photoelectrochemical reactions at or near the surface of the photocatalyst.

- **Dark oxidation processes**
  Generation of radicals in the absence of radiation, e.g., Fenton reaction (Fe$_{2+}$/H$_2$O$_2$), O$_3$ at high pH and O$_3$/H$_2$O$_2$.

- **Hydrothermal oxidation or wet (air) oxidation**
  Usually used for waste streams which are too dilute to incinerate, or too concentrated, too toxic or non-degradable for biological treatment. Suspended or dissolved materials are oxidised in water with dissolved oxygen at elevated temperature and pressure, e.g., sub-critical, critical and super-critical water oxidation (SUWOX).

- **Radiolysis**
  Irradiation of wastewater with high energy radiation ($\gamma$-rays) to produce *OH, *H, and hydrated electrons (e$_{aq}$).

- **Sonolysis**
  Generation of radicals such as *OH and hydroperoxyl radicals (*O$_2$H) by the dissociation of H$_2$O at high temperature and pressure conditions caused by the collapse of cavitation bubbles produced during the propagation of ultrasound waves in aqueous solution, or caused by the constrictions in hydraulic devices (e.g., valve, orifice, and venturi).

A review of the application of AOPs in wastewater treatment has been published by Gogate and Pandit (2004a). They classified the AOPs differently from above: cavitation, photocatalytic oxidation, Fenton chemistry, and chemical oxidation using ozonation and
H₂O₂, and they suggested that these technologies, when used alone, may not be economic or energy efficient. Subsequently, Gogate and Pandit (2004b) reviewed the combinations of these processes such as ultrasound/H₂O₂ or O₃, UV/H₂O₂ or O₃, O₂/H₂O₂, sono-photochemical oxidation, photo-Fenton process, sono-chemical oxidation with wet oxidation (SONIWO) and the cavitation oxidation process (CAV-OX) and concluded that the synergies resulted in higher oxidation rates due to the enhanced generation of *OH, and the process efficacy relied on the reactor conditions or configurations to achieve higher utilisation of oxidants or catalysts and better contact between *OH and the pollutants.

While many of these technologies have been implemented successfully in the treatment of domestic and industrial wastewaters, their application in greywater treatment has been limited. In the following review, emphasis has been placed on the applications of Fenton, Photo-Fenton and UVC/H₂O₂ processes.

2.6.3.1 Fenton Process
The reaction between dissolved iron and H₂O₂ was first described by Fenton in 1894, and the reaction can be described by Equations 2-1 and 2-2 (Benatti et al., 2006):

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \quad \text{Equation 2-1}
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \leftrightarrow \text{Fe}^{2+} + \cdot\text{O}_2\text{H} + \text{H}^+ \quad \text{Equation 2-2}
\]

Depending on the solution pH, ferrous and ferric ions can exist in the form of a range of hydrolysis species or other inorganic complexes. For pH 2 – 7 and in the absence of strong inorganic ligands, ferrous ion presents in the form of Fe²⁺ (aq). For the ferric ion, Fe³⁺ (aq) exists below pH 3, FeOH²⁺ (aq) at about pH 3, and Fe(OH)₂⁺ (aq) for pH 3 – 7 (Wadley and Waite, 2004). Therefore, Wadley and Waite suggested using the notation of Fe²⁺ and Fe³⁺ to represent the dissolved ferrous and ferric iron. However, as shown in the following review, most researchers used the notation of Fe²⁺ and Fe³⁺ instead of the exact species present in the water and this has been followed in this project.

The Fenton process usually involves four stages: pH adjustment, oxidation, neutralisation, and coagulation and precipitation (Benatti et al., 2006). Wadley and Waite (2004), Benatti et al. (2006) and Bautista et al. (2007) variously listed the following advantages of using the Fenton process for wastewater treatment:

- The reagents are easy-to-handle, inexpensive, abundant, non-toxic and environmentally benign in diluted form, and they possess oxidative and coagulative properties,
- No additional energy input required to activate H₂O₂, hence a cost effective method to
generate *OH,
- No special equipment required, and
- Short reaction time and high efficiency compared with some AOPs.

The actual mechanisms involved in reactions between the reagents, radicals, and organic substrate in the oxidation stage are yet to be completely understood (Wadley and Waite, 2004). However, some widely reported reactions are as in Equations 2-1 to 2-15 (Table 2-6), while others have also suggested the possible involvement of active oxidising species such as FeO$_{2}^{+}$ (Wadley and Waite, 2004).

**Table 2-6. Possible reactions between Fenton reagents and organic substrate in Fenton oxidation, listed variously by Neyens and Baeyens (2003), Wadley and Waite (2004), Benatti et al. (2006), Gulkaya et al.(2006), and Bautista et al. (2007).**

<table>
<thead>
<tr>
<th>Type of Reaction</th>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation of *OH and *O$_{2}$H by reactions between Fe$^{3+}$ or Fe$^{5+}$</td>
<td>Fe$^{2+} +$ H$<em>{2}$O$</em>{2} \rightarrow$ Fe$^{3+} +$ *OH + OH$^{-}$</td>
<td>2-1</td>
</tr>
<tr>
<td>with H$<em>{2}$O$</em>{2}$</td>
<td>Fe$^{3+} +$ H$<em>{2}$O$</em>{2} \leftrightarrow$ Fe$^{2+} +$ *O$_{2}$H + H$^{+}$</td>
<td>2-2</td>
</tr>
<tr>
<td>Scavenging of radicals by recombination of the radicals or by reactions with Fe$^{5+}$, Fe$^{3+}$ and H$<em>{2}$O$</em>{2}$</td>
<td>*OH + *OH $\rightarrow$ ½ O$<em>{2} +$ H$</em>{2}$O</td>
<td>2-3</td>
</tr>
<tr>
<td></td>
<td>*OH + *O$<em>{2}$H $\rightarrow$ O$</em>{2} +$ H$_{2}$O</td>
<td>2-4</td>
</tr>
<tr>
<td></td>
<td>H$<em>{2}$O$</em>{2} +$ *OH $\rightarrow$ *O$<em>{2}$H + H$</em>{2}$O</td>
<td>2-5</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+} +$ *OH $\rightarrow$ Fe$^{3+} +$ *O$_{2}$H + OH$^{-}$</td>
<td>2-6</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+} +$ *O$<em>{2}$H + H$^{+} \rightarrow$ Fe$^{3+} +$ H$</em>{2}$O$_{2}$</td>
<td>2-7</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+} +$ *O$<em>{2}$H $\rightarrow$ Fe$^{3+} +$ O$</em>{2} +$ H$^{+}$</td>
<td>2-8</td>
</tr>
<tr>
<td>Reactions initiated by the attack of organic substrate, RH, by radicals</td>
<td>RH + *OH $\rightarrow$ R$^{•}$ + H$_{2}$O</td>
<td>2-9</td>
</tr>
<tr>
<td></td>
<td>R$^{•}$ + O$<em>{2} \rightarrow$ RO$</em>{2}^{•}$ $\rightarrow$ degradation products</td>
<td>2-10</td>
</tr>
<tr>
<td></td>
<td>R$^{•}$ + H$<em>{2}$O$</em>{2} \rightarrow$ ROH + *OH</td>
<td>2-11</td>
</tr>
<tr>
<td></td>
<td>2R$^{•}$ $\rightarrow$ R–R</td>
<td>2-12</td>
</tr>
<tr>
<td></td>
<td>R$^{•}$ + Fe$^{2+} \rightarrow$ R$^{•}$ + Fe$^{3+}$</td>
<td>2-13</td>
</tr>
<tr>
<td></td>
<td>R$^{•}$ + Fe$^{3+} \rightarrow$ R$^{•}$ + Fe$^{2+}$</td>
<td>2-14</td>
</tr>
<tr>
<td></td>
<td>R$^{•}$ + H$_{2}$O $\rightarrow$ ROH + H$^{+}$</td>
<td>2-15</td>
</tr>
</tbody>
</table>

Usually, ferrous ion (Fe$^{2+}$) was used as the source of iron and its superiority over ferric ion (Fe$^{3+}$) has been demonstrated by Wang (2008) in the treatment of azo dye wastewater by the Fenton process. The effects of Fe$^{2+}$ or Fe$^{3+}$ dosage, H$_{2}$O$_{2}$ concentration, pH, and temperature were investigated and Wang (2008) reported the following findings:
Higher rate of dye degradation was observed when Fe\(^{2+}\) was used instead of Fe\(^{3+}\) although a similar extent of degradation was achieved (95% of about 0.07 mM dye was removed),

- Increased iron dosages and H\(_2\)O\(_2\) concentration accelerated the rate of dye degradation,
- Decrease in pH from 6.3 to 2.4 or 3.4 significantly improved the degradation rate, and
- Degradation rate deteriorated at temperature higher than 45°C.

The literature related to the Fenton process was reviewed by Gogate and Pandit (2004a) and the important operational parameters were identified as Fe\(^{2+}\) and H\(_2\)O\(_2\) dosages, initial concentration of pollutants, pH, and type of buffer used for pH adjustment. The degradation rate of pollutants was accelerated with increased Fe\(^{2+}\) concentration. However, excessive Fe\(^{2+}\) dosage only increased the degradation rate marginally and contributed to increased total dissolved solids. The need to remove residual dissolved iron and the problem related to sludge disposal have been pointed out by Bautista et al. (2007).

Gogate and Pandit (2004a) further discussed the adverse effect of excessive H\(_2\)O\(_2\) dosage in the overall degradation of pollutants due to the reaction between \(^*\)OH and excess H\(_2\)O\(_2\). The optimum pH condition was found to be 3 – 4, and the highest oxidation efficiency was reported when acetic acid/acetate buffer was used instead of phosphate and sulphate buffers which encouraged the formation of stable Fe\(^{3+}\) complexes. Problems such as corrosion of equipment (due to the acidic conditions) and inability to break down refractory chemicals (e.g., acetic acid, acetone, carbon tetrachloride, methylene chloride, \(n\)-paraffins, maleic acid, malonic acid, oxalic acid, and trichloroethane) were discussed by Gogate and Pandit (2004a). The effects of pH in Fenton processes have been summarised in Table 2-7.

Table 2-7. Effects of pH in processes using Fenton reagents, discussed variously by Gogate and Pandit (2004a), Gulkaya et al. (2006), Tekin et al. (2006), Bautista et al. (2007).

<table>
<thead>
<tr>
<th>pH</th>
<th>Effects</th>
<th>Consequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 2.5</td>
<td>Stabilisation of H(_2)O(_2) to form H(_3)O(_2^+)</td>
<td>Slow reaction between Fe(^{2+}) and H(_2)O(_2)</td>
</tr>
<tr>
<td></td>
<td>Reaction between H(^+) and (^*)OH</td>
<td>Inhibition of (^*)OH production</td>
</tr>
<tr>
<td></td>
<td>Formation of (Fe(^{II})(H(_2)O(_6))(^{2+})</td>
<td>Slow reaction with H(_2)O(_2), hence slows (^*)OH production</td>
</tr>
<tr>
<td></td>
<td>Inhibition of reaction between Fe(^{3+}) and H(_2)O(_2)</td>
<td>Inhibition of the regeneration of Fe(^{2+})</td>
</tr>
<tr>
<td>&gt; 4</td>
<td>Precipitation of Fe(^{3+}) as Fe(OH)(_3)</td>
<td>• Hinders regeneration of Fe(^{2+})</td>
</tr>
<tr>
<td></td>
<td>Formation of highly stable Fe(II) complexes with buffer</td>
<td>• Fe(OH)(_3) catalyses the decomposition of H(_2)O(_2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inhibition of (^*)OH production</td>
</tr>
</tbody>
</table>
Bautista et al. (2007) tested the Fenton process on wastewater collected from a cosmetic industry which was pre-treated with homogenisation, filtration, coagulation, neutralisation, flocculation, and air-pressure flotation. The aim of an additional Fenton process was to reduce the contaminant loadings in the treated water to the emission limit for discharge to the municipal sewer system. The researchers found highest removal of total organic carbon (TOC) at pH 2.5 – 3. The theoretical stoichiometric H₂O₂:COD ratio was reported as 2.12 g H₂O₂/g COD and it was concluded that a greater H₂O₂:COD ratio did not increase TOC removal. The optimisation of Fe²⁺ dosage was undertaken and, interestingly, samples with higher TOC had a lower threshold for Fe²⁺ dosage beyond which the removal of TOC was not improved. The researchers explained that, with higher initial concentration of organic matter, more organic radicals were formed which regenerated Fe²⁺ according to Equation 2-14 and consequently it favoured the scavenging of *OH by Fe²⁺ (Equation 2-6).

Bautista et al. (2007) also studied the effect of temperature at various Fe²⁺ dosage at a fixed stoichiometric H₂O₂:COD ratio. At low Fe²⁺ concentration, elevated temperature improved the rate and extent of TOC removal. Conversely, the combination of high temperature and high Fe²⁺ concentration caused rapid decomposition of H₂O₂, and favoured the occurrence of *OH consuming reactions (such as Equation 2-6) rather than oxidation of organic matter. The researchers used a Fe²⁺:H₂O₂ molar ratio of around 1:44, and commented on the large variations in this ratio that have been reported in the literature. Therefore, for the optimisation of the process in terms of Fe²⁺ and H₂O₂ dosages, Bautista et al. (2007) recommended dosing H₂O₂ according to the stoichiometric H₂O₂:COD ratio (i.e., 2.12 g H₂O₂/g COD), followed by the determination of the optimal Fe²⁺ dosage.

Gulkaya et al. (2006) also observed the large differences in the optimal Fe²⁺:H₂O₂ ratio in the literature and they concluded that the ratio depends on the type and loadings of contaminants in the wastewater. The aim of their study on the treatment of carpet dyeing wastewater was to determine the extent to which the Fe²⁺ and H₂O₂ dosages could be reduced, while keeping a constant optimal Fe²⁺:H₂O₂ ratio. They found that the optimal molar ratio fell within the range of 1:153 to 1:470 which achieved 90 – 95% COD removal (COD₀ = 2400 mg.L⁻¹). By maintaining the ratio within the range, the researchers demonstrated the possibility of substantially reducing the Fe²⁺ and H₂O₂ dosages without sacrificing the high level of COD removal. A significant improvement in overall TOC removal by the Fenton oxidation and the Fenton coagulation was reported when the temperature was raised from 25 to 40°C. Further increase in temperature to 50°C increased the extent of TOC removal in the oxidation stage, but not the coagulation stage. While reporting other studies which noted the adverse effect of temperature above 50°C (i.e., due to the decomposition of H₂O₂), the researchers did not explain why they obtained little difference between the treatments at 50 and 70°C.
Neyens and Baeyens (2003) discussed Fenton processes in three categories, i.e., when the molar ratio of $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ exceeded 2, equalled 1, and was less than 1. When the $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio exceeded 1, Fenton coagulation was the dominant process. Conversely, the oxidative property of Fenton reagents dominated when $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ was less than 1.

The Fenton process has been used by Benatti et al. (2006) to treat chemical laboratory wastewater, and the COD removal was maximised by using response-surface optimisation techniques in which $\text{H}_2\text{O}_2:\text{COD}$, $\text{Fe}^{2+}:\text{H}_2\text{O}_2$, and pH were used as the control factors. The required amount of $\text{H}_2\text{O}_2$ was added in three equal portions at intervals of 20 minutes. The oxidation stage was maintained at pH 4 for 4 hours before adjustment to 8 and subsequent settling for 15 hours. Although many reports suggested that up to 30 minutes was sufficient for the reaction to reach equilibrium (Gulkaya et al., 2006; Tekin et al., 2006; Bautista et al., 2007), the reaction time of 4 hours for the oxidation as suggested by Benatti et al. (2006) might not be excessive since others have also reported a longer oxidation time (Gogate and Pandit, 2004a). On the other hand, long settling times for the Fenton process have also been observed by Neyens and Baeyens (2003) and they recommended the use of a flocculant aid such as a polymer.

Benatti et al. (2006) reported an overall COD reduction of 92% at the optimal conditions of $\text{H}_2\text{O}_2:\text{COD} = 9:1$, $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:4.5$ and pH = 4. The researchers concluded that higher COD removal in the Fenton oxidation stage could minimise the quantity of sludge production in the subsequent coagulation stage. However, contaminants such as some heavy metals and sulphate were not adequately removed by the process and the installation of post-treatment systems was recommended to fulfil the discharge requirements.

The strong dependency of the optimal $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio on the type of wastewater has also been acknowledged by Tekin et al. (2006), and they applied the molar ratio of 1:150 to 1:250 to improve the biodegradability of different pharmaceutical wastewaters (measured as BOD$_5$:COD). The oxidative and coagulative properties of Fenton reagents were explored at different pH. No significant difference in COD removal was observed over pH 3 – 4.5 in the oxidation stage, or for pH 7 – 9 in the subsequent coagulation stage.

The dual function of Fenton reagents as oxidant and coagulant has also been investigated by Badawy and Ali (2006) in the treatment of combined industrial and domestic wastewater (COD = 1596 mg.L$^{-1}$). The process was compared with conventional coagulation treatment using FeCl$_3$ and coagulant aids such as cationic and anionic polymers, powdered activated carbon, and bentonite. While conventional coagulation improved the biodegradability of the wastewater, the researchers preferred the Fenton process which achieved higher removal of
soluble organic compounds and a lower volume of sludge. The optimal conditions for the Fenton process were 1.5 mM Fe$^{2+}$ and 16.2 mM H$_2$O$_2$ at pH 3 (molar ratio of Fe$^{2+}$:H$_2$O$_2$ of 1:11), which removed more than 90% of COD from the combined wastewater.

Kim et al. (2004) compared chemical coagulation and the Fenton process to treat textile industry wastewater which contained disperse and reactive dyestuffs. Different dyestuffs responded differently to the individual treatments, hence the researchers proposed to combine the two processes. A combination of chemical coagulation and Fenton process has also been studied for the treatment of industrial wastewater containing the herbicide trifluraline (COD = 2032 mg.L$^{-1}$), and 92% colour reduction (absorbance at 420 nm) and 63% COD removal were achieved (Martins et al., 2005).

For the treatment of domestic wastewater with low biodegradability, Ksibi (2006) concluded that the presence of ferrous ions did not improve the COD reduction, deodorisation, or disinfection of the wastewater compared with treatment by H$_2$O$_2$ alone. The experiments were conducted at around pH 7.4 as the researcher suggested that cost prohibited the acidification of the wastewater. Since the optimum pH for Fenton oxidation is widely reported to be 3 – 4, the conditions used by Ksibi for the Fenton process were probably not favourable for the generation of *OH, and this may explain why ferrous ions did not play a significant role in his study. Also, H$_2$O$_2$ is known to interfere with COD measurement (Talinli and Anderson, 1992), but the residual concentration of H$_2$O$_2$ in the sample was not measured before it was subjected to COD analysis as the researcher believed that the H$_2$O$_2$ would have decomposed completely under the experimental conditions (personal communication). Nevertheless, Ksibi (2006) found that in the presence of 15 mM H$_2$O$_2$ alone, approximately 85% COD reduction was achieved within 2 hours of treatment, and higher dosage of the oxidant (e.g., 25 mM) was necessary to improve the biodegradability (BOD:COD) of the wastewater from 0.11 to 0.47.

### 2.6.3.2 Photo-Fenton Process

Under UV irradiation (180-400 nm), Fe$^{3+}$ (or ferryl species, FeO$^{2+}$) can catalyse the formation of *OH, as shown in Equation 2-16 (Wadley and Waite, 2004):

$$\text{Fe}^{3+} + \text{H}_2\text{O} + h\nu \rightarrow \text{Fe}^{2+} + {^\circ}{\text{OH}} + \text{H}^+ \quad \text{Equation 2-16}$$

In conjunction with the reaction between Fe$^{2+}$ and H$_2$O$_2$ (Equation 2-1), the iron cycles between the +2 and +3 state and in theory, two moles of *OH could be produced by the photo-Fenton process per mole of H$_2$O$_2$ consumed (Wadley and Waite, 2004). Furthermore, the photolysis of H$_2$O$_2$ to *OH generates additional radicals (de Oliveira et al., 2007).
Gogate and Pandit (2004b) noted that the photo-Fenton process was generally more efficient than Fenton treatment. In some cases, use of sunlight instead of UV irradiation reduced the costs but a lower degradation rate of pollutants may result. While the presence of oxygen through aeration enhanced the process, the efficacy of using Fe$^{3+}$ ions was claimed to be significantly higher than Fe$^{2+}$ ions. In contrast to UV/H$_2$O$_2$ treatment, Gogate and Pandit (2004b) found no optimum H$_2$O$_2$ dosage beyond which the degradation rate was significantly reduced, but they suggested that a plateau might be observed with increased H$_2$O$_2$ concentration. Acidic conditions (about pH 3) were also reported to be favourable, mainly due to the conversion of carbonate and bicarbonate species to carbonic acid which has a low reactivity with OH$^-$ (Legrini et al., 1993).

In a comparison of the Fenton and the photo-Fenton processes for the treatment of painting industry effluent (COD = 80.75 mg L$^{-1}$), de Oliveira et al. (2007) found the highest COD and TOC removal with a solar-assisted photo-Fenton process, compared with Fenton treatment or when an artificial radiation source was used. Three iron sources were used in the photo-Fenton experiments: FeSO$_4$, Fe(NO$_3$)$_3$ and potassium ferrioxalate (K$_3$[Fe(C$_2$O$_4$)$_3$], obtained by mixing Fe(NO$_3$)$_3$ with K$_2$C$_2$O$_4$ solutions). The researchers found that the highest level of COD reduction occurred when FeSO$_4$ was used. The formation of Fe$^{3+}$ complex when Fe(NO$_3$)$_3$ was used resulted in poor performance of the photo-Fenton process, whereas the addition of K$_3$[Fe(C$_2$O$_4$)$_3$] increased the carbon loading to the wastewater. In the presence of 15 mM of Fe$^{2+}$ and 300 mM of H$_2$O$_2$, 99.5% COD reduction was achieved when the wastewater was irradiated by the sun for 6 hours.

Amat et al. (2004) compared the degradation of two commercial anionic surfactants, sodium dodecyl sulphate (SDS) and dodecylbenzenesulphonate (DBS), using the Fenton reagents (Fe$^{2+}$ or Fe$^{3+}$ with H$_2$O$_2$ in the presence or absence of solar radiation), photocatalysis (TiO$_2$ with solar irradiation) and photodegradation using solar sensitisers (pyrylium salt). They demonstrated that the addition of the solar sensitisers did not efficiently degrade the surfactants. Their further studies concluded that the photo-Fenton processes using solar radiation (0.1 mM of Fe$^{2+}$ or Fe$^{3+}$, and 1mM H$_2$O$_2$) had a higher rate of surfactant degradation than that of solar-TiO$_2$ treatment.

Sanly et al. (2006) treated water containing humic substances (DOC = 10 ppm) with a photo-Fenton process (UVA/Fe(ClO$_4$)$_3$/H$_2$O$_2$/pH 4). By fixing the dosage of Fe$^{3+}$ at 0.1 mM, the researchers observed an optimal Fe$^{3+}$:H$_2$O$_2$ molar ratio of 1:10 at which 80% of dissolved organic carbon (DOC) and 90% of A$_{254}$ were removed within 2.5 hours of irradiation. Ratios up to 1:20 were investigated but did not lead to significant improvement in the removal of DOC and A$_{254}$. 

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2.6.3.3 UV/H2O2 Process

The UV/H2O2 process is the most direct method for the generation of *OH through the photolysis of H2O2, as shown in Equation 2-17 (Tuhkanen, 2004):

$$\text{H}_2\text{O}_2 + h\nu \rightarrow 2 \,*\text{OH}$$  \hspace{1cm} \text{Equation 2-17}

Since H2O2 is a slightly stronger acid than H2O, it dissociates to form H⁺ and O₂⁻H according to Equation 2-18 (Ardon, 1964). Legrini et al. (1993) and Tang (2004) recognised that O₂⁻H also undergoes photolysis (Equation 2-19) and its molar absorption coefficient at 254 nm is 228 – 240 L.mol⁻¹.cm⁻¹ which is much higher than that of H2O2 (17.9 – 19.6 L.mol⁻¹.cm⁻¹):

$$\text{H}_2\text{O}_2 \stackrel{\text{hv}}{\rightarrow} \text{H}^+ + \text{O}_2\text{H}^-$$  \hspace{1cm} \text{Equation 2-18}

$$\text{H}_2\text{O}_2 / \text{O}_2\text{H}^- + h\nu \rightarrow 2 \,*\text{OH}$$  \hspace{1cm} \text{Equation 2-19}

In addition, H2O2 may decompose by dismutation reaction (Equation 2-20), which also produces *OH (Legrini et al., 1993; Tang, 2004):

$$\text{H}_2\text{O}_2 + \text{O}_2\text{H}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \,*\text{OH}$$  \hspace{1cm} \text{Equation 2-20}

Legrini et al. (1993) summarised three mechanisms for the reaction between *OH and organic substrates, namely hydrogen abstraction, electrophilic addition, and electron transfer. The reaction between *OH and an organic substrate (HRH) by hydrogen abstraction and their subsequent reactions are shown in Figure 2-1:

(a) H2O2 photolyses to *OH under irradiation,
(b) *OH reacts with HRH by hydrogen abstraction to form organic radicals (RH*),
(c) RH* reacts with dissolved oxygen to yield organic peroxyl radicals (RHO2*), which initiate subsequent thermal oxidation reactions as in (d), (e), (f), and (g),
(d) Heterolysis and generation of organic cations (RH⁺) and superoxide anions (O₂⁻*),
(e) 1,3-hydrogen shift and homolysis into *OH and carbonyl compound (RO),
(f) Reverse reaction of (c),
(g) Hydrogen abstraction of HRH by RHO₂*,
(h) O₂⁻* disproportionates in an aqueous system to form H₂O₂, and
(i) Polymerisation of unsaturated organic substrate initiated by RH* in an oxygen deficient system.

Electrophilic addition of *OH to the π-systems of unsaturated organic compounds leads to the formation of organic radicals (Equation 2-21) and its subsequent reaction pathways are similar to those described in Figure 2-1. The electron transfer occurs during the reduction of *OH to OH⁻ by an organic substrate (Equation 2-22) and it is of interest when hydrogen abstraction and electrophilic addition are not favoured due to multiple halogen substitution or
steric hindrance (Legrini et al., 1993):

\[
\begin{align*}
R_1R_2R_3 + \cdot\text{OH} & \rightarrow R_1R_2\cdot R_3OH & \text{Equation 2-21} \\
RX + \cdot\text{OH} & \rightarrow \text{OH}^- + RX^+ & \text{Equation 2-22}
\end{align*}
\]

\[
\begin{align*}
\text{RH}^+ & \rightarrow \text{O}_2^+ & \text{(h)} \\
\text{H}_2\text{O}_2 & \rightarrow \cdot\text{OH} & \text{Equation 2-22}
\end{align*}
\]

**Figure 2-1. Reaction between hydroxyl radicals (\(\cdot\text{OH}\)) and an organic substrate (HRH) by hydrogen abstraction and their subsequent reactions (Legrini et al., 1993).**

Ghaly et al. (2001) conducted a comparison of the degradation of 4-chlorophenol by direct photolysis, UV/H\(_2\)O\(_2\) and photo-Fenton processes. A high pressure mercury lamp (700W, 200 – 600 nm) was used in combination with H\(_2\)O\(_2\), and FeSO\(_4\) or Fe\(_2\)(SO\(_4\))\(_3\) was added as the source of iron when required. For UV irradiation alone (i.e., direct photolysis), the researchers found moderate degradation of 4-chlorophenol. By adding H\(_2\)O\(_2\), the degradation rate was enhanced and up to 98% 4-chlorophenol was removed by 20 mM H\(_2\)O\(_2\) within 30 minutes of irradiation. However, an adverse effect was observed when 50 mM H\(_2\)O\(_2\) was used which had a degradation rate lower than that of the direct photolysis, demonstrating the scavenging effect of excess H\(_2\)O\(_2\) on \(\cdot\text{OH}\). For photo-Fenton processes, the optimal conditions were found to be UV/1 mM Fe\(^{2+}\)/30 mM H\(_2\)O\(_2\)/pH 3 and UV/0.4 mM Fe\(^{3+}\)/10 mM H\(_2\)O\(_2\)/pH 3, and both achieved more than 99% 4-chlorophenol degradation within 7 and 4 minutes of treatment respectively. Note that the molar ratios of iron to H\(_2\)O\(_2\) are similar in both cases, i.e., 1:30 and 1:25 respectively, but a lower dosage of iron and H\(_2\)O\(_2\) and shorter reaction time were required when Fe\(_2\)(SO\(_4\))\(_3\) was used as the source of iron.
A UVC/H₂O₂ process was proposed by Yonar et al. (2006) to treat a medium-strength domestic wastewater collected from a non-industrial residential district in Turkey (COD = 336 ± 25 mg.L⁻¹ with 13.2 ± 0.8 NTU). A reduction of turbidity is necessary for the penetration of UV radiation and they examined the effects of different pre-treatments such as sedimentation, chemical coagulation, and filtration with filter papers. Sedimentation only reduced 20% COD and 31% turbidity. At the optimal dosage of 60 mg.L⁻¹ at pH 7, aluminium sulphate as a coagulant removed up to 39% and 84% of COD and turbidity, respectively. It was also reported that filter paper of 25 µm pore size was adequate as it removed 40% COD and 83% turbidity, although smaller pore size, such as 0.45 µm, provided further reduction. Various conditions such as pH, H₂O₂ dosage, and UV lamp power were studied. The generation of hydroxyl radicals in the process was pH-dependent and ionic radical scavengers such as carbonates and bicarbonates were diminished at lower pH. Maximal COD reduction was achieved at pH 3, however, the COD removal at pH 4 and 5 was only marginally lower. This led to consideration of operating the system at around pH 5 to avoid the problem of dealing with highly acidic solution and the practicality of acidification and subsequent neutralisation of a large volume of wastewater. The optimal H₂O₂ dosage was found to be 50 mg.L⁻¹. At higher dosages, the COD reduction was not significantly improved, possibly due to the formation of less powerful hydroperoxyl radicals (●O₂H) by the reaction between hydroxyl radicals and excess H₂O₂. It was also shown that the use of higher power UVC lamps shortened the reaction time for the same level of COD reduction.

An and Carraway (2002) studied photolytic and UVC/H₂O₂ treatment for the degradation of polycyclic aromatic hydrocarbons (PAHs) which had been solubilised in an anionic perfluorinated surfactant (PFS). Phenanthrene and pyrene were chosen to represent PAHs, and ammonium perfluorooctanoate (APFO) to represent the PFS. While the presence of APFO retarded the direct photolysis of phenanthrene but enhanced the photolysis of pyrene, the addition of H₂O₂ (10 mM) dramatically improved the degradation of the PAHs. The surfactant was found to be resistant to the treatment and the researchers considered this to be advantageous due to the possibility of recovering and reusing the surfactant. However, its resistance to treatment might also be problematic since APFO has been shown to have a long half-life in human blood and liver damage was observed in cynomolgus monkeys dosed with this PFS (Butenhoff et al., 2002; Butenhoff et al., 2004).

Annachhatre and Bhargava (1999) used vacuum-UV (VUV, 185 nm) irradiation and H₂O₂ to treat domestic wastewater (COD = 598 ± 304 mg.L⁻¹) which consisted of wastewater from a cafeteria and sewage from toilets. In addition to the photolysis of H₂O₂, VUV also causes photolysis of water to generate H⁺ and ●OH (Stefan, 2004). In the pilot-scale study,
Annachhatre and Bhargava added poly aluminium chloride and polymer as coagulant and flocculant aid in a swirl-flow clarifier where up to 40% of COD and 45% of total suspended solids were removed. The subsequent VUV/H₂O₂ treatment, however, only removed up to 23% of the remaining COD and further COD removal was achieved in the subsequent pressure sand filter (22%) and activated carbon column (76%). This gave an overall COD removal of about 90%. The relatively minor role of the VUV/H₂O₂ in the train of treatments was explained by the presence of suspended solids which hindered the penetration of VUV irradiation, and also the presence of nitrite and bicarbonates which scavenge *OH effectively.

### 2.6.3.4 Other AOPs

Zayas Pérez et al. (2007) combined commercial chemical coagulant/flocculant with UV/H₂O₂, UV/O₃, and UV/H₂O₂/O₃ processes for the treatment of coffee processing wastewater (COD = 4300 mg.L⁻¹). They found that coagulation/flocculation removed up to 67% of COD, and an overall COD reduction of 86% was achieved when combined with UV/H₂O₂ treatment. UV/H₂O₂/O₃ was claimed to be the most effective treatment among the three AOPs studied, with up to 87% of COD removed.

Han et al. (2004b) compared UVC (254 nm) and VUV (185 nm) irradiation for the degradation of some phenols (4-chlorophenol, hydroquinone, and 4-nitrophenol) in the presence or absence of TiO₂ slurry. It was shown that the presence of the photocatalyst enhanced the removal of TOC. In a similar study on the degradation of p-chlorobenzoic acid, Han et al. (2004a) investigated the effects of initial substrate concentration and different types of bubbling gases (i.e., air, O₂ and N₂). VUV-TiO₂ was the most efficient process, followed by VUV and UV-TiO₂ treatments, and direct photolysis of p-chlorobenzoic acid by UV had the lowest rate of mineralisation. While bubbling significantly increased the mass transfer in all treatments investigated, the rate of mineralisation by direct photolysis was not markedly affected by the type of bubbling gas used, whereas the presence of dissolved oxygen (DO) was highly beneficial in the UV/TiO₂, VUV, and VUV/TiO₂ treatments. The vital role of DO as an electron acceptor in semiconductor photocatalysis is well known (Mills and Lee, 2004), and the role of DO in the oxidation of organic pollutants by *OH is illustrated in Equations 2-9 and 2-10. However, the presence of DO is not always advantageous and some investigations reported an increased degradation rate of nitrogen-containing organic compounds (e.g., 3-amino-5-methylisoxazole) and chlorinated hydrocarbons in the absence of DO (Han et al., 2004b).

Kuo and Lin (2000) examined the photocatalytic degradation of carbofuran (10 mg.L⁻¹, TOC = 6.5 mg.L⁻¹) as a representative of XOCs. TiO₂ was immobilised on the agitator blades and
after 6 hours of irradiation with three 15 W low intensity UVC lamps, complete removal of carbofuran and up to 20% TOC removal were achieved, which implies partial mineralisation of carbofuran. Nakashima et al. (2002) investigated the decomposition of several endocrine disruptive chemicals (EDCs) by photocatalysis using low intensity UVA irradiation and TiO$_2$ immobilised on polytetrafluoroethylene (PTFE) mesh sheets. These EDCs included 17β-estradiol, bisphenol-A, and 2,4-dichlorophenol, and they were not directly photolysed by UVA irradiation alone. In the absence of UVA irradiation, these compounds were adsorbed to the stacked TiO$_2$-modified PTFE sheets to various extents within 1 hour: 85% for 17β-estradiol, 88% for bisphenol-A and 50% for 2,4-dichlorophenol. Using photocatalysis (UVA/TiO$_2$), more than 90% of each of the EDC (initial concentration = 90 $\mu$g.L$^{-1}$) was degraded after 30 minutes. Both of these investigations reported successful degradation of the compounds, and the benefit of using immobilised TiO$_2$ rather than in suspension was emphasized as it does not require an additional step to recover the photocatalyst. Gogate and Pandit (2004a) pointed out that successful immobilisation of TiO$_2$ on a support was method-dependent, as some coating methods affect catalytic activity, and the coating can be vulnerable to erosion and scouring caused by liquid flow.

Jefferson et al. (2003) also acknowledged the necessity of developing a low cost process to recover the photocatalyst after studying the treatment of greywater with UVC irradiation and TiO$_2$ in suspension. Subsequently, a membrane chemical reactor (MCR) was proposed by Rivero et al. (2006) in which side-stream cross-flow microfiltration (0.05 $\mu$m) was used to recycle the photocatalyst, and the organic contaminants in the shower greywater (BOD = 102.2 ± 28.4 mg.L$^{-1}$) were mineralised in the presence of up to 10 g.L$^{-1}$ TiO$_2$ in suspension under UVC irradiation. The problem of membrane fouling was minimised by the cross-flow arrangement and continuous aeration in the microfiltration module. While Rivero et al. demonstrated that the treatment achieved high quality permeate, with less than 10 mg.L$^{-1}$ BOD and 1 NTU turbidity remaining, the performance of the system to remove microbial loading was only reported as meeting “WHO standards for reuse” without further details given. Judd and Till (2000) found that the presence of protein facilitated the breakthrough and transportation of bacteria such as coliform species in cross-flow microfiltration (0.2 to 1.2 $\mu$m). While the pore size of the microfiltration membrane (0.05 $\mu$m) used by Rivero et al. would retain bacteria, viruses may remain an issue and therefore, a subsequent disinfection unit for the MCR might be necessary to provide multi-barrier protection of human health.

While TiO$_2$ (and its enhancement with transition metals such as Pt) offers superior efficiency of contaminant degradation, other photocatalysts such as ZnO, ZrO$_2$, CeO$_2$, CdS, and ZnS have also been used. The capability of these photocatalysts to utilise solar or near-UV irradiation has been considered as a major advantage for large scale applications (Gogate and
Sanly et al. (2006) used photocatalysis (UVA/TiO₂) to remove humic substances in water (DOC = 10 ppm), and they found that the rate of DOC and A₂₅₄ removal was increased at higher pH such that: pH 9 > pH 7 > pH 4. It was noted that the rate of degradation could be further enhanced by the addition of H₂O₂, which reduced the required irradiation time and allowed operation at neutral pH. Within 1 hour of UVA irradiation, 90% of DOC and 95% of A₂₅₄ were removed in the presence of 0.1 g.L⁻¹ TiO₂ and 1 mM H₂O₂ at pH 7.

As a sole treatment, AOPs are often associated with high costs compared with many physical and biological treatments (Marco et al., 1997; Ledakowicz, 1998). On the other hand, it has been observed that the biodegradability of most organic compounds increased with oxidation due to increased polarity and water solubility (Ledakowicz, 1998). These provide the basis for the integration of AOPs with biological treatments which has also been discussed by Gogate and Pandit (2004b). It should be noted that BOD₅:COD is frequently used to denote the biodegradability of the wastewater, but other measurements such as BOD₅:TOC have also been used (Ledakowicz, 1998).

Various configurations to combine biological treatments and AOPs are possible. AOPs could be used to remove toxic, refractory or inhibitory compounds prior to biological treatment; the biological system could also be considered as a pre-treatment to remove the majority of the contaminants so that the consumption of oxidants in subsequent AOPs can be reduced (Scott and Ollis, 1995).

The comprehensive literature review presented by Scott and Ollis (1995) covers the integration of biological treatment systems with chemical oxidation processes or AOPs for drinking water and wastewater treatments. More recent examples for the application of these integrated systems to water treatment are discussed below.

Genç et al. (2005) employed the combination of UVC/TiO₂/H₂O₂ to improve the biodegradability of a mixed wastewater from domestic and pre-treated industrial sources (COD = 90.2 mg.L⁻¹). The wastewater was filtered (0.45 µm) and 20 mM of H₂O₂ and 1g.L⁻¹ of TiO₂ (Degussa P25) were added. After 16.5 hours of irradiation with two 15 W UVC lamps, 78% of absorbance at 260 nm (A₂₆₀) and 43% of COD was removed and the biodegradability of the water (BOD₅:COD) was improved from 0.13 to 0.25.

Buchanan et al. (2004) studied the effects of UVC and VUV photooxidation on the biodegradability of natural organic matter (NOM) in drinking water. While acknowledging
the high energy requirement of the treatment, it was concluded that the VUV photooxidation as a pre-treatment to biological treatment enhances the biodegradability of NOM. Increased biodegradability of textile dyes and textile wastewater due to VUV photooxidation treatment has also been demonstrated (Al-Momani et al., 2002).

Li et al. (2003) conducted a study on the feasibility of constructed wetlands for the treatment of greywater (TOC = 80.2 – 93.8 mg.L\(^{-1}\)) for suburban and rural areas without a sewer system. The effluent from the wetland (TOC = 10 mg.L\(^{-1}\)) was treated further by a heterogeneous AOP (UVA/TiO\(_2\)) for the removal of residual organic substances and pathogens. It was demonstrated that three hours of UVA irradiation with 10 g.L\(^{-1}\)of TiO\(_2\) reduced the microbial content in the wetland effluent to a level acceptable for European bathing water quality (Table 2-3), and the residual TOC was about 6 mg.L\(^{-1}\). With longer irradiation time of up to 19 hours, the treated greywater was claimed to be suitable for reuse as an indirect potable water source such as groundwater recharge. However, it should be noted that the results reported in the study were based on the measurements of TOC while most standards or guidelines for the quality of reclaimed water (Table 2-3) are specified in terms of BOD levels.

Simultaneous application of photochemical and biological technologies for contaminated sites and industrial waste streams has also been proposed by using a UV- and fungicide-resistant strain of white rot fungus (Katayama and Matsumura, 1991). However, the possibility of environmental or health problems caused by this fungus due to its resistance to UV and fungicide was not discussed. Genetically modified organisms have also been reported for the biodegradation of XOCs in wastewater and similar concerns have been raised for the unknown behaviour of these organisms in the natural environment (Ledakowicz, 1998).
2.7 Summary

Greywater, a wastewater without input from toilets and industrial process water, varies significantly in its quantity and quality due to the activities involved in its production. Three main types of greywater have been identified: kitchen greywater, bathroom greywater, and laundry greywater. Generally, the reuse of kitchen greywater is discouraged due to its relatively high level of contaminants and relatively low volume produced.

Some proposed applications for greywater reuse include toilet flushing and garden irrigation, and concerns such as risks to public health, clogging of the distribution system, generation of offensive odour, and pollution of soil, surface water and groundwater have been raised. These concerns are also extended to xenobiotic organic compounds such as PPCPs, EDCs, and surfactants due to the lack of information regarding their toxicity, biodegradability and bioaccumulation properties, and the enormous and increasing variety of these compounds.

Technologies for greywater reuse include simple diversion systems or basic screening devices to sophisticated systems such as biological treatments, physical separation techniques, and chemical and advanced oxidation processes. Biological treatments are generally cheap and reliable but they usually require long treatment time, produce sludges, and are limited by the relatively low biodegradability of greywater. Physical separation techniques transfer pollutants from one medium to another, create the need to dispose of the separated or concentrated pollutants or sludges, and treatments such as ultrafiltration, nanofiltration and reverse osmosis are considered energy intensive. Chemical oxidation processes use oxidants such as O3 and H2O2 to oxidise contaminants, while AOPs rely on the generation of oxygen-containing intermediates such as *OH to achieve the mineralisation of pollutants and they are attractive alternatives which may destroy PPCPs, EDCs and surfactants in greywater. Many AOPs have been used in drinking water and wastewater treatment, however, their application in greywater reuse has so far been limited to photocatalysis.

Therefore, the aim of this project is to investigate the application of the Fenton, photo-Fenton, and UVC/H2O2 processes in greywater treatment, and the results are compared with alum and ferrous sulphate coagulation and their subsequent UVC/H2O2 treatment. The effects of the following parameters are determined:

- The use of pre-treatments (overnight settlement or coagulation),
- pH,
- Concentration of contaminant,
- Type of greywater,
• Dosage of reagents (alum, ferrous sulphate, and/or \( \text{H}_2\text{O}_2 \)), and
• Reaction/irradiation time.

While COD is used to measure the performance of the processes, the BOD\textsubscript{3} of the effluent produced from the optimised process is measured and compared against the different classes of reclaimed water as specified in the EPAV guidelines.
Chapter 3. Materials and Methods

The photo-reactor used in the experiments is described in Section 3.1, followed by potassium ferrioxalate actinometry which explains the procedures of measuring the intensity of the UVC lamps (Section 3.2). Section 3.3 outlines the analytical methods that have been used and the methods to determine the concentration of H₂O₂ stock solution and to remove excess H₂O₂ by catalase are also covered. Section 3.4 briefly describes the greywater used in the experiments, and Sections 3.5, 3.6 and 3.7 detail the experimental procedures for the coagulation, Fenton, photo-Fenton, and UVC/H₂O₂ processes, respectively.

The experimental plan comprised two stages. Stage 1 involved optimising the processes to treat greywaters collected by the researcher from home or in the laboratory. These greywaters were subjected to the coagulation, Fenton, photo-Fenton, and UVC/H₂O₂ processes. In Stage 2, the findings were tested on greywaters collected from a commercial accommodation and two households.

3.1 Photo-reactor

The photo-reactor used in this project was designed by Adele Parkinson (Parkinson, 2001). It had two lamp fixtures on opposite sides of the reactor and the ballasts were situated externally to minimise heat generation within the reactor. The lamp housing can be fitted with any bi-pin 15 W UV lamps of 25.5 mm diameter and 436 mm length. In this project, all experiments were conducted with two UVC lamps (Philips G15T8) of spectral peak at 254 nm. To prevent accidental exposure to harmful UV irradiation, the door of the reactor was connected to two safety switches which cut off power supply to both lamps should the door be opened during operation.

As shown in Figure 3-1, two quartz sleeves (internal diameter of 44 mm, 1 mm in thickness, and 470 mm in length) were situated in the centre of the reactor, and reflectors were installed to increase the irradiation efficiency. Each quartz sleeve held 500 mL of sample and the distance between the lamps and the quartz sleeves was approximately 6 cm on either side. For convenience, the quartz sleeves are referred to hereafter as QS1 and QS2. Due to the difference in irradiation intensity received by QS1 and QS2, possibly due to the design of the reactor, only QS1 was used in the experiments (refer to Table B-1 in Appendix B for the determined irradiation intensity).

The reactor was equipped with two sets of coolers to remove heat generated by the lamps.
Each cooler consisted of a circulation fan and a fin-type heat exchanger which was connected to an external water cooler (temperature setpoint at 7°C). One of the fans was operated continuously when the reactor was in operation while the other was controlled by a temperature controller which was set to maintain the reactor at 25°C.

The contents of the quartz sleeve were continuously stirred by bubbling gently with air supplied by a small air pump. The air passed through a scrubber/humidifier system before it was bubbled through the solution via a glass tube. The system included two parallel soda lime scrubbers for the removal of carbon dioxide (CO₂) and two parallel columns of deionised water for humidification. The soda lime was self-indicating and was replaced whenever its colour changed from pink to white towards the end of its capacity.

Figure 3-1. Photo-reactor.
3.2 Potassium Ferrioxalate Actinometry

The actinometric property of potassium ferrioxalate (K₃Fe(C₂O₄)₃) was first reported by Parker and Hatchard (1953; 1956) and various modifications have since been incorporated (Murov et al., 1993). This actinometer is sensitive to irradiation wavelength between 250 and 500 nm (Kuhn et al., 2004) and it was chosen to determine the irradiation intensity of the UVC lamps.

The net photochemical reaction of the actinometer can be described by the following equation (Murov et al., 1993):

\[
2\text{Fe}^{3+} + \text{C}_2\text{O}_4^{2-} \xrightarrow{\text{hv}} 2\text{Fe}^{2+} + 2\text{CO}_2.
\]  

Equation 3-1

1,10-Phenanthroline was added to react with the ferrous ions to form ferrous-phenanthroline complex and its absorbance at 510 nm was measured spectrophotometrically.

To determine irradiation intensity (Iₗ) of the UVC lamps, the following equation can be applied once other parameters in the equation have been determined experimentally (Murov et al., 1993):

\[
I_\lambda = \frac{A_{510} V_2 V_3}{\varepsilon d \Phi_\lambda t V_1}
\]

Equation 3-2

where \(I_\lambda\) is irradiation intensity of the lamp (mole of photons.s⁻¹),

\(A_{510}\) is the absorbance of irradiated actinometer solution against blank solution at 510 nm,

\(d\) is the pathlength of absorption cell used in the measurement of \(A_{510}\) (cm),

\(\varepsilon\) is the molar absorption coefficient of ferrous-phenanthroline complex at 510 nm (L.mol⁻¹.cm⁻¹),

\(\Phi_\lambda\) is the quantum yield of ferrous production at the wavelength of irradiation used,

\(t\) is the irradiation time (s),

\(V_1\) is the volume of irradiated actinometer solution withdrawn (mL),

\(V_2\) is the volume of actinometer solution irradiated (L), and

\(V_3\) is the volume of volumetric flask used for the dilution of irradiated aliquot (mL).

The quantum yield (\(\Phi_\lambda\)) of ferrous ions at various irradiation wavelengths has been reported by Murov et al. (1993). For the UVC lamps used, the value of \(\Phi_{254}\) was taken as 1.25.
3.2.1 Molar Absorption Coefficient ($\varepsilon$) of Ferrous-Phenanthroline Complex

The molar absorption coefficient ($\varepsilon$) of the ferrous-phenanthroline complex in Equation 3-2 can be determined from the gradient of the standard calibration graph. To plot this graph, 0.08 M ferrous sulphate solution (FeSO$_4$, Ajax Univar Analytical Reagent) was first standardised with 0.0167 M standard potassium dichromate solution (K$_2$Cr$_2$O$_7$, BDH AnalaR), using sodium salt of diphenylamine-\textit{p}-sulphonic acid (Aldrich, ACS Reagent) as the indicator in the presence of 10% orthophosphoric acid (BDH AnalaR) (Belcher and Nutten, 1960). For every 25 mL of the FeSO$_4$ solution used in the titration, an equal amount of 1 M H$_2$SO$_4$ (Ajax Univar Analytical Reagents) was added along with 4 drops of the indicator and 3 mL of 10% orthophosphoric acid.

During titration, the colourless solution turned green and the final volume of K$_2$Cr$_2$O$_7$ solution added to achieve a purple solution was recorded. The actual molarity of the FeSO$_4$ solution was then calculated stoichiometrically.

Upon the completion of standardisation, the FeSO$_4$ solution was diluted to $4\times10^{-4}$ M with 0.05 M H$_2$SO$_4$. To a series of six 50 mL volumetric flasks 0, 2, 6, 10, 14, 18 mL of the diluted FeSO$_4$ solution was transferred carefully and sufficient 0.05 M H$_2$SO$_4$ was added so that each volumetric flask was approximately half-filled. Subsequently, 2 mL of 0.2 wt% 1,10-phenanthroline solution (Sigma ACS Reagent) and 6 mL of sodium acetate buffer (Ajax Univar Analytical Reagent) were added and the mixture was diluted to the mark with 0.05 M H$_2$SO$_4$. It was found that 1,10-phenanthroline was insoluble in water when 0.2 wt% solution was prepared as per Murov et al. (1993), hence 0.05 M H$_2$SO$_4$ was used instead of water.

After shaking, the absorbance at 510 nm ($A_{510}$) of the red-coloured ferrous-phenanthroline complex was read (Unicam UV/vis Spectrophotometer, UV2-100) against the blank (i.e., the solution without FeSO$_4$). The cuvettes used were of 1 cm path length (i.e., $d = 1$ cm in Equation 3-2). The standard calibration graph and the determined molar absorption coefficient ($\varepsilon$) of ferrous-phenanthroline complex are shown in Appendix A.

3.2.2 Standardisation of Ferric Sulphate Stock Solution

The standardisation of ferric sulphate solution (Fe$_2$(SO$_4$)$_3$) was carried out as per Schwarzenbach (1957). Approximately 300 mL of MilliQ water (Millipore) was used to dilute 20 mL of 0.2 M Fe$_2$(SO$_4$)$_3$ solution (BDH). The mixture was boiled for five minutes with a few potassium persulphate crystals (BDH) to eliminate any Fe$^{2+}$ ions and 3.0 g of glycine (Ajax Unilab Laboratory Reagent) was then added. The solution was cooled to room
temperature and further diluted with MilliQ water to 1 L. Subsequently, 100 mL of this orange-coloured solution was warmed to approximately 40°C and 0.2 g of salicylic acid (BDH Laboratory Reagent) was added as the titration indicator, which turned the solution to purple colour.

This solution was then standardised with 0.1 M ethylenediaminetetraacetic acid (EDTA, BDH AnalaR) at about pH 4 while it was warm. The volume of EDTA solution required to change the purple solution to pure yellow was recorded and the actual molarity of the Fe₂(SO₄)₃ stock solution was calculated accordingly.

3.2.3 Measurement of A₅₁₀ for Irradiated Actinometer

Due to the light sensitivity of the actinometer solution, this procedure was conducted in the dark, illuminated only by red light. The actinometer solution was prepared by mixing the standardised ferric sulphate solution (Section 3.2.2) and 1.2 M potassium oxalate solution (K₂C₂O₄, Aldrich ACS Reagent) with MilliQ water to give 0.01 and 0.06 M, respectively, in the final solution.

Subsequently, 500 mL of the actinometer solution (i.e., V₂ = 0.5 L in Equation 3-2) was irradiated for 180 seconds (i.e., t = 180 s) in each quartz sleeve. The irradiated actinometer solution was then collected and 5 mL of the aliquot (i.e., V₁ = 5 mL) was added into a 50 mL volumetric flask (i.e., V₃ = 50 mL) which was half-filled with MilliQ water, 2.5 mL of sodium acetate buffer, and 10 mL of 0.2 wt% 1,10-phenanthroline solution. The solution was diluted to the mark with MilliQ water, shaken, and the A₅₁₀ was measured against MilliQ water. A blank was prepared in the same manner in which non-irradiated actinometer solution of the same volume as its irradiated counterparts was added to the volumetric flask. A₅₁₀ of the blank was subtracted arithmetically from A₅₁₀ of the irradiated sample.

The corrected A₅₁₀ of the actinometer irradiated by the UVC lamps is listed in Table B-1 (Appendix B). Using Equation 3-2 and information in Section 3.2 and Appendix A, the irradiation intensity (Iₓ) of the lamps was calculated (Table B-1). Appendix B also shows the calculation for the radiant energy (Qₓ) and fluence rate of the lamps.
3.3 Analytical Methods and Measurements

The following analytical parameters were measured according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1998) unless specified otherwise. These include dissolved oxygen (DO), five-day biochemical oxygen demand (BOD$_5$), chemical oxygen demand (COD), alkalinity, ion chromatography, total solids, total dissolved solids, total suspended solids, pH, conductivity, turbidity, fluorescence and absorbance.

This section also includes the verification of H$_2$O$_2$ concentration in the stock solution and the method of removing excess H$_2$O$_2$ in the sample with catalase.

3.3.1 Dissolved Oxygen (DO)

The measurement of DO level by DO meter (YSI 5000, Method 4500-O G) was compared with Winkler titration (iodometric method with azide modification, Method 4500-O C).

Samples of various DO levels were prepared by heating MilliQ water to 20, 30, 50, 70 and 90°C respectively and were collected in BOD bottles. The bottles were stoppered immediately and the contents were cooled to room temperature (22 ± 1°C) before DO measurement by the two methods.

The results comparing the two methods were shown to be comparable (Table C-1, Appendix C). Since the DO meter provides rapid response, is easy to use, and requires shorter analysis time, it was chosen to measure the changes in DO level for BOD$_5$ analysis.

3.3.2 Biochemical Oxygen Demand (BOD$_5$)

BOD$_5$ measurement was conducted as per Method 5210 B (APHA, 1998). The seeding material for the BOD$_5$ analysis was prepared by re-hydrating one capsule of BOD microbe (Cole-Parmer®) in 500 mL of the dilution water for 30 minutes under constant aeration.

For the seed controls, the manufacturer recommended dosing 25 mL of the seeding material. However, this was found to incur excessive DO depletion (Figure D-1(a)) Therefore, 15 mL of seeding material was chosen which gave at least 2 mg.L$^{-1}$ DO depletion and more than 1 mg.L$^{-1}$ residual DO as required in the standard method.

A glucose-glutamic acid (GGA) check was conducted for each batch of BOD$_5$ analyses to
monitor the quality of dilution water and seeding material. To achieve a BOD5 value of 198 ± 30.5 mg.L⁻¹, 4 mL of the seeding material was needed in the GGA check (Figure D-1(b)) and this amount of seeding material was also used in the BOD5 measurement of the samples.

Before BOD5 analysis, the pH of each sample was adjusted to between 6.5 and 7.5 with 1 M H₂SO₄ or 1 M NaOH (Ajax Univar Analytical Reagents). The sample volume to be added into each BOD bottle was estimated from its COD measurement and the following amounts were found to be adequate:

- COD between 400 and 600 mg.L⁻¹: 5 mL
- COD between 300 and 400 mg.L⁻¹: 10 mL
- COD between 100 and 300 mg.L⁻¹: 15 mL
- COD between 50 and 100 mg.L⁻¹: 30 mL
- COD less than 50 mg.L⁻¹: 50 mL

3.3.3 Chemical Oxygen Demand (COD)
COD reagents were prepared according to Method 5220 D (APHA, 1998) and consisted of potassium dichromate (K₂Cr₂O₇, BDH AnalaR), silver sulphate (Ag₂SO₄, Australian Chemical Reagents), mercuric sulphate (HgSO₄, BDH) and concentrated sulphuric acid (H₂SO₄, Ajax Univar Analytical Reagents). Two types of reagents were prepared: High-range reagent for measurement of samples between 90 and 900 mg.L⁻¹ COD while the low-range reagent was used when there was less than 90 mg.L⁻¹ COD in the sample. With at least two duplicates, 2.5 mL of sample was added into each reagent vial, shaken, and digested for 2 hours at 148°C in a Merck COD digester (Spectroquant® TR 420) before its absorbance was measured by a HACH spectrophotometer (DR/4000U).

Potassium hydrogen phthalate, also known as KHP (KHC₈H₄O₄, BDH AnalaR), was used as the standard; it has a theoretical COD value of 1.176 mg O₂ for every milligram of KHP (APHA, 1998). The standard calibration graphs are shown in Figure E-1. This information was entered into the HACH spectrophotometer which calculated the corresponding COD level after the absorbance of a sample was measured.

3.3.4 pH and Conductivity
The pH of sample was measured by SevenEasy™ pH meter (Mettler Toledo). The pH meter was calibrated regularly with buffer solutions at pH 4.0, 7.0 and 10.0 (Ajax). A HACH SensION156 meter was used to measure the conductivity of samples.
3.3.5 Alkalinity
Method 2320 B (APHA, 1998) was followed for the measurement of the alkalinity of greywater. Sodium carbonate (Na$_2$CO$_3$, Ajax Univar) was dried in an oven at 250°C for 4 hours before it was cooled in a desiccator. Subsequently, 0.05 N standard Na$_2$CO$_3$ solution was prepared and it was used to standardise hydrochloric acid (HCl, Ajax Univar) of 0.02 N and 0.1 N. A suitable concentration of HCl solution was then selected for the titration of the greywater sample. The volume of HCl required to achieve the end-point pH of 4.5 was then recorded for the calculation of total alkalinity of the greywater.

3.3.6 Ion Chromatography
The concentration of several anions in the greywater was measured by ion chromatography as described in Method 4110 B (APHA, 1998). These included chloride, orthophosphate and sulphate. Although nitrite, nitrate and bromide could also be measured by this method, their levels in the greywater sample were lower than the detection limit of 0.1 mg.L$^{-1}$. Before injection into the ion chromatograph, the samples were filtered with 0.45 µm Mille-HV PVDF cartridge filter.

The ion chromatograph (Dionex 2010i) used an Ionpac column (A54A-SC, 4 × 250 mm). The eluent solution contained 0.0017 M sodium bicarbonate (NaHCO$_3$, Ajax Univar) and 0.0018 M sodium carbonate (Na$_2$CO$_3$, Ajax Univar), and it carried the injected sample at the flow rate of 1 mL.min$^{-1}$. The separated anions were converted to their acid forms by regenerant solution (12.5 mM H$_2$SO$_4$), and were subsequently quantified by measuring their conductivity at a particular retention time against the standard calibration graphs. An integrator (Hewlett Packard 3390A) was used to record the peak area. A typical chart recorded by the integrator is shown in Figure F-1 (Appendix F). The calibration graphs for the measurement of the anions are shown in Figure F-2.

3.3.7 Total Solids, Total Dissolved Solids and Total Suspended Solids
The total solids, total dissolved solids and total suspended solids of the greywater samples were measured according to Method 2540 B, 2540 C and 2540 D, respectively (APHA, 1998). The samples for the measurement of total dissolved solids were dried in an oven at 180°C while the other samples were dried at 105°C. Whatman glass-microfiber filters (grade 934AH) were used for the measurement of total dissolved solids and total suspended solids.
3.3.8 Turbidity

Turbidity of samples was measured by HACH 2100AN turbidimeter and it was calibrated with StablCal® turbidity standard calibration kit (HACH).

3.3.9 Absorbance and Fluorescence

UV/vis Spectrophotometer UV2 (Unicam) was used for the measurement of absorbance over the wavelength range of 190 nm to 700 nm. Quartz cuvettes of 1 cm pathlength were used.

For fluorescence spectroscopy, a Perkin Elmer luminescence spectrometer (Model: LS 50B) was used. The emission was scanned from 200 to 600 nm and the excitation from 200 nm to 440 nm at 5 nm increments. The slit widths were both set at 5 nm, and the scan speed was 1200 nm.min⁻¹. The fluorescence intensity was recorded and plotted at each of the excitation and emission wavelengths.

3.3.10 Determination of H₂O₂ Concentration in Stock Solution

The permanganate titration method (H₂O₂.com, 2007) was used to verify the concentration of the hydrogen peroxide stock solution (50 wt%, Aldrich) which was stored at 5°C. Firstly, potassium permanganate solution of 0.06 M (KMnO₄, Standard Laboratories Analytical reagent) was standardised with sodium oxalate solution (Na₂C₂O₄, Aldrich A.C.S reagent) according to the method outlined by Harris (1998).

The H₂O₂ stock solution (2 g) was accurately weighed and diluted to 250 mL with MilliQ water in a volumetric flask. The diluted H₂O₂ solution (25 mL) was then transferred to a beaker containing 250 mL MilliQ water and 10 mL of concentrated sulphuric acid before it was titrated with the standardised 0.06 M KMnO₄ solution. The volume of the KMnO₄ solution required to establish a permanent pink colour in the solution was recorded and the average value was 19.2 mL after 6 repetitions. The actual concentration of the H₂O₂ stock solution was then determined stoichiometrically as 48.8%; the stock solution was checked periodically and the concentration did not decrease significantly over the period of storage.
3.3.11 Excess H$_2$O$_2$ Indicated by Merckoquant® Peroxide Test Strips and Its Removal by Catalase

H$_2$O$_2$ is known to interfere with many analytical measurements, including BOD$_5$, COD and absorbance (UV/vis spectrophotometry). Due to its decomposition to O$_2$, the presence of excess H$_2$O$_2$ reduces the actual BOD$_5$ values. For COD measurement, the reduction of potassium dichromate (K$_2$Cr$_2$O$_7$) by excess H$_2$O$_2$ results in falsely high readings (H$_2$O$_2$.com, 2007). This error in COD measurement and a proposed correction factor by Kang et al. (1999) are discussed in Appendix G. In addition, H$_2$O$_2$ absorbs radiation within the wavelength range of 200 to 300 nm (H$_2$O$_2$.com, 2007). Therefore, the removal of residual H$_2$O$_2$ in the sample is essential before these analyses.

To check the level of residual H$_2$O$_2$ in the sample, Merckoquant® peroxide test strips (Merck) was used as a quick colorimetric indication. Detailed description of the test strips and verification of their accuracy is included in Appendix G.

Catalase (from Aspergillus niger, Calbiochem®) was chosen to remove the excess H$_2$O$_2$. According to the manufacturer, the catalase is active within pH 2 – 12, and its activity is 5283 U.mg$^{-1}$ dry weight. To prepare the stock solution, 25 mg catalase was dissolved in 25 mL phosphate buffer (1.17 g Na$_2$HPO$_4$ and 0.57 g KH$_2$PO$_4$ in 250 mL MilliQ water, pH 7), and this corresponds to an activity of 5283 U.mL$^{-1}$. The solution is claimed to be stable for several weeks at 20°C or for several months at -20°C. For convenience, the stock solution was divided into several portions and frozen. When required, a portion was thawed and stored at 5°C over the period of about a month before it was consumed. This treatment did not affect the effectiveness of the catalase.

To every 30 mL of sample, 10 µL of the catalase solution was added. Within 2 hours of shaking at 100 rpm (B. Braun Certomat® shaker), the added catalase decomposed H$_2$O$_2$ to less than 2 mg.L$^{-1}$ (or 0.06 mM). According to Kang et al. (1999), this level of residual H$_2$O$_2$ corresponded to an error of 0.9 mg.L$^{-1}$ in COD measurement (Table G-1, Appendix G), and it is considered to be negligible. To account for the amount of COD contributed by the catalase, same amount of the catalase was added to 30 mL of MilliQ water and it resulted in less than 1.5 mg.L$^{-1}$ of COD. In some cases when high H$_2$O$_2$ dosages were used, 30 µL of the catalase solution was used to reduce the time required to decompose H$_2$O$_2$, and this corresponded to an increase of 5.5 mg.L$^{-1}$ COD. The COD contribution from the catalase has been deducted accordingly in all of the results presented. For the measurement of BOD$_5$ and absorbance, complete decomposition of H$_2$O$_2$ by the catalase was achieved to eliminate its impact on the analysis.
3.4 Greywater

Three categories of greywater were used in this project. These include the synthetic greywater prepared according to the CSIRO recipe (Section 2.5), greywater collected from the researcher’s home and samples from external sources.

The greywater from the researcher’s home was generated by the activities of laundry washing, teeth-brushing and showering. These were mixed with tap water at different ratios to produce greywater of different concentrations and compositions. These include shower greywater (SGW), teeth-brushing greywater (TGW), laundry greywater (LGW), low-range greywater (LR GW), mid-range greywater (MR GW) and high-range greywater (HR GW).

Untreated greywater was also collected from three other external sources with existing treatment or collection facilities: a backpacker and youth hostel accommodation (YHA in Katoomba, New South Wales, Australia) and the homes of two members of the Alternative Technology Association (ATA) in Brunswick and Heidelberg (Victoria, Australia).

Detailed description of the collection and preparation of these greywaters is in Chapter 4.
3.5 Sequential Chemical Coagulation and UVC/H₂O₂ Treatment

Chemical coagulation using alum and ferrous sulphate was studied as a pre-treatment to the UVC/H₂O₂ process. Figure 3-2 illustrates the experimental procedures. The effectiveness of the coagulants and their impacts on the subsequent UVC/H₂O₂ process are discussed in Chapter 5. Since the Fenton reagents also have coagulative properties, ferrous sulphate coagulation can be compared directly with the Fenton and photo-Fenton processes.

The alum stock solution (2 M) was prepared by dissolving Al₂(SO₄)₃·16H₂O (BDH AnalAr) in MilliQ water, and 2 M ferrous sulphate stock solution was prepared daily by dissolving ferrous sulphate (FeSO₄·7H₂O, BDH) in 0.05 M H₂SO₄.

The jar test was conducted with a B-Ker®2 Jar-Test Skid (Phipps and Bird) to determine the optimal pH condition and the dosages of Al³⁺ and Fe²⁺. Each of the jars contained 1 L of greywater which was stirred at 100 rpm during the addition of the coagulant, followed by pH adjustment with 1 M H₂SO₄ or 1 M NaOH. The solution was then stirred at 100 rpm for 5 minutes and then at 50 rpm for 30 minutes before settling for 60 minutes. Supernatant from each container was then withdrawn and analysed. Various jar test procedures were found in the literature but the above stirring speeds and times were found to be the most effective in this case.

The supernatant (500 mL) was subjected to UVC/H₂O₂ treatment without further pH adjustment. It was poured into the quartz sleeve (QS1) in the photo-reactor (Figure 3-1), and the required amount of 50% H₂O₂ solution was added. The sample was then irradiated with the UVC lamps while being bubbled gently by humidified, CO₂-free air. All 500 mL of the sample was collected upon the completion of the UVC/H₂O₂ treatment, and catalase was added. The sample was analysed once the residual H₂O₂ was less than 2 mg.L⁻¹.
Figure 3-2. Experimental procedures for the sequential coagulation (Fe$^{2+}$ or Al$^{3+}$) and UVC/H$_2$O$_2$ treatment.
3.6 Fenton and Photo-Fenton Processes

The Fenton and photo-Fenton processes were studied at different Fe$^{2+}$:H$₂$O$_₂$ and H$₂$O$_₂$:COD ratios, and two procedures were developed (Figure 3-3). Method 1 was used for the experiments involving SGW and TGW. For LGW, LR GW, MR GW and HR GW, Method 2 was used. Chapter 6 discusses the development of these procedures in detail.

As shown in Figure 3-3, the initial steps of both procedures are similar, i.e., the greywaters were acidified to pH 3.5 with 1 M H$₂$SO$_₄$, the required amount of Fe$^{2+}$ was added, followed by pH adjustment to 3. The source of Fe$^{2+}$ was ferrous sulphate (FeSO$_₄$.7H$₂$O, BDH) and 2 M FeSO$_₄$ solution was prepared daily by dissolving the iron salt in 0.05 M H$₂$SO$_₄$.

For the Fenton process, the required amount of H$₂$O$_₂$ was added to 500 mL of the greywater in a measuring cylinder (500 mL) and the reaction was allowed to take place whilst gently mixing the sample by bubbling with humidified, CO$_₂$-free air.

The photo-Fenton process was conducted in a similar manner except that the reaction took place in the quartz sleeve (QS1) of the photo-reactor (Figure 3-1). After adding the required amount of H$₂$O$_₂$, the UVC lamps were switched on and humidified, CO$_₂$-free air was gently bubbled through the sample for constant mixing.

After the oxidation stage of the Fenton and photo-Fenton processes, the treated sample was collected. In Method 1, the sample was immediately neutralised with 1 M NaOH and catalase was added to decompose any excess H$₂$O$_₂$ in the sample. After neutralisation, the sample was shaken at 100 rpm until the residual H$₂$O$_₂$ was less than 2 mg.L$^{-1}$, after which it was settled for 30 minutes and the supernatant collected and analysed.

When Method 2 was used, catalase was added upon the collection of the sample. It was then shaken at 100 rpm until the residual H$₂$O$_₂$ was less than 2 mg.L$^{-1}$. After settling for 30 minutes, the pH of the supernatant was adjusted to 7 with 1 M NaOH before analysis.
Figure 3-3. Experimental procedures for the Fenton and photo-Fenton processes.
3.7 UVC/H₂O₂ Treatment

Factors such as the effect of overnight settlement as a pre-treatment, H₂O₂ dosage, pH and initial COD level and type of greywater were investigated for their effects on the UVC/H₂O₂ process (Chapter 7).

Greywater was settled overnight to simulate the effect of a storage facility in which hair, lint and large particles were settled. The pH and COD content of the greywater were measured before and after settling overnight in a beaker. When necessary, the pH of the settled greywater was adjusted with 1 M H₂SO₄ or 1 M NaOH before the UVC/H₂O₂ treatment.

The UVC/H₂O₂ experiment was conducted in batch mode: 500 mL of the greywater was poured into the quartz sleeve (QS1) of the photo-reactor (Figure 3-1), and the required amount of 50% H₂O₂ solution was added. The sample was then irradiated with the UVC lamps while being bubbled gently with humidified, CO₂-free air. Upon completion of a required irradiation time, all 500 mL of the sample was collected and shaken after the addition of catalase. The sample was analysed once the residual H₂O₂ was less than 2 mg.L⁻¹.
Chapter 4. Greywaters Used in the Experiments

Several options for the source of greywater were considered. These include preparing greywater according synthetic greywater recipes that have been published in the literature, using greywater collected from the researcher’s home, and collecting raw greywater from external sources which have existing greywater treatment or collection facilities. These options are discussed in detail below.

4.1 Synthetic Greywater Recipe

Various synthetic greywater recipes were found in the literature (Section 2.5). Initially, the CSIRO recipe was selected for this project while it was in the process of being developed. The earlier recipe included sunscreen as one of the major ingredients instead of moisturiser as specified in the latest version of the recipe (Table 2-4). The latest version of the CSIRO recipe was released in the later stage of this project and due to time constraints, it was not tested.

In addition to the recipe, the CSIRO researchers also provided the preparation procedure which specified that all of the ingredients, except clay and secondary effluent, to be weighed and blended at low speed for 1 minute with approximately 50 mL of tap water. This concentrate is then diluted with the required amount of tap water and mixed for at least 9 hours at room temperature. Subsequently, clay is mixed with secondary effluent which is then added proportionally to the rest of the ingredients in the piping to a treatment facility.

Ideally, a synthetic greywater recipe should provide good repeatability in greywater quality since the individual ingredients can be measured and added according to the required quantity. However, early experiments showed that some ingredients such as sunscreen were not readily soluble in water and were separated from the prepared greywater due to the bubbling action in the photo-reactor. In addition, the representativeness of the synthetic greywater to real greywater is uncertain since the household and personal care products used in its preparation have not had interaction with the human body. Some ingredients in the products may be absorbed by skin, and the interaction of these products with sweat, saliva and dirt etc. is not taken into consideration.

Due to these problems and concerns, the use of synthetic greywater was halted. Instead, greywater was collected from the researcher’s home and its collection and preparation is detailed in Section 4.2.
4.2  Greywater Collected from the Researcher’s Home

Greywater was collected from the researcher’s home and it had the advantage of being readily available, and its quality could be controlled by using consistent amounts of household and personal care products.

Several considerations were made: Kitchen greywater was excluded in this study and bathroom and laundry greywaters were collected from the activities of showering, teeth-brushing and laundering clothes. As discussed previously, kitchen greywater is not recommended for recycle due to its relatively high level of contaminants (EPAV, 2001; Jefferson et al., 2004) and small volume (approximately 5% of water consumed by an average household in Melbourne) (Christova-Boal et al., 1996). For simplicity, the major household products used in the cleaning activities were limited to shampoo (Palmolive Softwash- Aloe Vera and Chamomile), toothpaste (Colgate® Fluoriguard®) and laundry powder (Omo High Performance Concentrate with Blue Powder). These products were chosen as they were recommended for their high market share (Diaper et al., 2005).

The production of the laundry, shower and teeth-brushing greywater at the researcher’s home was assessed, and the volume and COD level of these greywaters were measured (Section 4.2.1). These formed the basis for the preparation of greywater of different types and COD levels as described in Section 4.2.2.

4.2.1  Assessment of Typical Greywater Production in the Researcher’s Home

To assess the production of the laundry, shower and teeth-brushing greywater, the volume of each greywater stream and its corresponding COD level was measured and Table 4-1 shows the results for the grab samples.

For each greywater generation event, approximately 122 L of laundry greywater, 24 L of shower greywater, and 2.5 L of teeth-brushing greywater were produced and their average COD contents were 320 mg.L⁻¹, 118 mg.L⁻¹ and 257 mg.L⁻¹ respectively.

To minimise the amount of greywater to be transported to the laboratory, teeth-brushing greywater was collected in the laboratory, and only the first 2.5 minutes of shower and the discharge from the first wash cycle of the washing machine were collected from the researcher’s home. These greywaters were stored at 5°C and unused samples were discarded after 1 week.
Table 4-1. Greywater produced from laundry, shower and teeth-brushing activities at the researcher’s home, their respective volume and COD content.

<table>
<thead>
<tr>
<th>Type of Greywater</th>
<th>Volume Produced (L)</th>
<th>COD (mg.L(^{-1}))</th>
<th>Average COD (mg.L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laundry (first wash cycle)</td>
<td>27</td>
<td>723</td>
<td>320</td>
</tr>
<tr>
<td>Laundry (second wash cycle)</td>
<td>45</td>
<td>353</td>
<td></td>
</tr>
<tr>
<td>Laundry (rinse cycle)</td>
<td>40</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Laundry (spray and spin dry cycle)</td>
<td>10</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Total Laundry</td>
<td>122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shower (first 2.5 minutes wash)</td>
<td>12</td>
<td>212</td>
<td>118</td>
</tr>
<tr>
<td>Shower (second 2.5 minutes wash)</td>
<td>12</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Total Shower</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teeth-brushing</td>
<td>2.5</td>
<td>257</td>
<td>257</td>
</tr>
</tbody>
</table>

4.2.2 Preparation of the Greywater

Depending on the number of the individual laundry, shower and teeth-brushing activities, the volume and quality of the combined greywater vary on a daily basis.

It was estimated that on an average day, each of the three occupants in the researcher’s household brushed his/her teeth twice and had two showers. In addition, one load of laundry was washed with the washing machine. Based on this and the assessment of greywater production shown in Table 4-1, the estimated daily production of laundry greywater would be 122 L, 144 L for shower greywater (i.e., 24 L × 3 persons × 2 times daily) and 15 L for the teeth-brushing greywater (i.e., 2.5 L × 3 persons × 2 times daily). From mass balance, the mixture of these greywaters has a COD content of 213 mg.L\(^{-1}\) and is considered of low strength according to Ramon et al. (2004). This formed the basis for the preparation of low-range greywater (LR GW).

By mixing the collected greywater samples and/or diluting with various amounts of tap water, different greywaters were prepared: laundry greywater (L GW), shower greywater (SGW), teeth-brushing greywater (T GW), low-range greywater (LR GW), mid-range greywater (MR GW) and high-range-greywater (HR GW). Figure 4-1 shows the schematic diagram for the collection and preparation of the greywaters. The compositions of these greywaters are listed in Table 4-2 and their typical characteristics are given in Table 4-3.

In this project, LR GW was used as the main source of greywater for the comparison of different processes in Chapters 5 – 7, while the others were used only when the effects of the initial COD level and the type of greywater were investigated.
Figure 4-1. Schematic diagram for the collection and preparation of laundry greywater (LGW), shower greywater (SGW), teeth-brushing greywater (TGW), low-range greywater (LR GW), mid-range greywater (MR GW) and high-range greywater (HR GW).
Table 4-2. Composition of laundry, teeth-brushing and shower greywater, and of the three greywater mixtures.

<table>
<thead>
<tr>
<th>Source</th>
<th>LGW</th>
<th>TGW</th>
<th>SGW</th>
<th>LR GW</th>
<th>MR GW</th>
<th>HR GW</th>
</tr>
</thead>
<tbody>
<tr>
<td>First discharge from washing machine</td>
<td>50%</td>
<td>-</td>
<td>-</td>
<td>22.5%</td>
<td>28.0%</td>
<td>37.5%</td>
</tr>
<tr>
<td>First 2.5 minutes of shower</td>
<td>-</td>
<td>-</td>
<td>50%</td>
<td>25.0%</td>
<td>31.3%</td>
<td>41.7%</td>
</tr>
<tr>
<td>Teeth-brushing</td>
<td>-</td>
<td>100%</td>
<td>-</td>
<td>5.0%</td>
<td>6.3%</td>
<td>8.3%</td>
</tr>
<tr>
<td>Tap water</td>
<td>50%</td>
<td>-</td>
<td>50%</td>
<td>47.5%</td>
<td>34.4%</td>
<td>12.5%</td>
</tr>
</tbody>
</table>

Table 4-3. Characteristics of laundry, teeth-brushing and shower greywater, and of the three greywater mixtures.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LGW</th>
<th>TGW</th>
<th>SGW</th>
<th>LR GW</th>
<th>MR GW</th>
<th>HR GW</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₅ (mg.L⁻¹)</td>
<td>135</td>
<td>107</td>
<td>61</td>
<td>76</td>
<td>106</td>
<td>134</td>
</tr>
<tr>
<td>COD (mg.L⁻¹)</td>
<td>350</td>
<td>269</td>
<td>83</td>
<td>225</td>
<td>268</td>
<td>356</td>
</tr>
<tr>
<td>BOD₅:COD</td>
<td>0.39</td>
<td>0.40</td>
<td>0.73</td>
<td>0.34</td>
<td>0.40</td>
<td>0.38</td>
</tr>
<tr>
<td>pH</td>
<td>10.3</td>
<td>6.7</td>
<td>7.8</td>
<td>10.0</td>
<td>10.1</td>
<td>10.3</td>
</tr>
<tr>
<td>Total Suspended Solids (mg.L⁻¹)</td>
<td>29</td>
<td>147</td>
<td>7</td>
<td>19</td>
<td>23</td>
<td>31</td>
</tr>
<tr>
<td>Total Dissolved Solids (mg.L⁻¹)</td>
<td>504</td>
<td>218</td>
<td>69</td>
<td>205</td>
<td>267</td>
<td>425</td>
</tr>
<tr>
<td>Total Solids (mg.L⁻¹)</td>
<td>743</td>
<td>257</td>
<td>83</td>
<td>374</td>
<td>392</td>
<td>580</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>32.2</td>
<td>28.1</td>
<td>5.6</td>
<td>18.1</td>
<td>25.2</td>
<td>32.5</td>
</tr>
<tr>
<td>Conductivity (µS.cm⁻¹)</td>
<td>2060</td>
<td>556</td>
<td>227</td>
<td>1088</td>
<td>1268</td>
<td>1585</td>
</tr>
<tr>
<td>Cl⁻ (mg.L⁻¹)</td>
<td>31.8</td>
<td>18.3</td>
<td>12.8</td>
<td>23.6</td>
<td>21.1</td>
<td>23.0</td>
</tr>
<tr>
<td>NO₂⁻ (mg.L⁻¹)</td>
<td>0.1</td>
<td>N.D.</td>
<td>N.D.</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>NO₃⁻ (mg.L⁻¹)</td>
<td>0.1</td>
<td>1.5</td>
<td>N.D.</td>
<td>0.3</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>PO₄³⁻ (mg.L⁻¹)</td>
<td>107.1</td>
<td>52.9</td>
<td>N.D.</td>
<td>40.8</td>
<td>52.0</td>
<td>79.3</td>
</tr>
<tr>
<td>SO₄²⁻ (mg.L⁻¹)</td>
<td>97.9</td>
<td>8.2</td>
<td>6.3</td>
<td>43.6</td>
<td>50.9</td>
<td>66.4</td>
</tr>
</tbody>
</table>

N.D.: Not Detected
4.3 Greywater Collected from External Sources

4.3.1 Youth Hostel Association in Katoomba
The Youth Hostel Association (YHA) in Katoomba (New South Wales, Australia) uses an Aquacell G1 system (Clearwater Technology) to treat greywater collected from 3 showers and one washing machine. The greywater is collected in a pit and large particles are removed by a series of screens before the greywater enters the membrane bioreactor (MBR). Air is diffused into the greywater for the biological treatment and the submerged ultrafiltration membrane module removes particles, bacteria and viruses. A UV disinfection unit provides an additional barrier for the removal of pathogens before the effluent is used for toilet flushing.

The raw greywater was collected from the collection pit by Michael Conciatore (Clearwater Technology) and Danielle Baker (Ecowise Environmental) on 28th May 2008. Table 4-4 summarises its characteristics.

Table 4-4. Characteristics of the greywater from external sources.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Katoomba YHA</th>
<th>ATA Member (Brunswick)</th>
<th>ATA Member (Heidelberg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₅ (mg.L⁻¹)</td>
<td>55</td>
<td>312</td>
<td>391</td>
</tr>
<tr>
<td>COD (mg.L⁻¹)</td>
<td>140</td>
<td>530</td>
<td>590</td>
</tr>
<tr>
<td>BOD₅:COD</td>
<td>0.41</td>
<td>0.59</td>
<td>0.66</td>
</tr>
<tr>
<td>pH</td>
<td>7.75</td>
<td>7.46</td>
<td>7.73</td>
</tr>
<tr>
<td>Suspended Solids (mg.L⁻¹)</td>
<td>69</td>
<td>123</td>
<td>105</td>
</tr>
<tr>
<td>Total Dissolved Solids (mg.L⁻¹)</td>
<td>368</td>
<td>135</td>
<td>298</td>
</tr>
<tr>
<td>Total Solids (mg.L⁻¹)</td>
<td>431</td>
<td>280</td>
<td>458</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>39</td>
<td>222</td>
<td>197</td>
</tr>
<tr>
<td>Conductivity (μS.cm⁻¹)</td>
<td>506</td>
<td>168</td>
<td>357</td>
</tr>
</tbody>
</table>

4.3.2 Greywater from Members of Alternative Technology Association
With the assistance of Adam Maxey from the Alternative Technology Association (ATA), greywater samples were collected from the homes of two ATA members in Brunswick and Heidelberg (Victoria, Australia) on 18th and 25th June 2008 respectively. Both sites use Greywater Gardener 230™ (Waterwise Systems®), which collects greywater from bathroom and laundry in a pit and it is subsequently pumped to a surge tank. Lint, hair and coarse particles are screened and the greywater is stored temporarily before distribution for garden irrigation through drip feeders. The raw greywater was collected from the surge tank on both sites and its characteristics are also listed in Table 4-4.
Chapter 5.  Sequential Coagulation and UVC/H₂O₂ Treatment

The jar test procedure described in Section 3.5 was used to determine the optimal pH condition and coagulant dosage for the LR GW collected from the researcher’s home. Subsequently, the supernatant was subjected to UVC/H₂O₂ treatment. This chapter discusses the results of the jar test for Al³⁺ and Fe²⁺ coagulation and the subsequent UVC/H₂O₂ process (Sections 5.1 and 5.2, respectively). The effectiveness of the coagulants and their impacts as a pre-treatment to the UVC/H₂O₂ process are discussed in Section 5.3.

5.1 Alum Coagulation and Subsequent UVC/H₂O₂ Treatment

5.1.1 Al³⁺ Coagulation

The COD of the LR GW was 220 ± 11 mg.L⁻¹. The alum stock solution (2 M) was added to the greywater so that the concentration of Al³⁺ was between 0.4 and 2 mM (or 10.8 – 53.9 mg.L⁻¹ Al³⁺), and the solution was subsequently adjusted to pH 3 – 10.

White coloured flocs were first formed at 0.7 mM Al³⁺ at pH 4 (Table 5-1). As the Al³⁺ dosage increased, the range of pH that promoted coagulation also increased. At 2 mM Al³⁺, coagulation occurred between pH 4 and 9.

<table>
<thead>
<tr>
<th>Dosage of Al³⁺ (mM)</th>
<th>pH 3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.6</td>
<td>-</td>
<td>×</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>×</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>0.8</td>
<td>×</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>0.9</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>1.0</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>1.1</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>1.5</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
</tbody>
</table>

✓ Floc formation observed
× No floc formation observed
- Not tested
At pH 4, the COD removal increased with increased Al\(^{3+}\) dosage (Figure 5-1(a)), and approximately 71% of COD was removed by 2 mM of Al\(^{3+}\) at pH 4. However, Figure 5-1(b) shows that maximal COD removal occurred at pH 5 for both Al\(^{3+}\) dosages of 1.5 and 2 mM. The highest COD removal was 73% with 2 mM Al\(^{3+}\) at pH 5 and the residual COD in the supernatant was 59 mg.L\(^{-1}\).

![Figure 5-1. COD reduction of LR GW treated by alum coagulation: Effect of (a) Al\(^{3+}\) concentration, and (b) pH.](image)

Alum coagulation has been used by Pidou et al. (2008) to treat low-strength greywater collected from the baths, showers and hand basins in a student residential hall (BOD = 39 ± 17 and COD = 144 ± 63 mg.L\(^{-1}\)). The experiment was conducted at pH 4.5, 6 and 7, with Al\(^{3+}\) dosage of 1 – 18 mg.L\(^{-1}\) (0.04 – 0.67 mM). It was found that the coagulation was independent of pH between 4.5 and 7, and up to 68% BOD removal was achieved. Using another source of greywater collected from shower (BOD = 166 ± 37 mg.L\(^{-1}\) and COD = 575 ± 98 mg.L\(^{-1}\)), Pidou et al. demonstrated that higher BOD removal of up to 79% was achieved as pH decreased from 7 to 4.5; the alum dosage required to reach a plateau in BOD removal was reduced from 32 to 24 mg.L\(^{-1}\) (or 1.2 mM to 0.9 mM). They concluded that alum coagulation was suitable for the treatment of low-strength greywater while recalcitrant components in greywater of higher strength prevented the process from meeting the required residual BOD level of more stringent standards.

Since Pidou et al. (2008) used BOD removal as a parameter to measure the effectiveness of the alum coagulation, in contrast to the COD removal used in the present project, direct
comparison of the results was not possible. However, it was observed that Pidou et al. used a much lower dosage of Al\textsuperscript{3+} even though the initial COD level of their high-strength greywater was about 2.6 times higher than that of the LR GW. The difference in the required Al\textsuperscript{3+} dosage may be due to the fact that LR GW contained significant input from the laundry whereas their high-strength greywater was collected only from the shower. Since the conductivity of laundry greywater was high (Table 4-3), the LR GW may have very different ionic strength and zeta-potential from those of their high-strength greywater. Also, the nature of the organic compounds in each greywater would be different, i.e., laundry powder compared with toiletries such as shower gel and soap.

The optimal conditions for alum coagulation seem to vary significantly according to the type of water as Yonar et al. (2006) found that the optimal alum dosage was 60 mg.L\textsuperscript{-1} (2.2 mM Al\textsuperscript{3+}) at pH 7 for an untreated domestic wastewater collected from a residential district in Turkey (COD = 336 mg.L\textsuperscript{-1}). In Section 2.6.2, electcoagulation using aluminium as a sacrificial anode was described (Lin et al., 2005) and the effluent quality appeared to fluctuate significantly with the quality of the raw greywater.

5.1.2 Al\textsuperscript{3+} Coagulation Followed by UVC/H\textsubscript{2}O\textsubscript{2} Treatment

After alum coagulation (2 mM Al\textsuperscript{3+}/pH 5), the supernatant was subjected to UVC/H\textsubscript{2}O\textsubscript{2} treatment without further pH adjustment. Since a large portion of the initial COD in LR GW (up to 73%) was removed by alum coagulation, the UVC/H\textsubscript{2}O\textsubscript{2} treatment acted as a polishing step to improve the overall COD reduction.

As shown in Figure 5-2, the residual COD in the supernatant was 50 – 55 mg.L\textsuperscript{-1} and it remained relatively constant when exposed to UVC irradiation in the absence of H\textsubscript{2}O\textsubscript{2}. Significant reduction in COD was observed when 1 mM H\textsubscript{2}O\textsubscript{2} was added, and the remaining pollutants in the supernatant were oxidised, most likely by the \textsuperscript{\circ}OH generated from the photolysis of H\textsubscript{2}O\textsubscript{2}.

With a dose of 2 mM H\textsubscript{2}O\textsubscript{2}, the UVC/H\textsubscript{2}O\textsubscript{2} process reduced the COD level of the supernatant to 22 mg.L\textsuperscript{-1} after 30 minutes of irradiation (equivalent to a UV dose of 9,000 mJ.cm\textsuperscript{-2}). Extending the time to 1.5 hours, the residual COD was reduced to as low as 5 mg.L\textsuperscript{-1} and up to 92% of COD removal was achieved. This translated into an overall COD reduction of 98% when the COD removal by alum coagulation was also taken into account. Increasing the H\textsubscript{2}O\textsubscript{2} dosage to 3 mM led to only a slight improvement in the process performance.
Figure 5-2. COD of LR GW treated by UVC/H₂O₂ at pH 5 after alum coagulation (2 mM Al³⁺/pH 5) as a pre-treatment.
5.2 Ferrous Sulphate Coagulation and Subsequent UVC/H₂O₂ Treatment

5.2.1 Fe²⁺ Coagulation

Ferrous sulphate was chosen as the coagulant so that direct comparison could be made with the Fenton and photo-Fenton processes examined in Chapter 6.

For this experiment, the COD of LR GW was 230 ± 4 mg.L⁻¹. The concentration of Fe²⁺ added was 0.4 to 2 mM (or 22.3 – 111.7 mg.L⁻¹ Fe²⁺), and the solution pH was subsequently adjusted to pH 3 – 10. Floc formation was first observed at pH 3 when 1 mM Fe²⁺ was added (Table 5-2), and it was rusty brown in colour. As the concentration of Fe²⁺ increased to 2 mM, the pH at which coagulation took place spanned 3 and 5.

Table 5-2. Ferrous sulphate coagulation of LR GW.

<table>
<thead>
<tr>
<th>Dosage of Fe²⁺ (mM)</th>
<th>pH 3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>×</td>
<td>-</td>
<td>×</td>
<td>-</td>
<td>×</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>×</td>
<td>-</td>
<td>×</td>
<td>-</td>
<td>×</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.75</td>
<td>×</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>1.25</td>
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<td>✓</td>
<td>×</td>
<td>-</td>
<td>×</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.5</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>-</td>
<td>×</td>
<td>-</td>
<td>-</td>
<td>×</td>
</tr>
<tr>
<td>2.0</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
<td>×</td>
<td>-</td>
<td>-</td>
<td>×</td>
</tr>
</tbody>
</table>

✓  Floc formation observed
×  No floc formation observed
-  Not tested

The COD reduction increased from 3% to 49% when Fe²⁺ dosage increased from 0.75 to 1 mM (Figure 5-3). This corresponded to a reduction in residual COD level from 219 mg.L⁻¹ to 118 mg.L⁻¹. Further increase in Fe²⁺ concentration from 1 to 1.5 mM improved COD reduction by only 4%, and the lowest residual COD level obtained was 110 mg.L⁻¹.
In addition to incurring additional costs for chemicals, excessive dosage of Fe\(^{2+}\) should be avoided since Fe\(^{2+}\) also contributes to COD according to Method 5220 (APHA, 1998). Theoretically, 0.14 mg.L\(^{-1}\) of O\(_2\) is required to oxidise 1 mg.L\(^{-1}\) Fe\(^{2+}\) (AWWA, 2003) and each 1 mM Fe\(^{2+}\) added is equivalent to 8 mg.L\(^{-1}\) of COD. Therefore, higher Fe\(^{2+}\) concentration was not studied and the optimal Fe\(^{2+}\) dosage for the coagulation of LR GW was taken as 1 mM.

In addition to alum coagulation as discussed in Section 5.1.1, Pidou et al. (2008) used ferrous sulphate as a coagulant to treat their mixed source low-strength greywater and high-strength shower greywater. Similar to their results for alum coagulation, Fe\(^{2+}\) coagulation was not sensitive to pH between 4.5 and 7 when the low-strength greywater was used, and a residual BOD of between 1 and 7 mg.L\(^{-1}\) was achieved with 0.04 – 0.67 mM Fe\(^{2+}\) (1 – 18 mg.L\(^{-1}\)). For the shower greywater (BOD = 166 ± 37 mg.L\(^{-1}\)), the lowest residual BOD obtained was 30 mg.L\(^{-1}\) when the solution pH was 4.5 and with 0.79 mM Fe\(^{2+}\). Similar to the alum coagulation, the optimal conditions for Fe\(^{2+}\) coagulation appeared to vary significantly among different types of greywater.

5.2.2 Fe\(^{2+}\) Coagulation Followed by UVC/H\(_2\)O\(_2\) Treatment

Coagulation with ferrous sulphate (1 mM Fe\(^{2+}\)/pH 3) produced supernatant of COD level between 110 and 118 mg.L\(^{-1}\) (Figure 5-4). The subsequent UVC/H\(_2\)O\(_2\) process was conducted on the supernatant at its collected pH and in the presence of H\(_2\)O\(_2\) at 1 – 9 mM.
At 1 mM H$_2$O$_2$, only about 21% of the remaining COD in the supernatant was removed after 2 hours of irradiation. At 7 mM H$_2$O$_2$, the extent of COD removal increased to 83% within 1 hour of irradiation (UV dose of 18,000 mJ.cm$^{-2}$). The residual COD was 21 mg.L$^{-1}$ and the overall COD reduction was 91% when the COD reduction by Fe$^{2+}$ coagulation was taken into account. Only a slight improvement was achieved when 9 mM H$_2$O$_2$ was used.

**Figure 5-4.** COD of LR GW treated by UVC/H$_2$O$_2$ at pH 3 after ferrous sulphate coagulation (1mM Fe$^{3+}$/pH 3) as a pre-treatment.
5.3 Comparison of Al$^{3+}$ and Fe$^{2+}$ Coagulation as a Pre-Treatment to the UVC/H$_2$O$_2$ Process

Sections 5.1.1 and 5.2.1 presented the results of Al$^{3+}$ and Fe$^{2+}$ coagulation for the treatment of LR GW. Under optimal conditions, 73% of COD was removed by Al$^{3+}$ coagulation (2 mM/pH 5) alone and 49% was removed by Fe$^{2+}$ coagulation (1 mM/pH 3) alone. Thus, the degree of COD removal and the optimal conditions depend on the type of coagulant used. Another observation was that the supernatant from Fe$^{2+}$ coagulation was yellowish compared with Al$^{3+}$ and this may not be aesthetically desirable. When Al$^{3+}$ coagulation was followed by the UVC/H$_2$O$_2$ process, an overall COD reduction of 98% (residual COD = 5 mg.L$^{-1}$) was achieved with 2 mM H$_2$O$_2$ within 1.5 hours of irradiation; the Fe$^{2+}$ coagulation and subsequent UVC/H$_2$O$_2$ process required a shorter irradiation time (1 hour) but less COD was removed (91%), and a higher H$_2$O$_2$ dosage was needed (7 mM). Thus, although good removal of COD was obtained with either alum or ferrous sulphate coagulation followed by UVC/H$_2$O$_2$ treatment, the process using alum is preferable due to slightly higher COD removal, lower dosage of H$_2$O$_2$ required and no residual colour in the treated water.

Since a large proportion of COD in the raw LR GW was removed by both coagulants, the UVC/H$_2$O$_2$ process served merely as a polishing step. While recognising the advantage of coagulation to reduce the turbidity of greywater and hence enhance the subsequent UVC/H$_2$O$_2$ treatment, issues such as sludge disposal arise with the use of coagulation. Unlike sludge produced from potable water treatment, its counterpart produced in wastewater treatment plants is often considered a regulated waste. For example, under the Environmental Protection Act 1994 in Queensland (Australia), it is required to have a licence or development approval for the disposal, incineration, recycling, processing, treatment, transportation and storage of alum sludge produced from commercial or industrial wastewater treatment facilities (EPAQ, 2007).

The presence of xenobiotic organic compounds (XOCs) in greywater, which may include PPCPs, EDCs and surfactants, was discussed in Section 2.3. The ever expanding list of XOCs and the lack of information about their toxicity, biodegradability and bioaccumulation properties are major concerns (Ledakowicz, 1998; Eriksson et al., 2003; Palmquist and Haneus, 2004; Ying et al., 2004). Since coagulation removes contaminants by forming flocs that are readily settled, some of these XOCs may be physically separated by the coagulation and concentrated in the sludge. Due to its capability of mineralising organic compounds, the UVC/H$_2$O$_2$ treatment has the potential of destroying the XOCs in greywater and this makes it an appealing option. Further investigation of the UVC/H$_2$O$_2$ process as a main treatment is detailed in Chapter 7.
Chapter 6. Fenton and Photo-Fenton Processes

Many factors affect the performance of the Fenton and photo-Fenton processes and they include the type of iron (ferrous or ferric), pH, temperature, Fe:H$_2$O$_2$ ratio and H$_2$O$_2$:COD ratio and some of the findings in the literature are summarised below:

- Researchers such as Neyens and Baeyens (2003), Badawy and Ali (2006), and Bautista et al. (2007) used only Fe$^{2+}$ in their studies of the Fenton process; Wang et al. (2008) reported a higher degradation rate of azo dye when Fe$^{2+}$ was used instead of Fe$^{3+}$. For the photo-Fenton process, the type of iron salts used and hence the effectiveness of the process appeared to vary according to the type of water being treated: Gogate and Pandit (2004b) reported better performance using Fe$^{3+}$ while de Oliveira et al. (2007) claimed that the formation of Fe$^{3+}$ complex resulted in poor COD removal by the photo-Fenton process when Fe(NO$_3$)$_3$ was used instead of FeSO$_4$.

- For the oxidation and coagulation stages, Tekin et al. (2006) did not observe significant difference in COD removal between pH 3 – 4.5 and 7 – 9 for the respective stage.

- Gulkaya et al. (2006) reported higher TOC removal during the oxidation stage of the Fenton process when the temperature was elevated from 25°C to 50°C. In contrast, in the review by Gogate and Pandit (2004a), the optimal temperature was reported as 30°C whereas some claimed that the performance was unaffected between 10 and 40°C, and that higher temperature accelerated the decomposition of H$_2$O$_2$ and reduced process performance.

Therefore, in this study the source of iron was limited to ferrous sulphate and the pH for the oxidation and coagulation stages was fixed at 3 and 7, respectively. All experiments were conducted at 25 ± 3°C. The focus of the investigation was to determine the optimal Fe$^{2+}$:H$_2$O$_2$ and H$_2$O$_2$:COD ratios.

The experimental procedures for the Fenton and photo-Fenton processes were described in Section 3.6. Using LR GW prepared as per Section 4.2.2, Section 6.1 investigates the effect of Fe$^{2+}$:H$_2$O$_2$ ratio and the results are compared with the sequential Fe$^{2+}$ coagulation and UVC/H$_2$O$_2$ treatment (Sections 5.2.1 and 5.2.2). Section 6.2 studies the effect of H$_2$O$_2$:COD ratio by varying initial COD level and using different types of greywater while keeping the Fe$^{2+}$ concentration constant. Finally, Section 6.3 summarises the findings for the Fenton and photo-Fenton processes. All results reported in the following sections are based on the overall COD removal, i.e., from the combination of the oxidation and coagulation stages of the Fenton and photo-Fenton processes.
6.1 Effect of Fe$^{2+}$:H$_2$O$_2$ Ratio

As per Bautista et al. (2007), the optimisation of the processes was carried out by determining the optimal H$_2$O$_2$ dosage at a fixed Fe$^{2+}$ concentration, followed by varying the Fe$^{2+}$ dosage at the optimal H$_2$O$_2$ dosage for the greywater of a fixed initial COD level.

6.1.1 H$_2$O$_2$ Concentration

In Section 5.2.1, the optimal Fe$^{2+}$ dosage for the coagulation of LR GW was found to be 1 mM. To allow direct comparison, this Fe$^{2+}$ dosage was used as the first trial to treat the LR GW by the Fenton (Figure 6-1(a)) and photo-Fenton processes (Figure 6-1(b)) in the presence of 1 – 15 mM H$_2$O$_2$. The LR GW had a COD of 231 ± 9 mg.L$^{-1}$.

For the Fenton process, the lowest COD level of 122 mg.L$^{-1}$ was achieved with 1 mM Fe$^{2+}$/5 mM H$_2$O$_2$ within a reaction time of 30 minutes (45% COD removal). Increasing H$_2$O$_2$ dosage to above 5 mM H$_2$O$_2$ decreased COD removal, possibly due to the scavenging of *OH by excess H$_2$O$_2$ (Gogate and Pandit, 2004a).

For all H$_2$O$_2$ concentrations used, the residual COD remained relatively constant for the reaction time between 30 minutes and 3 hours. This coincides with the reports by Gulkaya et al. (2006), Tekin et al. (2006) and Bautista et al. (2007) that the time required for the oxidation stage of the Fenton process to reach a plateau is up to about 30 minutes (some used the term “equilibration time”). Measurement of residual H$_2$O$_2$ by Merckoquant® test strip (Section 3.3.11) showed that more than 25 mg.L$^{-1}$ H$_2$O$_2$ (or 0.74 mM) remained in the water over the entire reaction time for H$_2$O$_2$ dosages of 5 mM and above, whereas it remained consistently at about 10 mg.L$^{-1}$ for the initial H$_2$O$_2$ dosage of 1 mM. This suggests that no further reaction took place after 30 minutes. Compared with the Fenton process, a similar level of COD removal (43%) and residual COD (131 mg.L$^{-1}$) was achieved when 1 mM H$_2$O$_2$ was dosed for the photo-Fenton process (Figure 6-1(b)). After 30 minutes of irradiation, the residual H$_2$O$_2$ in the system decreased to about 5 mg.L$^{-1}$ (i.e., half that of the Fenton process) and it disappeared almost completely within 1 hour. In these cases, coagulation, rather than oxidation, may be the main mechanism for COD removal.

The photo-Fenton process achieved almost twice as much COD removal at the H$_2$O$_2$ dosage of 5 mM and above. With 10 mM H$_2$O$_2$, 83% COD was removed after 1.5 hours irradiation and the residual COD was 38 mg.L$^{-1}$; for the same H$_2$O$_2$ dosage and reaction time, the Fenton process only achieved 38% removal and 140 mg.L$^{-1}$ COD remained. At this point, the residual H$_2$O$_2$ was 2 mg.L$^{-1}$ (or 0.06 mM) and extending the irradiation to 2 or 3 hours only marginally reduced the COD to 36 and 32 mg.L$^{-1}$, respectively.
Figure 6-1. COD of LR GW treated by (a) Fenton process, and (b) photo-Fenton process in the presence of 1 mM Fe$^{2+}$.
The good performance of the photo-Fenton process compared with the Fenton process can be explained by the occurrence of more reactions that generate \( ^\cdot \text{OH} \): In addition to the Fenton reaction between \( \text{Fe}^{2+} \) and \( \text{H}_2\text{O}_2 \) (Equation 2-1), \( ^\cdot \text{OH} \) is also produced from water in the presence of \( \text{Fe}^{3+} \) under UV irradiation (Equation 2-16) and the direct photolysis of \( \text{H}_2\text{O}_2 \) (Equation 2-17). These results are consistent with the review by Gogate and Pandit (2004b), who reported significantly higher efficacy of the photo-Fenton process.

Since COD removal was not significantly improved as the \( \text{H}_2\text{O}_2 \) concentration increased from 10 mM to 12.5 and 15 mM, possibly due to the scavenging effect of excess \( \text{H}_2\text{O}_2 \) and the presence of recalcitrant compounds, 10 mM appeared to be the optimal \( \text{H}_2\text{O}_2 \) dosage for the treatment of LR GW by the photo-Fenton process.

As discussed previously for the Fenton process, it appeared that coagulation was the main mechanism involved in the removal of COD from LR GW. Hence in Section 6.1.1.1, the Fenton process is compared with ferrous sulphate coagulation; the effectiveness of the photo-Fenton process is evaluated against that of the sequential ferrous sulphate coagulation and UVC/\( \text{H}_2\text{O}_2 \) in Section 6.1.1.2 since both systems involve the use of UVC irradiation, \( \text{Fe}^{2+} \) and \( \text{H}_2\text{O}_2 \).

6.1.1.1 Comparison of \( \text{Fe}^{2+} \) Coagulation with Fenton Process

The main difference between the \( \text{Fe}^{2+} \) coagulation and the Fenton processes is the sequence of \( \text{Fe}^{2+} \) dosage and pH adjustment, and the latter also requires the addition of \( \text{H}_2\text{O}_2 \). For \( \text{Fe}^{2+} \) coagulation in Section 5.2.1, \( \text{Fe}^{2+} \) was added to the raw LR GW (pH 10) before subsequent acidification to pH 3, whereas for the Fenton process, \( \text{Fe}^{2+} \) was added to acidified LR GW (pH 3.5) before final pH adjustment to 3 and the subsequent addition of \( \text{H}_2\text{O}_2 \).

Figure 6-2 shows the colour changes of the solutions for the different \( \text{Fe}^{2+} \) dosing regime: a rusty-coloured floc formed and settled readily when \( \text{Fe}^{2+} \) was added directly to the raw LR GW, whereas no floc formation was observed when \( \text{Fe}^{2+} \) was added to its acidified counterpart. The change in colour and floc formation in the former regime can be explained by the formation of ferric hydroxide (\( \text{Fe(OH)}_3 \)) which is reddish-brown in colour. According to Bratby (2006), ferrous sulphate reacts with alkalinity to form ferrous hydroxide (\( \text{Fe(OH)}_2 \)) and at pH > 8.5, it is oxidised to \( \text{Fe(OH)}_3 \) in the presence of dissolved oxygen. Upon the addition of \( \text{H}_2\text{O}_2 \) in the latter case (i.e., at the oxidation stage of the Fenton process), slight yellowish floc formation was observed which settled readily. Subsequent neutralisation (coagulation stage), however, did not promote floc formation.

Despite the differences in the methods, the \( \text{Fe}^{2+} \) coagulation (1 mM \( \text{Fe}^{2+} \)/pH 3) resulted in a
supernatant of 118 mg.L\(^{-1}\) COD, which was similar to 122 mg.L\(^{-1}\) COD remaining in the water treated by the Fenton process (1 mM Fe\(^{2+}\)/5 mM \(\text{H}_2\text{O}_2\)). This suggests that the coagulation process is more desirable than the Fenton process for the treatment of LR GW since similar COD removal was achieved without the addition of \(\text{H}_2\text{O}_2\).

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**Figure 6-2. Differences in solution colour and floc formation by adding 1 mM Fe\(^{2+}\) to raw LR GW (pH 10) and acidified LR GW (pH 3.5).**

6.1.1.2 Comparison of the Sequential Fe\(^{2+}\) Coagulation and UVC/H\(_2\)O\(_2\) Treatment with Photo-Fenton Process

The sequential treatment of LR GW by Fe\(^{2+}\) coagulation (1 mM Fe\(^{2+}\)/pH 3) and UVC/7 mM \(\text{H}_2\text{O}_2\)/pH 3 achieved an overall COD reduction of 91% within 1 hour of irradiation and the residual COD was 21 mg.L\(^{-1}\) (Section 5.2.2). For the photo-Fenton process, a higher \(\text{H}_2\text{O}_2\) dosage (10 mM) and longer irradiation time (1.5 hours) was required for an overall COD reduction of 83%, and the residual COD was almost two times higher (38 mg.L\(^{-1}\)).

The poorer performance of the photo-Fenton process may be explained by the formation of flocs upon the addition of \(\text{H}_2\text{O}_2\). The flocs caused the solution to become more turbid and the bubbling action in the photo-reactor kept the flocs in suspension which may have reduced the penetration of UVC radiation into the medium.

As mentioned in Section 6.1.1.1, slightly yellowish flocs were formed when \(\text{H}_2\text{O}_2\) was added to the acidified LR GW which contained 1 mM Fe\(^{2+}\). For LR GW, this occurred during the oxidation stage of both of the Fenton and photo-Fenton processes and pH neutralisation did not promote floc formation in the subsequent coagulation stage. This did not seem to follow the four stages outlined by Gogate and Pandit (2004a) and Benatti et al. (2006), i.e., pH adjustment, oxidation, neutralisation and coagulation. Further discussion about this phenomenon is included in Section 6.2 which describes the treatment of greywaters of different types and concentrations by the Fenton and photo-Fenton processes.
6.1.2 Fe$^{2+}$ Concentration

Gogate and Pandit (2004a; 2004b) discussed the drawbacks of excess iron dosage: additional COD incurred by the presence of Fe$^{2+}$, scavenging of radicals by Fe$^{2+}$ (Equation 2-6), and increase in total dissolved solids due to the iron salts (Fe$^{2+}$ or Fe$^{3+}$).

As previously described in Section 5.2.1, the Fe$^{2+}$ concentration required for coagulation was determined as 1 mM and this was used in the first trial of the Fenton and photo-Fenton processes at different H$_2$O$_2$ dosage (Section 6.1.1) so that direct comparison with Fe$^{2+}$ coagulation can be made (Sections 6.1.1.1 and 6.1.1.2). This Fe$^{2+}$ dosage appeared to be adequate for the treatment of LR GW, hence higher Fe$^{2+}$ dosage was not attempted in this project. However, lower Fe$^{2+}$ dosage at 0.75 mM was investigated in the presence of 10 mM H$_2$O$_2$ (Figure 6-3), and the result for the UVC/H$_2$O$_2$ process (Section 7.2.2), i.e., with 0 mM Fe$^{2+}$, is included here as a comparison.

![Figure 6-3. Effect of different Fe$^{2+}$ concentrations on the COD of LR GW treated by Fenton and photo-Fenton process in the presence of 10 mM H$_2$O$_2$.](image-url)
For the Fenton process, a slight reduction in the extent of COD removal was observed when lower Fe\(^{2+}\) was used. Interestingly, for the photo-Fenton process, the extent of COD reduction was similar despite increasing Fe\(^{2+}\) concentrations from 0 to 0.75 and 1 mM. However, the rate of COD removal increased significantly with increasing Fe\(^{2+}\) dosage. Compared with UVC/10 mM H\(_2\)O\(_2\) treatment, the required irradiation time was reduced from 3 hours to 1.5 hours when 1 mM Fe\(^{2+}\) was added. This effectively halved the UV dose from 54,000 mJ.cm\(^{-2}\) to 27,000 mJ.cm\(^{-2}\).

However, it should be pointed out that the UVC/H\(_2\)O\(_2\) process, i.e., at 0 mM Fe\(^{2+}\), removes COD by a different mechanism from the photo-Fenton process. The former depends almost entirely on the generation of radicals such as \(^{\circ}\)OH to oxidise the pollutants, while the photo-Fenton process also relies on the coagulative property of the Fenton reagents, and hence the issues of sludge generation discussed in Section 5.3 are also applicable to the photo-Fenton process.

From this study, 1 mM Fe\(^{2+}\) was considered the optimal Fe\(^{2+}\) dosage for the treatment of LR GW by the Fenton and photo-Fenton processes. The optimal molar ratios of Fe\(^{2+}\):H\(_2\)O\(_2\) for the Fenton and photo-Fenton process were 1:5 and 1:10, respectively.

While the theoretical optimal Fe\(^{2+}\):H\(_2\)O\(_2\) ratio was reported to be close to 1:10 (Wadley and Waite, 2004), it varies significantly in the literature, e.g., 1:153 – 1:470 (Gulkaya et al., 2006), 1:4.5 (Benatti et al., 2006), 1:150 – 1:250 (Tekin et al., 2006), 1:11 (Badawy and Ali, 2006) and 1:44 (Bautista et al., 2007). Gulkaya et al. (2006) also remarked on the large variation in the optimal Fe\(^{2+}\):H\(_2\)O\(_2\) ratio and concluded that the ratio depends on the type and loading of the contaminants in the wastewater.
6.2 Effect of H$_2$O$_2$:COD Ratio

To investigate the effect of H$_2$O$_2$:COD ratio on the effectiveness of the Fenton and photo-Fenton processes, greywater of different types and COD levels was used. These include laundry greywater (LGW), shower greywater (SGW), teeth-brushing greywater (TGW), high-range greywater (HR GW), mid-range greywater (MR GW) and low-range greywater (LR GW); their collection and preparation have been described in Section 4.2.

For both the Fenton and photo-Fenton processes, the Fe$^{2+}$ concentration was fixed at 1 mM. Two H$_2$O$_2$ dosages were studied: 10 mM H$_2$O$_2$ and the other according to the theoretical optimal H$_2$O$_2$:COD ratio of 2.12 g H$_2$O$_2$/g COD (Bautista et al., 2007). Table 6-1 shows the theoretical optimal H$_2$O$_2$ dosage for each of the greywaters used.

<table>
<thead>
<tr>
<th>Type of Greywater</th>
<th>COD (mg.L$^{-1}$)</th>
<th>Theoretical Optimal H$_2$O$_2$ Dosage$^*$ (mM)</th>
<th>Type of Greywater</th>
<th>COD (mg.L$^{-1}$)</th>
<th>Theoretical Optimal H$_2$O$_2$ Dosage$^*$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LGW</td>
<td>401</td>
<td>25.0</td>
<td>HR GW</td>
<td>372</td>
<td>23.2</td>
</tr>
<tr>
<td>TGW</td>
<td>282</td>
<td>17.6</td>
<td>MR GW</td>
<td>283</td>
<td>17.6</td>
</tr>
<tr>
<td>SGW</td>
<td>112</td>
<td>7.0</td>
<td>LR GW</td>
<td>226</td>
<td>14.1</td>
</tr>
</tbody>
</table>

* Calculated according to the theoretical H$_2$O$_2$:COD ratio of 2.12 g H$_2$O$_2$/g COD (Bautista et al., 2007).

These greywaters responded differently when the Fenton reagents were added and two procedures were developed as described in Section 3.6 (Figure 3-3). The initial steps were similar: the greywaters were acidified to around pH 3.5 with 1 M H$_2$SO$_4$ before the addition of 1 mM Fe$^{2+}$ and subsequent adjustment of pH to 3. For Method 1, H$_2$O$_2$ was then added and oxidation was allowed to take place for a specific time, followed by pH neutralisation which was accompanied by the formation of flocs during the subsequent coagulation stage. Finally, catalase was added to remove the residual H$_2$O$_2$. For Method 2, catalase was added after the required time for oxidation, followed by settlement and subsequent neutralisation of the supernatant with 1 M NaOH.

It was found that Method 1 was suitable for SGW and TGW, but for LGW, LR GW, MR GW and HR GW, floc formation was observed upon the addition of H$_2$O$_2$, and the oxidation and coagulation appeared to occur simultaneously. When Method 1 was used, the flocs disappeared after adjustment of pH to 7 and no coagulation took place during the
“coagulation stage”. Hence, Method 2 was developed to separate the flocs by settlement before the supernatant was withdrawn and subsequently neutralised.

Using LGW as an example, the Fenton process (1 mM Fe\(^{2+}/10\) mM H\(_2\)O\(_2\)) achieved up to 52% of COD removal by using Method 2 (Figure 6-4(b)); as a result of the flocs being redissolved after neutralisation, only about 14% of COD was removed when Method 1 was used (Figure 6-4(a)). This shows that a large portion of the COD in LGW was removed during the coagulation stage of the Fenton process and its effectiveness relies on the use of an appropriate procedure. Similarly for the photo-Fenton process (UVC/1 mM Fe\(^{2+}/10\) mM H\(_2\)O\(_2\)), Method 2 resulted in 58% COD removal in LGW, almost twice as much as for Method 1 (33%). In addition, increasing the H\(_2\)O\(_2\) concentration to the theoretical optimal dosage of 25 mM enhanced the COD removal by the photo-Fenton process to 53% and 68% for Method 1 and 2, respectively; however, such increase in H\(_2\)O\(_2\) dosage did not improve the performance of the Fenton process regardless of the method used.

For TGW, some fine flocs were formed upon the addition of H\(_2\)O\(_2\) but continued with the procedures of Method 1, substantial formation of off-white flocs was observed once the pH was adjusted to neutral. For the Fenton process, a similar level of COD removal was achieved when 10 and 17.6 mM H\(_2\)O\(_2\) was added to the system, i.e., 18% and 21% respectively (Figure 6-4(c)). For the photo-Fenton process, the extent of COD removal increased from 63% to 91% with the increased H\(_2\)O\(_2\) dosage.

SGW had the lowest COD level (112 mg.L\(^{-1}\)) and Method 1 was used for the Fenton and photo-Fenton processes. Figure 6-4(d) shows the superiority of the photo-Fenton process over the Fenton process. Increasing the H\(_2\)O\(_2\) dosage from 7 to 10 mM did not improve the extent or rate of COD removal for both processes. After only 10 minutes of reaction time for the oxidation stage, the Fenton process removed up to 66% of COD, and longer reaction time only marginally improved the quality of the effluent. A higher COD removal of up to 98% was achieved with the photo-Fenton process when the sample was irradiated for half an hour during the oxidation stage.

Using Method 2, the Fenton process (1 mM Fe\(^{2+}/10\) mM H\(_2\)O\(_2\)) removed 46%, 49%, 38% of COD in HR GW, MR GW and LR GW, respectively (Figure 6-5(a)-(c)). Adding H\(_2\)O\(_2\) according to the theoretical optimal dosages (Table 6-1) did not improve the extent of COD removal. With 10 mM H\(_2\)O\(_2\), the photo-Fenton process was more effective, with COD removal of 56%, 87% and 86% achieved for HR GW, MR GW and LR GW, respectively. Increasing the H\(_2\)O\(_2\) dosages to the theoretical optimal values only improved the effectiveness of the treatment of HR GW, for which the COD removal was increased to 72%.
Figure 6-4. COD of greywater treated by the Fenton and photo-Fenton processes in the presence of 1 mM Fe$^{2+}$: (a) LGW (Method 1)$^#$, (b) LGW (Method 2)$^*$, (c) TGW (Method 1)$^#$, and (d) SGW (Method 1)$^#$.

$^#$ Method 1: After oxidation stage, sample was subjected to pH neutralisation before settlement

$^*$ Method 2: After oxidation stage, sample was settled before pH neutralisation
Figure 6-5. COD of greywater by the Fenton and photo-Fenton processes in the presence of 1 mM Fe^{2+}: (a) HR GW, (b) MR GW, and (c) LR GW.
Method 2 was used, i.e., after oxidation stage, sample was settled before pH neutralisation.
This study showed that different types of greywater exhibited markedly different properties when Fenton reagents were used. While SGW followed the typical steps described by Gogate and Pandit (2004a) and Benatti et al. (2006), (i.e., acidification, oxidation, pH neutralisation, and coagulation), some fine flocs were formed once H₂O₂ was added to TGW, but most coagulation occurred after pH neutralisation. For those containing a large proportion of input from the laundry (LGW, HR GW, MR GW and LR GW), floc formation upon the addition of H₂O₂ suggested that the oxidation and coagulation took place simultaneously. Discussion of this observation has not been found in the literature, although Neyens and Baeyens (2003) noted that large amounts of small flocs were observed during the Fenton oxidation stage, which took a very long time to settle out, and hence recommended the use of polymer to promote coagulation.

It should be pointed out that the occurrence of flocs during the oxidation stage of the photo-Fenton process may impede the penetration of UV radiation and reduce the effectiveness of the process. Also, the difference in the response of the greywaters to the treatments may be due to the type of contaminants present, but not the initial COD levels: for example, MR GW and TGW had similar COD level but the floc formation took place at different stages.

Based on the theory of particle-particle interaction derived by Derjaguin, Landau, Verwey and Overbeek (DLVO Theory), the use of coagulant compresses the electrical double layer and reduces the zeta-potential, hence results in the reduction of repulsive forces that exist between the particles. The particles come together due to Brownian movement and remain attached due to van der Waals forces of attraction (Crittenden et al., 2005). The stability of a colloidal system depends on the thickness of the electrical double layer and the zeta-potential, which are greatly affected by ionic strength of the system. Since ionic strength is associated with the level of total dissolved solids and conductivity of the solution, high conductivity of the medium (i.e., level of salts) reduces the zeta-potential. Examination of Table 4-3 shows that the greywaters had very different conductivity: Those with laundry input had conductivities higher than 1000 µS.cm⁻¹; in relation to LGW, which had the highest conductivity of 2060 µS.cm⁻¹, those of TGW and SGW were approximately 4 and 9 times lower, respectively. This suggests that, under the conditions during the oxidation stage of the Fenton and photo-Fenton processes, those greywaters with laundry input were prone to coagulation due to their high conductivity and as a result, the electrical double-layer was compressed and the zeta-potential reduced.

Depending on the cleaning activities in a household that lead to the generation of greywater, the washing machine may be the main source for greywater during a particular time of the day, and greywaters from shower or hand basin may predominate at other times. Since the
quality and quantity of greywater vary significantly even within a single household (Jefferson et al., 2000), this may prove to be problematic as floc formation may occur at different stages of the processes which requires different procedures for settlement or pH adjustment, or their effectiveness in COD removal may be jeopardised. Therefore, the variation in the response of different types of greywaters to the Fenton and photo-Fenton processes presents a major challenge in the application of these processes in greywater treatment. Careful process design which includes the selection or exclusion of a particular type(s) of greywater may reduce the variation in greywater quality. Such variation may also be decreased with the use of a storage facility to allow mixing prior to treatment, and/or by applying the processes to larger scale recycling projects which collect large volumes of greywater from multiple sources that may achieve homogenisation of the influent.
6.3 Summary of Findings for the Fenton and Photo-Fenton Processes

In this study, the focus of investigation for the Fenton and photo-Fenton processes was the effect of Fe$^{2+}$:H$_2$O$_2$ and H$_2$O$_2$:COD ratios.

Using LR GW as an example and at a fixed Fe$^{2+}$ dosage (1 mM), the effect of H$_2$O$_2$ addition ranging from 1 – 15 mM was investigated. For the Fenton process, COD removal of 33% – 45% was achieved after 30 minutes reaction time for the oxidation stage. Longer reaction time (up to 3 hours) did not improve the COD removal, despite the presence of significant residual H$_2$O$_2$ which remained relatively constant. It appeared that most of the COD was removed during the coagulation stage of the Fenton process since the photo-Fenton process with 1 mM H$_2$O$_2$ achieved similar level of COD removal. For the photo-Fenton process, the optimal H$_2$O$_2$ dosage was 10 mM, beyond which no significant improvement was made probably due to the scavenging of *OH by excess H$_2$O$_2$. The photo-Fenton process (1 mM Fe$^{2+}$/10 mM H$_2$O$_2$) achieved up to 83% of COD removal after 1.5 hours of irradiation during the oxidation stage.

Once the optimal H$_2$O$_2$ dosage was established, a lower Fe$^{2+}$ dosage of 0.75 mM was used. This was found to reduce the rate but not the extent of COD removal for the photo-Fenton process, whereas for the Fenton process the extent of COD removal deteriorated by about 5%. Higher Fe$^{2+}$ concentration was not investigated since excess dosage of ferrous sulphate may result in increased COD and total dissolved solids. Therefore, 1 mM Fe$^{2+}$ appeared to be adequate for treatment of LR GW and the optimal molar ratio of Fe$^{2+}$:H$_2$O$_2$ for the Fenton and photo-Fenton processes was 1:5 and 1:10 respectively.

The Fenton process (1 mM Fe$^{2+}$/5 mM H$_2$O$_2$) had a similar efficacy for COD removal as Fe$^{2+}$ coagulation (Section 6.1.1.1). However, Fe$^{2+}$ coagulation is favoured since it does not require the addition of H$_2$O$_2$. Similarly, the photo-Fenton process (1 mM Fe$^{2+}$/10 mM H$_2$O$_2$) was compared with the sequential Fe$^{2+}$ coagulation (1 mM Fe$^{2+}$) and UVC/7 mM H$_2$O$_2$ treatment (Section 6.1.1.2). Despite longer irradiation time and higher H$_2$O$_2$ dosage, twice as much COD remained in the water treated by the photo-Fenton process, possibly due to the formation of flocs during the oxidation stage which reduced the penetration of UVC radiation.

The determination of the optimal H$_2$O$_2$:COD ratio was complicated by the different types and concentrations of greywater used. Two methods were developed for the processes involving the use of Fenton reagents. Method 1 was the typical procedure as described by Gogate and Pandit (2004a), which was used to treat SGW and TGW. For greywaters containing laundry
input, floc formation occurred during the oxidation stage and if Method 1 was used, the flocs re-dissolved and the extent of COD removal deteriorated substantially. This prompted the development of Method 2, which allowed settlement of the flocs before pH neutralisation of the solution. Discussion on floc formation during the oxidation stage and its disappearance after neutralisation has not been found in the literature. The variation in the response of different types of greywater to the Fenton and photo-Fenton processes is attributed to the high conductivity of those greywaters with input from laundry, which in effect reduced the zeta-potential and compressed the electrical double-layer of the particles in suspension, and resulted in the greywaters being prone to coagulation under the conditions used in the oxidation stage of the processes.

For all the greywater types studied in this work, dosing H_2O_2 according to the theoretical optimal ratio of 2.12 g H_2O_2/g COD (Bautista et al., 2007) for the Fenton process did not provide better COD removal than when 10 mM H_2O_2 was used. However for the photo-Fenton process, enhanced COD removal was observed for LGW, TGW and HR GW when H_2O_2 was dosed in accordance with the theoretical optimal ratio. In short, the Fenton process did not adequately remove COD and the photo-Fenton process achieved COD removal of up to 68%, 91%, 98%, 72%, 87% and 86% for LGW, TGW, SGW, HR GW, MR GW and LR GW, respectively. The optimisation of the processes depends greatly on the types of greywater and the COD loadings.

In addition to the requirement for optimisation of multiple parameters, one major challenge to the application of the Fenton and photo-Fenton processes in greywater treatment is the variation in the types of greywater, causing floc formation to occur at different stages of the processes. While the flocs formed during the oxidation stage of the photo-Fenton process may reduce the penetration of UV radiation, effectiveness of the Fenton and photo-Fenton processes may also decrease as a result of the flocs being re-dissolved if appropriate procedures for settlement and pH adjustment were not followed. Furthermore, the treated water from both of the Fenton and photo-Fenton processes was yellowish and not aesthetically pleasant due to the residual iron salt in the effluent. Also, the issue of sludge disposal needs to be considered since coagulation is involved.
Chapter 7. UVC/H₂O₂ Treatment

This chapter details the findings for the treatment of greywater by UVC/H₂O₂. Tuhkanen (2004) identified that the rate of \( \bullet \text{OH} \) formation from \( \text{H}_2\text{O}_2 \) photolysis is the limiting factor for the oxidation of contaminants. In this chapter, several factors that affect the formation of \( \bullet \text{OH} \) are investigated.

Using LR GW as the main source of greywater, the impact of overnight settlement as a pre-treatment to the UVC/H₂O₂ process is discussed in Section 7.1. The results of COD reduction at various \( \text{H}_2\text{O}_2 \) dosages are presented in Section 7.2 and they are discussed in relation to the changes in absorbance and fluorescence characteristics of the treated water. In Section 7.3, the effect of pH on the process is investigated, following which the \( \text{BOD}_5 \), total suspended solids, turbidity and the level of \textit{Escherichia coli} of the treated water are compared with the requirements of Class A and Class B reclaimed water as specified by the EPAV (Table 2-2) in Section 7.4. The change in the biodegradability of settled LR GW during the UVC/H₂O₂ treatment is then evaluated in Section 7.5. Subsequently, these findings are applied to treat other greywaters collected from the researcher’s home to assess the effect of the initial COD level and the type of greywater on the treatment (Section 7.6). The results are summarised in Section 7.7.

7.1 Effect of Overnight Settlement

Due to the variability of greywater production and its demand, storage of greywater is usually needed for its optimum reuse (as discussed in Section 2.3). Therefore, the greywater was subjected to overnight settlement to simulate the effect of a storage facility in which hair, lint, and large particles were settled. In addition, there was concern regarding the turbidity of the greywater which may inhibit the penetration of UVC irradiation. Hence, by reducing the turbidity of greywater through settling overnight, this study was to investigate if the effectiveness of the UVC/H₂O₂ process was enhanced.

LR GW prepared as per Section 4.2 was used as the main source of greywater in this study. The raw LR GW had a COD of 235 mg.L\(^{-1}\), a turbidity of 13.3 NTU and its pH was 10. Settling the greywater overnight reduced the COD by 13\%, turbidity by 31\%, and pH by 0.5 units.

The raw LR GW and its settled counterpart (COD = 195 mg.L\(^{-1}\)) were both subjected to UVC/10 mM \( \text{H}_2\text{O}_2 \) treatment at an initial pH of 10, and a fairly similar rate of COD removal
was observed (Figure 7-1). After 3 hours of the treatment, 84% of COD in the raw greywater was removed (residual COD = 38 mg.L⁻¹) whereas 85% COD removal was obtained for the settled greywater (residual COD = 30 mg.L⁻¹).

Despite a reduction of 13% in COD and 31% in turbidity, overnight settlement did not greatly enhance the effectiveness of the UVC/H₂O₂ process for this greywater. The overall COD reduction for the sequential overnight settlement and UVC/H₂O₂ treatment was 87%, only 3% higher than that of the raw LR GW treated directly by the UVC/H₂O₂ process. This suggests that the turbidity level of the greywater was not high enough to have significant impact on the penetration of UVC radiation, and hence overnight settlement did not improve the effectiveness of the subsequent UVC/H₂O₂ treatment significantly.

![Figure 7-1. COD of raw and settled LR GW treated by UVC/10 mM H₂O₂ at initial pH of 10.](image-url)
7.2 Effect of H$_2$O$_2$ Dosage

7.2.1 Preliminary Study

Prior to investigating the effect of H$_2$O$_2$ dosage on UVC/H$_2$O$_2$ treatment (Section 7.2.2), a preliminary study was conducted to determine the pH, minimum H$_2$O$_2$ dosage and irradiation time for COD reduction to occur. The pH of the settled LR GW was adjusted to pH 3, 5, 7 or 10 with 1 M H$_2$SO$_4$ or 1 M NaOH. Subsequently, H$_2$O$_2$ was added so that its concentration was between 3 and 5 mM in the greywater, which was then exposed to UVC irradiation for up to 2 hours. As a trial, a 35 mL aliquot was collected at each sampling time over the course of treatment. As a result of periodically withdrawing the aliquots, the volume of sample being irradiated decreased, and in turn, the surface area exposed to irradiation decreased. The results are shown in Figure 7-2.

Figure 7-2. COD of settled LR GW treated by UVC/H$_2$O$_2$ at initial pH in the range of 3 – 10, with (a) 3 mM H$_2$O$_2$, (b) 3.5 mM H$_2$O$_2$, (c) 4 mM H$_2$O$_2$, and (d) 5 mM H$_2$O$_2$. 

COD (mg.L$^{-1}$) vs. Irradiation Time (h) for different pH conditions.
The general trend across Figure 7-2(a) to (d) shows increased COD removal with increasing \( \text{H}_2\text{O}_2 \) dosage and irradiation time. While 3, 3.5 and 4 mM \( \text{H}_2\text{O}_2 \) led to similar COD removal, up to 60% was removed with 5 mM \( \text{H}_2\text{O}_2 \) after 2 hours irradiation. Higher COD removal with longer irradiation time is expected since there was significant excess \( \text{H}_2\text{O}_2 \) in the irradiated samples (> 0.74 mM according to the Merckoquant® peroxide test strip).

An important observation from this preliminary study was that the initial pH of the settled LR GW appeared to have a minor effect on the UVC/\( \text{H}_2\text{O}_2 \) treatment and it was not as significant as described by Yonar et al. (2006). This is shown in Figure 7-2 by the relatively small differences in the residual COD level at various initial pH for the same \( \text{H}_2\text{O}_2 \) dosage. Furthermore, operating at the initial pH of 10 gave slightly better COD removal, e.g., at 5 mM \( \text{H}_2\text{O}_2 \) (Figure 7-2 (d)). In the following section, the optimal \( \text{H}_2\text{O}_2 \) dosage for the treatment of the settled LR GW by UVC/\( \text{H}_2\text{O}_2 \) was determined at the initial pH of 10 while the effect of pH was investigated in Section 7.3.

### 7.2.2 Optimal \( \text{H}_2\text{O}_2 \) Dosage

For the treatment of a domestic wastewater collected from a non-industrial residential district (COD = 336 ± 25 mg.L\(^{-1}\)), Yonar et al. (2006) reported that 50 mg.L\(^{-1}\) (1.5 mM) of \( \text{H}_2\text{O}_2 \) resulted in 25 mg.L\(^{-1}\) of residual COD after 1 hour of radiation with a 15 W monochromatic UVC lamp at pH 3. Ghaly et al. (2001) found that 20 mM was the optimal \( \text{H}_2\text{O}_2 \) dosage for degradation of \( p \)-chlorophenol (100 mg.L\(^{-1}\)), using a 700 W high-pressure UV lamp. When treating water containing Remazol Black-B dye (35 – 37.5 mg.L\(^{-1}\)), Ince (1999) concluded that 15 mM \( \text{H}_2\text{O}_2 \) gave the highest rate of degradation when a 1 kW medium pressure Hg lamp was used. While direct comparison of these investigations was not possible due to the differences in reactor design, lamp selection, and the type and concentration of the contaminants, it demonstrates the importance of determining the optimal \( \text{H}_2\text{O}_2 \) dosage to achieve satisfactory removal of the contaminants.

In this study, the effect of \( \text{H}_2\text{O}_2 \) dosage on the UVC/\( \text{H}_2\text{O}_2 \) process was investigated using settled LR GW at the initial pH of 10. The COD of the batches of the settled LR GW ranged from 187 to 208 mg.L\(^{-1}\). The \( \text{H}_2\text{O}_2 \) concentrations were between 3.5 and 15 mM. The results in Figure 7-3 indicate that only a small amount of the COD was removed when the greywater was irradiated in the absence of \( \text{H}_2\text{O}_2 \). Significant COD removal was observed when 3.5 mM \( \text{H}_2\text{O}_2 \) was added and its extent increased with increasing \( \text{H}_2\text{O}_2 \) concentration. With \( \text{H}_2\text{O}_2 \) dosage of 10 mM, the COD level in the water reduced to 30 mg.L\(^{-1}\) after 3 hours irradiation (equivalent UV dose of 54,000 mJ.cm\(^{-2}\)). This corresponded to 85% COD removal or an overall COD removal of 87% when the removal by overnight settlement was included.
Despite a 50% increase in H\(_2\)O\(_2\) dosage from 10 to 15 mM, only a relatively small improvement in the rate of COD reduction was observed (Figure 7-3). To better demonstrate the relationship between the rate of COD removal and the H\(_2\)O\(_2\) dosages, the reaction rate constants were determined by simplifying the order of the reaction as pseudo first-order, i.e., the concentration of *OH was assumed to remain constant throughout the period of reaction (Tuhkanen, 2004). This assumption is valid only when the amount of excess H\(_2\)O\(_2\) in the system does not deplete significantly.

The overall kinetics of the COD removal can be expressed by a second-order reaction (Equation 7-1). At a given H\(_2\)O\(_2\) dosage, the pseudo first-order rate constant (\(k'\)) for COD reduction is given by Equation 7-2, where COD\(_0\) and COD\(_t\) are the COD at irradiation time 0 and t, respectively:

\[
r = k [\text{COD}][\text{H}_2\text{O}_2]
\]

\[
\ln \frac{\text{COD}_t}{\text{COD}_0} = -k't
\]

By plotting ln(COD\(_t\))/ln(COD\(_0\)) versus time (t) (Figure 7-4), the value of \(k'\) for each H\(_2\)O\(_2\) dosage was obtained and are given in Table 7-1. As shown in Figure 7-4, the linear relationship in Equation 7-2 was valid up to 3 hours of irradiation, except for 15 mM H\(_2\)O\(_2\).
The corresponding $R^2$ values for all $\text{H}_2\text{O}_2$ dosages were at least 0.97 (Table 7-1).

**Table 7-1. Pseudo first-order rate constant ($k'$) and the corresponding $R^2$ value for different $\text{H}_2\text{O}_2$ concentrations.**

<table>
<thead>
<tr>
<th>Molarity of $\text{H}_2\text{O}_2$ (mM)</th>
<th>$k'$ (h$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>0.1696</td>
<td>0.97</td>
</tr>
<tr>
<td>5</td>
<td>0.3212</td>
<td>0.98</td>
</tr>
<tr>
<td>7</td>
<td>0.4657</td>
<td>1.00</td>
</tr>
<tr>
<td>10</td>
<td>0.6413</td>
<td>1.00</td>
</tr>
<tr>
<td>15</td>
<td>0.8162</td>
<td>1.00</td>
</tr>
</tbody>
</table>

By plotting the $k'$ against the concentration of $\text{H}_2\text{O}_2$, the rate constant $k$ in Equation 7-1 was determined as $0.0637 \text{ mM}^{-1}.\text{h}^{-1}$ (Figure 7-5) and it clearly demonstrated that the rate of COD removal increased proportionally with increasing $\text{H}_2\text{O}_2$ concentration, and that the linear relationship was not valid beyond 10 mM $\text{H}_2\text{O}_2$. This can be explained by the scavenging of $\cdot \text{OH}$ by excess $\text{H}_2\text{O}_2$ as suggested by Gogate and Pandit (2004a), Yonar et al. (2006), and Azam and Hamid (2006). While a higher dosage of $\text{H}_2\text{O}_2$ increased the amount of $\cdot \text{OH}$ produced from photolysis, it in turn reacts with $\text{H}_2\text{O}_2$ to form the less reactive $\cdot \text{O}_2\text{H}$ (Equation 2-5), and so decreases the rate of COD reduction.

**Figure 7-4. Determination of pseudo first-order rate constant ($k'$).**

**Figure 7-5. Effect of $\text{H}_2\text{O}_2$ dosage on the initial rate constant of COD reduction ($k'$).**
As discussed previously, the pseudo first-order reaction, or the linear relationship in Equation 7-2, was based on the assumption of a constant \( \bullet \)OH concentration during the reaction (Tuhkanen, 2004). Effectively, the \( \text{H}_2\text{O}_2 \) concentration should also remain constant for the assumption to be valid.

For all the \( \text{H}_2\text{O}_2 \) dosages used, the concentration of excess \( \text{H}_2\text{O}_2 \) remained higher than 25 mg.L\(^{-1}\) (or 0.74 mM) during the first 2 hours of irradiation (Table 7-2). As the irradiation time extended to 3 hours, the excess \( \text{H}_2\text{O}_2 \) varied from 10 to 25 mg.L\(^{-1}\) (or 0.3 to 0.74 mM), except for the dosage of 15 mM, which only had 5 mg.L\(^{-1}\) (0.15 mM) \( \text{H}_2\text{O}_2 \) remaining in the treated sample. This may explain why the linear relationship for the \( \text{H}_2\text{O}_2 \) dosage of 15 mM \( \text{H}_2\text{O}_2 \) was not valid up to 3 hours of irradiation (Figure 7-4), as the remaining 0.15 mM \( \text{H}_2\text{O}_2 \) at this point may have been too little to sustain the constant production of \( \bullet \)OH.

Examination of Table 7-2 also reveals why extending the UVC/10 mM \( \text{H}_2\text{O}_2 \) treatment from 3 to 5 hours did not provide significant COD reduction in the effluent (Figure 7-3), as there was only 10 mg.L\(^{-1}\) \( \text{H}_2\text{O}_2 \) (or 0.3 mM) remaining in the solution at this point.

<table>
<thead>
<tr>
<th>Initial ( \text{H}_2\text{O}_2 ) Dosage (mM)</th>
<th>Concentration of Excess ( \text{H}_2\text{O}_2 \star ) (mg.L(^{-1})) at Irradiation Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>&gt; 25 &gt; 25 &gt; 25 25 5</td>
</tr>
<tr>
<td>5</td>
<td>&gt; 25 &gt; 25 &gt; 25 25 5</td>
</tr>
<tr>
<td>7</td>
<td>&gt; 25 &gt; 25 &gt; 25 ~ 20 5</td>
</tr>
<tr>
<td>10</td>
<td>&gt; 25 &gt; 25 &gt; 25 10 2</td>
</tr>
<tr>
<td>15</td>
<td>&gt; 25 &gt; 25 &gt; 25 5 2</td>
</tr>
</tbody>
</table>

* The excess \( \text{H}_2\text{O}_2 \) in the sample were measured by Merckoquant® peroxide test strips as per Section 3.3.11.

Interestingly, the concentration of excess \( \text{H}_2\text{O}_2 \) after 3 hours of irradiation was lower when the initial \( \text{H}_2\text{O}_2 \) dosages were high (Table 7-2). This may be explained by the scavenging of \( \bullet \)OH by excess \( \text{H}_2\text{O}_2 \); increasing \( \text{H}_2\text{O}_2 \) concentration leads to higher production of \( \bullet \)OH, which consumes more \( \text{H}_2\text{O}_2 \) to form less reactive \( \bullet \text{O}_2\text{H} \) (Equation 2-5), and hence accelerates the depletion of \( \text{H}_2\text{O}_2 \).

In short, the optimal \( \text{H}_2\text{O}_2 \) dosage is a trade-off between the oxidation of pollutants in the greywater and the scavenging effect of excess \( \text{H}_2\text{O}_2 \) in the system. For the treatment of settled LR GW by UVC/\( \text{H}_2\text{O}_2 \), the optimal \( \text{H}_2\text{O}_2 \) dosage was found to be 10 mM.
7.2.3 Absorbance Spectrophotometry

During the treatment by the UV/H$_2$O$_2$ process, organic compounds can be eliminated by direct photolysis or the attack by *OH produced from the photolysis of H$_2$O$_2$ (Tuhkanen, 2004). To elucidate the changes in the organic compounds in settled LR GW treated by UVC irradiation alone (i.e., 0 mM H$_2$O$_2$) and UVC/10 mM H$_2$O$_2$, the samples were filtered (0.45 µm, Millex-HV PVDF filter) and diluted with MilliQ water (1:4) before measuring their absorbance over the wavelength range of 190 – 400 nm. The results shown in Figure 7-6(a) and (b) are superimposed on a chart showing the absorption region of different organic functional groups (Masschelein, 2002).

The settled LR GW had strong absorbance at 190 – 210 nm, and a second peak spanned 210 – 240 nm (Figure 7-6(a)). These coincide with the absorption region of many organic compounds which contain functional groups such as $\geq$C=O, $\geq$C=N, C=$\equiv$(C=)=$\equiv$C, R$\equiv$COOH, R$\equiv$COO$\equiv$R', R$\equiv$CO$\equiv$NH$\equiv$R', R$\equiv$S$\equiv$CO$\equiv$R', R$\equiv$C$\equiv$C$\equiv$COOH, and $\equiv$C$\equiv$C$\equiv$CO$\equiv$S$\equiv$R', $\equiv$SH, and $\equiv$O. Despite little absorbance at 254 nm (i.e., UVC radiation), there was significant reduction in absorbance at 190 – 240 nm after 1 hour of irradiation alone. Longer irradiation led to lower absorbance across the region but the decrease was marginal after 3 hours.

Although the absorbance of the settled LR GW at 254 nm appears to be very low in Figure 7-6(a) ($A_{254} = 0.035$), calculation according to the Beer-Lambert law in Equation 7-3 (Oppenländer, 2003) revealed that, after taking into account the dilution factor, about 33% of the incident UVC radiation was absorbed.

$$\text{Absorbance} = \log \frac{\text{Intensity of Incident Radiation}}{\text{Intensity of Transmitted Radiation}}$$  \hspace{1cm} \text{Equation 7-3}

According to the chart of Masschelein (2002), the following functional groups absorb UVC radiation: C=$\equiv$(C=)$\equiv$C, $\equiv$, $\equiv$, $\equiv$, $\equiv$, $\equiv$, and $\equiv$, i.e., those with conjugated double-bonds and aromatic rings. The electronic excitation of these groups by the UVC radiation promotes one electron from ground-state to excited-state (Equation 7-4), and as suggested by Legrini et al. (1993) and Oppenländer (2003), the subsequent transfer of the electron to ground-state molecular oxygen (Equation 7-5) produces radical ions. These radical ions can recombine or rearrange, or undergo other reactions such as the hydrolysis of the radical cation, which may have caused the reduction in the absorbance between 190 – 240 nm as shown in (Figure 7-6(a)).

$$C \xrightarrow{hv} C^*$$  \hspace{1cm} \text{Equation 7-4}

$$C^* + O_2 \rightarrow C^{**} + O_2^-$$  \hspace{1cm} \text{Equation 7-5}
Figure 7-6. Absorbance of settled LR GW treated by a) UVC irradiation alone, and b) UVC/10 mM H$_2$O$_2$, at the initial pH of 10*.

* Sample was filtered (0.45 $\mu$m) and diluted with MilliQ water (1: 4)
Since the COD of the settled LR GW remained relatively constant when exposed to UVC irradiation alone (Figure 7-3), the reduction in absorbance in Figure 7-6(a) indicated that some changes in the chemical structures of the contaminants occurred but did not lead to substantial mineralisation of the compounds. This is consistent with the observation by Legrini et al. (1993) that, although UVC irradiation may be useful for the degradation of substituted aromatics, the organics in water (especially the halogenated aliphatic compounds) cannot be effectively removed by irradiation alone.

In contrast, greater reduction in absorbance was observed when 10 mM of H₂O₂ was added to the system (Figure 7-6(b)). The UVC/H₂O₂ treatment changed the organic constituents of the greywater largely within the first hour of the treatment, and a slight increase in absorbance at greater than 235 nm was observed. Extending the irradiation time to 3 hours further reduced the absorbance across all the measured wavelengths. This indicates that the *OH radicals generated from the photolysis of H₂O₂ attacked the organic compounds and produced intermediates that absorbed radiation at other wavelengths, which were subsequently destroyed as the treatment proceeded. Accompanied by 85% of COD removal in the settled LR GW (Figure 7-3) after 3 hours of the UVC/10 mM H₂O₂ treatment, it can be deduced that the COD reduction in the greywater was achieved by the mineralisation of the organic contaminants by *OH, rather than by direct photolysis of the contaminants.

### 7.2.4 Fluorescence Spectroscopy

Fluorescence spectroscopy has been used to characterise dissolved organic matter (DOM) in drinking water sources (Rosario-Ortiz et al., 2007) and wastewater treatment plant effluent (Nguyen et al., 2007), and as a surrogate for BOD measurement in natural waters and wastewaters (Reynolds and Ahmad, 1997; Hudson et al., 2008). The excitation-emission matrix (EEM) of DOM can be divided into 5 regions which characterise specific components of DOM such as aromatic proteins, humic and fulvic-like materials, and microbial by-products. These are detailed in Figure 7-7(a) (Rosario-Ortiz et al., 2007).

In their review of the fluorescence properties of water and wastewaters, Hudson et al. (2008) described the use of the increases in Regions I, II, and IV of the fluorescence signature to indicate the anthropogenic impacts of wastewaters to natural waters. The tryptophan-like (Regions II and IV) and tyrosine-like (Region I) materials may be transported into a system (i.e., allochthonous) or be created within the system (autochthonous) and they are common in wastewaters. They are often associated with microbial activities, and may represent the presence of bioavailable, labile organic substrate, or the product of microbial or algal activity.
Using the method described in Section 3.3.9, EEMs were obtained for the settled LR GW and the samples treated by UVC/10 mM H₂O₂ (Figure 7-7(b) – (f)). The settled LR GW exhibited strong fluorescence in Regions I, II, III and V, and to a lesser extent in Region IV (Figure 7-7(b)). This is in accordance with the report of Hudson et al. (2007), i.e., the EEMs of untreated wastewaters typically comprise a broad humic-type peak in Region V with intense peaks in Regions I, II, and IV. The weaker fluorescence intensity in Region IV of the settled LR GW may be explained by the exclusion of toilet input to the greywater, since fluorescence in Region IV is typically associated with microbial by-products.

The presence of other peaks in the EEM may be explained by the use of fluorescent whitening agents (FWAs) in laundry detergents. FWAs have been detected at µg.L⁻¹ levels in the effluents of wastewater treatment plants, and Westerhoff et al. (2001) found that FWAs such as Tinopal AMS-GX, CBS-X, and 5BM-GX had EEM peaks with excitation/emission wavelength (λₑₓ: λₑₘ) of 260 nm:430 nm, 260 nm:540 nm, and 400 nm:460 nm, respectively.

As observed in Figure 7-7(b), the large area of the peak in Region V exceeded the maximum intensity on the scale, suggesting the settled LR GW may require dilution to give more accurate depiction of the fluorescence footprint. As Hudson et al. (2007) pointed out, the fluorescence analysis of high concentration solutions such as untreated sewage may be affected by inner filtering, due to the absorption and re-emission of the emitted energy at a longer wavelength by surrounding fluorophores. Nevertheless, in relation to the EEMs of the samples treated by UVC/H₂O₂ (Figure 7-7(c)-(f)), the sharp decrease in the intensity of all peaks in Figure 7-7(b) demonstrates that the fluorescent compounds in the settled LR GW were readily broken down even after one hour of treatment (Figure 7-7(c)); the main residual fluorophores absorbed in the same region as fulvic acid (Region III), while the peaks in Region I, II and V were still significant.

As the treatment proceeded to 2 hours (Figure 7-7(d)), all the peak intensities in Region I, II, III and V were reduced and interestingly, a new peak was observed at 400 nm:460 nm in Figure 7-7(d). After 3 hours irradiation (Figure 7-7(e)), this new peak was diminishing along with the peak in Region III, but a slight increase in peak intensity in Region I and II was also observed. Some of these aromatic proteins remained after 5 hours of treatment.

These observations indicated the complexity of reactions that occurred during the UVC/H₂O₂ treatment. While some compounds were broken down, intermediates were formed which may exhibit different fluorescent properties before their eventual destruction. This is consistent with the absorbance results (Figure 7-6(b)) regarding the increase in absorbance at different wavelengths indicating the production of reaction intermediates.
Figure 7-7. Fluorescence Excitation-Emission Matrices during the treatment of settled LR GW by UVC/10 mM H₂O₂ at the initial pH of 10.
7.3 Effect of pH

The preliminary study in Section 7.2.1 suggested that the pH of the settled LR GW played a minor role in the UVC/H$_2$O$_2$ treatment. In this section, further investigation was conducted according to the procedure described in Section 3.7. Using 1 M H$_2$SO$_4$ or 1 M NaOH, the settled LR GW was adjusted to pH 3, 7 or 10 prior to treatment. In addition to the optimal H$_2$O$_2$ dosage of 10 mM as determined in Section 7.2.2, 7 mM H$_2$O$_2$ was also studied. The results are shown in Figure 7-8.

Regardless of the initial pH, the UVC/H$_2$O$_2$ treatment achieved a lower level of residual COD with 10 mM H$_2$O$_2$. However, for both H$_2$O$_2$ concentrations, pH was shown to have a relatively minor effect on the extent of COD reduction. In addition, pH 10 resulted in a slightly lower residual COD compared with its neutral and acidic counterparts. This verified the findings from the preliminary study in which lower H$_2$O$_2$ concentrations were used (Figure 7-2). These results appear to contradict the common perception that acidic conditions are preferable for UV/H$_2$O$_2$ processes (Tuhkanen, 2004; Yonar et al., 2006), and for other AOPs (Liao et al., 2001; Gogate and Pandit, 2004b).

Gogate and Pandit (2004b) suggested that the exact optimal pH value depends on the acid dissociation constant ($K_a$) of the contaminant of concern, however, pH within the range of 2 – 3.5 is suitable for the operation of AOPs (Gogate and Pandit, 2004b; Schrank et al., 2007). For the UVC/H$_2$O$_2$ treatment of a domestic wastewater collected from residential district, Yonar et al. (2006) concluded that the optimal pH was 3 and decrease in COD removal was pronounced only when the pH was greater than 5. Frequently the requirement to operate AOPs at low pH is attributed to the alkalinity of the water, as carbonate and bicarbonates are effective scavengers for *OH (Tuhkanen, 2004).

In the following sections, the possible reasons for the contradiction between the present study and the results reported in the literature are explored. Section 7.3.1 describes the changes in pH observed during the UVC/H$_2$O$_2$ treatment. In Section 7.3.2, the scavenging of *OH by carbonate/bicarbonate species and chloride anions, and their competition for the radicals at different pH are discussed in relation to the experimental results. The level of carbonate/bicarbonate species that impair the effectiveness of the UVC/H$_2$O$_2$ treatment is determined and the remedy for treating greywater with high carbonate/bicarbonate level is demonstrated. The way that pH affects the photolysis of H$_2$O$_2$ and its dissociated form, O$_2$H$,^-$, is further discussed from the perspective of their respective molar absorption coefficients at 254 nm (Section 7.3.3). Finally, these theories and the experimental observations are summarised in Section 7.3.4.
Figure 7-8. COD of settled LR GW treated by UVC/H$_2$O$_2$ at initial pH of 3, 7 and 10, with (a) 7 mM H$_2$O$_2$ and (b) 10 mM H$_2$O$_2$. 
7.3.1 Change in pH during UVC/H\textsubscript{2}O\textsubscript{2} Treatment

The effect of pH on the UVC/H\textsubscript{2}O\textsubscript{2} process is complicated by the fact that, in most cases, the pH of the solution changes during the treatment. Using H\textsubscript{2}O\textsubscript{2} dosages of 7 and 10 mM as examples, the changes in pH are depicted in Figure 7-9, for which the initial pH of the settled LR GW was 3, 7 or 10.

![Figure 7-9. pH of settled LR GW during UVC/H\textsubscript{2}O\textsubscript{2} treatment at initial pH of 3, 7 and 10, with (a) 7 mM H\textsubscript{2}O\textsubscript{2} and (b) 10 mM H\textsubscript{2}O\textsubscript{2}.](image-url)
A similar trend was observed for both \( \text{H}_2\text{O}_2 \) concentrations. For initial pH 3, there was little, if any, change in pH during the irradiation. In contrast, a decrease in pH was observed for initial pH of 7 and 10, with greater extent of decrease observed in the latter. This was followed by a period of relatively stable pH before a slight increase towards the end of irradiation.

Although \( \text{H}_2\text{O}_2 \) is a weak acid (Section 2.6.3.3), it did not cause the pH reduction during the UVC/\( \text{H}_2\text{O}_2 \) treatment. Using the initial pH of 10 as an example, the addition of 7 mM \( \text{H}_2\text{O}_2 \) to the settled LR GW resulted only in a pH reduction of less than 0.1 units. The pH reduction during the treatment is usually associated with the oxidation of organic compounds to mineral acids, carbon dioxide and their acidic intermediates (Crittenden et al., 1999). For the initial pH of 7 and 10 (Figure 7-9), the gradual increase in pH towards the end of irradiation can be explained by the mineralisation of the acidic intermediates.

Despite the substantial difference between the initial pH of 7 and 10, the production of acidic intermediates resulted in fairly similar pH conditions during the irradiation. This may explain the small difference in COD reduction for greywater with initial pH of 7 and 10 (Figure 7-8). Except for the initial pH of 3, the other pH conditions resulted in a treated water of pH 6 – 8, which fulfilled the requirement of many standards or guidelines as listed in Table 2-3. Therefore, further pH adjustment of the effluent is not necessary, and the pH adjustment of large volumes of water, which may incur additional costs and may not be feasible, is avoided.

### 7.3.2 Bicarbonate/Carbonate Species and Chloride Anions

A commonly discussed phenomenon is the scavenging effect of the alkalinity on \( \cdot\text{OH} \) (Tuhkanen, 2004), and in particular, the pH dependence of AOPs is frequently associated with the presence of bicarbonate/carbonate species (Liao et al., 2001).

Consider the \( \text{CO}_2/(\text{H}_2\text{CO}_3)/\text{HCO}_3^-/\text{CO}_3^{2-} \) equilibria in Equation 7-6, and the composition of each component at various pH as illustrated in Figure 7-10 (Oppenländer, 2003):

\[
\text{CO}_2(\text{gas}) \rightleftharpoons \text{CO}_2(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{HCO}_3^- (\text{aq}) \rightleftharpoons \text{CO}_3^{2-} (\text{aq}) \quad \text{Equation 7-6}
\]

Figure 7-10 shows that \( \text{CO}_3^{2-} \) is the predominant species at pH greater than 12. At pH 10.3, \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) exist in approximately the same proportion. As pH decreases to about 8.2, \( \text{CO}_3^{2-} \) diminishes and \( \text{HCO}_3^- \) exists almost exclusively. The equilibrium shifts towards carbonic acid with further pH reduction, and at pH < 4.3, \( \text{CO}_2(\text{aq}) \) is the main component since only 0.1% of the dissolved \( \text{CO}_2 \) reacts with water to form \( \text{H}_2\text{CO}_3(\text{aq}) \) (Oppenländer, 2003).
The HCO$_3^-$/CO$_3^{2-}$ anions scavenge $^\cdot$OH effectively to form carbonate radical anion, CO$_3^{\cdot-}$, which has a lower oxidation potential and higher selectivity than $^\cdot$OH in its reactions with organic compounds (Legrini et al., 1993; Liao et al., 2001; Tuhkanen, 2004):

\[ ^\cdot \text{OH} + \text{HCO}_3^- \rightarrow \text{CO}_3^{\cdot-} + \text{H}_2\text{O} \quad \text{Equation 7-7} \]

\[ ^\cdot \text{OH} + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{\cdot-} + \text{OH}^- \quad \text{Equation 7-8} \]

Since the HCO$_3^-$/CO$_3^{2-}$ species are converted to carbonic acid in acidic conditions, which has a very low reactivity with $^\cdot$OH, the scavenging effect of these anions on $^\cdot$OH can be suppressed (Liao et al., 2001). As more than 95% of the species exist as CO$_2$(aq)/H$_2$CO$_3$ at pH 5 (Figure 7-10), this may explain why Yonar et al. (2006) observed significant deterioration in the effectiveness of the UVC/H$_2$O$_2$ process only when the pH was higher than 5.

In contrast, acidic conditions enhance the scavenging of $^\cdot$OH by chloride anions (Liao et al., 2001). Equation 7-9 shows the scavenging of $^\cdot$OH by Cl$^-$ to form HOCl$^\cdot$; its reverse reaction has a rate constant of similar magnitude. A subsequent protonation reaction of HOCl$^\cdot$ to form Cl$^\cdot$ and H$_2$O as described in Equation 7-10 has a significantly higher rate constant compared with its reverse reaction:

\[ ^\cdot \text{OH} + \text{Cl}^- \quad \text{k} = (4.3 \pm 0.4) \times 10^9 \text{ M}^{-1}\text{s}^{-1} \quad \rightarrow \quad \text{HOCl}^\cdot \quad \text{Equation 7-9} \]

\[ \text{HOCl}^\cdot + \text{H}^+ \quad \text{k} = (2.1 \pm 0.7) \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \quad \rightarrow \quad \text{Cl}^\cdot + \text{H}_2\text{O} \quad \text{Equation 7-10} \]
The pK value of the reverse reaction in Equation 7-10 was reported as 7.2, and Liao et al. (2001) argued that, in the presence of chloride, this is the critical value which affects the concentration of \( \cdot \text{OH} \). At pH > 7.2, the equilibrium in Equation 7-10 shifts towards the left and HOCl\(^*\) is the predominant species in the system. A higher concentration of HOCl\(^*\), in turn, reduces the scavenging of \( \cdot \text{OH} \) by Cl\(^-\) by favouring the reverse reaction in Equation 7-9. Therefore, high pH conditions increase the scavenging effect of HCO\(_3\)\(^-\)/CO\(_3\)\(_2\)^- for \( \cdot \text{OH} \) but reduce that of Cl\(^-\).

In their study on the scavenging of \( \cdot \text{OH} \) by Cl\(^-\) and HCO\(_3\)\(^-\)/CO\(_3\)\(_2\)^- species, Liao et al. (2001) used \( n \)-chlorobutane (BuCl) as a probe compound to indicate the concentration of \( \cdot \text{OH} \). The ratio of Cl\(^-\) and HCO\(_3\)\(^-\)/CO\(_3\)\(_2\)^- was expressed as \( [\text{Cl}^-]/c_T \), where \( c_T = [\text{NaHCO}_3] = [\text{H}_2\text{CO}_3\text{*}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \) is the sum of [CO\(_2\)(aq)] and [H\(_2\)CO\(_3\)]. The study was conducted at pH 2 – 9, and by fixing the \( c_T \) at 25 mM, the molarity of Cl\(^-\) was varied so that the \([\text{Cl}^-]/c_T\) ratio was 1, 10, and 100, respectively. The findings were presented in terms of \( c_{\cdot \text{OH}, j/i} \), which can be understood as the ratio of the pseudo first-order rate constant for the disappearance of BuCl (\( k_{\text{BuCl}} \)) as it reacts with \( \cdot \text{OH} \) at two experimental conditions \( j \) and \( i \) (Figure 7-11).

![Figure 7-11. Effect of pH on \( c_{\cdot \text{OH}, j/i} \) for \([\text{Cl}^-]/c_T = 1, 10, 100 \) (\( c_T = 25 \text{ mM}, [\text{BuCl}]_0 = 16 \mu \text{M} \)) (Liao et al., 2001).](image)

\( c_{\cdot \text{OH}, j/i} \) is defined as the ratio of steady-state \( \cdot \text{OH} \) concentrations at two experimental conditions \( j \) and \( i \), i.e., \( c_{\cdot \text{OH}, j/i} = [\cdot \text{OH}]_j/[\cdot \text{OH}]_i \). Since \( n \)-chlorobutane (BuCl) was used as the probe for \( \cdot \text{OH} \), \( c_{\cdot \text{OH}, j/i} \) can also be expressed as \( c_{\cdot \text{OH}, j/i} = (k_{\text{BuCl}})_j/(k_{\text{BuCl}})_i \).

A similar trend can be observed for each \([\text{Cl}^-]/c_T\) ratio: the \( c_{\cdot \text{OH}, j/i} \) value increased with increasing pH, a peak or plateau was then reached where the maximal \( c_{\cdot \text{OH}, j/i} \) was obtained before it decreased with further increase in pH. The peaks shifted from pH 4 to 5 as the ratio...
of [Cl]/cT increased from 1 to 10, and when [Cl]/cT = 100, the plateau was between pH 5 and 7 (Liao et al., 2001). This indicates that an increase in the [Cl]/cT ratio causes the maximum production of *OH to shift to higher pH. However, it should be noted that the values of c_{OH, j/i} at the peak or plateau were in descending order as the [Cl]/cT ratio increased: the c_{OH, j/i} value at [Cl]/cT = 1 was double that when [Cl]/cT = 10, and it was about ten times higher when compared with that of [Cl]/cT = 100. Furthermore, the c_{OH, j/i} value decreased as the molarity of Cl⁻ increased at a specific pH. Using pH 2 as an example, c_{OH, j/i} decreased from 1 to approximately 0.2, and subsequently 0.07 with increasing [Cl]/cT ratio. Respectively, this can be translated to 20% and 7% of the amount of *OH that is produced when [Cl]/cT = 1 as this ratio increased to 10 and 100.

Through their study, Liao et al. (2001) demonstrated that the scavenging effect of *OH by Cl⁻ can be counteracted to a certain extent by increasing the pH. They also concluded that *OH is much more sensitive to the change in pH than to [Cl⁻]. Importantly, their study highlighted the fact that these anions and their interactions with pH have to be considered carefully during the optimisation of AOPs.

In the UVC/H₂O₂ treatment of Acid Orange 7, Behnajady et al. (2004) found that the “rate of photo-destruction” of the anionic acidic dye was lower in acidic conditions. They suggested that the Cl⁻ ions from the addition of HCl used for pH adjustment reacted with *OH to produce inorganic radical ions which have lower reactivity than *OH, and did not contribute to the destruction of the dye.

The Carbonate/Bicarbonate Species and Chloride Anions in the Settled LR GW
The measurement of total alkalinity was described in Section 3.3.5. To achieve the end-point pH of 4.5, 13.55 mL of the standardised 0.02 N HCl was consumed and this corresponded to a total alkalinity, [Alk], of 133.2 mg.L⁻¹ CaCO₃.

Considering the equilibrium distribution of the CO₂/(H₂CO₃)/HCO₃⁻/CO₃²⁻ as shown in Equation 7-6, the equilibrium constants can be expressed as in Equations 7-11, 7-12, and 7-13. By rearranging these equations with the total alkalinity ([Alk]) and total concentration of carbonate (cT) as defined in Equations 7-14 and 7-15, Equation 7-16 can be derived to establish the relationship between cT and [Alk] (Stumm and Morgan, 1996):

\[
K_1 = \frac{[H^+][HCO_3^-]}{[CO_2(g)] + [H_2CO_3]} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}
\]  
Equation 7-11

\[
K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}
\]  
Equation 7-12

\[
K_w = [H^+][OH^-]
\]  
Equation 7-13
The equilibrium constants $K_1$, $K_2$, and $K_w$ are $4.47 \times 10^{-7}$, $4.68 \times 10^{-11}$, and $1 \times 10^{-14}$, respectively, at 25°C (Stumm and Morgan, 1996).

With $[\text{Alk}]=133.2 \text{ mg.L}^{-1} \text{ CaCO}_3$ and at the pH of 9.95, the $c_T$ of the settled LR GW was calculated as 96.0 mg.L$^{-1}$ CaCO$_3$ (1.0 mM) according to Equation 7-16. Using ion chromatography (Section 3.3.6), the chloride level of the LR GW was determined as 23.6 mg.L$^{-1}$ or 0.7 mM (Table 4-3), which was higher than that of some bathroom greywaters (0.25 – 0.5 mM) but within the range of laundry greywater (0.25 – 2.5 mM) found in the literature (Eriksson et al., 2002). Hence the $[\text{Cl}^-]/c_T$ ratio of LR GW was 0.7, lower than the ratio of 1 studied by Liao et al. (2001). This suggests that the concentration of chloride in the settled LR GW may not be sufficient to compete with the $\text{HCO}_3^-/\text{CO}_3^{2-}$ species for the scavenging of $^•\text{OH}$, and therefore, these phenomena as discussed by Liao et al. (2001) did not adequately explain the slightly enhanced performance of the UVC/H$_2$O$_2$ process at the initial pH of 10 (Figure 7-8). For samples with higher concentrations of Cl$^-$, its competition with $\text{HCO}_3^-/\text{CO}_3^{2-}$ for $^•\text{OH}$ may become prominent and operating at higher pH may prove to be beneficial for the UVC/H$_2$O$_2$ treatment.

**Addition of NaHCO$_3$ to the Settled LR GW**

According to the data compiled by Eriksson et al. (2002), the pH and alkalinity level of greywater from various sources are listed in Table 7-3. The $c_T$ of each greywater was then estimated according to Equation 7-16. Compared with those in the table, the $c_T$ of the settled LR GW (96 mg.L$^{-1}$ CaCO$_3$ or 1 mM) was higher than the shower and bathroom greywaters, lower than the greywater mixture, but fell within the range of the laundry greywater.

**Table 7-3. Alkalinity and pH of greywater from various sources (Eriksson et al., 2002) and the estimated total concentration of carbonate ($c_T$).**

<table>
<thead>
<tr>
<th>Type of Greywater</th>
<th>pH</th>
<th>Alkalinity</th>
<th>Total Concentration of Carbonate ($c_T$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bathroom</td>
<td>6.4 – 8.1</td>
<td>24 – 43</td>
<td>24 – 81</td>
</tr>
<tr>
<td>Shower</td>
<td>6.7 – 7.4</td>
<td>48 – 67</td>
<td>52 – 97</td>
</tr>
<tr>
<td>Laundry</td>
<td>9.3 – 10.0</td>
<td>83 – 200</td>
<td>55 – 183</td>
</tr>
<tr>
<td>Mixture</td>
<td>5.0 – 7.0</td>
<td>149 – 198</td>
<td>182 – 3508</td>
</tr>
</tbody>
</table>

* Estimated according to Equation 7-16.
In this section, various amounts of sodium bicarbonate (NaHCO$_3$, Ajax Univar) was added to the settled LR GW to determine the extent to which the UVC/10 mM H$_2$O$_2$ treatment may be impaired by the presence of CO$_3^{2-}$/HCO$_3^-$ species. The required amount of NaHCO$_3$ was added so that the initial c$_T$ of the greywater was increased to 3, 10, 20 and 100 mM respectively. Before being treated by UVC/10 mM H$_2$O$_2$, the pH of the solution was carefully adjusted to 10. Instead of using 1 M NaOH as described in Section 3.7, of which a large quantity was required due to the increased buffer capacity of the settled LR GW with the additional NaHCO$_3$, NaOH pellets was dissolved in a small volume of the greywater and subsequently used for pH adjustment.

Figure 7-12 shows that the COD reduction was similar for the initial c$_T$ of 1 and 3 mM; when the initial c$_T$ was increased to 10 mM, however, deterioration of the process performance became apparent. With 3 hours of irradiation, the overall COD removal decreased from 85% to 78% as the initial c$_T$ increased from 1 mM to 10 mM; further increase of the initial c$_T$ to 100 mM resulted in an overall COD removal of only 24% and 154 mg.L$^{-1}$ of COD remained in the effluent.

This demonstrates the resistance of the process to the presence of at least 3 mM of carbonate/bicarbonate species (300 mg.L$^{-1}$ CaCO$_3$), and the scavenging of *OH by the anions was prominent when the initial c$_T$ was 10 mM and above.

Using the initial c$_T$ of 100 mM as an example, the impact of pH on the UVC/H$_2$O$_2$ treatment of greywater containing high level of carbonate/bicarbonate species was evaluated. Once the required amount of NaHCO$_3$ was added to the settled LR GW, its pH was adjusted with concentrated H$_2$SO$_4$ or NaOH pellets to 3, 5, 7 or 10, respectively. The solution effervesced profusely during acidification due to the formation of CO$_2$, and was subjected to the UVC/10 mM H$_2$O$_2$ treatment only after the bubbling ceased.

The results in Figure 7-13 clearly indicate the performance of the UVC/H$_2$O$_2$ treatment was similar for pH 3 and 5 despite the presence of 100 mM carbonate/bicarbonate species in the sample initially. At pH 7, the decrease in the extent of COD removal was only noticeable after 2 hours of irradiation, whereas the effectiveness of the UVC/H$_2$O$_2$ treatment was severely impaired when operated at pH 10. These results are consistent with the findings of Yonar et al. (2006), and as shown in the CO$_2$/H$_2$CO$_3$/HCO$_3^-$/CO$_3^{2-}$ equilibria (Figure 7-10), acidification of the system to less than pH 5 converts the carbonate/bicarbonate species to carbonic acid which has a very low reactivity with *OH (Liao et al., 2001). Therefore, by operating at pH < 5, the problem of high concentrations of HCO$_3^-$/CO$_3^{2-}$ species can be alleviated and the greywater can be treated effectively by the UVC/H$_2$O$_2$ process.
Figure 7-12. COD of settled LR GW treated by UVC/10 mM H₂O₂ at the initial pH of 10 in the presence of various total concentration of carbonate.

Figure 7-13. COD of settled LR GW treated by UVC/10 mM H₂O₂ at various initial pH in the presence of 100 mM total concentration of carbonate.
7.3.3 pH-Dependence of the Photolysis of H$_2$O$_2$ and O$_2$H$^-$

In Section 7.3.2, the relatively minor role of pH in the treatment of settled LR GW by UVC/H$_2$O$_2$ was explained by:

- The formation of mineral acids, carbon dioxide and acidic organic intermediates which resulted in similar operating pH despite the difference in initial pH of 7 and 10,
- Low concentrations of carbonate/bicarbonate species and chloride, and hence the scavenging of $^*$OH was minimal regardless of the pH conditions; the process was resistant to the presence of at least 3 mM of carbonate/bicarbonate species (or equivalent to 300 mg.L$^{-1}$ CaCO$_3$).

However, the slightly enhanced COD reduction at the initial pH of 10 (Figure 7-8) remained unexplained. In this section, the pH-dependence of the UVC/H$_2$O$_2$ treatment is discussed from the perspective of the dissociation of H$_2$O$_2$ and its subsequent photolysis.

The photolysis of H$_2$O$_2$ by UV irradiation produces a complex mixture of transient radicals. These include the cleavage of the H$_2$O$_2$ molecule to 2 $^*$OH radicals (Equation 2-17), and the production of other radicals such as $^*$O$_2$H and O$_2$$^*$ which may also enhance the oxidising ability of the process (Tang, 2004). Importantly, the pH dependence of the photolysis of H$_2$O$_2$ has been reported and the rate of photolysis increases in more alkaline conditions (Legrini et al., 1993; Tang, 2004).

Considering the slight acidity of H$_2$O$_2$ in Equation 2-18, its dissociation constant ($K_a$) has been reported as $1.78 \times 10^{-12}$ at 20$^\circ$C (Ardon, 1964), and the relationship between pH and $pK_a$ can be expressed as:

$$\text{pH} = pK_a + \log \frac{[O_2H^-]}{[H_2O_2]}$$

Equation 7-17

With the $pK_a$ value of 11.75, it can be deduced from Equation 7-17 that more H$_2$O$_2$ dissociates to O$_2$H$^-$ at pH > $pK_a$. In addition, the generation of $^*$OH by the dismutation reaction (Equation 2-20) is also maximal when pH = $pK_a$ (Legrini et al., 1993; Tang, 2004).

The importance of the dissociation of H$_2$O$_2$ to O$_2$H$^-$ and its pH-dependence becomes more apparent when considering the significantly higher molar absorption coefficient ($\varepsilon_{254}$) of O$_2$H$^-$ (228 – 240 L.mol$^{-1}$.cm$^{-1}$) in comparison with that of H$_2$O$_2$ (17.9 – 19.6 L.mol$^{-1}$.cm$^{-1}$) (Legrini et al., 1993; Tang, 2004). To demonstrate how these affect the UVC/H$_2$O$_2$ process, the relationship between $\varepsilon_{254}$, the absorbance of a component in a mixture, and the fraction of spectral radiant power absorbed by the component is derived below.
The Beer-Lambert law quantifies the strength of absorption of UV/vis radiation (Oppenländer, 2003):

\[ A_{\lambda, n} = \log \frac{P_{\lambda, n}^0}{P_{\lambda, n}^{\text{trans}}} = \varepsilon_{\lambda, n} c l \]  

Equation 7-18

where \( A_{\lambda, n} \) is the decadic absorbance of a beam of collimated monochromatic radiation in a homogeneous isotropic medium (Verhoeven, 1996), \( P_{\lambda}^0 \) is the incident spectral radiant power (W), \( P_{\lambda}^{\text{trans}} \) is the transmitted spectral radiant power (W), \( \varepsilon_{\lambda, n} \) is the molar absorption coefficient of the substrate (L.mol\(^{-1}\).cm\(^{-1}\)), \( c \) is the concentration of the substrate (mol.L\(^{-1}\)), and \( l \) is the irradiation pathlength (cm).

For a multi-component system such as the mixture of LR GW, H\(_2\)O\(_2\) and O\(_2\)H\(_{-}\), the Beer-Lambert law (Equation 7-18) can be expanded to Equation 7-19 since absorbance is an additive property (Oppenländer, 2003). Equation 7-20 can be obtained by rearranging Equation 7-19:

\[ A_{\lambda, n} = \log \frac{P_{\lambda, n}^0}{P_{\lambda, n}^{\text{trans}}} = \log \frac{P_{\lambda, n}^0}{P_{\lambda, n}^{\text{abs}}} = \sum_{n=1}^{n=m} \frac{\varepsilon_{\lambda, n} c_n l}{P_{\lambda, n}^{\text{abs}}} \]  

Equation 7-19

\[ P_{\lambda, n}^{\text{abs}} = P_{\lambda}^0 \left(1 - 10^{-\frac{A_{\lambda, n} c_l}{c_n l}} \right) \]  

Equation 7-20

where \( A_{\lambda, n} \) is the absorbance of the multi-component mixture, \( P_{\lambda, n}^{\text{abs}} \) is the spectral radiant power absorbed by the mixture (W), \( \varepsilon_{\lambda, n} \) is the molar absorption coefficient of all radiation absorbing species \( n \) (L.mol\(^{-1}\).cm\(^{-1}\)), and \( c_n \) is the concentration of species \( n \) (mol.L\(^{-1}\)).

According to Pfoertner (1998), the absorbed spectral radiant power of a specific component \( i \), \( (P_{\lambda, i}^{\text{abs}}) \) is related to \( P_{\lambda, n}^{\text{abs}} \) by:

\[ \frac{P_{\lambda, i}^{\text{abs}}}{P_{\lambda, n}^{\text{abs}}} = \frac{\varepsilon_{\lambda, i} c_i l}{\sum_{n=1}^{n=m} \varepsilon_{\lambda, n} c_n l} \]  

Equation 7-21

Therefore, by substituting Equation 7-20 into Equation 7-21, Equation 7-22 can be obtained and it establishes the relationship between the fraction of the incident spectral radiant power absorbed by the component \( i \) (\( F_{\lambda, i} \)) and its molar absorption coefficient (\( \varepsilon_{\lambda, i} \)) (Pfoertner, 1998; Bolton, 1999):

\[ F_{\lambda, i} = \frac{P_{\lambda, i}^{\text{abs}}}{P_{\lambda}^0} = \frac{\varepsilon_{\lambda, i} c_i l (1 - 10^{-\frac{A_{\lambda, i} c_l}{c_i l}})}{\sum_{n=1}^{n=m} \varepsilon_{\lambda, n} c_n l} = \frac{A_{\lambda, i} c_i l (1 - 10^{-A_{\lambda, n} c_i l})}{A_{\lambda, n} c_i l} \]  

Equation 7-22
Effect of pH on the Photolysis of H$_2$O$_2$ in Settled LR GW

The effect of pH on the treatment of settled LR GW by the UVC/H$_2$O$_2$ process is examined by considering the dissociation of H$_2$O$_2$ to O$_2$H$^-$ at various pH and their respective absorption of the incident spectral radiant power.

Using the initial H$_2$O$_2$ concentration of 10 mM as an example, the amounts of H$_2$O$_2$ dissociated to O$_2$H$^-$ at different pH were calculated using Equation 7-17 and are tabulated in Table 7-4. The following observations can be made:

- Within pH 3 – 7, the dissociation of H$_2$O$_2$ is negligible,
- At pH 10, about 1.7% of the initial H$_2$O$_2$ presents as O$_2$H$^-$,
- When pH = pK$_a$ = 11.75, H$_2$O$_2$ and O$_2$H$^-$ exist in the same proportion, and
- Almost complete dissociation of H$_2$O$_2$ to O$_2$H$^-$ occurs at pH 14.

As shown in Table 7-4, the absorbance ($A_\lambda$) of H$_2$O$_2$ and O$_2$H$^-$ in the settled LR GW were calculated according to the Beer-Lambert Law (Equation 7-18). The molar absorption coefficients at 254 nm ($\varepsilon_{254}$) of H$_2$O$_2$ and O$_2$H$^-$ were taken as 19.6 and 240 L.mol$^{-1}$.cm$^{-1}$, respectively (Legrini et al., 1993; Tang, 2004). The $A_{254}$ of the settled LR GW was measured as 0.48 by Unicam UV/vis Spectrophotometer (UV2-100), using cuvettes of 1 cm pathlength. The quartz sleeve of the photo-reactor has an internal diameter of 4.4 cm, and the average pathlength ($l$) of radiation in the quartz sleeve in the photo-reactor was 3.46 cm. Therefore, the equivalent $A_{254}$ of the greywater in the quartz sleeve of the photo-reactor was 1.66 with $l = 3.46$ cm (Equation 7-18). The fraction of incident spectral radiant power absorbed by the individual components ($F_{\lambda,i}$) was then calculated using Equation 7-22.

In acidic conditions, the dissociation of H$_2$O$_2$ to O$_2$H$^-$ was negligible. As the initial pH increased from 7 to 10, the H$_2$O$_2$ concentration decreased from 10 mM to 9.83 mM and the $F_{\lambda,i}$ absorbed by H$_2$O$_2$ reduced from 28.9% to 26.9%. Despite only 1.7% of H$_2$O$_2$ being dissociated to O$_2$H$^-$ at pH 10, the $F_{\lambda,i}$ of O$_2$H$^-$ increased from 0% to 5.9%. In total, 32.8% of the incident spectral radiant power was absorbed by H$_2$O$_2$ and O$_2$H$^-$ at pH 10 and this corresponded to a net increment of 3.9% compared with that absorbed by H$_2$O$_2$ alone at pH 7. Correspondingly, the $F_{\lambda,i}$ absorbed by the settled LR GW reduced from 70.7% to 66.9%.

Despite only a small amount of O$_2$H$^-$ being produced, this increase in the combined $F_{\lambda,i}$ absorbed by H$_2$O$_2$ and O$_2$H$^-$ can be explained by the significantly higher $\varepsilon_{254}$ of O$_2$H$^-$, which is about 12 times higher than that of H$_2$O$_2$. Since both H$_2$O$_2$ and O$_2$H$^-$ absorb UVC irradiation to produce *OH according to Equation 2-19, this implies that more *OH can be produced when H$_2$O$_2$ dissociates to O$_2$H$^-$ at higher pH such as pH 10.
Table 7-4. Effect of pH on the dissociation of H$_2$O$_2$ and the fraction of spectral radiant power absorbed by H$_2$O$_2$ and O$_2$H$^-$ in settled LR GW treated by UVC/10 mM H$_2$O$_2$.

<table>
<thead>
<tr>
<th>pH</th>
<th>Dissociation of H$_2$O$_2$ (1)</th>
<th>A$_{254}$ $l = 3.46$ cm (2)</th>
<th>Fraction of Incident Spectral Radiant Power Absorbed, $F_{\lambda,i}$ (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[H$_2$O$_2$] (mM)</td>
<td>[O$_2$H$^-$] (mM)</td>
<td>H$_2$O$_2$</td>
</tr>
<tr>
<td>3</td>
<td>10.00</td>
<td>$1.78 \times 10^{-8}$</td>
<td>0.68</td>
</tr>
<tr>
<td>5</td>
<td>10.00</td>
<td>$1.78 \times 10^{-6}$</td>
<td>0.68</td>
</tr>
<tr>
<td>7</td>
<td>10.00</td>
<td>$1.78 \times 10^{-4}$</td>
<td>0.68</td>
</tr>
<tr>
<td>10</td>
<td>9.83</td>
<td>0.17</td>
<td>0.67</td>
</tr>
<tr>
<td>11</td>
<td>8.49</td>
<td>1.51</td>
<td>0.58</td>
</tr>
<tr>
<td>11.75</td>
<td>5.00</td>
<td>5.00</td>
<td>0.34</td>
</tr>
<tr>
<td>14</td>
<td>0.06</td>
<td>9.94</td>
<td>0.00</td>
</tr>
</tbody>
</table>

(1) Calculated according to Equation 7-17, with initial H$_2$O$_2$ concentration of 10 mM.
(2) The quartz sleeve in the photo-reactor had an internal diameter of 4.4 cm. Average pathlength was 3.46 cm.
(3) Calculated according to Equation 7-18 by taking $\varepsilon_{254}$ of H$_2$O$_2$ as 19.6 L.mol$^{-1}$.cm$^{-1}$ (Oppenländer, 2003).
(4) Calculated according to Equation 7-18, by taking $\varepsilon_{254}$ of O$_2$H$^-$ as 240 L.mol$^{-1}$.cm$^{-1}$ (Legrini et al., 1993).
(5) The A$_{254}$ of LR GW was 0.48, which was determined experimentally using Unicam UV/vis Spectrophotometer (UV2-100) with 1 cm quartz cuvette. For pathlength of 3.46 cm, the corresponding A$_{254}$ can be calculated according to Equation 7-18, i.e., for constant $\varepsilon_c$, $A_1/A_2 = l_1/l_2$.
(6) Calculated according to Equation 7-22.

As discussed in Section 7.2.2, the COD of the settled LR GW remained relatively constant under UVC irradiation in the absence of H$_2$O$_2$ (Figure 7-3(a)). As this was accompanied by a reduction in its absorbance between 190 and 240 nm (Figure 7-6(a) in Section 7.2.3), it can be deduced that the organic compounds in the greywater underwent some changes in the chemical structures but were not mineralised by direct photolysis, i.e., any absorption of the incident spectral radiant power by the components of the greywater did not result in COD reduction. Hence, the dissociation of H$_2$O$_2$ to O$_2$H$^-$ at high pH and the significantly higher $\varepsilon_{254}$ of O$_2$H$^-$ allow this fraction of the incident spectral radiant power to be utilised by O$_2$H$^-$ to produce more $^\bullet$OH, and this may explain the slight improvement in COD removal when the settled LR GW was treated by UVC/H$_2$O$_2$ at the initial pH of 10 (Figure 7-8).

However, it should be noted that this advantage may only be applicable at the beginning of the UVC/H$_2$O$_2$ treatment. Due to the production of acidic oxidation products as described in Section 7.3.1, the pH of the solution became close to neutral during the irradiation (Figure 7-9). As a result, the benefits from the formation of O$_2$H$^-$ at high initial pH diminished as the treatment proceeded.
Another observation from Table 7-4 was that the effect of initial pH on the combined $F_{\lambda,i}$ absorbed by $\text{H}_2\text{O}_2$ and $\text{O}_2\text{H}^-$ appeared to be much greater for pH above 10. By increasing the pH to 11, the combined $F_{\lambda,i}$ absorbed by $\text{H}_2\text{O}_2$ and $\text{O}_2\text{H}^-$ was dramatically increased from 32.8% to 52.4%. This suggests that more COD in the settled LR GW could be removed by operating the UVC/$\text{H}_2\text{O}_2$ treatment at pH > 10, and while maintaining the same pH level during the treatment.

These prompted further investigations of the treatment of settled LR GW by UVC/10 mM $\text{H}_2\text{O}_2$ by operating at pH > 10 and by maintaining the solution pH at 10 during irradiation. The experiments in Figure 7-8(b) were repeated, and in addition, initial pH of 11, 11.75 and 12 were used. The results in Figure 7-14 show that the performance of the process decreased when the initial pH was increased from 10 to 11, and the deterioration was even more pronounced when the initial pH was 11.75 and above. At 3 hours irradiation, the overall COD removal decreased from 85% to 73.5% as the initial pH increased from 10 to 11, and it decreased further to 39.4% and 36.9% at pH 11.75 and 12, respectively.

Examining the concentration of excess $\text{H}_2\text{O}_2$ in the treated sample (Table 7-5) revealed that less excess $\text{H}_2\text{O}_2$ remained in the treated water at higher initial pH: For the initial pH of 7, 10 and 11, there was 10 mg.L$^{-1}$ of excess $\text{H}_2\text{O}_2$ after 3 hours irradiation, whereas less than 1 mg.L$^{-1}$ $\text{H}_2\text{O}_2$ remained for the initial pH of 11.75 and above. This is attributed to the decomposition of $\text{H}_2\text{O}_2$ to $\text{O}_2$ and water, and the rate increases with increasing pH ($\text{H}_2\text{O}_2$.com, 2007).

Possibly for the same reason, maintaining the pH at 10 also resulted in poorer COD removal by the UVC/10 mM $\text{H}_2\text{O}_2$ treatment (Figure 7-15). After 3 hours irradiation, the COD removal reduced from 85% to 72% when the pH was maintained at 10, and only 5 mg.L$^{-1}$ $\text{H}_2\text{O}_2$ remained in the sample, which was half the amount of that without maintaining the pH.

In conclusion, due to the dissociation of $\text{H}_2\text{O}_2$ to $\text{O}_2\text{H}^-$ and the significantly higher $\varepsilon_{254}$ of $\text{O}_2\text{H}^-$, the treatment of the settled LR GW by UVC/$\text{H}_2\text{O}_2$ at the initial pH of 10 resulted in a slight improvement in COD removal compared with its neutral or acidic counterparts. While this benefit diminished during the treatment due to the production of mineral acids, carbon dioxide and acidic intermediates, it has been demonstrated that operating at the initial pH of higher than 10 or maintaining the pH at 10 were disadvantageous due to the rapid decomposition of $\text{H}_2\text{O}_2$ to $\text{O}_2$ and water.
Figure 7-14. COD of settled LR GW treated by UVC/10 mM H$_2$O$_2$ at initial pH of 3, 7, 10, 11, 11.75 and 12.

Table 7-5. Concentration of excess H$_2$O$_2$ in settled LR GW treated by UVC/10 mM H$_2$O$_2$ process at different initial pH.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Concentration of Excess H$_2$O$_2$* (mg.L$^{-1}$) at Irradiation Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>N. A.</td>
</tr>
<tr>
<td>7</td>
<td>N. A.</td>
</tr>
<tr>
<td>10</td>
<td>N. A.</td>
</tr>
<tr>
<td>11</td>
<td>N. A.</td>
</tr>
<tr>
<td>11.75</td>
<td>&gt; 25</td>
</tr>
<tr>
<td>12</td>
<td>&gt; 25</td>
</tr>
</tbody>
</table>

* All indicated values of excess H$_2$O$_2$ in the sample were measured by Merckoquant® peroxide test strips. N. A.: Not Applicable
Figure 7-15. COD of settled LR GW treated by UVC/10 mM H₂O₂ at an initial pH of 10 and maintaining at pH 10 during the treatment.
Summary of Effect of pH: Theories versus Experimental Results

In Section 7.2, the settled LR GW was subjected to UVC/H$_2$O$_2$ treatment at the initial pH of 3, 7 and 10. In contrast to the literature, acidic pH conditions did not improve the effectiveness of the UVC/H$_2$O$_2$ treatment. Although similar levels of COD removal were achieved, pH 10 appeared to enhance the COD removal slightly.

Despite the difference in the initial pH of 7 and 10, the formation of mineral acids, carbon dioxide and acidic intermediates reduced the solution pH to nearly neutral and hence resulted in similar operating conditions during the UVC/H$_2$O$_2$ treatment (Section 7.3.1). In Sections 7.3.2 and 7.3.3, the effects of pH on the treatment were discussed from the perspective of CO$_3^{2-}$/HCO$_3^-$ and Cl$^-$ concentrations, and the dissociation of H$_2$O$_2$ to O$_2$H$^-$. At high pH:

- Scavenging of $^\cdot$OH by CO$_3^{2-}$/HCO$_3^-$ species is increased,
- Scavenging of $^\cdot$OH by Cl$^-$ is reduced, and
- H$_2$O$_2$ dissociates to O$_2$H$^-$, leading to increased $^\cdot$OH production due to the significantly higher molar absorption coefficient ($\varepsilon_{254}$) of O$_2$H$^-$ compared with that of H$_2$O$_2$.

The HCO$_3^-$/CO$_3^{2-}$ and Cl$^-$ anions in the settled LR GW were 1 mM and 0.7 mM, respectively. This gave a [Cl$^-$/cT ratio of 0.7, which was lower than the ratio of 1 studied by Liao et al. (2001), suggesting weak competition between the anions for the scavenging of $^\cdot$OH. Therefore, the reduced scavenging of the radicals by Cl$^-$ at high pH was not sufficient to compensate those reacted with HCO$_3^-$/CO$_3^{2-}$, and these phenomena did not adequately explain the slightly enhanced performance of the UVC/H$_2$O$_2$ process at the initial pH of 10.

The cT of the settled LR GW was higher than for some shower and bathroom greywaters reported in the literature, similar to those from laundries but lower than some greywater mixtures. With the addition of NaHCO$_3$ to the settled LR GW, it was demonstrated that the UVC/H$_2$O$_2$ treatment was resistant to the presence of at least 3 mM of cT (or 300 mg.L$^{-1}$ CaCO$_3$). For the initial cT $\geq$ 10 mM, however, operating between pH 3 and 5 was essential to convert the CO$_3^{2-}$/HCO$_3^-$ anions to carbonic acid which has a very low reactivity with $^\cdot$OH.

The slightly enhanced COD removal at the initial pH of 10 was attributed to the dissociation of H$_2$O$_2$ to O$_2$H$^-$ at high pH and the significantly higher $\varepsilon_{254}$ of O$_2$H$^-$, which resulted in the production of more $^\cdot$OH from the photolysis of both H$_2$O$_2$ and O$_2$H$^-$. However, this benefit of operating at high pH was lost during the course of the UVC/H$_2$O$_2$ treatment since the pH reduced considerably due to the production of acidic compounds. Maintaining the pH at 10 or operating at an initial pH of higher than 10, however, resulted in poorer COD removal due to the higher decomposition rate of H$_2$O$_2$ to O$_2$ and water in these conditions.
7.4 BOD$_5$, Total Suspended Solids, Turbidity, pH and *Escherichia coli* Level of LR GW

As described in Sections 7.2 and 7.3, the optimal condition for the treatment of the settled LR GW was 10 mM H$_2$O$_2$ at initial pH of 10 and 3 hours of UVC irradiation. Overnight settlement and the UVC/10 mM H$_2$O$_2$ process successfully removed 87% of COD in the LR GW, leaving a residual COD of 30 mg L$^{-1}$. The BOD$_5$ level, total suspended solids, turbidity and pH of the treated water were measured according to the methods described in Section 3.3 or the Standard Methods for the Examination of Water and Wastewater (APHA, 1998), and the outcomes compared with the requirement of Class A and Class B reclaimed water as specified by the EPAV (2003) (Table 7-6).

<table>
<thead>
<tr>
<th>Requirement for Reclaimed Water</th>
<th>Quality of Water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Class A</strong></td>
<td><strong>Class B</strong></td>
</tr>
<tr>
<td>BOD$_5$ (mg L$^{-1}$)</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Total Suspended Solids (mg L$^{-1}$)</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>pH</td>
<td>6 – 9</td>
</tr>
<tr>
<td><em>Escherichia coli</em> (orgs/100 mL)</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

The BOD$_5$ of the treated water fell between the requirement for Class A and Class B reclaimed water. Although its content of total suspended solids and turbidity level exceeded the specification for Class A reclaimed water, the former parameter was adequate for the Class B category, which is suitable for agricultural and industrial uses without direct contact with humans (Table 2-2). Since the main function of UVC/H$_2$O$_2$ treatment is to oxidise the organic pollutants in the greywater, it was not expected to reduce the total suspended solids and turbidity of the LR GW, and the small reductions in these parameters were attributed to settling the greywater overnight. Therefore, additional treatment such as filtration may be necessary should higher quality reclaimed water be required.

As discussed in Section 7.3.1, the formation of mineral acids, carbon dioxide and acidic intermediates during the UVC/H$_2$O$_2$ treatment reduced the pH of the greywater to nearly neutral, which also falls within the requirement of all classes of reclaimed water. Therefore, additional pH neutralisation of the treated water is not required.
As shown in Table 2-2, all classes of reclaimed water have the same requirement for the levels of BOD₅, total suspended solids and pH except for Class A. The main difference between Classes B, C and D is the content of *Escherichia coli*. While Class A reclaimed water should contain less than 10 orgs/100 mL of *E. coli*, Class B, C and D require less than 100, 1000 and 10,000 orgs/100 mL of *E. coli*, respectively.

Using the Colilert® method (Indexx Laboratories), the *E. coli* levels in the greywater were measured by Ecowise Environmental. Both the raw and settled LR GW had less than 10 orgs/100 mL of *E. coli* (Table 7-6), which is very low compared with some reported values in the literature of up to $2.82 \times 10^6$ per 100 mL. Nevertheless, less than 1 org/100 mL of *E. coli* was detected after 1 hour of exposure to the UVC irradiation, which corresponded to a UV dose of 18,000 mJ.cm⁻². Although the initial *E. coli* level in LR GW was very low, this UV dose was expected to inactivate the microorganisms of higher loadings since it was very much higher than that used by Gilboa and Friedler (2008). The researchers examined the disinfection of greywater treated by rotary biological contactor (RBC) followed by sedimentation. The greywater was collected from showers, baths and wash-basins of 14 flats and it contained $1.6 \times 10^7$ cfu.mL⁻¹ heterotrophic plate count (HPC), $3.8 \times 10^4$ cfu/100 mL faecal coliforms, $9.9 \times 10^3$ cfu/100 mL *Staphylococcus aureus*, $3.3 \times 10^3$ cfu/100 mL *Pseudomonas aeruginosa* and 4.6 cfu/100 mL *Clostridium perfringens*. They found that a UV dose of up to 439 mJ.cm⁻² eliminated all but HPC in the water, and faecal coliforms were the most resistant at lower UV dose such as 69 mJ.cm⁻². Due to their ability to self-aggregate, faecal coliforms survived low doses of radiation despite the low concentration of suspended solids in the water.

In conclusion, the treatment of LR GW by overnight settlement and 3 hours of UVC/10 mM H₂O₂ resulted in an effluent that fulfilled the requirement of Class B reclaimed water as specified by EPAV. To meet a more stringent requirement, further treatment of the effluent is required to reduce its BOD₅ level, total suspended solids and turbidity.
7.5 Change in Biodegradability (BOD₅:COD) of Settled LR GW during UVC/H₂O₂ Treatment

The settled LR GW had a BOD₅ and COD of 42 mg.L⁻¹ and 191 mg.L⁻¹, respectively (Table 7-7). This indicated that the biodegradability, measured as BOD₅:COD, of the greywater was 0.22 and similar to that reported by Jefferson et al. (2000). These authors discussed the low biodegradability of greywater in comparison with municipal wastewater which usually has a BOD₅:COD of 0.4 – 0.8 (Marco et al., 1997; Ledakowicz, 1998; Al-Momani et al., 2002).

As discussed in Section 2.6.3.4, AOPs are frequently integrated with biological treatments, either as a pre-treatment to remove toxic or inhibitory compounds and to improve the biodegradability of the contaminants in the water, or as a subsequent polishing step to lower the costs involved in the AOPs. Suggestions for such integration can be found in the work of Thomson (2002), Li et al. (2003), Buchanan et al. (2004), and Genç et al. (2005).

In this section, the BOD₅ and COD of the settled LR GW were measured during the UVC/10 mM H₂O₂ treatment (Table 7-7). As shown in the table, the biodegradability of the settled LR GW increased as the treatment proceeded; after 2 hours of treatment, the BOD₅:COD increased from 0.22 to 0.41, which is comparable with that of municipal wastewater. Extending the treatment to 5 hours improved the BOD₅:COD to 0.58. This shows that the UVC/H₂O₂ treatment can be used to improve the biodegradability of greywater. It should also be noted that, after 2 hours of treatment, the BOD₅ of the effluent was 20 mg.L⁻¹, which fulfilled the requirement of Class B reclaimed water (Section 7.4). Therefore, subsequent biological treatment, in conjunction with treatment such as filtration to remove suspended solids, may further reduce the BOD₅ of this water to meet the more stringent requirement of Class A reclaimed water.

Table 7-7. BOD₅, COD and biodegradability (BOD₅:COD) of settled LR GW treated by UVC/10 mM H₂O₂ at the initial pH of 10.

<table>
<thead>
<tr>
<th>Irradiation Time (h)</th>
<th>BOD₅ (mg.L⁻¹)</th>
<th>COD (mg.L⁻¹)</th>
<th>BOD₅:COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>42</td>
<td>191</td>
<td>0.22</td>
</tr>
<tr>
<td>1</td>
<td>32</td>
<td>112</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>49</td>
<td>0.41</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>30</td>
<td>0.48</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>23</td>
<td>0.58</td>
</tr>
</tbody>
</table>
7.6 Effect of Initial COD Level and Greywater Type

Using LR GW, the effects of overnight settlement as a pre-treatment, H₂O₂ dosage and pH on the UVC/H₂O₂ process were investigated in Sections 7.1 to 7.3. In this section, these findings are applied to other greywaters collected from the researcher’s home, i.e., MR GW, HR GW, LGW, TGW and SGW (Section 4.2). The compositions and characteristics of these greywaters are listed in Table 4-2 and Table 4-3, respectively. These greywaters are of different initial COD level and type, and their influences on the sequential overnight settlement and UVC/H₂O₂ treatment are discussed below.

7.6.1 Overnight Settlement

The greywaters prepared as per Section 4.2.2 were well mixed before settling overnight, and Table 7-8 shows the reduction in their COD level, pH and turbidity. For comparison, the data for LR GW was included.

<table>
<thead>
<tr>
<th>Type of Greywater</th>
<th>COD (mg.L⁻¹)</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial Value</td>
<td>Reduction (%)</td>
<td>Initial Value</td>
</tr>
<tr>
<td>HR GW</td>
<td>349</td>
<td>4.6%</td>
<td>10.3</td>
</tr>
<tr>
<td>MR GW</td>
<td>267</td>
<td>3.0%</td>
<td>10.1</td>
</tr>
<tr>
<td>LR GW</td>
<td>225</td>
<td>13.1%</td>
<td>10.0</td>
</tr>
<tr>
<td>LGW</td>
<td>342</td>
<td>6.5%</td>
<td>10.3</td>
</tr>
<tr>
<td>TGW</td>
<td>265</td>
<td>1.0%</td>
<td>6.7</td>
</tr>
<tr>
<td>SGW</td>
<td>105</td>
<td>23.1%</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Overnight settlement resulted in 1% to 23% COD removal in these greywaters, and their pH decreased by up to 0.7 units; the reduction in turbidity varied from 2% to 41%. SGW had the lowest levels of total solids, total dissolved solids and total suspended solids (Table 4-3) and only 2% of the turbidity was removed after settling overnight. For TGW, there was only 1% COD reduction although up to 52.3% of the turbidity was removed by settling, thus the particulate content of the toothpaste did not incur COD. These particulate materials are most likely the polishing agent or abrasive used in the toothpaste. In this case, these materials are dicalcium phosphate dihydrate and silica according to “Oral Care – Facts about Toothpaste” from Colgate® (2006b).
7.6.2 Alkalinity, Total Concentration of Carbonate (c_T) and Chloride Concentration of Greywaters Collected from the Researcher’s Home

The alkalinity of the greywaters was measured as per Section 3.3.5 and their respective total concentration of carbonate estimated using Equation 7-16 (Table 7-9). In comparison with the c_T of some greywaters in the literature (Table 7-3), settled LGW and SGW fell within the range of the laundry and shower greywater, respectively; c_T for the settled TGW was higher than for the bathroom greywater, and the settled HR GW was in the lower range of the greywater mixture.

Table 7-9. Alkalinity and pH of the settled greywaters collected from the researcher’s home and the estimated total concentration of carbonate (c_T).

<table>
<thead>
<tr>
<th>Type of Greywater</th>
<th>pH</th>
<th>Alkalinity</th>
<th>Total Concentration of Carbonate (c_T)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mg.L⁻¹CaCO₃</td>
<td>mM</td>
</tr>
<tr>
<td>Settled HR GW</td>
<td>9.73</td>
<td>229.5</td>
<td>2.3</td>
</tr>
<tr>
<td>Settled MR GW</td>
<td>9.80</td>
<td>168.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Settled LR GW</td>
<td>9.95</td>
<td>133.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Settled LGW</td>
<td>9.92</td>
<td>211.3</td>
<td>2.1</td>
</tr>
<tr>
<td>Settled TGW</td>
<td>6.80</td>
<td>117.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Settled SGW</td>
<td>7.23</td>
<td>70.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>

*Estimated according to Equation 7-16.

Using the concentrations of Cl⁻ shown in Table 4-3, the [Cl⁻]/c_T ratios of these greywaters were found to be within the range of 0.3 – 0.7, indicating that when treated by UVC/H₂O₂ the pH of these greywaters should not affect the competition between the Cl⁻ and CO₃²⁻/HCO₃⁻ species for the scavenging of \( \cdot OH \) (Section 7.3.2).

In Section 7.3.2, the initial pH of the settled LR GW (pH 3 – 10) was found to have minimal effect on the performance of the UVC/H₂O₂ treatment, which was resistant to the presence of at least 300 mg.L⁻¹ of CO₃²⁻/HCO₃⁻ species, i.e., c_T = 3 mM. In addition, maintaining the pH at 10 or operating at higher pH did not improve the COD removal due to higher decomposition rate of H₂O₂ to O₂ and water (Section 7.3.3).

The settled TGW and SGW had a pH of about 7, whereas the other greywaters had a pH close to 10. As shown in Table 7-9, all these settled greywaters had c_T of less than 3 mM, inferring that the scavenging of \( \cdot OH \) by CO₃²⁻/HCO₃⁻ should not be significant. Hence, acidification of these greywaters was not necessary and they were treated by UVC/H₂O₂ at their collected pH after settling overnight. The results are shown in Section 7.6.3.
7.6.3 UVC/H₂O₂ Treatment of Greywaters Collected from the Researcher’s Home

The optimal H₂O₂ dosage for the treatment of settled LR GW by UVC/H₂O₂ was determined as 10 mM (Section 7.2.2). With 195 mg.L⁻¹ COD in the settled LR GW, the optimal \( \text{H}_2\text{O}_2: \text{COD} \) ratio was 0.05 mM \( \text{H}_2\text{O}_2 \) per mg.L⁻¹ COD (or 1.7 g \( \text{H}_2\text{O}_2 \) per g COD).

In this section, the greywaters collected from the researcher’s home were settled overnight before subsequent UVC/H₂O₂ treatment using this \( \text{H}_2\text{O}_2: \text{COD} \) dosing ratio. The COD of the settled HR GW and LGW were similar, i.e., 344 mg.L⁻¹ and 350 mg.L⁻¹, respectively. Hence 18 mM \( \text{H}_2\text{O}_2 \) was added to these greywaters. For the settled MR GW and TGW of about 260 mg.L⁻¹ COD, the \( \text{H}_2\text{O}_2 \) dosage was 13.3 mM. The settled SGW had a COD of 87 mg.L⁻¹ and 4.5 mM \( \text{H}_2\text{O}_2 \) was used. As discussed in Section 7.6.2, these greywaters had total concentration of carbonate \( (c_T) \) of less than 3 mM, indicating a potentially minor scavenging effect of the \( \text{CO}_3^{2-}/\text{HCO}_3^- \) species irrespective of the pH condition. Therefore, they were treated at their collected pH after overnight settlement and the results are in Figure 7-16.

![Figure 7-16](image-url)

Figure 7-16. UVC/H₂O₂ treatment of the greywaters collected from the researcher’s home, using \( \text{H}_2\text{O}_2 \) dosages at 0.05 mM \( \text{H}_2\text{O}_2 \) per mg.L⁻¹ COD: (a) Settled LR GW, MR GW and HR GW, and (b) Settled LGW, TGW and SGW.
Since LR GW, MR GW and HR GW were only different in the amount of tap water added for dilution, Figure 7-16(a) shows that, by dosing according to the optimal H$_2$O$_2$:COD ratio, the UVC/H$_2$O$_2$ treatment adequately treated the greywaters of different COD levels. For the treatment of settled MR GW, similar COD removal was achieved within the same irradiation time as for settled LR GW; both achieved about 85% COD removal after 3 hours irradiation, with residual COD of 39 mg.L$^{-1}$ and 30 mg.L$^{-1}$, respectively. For the settled HR GW, 5 hours of treatment was required to reduce the COD to 46 mg.L$^{-1}$ (86.8% COD removal). At this point, only 2 mg.L$^{-1}$ H$_2$O$_2$ (0.06 mM) remained in the effluent, therefore, extending irradiation time was not expected to improve the COD reduction.

HR GW and LGW had similar levels of COD although their compositions were rather different. As per Table 4-2, HR GW consisted of 37.5% of the first discharge from washing machine, 41.7% from shower, and the rest was TGW and tap water. In contrast, LGW was prepared by mixing the first discharge from washing machine with tap water in equal proportions. Despite this difference, the UVC/H$_2$O$_2$ treatment achieved similar COD removal for the settled HR GW and LGW (Figure 7-16 (a) and (b)). Likewise, although MR GW consisted of only 6.3% of TGW, the trends of COD removal were similar for these cases. The settled SGW had the lowest COD amongst all the greywaters. With only 1 hour of UVC/4.5 mM H$_2$O$_2$ treatment, the COD reduced from 87 mg.L$^{-1}$ to 23 mg.L$^{-1}$, and increasing irradiation time to 2 hours resulted in a small improvement to give a residual COD of 13 mg.L$^{-1}$. These results are summarised in Table 7-10.

Thus, it can be concluded that the initial COD level, rather than the greywater type, appears to be the major determinant for the removal of COD by the UVC/H$_2$O$_2$ process, and this can be attributed to the non-selective oxidising property of *OH (Oppenländer, 2003). By dosing H$_2$O$_2$ according to the determined optimal ratio of 0.05 mM H$_2$O$_2$ per mg.L$^{-1}$ COD, the UVC/H$_2$O$_2$ process was shown to be capable of treating all the greywater types tested.

### Table 7-10. COD reduction of settled greywaters after UVC/H$_2$O$_2$ treatment.

<table>
<thead>
<tr>
<th>Type of Greywater</th>
<th>Irradiation Time (h)</th>
<th>Residual COD (mg.L$^{-1}$)</th>
<th>COD Removal (%)</th>
<th>Overall COD Removal (%)$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR GW</td>
<td>5</td>
<td>46</td>
<td>86.8%</td>
<td>87.4%</td>
</tr>
<tr>
<td>MR GW</td>
<td>3</td>
<td>39</td>
<td>85.0%</td>
<td>86.1%</td>
</tr>
<tr>
<td>LR GW</td>
<td>3</td>
<td>30</td>
<td>84.7%</td>
<td>86.1%</td>
</tr>
<tr>
<td>LGW</td>
<td>5</td>
<td>54</td>
<td>84.6%</td>
<td>85.9%</td>
</tr>
<tr>
<td>TGW</td>
<td>3</td>
<td>33</td>
<td>87.3%</td>
<td>89.8%</td>
</tr>
<tr>
<td>SGW</td>
<td>1</td>
<td>23</td>
<td>74.2%</td>
<td>79.7%</td>
</tr>
</tbody>
</table>

* COD removal by overnight settlement was taken into account
7.7 Summary of Findings for the UVC/H₂O₂ Process

The conditions investigated for the UVC/H₂O₂ process include overnight settlement as a pre-treatment, H₂O₂ dosage, pH and, initial COD level and greywater type.

LR GW was the main type of greywater used for the investigation. Possibly due to the low turbidity and suspended solids of LR GW, settling overnight did not enhance the UVC/H₂O₂ process significantly. While the settlement removed 13% COD, an overall reduction of 87% was achieved when it was combined with UVC/10 mM H₂O₂/pH 10 treatment (residual COD = 30 mg.L⁻¹). Higher H₂O₂ dosage only slightly improved the COD removal probably due to the scavenging of *OH by the excess H₂O₂. For the settled LR GW, the optimal H₂O₂ dosage was determined as 10 mM and the optimal H₂O₂:COD ratio was 0.05 mM per mg.L⁻¹ COD (or 1.7 g H₂O₂ per g COD). The COD removal followed a second-order kinetic equation, \( r = 0.0637 \text{[COD]} \times \text{[H₂O₂]} \), up to 10 mM H₂O₂.

In the absence of H₂O₂, UVC irradiation alone removed only a small amount of COD in the settled LR GW. As evidenced by a reduction in absorbance in the range of 190 – 240 nm, the contaminants underwent changes in chemical structure but were not mineralised by direct photolysis. The addition of 10 mM H₂O₂ led to substantial COD removal and therefore attack by *OH was most likely the main mechanism responsible for the mineralisation of the contaminants. Absorbance and fluorescence results showed the formation of intermediates which were subsequently destroyed towards the end of treatment.

In contrast to the literature, which frequently recommends that AOPs be operated in acidic conditions, the initial pH of the settled LR GW was found to have only a minor effect on the UVC/H₂O₂ treatment. The effect of pH on the UVC/H₂O₂ process was discussed in terms of the change in pH during treatment, competition between HCO₃⁻/CO₃²⁻ and Cl⁻ for the scavenging of *OH, and the dissociation of H₂O₂ to O₂H⁻:

- Due to the low concentration of HCO₃⁻/CO₃²⁻ in the settled LR GW (1 mM), operating at pH 3 was not essential to suppress the reactivity of these anions with *OH.
- Despite the difference in the initial pH of 7 and 10, the formation of mineral acids, carbon dioxide and acidic intermediates resulted in similar pH conditions of close to neutral during the oxidation.
- The concentration of Cl⁻ in the settled LR GW was low (0.7 mM), and with the [Cl⁻]/c₉ ratio at the low value of 0.7, the reduced scavenging of *OH by Cl⁻ at high pH was not sufficient to compensate the increased reaction between HCO₃⁻/CO₃²⁻ and *OH; hence this did not explain the slightly enhanced COD removal at the initial pH of 10.
- The enhanced COD removal at the initial pH of 10 is attributed to the dissociation of H₂O₂.
to \(O_2\H^+ \) at high pH and the significantly higher \(\varepsilon_{254}\) of \(O_2\H^+\). According to calculation, only 1.7% of \(H_2O_2\) dissociates to \(O_2\H^+\) at pH 10 but there is a net increment of 3.9% in the incident photon flow absorbed by \(H_2O_2\) and \(O_2\H^+\) compared with that at pH 3 and 7, which leads to higher production of \(^{\circ}\OH\) and thus enhanced the COD removal.

It was found that the UVC/\(H_2O_2\) process was resistant to at least 3 mM of \(c_T\) and its performance decreased when the initial \(c_T\) was greater than 10 mM; for the initial \(c_T\) of 100 mM, operating at pH 3 – 5 was essential to convert \(HCO_3^-/CO_3^{2-}\) to carbonic acid which has a low reactivity with \(^{\circ}\OH\). As the UVC/\(H_2O_2\) treatment proceeded, the formation of acidic oxidation products decreased the solution pH from 10 to 6.6 – 7.8 thereby diminishing the benefits of the formation of \(O_2\H^+\) at high initial pH. Although dissociation of \(H_2O_2\) to \(O_2\H^+\) at high pH increased the production of \(^{\circ}\OH\) in theory, maintaining the pH at 10 or operating at higher initial pH resulted in poorer process performance, this was attributed to the accelerated decomposition of \(H_2O_2\) to \(O_2\) and water.

Despite 87% COD of the LR GW being removed by overnight settlement and 3 hours of the subsequent UVC/10 mM \(H_2O_2\) treatment, the \(BOD_5\), total suspended solids content and turbidity of the effluent were higher than the requirement of Class A reclaimed water as specified by the EPAV (2003). However, the effluent fell within Class B category. Additional treatment such as filtration may be required to fulfil more stringent requirements. The \(E.\ coli\) level in the raw and settled LR GW was low (10 orgs/100 mL) and it was reduced to less than 1 org/100 mL after 1 hour of UVC/\(H_2O_2\) treatment, in spite of the high turbidity in the water. This was expected as this UV dose of 18,000 \(mJ.cm^{-2}\) was very much higher than that needed for disinfection, e.g., as Gilboa and Friedler (2008) used for UV disinfection of greywater (UV dose up to 439 \(mJ.cm^{-2}\)).

The UVC/10 mM \(H_2O_2\) treatment increased the biodegradability of the settled LR GW from 0.22 to 0.41 within 2 hours, after which only 20 mg.L\(^{-1}\) of \(BOD_5\) remained, and so the treated water complied with the requirement of Class B reclaimed water. This illustrated the potential of utilising the UVC/\(H_2O_2\) process as a pre-treatment to biological systems when dealing with greywater of low biodegradability.

As \(^{\circ}\OH\) is a non-selective oxidant (Oppenländer, 2003), the UVC/\(H_2O_2\) process was found to be sensitive to the initial COD level in the greywater, but not the greywater type. By dosing \(H_2O_2\) according to the determined optimal ratio of 0.05 mM \(H_2O_2\) per mg.L\(^{-1}\) COD, the UVC/\(H_2O_2\) process was shown to be capable of treating greywater of different concentrations and constituents.
Chapter 8. Process Comparison

Chapter 5 presented the results of treating LR GW with alum or ferrous sulphate coagulation, with subsequent treatment by UVC/H₂O₂. The investigation of the Fenton and photo-Fenton processes was conducted in Chapter 6 and the focus was on the optimisation of the Fe²⁺:H₂O₂ and H₂O₂:COD ratios. In Chapter 7, the greywater was settled overnight to simulate the effect of storage and the effects of H₂O₂ dosage, pH, initial COD levels and types of greywater were examined for the subsequent UVC/H₂O₂ process.

In this chapter, these processes are compared using parameters such as the COD removal, type of treatment, sludge formation, complexity in operation, pH condition, visual aesthetics of the effluent, and energy requirement (Table 8-1).

Table 8-1. Comparison of different processes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al³⁺</th>
<th>Al³⁺ + UVC/H₂O₂</th>
<th>Fe²⁺</th>
<th>Fe²⁺ + UVC/H₂O₂</th>
<th>Fenton</th>
<th>Photo-Fenton</th>
<th>Settle + UVC/H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD Removal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moderate (73%)</td>
<td>High</td>
<td>Low (49%)</td>
<td>High (91%)</td>
<td>Low (45%)</td>
<td>High (83%)</td>
<td>High (87%)</td>
<td></td>
</tr>
<tr>
<td>Type of Treatment</td>
<td>Physical separation and chemical oxidation</td>
<td>Physical separation and chemical oxidation</td>
<td>Physical separation and chemical oxidation</td>
<td>Physical separation and chemical oxidation</td>
<td>Physical separation and chemical oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sludge Formation</td>
<td>Significant</td>
<td>Significant</td>
<td>Significant</td>
<td>Significant</td>
<td>Significant</td>
<td>Significant</td>
<td>Little</td>
</tr>
<tr>
<td>Complexity in Operation</td>
<td>Low</td>
<td>Moderate</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>pH Condition</td>
<td>Acidic</td>
<td>Acidic</td>
<td>Acidic</td>
<td>Acidic</td>
<td>Acidic → neutral</td>
<td>Acidic → neutral</td>
<td>Any</td>
</tr>
<tr>
<td>Visual Aesthetics of Effluent</td>
<td>Clear</td>
<td>Clear</td>
<td>Yellowish</td>
<td>Yellowish</td>
<td>Yellowish</td>
<td>Yellowish</td>
<td>Slightly turbid</td>
</tr>
<tr>
<td>Energy Requirement</td>
<td>Low</td>
<td>Medium</td>
<td>Low</td>
<td>Medium</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
</tbody>
</table>

Al³⁺: Alum coagulation (2 mM Al³⁺/pH 5)
Al³⁺ + UVC/H₂O₂: Combined alum coagulation (2 mM Al³⁺/pH 5) and UVC/H₂O₂ treatment (1.5 hours/2 mM H₂O₂/pH 5)
Fe²⁺: Iron coagulation (1 mM Fe²⁺/pH 3)
Fe²⁺ + UVC/H₂O₂: Combined iron coagulation (1 mM Fe²⁺/pH 3) and UVC/H₂O₂ treatment (1 hour/7 mM H₂O₂/pH 3)
Fenton: Fenton process (1 mM Fe²⁺/5 mM H₂O₂; Oxidation stage: 0.5 hour at pH 3, Coagulation stage at pH 7)
Photo-Fenton: Photo-Fenton Process (UVC/1 mM Fe²⁺/10 mM H₂O₂; Oxidation stage: 1.5 hours at pH 3, Coagulation stage at pH 7)
Settle + UVC/H₂O₂: Overnight Settlement and subsequent UVC/H₂O₂ (3 hours/10 mM H₂O₂ at pH 10)
The COD removal of the optimised processes is summarised in Table 8-1. Al\textsuperscript{3+} and Fe\textsuperscript{2+} coagulation removed 73% and 49% COD of the LR GW, respectively, whereas the Fenton process removed only 45% COD. All the other processes achieved satisfactory COD removal, the highest being the sequential Al\textsuperscript{3+} coagulation and UVC/H\textsubscript{2}O\textsubscript{2} (98%), followed by the sequential Fe\textsuperscript{2+} coagulation and UVC/H\textsubscript{2}O\textsubscript{2} (91%), overnight settlement and UVC/H\textsubscript{2}O\textsubscript{2} (87%), and the photo-Fenton process (83%).

Of these processes, the alum and iron coagulation were physical separation techniques, i.e., the COD reduction in the effluent was achieved by floc formation which settled out from the solution to form sludge which requires disposal. The other processes which involved the use of Fenton reagents also generated a large amount of chemical sludge as they exploited the coagulative properties of the reagents. Conversely, the sequential overnight settlement and UVC/H\textsubscript{2}O\textsubscript{2} treatment had the advantage of low sludge production, in which only lint, hair and larger particles were settled out from the greywater during overnight settlement (13% COD removal) and most of the COD removal was via mineralisation of the organic compounds during the oxidation process.

Other than the issue of sludge disposal, the presence of xenobiotic organic compounds (XOCs) in greywater, which may include PPCPs, EDCs and surfactants, are major concerns due to the lack of information about their toxicity, biodegradability and bioaccumulation properties and their ever expanding list (Ledakowicz, 1998; Eriksson et al., 2003; Palmquist and Hanæus, 2004; Ying et al., 2004). Depending on their chemical characteristics, these XOCs may be physically separated by coagulation and concentrated in the sludge. Therefore, the UVC/H\textsubscript{2}O\textsubscript{2} process is appealing for the treatment of greywater due to its ability to destroy organic compounds in greywater by oxidation without the generation of sludge.

From an operational point of view, the coagulation process using alum or ferrous sulphate was simple, it involved the dosage of coagulant, pH adjustment, and settlement. The overnight settlement and UVC/H\textsubscript{2}O\textsubscript{2} treatment was also relatively straightforward and capable of treating different types of greywater: pH adjustment was not required when the concentration of carbonate/bicarbonate species was low and the effectiveness of the process can be controlled by dosing H\textsubscript{2}O\textsubscript{2} according to the initial COD level. The sequential coagulation and UVC/H\textsubscript{2}O\textsubscript{2} treatments required more effort as both processes had to be optimised to achieve high COD removal. The use of Fenton reagents was complicated by the optimisation of multiple parameters such as pH, Fe\textsuperscript{2+}:H\textsubscript{2}O\textsubscript{2} ratio, H\textsubscript{2}O\textsubscript{2}:COD ratio, and the reaction/irradiation time during the oxidation stage. In addition, the variability in the quality and different types of greywater present a major challenge to the Fenton and photo-Fenton processes as incorrect operating procedure may result in poor process performance. Hence,
careful design considerations in terms of storage facility and the selection or exclusion of appropriate types of greywater are particularly important for the Fenton or photo-Fenton processes, and the homogeneity of the greywater may be improved for recycling projects at larger scale where larger groups of users are involved and higher volumes of greywater are produced.

Furthermore, most of the processes need to be operated in acidic conditions (pH 3 – 5). This requires additional equipment and chemicals for pH adjustment, appropriate choice of material for the equipment and piping design, and the careful consideration of the feasibility of acidifying a large volume of water (and its subsequent neutralisation). In contrast, UVC/H$_2$O$_2$ was capable of treating the settled LR GW at a wide range of pH from 3 to 10. With low concentrations of HCO$_3$-/CO$_3^{2-}$ and Cl$^-$, the initial pH condition of the greywater had a relatively minor effect on the UVC/H$_2$O$_2$ process and its effectiveness for COD removal. For greywaters that have a significant laundry input and thus are usually of high pH, the generation of mineral acids, carbon dioxide and acidic intermediates during the UVC/H$_2$O$_2$ process reduces the pH of the greywater to close to neutral without the addition of acid, and the pH of the treated water falls within the requirement of pH 6 – 9 of many guidelines or standards as listed in Tables 2-2 and 2-3.

The use of Fe$^{2+}$ in many of the processes created issues regarding the visual aesthetics of the treated water. This water was slightly yellowish in colour and it may stain the toilet bowl or urinal if it were used for toilet flushing. For the overnight settlement and UVC/H$_2$O$_2$ treatment, the treated water was slightly turbid. While it fulfilled the requirement for Class B reclaimed water as specified by EPAV, further treatment such as filtration may be needed to remove suspended solids so that treated water of higher quality can be obtained.

For all the processes achieving higher than 83% COD removal, the main energy consumption was for the operation of UV lamps. The sequential Fe$^{2+}$ coagulation and UVC/H$_2$O$_2$ process required 1 hour of irradiation to achieve 91% COD removal (UV dose = 18,000 mJ.cm$^{-2}$); 1.5 hours of irradiation (UV dose = 27,000 mJ.cm$^{-2}$) was needed for the sequential Al$^{3+}$ coagulation and UVC/H$_2$O$_2$ process and the photo-Fenton process to achieve 98% and 83% of COD removal, respectively. Despite having the advantages of simplicity in operation, flexibility in the operating pH condition, and low sludge production, the overnight settlement followed by UVC/H$_2$O$_2$ treatment required the longest irradiation time of 3 hours to achieve 87% of COD reduction, i.e., equivalent to a UV dose of 54,000 mJ.cm$^{-2}$. Figures-of-merit such as electrical energy per mass ($E_{EM}$) or per order of removal ($E_{EO}$) are frequently used to measure the process effectiveness, with their proposed applications for high and organic concentrations, respectively (Bolton et al., 2001):
Greywater Treatment by Fenton, Photo-Fenton and UVC/H₂O₂ Processes

W. H. Chin

\[
E_{EM} = \frac{P \times t \times 10^6}{V(C_i - C_f)} \quad \text{Equation 8-1}
\]

\[
E_{EO} = \frac{P \times t \times 10^3}{V \times \log \frac{C_i}{C_f}} \quad \text{Equation 8-2}
\]

where \( P \) is the lamp power (kW),
\( t \) is the time (h),
\( V \) is the volume of sample irradiated (L), and
\( C_i \) and \( C_f \) are the initial and final concentrations of pollutant (mg.L\(^{-1}\)), respectively.

Using these definitions and with 500 mL of greywater irradiated by two 15 W UVC lamps in the photo-reactor (Chapter 3), the \( E_{EM} \) and \( E_{EO} \) for the process were calculated and summarised in Table 8-2.

<table>
<thead>
<tr>
<th>Process</th>
<th>Irradiation Time (h)</th>
<th>Initial COD Level (mg.L(^{-1}))</th>
<th>Final COD Level (mg.L(^{-1}))</th>
<th>( E_{EM} ) (kWh.kg(^{-1}))</th>
<th>( E_{EO} ) (kWh.m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{2+}) Coagulation + UVC/H₂O₂</td>
<td>1</td>
<td>234</td>
<td>21</td>
<td>282</td>
<td>57</td>
</tr>
<tr>
<td>Al(^{3+}) Coagulation + UVC/H₂O₂</td>
<td>1.5</td>
<td>231</td>
<td>5</td>
<td>398</td>
<td>54</td>
</tr>
<tr>
<td>Photo-Fenton</td>
<td>1.5</td>
<td>222</td>
<td>38</td>
<td>489</td>
<td>117</td>
</tr>
<tr>
<td>Overnight settlement + UVC/H₂O₂</td>
<td>3</td>
<td>235</td>
<td>30</td>
<td>878</td>
<td>201</td>
</tr>
</tbody>
</table>

These figures are much higher than those reported in the literature, for example, \( E_{EM} \) of 10 kWh.kg\(^{-1}\) (Yonar et al., 2006) and \( E_{EO} \) of 4 kWh.m\(^{-3}\) (Crittenden et al., 1999). Although the high energy demand of these processes must be acknowledged, their potential in the application of greywater has been demonstrated particularly in the case of the UVC/H₂O₂ process. Improvement in the energy efficiency may be achieved by optimisation of the reactor design which includes the investigation of different types of lamp and photo-reactor with different configurations (annular reactors with coaxial or perpendicular lamp positions, external lamp with reflectors, contact-free photo-reactor etc.). Other radiation sources such as solar radiation may prove to be an attractive alternative, while the use of renewable energy such as solar power may be advantageous to reduce the carbon-footprint of this process. As demonstrated, the process is capable of increasing the biodegradability of greywater. Therefore, it could be used to partially oxidise the contaminants before a subsequent biological treatment.
Chapter 9. Greywaters Collected from External Sources

As discussed in Chapters 5 – 7, greywaters collected from the researcher’s home were subjected to sequential alum or ferrous sulphate coagulation and UVC/H₂O₂ treatment, Fenton and photo-Fenton processes, and the overnight settlement and UVC/H₂O₂ process. In this chapter, the experience and findings gained from previous experiments are applied to greywater collected from external sources, which include the Youth Hostel Association (YHA) in Katoomba (New South Wales, Australia) and the homes of two members of the Alternative Technology Association (ATA) in Brunswick and Heidelberg (Victoria, Australia). For convenience, these greywaters are referred to hereafter as YHA, ATA-B and ATA-H greywaters, respectively. The descriptions of the sites and the characteristics of these greywaters are in Section 4.3.

The YHA is a service provider for commercial lodging; hence limited requests could be made for the monitoring of their greywater production. Although the personnel from Clearwater Technology and Ecowise Environmental collected the greywater sample early in the morning to avoid the peak hours for showers, there may not be significant input from the laundry since it was uncertain if the washing machine was used prior to the collection of greywater. Hence, the greywater collected from YHA probably contained mainly shower greywater. As shown in Table 4-4, the YHA greywater had the lowest COD content amongst all the greywaters collected from external sources but its levels of conductivity and total dissolved solids were the highest, suggesting high level of salts in the greywater. Also, it contained large brownish particles which settled readily.

In contrast, the ATA-B and ATA-H greywaters appeared highly turbid and the particles were whitish in colour. Compared with the greywaters collected from the researcher’s home (Table 4-3), these greywaters had significantly higher levels of BODs, COD, turbidity and suspended solids. As the ATA members are conscientious about their water consumption, the use of appliances such as front-loader washing machines and water efficient showerheads may have resulted in a lower production of greywater with more concentrated levels of contaminants.

In Section 9.1, the application of sequential alum or ferrous sulphate coagulation and UVC/H₂O₂ treatment to the YHA, ATA-B and ATA-H greywaters is discussed. Section 9.2 details their treatment by the Fenton and photo-Fenton processes, and the results from overnight settlement and UVC/H₂O₂ treatment are presented in Section 9.3. The findings from these experiments are summarised in Section 9.4.
9.1 Sequential Coagulation and UVC/H₂O₂ Treatment

The YHA greywater had the lowest COD (140 mg.L⁻¹) compared with the ATA-B and ATA-H greywaters which had COD levels of 530 mg.L⁻¹ and 590 mg.L⁻¹, respectively.

The experimental procedures for the coagulation and subsequent UVC/H₂O₂ treatment were detailed in Section 3.5. These greywaters were treated by alum (2 mM Al³⁺) and ferrous sulphate (1 mM Fe²⁺) at pH 3 – 10. Figure 9-1 shows the colour of the floc, if any, that was formed. Notably, the alum flocs were white while ferrous sulphate produced yellow/orange coloured flocs in various shades. When Fe²⁺ was used, no floc formation was observed for pH 3 – 6 for the ATA-B greywater and pH 5 – 6 for the ATA-H greywater. In contrast, alum coagulation produced flocs for all three of the greywaters at all the pH conditions studied, but the settleability varied.

Regardless of pH, alum and ferrous sulphate coagulation reduced the COD of the YHA sample to 29 – 37 mg.L⁻¹ and 33 – 40 mg.L⁻¹, respectively (Figure 9-2). The residual COD in the supernatants was considered low and so they were not subjected to further UVC/H₂O₂ treatment.

Addition of alum to the ATA-B greywater resulted in floc formation for pH 3 – 10. However at pH 3, significant amount of the flocs remained suspended even after 1 hour of settling. In
In this case, the optimal pH was taken as 7 as the flocs formed at pH 6 and 7 settled most readily to produce supernatant of 57 – 59 mg.L\(^{-1}\) COD, corresponding to about 89% COD removal (Figure 9-2(a)). For Fe\(^{2+}\), no coagulation took place in the acidic conditions; at pH 7, the residual COD level was 48 mg.L\(^{-1}\), with up to 91% of COD removed (Figure 9-2(b)).

The supernatant of ATA-B greywater was then treated by the UVC/H\(_2\)O\(_2\) process without further pH adjustment. A concentration of 3 mM H\(_2\)O\(_2\) was chosen as suitable for the COD level in these samples, based on the data in Figure 5-2. Figure 9-3 shows that the UVC/H\(_2\)O\(_2\) treatment gave similar results for both supernatants and 16 – 21 mg.L\(^{-1}\) COD remained in the effluent after 2 hours of irradiation. The sequential alum coagulation and UVC/H\(_2\)O\(_2\) treatment and its counterpart using ferrous sulphate coagulation achieved an overall COD removal of 97% and 96%, respectively.

For the ATA-H greywater, alum coagulation at pH 6 produced the lowest COD level of 75 mg.L\(^{-1}\) (87% COD removal). Slightly higher residual COD of 82 mg.L\(^{-1}\) (86% COD removal) was obtained when coagulation with ferrous sulphate took place at pH 7; no floc formation was observed at pH 5 and 6 (Figure 9-2). In the presence of 5 mM H\(_2\)O\(_2\) and 2 hours of irradiation, the UVC/H\(_2\)O\(_2\) process further reduced the COD level to 15 mg.L\(^{-1}\) when pre-treated with alum, or 27 mg.L\(^{-1}\) when ferrous sulphate was used. These resulted in overall COD reductions of 97% and 95%, respectively (Figure 9-3).
The dosages of coagulants and H$_2$O$_2$ used in this section were based on those used in the previous experiments on LR GW (Chapter 5) and they were adequate when applied to these greywaters of different concentrations, types and sources. Most COD (66% – 91%) in all greywaters was removed by coagulation. Depending on the required quality of the effluent, coagulation alone may be sufficient for the YHA sample which had the lowest initial COD content. For the ATA-B and ATA-H greywaters, the use of UVC/H$_2$O$_2$ as a subsequent treatment to coagulation produced effluents of good quality, with a minimal COD removal of 95%.

The pH for coagulation needs to be optimised for each greywater. While the optimal pH for the alum and ferrous sulphate coagulation of LR GW was 5 and 3 respectively, pH 6 and 7 appeared to be suitable for the YHA, ATA-B and ATA-H greywaters and so avoided the issue of acidifying a large volume of water.
9.2 Fenton and Photo-Fenton Processes

Section 3.6 described the experimental procedures for the Fenton and photo-Fenton processes and they were applied to the YHA, ATA-B and ATA-H greywaters using a fixed Fe$^{2+}$ concentration of 1 mM. H$_2$O$_2$ was added according to the theoretical stoichiometric H$_2$O$_2$:COD ratio of 2.12 g H$_2$O$_2$/g COD as reported by Bautista et al. (2007), i.e., 8.7 mM, 33 mM and 36.8 mM for the YHA, ATA-B and ATA-H greywater, respectively. The oxidation stage was operated at pH 3, before subsequent neutralisation to pH 7 for the coagulation to take place.

Treatment of YHA greywater (COD = 140 mg.L$^{-1}$) by the Fenton and photo-Fenton processes produced effluents of similar qualities (Figure 9-4). Slightly yellowish water was collected from the oxidation stage, with some particles which settled readily. However, these particles were not flocs but the suspended solids in the raw YHA greywater. When the pH of the solution was neutralised, orange coloured flocs were formed which also settled easily.

Figure 9-4. COD of YHA, ATA-B and ATA-H greywaters treated by (a) Fenton process and (b) photo-Fenton process.
With just 10 minutes of reaction time during the oxidation stage of the Fenton process, 31 mg.L\(^{-1}\) of COD remained in the treated water from YHA (Figure 9-4). By extending the reaction time to 1 hour, the residual COD was reduced further to 18 mg.L\(^{-1}\). In contrast, the photo-Fenton process produced an effluent of 22 mg.L\(^{-1}\) COD with 10 minutes of UVC irradiation. Increasing the irradiation time to 1 hour, however, only marginally decreased the COD level by 4 mg.L\(^{-1}\). In this case, the Fenton process achieved 87% COD removal and the photo-Fenton process did not greatly improve the extent of COD removal, contrary to that observed in Chapter 6. While the CODs of the effluents from the Fenton and photo-Fenton processes were approximately half those produced from the alum and ferrous sulphate coagulation (Section 9.1), the former processes also incur additional costs due to the requirement for pH adjustment, the use of H\(_2\)O\(_2\) and/or UVC irradiation.

The collected ATA-B greywater was highly turbid (222 NTU) and had a COD level of 514 mg.L\(^{-1}\). During the oxidation stage of the Fenton and photo-Fenton processes, the acidified sample turned slightly yellow and flocs started to form upon the addition of H\(_2\)O\(_2\) (33 mM). Over time (with or without irradiation), the flocs became orange and instead of settling, scum was formed on the surface of the water while the solution became clearer. As shown in Figure 9-5, this was observed for both of the Fenton and photo-Fenton processes. Subsequent pH neutralisation led to the formation of orange-coloured flocs which settled readily.

![Figure 9-5. Changes in the appearance of ATA-B greywater after the oxidation stage of (a) Fenton process, and (b) photo-Fenton process.](image_url)
For COD removal in ATA-B greywater, the photo-Fenton process was more effective than the Fenton process (Figure 9-4). For the Fenton process, the COD level in the treated water reduced from 45 to 28 mg.L\(^{-1}\) when the reaction time during the oxidation stage was extended from 10 minutes to one hour; with UVC irradiation, the residual COD was halved from 28 mg.L\(^{-1}\) to 14 mg.L\(^{-1}\). The Fenton and photo-Fenton processes removed 95% and 97% of COD in the raw ATA-B greywater, respectively, similar to that of the sequential coagulation and UVC/H\(_2\)O\(_2\) treatment as discussed in Section 9.1. However, 33 mM H\(_2\)O\(_2\) was added for the Fenton and photo-Fenton processes, which was 11 times higher than that used for the sequential coagulation and UVC/H\(_2\)O\(_2\) treatment, regardless of whether Al\(^{3+}\) or Fe\(^{2+}\) was used in the coagulation. Nevertheless, the UVC/H\(_2\)O\(_2\) process needed twice the irradiation time required by the photo-Fenton process.

Similar to the ATA-B greywater (Figure 9-5), the acidified ATA-H greywater with added ferrous sulphate turned yellow and scum was formed upon the addition of H\(_2\)O\(_2\). Subsequent pH neutralisation also produced orange-coloured flocs which settled easily. The raw ATA-H greywater had an initial COD level of 579 mg.L\(^{-1}\). After one hour treatment during the oxidation stage, 98% COD was removed by the photo-Fenton process (residual COD = 14 mg.L\(^{-1}\)), higher than 91% that was obtained by the Fenton process (residual COD = 52 mg.L\(^{-1}\)) (Figure 9-4). Compared with the sequential coagulation by alum or ferrous sulphate and UVC/H\(_2\)O\(_2\) treatment (Section 9.1), a similar level of COD removal was achieved but the Fenton and photo-Fenton processes consumed a much higher amount of H\(_2\)O\(_2\): 36.8 mM H\(_2\)O\(_2\) compared with 5 mM used in the sequential coagulation and UVC/H\(_2\)O\(_2\) treatment. However, the Fenton and photo-Fenton processes took only half of the reaction/irradiation time compared with the UVC/H\(_2\)O\(_2\) treatment.

The Fenton and photo-Fenton processes led to good COD reductions for the YHA, ATA-B and ATA-H greywaters. Higher COD removal was obtained with the photo-Fenton process when the initial COD level of the greywater was high, such as for ATA-B and ATA-H greywaters. The Fenton and photo-Fenton processes gave similar COD removals as the sequential coagulation (Al\(^{3+}\) or Fe\(^{2+}\)) and UVC/H\(_2\)O\(_2\) treatment, but significantly higher H\(_2\)O\(_2\) dosage was required. However, they required a shorter reaction/irradiation time.

The formation of scum during the Fenton or photo-Fenton process (Figure 9-5) was not encountered in the experiments using greywaters collected from the researcher’s home. In contrast to the formation of flocs that settled readily during the oxidation stage for the LGW, LR GW, MR GW and HR GW, scum was formed for both of the ATA-B and ATA-H greywaters.
Despite having COD levels of much higher than all greywaters collected from the researcher’s home, the conductivity of the ATA-B and ATA-H greywaters was close to those of TGW and SGW, suggesting a low level of salts in the cleaning products used by the ATA members. Although both processes achieved a high level of COD removal, the formation of scum prompted the necessity of using a separation device to produce effluent that is aesthetically acceptable. In addition, it was necessary to clean of the quartz sleeve in the photo-reactor between each batch of treatment to prevent the build up of scum that may reduce the penetration of UV radiation.

Considering the variation in the quality of greywater in a single household and the differences in its response to the Fenton and photo-Fenton treatment, the application of these processes in greywater treatment may prove to be difficult. Selecting or excluding a particular source of greywater and the use of a storage tank may reduce such variation, and careful process design to manage the scum may be required. Also, the application of these processes in recycling project of larger scale may improve the homogeneity of greywater influent since larger groups of users are involved and higher volumes of greywater are collected.
9.3 Overnight Settlement and UVC/H$_2$O$_2$ Treatment

The treatment of LR GW by overnight settlement and subsequent UVC/H$_2$O$_2$ showed that 10 mM was the optimal H$_2$O$_2$ dosage when the COD of the settled LR GW was 187 – 208 mg.L$^{-1}$ (Figure 7-3). This corresponded to a H$_2$O$_2$ dosage of approximately 0.05 mM H$_2$O$_2$ per mg.L$^{-1}$ COD. Consequently, the settled YHA, ATA-B and ATA-H greywaters were subjected to the UVC/H$_2$O$_2$ treatment using this dosing ratio (Figure 9-6(a)). For comparison, H$_2$O$_2$ dosage of 10 mM was also used for the settled ATA-B and ATA-H greywaters (Figure 9-6(b)).

The total concentrations of carbonate for the YHA, ATA-B and ATA-H greywaters were 1.95 mM, 0.62 mM and 1.43 mM, respectively. As discussed in Section 7.3.2, the UVC/H$_2$O$_2$ process was found to be tolerant to the presence of at least 3 mM of CO$_3^{2-}$/HCO$_3^-$ and therefore these greywaters were settled overnight and subsequently treated by UVC/H$_2$O$_2$ without pH adjustment.

![Figure 9-6. COD of settled YHA, ATA-B and ATA-H greywaters treated by UVC/H$_2$O$_2$ with (a) H$_2$O$_2$ dosages at 0.05 mM H$_2$O$_2$ per mg.L$^{-1}$ COD, and (b) 10 mM H$_2$O$_2$.](image-url)
The initial COD level in YHA greywater was 116 mg L\(^{-1}\), of which 62% was readily removed by settling overnight (residual COD = 44 mg L\(^{-1}\)). The settled greywater of pH 7.8 was subjected to UVC/2 mM H\(_2\)O\(_2\) treatment and after 1.5 hours of irradiation, the effluent had a COD as low as 14 mg L\(^{-1}\) (Figure 9-6(a)). Since BOD\(_5\) of a sample is always less than its COD value, the BOD\(_5\) of this effluent was not measured but it is expected to fall within the minimal requirement of 20 mg L\(^{-1}\) for reclaimed water as specified by EPAV (Table 2-2).

For the raw ATA-B greywater (COD = 530 mg L\(^{-1}\)), 20 – 23% of the COD was removed by overnight settlement and the settled greywater (pH 6.9) had a COD level of 426 mg L\(^{-1}\). Even with 5 hours of irradiation, the UVC/23 mM H\(_2\)O\(_2\) treatment removed only 66% of the COD in the settled greywater to produce effluent with residual COD of 144 mg L\(^{-1}\) (Figure 9-6(a)). Although the overall COD reduction was 73%, the quality of the effluent was not satisfactory as it contained 63 mg L\(^{-1}\) BOD (Table 9-1), significantly higher than the required 20 mg L\(^{-1}\) for Class B reclaimed water (Table 2-2). Using lower H\(_2\)O\(_2\) dosage (10 mM), the residual COD level was 196 mg L\(^{-1}\) after 5 hours of irradiation (Figure 9-6(b)).

Similarly for the ATA-H greywater (COD = 590 mg L\(^{-1}\)), the settled greywater had a COD of 477 – 482 mg L\(^{-1}\) or equivalent to 18 – 19% COD removal by the overnight settlement. Subsequently, the settled water (pH 7.4) was treated by UVC/25 mM H\(_2\)O\(_2\), which reduced the COD level to 176 mg L\(^{-1}\) after 5 hours irradiation (Figure 9-6(a)). The overall COD removal was about 70% and the BOD level of the effluent was 107 mg L\(^{-1}\) (Table 9-1). The settled greywater was also treated by UVC/10 mM H\(_2\)O\(_2\) and 5 hours of irradiation resulted in a residual COD of 260 mg L\(^{-1}\) (Figure 9-6(b)).

Thus, it was shown that YHA greywater was readily treated by the overnight settlement and UVC/H\(_2\)O\(_2\) treatment. With most COD removed by settling overnight, the majority of the contaminants were suspended solids. In contrast, the COD removal of the ATA-B and ATA-H greywaters was not satisfactory and the treated waters had BOD\(_5\) levels significantly higher than the minimal value for reclaimed water as required by EPAV. Despite the high turbidity of ATA-B and ATA-H greywaters, the \textit{E. coli} level was reduced from > 2400 orgs/100 mL to less than 1 org/100 mL after 1 hour of UVC/H\(_2\)O\(_2\) treatment. This was expected as the UV dose of 18,000 mJ cm\(^{-2}\) was very much higher than that needed for disinfection as noted previously in the work of Gilboa and Friedler (2008).

Using the settled ATA-B greywater as an example, a different H\(_2\)O\(_2\) dosing regime was developed in an attempt to improve the COD removal: An initial H\(_2\)O\(_2\) dose to give 10 mM was used, and subsequently an equal amount of H\(_2\)O\(_2\) was added after 2 hours of irradiation, i.e., equivalent to an initial concentration of 20 mM of H\(_2\)O\(_2\) was dosed in fed-batch mode.
As shown in Figure 9-7, the use of 10 and 23 mM H₂O₂ resulted in a similar level of COD removal within 2 hours of the UVC/H₂O₂ treatment; a lower rate of COD removal was observed in the former case when the irradiation time was extended to 3 hours and beyond. As only 10 mg.L⁻¹ (or 0.3 mM) of H₂O₂ remained in the solution at this point, this decrease in the rate of COD removal can be explained by the depletion of H₂O₂ during the treatment from which the generation of *OH cannot be sustained. In contrast, the residual H₂O₂ was more than 2.5 times higher when the initial H₂O₂ concentration was 23 mM. Since excess H₂O₂ can also act as a scavenger to *OH (Yonar et al., 2006), dosing H₂O₂ in the fed-batch mode should reduce the scavenging effect of excess H₂O₂ due to the presence of a lower H₂O₂ concentration, and also overcome the issue of H₂O₂ depletion.

Results in Figure 9-7 show that operating in the fed-batch mode significantly reduced the irradiation time and H₂O₂ dosage compared with using the initial H₂O₂ concentration of 23 mM: irradiation time was cut by 2 hours (equivalent to 36,000 mJ.cm⁻² reduction in UV dose), and H₂O₂ dosage was decreased by 3 mM. However, a similar level of COD remained in the effluent (156 mg.L⁻¹), suggesting that other factors may be imped ing the process.

Figure 9-7. COD of settled ATA-B greywater treated by UVC/H₂O₂, using initial H₂O₂ concentrations of 10 mM and 23 mM and fed-batch mode (10 mM H₂O₂ at 0 and 2 hours).
One possibility was the high COD content in the settled ATA-B greywater. In Section 7.6, the UVC/H₂O₂ treatment appeared to be affected by high concentrations of COD in the greywaters. While a similar percentage of COD removal was obtained within the same irradiation time for the treatment of the settled LR GW and MR GW, longer irradiation time was required for the settled HR GW and the treated water contained slightly higher residual COD (Figure 7-16(a)). The settled ATA-B greywater contained 426 mg.L⁻¹ COD which was about 80 mg.L⁻¹ higher than that of the settled HR GW, therefore, the settled ATA-B greywater it was diluted with tap water before UVC/H₂O₂ treatment to determine if high COD concentration was a limiting factor.

The diluted settled ATA-B greywater had a COD content of 198 mg.L⁻¹, similar to that of settled LR GW (Figure 7-16). Using the same H₂O₂ dosage as for the settled LR GW, i.e., 10 mM, Figure 9-8 shows that less COD was removed from the diluted settled ATA-B greywater than the settled LR GW. After 3 hours of treatment, 85 mg.L⁻¹ COD remained in the treated ATA-B sample, compared with 30 mg.L⁻¹ in the treated LR GW. This indicated that the high concentration of COD in the settled ATA-B greywater was not the limiting factor. Therefore, it is possible that the ATA-B greywater contained recalcitrant organic compounds which could not be oxidised by the UVC/H₂O₂ treatment.

Figure 9-8. COD of settled LR GW and diluted settled ATA-B greywater treated by UVC/10 mM H₂O₂.
Examination of the turbidity of the diluted settled ATA-B greywater, however, suggested that the suspended solids in the greywater may have hindered the penetration of the UVC radiation and hence reduced the photolysis of H$_2$O$_2$ to $\cdot$OH. The diluted settled ATA-B greywater had a turbidity level of 103 NTU, which was about 11 times higher than that of the settled LR GW. This was further supported by the residual H$_2$O$_2$ in the treated water; for the diluted settled ATA-B greywater, more than 25 mg.L$^{-1}$ H$_2$O$_2$ remained after 3 hours of treatment, compared with only 10 mg.L$^{-1}$ in the settled LR GW after treatment. This suggested that the photolysis of H$_2$O$_2$ was inhibited in the diluted settled ATA-B greywater. Since overnight settlement did not result in adequate reduction in suspended solids, other physical treatment such as filtration may be required as a pre-treatment to the UVC/H$_2$O$_2$ process for greywater of very high turbidity.

As discussed in Section 7.5, the biodegradability of the settled LR GW was improved by UVC/H$_2$O$_2$ treatment. The feasibility of using the AOP as a pre-treatment to a biological system was examined for the settled ATA-B and ATA-H greywaters. The COD of these greywaters during the UVC/H$_2$O$_2$ treatment (Figure 9-6(a)) is tabulated in Table 9-1 along with the measured BOD$_5$ levels. The changes in biodegradability (BOD$_5$:COD) of these greywaters during the UVC/H$_2$O$_2$ treatment are shown in Figure 9-9.

Table 9-1. BOD$_5$ and COD of the settled ATA-B and ATA-H greywaters during the UVC/H$_2$O$_2$ treatment.

<table>
<thead>
<tr>
<th>Irradiation Time (h)</th>
<th>Settled ATA-B Greywater</th>
<th>Settled ATA-H Greywater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BOD$_5$ (mg.L$^{-1}$)</td>
<td>COD (mg.L$^{-1}$)</td>
</tr>
<tr>
<td>0</td>
<td>251</td>
<td>426</td>
</tr>
<tr>
<td>1</td>
<td>146</td>
<td>316</td>
</tr>
<tr>
<td>2</td>
<td>121</td>
<td>248</td>
</tr>
<tr>
<td>3</td>
<td>89</td>
<td>183</td>
</tr>
<tr>
<td>5</td>
<td>63</td>
<td>144</td>
</tr>
</tbody>
</table>

The settled ATA-B and ATA-H greywaters had a BOD$_5$:COD of 0.59 and 0.66, respectively. These were similar to municipal wastewater (Section 7.5), indicating that the contaminants in these greywaters were biodegradable. This can be explained by the use of biodegradable and eco-friendly cleaning products by the ATA members. In contrast to the settled LR GW which had a BOD$_5$:COD of 0.22 (Table 7-7), the UVC/H$_2$O$_2$ treatment reduced the biodegradability of the settled ATA-B and ATA-H greywaters. Therefore, a biological system may be more appropriate for the treatment of these greywaters, and a subsequent UVC/H$_2$O$_2$ process may be employed as a polishing step to reduce the time required for the biological treatment and to improve the quality of the effluent.
From this study, it can be concluded that the overnight settlement and UVC/H₂O₂ treatment can be used for the removal of COD in YHA greywater but substantial amounts of contaminants were removed by settling overnight. Due to the costs involved for the construction of photo-reactor, the energy consumption and the use of H₂O₂, the subsequent UVC/H₂O₂ treatment may not be an appropriate option to remove the remaining 44 mg.L⁻¹ of COD in the settled YHA greywater. For the settled ATA-B and ATA-H greywaters, a significant amount of COD remained in the effluent even after 5 hours of irradiation during the UVC/H₂O₂ treatment. The residual BOD₅ level of the treated ATA-B and ATA-H greywaters was 63 and 107 mg.L⁻¹, respectively, and they did not meet the minimal requirement for reclaimed water as specified by EPAV.

Using ATA-B greywater as an example, it was demonstrated that changing the H₂O₂ dosing regime to fed-batch mode substantially reduced the H₂O₂ dosage and irradiation time but the extent of COD removal was not improved. It was found that high concentration of COD in the greywater was not the limiting factor, but high level of turbidity and suspended solids (Table 4-4) may have hindered the penetration of UVC radiation and hence reduced the performance of the UVC/H₂O₂ process.

It is suggested that a biological treatment may be more appropriate for the treatment of ATA-B and ATA-H greywaters which had high biodegradability.
9.4 Summary of Findings for the Treatment of Greywaters Collected from External Sources

The YHA, ATA-B and ATA-H greywaters were treated by sequential alum or ferrous sulphate coagulation and UVC/H$_2$O$_2$, Fenton and photo-Fenton processes, and overnight settlement and UVC/H$_2$O$_2$. The COD of YHA greywater was about 90 mg.L$^{-1}$ lower than that of LR GW collected from the researcher’s home (about 225 mg.L$^{-1}$), whereas the initial COD level of the ATA-B and ATA-H greywaters were 530 and 590 mg.L$^{-1}$, respectively. The removal of COD in these greywaters by the investigated processes is summarised in Table 9-2.

Table 9-2. The COD removal of YHA, ATA-B and ATA-H greywaters resulted from different treatments.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>YHA Greywater</th>
<th>ATA-B Greywater</th>
<th>ATA-H Greywater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Residual COD</td>
<td>COD Removal (%)</td>
<td>Residual COD</td>
</tr>
<tr>
<td></td>
<td>(mg.L$^{-1}$)</td>
<td>(%)</td>
<td>(mg.L$^{-1}$)</td>
</tr>
<tr>
<td>Alum Coagulation</td>
<td>29</td>
<td>74.3%</td>
<td>57</td>
</tr>
<tr>
<td>Ferrous Sulphate Coagulation</td>
<td>33</td>
<td>71.9%</td>
<td>48</td>
</tr>
<tr>
<td>Alum Coagulation + UVC/H$_2$O$_2$</td>
<td>-</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>Ferrous Sulphate Coagulation + UVC/H$_2$O$_2$</td>
<td>-</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>Fenton Process</td>
<td>18</td>
<td>87.5%</td>
<td>28</td>
</tr>
<tr>
<td>Photo-Fenton Process</td>
<td>18</td>
<td>87.4%</td>
<td>14</td>
</tr>
<tr>
<td>Overnight Settlement</td>
<td>44</td>
<td>62.0%</td>
<td>426</td>
</tr>
<tr>
<td>Overnight Settlement + UVC/H$_2$O$_2$</td>
<td>14</td>
<td>88.2%</td>
<td>144</td>
</tr>
</tbody>
</table>

For the YHA greywater, the suspended solids appeared to be the major source of COD. This was evident as after settling overnight, only 44 mg.L$^{-1}$ COD remained in the water (51% COD removal). As a result, UVC/H$_2$O$_2$ may not be appropriate as a subsequent treatment due to the costs involved in the construction of a photo-reactor, the energy requirement for irradiation and the use of H$_2$O$_2$. Simple treatment options such as alum and ferrous sulphate
coagulation produced effluents of 29 – 37 mg.L⁻¹ and 33 – 40 mg.L⁻¹ COD respectively, but they were only marginally lower than those from overnight settlement. The Fenton and photo-Fenton processes removed a similar amount of COD from YHA greywater and the residual COD in the treated water was as low as 15 mg.L⁻¹.

For the ATA-B and ATA-H greywaters, sequential alum or ferrous sulphate coagulation and UVC/H₂O₂ treatment reduced the COD levels to 15 – 27 mg.L⁻¹, regardless of the coagulant used. Effluents of similar quality were achieved by the photo-Fenton process with half the irradiation time but at the expense of a much higher H₂O₂ dosage. A higher level of COD removal was obtained by the photo-Fenton process, compared with the Fenton process, which is consistent with the findings in Section 6.1.1; it was found that the operation of these processes was not as straightforward as the sequential coagulation and UVC/H₂O₂ treatment. In previous experiments using LR GW, MR GW, HR GW and LGW from the researcher’s home (Section 6.2), floc formation was observed during the oxidation stage of the Fenton and photo-Fenton processes. For ATA-B and ATA-H greywaters, however, scum formed, resulting in the necessity of adequate separation devices and/or regular cleaning of the photo-reactor. The variation in the response to these processes remains a difficulty when dealing with greywater of various types and contaminant levels, and it remains a major challenge to the application of these processes in greywater treatment. While such variation may be more pronounced in a single household and should be taken into consideration during the design of the process, the consistency of the greywater may be improved in the case of large scale recycling projects (e.g., apartment blocks) where larger volumes of greywater would be collected and mixed before its subsequent treatment.

Overnight settlement followed by UVC/H₂O₂ treatment was not adequate for the treatment of ATA-B and ATA-H greywaters. Despite using the optimal H₂O₂:COD ratio as determined previously for the LR GW (Section 7.2.2), only 70% – 73% overall COD removal was achieved and the residual COD was 144 – 176 mg.L⁻¹. Dosing H₂O₂ by fed-batch mode substantially reduced the H₂O₂ dosage and irradiation time but the extent of COD removal was not improved. The high concentration of COD in these greywaters was not the limiting factor since the treatment of the sample diluted to similar COD level as LR GW also resulted in poorer COD removal. While the presence of recalcitrant organic chemicals may explain part of the reason for the limitation, it was suggested that the high turbidity levels of these greywaters (Table 4-4) may have hampered the performance of the UVC/H₂O₂ process by hindering the penetration of UVC radiation and hence reduced the photolysis of H₂O₂ to *OH.

The use of eco-friendly, biodegradable cleaning products by ATA members resulted in the
generation of highly biodegradable greywater in their households. Therefore, a biological system may be more appropriate for the treatment of the ATA-B and ATA-H greywaters.

In this chapter, the findings obtained from the application of coagulation, Fenton and photo-Fenton processes, and UVC/H₂O₂ in the treatment of greywater collected from the researcher’s home were applied to greywaters collected from external sources. While various degrees of success were obtained after optimisation of the processes, the effectiveness of treatment was found to depend largely on the quality and type of the greywater. In addition, the importance of consistency in the quality of the greywater cannot be over-emphasized. While the quality of greywater generated in a single household varies significantly, such variation may be reduced with the use of a storage facility to mix the inputs to achieve a more homogeneous stream and/or by the selection or exclusion of different type of greywaters. These processes may be more suitable for greywater recycling projects at larger scale (for instance multi-storey dwellings, apartment blocks, schools and hospitals) where larger populations of users are involved and higher volumes of greywaters are produced.
Chapter 10. Conclusions and Recommendations

10.1 Conclusions

The application of AOPs in greywater treatment has hitherto been limited to heterogeneous systems such as UV/TiO₂. Three homogeneous AOPs, namely Fenton, photo-Fenton and UVC/H₂O₂ processes, were investigated for their applicability in greywater treatment; comparison was made with conventional coagulation using alum or ferrous sulphate. The treatment of LR GW by these processes was optimised and the optimal conditions were:

- Alum coagulation (2 mM Al³⁺/pH 5)
- Sequential alum coagulation (2 mM Al³⁺/pH 5) and UVC/H₂O₂ treatment (1.5 hours/2 mM H₂O₂/pH 5)
- Ferrous sulphate coagulation (1 mM Fe²⁺/pH 3)
- Sequential ferrous sulphate coagulation (1 mM Fe²⁺/pH 3) and UVC/H₂O₂ treatment (1 hour/7 mM H₂O₂/pH 3)
- Fenton process (1 mM Fe²⁺/5 mM H₂O₂; Oxidation stage: 0.5 hour at pH 3, Coagulation stage: pH 7)
- Photo-Fenton Process (UVC/1 mM Fe²⁺/10 mM H₂O₂; Oxidation stage: 1.5 hours at pH 3, Coagulation stage: pH 7)
- Overnight Settlement and UVC/H₂O₂ (3 hours/10 mM H₂O₂ at pH 10).

Seven parameters were used to compare the effectiveness of these processes: COD removal, type of treatment, sludge formation, complexity in operation, pH condition, visual aesthetic of effluent, and energy requirement.

The effectiveness of ferrous sulphate coagulation and the Fenton process was low for the treatment of LR GW. Under the conditions studied, less than 50% of COD was removed, the next best was alum coagulation which removed 73% COD. A higher level of COD removal was obtained by the photo-Fenton process (83%), overnight settlement and subsequent UVC/H₂O₂ treatment (87%), sequential ferrous sulphate coagulation and UVC/H₂O₂ treatment (91%), and sequential alum coagulation and UVC/H₂O₂ treatment (98%).

The processes investigated in this project employed physical separation and/or chemical oxidation. All these processes, except overnight settlement and UVC/H₂O₂ treatment, included coagulation which removed a significant proportion of COD in the greywater. Many of the compounds in greywater are xenobiotic (such as PPCPs, EDCs and surfactants) and they are of major concern due to the lack of information about their toxicity, biodegradability...
and bioaccumulation properties. With coagulation, some of these compounds may be concentrated in the sludge and hence the issue of dealing with a large volume of chemical sludge arises. For overnight settlement and UVC/H₂O₂ treatment, only 13% COD in the raw LR GW was removed by settlement while the majority of the contaminants were chemically destroyed or mineralised in the subsequent oxidation stage.

Considering the ease of operation, alum or ferrous sulphate coagulation was relatively straightforward and simple. When coupled with a subsequent UVC/H₂O₂ treatment, these processes had a moderate level of complexity due to the additional requirement for optimising the H₂O₂ dosage.

For Fenton and photo-Fenton processes, their operation was complicated by the optimisation of multiple parameters such as pH, Fe²⁺:H₂O₂, H₂O₂:COD and reaction/irradiation time. In addition, when treating greywaters of various types, customised operation procedures and different considerations in process design would be required. While the conventional procedures as described by Gogate and Pandit (2004a) and Benatti et al. (2006) were appropriate for SGW and TGW, the formation of flocs that settled readily was observed during the oxidation stage for the treatment of LGW, LR GW, MR GW and HR GW. If settlement of the solution was not allowed before neutralising the pH, the flocs disappeared and resulted in poor COD removal. The formation of flocs during the oxidation is attributed to the high conductivity of these greywaters with significant laundry input, which reduces the zeta-potential by compressing the electrical double-layer between the suspended particles. Although Neyens and Baeyens (2003) commented on the formation of fine flocs during the oxidation stage which took a long time to settle, discussion on the simultaneous occurrence of oxidation and coagulation and the disappearance of flocs during pH adjustment has not been found in the literature.

For the treatment of ATA-B and ATA-H greywaters by Fenton and photo-Fenton processes, scum was formed during the oxidation stage although subsequent pH neutralisation produced substantial flocs that settled readily. To improve the appearance of the effluent, an additional separation device was necessary to remove the scum. Furthermore, regular cleaning of the photo-reactor was required for the photo-Fenton process to prevent the accumulation of scum which may inhibit the penetration of UV radiation. Therefore, the variation in the quality and type of greywater presents a major challenge particularly to the application of Fenton and photo-Fenton processes in greywater treatment. In addition to appropriate design of the process, consistency in the quality of the greywater may be improved by selecting or excluding certain types of greywater, and with the use of storage of appropriate capacity to allow mixing. Also, in larger scale recycling projects that involve larger populations of users,
the variation in the quality of the influent may be reduced.

In contrast to the literature that frequently recommends the operation of AOPs in acidic conditions, it was found that the initial pH condition of settled LR GW did not strongly affect the performance of UVC/H₂O₂ treatment. For initial pH of 3, 7 and 10, the levels of COD removal were similar but a slightly lower residual COD was obtained when the initial pH was 10. It was demonstrated that:

- The [Cl⁻] and cₜ in the settled LR GW were 0.7 mM and 1 mM, respectively, and they were both higher than those of bathroom greywaters but within the range of laundry greywaters as reported in the literature (Eriksson et al., 2002). With the [Cl⁻]/cₜ ratio at the low value of 0.7, the reduced scavenging of *OH by Cl⁻ at high pH was not sufficient to compensate for the radicals that reacted with HCO₃⁻/CO₃²⁻. Therefore, this did not explain the enhanced COD removal when the initial pH of the greywater was 10. By increasing the cₜ with the addition of NaHCO₃ to the settled LR GW, the UVC/H₂O₂ treatment was found to be tolerant to the presence of at least 3 mM of HCO₃⁻/CO₃²⁻; when the initial cₜ exceeded 10 mM, the deterioration in the performance was noticeable and operating between pH 3 – 5 alleviated the impact of HCO₃⁻/CO₃²⁻ by converting them to CO₂ and carbonic acid which has low reactivity with *OH.

- Despite the difference between the initial pH of 7 and 10, the formation of mineral acids, carbon dioxide and acidic intermediates during the UVC/H₂O₂ treatment resulted in similar operating conditions of between pH 6 and 8.

- In addition to the reported acceleration in the rate of H₂O₂ photolysis in alkaline conditions, the slightly higher COD removal is attributed to the dissociation of H₂O₂ to O₂/H⁻ at initial pH of 10 and the significantly higher ε₂₅₄ of O₂H⁻, although this benefit soon diminished due to the production of acidic intermediates that reduced the solution pH. Operating at higher initial pH or maintaining pH at 10, however, did not improve the treatment and this was attributed to the accelerated decomposition of H₂O₂ to O₂ and water at these pH conditions.

While pH adjustment was not necessary for the settled LR GW before UVC/H₂O₂, the formation of mineral acids, carbon dioxide and acidic intermediates during the treatment reduced the initial pH of the greywater from 10 to nearly neutral. This is advantageous since the pH of the effluent fulfilled the requirement of many standards or guidelines for reclaimed water (Tables 2-2 and 2-3) and therefore did not require further adjustment. All other processes need to be operated in acidic conditions and the feasibility of acidifying and subsequently neutralising a large volume of greywater, the additional costs for chemicals and equipment, and the use of adequate material for piping and equipment should be considered. Visually, alum coagulation produced effluent that was clear and free of colour, with or
without the subsequent UVC/H₂O₂ treatment. In contrast, those processes involving the use of ferrous sulphate imparted a yellow tint in the treated water due to the residual iron. This may not be aesthetically acceptable as the treated water may stain toilet bowls and urinals if used for toilet flushing.

In summary, for the treatment of LR GW, the overnight settlement and subsequent UVC/H₂O₂ process had the following advantages over the other processes investigated:

- High level of COD removal was achieved and most of the contaminants in the raw greywater were mineralised by the oxidation process, i.e., chemically destroyed and not physically separated from the water and transferred to another medium.
- The process could be applied to different types of greywaters due to the non-selectivity of *OH.
- Its operation was moderate in complexity, which required the optimisation of H₂O₂ dosage according to the initial COD level of the greywater.
- No pH adjustment was required during the process.
- The treated effluent was not coloured although it remained slightly turbid.

While 31% turbidity in LR GW was removed by settling overnight, a slight reduction during the UVC/H₂O₂ treatment did not result in effluent that fulfilled the requirement of Class A reclaimed water as specified by EPAV. The effluent appeared slightly turbid and filtration may be required to reduce the levels of suspended solids and turbidity of the effluent if more stringent requirements are to be met. An example for the integration of AOP with membrane filtration is the work of Rivero et al. (2006), who combined UV/TiO₂ treatment with a side-stream cross-flow microfiltration unit. The removal of suspended solids should be carried out prior to the UVC/H₂O₂ treatment, especially for the treatment of highly turbid greywaters such as ATA-B and ATA-H, for which the poorer process performance was attributed to the reduced penetration of UVC radiation due to the suspended solids.

The UVC/H₂O₂ process provided additional benefits due to the disinfection property of UVC radiation, which resulted in the survival of less than 1 org/100 mL of *E. coli* in the effluent of settled LR GW, ATA-B and ATA-H greywaters. While the UV dose to achieve an adequate level of COD removal was much higher than those used in greywater disinfection (Gilboa and Friedler, 2008), subsequent disinfection such as by chlorination may be required to ensure the safety of reusing the treated water and to provide a multi-barrier system for the purpose of risk management.

Due to the level of sophistication of the UVC/H₂O₂ treatment, this process is more applicable to a greywater recycling project of a larger scale, such as multi-storey dwellings, apartment
blocks, schools and hospitals etc. For the treatment of LR GW, overnight settlement and subsequent UVC/H₂O₂ process produced an effluent that fulfilled the requirement of Class B reclaimed water as specified by EPA (Table 2-2), which is suitable for non-potable urban uses (with controlled public access), agricultural irrigation (e.g., cooked/processed food crops for human consumption), and industrial applications with no potential exposure to workers.

10.2 Recommendations

The potential of UVC/H₂O₂ for the treatment of greywater has been demonstrated although the high energy requirement for the operation of UVC lamps must be acknowledged. Therefore further research into the optimisation of reactor design is highly recommended. These include the investigation of different types of lamp and photo-reactor with different configurations (annular reactors with coaxial or perpendicular lamp positions, external lamp with reflectors, contact-free photo-reactor etc.) to improve the efficiency of the process. Other irradiation sources such as solar irradiation may prove to be an attractive alternative, while the use of renewable energy such as solar power may be advantageous to reduce the carbon-footprint of this process.

Another possibility is the utilisation of the UVC/H₂O₂ process as a pre-treatment to biological treatment. As shown in this study, the biodegradability (BOD₅:COD) of LR GW was increased from 0.22 to 0.41. Therefore, for the treatment of greywater with low biodegradability, partially oxidising the contaminants by the UVC/H₂O₂ process before subsequent biological treatment is particularly useful since it may not always be feasible to rely solely on AOPs to achieve the required COD removal. With such integration, problems with the low biodegradability of greywater can be overcome while reducing the costs involved in the operation of the UVC/H₂O₂ process (e.g., energy demand and chemicals). For greywaters such as ATA-B and ATA-H that had high biodegradability, a biological system may be more feasible.

This study demonstrated that the selection of a process for greywater treatment relies greatly on the quality and type of the greywater. While safety for the reuse of greywater should be of the highest priority, it is important to recognise that the level of treatment should reflect the application of the reclaimed water, i.e., the concept of “fit-for-purpose”. In addition, issues such as the consistency (or variation) in the quality of raw greywater and its concentration and type of contaminants (e.g., biodegradability, BOD₅ or COD, turbidity and level of suspended solids etc.), the requirement for sludge disposal, and risk management strategy that includes multi-barrier protection should be carefully considered. As the public becomes more aware of their water usage and the pressure that it imposes on the water supply system,
it is foreseeable that the production of greywater will be reduced and this should be incorporated into the design of a process for the treatment of greywater with high concentrations of contaminants.

In their review of greywater treatment options and applications, Pidou et al. (2007) identified the current issue of focusing on treatment performance without evaluating the sustainability of a suitable technology for greywater treatment. While they discussed the feasibility of different technologies by examining the pay-back period and the water savings of the technologies, figures-of-merit such as the electrical energy per order of magnitude of removal ($E_{EO}$), and the electrical energy per mass of removal ($E_{EM}$) (Stefan, 2004) should also be evaluated. In this project, the processes that have been investigated demonstrated various degrees of success in their applicability in the treatment of greywater. Further research is strongly recommended to examine their feasibility in terms of the energy consumption and the economics. An assessment tool proposed by Memon et al. (2005) may prove to be useful for the evaluation of the sustainability of a greywater recycling project. This tool employs the “whole-life cycle” approach, incorporates different modules to calculate the net cost of producing the treated water, and it takes into account the capital cost, operation cost and planned/unplanned maintenance cost, together with input of information such as scale of the recycle scheme, number of residents, period of operation time, volume of the greywater generated and the consumption of treated water.
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Appendices

Appendix A. Determination of the Molar Absorption Coefficient (\(\varepsilon\)) of Ferrous-Phenanthroline Complex

Procedures for the determination of the molar absorption coefficient (\(\varepsilon\)) of the ferrous-phenanthroline complex were described in Section 3.2.1. Figure A-1 shows the standard calibration graph, in which the linear relationship between the absorbance at 510 nm (\(A_{510}\)) of the ferrous-phenanthroline complex and the concentration of the Fe\(^{2+}\) is shown. The \(\varepsilon\) of ferrous-phenanthroline complex determined from three experimental data sets was \(1.1135 \times 10^4\) L.mol\(^{-1}\).cm\(^{-1}\), which is comparable with the value of \(1.11 \times 10^4\) L.mol\(^{-1}\).cm\(^{-1}\) reported by Murov et al. (1993).

![Figure A-1. Standard calibration graph for potassium ferrioxalate actinometry.](image)

\[ A_{510} = 1.1135 \times 10^4 \times \frac{[Fe^{2+}]}{M} \]
Appendix B. Irradiation Intensity ($I_\lambda$), Radiant Energy ($Q_\lambda$), and Fluence Rate of the UVC Lamps

The absorbance at 510 nm ($A_{510}$) of the potassium ferrioxalate actinometer was measured according to Section 3.2.3. For non-irradiated actinometer or the blank, the average $A_{510}$ with reference to MilliQ water was 0.025 ± 0.001 (three repetitions). Since it is lower than 0.06, this indicates that the actinometer solutions were of good quality (Murov et al., 1993). The $A_{510}$ of the actinometer irradiated by the UVC lamps was determined and corrected by subtracting arithmetically the $A_{510}$ of the blank sample from that of the irradiated sample, i.e.,

$$A_{510}^{(\text{Irradiated sample})} (\text{w.r.t. blank}) = A_{510}^{(\text{Irradiated sample})} (\text{w.r.t. water}) - A_{510}^{(\text{blank})} (\text{w.r.t. water}).$$

The corrected $A_{510}$ values of the irradiated actinometer are shown in Table B-1.

Using Equation 3-2 and the information in Section 3.2 and Appendix A, the average irradiation intensity ($I_\lambda$) of the UVC lamps was calculated (Table B-1).

From Planck’s Law of Radiation, the radiant energy carried by each photon at a specific wavelength ($Q_\lambda$) was calculated according to Equation B-1 by approximating at the spectral peak of each lamp (Bolton, 1999; Oppenländer, 2003):

$$Q_\lambda = \frac{N_A h c_0}{\lambda} = \frac{1.1963 \times 10^5}{\lambda}$$

where $Q_\lambda$ is radiant energy (kJ.mol$^{-1}$) at wavelength $\lambda$ (nm), $N_A$ is Avogadro’s number ($6.022 \times 10^{23}$ mol$^{-1}$), $h$ is Planck’s constant ($6.6261 \times 10^{-34}$ J.s), and $c_0$ is speed of light in vacuum ($2.9979 \times 10^8$ m.s$^{-1}$).

Finally, the fluence rate for each lamp was determined according to Equation B-2 and UV dose or fluence was given by the average fluence rate times the exposure time (Equation B-3) (Bolton, 1999):

$$\text{Fluence Rate} = \frac{I_\lambda \times Q_\lambda \times 10^6}{\text{Cross - Sectional Area}}$$

$$\text{Fluence} = \text{Fluence Rate} \times \text{Exposure Time}$$

where the fluence rate is defined as the radiant power of all wavelengths passing through an infinitesimally small sphere of cross-sectional area $dA$, divided by $dA$ (mW.cm$^{-2}$), $I_\lambda$ is irradiation intensity determined as in Equation 3-2 (mole of photons.s$^{-1}$), $Q_\lambda$ is radiant energy calculated according to Equation B-1 (kJ.mol$^{-1}$), and the exposure time is in s.
The internal diameter of the quartz sleeve was 4.4 cm and the height of actinometer in the quartz sleeve was 39 cm and it was measured while being bubbled gently by humidified CO₂-free air. Hence, the cross-sectional area of liquid in each quartz sleeve exposed to irradiation was 171.6 cm².

As shown in Table B-1, the difference between the fluence rates received by the quartz sleeves QS1 and QS2 in the photo-reactor (Section 3.1) ranged from 7% to 13%, depending on the lamp used. To minimise error, only QS1 was used in the experiments.

Table B-1. Absorbance at 510 nm (A₅₁₀) of irradiated actinometer by the UVC lamps and its respective irradiation intensity (Iₜ), radiant energy (Qₜ) and fluence rate.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quartz Sleeve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>QS1</td>
</tr>
<tr>
<td>Absorbance at 510 nm, A₅₁₀ #</td>
<td>0.902 ± 0.049</td>
</tr>
<tr>
<td>Irradiation Intensity, Iₜ</td>
<td>1.80 ± 0.10</td>
</tr>
<tr>
<td>(×10⁻⁶ mole of photon.s⁻¹)</td>
<td></td>
</tr>
<tr>
<td>Radiant Energy, Qₜ (kJ.mol⁻¹)</td>
<td>471.54</td>
</tr>
<tr>
<td>Fluence Rate (mW.cm⁻²)</td>
<td>4.95 ± 0.27</td>
</tr>
</tbody>
</table>

# Corrected for the absorption of blank (non-irradiated actinometer)
Appendix C. Comparison of Dissolved Oxygen Measurement by DO meter and Winkler Titration

Table C-1. Comparison of dissolved oxygen (DO) measurement by DO meter and Winkler titration (three repetitions).

<table>
<thead>
<tr>
<th>Heated MilliQ Water (°C)</th>
<th>Measurement by DO meter</th>
<th>Winkler Titration</th>
<th>DO (mg.L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure (mbar)</td>
<td>Temperature (°C)</td>
<td>DO (mg.L⁻¹)</td>
</tr>
<tr>
<td>20</td>
<td>1005</td>
<td>19.75</td>
<td>8.88</td>
</tr>
<tr>
<td></td>
<td>1005</td>
<td>19.83</td>
<td>8.73</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>19.65</td>
<td>9.05</td>
</tr>
<tr>
<td>30</td>
<td>1001</td>
<td>19.63</td>
<td>7.77</td>
</tr>
<tr>
<td></td>
<td>1006</td>
<td>19.70</td>
<td>7.66</td>
</tr>
<tr>
<td></td>
<td>1005</td>
<td>20.08</td>
<td>7.67</td>
</tr>
<tr>
<td>50</td>
<td>1000</td>
<td>19.64</td>
<td>5.57</td>
</tr>
<tr>
<td></td>
<td>1006</td>
<td>19.80</td>
<td>5.85</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>20.24</td>
<td>5.87</td>
</tr>
<tr>
<td>70</td>
<td>1005</td>
<td>19.74</td>
<td>4.12</td>
</tr>
<tr>
<td></td>
<td>1005</td>
<td>19.93</td>
<td>4.36</td>
</tr>
<tr>
<td></td>
<td>999</td>
<td>20.23</td>
<td>3.75</td>
</tr>
<tr>
<td>90</td>
<td>1003</td>
<td>19.60</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td>1006</td>
<td>19.81</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>996</td>
<td>19.98</td>
<td>2.15</td>
</tr>
</tbody>
</table>
Appendix D. BOD₅ Measurement: Dosage of Seeding Material in Seed Control and GGA Test

Figure D-1. BOD₅ study for the dosage of seeding material in: (a) Seed control, and (b) Glucose-Glutamic Acid (GGA) check.
Appendix E. Standard Calibration Graphs for Low-Range and High-Range COD Reagents

Figure E-1. Calibration graphs of KHP standard solutions for (a) High-range COD reagent, and (b) Low-range COD reagent.

(a) Absorbance at 620 nm, $A_{620}$

- $A_{620} = 3.6174 \times 10^{-4} \times \text{COD}$
- $R^2 = 0.9965$

(b) Absorbance at 420 nm, $A_{420}$

- $A_{420} = -0.0027 \times \text{COD} + 0.2368$
- $R^2 = 0.9929$
Appendix F. Ion Chromatography and Standard Calibration Graphs

Figure F-1. Ion chromatography: typical graph recorded by the integrator for a standard solution consisting of Cl\(^-\), NO\(_2\)\(^-\), Br\(^-\), NO\(_3\)\(^-\), PO\(_4\)\(^{3-}\), and SO\(_4\)\(^{2-}\) anions.

To determine the calibration graphs, chemicals of analytical grade were used to prepare the standard solutions (included NaCl, NaNO\(_2\), NaBr, NaNO\(_3\), KH\(_2\)PO\(_4\) and K\(_2\)SO\(_4\)). Various concentrations of the standard solutions were prepared as shown in Table F-1. Figure F-2 shows the calibration graphs for each anion and their corresponding gradients and R\(^2\) values are listed in Table F-1.

Table F-1. Concentration of Cl\(^-\), NO\(_2\)\(^-\), Br\(^-\), NO\(_3\)\(^-\), PO\(_4\)\(^{3-}\), and SO\(_4\)\(^{2-}\) standard solutions, their corresponding gradient of calibration graphs and R\(^2\) value.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Concentration of Standard Solutions (mg.L(^{-1}))</th>
<th>Gradient of Calibration Graph</th>
<th>R(^2) Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution 1</td>
<td>Solution 2</td>
<td>Solution 3</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>2.0</td>
<td>5.0</td>
<td>20.0</td>
</tr>
<tr>
<td>NO(_2)(^-)</td>
<td>1.2</td>
<td>3.0</td>
<td>12</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>1.2</td>
<td>3.0</td>
<td>12.0</td>
</tr>
<tr>
<td>NO(_3)(^-)</td>
<td>1.2</td>
<td>3.0</td>
<td>12.0</td>
</tr>
<tr>
<td>PO(_4)(^{3-})</td>
<td>1.2</td>
<td>3.0</td>
<td>12.0</td>
</tr>
<tr>
<td>SO(_4)(^{2-})</td>
<td>8.0</td>
<td>20.0</td>
<td>80.0</td>
</tr>
</tbody>
</table>
Figure F-2. Calibration graphs for ion chromatography of anions: (a) Cl⁻, (b) NO₂⁻, (c) Br⁻, (d) NO₃⁻, (e) PO₄³⁻, and (f) SO₄²⁻.
Appendix G. Excess H$_2$O$_2$: Error in COD Measurement and Indication by Merckoquant® Peroxide Test Strip

As discussed in Section 3.3.11, excess H$_2$O$_2$ gives falsely high readings in COD measurement. Kang et al. (1999) proposed a correction factor, and the errors in COD measurements at various concentrations of residual H$_2$O$_2$ were calculated accordingly (Table G-1). As shown in the table, 2 mg.L$^{-1}$ of residual H$_2$O$_2$ introduces 0.9 mg.L$^{-1}$ of error in COD measurement.

### Table G-1. Various concentrations of H$_2$O$_2$ and their corresponding errors in COD measurement using correction factor proposed by Kang et al. (1999).

<table>
<thead>
<tr>
<th>Hydrogen Peroxide Concentration, [H$_2$O$_2$] (mg.L$^{-1}$)</th>
<th>Molarity (mM)</th>
<th>Error in COD Measurement, f[H$_2$O$_2$]$^*$ (mg.L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.02</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
<td>2.4</td>
</tr>
<tr>
<td>10</td>
<td>0.29</td>
<td>4.7</td>
</tr>
<tr>
<td>25</td>
<td>0.74</td>
<td>11.7</td>
</tr>
</tbody>
</table>

*$f$ is the correction factor proposed by Kang et al. (1999) (i.e. $f = 0.4706 - 4.06 \times 10^{-5} \times [H_2O_2]$)

Verification of COD Correction Factor and Merckoquant® Peroxide Test Strip

A study was conducted to verify the correction factor proposed by Kang et al. (1999) and the use of Merckoquant® peroxide test strips to test residual H$_2$O$_2$ in greywater.

LR GW was prepared as described in Section 4.2, and H$_2$O$_2$ was added to a series of LR GW samples so that each sample contained 0, 0.5, 2, 5, 10, and 25 mg.L$^{-1}$ of H$_2$O$_2$, respectively (or 0.02, 0.06, 0.15, 0.29, and 0.74 mM). Merckoquant® peroxide test strips were dipped into these greywaters for one second and the colour change of the strips was recorded after 15 seconds.

As shown in Figure G-1, the colour changes of the test strips closely matched the corresponding colour chart. The result was satisfactory and greywater did not appear to interfere with the test.

The COD of these greywaters was then measured. As shown in Table G-2, the presence of H$_2$O$_2$ in greywater increased its COD level and the extent of increment generally followed...
the trend as shown in Table G-1, except when the concentration of H$_2$O$_2$ was 0.5 and 2 mg.L$^{-1}$. In such cases, the error inherent to COD measurement was higher than the interference caused by H$_2$O$_2$, possibly due to the manual transfer of sample aliquots into COD reagent vials.

![Colorimetric indication by Merckoquant® peroxide test strip for greywater containing 0, 0.5, 2, 5, 10, and 25 mg.L$^{-1}$ of H$_2$O$_2$.](image)

**Figure G-1.** Colorimetric indication by Merckoquant® peroxide test strip for greywater containing 0, 0.5, 2, 5, 10, and 25 mg.L$^{-1}$ of H$_2$O$_2$.

**Table G-2.** Error in COD measurement due to the presence of H$_2$O$_2$.

<table>
<thead>
<tr>
<th>Hydrogen Peroxide</th>
<th>Average COD (mg.L$^{-1}$)</th>
<th>Error in COD Measurement in the Presence of H$_2$O$_2$ (mg.L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration, [H$_2$O$_2$] (mg.L$^{-1}$)</td>
<td>Molarity (mM)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>292 ± 2</td>
</tr>
<tr>
<td>0.5</td>
<td>0.02</td>
<td>294 ± 6</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
<td>297 ± 2</td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
<td>294 ± 2</td>
</tr>
<tr>
<td>10</td>
<td>0.29</td>
<td>296 ± 4</td>
</tr>
<tr>
<td>25</td>
<td>0.74</td>
<td>307 ± 2</td>
</tr>
</tbody>
</table>