CRANFIELD UNIVERSITY

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Advanced oxidation processes for wastewater reuse – removal of micropollutants

School of Applied Science
MSc by Research

Master of Science
Academic Year: 2011- 2013

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ABSTRACT

The removal of micropollutants (MPs) from secondary municipal wastewater by an advanced oxidation process (AOP) based on UV irradiation combined with hydrogen peroxide (UV/H_2O_2) has been assessed through pilot-scale experiments incorporating microfiltration (MF) and reverse osmosis (RO). Tests employed low concentrations of a range of emerging contaminants of concern, and the water quality varied by blending of waters from different sources.

Under optimum H_2O_2 and lamp power conditions, the process achieved >99% removal of N-nitrosodimethylamine (NDMA) and endocrine disrupting compounds (EDCs) from all waters. Pesticide removal, in particular metaldehyde, atrazine and 2, 4 5-T, was dependent on water transmittance (UVT), and levels of Total Organic Carbon (TOC) and other hydroxyl radical ($HO^.$) scavengers. Chloroform, a trihalomethane (THM), was not readily degraded (<10% removal in either stream), as was TOC removal.

Further analysis of metaldehyde removal identified UVT, reaction time, and H_2O_2 dose to be influential parameters in determining degradation as a function of UV dose. In comparison, the impact of H_2O_2 dose and UVT was negligible on NDMA degradation; removal increased from 89 to >98% on increasing the UV dose from 200 to 680 mJ cm^{-2} from the MF permeate. Nitrite by-products were observed at elevated levels, promoted by low pH and high UV doses.

An operational cost assessment revealed energy consumption to account for 65% with lamp replacement contributing 25%. A comparison of three unit process sequences, based on MF, RO, AOP and activated carbon (AC), revealed MF-RO-AOP to be the most cost effective provided management of the RO concentrate stream incurs no significant cost. Results demonstrated AOPs to satisfactorily reduce levels of the more challenging recalcitrant MPs to meet stringent water quality standards for wastewater reuse, but that practical limitations exist and the cost penalty is significant.

Keywords: AOP, UV/H_2O_2, wastewater reuse, micropollutants, metaldehyde, NDMA.

ACKNOWLEDGEMENTS

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AOP	Advanced oxidation process
BBD	Box-Behnken design
CAS	Conventional activated sludge
CIP	Clean in place
DBP	Disinfection by-product
ECC	Emerging contaminants of concern
EDC	Endocrine disrupting compound
EED	Electrical energy demand
EEO	Electrical energy per order
GAC	Granular activated carbon
HO	High output
IPR	Indirect potable reuse
LP	Low pressure
MF	Microfiltration
MP	Micropollutant
NOM	Natural organic matter
NDMA	N-nitrosodimethylamine
OPEX	Operational expenditure
ORP	Oxidation reduction potential
PhACs	Pharmaceutically active compounds
PCPs	Personal care products
PNEC	Proposed predicted no effect concentration
SUVA	Specific UV absorbance
RO	Reverse osmosis
THM	Trihalomethane
THMFP	Trihalomethane formation potential
TOC	Total organic carbon
UV	Ultraviolet
UVA	UV Absorbance
UVT	UV Transmittance
WWTP	Wastewater treatment plant

1 Introduction

1.1 Background

Increasing pressure on global water resources, driven by population and industrial growth in urban areas and the possible exacerbation by future climatic conditions (Asano, 2005) demands further consideration of safe supply options. Wastewater reclamation is becoming an increasingly attractive solution to conserve freshwater supplies, and is more economically viable than seawater desalination (Cotes *et al.*, 2004) in non-arid regions. However, one of the major concerns for wastewater reuse is the ever growing number of micropollutants being introduced into sewerage catchments that are resistant to removal using conventional wastewater treatment works (WWTPs) (Drewes *et al.*, 2002; Bolong *et al.*, 2009). Though generally found at low concentrations (Loos *et al.*, 2009) the associated long term risk of some micropollutants to human health and the environment is still unknown and strongly influences public acceptance.

Each UK water utility company is required by law to produce a water resources management plan (WRMP) every five years as a foundation of the water supply and demand planning for the following 25 year period. It is expected that water demand within the greater London region will substantially increase in the next few years due to planned population and economic growth, coupled with existing stressed water resources from low effective rainfall use as well as recent drought events. One of the options incorporated in the Thames Water WRMP plan is to investigate the feasibility of 'planned' indirect potable reuse (IPR) for future augmentation of water resources. This then led to the implementation of a 0.6 MLD pilot plant based in North London, with the aim of studying the most current municipal wastewater reuse technologies. The pilot plant was designed on existing global, full-scale IPR reclamation plants using the 'multi-barrier' approach of microfiltration (MF), reverse osmosis (RO) and advanced oxidation process (AOP).

Extensive water quality studies are also being undertaken to evaluate the ability of the advanced treatment processes to reliably remove constituents from the

reclaimed water. Of particular interest are "contaminants of emerging concern", whose potential impacts to human health and the environment are not fully understood and demand continued review (Reardon, 2010; NWRI, 2010). These include endocrine disrupting compounds (EDCs), pharmaceuticals, disinfection by-products (DBPs), pesticides/herbicides and personal care products (PCP), which are monitored on a routine basis to identify their presence and level of detection. However, for some chemicals their removal cannot be sufficiently established due to limited frequency of occurrence (i.e. seasonal use and changes to the upstream sewerage catchment etc.) and with only trace levels existing in the source effluent. Furthermore, the RO process is an effective barrier to most recalcitrant micropollutants (Wintgens *et al.*, 2004; Sahar *et al.*, 2011), presenting contaminant levels that are extremely low (ng per litre range) or below the analytical detection limit. It is thus preferable to conduct trials that determine the absolute degradation efficiency of the AOP to ensure all possible risks are mitigated and so reliably inform full-scale implementation. Also, it allows optimisation of key performance parameters, relative cost data to be obtained, and overall comparison with other advanced treatment processes.

1.2 Aims and objectives

This study aims to assess the efficacy of advanced oxidation process, UV irradiation combined with hydrogen peroxide (H_2O_2), on treating a range of micropollutants of concern, related to this particular wastewater reuse scheme. The principal objectives comprise:

1. establish optimum conditions for the AOP in terms of power input and H_2O_2 dose on MF and RO feedwater quality.

2. assessment of micropollutant degradation, particularly metaldehyde and NDMA.

3. evaluate the relative cost performance of AOP in comparison to other advanced treatment process trains.

4. Assess by-product formation under representative operating conditions.

The work is presented as a brief review of the pertinent literature (Chapter 2) followed by two papers. Chapter 3 reports the performance of the Advanced oxidation for micropollutant removal generally and metaldehyde specifically, metaldehyde being the most recalcitrant of the chemicals studied. This paper includes a cost comparison with alternative process treatment options, and has been submitted to Water Research. The second paper (Chapter 4) focuses on disinfection byproduct removal and formation and is to be submitted to Water Science and Technology.

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2 Literature Review

2.1 Introduction

A basic "blind" literature survey on advanced oxidation processes (AOP) for water and wastewater treatment published between 1990 and 2012 was conducted using the search engine Scopus (Scopus, 2013).

The search terms "AOP" combined with either "water treatment" or "wastewater treatment" were applied to titles, abstracts and keywords, with their outcomes provided in Figure 2-1. This indicates a growing interest in the subject area over recent years, particularly from around 2004 – attributable to the promulgation of legislation (i.e. tightening of water quality standards), and ever-increasing concerns over environmental impacts and water resource management. Most publications appear to focus on AOP for water treatment, for which 450 articles have been generated in the stated period – almost 60% more than those based on wastewater treatment. In addition, "AOP" and "reuse" were also searched for, highlighting a rise in the number of publications in the last ten years (125 in total) but not as substantial as those in water treatment (Figure 2-1). No distinction was made between industrial and municipal applications.

For further review and comparison, individual AOPs (e.g. "ozone" and "UV/H_2O_2") were searched for in combination with the three water type classifications identified above. Figure 2-2 displays the results of these searches, evidently showing Fenton's reagent to have a significantly higher number of publications (3,653), followed by ozone (O_3)/UV (1,539) and titanium dioxide (TiO_2)/UV (1,210), respectively. Publications on UV/H_2O_2 numbered to 1,130 articles in total, with only 21 of these registered as concerning "micropollutants" (although this term does not capture all papers on pollutants present at trace levels. These trends could possibly suggest that the other AOPs are more established, cost effective or limited to certain applications.
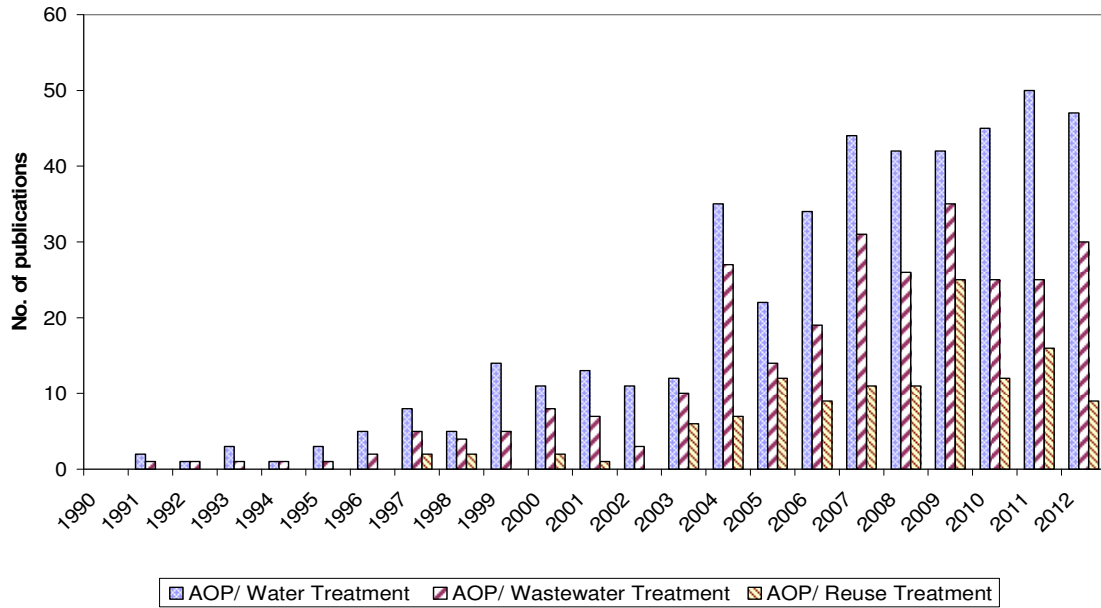
Figure 2-1 No. of publications considering the terms "AOP" and "water treatment", "wastewater treatment" or "reuse" for the period 1990-2012.
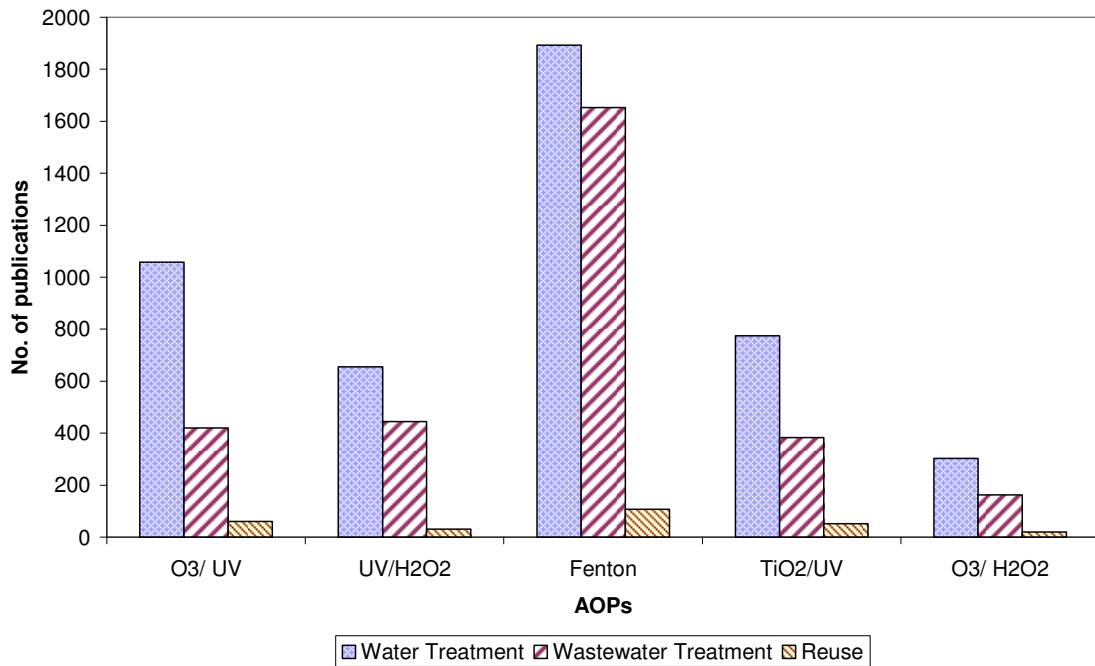
Figure 2-2 No. of publications considering the major AOPs in combination with either of the three treatment classifications for the period 1990-2012.

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2.2 Overview of AOPs

2.2.1 Introduction

Advanced oxidation processes (AOPs) have been identified as a promising alternative to conventional treatment for removing a wide range of organic constituents in contaminated water and wastewaters. Their development and application has been studied extensively over the last few decades (Figure 2-2) using a variation of combined oxidants, catalysts and radiation. Some of these include Fentons reagent (Fe_2^+/ H_2O_2), ozone and hydrogen peroxide (O_3/H_2O_2), UV with ozone (UV/O_3), hydrogen peroxide (UV/H_2O_2) and titanium dioxide (UV/TiO_2); the more established and commercially available processes (Suty *et al.*, 2004) utilised for water purification (drinking, wastewater and groundwater treatment). AOPs have the potential to achieve full mineralisation, or possible transformation to less potent products (Bolton, 2001), and are thus considered appropriate for drinking water and industrial applications.

An AOP is typically characterised by the formation of hydroxyl radicals ($^.OH$) (Glaze *et al.*, 1987) to induce the oxidation and degradation of target contaminants, predominately organic materials. $^.OH$ radicals are well known for being one of the most powerful, non-selective and short lived oxidants (Sanches *et al.*, 2010), potentially producing a large number of reactions, suitable for multiple treatment objectives. These reactions are highly accelerated, exhibiting rate constants in the range of 10^8 –10^{10} M^{-1} s^{-1} (Parsons, 2004) – an order of magnitude faster than molecular ozone.

Contaminant degradation rates are generally proportional to the rate constant for the species with $^.OH$ radical. However, the degradation rates can be impacted by background organic compounds present in source water (Hoigne, 1988) and scavengers of $^.OH$ such as organic carbon and bicarbonate/ carbonate ions (Wu and Linden, 2008). Under such circumstances complete mineralisation may only be achievable at extended treatment times and with excessive chemical usage, unlikely to be economically or practically favourable at larger scales (Wadley and Waite, 2004).

UV based AOPs are gaining particular interest worldwide from a regulatory perspective for drinking water and for providing additional protection barriers for water remediation applications.

2.2.2 Ultraviolet (UV) photolysis

The application of UV for disinfecting water dates back to several decades in Europe in particular. In more recent years the use of chlorine as a primary disinfectant has started to be phased out in some regions due to its limited ability to effectively inactivate some micro-organisms, and specifically *Cryptosporidium* (Craik *et al.*, 2001), without generating significant levels of disinfection by-products. Conventional sources of UV radiation (200-400 nm) for water treatment comprise low pressure (LP-UV) and medium pressure (MP-UV) mercury (Hg) lamps with high and low intensities. LP lamps emit essentially monochromatic light at 253.7 nm, whilst MP polychromatic light sources emit in the wavelength range of 200 – 800 nm. Apart from their difference in spectral wavelength, LP lamps offer more efficiency, consume less power and have a longer lamp life (Stefan, 2004), compared to the smaller footprint and higher output provided by the MP lamps. The optimal wavelength for disinfection is UV-C, or the germicidal range (200 – 280 nm), provided by both lamp types.

UV light also provides a means of degrading organic matter through a direct photolysis. This can be effective for compounds that exhibit large molar absorption coefficients and high quantum yields across the lamps emission spectrum (Wu and Linden, 2008). The energy associated with the molecular bonds must be lower than that absorbed from the UV photons to initiate photolysis (Bolton, 2001). These factors must be considered in lamp selection, since the wavelength spectrum needs to be within the range of the target pollutant. The process performance is also affected by various water quality components, such as UV transmittance (UVT), turbidity/ suspended solids and foulants such as organic matter and iron that can precipitate onto the quartz sleeves (Linden *et al.*, 2004). In general, the relative efficiency of UV photolysis in degrading most micropollutants is low, but in combination with a chemical oxidant their elimination rate can be greatly enhanced.

2.2.3 UV and hydrogen peroxide (UV/H_2O_2)

The UV/H_2O_2 process is among the most studied AOPs and has become a key polishing step in full scale systems for wastewater reuse (Royce *et al.*, 2010). UV-photolysis of H_2O_2 activates the formation of ·OH by homolytic cleavage of the central HO-OH bond (Clarke and Knowles, 1982; Chang and Young, 2000), yielding the formation of two ·OH per mole of H_2O_2.

$$H_2O_2 + h\nu \rightarrow 2\bullet OH \tag{2-1}$$

The efficiency of the reaction pathway is limited by the low molar absorption coefficient of H_2O_2 at 254 nm (19.6 M^{-1} cm^{-1}; Baxendale and Wilson, 1957), demanding a high H_2O_2 concentration to generate sufficient ·OH radicals. However, high concentrations of H_2O_2 cause scavenging of the ·OH radicals, impairing the process efficacy (Wang *et al.*, 2000).

$$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O \tag{2-2}$$
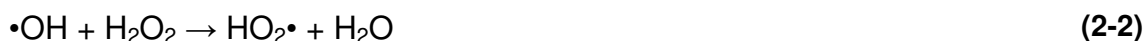
2.2.4 UV and ozone (UV/O_3)

Ozone (O_3) has traditionally been used for disinfection and oxidation (taste and odour control, colour removal and micropollutant detoxification) in drinking water treatment plants (Langlais *et al.*, 1991; Hoigne, 1998; von Gunten, 2003). However, it is a selective oxidant compared to ·OH, and the production of ·OH radicals via O_3 decomposition is relatively low. Combining ozone with UV irradiation, H_2O_2, or both, enhances ·OH generation.

The photolysis of O_3 by UV leads to the formation of H_2O_2 and O_2, whereby H_2O_2 reacts further with O_3 to produce the ·OH radical (Bolton, 2001).

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \tag{2-3}$$

$$O_3 + H_2O_2 \rightarrow 2 \bullet OH + 3 O_2 \tag{2-4}$$

$$H_2O_2 + h\nu \rightarrow 2 \bullet OH \tag{2-5}$$

This process can be extremely effective because of its high oxidation potential as a result of the high molar absorption coefficient at 254 nm of O_3 (3301 M^{-1}

cm^{-1}; (Gottschalk *et al.*, 2000) as well as contaminants being exposed to both oxidants. The production of O_3 incurs relatively high capital and operational costs, and ozonation also leads to the generation of bromate (a carcinogenic DBP) in waters containing bromide (IJpelaar *et al.*, 2002). Nonetheless, this particular process has been extensively applied to groundwater treatment (Collivignarelli and Sorlini, 2004).

2.2.5 UV and titanium dioxide (UV/TiO$_2$)

Although one of the least established and commercially developed AOPs for full-scale treatment, UV/TiO$_2$ has been demonstrated at bench scale to decompose natural organic matter (NOM) (Huang *et al.*, 2008; Gerrity *et al.*, 2009) as well as providing disinfection (Pablos *et al.*, 2013). The process does not require any chemical addition to produce ·OH radicals, which are generated by virtue of the semiconductor properties of the TiO$_2$. TiO$_2$ acts as a photocatalyst when exposed to UV at irridation wavelengths less than 380 nm (Tran *et al.*, 2009). Energetically excited electrons transfer from valence to the conductance band, thereby creating highly reactive charged holes – at an oxidation potential higher than fluorine – and subsequently ·OH radicals. Compounds are either directly oxidised in solution or degraded on the surface of the TiO$_2$ particle.

Using TiO$_2$ has several advantages in that it is relatively inexpensive to produce, is largely inert and not harmful to the environment. Additionally, the photocatalyst process can be powered by a renewable energy source using natural solar radiation, although this source of UV light is limited in the UV-A wavelength radiation required for photoactivation of the catalyst (Ljubas, 2005). There are also engineering issues surrounding the separation of the TiO$_2$ from the treated water.

2.3 Micropollutants removal

2.3.1 Introduction

The ongoing development of analytical methods has revealed a large number of chemicals of possible concern detectable at trace levels in the environment.

Typically referred to as micropollutants (MPs), these are chemicals considered to cause potentially adverse health effects at concentrations in the milligram/nanogram per litre range (WHO, 2004; Holm, 2011), which originate predominately from anthropogenic sources (industry, agriculture and domestic households).

Environmental quality standards for several organic MPs that may be released into surface waters have been promulgated via regulations such as the European Water Framework Directive (WFD) (EC, 2000). However, there are several other emerging contaminants of concern (ECC) that are currently unregulated and are not monitored, particularly in wastewater effluents. These include endocrine disrupting compounds (EDCs), pharmaceuticals, disinfection by-products (DBPs), pesticides/herbicides and personal care products (PCP). Unknown health and environmental risks associated with some of these contaminants and their treatability pose significant challenges to wastewater reclamation, especially for waters intended for human consumption. The occurrence and fate of major emerging contaminants in various water bodies, including wastewaters has been studied (Ternes and Joss, 2006; Auriol *et al.*, 2006) and monitored across various advanced and conventional treatment processes (Snyder *et al.*, 2007; Gonzalez *et al.*, 2007; Ruel *et al.*, 2011).

2.3.2 Disinfection by-products (DBPs)

One more established group of concern are DBPs, produced from the reaction of NOM with chlorine, to form trihalomethanes (THMs) and halocetic acids (HAA), or chloramines to generate *N*-nitrosodimethylamine (NDMA). NDMA is a highly recalcitrant compound attributed to its hydrophilic properties, poor biodegradability and low molecular weight and volatility (Mitch *et al.*, 2003). Ancillary processes such as membranes, air stripping and granular activated carbon (GAC) are unable to adequately remove NDMA. A maximum removal of 65-70% has been reported for reverse osmosis (RO) (Krauss *et al.*, 2010; Joss *et al.*, 2011), presenting a risk to wastewater reuse plants applying chloramination to control biofouling (Farre *et al.*, 2011).

Direct UV photolysis has been largely cited as an efficient treatment process for eradicating NDMA because of a favourable quantum yield and molar absorption coefficient, i.e. strong absorbance at 225-250 nm radiation (Mitch *et al.*, 2003; Sharpless and Linden, 2003). Removal can be marginally enhanced in acidic conditions (Stefan and Bolton, 2002) and with ·OH radical (Lee *et al.*, 2007). However, the presence of NOM and nitrates has been shown to restrict NDMA destruction (Liang *et al.*, 2003) and the yield of UV by-products (nitrite, assimilable organic carbon (AOC)) can be higher at lower wavelengths (Toor and Mohseni, 2007). AOP removal of the halogenated derived DBPs (THMs and HAAs) has focussed on reducing the concentration of precursors, specifically NOM. Fenton's and photo-Fenton processes have been demonstrated to remove over 90% of dissolved organic carbon (DOC) in upland catchment waters. However, the UV/H_2O_2 process achieved only a ~65% reduction over a longer reaction time (Murray and Parsons, 2004). Similar outcomes were also observed by Goslan *et al.*, (2006). Chin and Bérubé (2005) observed substantial DOC mineralisation from applying UV/O_3 as well as reduction in THM and HAA formation potential (THMFP & HAAFP). Combined UV/TiO_2 also produced a significant degradation of DOC, although higher concentrations of TiO_2 were required and THMFP was shown to be slightly elevated (Gerrity *et al.*, 2009).

2.3.3 Pesticides

The use and type of pesticides for wide-ranging applications within the agricultural sector has developed significantly over the past 50 years, and these can readily contaminate raw drinking water sources through run-off. Among those of concern in drinking waters are atrazine and, most recently, metaldehyde. Atrazine is identified as a priority pollutant in the European WFD (EC, 2000) because of its environmental persistence and detrimental health affects (Hincapié *et al.*, 2005). The detection of metaldehyde has been widely reported in UK water sources (Water UK, 2009) and is not readily removed by conventional water treatment technologies (GAC and ozone) (Autin *et al.*, 2012).

Bench scale experiments conducted by Sanches et al., (2010) revealed efficient degradation of atrazine, diuron and other pesticides through applying LP UV photolysis (dose of 1500 mJ cm^{-2}). The addition of oxidants (TiO$_2$ and H$_2$O$_2$) had very little impact on the overall removal rate as identified with NDMA (Sharpless and Linden, 2003). Isoproturon was not readily degraded by the AOPs applied. In other research, a 90% conversion of atrazine was recorded (Chiron et al., 2000; Ijpelaar et al., 2002), though the latter study concerned surface waters at a UV dose of 3000 mJ cm^{-2} - highlighting the importance of UVT. Autin et al., (2012) investigated UV/H$_2$O$_2$ and UV/TiO$_2$ to remove metaldehyde to a comparable extent, though the TiO$_2$ process was inhibited by background organics in natural waters.

2.3.4 Endocrine disrupting compounds (EDCs)

EDCs are widespread in the environment and consist of natural oestrogens (estrone (E1) and 17β-estradiol (E2)) along with synthetic xenoestrogens (17 α-ethynylestradiol), phthalates and many more, that have been shown to affect/interfere with the action of hormones in the endocrine system (Jobling et al., 1998). Sewage effluents have been identified as being a major source of natural estrogenic chemicals in the aquatic environment (Desbrow et al., 1996; Folmar et al., 1996), receiving much interest over the last twenty years. Although partial biological removal of EDCs is recognised from conventional WWTP (Ternes and Joss, 2006), the reported data on reliability and extent of treatment is limited.

The application of a UV/H$_2$O$_2$ AOP was found to be effective in degrading E2, EE2 and bisphenol A (>90%) compared to direct UV photolysis in natural waters (Rosenfeldt and Linden, 2004). Liu and Liu (2004) also observed similar results for E1 and E2, though photolysis rates were increased with MP lamps and at a higher pH value. In a subsequent study (Linden et al., 2007), the EDC breakdown products following AOP (UV/H$_2$O$_2$) were examined, showing no transformation of oestrogenic activity. This was also identified by Benotti et al., (2009), who applied UV/TiO$_2$ to natural surface waters and found that that an

energy demand of 0.53 kWh m^{-3} was needed to remove most EDCs to below the detection limit.

2.3.5 Pharmaceuticals and Personal care products (PCPs)

Over the past few years much attention has been paid to pharmaceutically active compounds (PhACs) and PCPs (i.e. detergents, antimicrobials etc) detected in various aqueous matrices. Though generally found at low concentrations (ng L^{-1}), as with EDCs the long-term exposure to such chemicals poses a potential risk to the environment and humans. Studies have highlighted that PCPs and PhACs are not adequately biodegraded by conventional WWTP (Okuda *et al.*, 2008), requiring advanced treatment to satisfy water reuse standards. Klavarioti *et al.* (2009), in reviewing AOPs for removing PhACs, concluded that compounds are easily degraded to detection limits in ground and surface waters but that the economics were unfavourable. Varied degradation rates for PhACs have been reported from applying UV/H$_2$O$_2$ to wastewaters as at different effluent organic matter (EfOM) concentrations (Rosario-Ortiz *et al.*, 2010)

2.4 Summary

AOPs have been proven to eradicate a wide range of trace organic micropollutants in various water matrices. UV/H$_2$O$_2$ and UV/O$_3$ provide the most established technologies and have been applied at full scale for drinking water and wastewater reclamation. Heterogeneous photocatalytic processes, such as UV/TiO$_2$, are attracting increasing attention because of their potential to be powered by renewable energy sources (i.e. solar irradiation) as well as using low cost consumables. However, there remain several engineering challenges that require further development before full-scale implementation. MP removal efficiency is shown to be impacted by the presence of inorganic compounds (bicarbonate/ carbonate) and NOM in the treated water.

The theory, kinetics and mechanisms behind photo-oxidation are generally well understood (Crittenden *et al.*, 1999). Thus, the present research is giving more attention to the optimisation and design of UV based AOPs, considering their

relatively high energy consumption and intensive use of chemicals. One area of ultimate concern is the chemical nature (and specifically toxicity) and extent of formation of degradation by-products (including biodegradable organics). Even though literature data exists on this issue, there remains a paucity of knowledge relating to pharmaceutical and PPCP by-products in particular.

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3 Advanced oxidation for micropollutant removal in wastewater reuse: efficacy and relative operational cost

James, C.P., Germain-Cripps, E., MacAdam-Sproat, J., Judd, S., 2013. Advanced oxidation for micropollutant removal in wastewater reuse: efficacy and relative cost. Submitted to *Water Research*.

3.1 Introduction

Over the past 20 years, there has been an increased awareness of the incidence of certain micropollutants (MPs) in the environment and a concomitant increase in the study of their fate and removal by water treatment technologies. This is particularly germane to recovered and reused wastewater, which demands implementation of advanced treatment technologies to attain water of a quality comparable to treated raw waters with respect to the MP levels.

MPs are chemicals considered to cause potentially adverse health effects at concentrations in the milligram/nanogram per litre range (WHO, 2004; Holm, 2011). They may originate from natural or anthropogenic sources, such as industry, agriculture and domestic households. Environmental quality standards for several organic MPs that may be released into surface waters have been promulgated via regulations such as the European Water Framework Directive (WFD) (EC, 2000). However, there are several other emerging chemicals of concern that are currently unregulated and not monitored, particularly in wastewater effluents. Specifically, the difficulty in effectively managing and reliably treating diffuse sources of pollution poses a significant challenge to wastewater reclamation, especially if intended for human consumption. Moreover, most national drinking water standards, e.g. as prescribed by Drinking Water Directive (EC, 1998) in Europe, have not incorporated specific regulations for most MPs.

Research into removal or fate of MPs has mainly focused on organic compounds often classified as disinfection by-products (DBPs), pharmaceuticals, pesticides, and endocrine disrupting compounds (EDCs).

EDCs are widespread in the environment and consist of natural oestrogens (estrone (E1) and 17β-estradiol (E2)) along with synthetic xenoestrogens (17 α-ethynylestradiol), phthalates and many more, that have been shown to affect/interfere with the action of hormones in the endocrine system (Jobling *et al.*, 1998). Sewage effluents have been identified as being a major source of natural estrogenic chemicals in the aquatic environment (Desbrow *et al.*, 1996; Folmar *et al.*, 1996). Research conducted over the past 15-20 years has highlighted the limited removal capability of conventional wastewater treatment systems to levels that are deemed acceptable according to Environment Agency (2004) predicted no-effect concentration (PNEC) guideline values for ecological protection.

The use and type of pesticides for wide-ranging applications within the agricultural sector has developed significantly over the past 50 years, and these can readily contaminate raw drinking water sources through run-off. Regulatory limits for pesticide levels in EU drinking waters are 0.1 µg L^{-1} for an individual pesticide and 0.5 µg L^{-1} in total. Among those of concern in drinking waters are atrazine and, most recently, metaldehyde. The latter has been shown to be widely detected in UK water sources (Water UK, 2009) and is not readily removed by conventional water treatment technologies (Autin *et al.*, 2012).

Advanced oxidation processes (AOPs) have been identified as a promising alternative to conventional treatment for removing organic constituents in contaminated waters. They are characterised by the generation of highly reactive and non-selective hydroxyl radicals (HO$^.$). The UV/H_2O_2 process is among the most studied AOP and reported to be effective at degrading recalcitrant MPs, including NDMA (Poussade *et al.*, 2009) and various pharmaceuticals and EDCs (Drewes *et al.*, 2002; Snyder *et al.*, 2007) for indirect potable reuse (IPR). A UV/H_2O_2 step may be installed as a final step in IPR schemes following reverse osmosis (RO) to remove traces of compounds permeating the RO membrane (Royce *et al.*, 2010). AOPs can potentially achieve full mineralisation, or at least degradation to less potent products (Bolton, 2001), whereas RO leaves MPs unchanged in the waste stream,

demanding further management. Both processes are energy and chemically intensive.

Previous studies of MP fate using UV/ H_2O_2 treatment have been primarily determined at trace level concentrations or conducted at bench scale to elucidate degradation mechanisms and H_2O_2 ratio for process optimisation. Therefore further research is required, particularly at pilot scale, for representative water quality and operational conditions to assess the true cost benefit or penalty of the process. This study reports the effectiveness of UV/ H_2O_2 for the degradation of selected MPs of emerging concern and focused on highly recalcitrant compounds, particularly metaldehyde, that currently present a significant challenge to the water industry. The cost and performance of the AOP for removal of such compounds for different feedwater qualities, and specifically transmittance, were compared to that of other candidate processes. The key operating parameters of UV and H_2O_2 dose were adjusted and the impact on metaldehyde destruction evaluated.

3.2 Materials and methods

3.2.1 Pilot plant and chemical reagents

The pilot plant (Fig. 3-1), details of which are provided elsewhere (Raffin *et al*, 2011), treated 600 m^3 d^{-1} of final effluent from a conventional activated sludge (CAS)-based wastewater treatment works. The process consisted of a pre-filter, microfiltration (MF), reverse osmosis (RO) and a advanced oxidation process (AOP), based on a combination of UV irradiation and H_2O_2 dosing (UV/H_2O_2), downstream of the MF (AOP1) and the RO (AOP2).

Each AOP comprised a flow-through UV reactor (Trojan UVPhox[TM], Model 12AL30) equipped with 12 low-pressure/high-output (LP/HO) amalgam lamps with nominal output power from the lamps varies from 60 to 100%, with an automatic sleeve wiping and clean-in-place (CIP) system, the latter using citric acid for iron fouling mitigation (or scaling on the quartz sleeves, i.e. fouling). H_2O_2 was dosed upstream of both UV reactors with static mixers in-line. UV transmittance (at 254 nm), intensity and power were monitored online for each

reactor, along with temperature, and independent flowmeters fitted to each stream. Selected MPs (Table 3-4) were dosed at concentrations generally between 0.2 and 2 µg L^{-1} into the feed via glass ampoules and/or pipetted from solutions of the compounds dissolved in water/acetone. Acetone added up 15% to the organic carbon, but assumed to be inert under the AOP operating conditions employed, based on previous studies (Hernandez *et al.*, 2002). All MPs were of an analytical grade and provided by Sigma Aldrich, with the exception of the EDC compounds (*E1*, *E2* and *EE2*) which were from QMX Laboratories (Essex, UK).
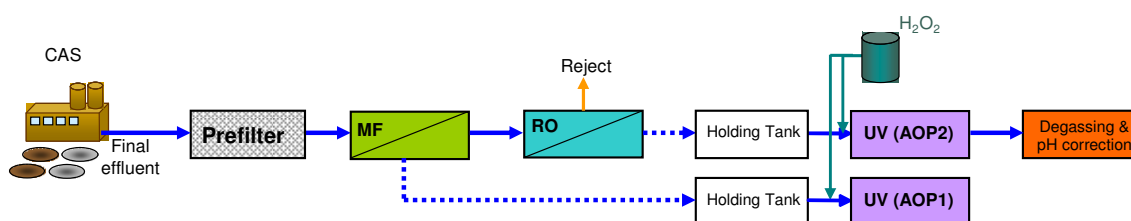
Figure 3-1   Pilot plant schematic

3.2.2 Experimental procedure

Feed water quality was varied by blending of the MF and RO permeate streams (Table 3-1). Selected MPs were then dosed at concentrations generally between 0.2 and 2 µg L^{-1}. Concentrations were based on those typically arising in secondary wastewater, as identified in the literature and regulatory guidelines (WSR, 2010), or else constrained by their limit of detection as advised by the laboratory (Thames Water Analytical Laboratories, Reading). Spiking in this manner allowed percentage removal values to be accurately calculated due to trace levels detected in pilot plant feed and membrane product waters for the compounds studied (Appendix A). Operating conditions for each AOP stream (Table 3-2) were determined from the optimum UV lamp input power and H$_2$O$_2$ dose for each AOP stream for efficient removal of target MPs to the required log reduction, based on outcomes of scoping trials.

Chemicals were prepared to a required concentration and dosed directly into a 1 m^3 storage tank, fitted with a submersible mixing pump, for holding the

MF/RO permeate or blend. This feedwater was pumped to the UV unit with in-line H_2O_2 dosing upstream of a static mixer at flow rates of 1-3 m^3 h^{-1}, providing residence times of 120-180 seconds. Each experiment lasted ~40 mins, comprising feed solution mixing for 20 minutes followed by 20 minutes of AOP treatment with accompanying sampling of inlet and outlet streams.

A daily 5 wt% citric acid CIP was performed on AOP1 to minimise sleeve fouling. The reactor was flushed through with the normal permeate stream following each experiment. Experiments were conducted separately for the DBP compounds and metaldehyde to ensure no competition between the two sets of reactions; the EDCs, pesticides and herbicides were combined in the same bulk feedwater solution as applied in other studies (MWH Global, 2007). Duplicate samples were taken from the feed tank and triplicate samples collected post AOP at various intervals (5, 10, 15 minutes) for each MP compound. Tests were repeated for any apparently anomalous results.

Sampling and analysis was conducted for MPs along with standard sanitary determinants. All compounds were analysed by Thames Water Laboratories (Reading, UK), other than THMs which were assayed by Severn Trent Services (Coventry, UK). EDCs, atrazine and terbutryn were analysed by liquid chromatography with mass spectrophotometric detection (MS), whilst the remaining herbicides, metaldehyde and NDMA were analysed by gas chromatography (GC). THMs were analysed by purge-and-trap GC with MS. H_2O_2 concentration was determined with a photometric cell test Spectroquant Nova 60, from Merck. UV absorbance of samples (UV_{254}) was measured using a Genesys 10 UV spectrophotometer (Thermo Fisher Scientific Inc.). TOC was measured with an AstroTOC analyser from Hach Lange (Hach Lange Ltd., Salford, UK).

The optimisation trials were based on metaldehyde, the most recalcitrant of the micropollutants examined. Three equally-spaced H_2O_2 doses and power inputs were employed with each stream (MF permeate, RO permeate, and Blend) and correlated with metaldehyde removal (Table 3-3). This approach allowed Box-Behnken programme design (Box and Behnken, 1960; Raffin et al., 2011) to be

applied, reducing the number of experiments for a three-level, three-parameter study from 27 for a 3^n factorial design to 15. From this, the influence of the three operating parameters (H_2O_2, Power Input & UV-transmittance) can determine the inputs required to achieve an optimum removal of metaldehyde.

Table 3-1 Mean and standard deviation values of feedwater quality parameters for each stream.

Compound	Unit	MF permeate	RO permeate	MF/RO Blend
Alkalinity as $CaCO_3$	$mg.L^{-1}$	212 ± 12.4	< 16	-
Conductivity	$\mu S\ cm^{-1}$	1061 ± 15.3	20.8 ± 2.35	-
pH		7.3 ± 0.07	5.5 ± 0.05	7.14 ± 0.14
Hardness Total as $CaCO_3$	$mg.L^{-1}$	332.9 ± 16.7	< 29	-
Total Organic Carbon (TOC)	$mg.L^{-1}$	7.7 ± 0.73	0.2 ± 0.17	4.85 ± 0.11
Turbidity	NTU	0.14 ± 0.21	0.08 ± 0.02	-
UV absorbance at 254 nm (UV_{254})	cm^{-1}	0.18 ± 0.002	0.001 ± 0.002	0.11 ± 0.008
UV transmittance (UVT)	%	66 ± 0.82	98.8 ± 0.41	76.2 ± 1.44
Specific UV Absorbance (SUVA)	$L.mg^{-1}.m.$	2.34	0.5	2.26

Table 3-2 Operational conditions for the AOP spiking trials

Parameter	AOP1	AOP2
Feed water	MF filtrate	RO permeate
Lamp power set-point (%)	100%	60%
Power Input P / Optimal Range (kWh)	2.82/ 1.68 – 2.82	1.78/ 1.78 – 2.98
Lamp Life (h)	1380	1100
Peroxide dose/ Optimal Range ($mg\ L^{-1}$)	16/ 6-20	3/ 1-3
Treatment capacity ($m^3\ h^{-1}$)	3	3
Reactor volume (m^3)	0.098	0.098
Theoretical contact time (s)	approx. 120	approx. 120

Table 3-3   Parameters and their levels for Box-Behnken analysis

Param. #	Parameters	Levels
X_1	H_2O_2 dose (mg L^{-1})	3, 9.5, 16
X_2	UV-T (%)	65, 82, 98
X_3	Power input (kWh)	1.68, 2.33, 2.98

Evaluated efficiency values were based on electrical energy per order (E_{EO}), as used by previous workers studying similar AOP systems for performance specification (Bolton *et al*, 2001). In addition, specific energy demand (E_D) was also calculated to provide values where actual contaminant concentrations failed to achieve a 90% (or 1 log) reduction and to benchmark against other advanced technologies such as RO. E_{EO} is defined as the electrical energy in kWh required to reduce the concentration of a contaminant by one order of magnitude in 1 m^3:

$$E_{EO} = P/F \log (c_i/c_f) \tag{3-1}$$

where P is the electrical power (kW) of the UV system, F is the flow rate (m^3/ h), and C_i and C_f the initial and final contaminant concentrations (mg L^{-1}). E_D is the electrical energy (kWh) consumed per unit volume (1m^3) of water treated:

$$E_D = Pt/60V \tag{3-2}$$

where P is the electrical power (kW) of the UV system, t is the time (h) and V the volume of water treated (m^3).

3.3 Results and discussion

3.3.1 MP removal

Measured concentrations (Table 3-4) revealed all the MPs studied with the exception of TTHMs to be removed by at least 98% when applying AOP to the RO permeate at an H_2O_2 dose of 3 mg L^{-1} and an E_D of 0.62 kWh m^{-3}. In contrast, application to the MF permeate was much less effective in removing

herbicides and pesticides generally, and metaldehyde in particular. Even at very high H_2O_2 doses of 16 mg L^{-1} with E_D levels of 0.93 kWh m^{-3}, metaldehyde removal remained below 50%. Estrogenic substances (E1, E2 and EE2), on the other hand, were readily degraded (>99%) in both streams. These observations are consistent with those reported elsewhere (IJpelaar et al., 2010; Rosenfeldt and Linden, 2004) for UV doses of 600-1000 mJ cm^{-2} and H_2O_2 concentrations of 10-15 mg L^{-1}; >90% removal of these compounds was reported based on bench-scale UV/H_2O_2. Further analysis of the THMs revealed chloroform to be particularly recalcitrant even at higher UV doses applied to the higher-purity AOP2 steam. It is widely recognised that chloroform is resistant to oxidation (Pera-Titus et al., 2004), as evidenced by a second order rate constant value ~60 times lower than that of NDMA for reaction with $^{\cdot}$OH (Sharpless and Linden, 2003a; Crittenden et al., 2005).

Table 3-4   Micro-pollutant removal results for Post MF and RO streams under optimum process conditions (power input and H_2O_2 dose).

Stream	Classifi-cation	Compound	Inlet Conc. ($\mu g.l^{-1}$)	% removal	Log reduction	UV Dose (mJ cm^{-2})	E_D (kWh m^{-3})	E_{EO} (kWh m^{-3})
AOP 1 (post-MF)	EDC	E1 Estrone	0.2	99	2.16	695	0.95	0.44
	EDC	E2 17- β Estradiol	0.2	99	2.11	695	0.95	0.45
	EDC	EE2 α Ethinyl Estradiol	0.2	99	2.32	695	0.95	0.41
	Herbicide	2,4-D	1	89	0.98	727	0.95	-
	Herbicide	Mecoprop	1	98	1.61	727	0.95	0.59
	Herbicide	2,4 5-T	1	85	0.83	727	0.95	-
	Pesticide	Atrazine	2	88	0.92	713	0.95	-
	Pesticide	Terbutryn	2	96	1.38	713	0.95	0.69
	Volatile	NDMA	0.2	98	1.62	678	0.95	0.59
	Pesticide	Metaldehyde	2	45	0.26	739	0.93	-
	Volatile	TTHM	50	52	0.32	739	0.94	-
AOP 2 (post-RO)	EDC	E1 Estrone	0.2	99	3.25	2026	0.62	0.19
	EDC	E2 17- β Estradiol	0.2	99	3.21	2026	0.62	0.19
	EDC	EE2 α Ethinyl Estradiol	0.2	99	3.18	2026	0.62	0.19
	Herbicide	2,4-D	1	99	2.72	1825	0.62	0.23
	Herbicide	Mecoprop	1	99	2.60	1825	0.62	0.24

Stream	Classification	Compound	Inlet Conc. ($\mu g.l^{-1}$)	% removal	Log reduction	UV Dose ($mJ\ cm^{-2}$)	E_D (kWh m^{-3})	E_{EO} (kWh m^{-3})
	Herbicide	2,4 5-T	1	99	2.70	1825	0.62	0.23
	Pesticide	Atrazine	2	98	1.62	1775	0.62	0.39
	Pesticide	Terbutryn	2	99	2.40	1775	0.62	0.26
	DBP	NDMA	0.2	99	2.39	1845	0.62	0.26
	Pesticide	Metaldehyde	0.2	98	1.70	2003	0.62	0.36
	DBP	TTHM	0.2	68	0.50	1861	0.60	-

Differences in measured removal between the two permeate streams reflect those in UV transmittance (UVT) (Table 3-1), which is near total for the RO permeate compared with only 65% for the MF permeate. Higher doses of H_2O_2 in AOP1 were thus needed to compensate for the lower photon absorption efficiency (Tuhkanen, 2004). Moreover, competition for $\cdot$OH was greater in the MF stream due to significantly higher levels of scavengers (organic carbon, chloride and bicarbonate/carbonate ions), manifested as a higher E_{EO} value. pH would also be expected to influence oxidation efficiency since increasing pH converts more of the dissolved CO_2 to bicarbonate and so promotes scavenging (Liao and Gurol, 1995). However, reducing the MF permeate pH from ~7.2 to 5.5 was found to produce only a marginal increase (<10%) in metaldehyde removal efficiency. Other contributory factors, such as scaling/fouling of the lamp sleeves and other MF permeate water quality parameters (Stefan, 2004), would also be expected to reduce UV intensity and so AOP efficacy.

3.3.2 Metaldehyde removal

Tests conducted on metaldehyde specifically demonstrated increased removal with increasing UV and H_2O_2 dose (Fig. 3-2). However, metaldehyde was only significantly removed when the AOP was applied to the RO permeate, since the received UV dose was around five times greater than that for the MF permeate. Removal exceeded 95% at a peroxide dose of 2 mg L^{-1} and an E_D of ~0.7 kWh m^{-3} (Fig. 3-3). Other studies have reported similar removal rates (Autin $et\ al.$, 2012), citing lower UV fluences of 600 mJ cm^{-2} for laboratory grade water, but at considerably higher H_2O_2 doses of 272 mg L^{-1}.

For MF permeate, energy inputs above 0.75 kWh m^{-3} achieved no more than 40% removal (Fig. 3-3). Removal from MF permeate at a UV dose of around 460 mJ cm^{-2} ranged from 3 to 45% according to H_2O_2 concentration (Fig. 3-4). However, it should be noted that an increase in UV dose did not always show a linear relationship with metaldehyde removal as observed in Figure 3-2 at H_2O_2 doses of 9 and 20 mg L^{-1}. These anomalous results could relate to a change in the peroxide concentration (lower dose applied) or water quality conditions i.e. increased radical scavengers, therefore impeding the efficacy of the treatment process. In addition, the analytical error margins observed for 9mg L^{-1} of H_2O_2 at a UV dose of ~220 mJ cm^{-2} (see Fig. 3-2) is relatively substantial (25%) and cannot be ruled out as underlying factor.

The high UV doses required for metaldehyde destruction, could suggest that direct photolysis has a significant influence. Removal is, however, improved by the H_2O_2 addition, particularly in poorer water quality. A higher H_2O_2 concentration may thus further increase degradation, provided the peroxide itself does not scavenge the hydroxyl radicals at these high concentrations as suggested by other authors (Galbraith *et al.*, 1992). The relationship between UV dose and energy demand for each stream (Figure 3-5) indicates that higher UV doses are only attainable at the upper limits of UV transmittance at comparable energy demand. UV doses above 2000 mJ cm^{-2} with >2 mg L^{-1} H_2O_2 appear sufficient to attain >90% removal of metaldehyde.
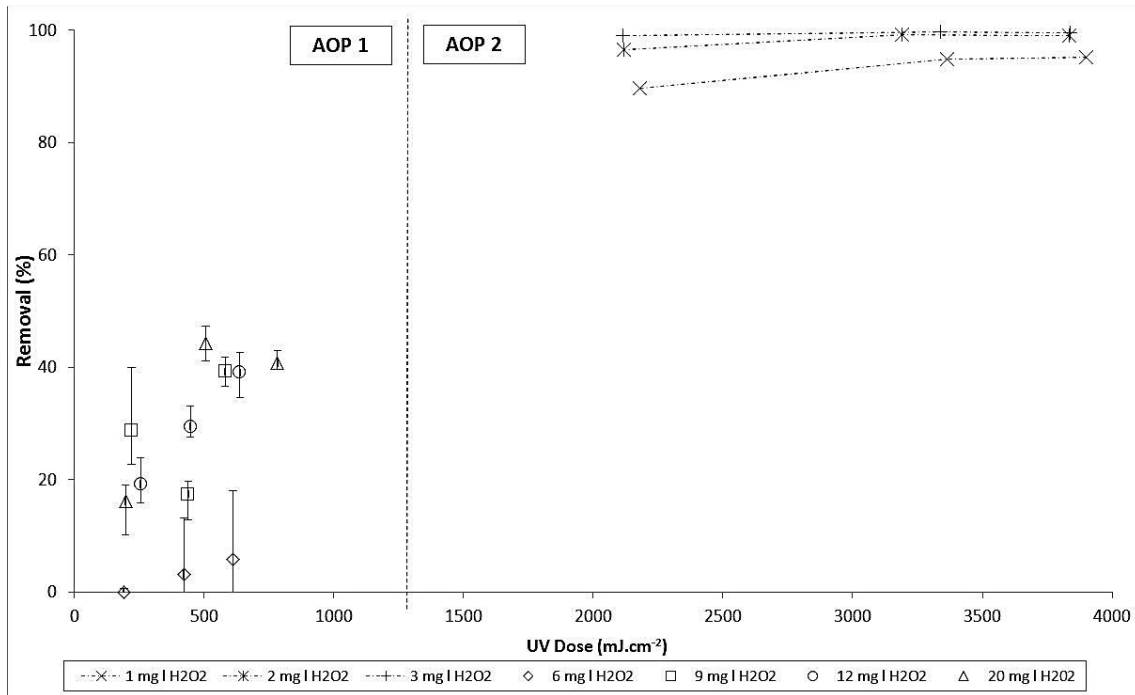
Figure 3-2   Effect of UV and H₂O₂ dose on the removal of metaldehyde from MF permeate (AOP1) and RO permeate (AOP2).
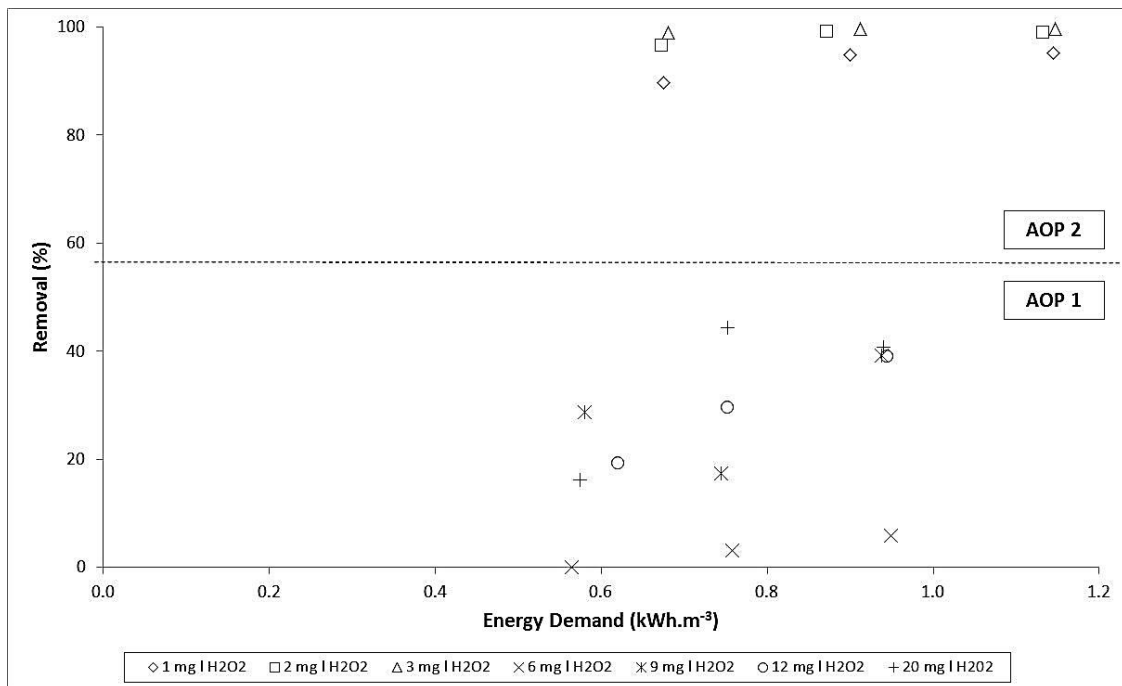
Figure 3-3   E_D data for metaldehyde degradation in MF (AOP1) and RO (AOP2) permeate as a function of H₂O₂ dose.
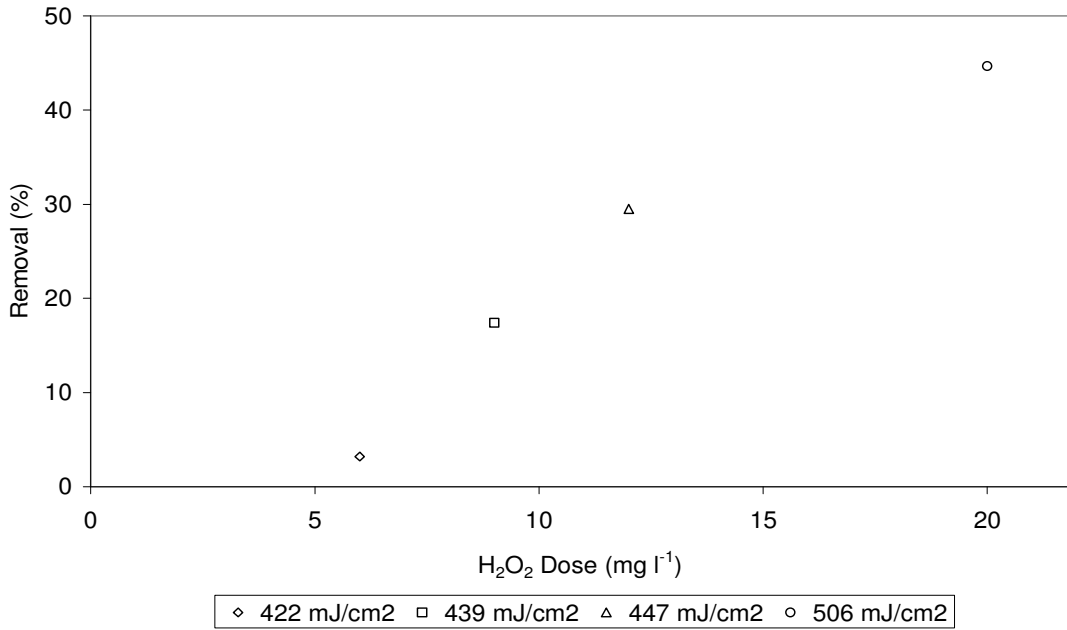
Figure 3-4   Metaldehyde removal from MF permeate as a function of H_2O_2 dose at a UV dose of 422-506 mJ cm^{-2} and a power of 2.25kW.
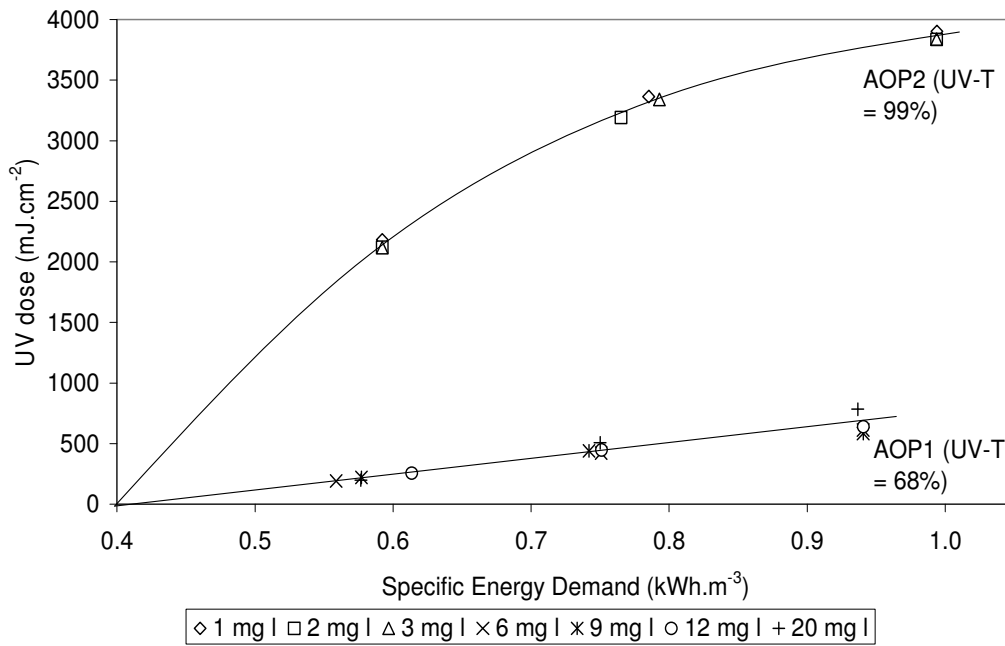
Figure 3-5   Influence of UVT on the UV dose output as a function of energy input at various H_2O_2 concentrations (1-20 mg L^{-1}) in streams AOP 1 and 2.

3.3.2.1 Effect of residence time

Figure 3-6 shows the influence of retention time (RT) on metaldehyde removal from the MF permeate. Removal appears to increase from 40% to >75% on trebling RT from around two minutes, depending upon the power applied. UV intensity levels were increased 1.5-2 fold at extended RTs, relative to the lamp power input (3.1 mW cm^{-2} at 1.67 kW; 8.9 mW cm^{-2} at 2.82 kW). This probably results from improved UV$_{254}$ transmittance (Stefan, 2004), which increased after AOP treatment in all experiments at higher UV doses in particular – presumably as a result of the rupturing of conjugated bonds in the NOM molecular structure (Toor and Mohseni, 2007).
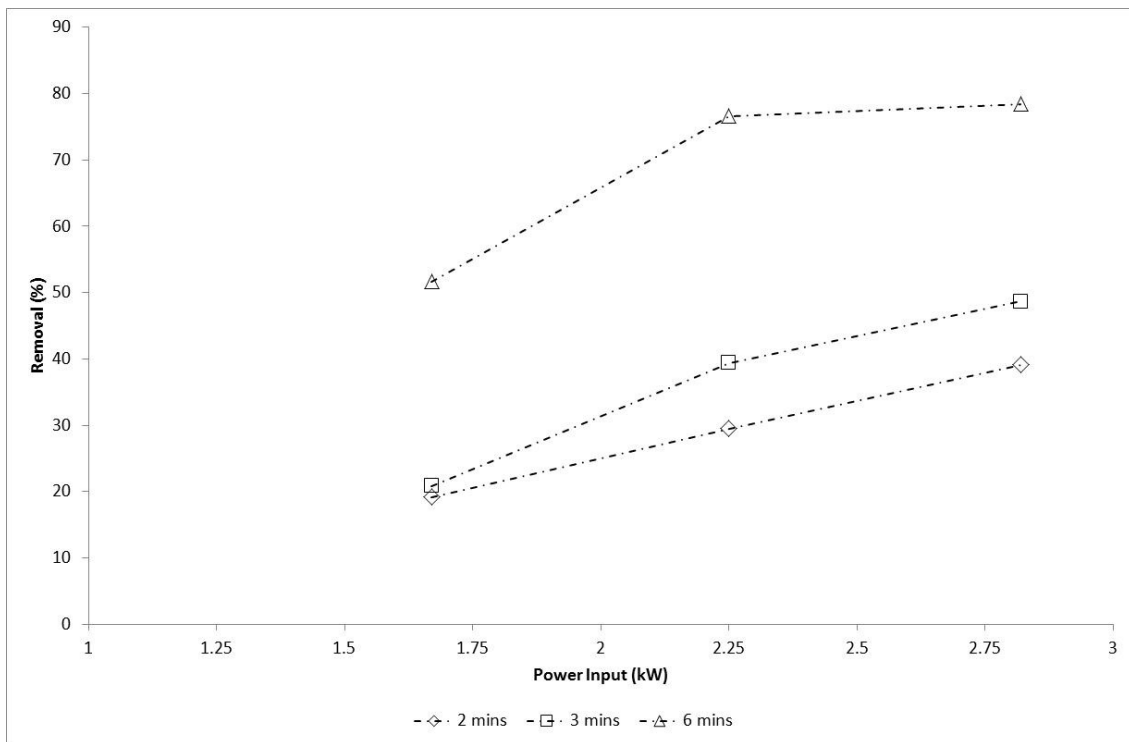
Figure 3-6   **Influence of residence time on the degradation of metaldehyde in MF permeate as a function of power input, 16 mg L^{-1} H$_2$O$_2$.**

3.3.2.2 Effect of UV transmittance

The influence of UV$_{254}$ transmittance (UVT$_{254}$) was studied through blending of the MF and RO permeate streams in conjunction with power input and peroxide dose using a Box-Behnken experimental design based on the levels indicated in Table 3-3.   The analysis (Table 3-5) reveals UVT$_{254}$ and H$_2$O$_2$ dose to be the

only significantly influential parameters on metaldehyde removal (p-value <0.05 for the linear coefficient in both cases). Power input appeared to have no significant impact on metaldehyde reduction, with a p-value of 0.18, probably because of the limited range of power input applied (1.66 - 2.82 kW). The blended MF/RO stream (50:50) increased UVT from ~67% cm^{-1} in the MF stream to ~78% cm^{-1} (Fig. 3-7). Consequently, based on the same conditions optimised for the MF permeate (16 mg.L^{-1} H$_2$O$_2$ and 2.82 kW power input), permeate metaldehyde levels were almost halved: removal was increased from 70 to 87%. UV transmittance thus appears to be a significant parameter in determining the economic viability of AOP treatment for MP removal.

Table 3-5   Statistical analysis results from Box-Behnken experimental design based on metaldehyde removal as the response parameter.

Parameter		Coefficient	P-value
Linear coefficients	Intercept	-570	0.022
	H$_2$O$_2$ dose (mg L^{-1})	16.17	0.014
	UV-T (%)	11.43	0.043
Quadratic coefficients	(H$_2$O$_2$ dose (mg L^{-1}))^2	-0.27	0.101
	(UV-T (%))^2	-0.04	0.117
Interaction coefficients	H$_2$O$_2$ dose (mg l) x UV-T (%)	-0.1	0.086

Removal (%)

100

80

60

40

20

0

0   500   1000   1500   2000   2500   3000   3500   4000   4500

UV Dose (mJ.cm^{-2})

◇ MF UV-T (67%)   □ Blend UV-T (78%)   △ RO UV-T (99%)
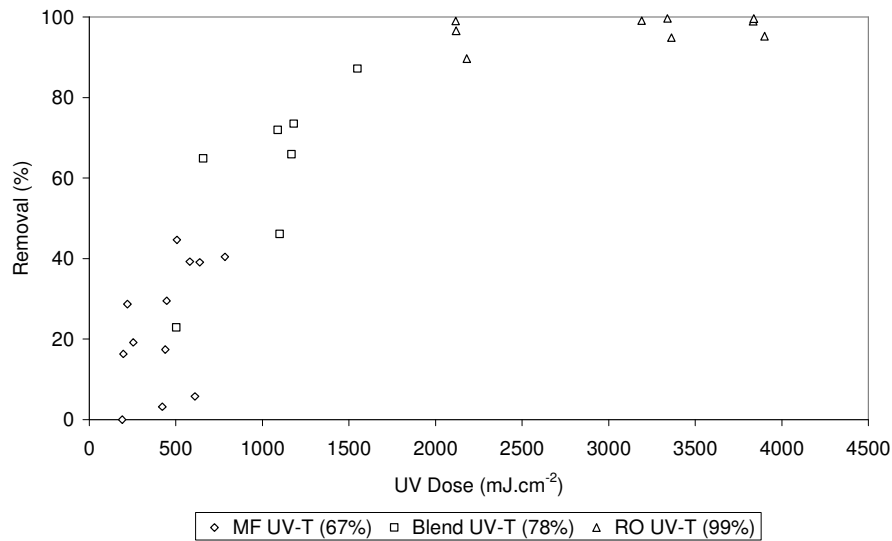
Figure 3-7   Effect of UVT on metaldehyde removal as a function of UV dose and H$_2$O$_2$ concentration, 6-16 mg L^{-1}, on the MF, blended and RO streams at 1.68-2.98kW power input.

3.3.3 Operating expenditure (OPEX)

The operating cost of applying a UV/H$_2$O$_2$ AOP for MP removal is determined primarily by:

- the energy demand of the UV device, which is in turn governed by the water quality,

- the replacement frequency of critical, high-cost components, and

- the hydrogen peroxide demand.

The water quality determines both UV transmittance and the degree of hydroxyl radical scavenging/quenching by bicarbonate and organic matter, which then increases the required dose of both H$_2$O$_2$ and UV (Linden *et al.*, 2007). This is apparent from comparison of the MF and RO permeate data, with MF permeate demanding increased peroxide and energy input to attain practical UV doses.

The individual operating expenditure (OPEX) components are provided in Table 3-6. Correlations of UV dose vs. power input for the upper and lower water quality limits (Fig. 3-5) can be used in conjunction with the trends for

metaldehyde removal vs. (i) UV dose provided at different water qualities (Fig. 3-7), and (ii) peroxide concentration (Fig. 3-4) to generate energy and chemical demand correlations as a function of water quality.

Table 3-6   Treatment conditions and costs assumed for OPEX calculations.

Parameter	MF-AOP	MF-AC-AOP	MF-RO-AOP
E_D, kWh.m^{-3}	2.17	0.77	0.50
UV dose, mJ cm^2	2600	2196	2181
% removal	77	82	80
H_2O_2 dose, mg L^{-1}	16	5	1
OPEX £ m^3			
Energy	0.241	0.092	0.072
Chemicals	0.033	0.008	0.002
Maintenance	0.099	0.099	0.099
TOTAL	0.373	0.199	0.173

It is of interest to compare OPEX values of different treatment options for attaining a nominal target of >75% metaldehyde removal. OPEX values relating to the MF-RO process have been recently reported. A study of municipal wastewater reuse based on the same plant as that employed in the current study provided projected costs of £0.069-0.084 m^{-3} for the MF process and £0.19-0.23 m^{-3} for the complete MF-RO process for flows of 25-100 MLD (Raffin, 2012). This compares with costs of £0.25-0.26 m^{-3} calculated for a similar MF-RO process (Garcia *et al*, 2013) for the same range of flow. The 62% figure for the mean proportion of the MF-RO OPEX attributed to the RO stage is very similar to the same parameter for the proportion of the energy demand (58%) averaged across six MF-RO municipal wastewater reuse plants worldwide (Raffin *et al*, 2013).

Since it is evident that the OPEX of the MF-AOP plant is a function of the UV transmittance, it is appropriate to consider the option of activated carbon (AC) for removing TOC contributing to the UVT$_{254}$. Recent trials (Hatt *et al*, 2013) have explored the options of employing powdered AC upstream of the MF, as

well as downstream granular media beds (GAC). The outcomes suggest that either of these options can achieve 60-70% removal of UVT_{254} from secondary wastewater, at a ~1500 bed volume capacity in the case of GAC. Based on a projected regeneration cost of £0.31-0.44 per kg (Supplier, 2013) and assuming a 5-10% loss of GAC per regeneration, this provides a GAC cost of £0.09 - 0.16 per m^{-3} of water treated.

The computed AOP E_D and peroxide demand values associated with the treatment of water from MF, MF-AC, and MF-RO were determined from the water quality correlations based on >75% metaldehyde removal. Combining the associated OPEX of these demand data (based on the assumptions listed in Table 3-6) allows the OPEX of the AOP stage to be determined for each of these streams (Table 3-7). These can then be combined with the costs relating to the other unit operations (Table 3-8) to general total OPEX values of the key candidate process treatment schemes (Figure 3-8), which exclude both labour and disposal costs but are otherwise based on similar conditions of feedwater quality (secondary municipal effluent).

Table 3-7   Calculated OPEX for AOP process within three treatment schemes for >75% metaldehyde removal.

Parameter	Unit	MF-AOP	MF-RO-AOP
Pump - kW rating	kW		0.25
Lamp Power	kWh	2.82	1.78
H_2O_2 Dosing	mg L^{-1}	16	3
H_2O_2 Pump – kW rating	kW		0.015
Lamp Life	H		~9000
Citric Acid CIP Frequency	no. y^{-1}		26
Citric Acid CIP Conc.	ppm		2500
<u>Assumptions for OPEX analysis</u>		Value	Source
Electricity	£ kWh^{-1}	0.11	Energy EU, 2012
H_2O_2 (35% w/v)	£ L^{-1}	0.59	Supplier
Citric acid solution (50% w/v)	£ L^{-1}	1.59	Supplier
Lamp costs	£/lamp	223	Supplier

Table 3-8   Comparable unit process OPEX, £ m⁻³

Process	Min	Max	Source
MF	0.069	0.084	Raffin (2012)
Total, MF-RO	0.19	0.228	Raffin (2012)
	0.25	0.26	Garcia *et al*, (2013)
%RO of total	0.62	0.62	Raffin (2012)
AOP, post MF	0.373		James *et al* (this study)
AOP, post RO	0.176		James *et al* (this study)
AOP, post AC	0.199		James *et al* (this study)
GAC	0.09	0.16	Hatt *et al*, (2013)

The OPEX data (Figure 3-8) indicate the MF-RO-AOP process to be slightly lower in cost (by ~20%) than either of the two other enhanced treatment process options (MF-AOP or MF-AC-AOP), whose OPEX values are comparable. However, the MF-RO-AOP option incurs an additional capital cost from the RO process stage, and relies on an appropriate route for disposal of the RO concentrate stream. All three options are considerably more costly, by between 70 and 190%, than the "standard" two-stage MF-RO process.
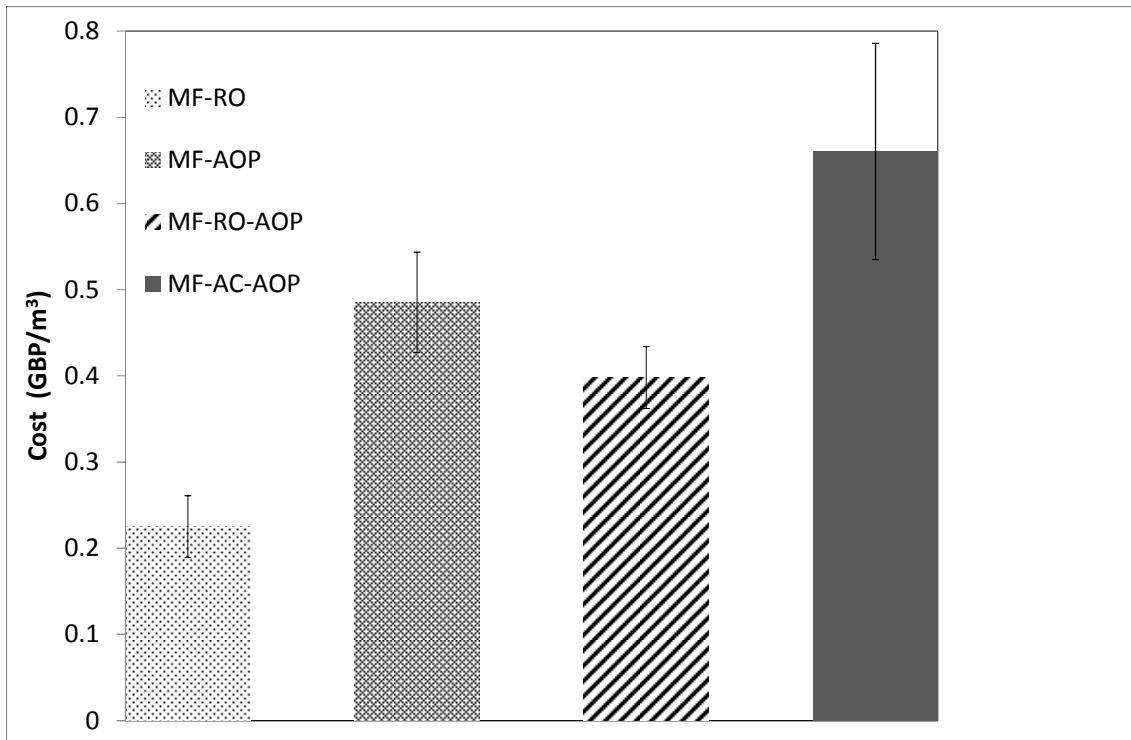
Figure 3-8   Projected OPEX values of four treatment schemes, based on 77-90% removal of metaldehyde from secondary municipal wastewater.

3.4 Conclusions

An extensive pilot-scale study of the efficacy of an advanced oxidation process for water reuse has been conducted. Results indicate feedwater UV transmittance as being pivotal to the process economic viability, since this factor dramatically impacts on energy and/or oxidative chemical demand. For the benchmark, and most conservative, case of metaldehyde removal of >75%, the MF-RO-AOP process is around 20% lower in OPEX than the MF-AOP and MF-AC-AOP options and provides a higher water quality. However, this is at the expense of an additional process stage and/or a significant waste stream volume. The OPEX of the enhanced processes can be up to 2.2 times that of the MF-RO process.

Metaldehyde represents one of the most recalcitrant of all micro-pollutants, along with the disinfection by-product, chloroform. Tests suggest that most other MPs are removed by at least 85% under the conditions employed in the study, with the estrogenic substances being more than 99% removed down to

levels of 1 ng L^{-1}. Under such conditions of reduced energy demand, the OPEX of the MF-AOP process would be in the range of £0.32-0.40 m^{-3} – 50-70% higher in OPEX than the MF-RO process but without the requirement for concentrate management.

A critically important factor in further development of treatment processes for recalcitrant micropollutants is projected future trends in technology improvement. Whilst activated carbon technology can be considered mature, current developments in UV technology indicate a significant reduction in energy demand to be attainable from the use of LED (light-emitting diode) technology. UV disinfection devices for water treatment have not yet been commercialised but it is not unreasonable to assume energy reductions in the region of 40-50% over conventional UV technologies from such devices, making the MF-AOP process comparable in OPEX to MF-RO. Moreover, the AOP offers the additional benefit of being intermittent and/or adjustable, such that the process can be applied seasonally during periods of high contaminant levels rather than 100% of the time. It must therefore be concluded that the development of LED UV may prove pivotal in future municipal water reuse plants if removal of recalcitrant micropollutants is prioritised.

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4 The impact of advanced oxidation (UV/H2O2) on disinfection/ byproduct formation and removal

James, C.P., Germain-Cripps, E., Judd, S., 2013. The impact of advanced oxidation (UV/H2O2) on disinfection/ byproduct formation and removal. To be submitted to *Water Science and Technology*

4.1 Introduction

Application of chemical disinfectants for sanitising treated waters can promote the formation of by-products that pose human health risks. Such compounds, referred to as disinfection by-products (DBPs), can be produced from the reaction of natural organic matter with chlorine - to form trihalomethanes (THMs) and halocetic acids (HAA) - or chloramines to generate nitrosamines, in particular *N*-nitrosodimethylamine (NDMA). These compounds are all recognised as probable human carcinogens (Singer, 1999; Pehlivanoglu-Mantas *et al.*, 2006). NDMA may already be present in industrial wastewaters, but is generally agreed that various NDMA precursors are abundant in treated secondary effluent and can lead to NDMA concentrations well of up to 790 ng L^{-1} (Sedlack *et al*, 2005). This then generates further concern for wastewater reclamation facilities that typically chlorinate or chloraminate source waters to control membrane biofouling. Consequently, studies conducted in this area have been focused on reducing DBP precursors and managing the NDMA formation potential, with recent emphasis on NDMA prompted by the proposed WHO (2008) guideline value of 100 ng L^{-1} and some countries setting action levels up to 10 ng L^{-1}.

It is widely recognised that advanced polishing processes such as reverse osmosis (RO) are not absolute barriers to DBPs; a maximum of 70% rejection has been reported for NDMA (Krausse *et al.*, 2010), whilst for some THM compounds high initial rejection has been observed which then gradually decreases over time (Xu *et al.*, 2005). For this reason UV-based advanced oxidation processes (AOPs, and typically UV/H_2O_2) are installed as a final step in a number of indirect potable reuse (IPR) schemes. AOPs can photolytically

destroy trace organic contaminants and provide effective disinfection of pathogens (Pereria *et al*, 2007). However, AOPs can also generate undesirable degradation by-products that have been shown, in some cases, to increase THM yields following downstream chlorination (Dotson *et al.*, 2010).

This current study aimed to assess impact of a UV/H_2O_2 AOP on the removal of NDMA and THMs at pilot scale. Few studies have focused on THM removal efficiency from application of UV/H_2O_2, focusing more on NOM reduction and the effect of degradation products. Whilst efficient NDMA removal has already been successfully identified at full-scale reuse plants using AOP (Poussade *et al.*, 2009), the present research encompasses the evaluation of the influence of different feedwater qualities and AOP operating parameters (namely UV and H_2O_2 dose) on NDMA degradation along with associated by-product formation.

4.2 Materials and methods

4.2.1 Pilot plant

The 600 m^3 d^{-1} pilot plant, details of which are provided elsewhere (Raffin *et al*, 2011; James *et al*, 2013), treated final effluent from a conventional activated sludge (CAS) based wastewater treatment works. The process consisted of a pre-filter, microfiltration (MF), reverse osmosis (RO) and an advanced oxidation processes (AOP), based on a combination of UV irradiation and H_2O_2 dosing (UV/H_2O_2), downstream of the MF (AOP1) and the RO (AOP2). The AOP units comprised a pumped flow-through UV reactor (Trojan UVPhox[TM], Model 12AL30) equipped with 12 low-pressure/high-output (LP/HO) amalgam lamps with nominal output power from the lamps varying from 60 to 100%, automatic sleeve wiping and a clean in place (CIP) system based on citric acid. H_2O_2 was dosed upstream of both UV reactors with static mixers in-line. UV transmittance (at 254 nm), intensity and power were monitored online for each reactor, along with temperature, and independent flowmeters fitted to each stream.

4.2.2 Experimental procedure

Experiments were performed using the same operating conditions (Table 4-1), feed water quality (Table 4-2) and procedures employed in previous studies by

James *et al* (2013). Analytical grade NDMA and THM standard solutions, provided by Sigma Aldrich, were dosed via glass ampoules into the feed storage tank to achieve a concentration of 0.2 and 50 µg L^{-1}, respectively. Concentration levels were based on those typically arising in secondary wastewater, as identified in the literature and regulatory guidelines (WSR, 2000), or else constrained by their limit of detection as advised by the laboratory (Thames Water Analytical Laboratories, Reading). Spiking in this manner allowed % removal values to be accurately calculated.

Analysis of NDMA was performed using gas chromatography (GC) and THMs were examined by purge-and-trap GC with mass spectrometry. Samples were also analysed for standard nutrient determinants (ammonium, nitrate and nitrite), total organic carbon (TOC) and the key disinfection by-product bromate (and its precursor bromide). Ion chromatography was used to analyse bromate and bromide, and standard colorimetric methods were employed for nitrogen compounds. TOC was measured with an AstroTOC analyser from Hach Lange (Hach Lange Ltd., Salford, UK). All compounds were analysed by Thames Water Laboratories (Reading, UK), with the exception of THMs, which were assayed by Severn Trent Services (Coventry, UK).

Table 4-1   Operational conditions for the AOP spiking trials.

Parameter	AOP1	AOP2
Feed water	MF filtrate	RO permeate
Lamp power set-point (%)	100%	60%
Power Input P [Optimal Range] (kWh)	2.82 [1.68 – 2.82]	1.78 [1.78 – 2.98]
Lamp Life (h)	1380	1100
Peroxide dose [Optimal Range] (mg L^{-1})	16 [6-20]	3 [1-3]
Treatment capacity (m^3 h^{-1})	3	3
Reactor volume (m^3)	0.098	0.098
Theoretical contact time (s)	approx. 120	approx. 120

Table 4-2   **Mean and standard deviations values of feedwater quality for each stream.**

Compound	Unit	MF permeate	RO permeate
Alkalinity as $CaCO_3$	$mg.L^{-1}$	212 ± 12.4	< 16
Conductivity	$\mu S\ cm^{-1}$	1061 ± 15.3	20.8 ± 2.35
pH		7.3 ± 0.07	5.5 ± 0.05
Hardness Total as $CaCO_3$	$mg.L^{-1}$	332.9 ± 16.7	< 29
Total Organic Carbon (TOC)	$mg.L^{-1}$	7.7 ± 0.73	0.2 ± 0.17
Turbidity	NTU	0.14 ± 0.21	0.08 ± 0.02
UV absorbance at 254 nm (UV_{254})	cm^{-1}	0.18 ± 0.002	0.005 ± 0.002
UV transmittance (UVT)	%	66 ± 0.82	98.8 ± 0.41
Specific UV Absorbance (SUVA)	$L.mg^{-1}.m.$	2.34	0.5

4.3 Results and discussion

4.3.1 NDMA and THM removal

Table 4-3 summarises the results from the DBP spiking studies. The AOP achieved significant removal of NDMA above 98% when applied to both MF and RO permeate under varying H_2O_2 and UV doses. In comparison, THMs were shown not to be readily degraded for both streams. Applying UV and H_2O_2 doses of 1861 mJ cm^{-2} and 3 mg L^{-1} respectively to the higher-purity RO permeate led to a TTHM reduction of only 68%. Among the four THM's analysed, chloroform followed by dichlorobromomethane were the most recalcitrant species (Figure 4-1), with chloroform removal being less than 10%. Similar trends in removal of these two species following UV/H_2O_2 treatment were also reported by Lamsal *et al* (2011), accompanied by slightly greater TTHM removal overall (77%). Chloroform in particular is not readily oxidised (Bolton, 2001), as evidenced by a second order rate constant value ~60 times lower than that of NDMA for reaction with ·OH (Sharpless and Linden, 2003; Crittenden *et al.*, 2005). Removal of bromoform was relatively consistent across both MF and RO streams.

Table 4-3   DBP removal results for post MF and RO streams under optimum conditions (power input and H2O2 dose).

Stream	Compound	Inlet Conc. ($\mu g.l^{-1}$)	% removal	Log reduction	UV Dose ($mJ\ cm^{-2}$)	E_D ($kWh\ m^{-3}$)
AOP 1 (post MF)	NDMA	0.2	98	1.62	678	0.95
	THMs	50	52*	0.32	739	0.94
AOP 2 (post RO)	NDMA	0.2	99	2.39	1845	0.62
	THMs	50	68*	0.50	1861	0.60

* Weighted average
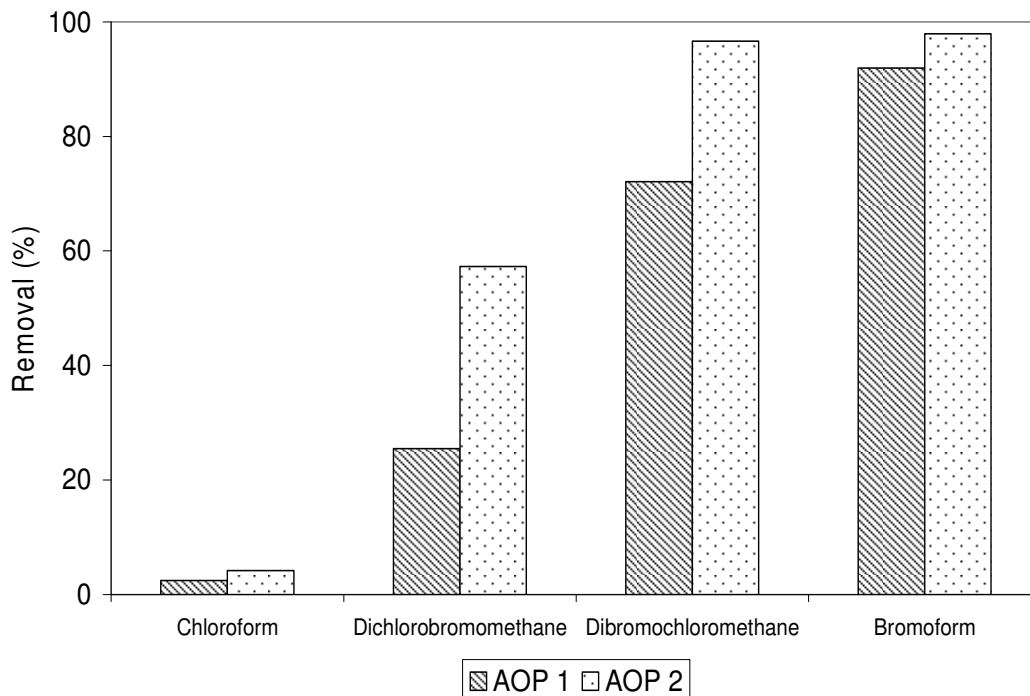
Figure 4-1   Removal of THM compounds under optimised conditions in the MF and RO permeates.

Further tests conducted more specifically on NDMA showed removal rates to increase with higher UV doses, as demonstrated in the MF permeate (Fig. 4-2). Increased H_2O_2 doses made minimal impact on removal efficiency as UV alone achieved 96% removal, only 2-3% less than applying 6–12 mg l^{-1} of peroxide to the MF stream. Interestingly, the lower H_2O_2 concentrations tested in this study, showed better removal of NDMA, although marginal, this supports the fact that

H_2O_2 scavenges $^{\cdot}OH$, generating a less effective $^{\cdot}HO_2$ radical (Wang $et\ al.$, 2000). All tests performed on the RO permeate reduced NDMA to the limit of detection (Fig 4-2) regardless of the UV and H_2O_2 doses employed. Differences in the UV absorbance between MF and RO permeate thus appear to have marginal influence on NDMA removal. Moreover, the presence of TOC and nitrates evident in the MF permeate (see Table 4-4) were not significantly inhibitory to NDMA destruction, as noted by other authors (Liang $et\ al.$, 2003). The energy required for 90% degradation of NDMA in the MF water was 0.56kWh m^{-3}, at an approx. UV dose of 200 mJ cm^{-2} (Fig. 4-3), slightly higher than energy values of 0.44kWh m^{-3} reported in other studies for NDMA removal (Katsoyiannis $et\ al.$, 2011). These results clearly indicate photolysis to be the principal mechanism for NDMA degradation in wide agreement with the literature.
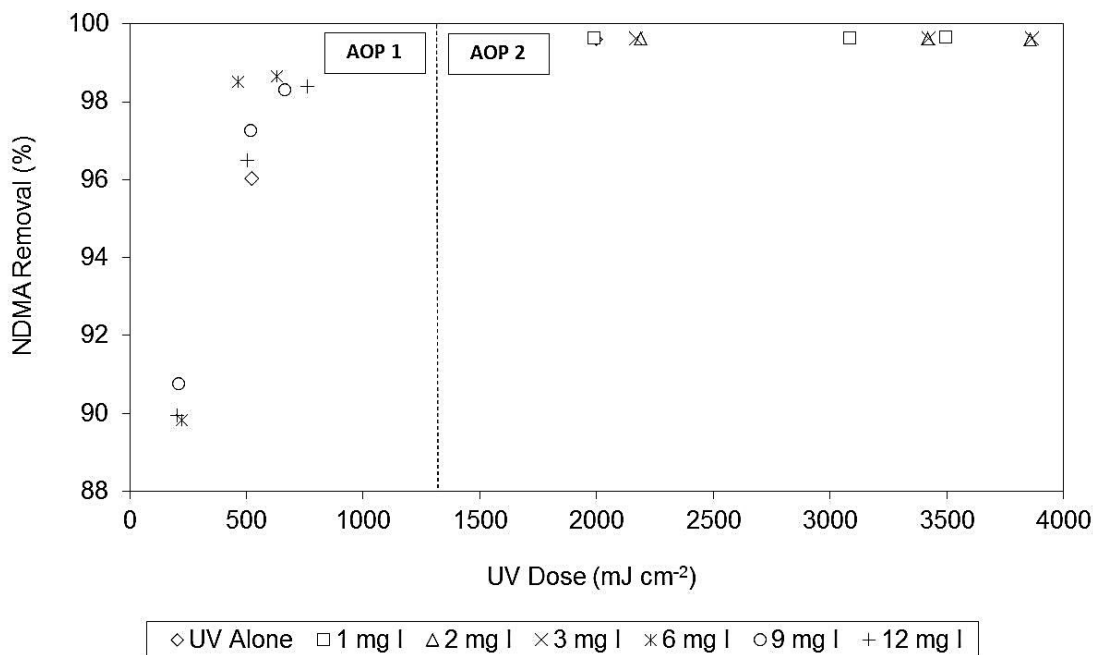
Figure 4-2   Effect of UV and H_2O_2 dose on the removal of NDMA from MF (AOP1) and RO (AOP2) permeate.
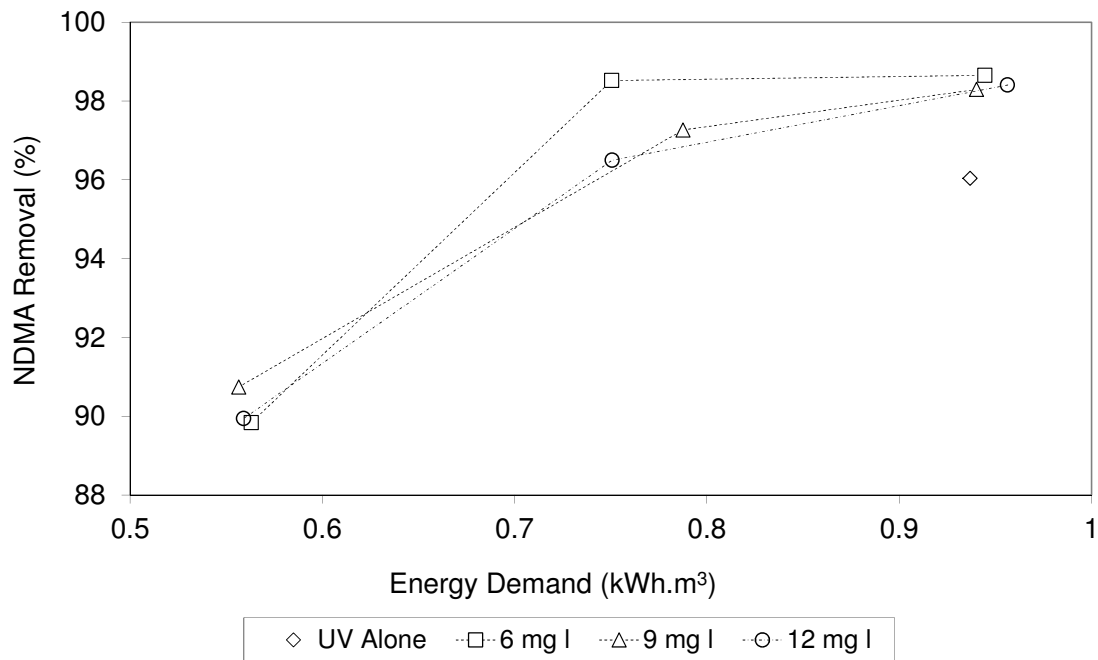
Figure 4-3   E$_D$ data for NDMA degradation in the MF permeate as a function of H$_2$O$_2$ dose.

4.3.2 By-product formation

Feed and treated water quality data from the MP removal studies (Table 4-4) reveal almost negligible bromate generation from the low levels of feed bromide (a 5% increase in the background level of 2.1 µg L^{-1}), but rather more significant nitrite formation. Generation of nitrite (NO$_2$$^-$-N), associated with photolysis of nitrate (NO$_3$$^-$-N) (Sharpless and Linden, 2001; Keen *et al.*, 2012), increased its yield by 66% and 2900% on average in the MF and RO streams respectively. Levels were increased on average to 0.03 - 0.102 mg L^{-1}, close to or exceeding the UK DWI (2000) standard of 0.1 mg L^{-1} for drinking water. Conversion of NO$_3$$^-$-N to NO$_2$$^-$-N does not appear to be promoted by the higher nitrate content in the MF stream, but this may relate more to higher UV doses as demonstrated in the RO stream (IJpelaar *et al.*, 2002) combined with the lower pH (Sharpless *et al*, 2003). However, high H$_2$O$_2$ levels may suppress nitrite formation, yielding a lower % increase in the MF stream (16 mg L^{-1} H$_2$O$_2$) than the RO permeate (3 mg L^{-1}), as previously reported by Lu *et al* (2009). The low bromate formation would also seem to corroborate reports of H$_2$O$_2$ reducing oxidised hypobromite

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($^{\cdot}$OBr$^-$) back to bromide rather than bromate (Von Gunten and Oliveras, 1997; Kruithof *et al.*, 2007).

Table 4-4   Selected water quality results before and after AOP, for the MF and RO streams.

Parameter	Unit	MF permeate			RO permeate		
		Inlet	Outlet	Diff., (+/-)	Inlet	Outlet	Diff., (+/-)
Ammoniacal Nitrogen as N	mg L^{-1}	0.7	0.46	0.24	0.14	0.04	0.1
Nitrite as N	mg L^{-1}	0.06	0.1	-0.04	0.001*	0.03	-0.029
Nitrate as N	mg L^{-1}	18.2	18.2	0	1.08	1.05	0.03
Tot Nitrogen oxidised as N	mg L^{-1}	18.3	18.3	0	1.08	1.08	0
Alkalinity as HCO$_3$	mg L^{-1}	260	257	3	20*	20*	0
Silica, reactive (SiO$_2$)	mg L^{-1}	14.3	13.9	0.4	0.4*	0.4*	0
pH		7.3	7.3	0	5.53	5.46	0.07
Turbidity (FTU)	FTU	0.16	0.21	-0.05	0.09	0.09	0
Bromide	mg L^{-1}	0.12	0.14	-0.02	0.004*	0.098	-0.094
Bromate	µg L^{-1}	2.14	2.26	-0.12	0.2*	0.29	-0.09
Total Organic Carbon, (TOC)	mg L^{-1}	13.7	13.1	0.6	2.08	2.30	-0.22
Colour	mg L^{-1} Pt/Co	21.5	13	8.5	0.5*	0.5*	0
H$_2$O$_2$ residual	mg L^{-1}	-	13.3	-	-	1.55	-
UV-T$_{254}$	%	68.2	76.8	-8.6	99.2	99.9	-0.7

* Lowest limit of detection.

TOC reduction appears to be negligible in both streams, confirming outcomes from other studies where high UV doses (1500 – 10,000 mJ cm^{-2}) with H$_2$O$_2$ concentrations (20 - 51 mg L^{-1}) have been applied yielding only modest mineralisation rates of 15-50% (Sarathy and Mosheni, 2009; Goslan *et al.*, 2006;); the latter study deemed uneconomical in practice. However, colour removal from the MF permeate was more significant (~40%), suggesting partial oxidation to less complex molecules. This then raises the possibility of generation of more assimilable organic matter (Toor and Mohseni, 2007),

increasing the propensity for biofouling in the downstream network. Moreover, the high H_2O_2 residual in the MF stream (13.3mg l^{-1}) would require quenching prior to further use, incurring additional treatment costs downstream of the AOP.

4.4 Conclusions

A pilot-scale study of the efficacy of UV/ H_2O_2-based advanced oxidation for municipal wastewater reuse has shown NDMA to be significantly less recalcitrant than other organic micropollutants (THMs). The added NDMA was removed by 89 - >98% at UV doses of 200-680 mJ cm^{-2} from the MF permeate, with complete removal (>99%) observed in the RO stream at doses above 1800 mJ cm^{-2}. Under optimum conditions, both MF and RO AOP streams were able to achieve the stringent threshold standard of 10 ng L^{-1}. The addition of H_2O_2 provided negligible impact on NDMA degradation, but suppressed formation of nitrogenous DBPs (nitrite) as a consequence of applying high UV doses. Results indicate that nitrite levels are slightly increased by the action of low pressure UV irradiation.

Chloroform and dichlorobromomethane were not readily degraded by the UV/H_2O_2 process in either the MF or RO permeates as was evident with TOC, although the latter was partially oxidised as observed by colour reduction and improved UV_{254}. Failure to mineralise organics resistant to AOP may increase the DBP formation potential if a residual disinfectant (i.e. chlorine or chloramine) is employed, which is likely to be required for reuse distribution.

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5 Conclusions

An extensive pilot-scale study to assess the efficacy of UV/ H_2O_2-based advanced oxidation in terms of micropollutant removal and relative cost for water reuse has been conducted. From the research the following conclusions can be drawn:

- Metaldehyde represents one of the most recalcitrant of all micro-pollutants, along with the disinfection by-product, chloroform. Tests suggest that most other MPs are removed by at least 85% under the conditions employed in the study, with the estrogenic substances being more than 99% removed down to levels of 1 ng L^{-1}. OPEX costs for MF-AOP treatment are still 50-70% higher than those for the MF-RO process but without the costs associated with concentrate management.

- An evaluation of metaldehyde removal has shown higher levels of UV transmittance (UVT) and H_2O_2 doses, and longer hydraulic retention times are required to enhance its mineralisation for a given UV dose. The impact of feedwater UV transmittance is critical in determining the economic viability of AOP, since this factor dramatically impacts on energy and/or oxidative chemical demand. For the less challenging removal target for metaldehyde of 75%, the MF-RO-AOP process train provides lower OPEX and enhanced water quality compared to the MF-AOP and MF-AC-AOP options examined. Future studies should therefore be focused developing a less costly alternative to activated carbon for removing UV-absorbance/ DOC to similar levels upstream of the MF-AOP process.

- Direct UV photolysis is the principal mechanism for NDMA degradation in agreement with those from previous studies. The impact of H_2O_2 and water quality (UVT) on removal rates was negligible in this case: a benchmark 1 log reduction was achievable in the MF permeate by applying a UV dose of ~200 mJ cm^{-2}. Under optimum conditions, both MF and RO-AOP streams were able to achieve the stringent threshold standard of 10 ng L^{-1} for NDMA.

The THM compounds chloroform and dichlorobromomethane were not readily degraded by the UV/H_2O_2 process in either the MF or RO permeates. The fate of chloroform should be assessed further to determine the efficacy of AOP and removal thresholds by applying higher UV and H_2O_2 doses than those applied in this current study, particularly in the RO permeate where UVT is not limiting.

- The extent of by-product formation was limited to standard sanitary determinants and TOC. Nitrite (as N) yields were significantly elevated in the RO-AOP stream, promoted by a low pH and higher applied UV doses. Although initial nitrate (as N) levels were higher in the MF permeate, the conversion to nitrite was suppressed by the addition of H_2O_2. These results indicate that nitrite levels are increased by the action of low pressure UV irradiation, possibly exceeding drinking water standards. Mineralisation of TOC was shown to be limited, highlighting the need to monitor assimilable organic carbon (AOC) in the treated water. AOC measurement would offer an improved understanding of the biological stability of the water with reference to biofilm formation propensity, which can potentially promote DBP formation in the presence of residual chemical disinfectant. Such by-product formation could be ameliorated by additional treatment (GAC) downstream of the AOP for removal of nitrite, organic carbon and residual H_2O_2.

- The practical implications of these findings are that OPEX of the enhanced processes can be up to 2.2 times that of the MF-RO process, the AOPs thus presenting a high cost. This being the case, it is questionable that AOPs are required for water reuse given that RO provides a robust barrier to almost all other MPs other than NDMA whose formation can be controlled. Having said this, current developments in UV technology indicate a significant reduction in energy demand to be attainable from the use of LED (light-emitting diode) technology, potentially making the MF-AOP process comparable in OPEX to MF-RO. At the present time, AOP is the only reliable means of removing metaldehyde and NDMA to trace levels, though more focus on catchment management and improved operational practices could lessen their

presence in source waters. Moreover, the AOP offers the additional benefit of being intermittent and/or adjustable, such that the process can be applied seasonally during periods of high contaminant levels (i.e. autumn/winter periods in UK for pesticides) rather than 100% of the time. Online instrumentation can also regulate its application, providing the contaminants can be monitored in real-time through broad spectrum analysers or else surrogate indicators (i.e. DBP precursors such as TOC combined with pH, oxidation reduction potential (ORP) and temperature), can be reliably employed. It must therefore be concluded that the development of LED UV may prove pivotal in future municipal water reuse plants if removal of recalcitrant micropollutants is prioritised and AOPs remain the only viable means for their control.

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APPENDICES

Appendix A : Micropollutant detection levels in pilot plant source water and membrane product treatment stages

Detected Compound	Units	STW Settled Sewage				Pilot Plant Raw Water				Post MF				Post RO			
		No. of samples	Average	Max	Min	No. of samples	Average	Max	Min	No. of samples	Average	Max	Min	No. of samples	Average	Max	Min
E1 Estrone	ng/l	14	37.86	54.90	7.80	64	4.03	15.81	<0.04	42	2.47	17.00	<0.04	47	0.27	3.52	<0.04
E2 17 beta Estradiol	ng/l	14	12.88	21.40	2.60	76	1.28	7.36	<0.03	49	0.87	8.00	<0.03	61	0.08	<0.67	<0.03
EE2 17 alpha Ethinyl Estradiol	ng/l	14	0.19	0.61	<0.04	65	1.19	9.74	<0.04	39	0.75	6.26	<0.04	47	0.07	0.64	<0.04
2 4 5 -T (2,4,5-Trichlorophenoxyacetic acid)	µg/l	8	<0.006	<0.01	<0.002	73	0.01	0.01	<0.002	48	0.004	<0.02	<0.002	53	<0.002	<0.002	<0.002
2 4 -D (2,4-Dichlorophenoxyacetic acid)	µg/l	8	0.05	0.33	<0.002	84	0.02	0.62	<0.002	59	0.017	0.11	<0.002	64	<0.002	<0.002	<0.002
Mecoprop	µg/l	8	0.05	0.17	<0.003	73	0.02	0.10	0.01	48	0.02	0.07	<0.003	53	<0.003	<0.003	<0.003
Metaldehyde	µg/l	8	0.06	0.11	0.03	63	0.06	0.20	0.03	39	0.07	0.21	0.03	43	<0.004	<0.004	<0.004
Atrazine	µg/l	13	0.02	0.03	0.004	87	0.02	0.03	0.00	60	0.03	0.03	0.01	66	<0.0055	<0.006	<0.003
Terbutryn	µg/l	14	0.08	0.37	0.01	73	0.06	<0.65	<0.004	50	0.06	<0.65	<0.004	52	<0.012	<0.065	<0.002
THM Total	µg/l	10	1.66	2.50	1.20	80	1.11	2.50	0.30	60	1.29	2.60	<0	62	0.16	4.83	<0
NDMA	µg/l	11	0.004	<0.009	<0.0036	85	0.004	0.01	<0.0036	59	0.004	0.01	<0.0036	65	0.001	0.01	<0.0009