

# Micropollutant removal by advanced oxidation of microfiltered secondary effluent for water reuse

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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<sub>2</sub>O<sub>2</sub>) has been assessed through pilot-scale experiments incorporating microfiltration (MF) and reverse osmosis (RO). Initial tests employed low concentrations of a range of key emerging contaminants of concern, subsequently focusing on the highly recalcitrant compound metaldehyde (MA), and the water quality varied by blending MF and RO permeate.

Under optimum H<sub>2</sub>O<sub>2</sub> and lamp power conditions, AOP achieved significant removal (>99%) of N-nitrosodimethylamine (NDMA) and endocrine disrupting compounds (EDCs) for all waters. Pesticide removal, in particular metaldehyde, atrazine and 2, 4 5-Trichlorophenoxyacetic acid, was dependent on water transmittance (UVT), and levels of TOC and other hydroxyl radical ( $\cdot$ OH) scavengers. Further analysis of MA removal showed UVT, hydraulic retention time and H<sub>2</sub>O<sub>2</sub> dose to be influential parameters in determining degradation as a function of UV dose.

A cost assessment revealed energy consumption to account for 65% of operating expenditure 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 incurred 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 significant.

Keywords: Advanced oxidation; Wastewater reuse; Micropollutants; Metaldehyde; Operating cost.

## 1 Introduction

Over the past 20 years, there has been 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 can cause potentially adverse health effects at concentrations in the milligram/nanogram per litre range (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.

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 17 $\beta$ -estradiol (E2)) along with synthetic xenoestrogens (17  $\alpha$ -ethynylestradiol), phthalates and many more, known to affect/interfere with the action of hormones in the endocrine system (Hotchkiss *et al.*, 2008). Sewage effluents have been identified as being a major source of natural estrogenic chemicals in the aquatic environment (Desbrow *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.

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  $\mu\text{g L}^{-1}$  for an individual pesticide and 0.5  $\mu\text{g L}^{-1}$  in total. Among those of concern in drinking waters are atrazine and, most recently, metaldehyde (MA). 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), characterised by the generation of highly reactive, non-selective hydroxyl radicals ( $\cdot\text{OH}$ ), offer a promising alternative to conventional treatment for removing organic constituents in contaminated waters. The UV/H<sub>2</sub>O<sub>2</sub> process is amongst the most studied AOP and reported to be effective at degrading recalcitrant MPs such as NDMA (Poussade *et al.*, 2009) and various pharmaceuticals and EDCs (Benotti *et al.*, 2009; Snyder *et al.*, 2007) for indirect potable reuse (IPR) and, in the case of surface water treatment generally, metaldehyde (Autin *et al.*, 2013). Such a process installed downstream of the membrane filtration step of an IPR scheme to remove traces of compounds permeating the RO membrane (Royce *et al.*, 2010) can potentially achieve full mineralisation of MPs (Matilainen and Sillanpää, 2010), whereas reverse osmosis (RO) leaves MPs unchanged in the waste stream thus demanding further management. However, both RO and AOPs are energy and chemically intensive and thus incur a significant cost. Whilst previous studies of AOPs at bench scale have elucidated degradation mechanisms and H<sub>2</sub>O<sub>2</sub> dosing requirements (or hydroxyl rate constants) for MP removal (Sanches *et al.*, 2010; Rosario-Ortiz *et al.*, 2010; Katsoyiannis *et al.*, 2011; Baeza and Knappe, 2011), representative costs and performance from larger scale demonstration against real waters have not been quantified.

This study aims to determine both the effectiveness and cost of a UV/H<sub>2</sub>O<sub>2</sub> process for treating MPs of emerging concern, and the most highly recalcitrant of these in particular MA, which currently presents a significant challenge to the water industry. Impacts of key parameters, specifically feedwater transmittance, are assessed and process costs compared with those of other candidate processes recently demonstrated on the same large pilot scale.

## 2 Materials and methods

### 2.1 Pilot plant and chemical reagents

The pilot plant (Fig. 1), details of which are provided elsewhere (Raffin *et al.*, 2011), treated 600 m<sup>3</sup> d<sup>-1</sup> 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 an advanced oxidation process (AOP), based on a combination of UV irradiation and H<sub>2</sub>O<sub>2</sub> dosing (UV/H<sub>2</sub>O<sub>2</sub>), downstream of the MF (AOP1) and the RO (AOP2).

Each AOP comprised a flow-through UV reactor (Trojan UVPhox<sup>TM</sup>, 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%. AOP1 reactor was fitted 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<sub>2</sub>O<sub>2</sub> 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) were dosed at concentrations generally between 0.2 and 2 µg L<sup>-1</sup> into the feed via glass ampoules and/or pipetted from solutions of the compounds dissolved in water/acetone, the latter adding 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).

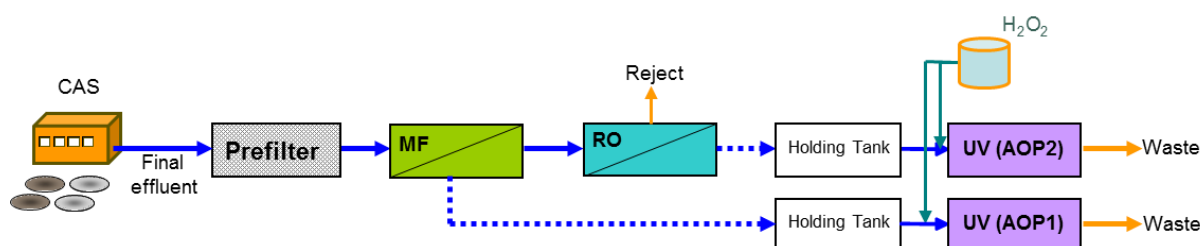


Figure 1. Pilot plant schematic

### 2.2 Experimental procedure

Feed water quality was varied by testing either the MF, RO or an equal blend of the two permeate streams (Table 1). MPs were then dosed at concentrations based on those typically arising in secondary wastewater, as identified in the literature (Lundstrom *et al.*, 2010; Martin Ruel *et al.*, 2011) and regulatory guidelines (WSR, 2010), or else constrained by their limit of detection as advised by the laboratory (Thames Water Analytical Laboratories, Reading) to allow % removal values to be accurately calculated. Operating conditions for each AOP stream (Table 2) were determined from the optimum UV lamp input power and H<sub>2</sub>O<sub>2</sub> dose for each AOP stream for efficient removal of target MPs to the required log reduction, based on outcomes of initial scoping trials.

Chemicals were prepared to a required concentration and dosed directly into a 1 m<sup>3</sup> 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<sub>2</sub>O<sub>2</sub> dosing upstream of a static mixer at flow rates of 1-3 m<sup>3</sup> h<sup>-1</sup>, providing residence times of 120-180 s. An experimental test comprised feed solution mixing for 20 minutes, to ensure a homogeneous solution, followed

by once-through AOP treatment for 20 minutes. Sampling of the outlet stream was timed to allow for the above residence time.

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 NDMA and MA 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, 2007). Duplicate samples for each MP compound were taken from the feed tank and triplicate samples collected post-AOP at 5, 10, and 15 minute intervals. Tests were repeated for any apparent anomalies.

Sampling and analysis was conducted for MPs along with standard sanitary determinants. All compounds were analysed by Thames Water Laboratories (Reading, UK) using standard methods (APHA, 2005). EDCs, atrazine and terbutryn were analysed by liquid chromatography with mass spectrophotometric detection (LS-MS-MS), ion chromatography (IC) was used to analyse NDMA, whilst the remaining herbicides and MA were analysed by gas chromatography (GC-MS).

**Table 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 <sub>3</sub>	mg.L <sup>-1</sup>	212 ± 12.4	< 16	-
Conductivity	µS cm <sup>-1</sup>	1061 ± 15.3	20.8 ± 2.35	-
pH		7.3 ± 0.07	5.5 ± 0.05	7.14 ± 0.14
Hardness Total as CaCO <sub>3</sub>	mg.L <sup>-1</sup>	332.9 ± 16.7	< 29	-
Total Organic Carbon (TOC)	mg.L <sup>-1</sup>	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 <sub>254</sub> )	cm <sup>-1</sup>	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 <sup>-1</sup> .m.	2.34	0.5	2.26

**Table 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 <sup>-1</sup> )	16/ 6-20	3/ 1-3
Treatment capacity (m <sup>3</sup> h <sup>-1</sup> )	3	3
Reactor volume (m <sup>3</sup> )	0.098	0.098
Theoretical contact time (s)	approx. 120	approx. 120

The optimisation trials were based on MA, the most recalcitrant of the micropollutants examined. Three equally-spaced H<sub>2</sub>O<sub>2</sub> doses and power inputs were employed with each stream (MF permeate, RO permeate, and blend) and correlated with MA removal (Table 3). This approach allowed Box-Behnken 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<sup>n</sup> factorial design to 15.

**Table 3:** Parameters and their levels, Box-Behnken analysis

Param. #	Parameters	Levels
X <sub>1</sub>	H <sub>2</sub> O <sub>2</sub> dose (mg L <sup>-1</sup> )	3, 9.5, 16
X <sub>2</sub>	UV-T (%)	65, 82, 98
X <sub>3</sub>	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 (Bolton *et al*, 2001), along with specific energy demand ( $E_D$ ) to benchmark against other advanced technologies such as RO.  $E_{EO}$  is defined by these authors as the electrical energy in kWh required to reduce the concentration of a contaminant by one order of magnitude in 1 m<sup>3</sup>.

$$E_{EO} = P/(Q \log (c_i/c_f)) \quad 1$$

where  $P$  is the electrical power (kW) of the UV system,  $Q$  is the flow rate (m<sup>3</sup>/h), and  $C_i$  and  $C_f$  the initial and final contaminant concentrations (mg L<sup>-1</sup>). Specific energy demand ( $E_D$ ), the electrical energy (kWh) consumed per unit volume of water treated, was also calculated so as to provide a further benchmark in cases where 90% (or 1 log) reduction was not achieved:

$$E_D = P/Q \quad 2$$

### 3 Results and discussion

#### 3.1 MP removal

Measured concentrations (Table 4) revealed all the MPs studied to be removed by at least 97% when applying AOP to the RO permeate at an H<sub>2</sub>O<sub>2</sub> dose of 3 mg L<sup>-1</sup> and an  $E_D$  of 0.62 kWh m<sup>-3</sup>. In contrast, application to the MF permeate was much less effective in removing herbicides and pesticides generally, and MA in particular. Even at very high H<sub>2</sub>O<sub>2</sub> doses of 16 mg L<sup>-1</sup> with  $E_D$  levels of 0.93 kWh m<sup>-3</sup>, MA 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<sup>-2</sup> and H<sub>2</sub>O<sub>2</sub> concentrations of 10-15 mg L<sup>-1</sup>; >90% removal of these compounds was reported based on bench-scale UV/H<sub>2</sub>O<sub>2</sub>.

Differences in measured removal between the two permeate streams reflect those in UV transmittance (UVT) (Table 1), which is near total for the RO permeate compared with only 65% for the MF permeate. Higher doses of H<sub>2</sub>O<sub>2</sub> in AOP1 were thus needed to compensate for the lower photon absorption efficiency (Tuhkanen, 2004). Moreover, competition for ·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<sub>2</sub> 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. 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.

**Table 4:** Micro-pollutant removal results for Post MF and RO streams under optimum process conditions (power input and H<sub>2</sub>O<sub>2</sub> dose).

Stream	Classification	Compound	Inlet Conc. (µg.l <sup>-1</sup> )	% removal	Log reduction	UV Dose (mJ cm <sup>-2</sup> )	E <sub>D</sub> (kWh m <sup>-3</sup> )	E <sub>EO</sub> (kWh m <sup>-3</sup> )
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	-
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
	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

### 3.2 Metaldehyde removal

Tests conducted on MA specifically demonstrated increased removal with increasing UV and H<sub>2</sub>O<sub>2</sub> dose (Fig. 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<sup>-1</sup> and an E<sub>D</sub> of ~0.7 kWh m<sup>-3</sup> (Fig. 3). Other studies have reported similar removal rates (Autin *et al.*, 2012), citing lower UV fluences of 600 mJ cm<sup>-2</sup> for laboratory grade water, but at considerably higher H<sub>2</sub>O<sub>2</sub> doses of 272 mg L<sup>-1</sup>. For MF permeate, energy inputs above 0.75 kWh m<sup>-3</sup> achieved no more than 40% removal (Fig. 3). Removal from MF permeate at a UV dose of around 460 mJ cm<sup>-2</sup> ranged from 3 to 45% according to H<sub>2</sub>O<sub>2</sub> concentration (Fig. 4).

Removal is, however, improved by H<sub>2</sub>O<sub>2</sub> addition, particularly in poorer water quality. An increased H<sub>2</sub>O<sub>2</sub> concentration may thus further increase degradation, provided the peroxide itself does not scavenge ·OH at these elevated concentrations as suggested by other authors (Galbraith *et al.*, 1992). The relationship between UV dose and energy demand for each stream (Figure 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<sup>-2</sup> with at >2 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> appear sufficient to attain >90% removal of MA.

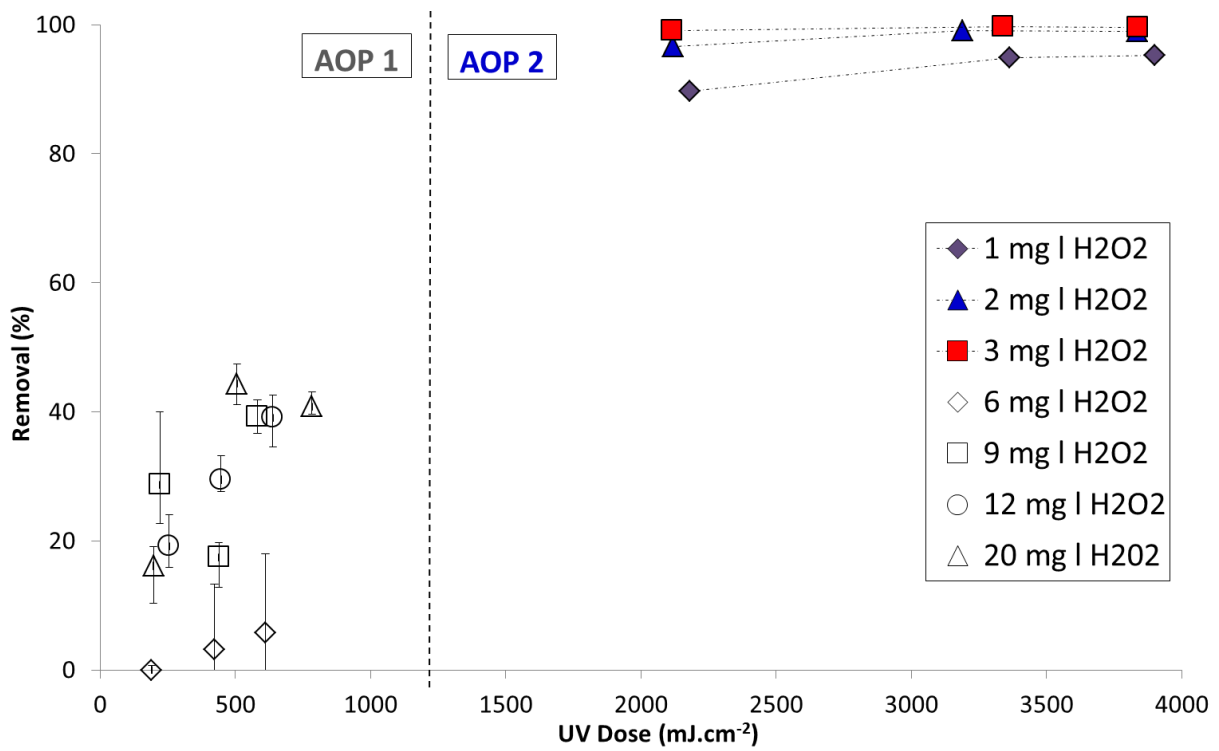


Figure 2. Effect of UV and H<sub>2</sub>O<sub>2</sub> dose on the removal of metaldehyde from MF permeate (AOP1) and RO permeate (AOP2).

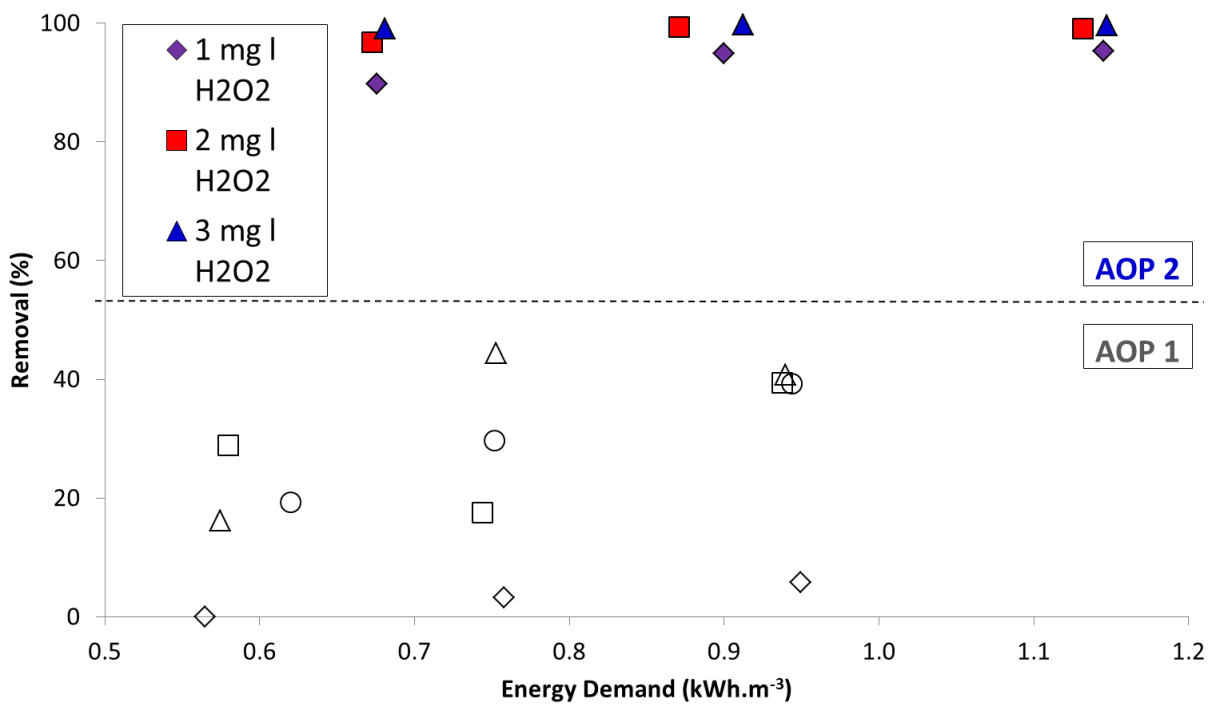


Figure 3.  $E_D$  data for metaldehyde degradation in MF (AOP1) and RO (AOP2) permeate as a function of H<sub>2</sub>O<sub>2</sub> dose.

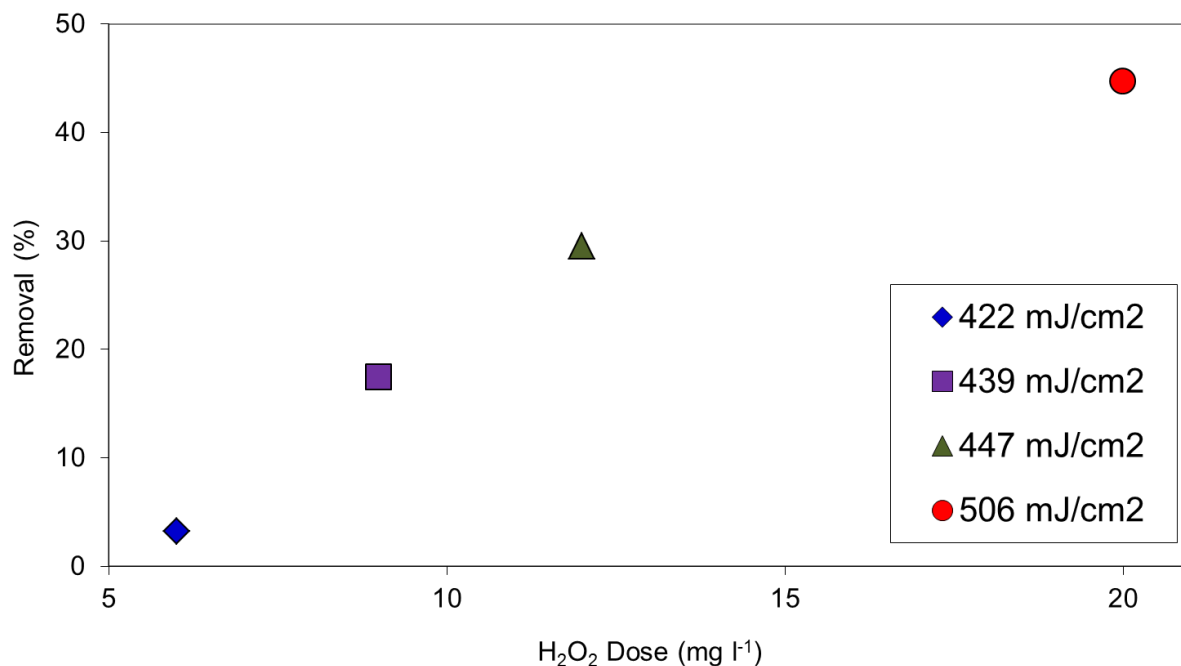


Figure 4. Metaldehyde removal from MF permeate as a function of H<sub>2</sub>O<sub>2</sub> dose at UV dose 422-506 mJ cm<sup>-2</sup> and a power of 2.25kW.

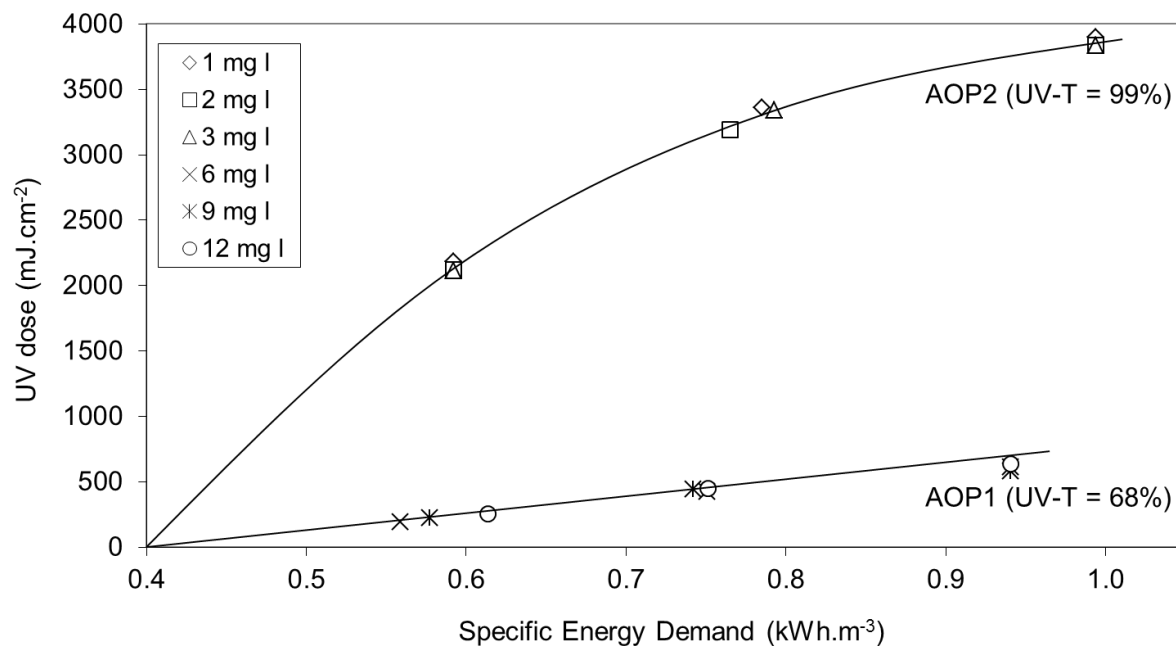


Figure 5. Influence of UVT on the UV dose output as a function of energy input at various H<sub>2</sub>O<sub>2</sub> concentrations (1-20 mg L<sup>-1</sup>) in streams AOP 1 and 2.

### 3.3 Effect of residence time

Figure 6 shows the influence of retention time (RT) on MA 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<sup>-2</sup> at 1.67 kW; 8.9 mW cm<sup>-2</sup> at 2.82 kW). This probably results from improved UV<sub>254</sub> 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).

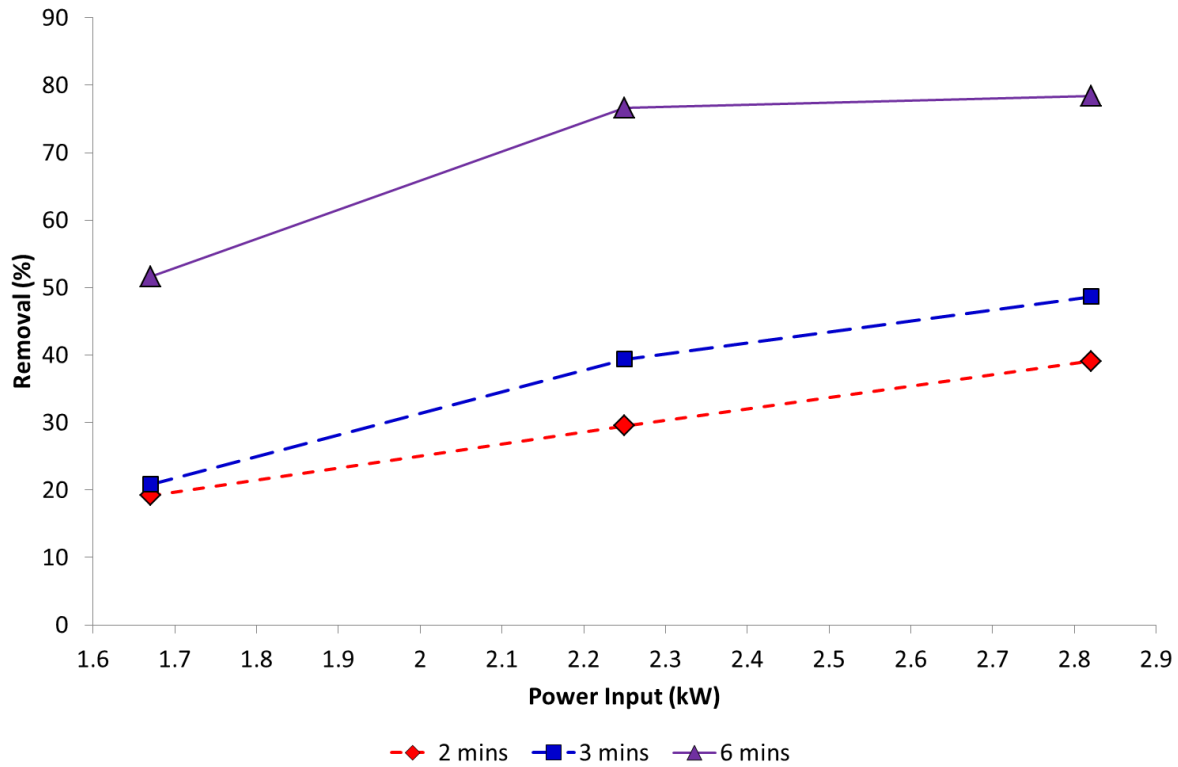


Figure 6. Influence of residence time on the degradation of metaldehyde in MF permeate as a function of power input, 16 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>.

### 3.4 Effect of UV transmittance (UVT)

The influence of UVT was quantified through blending of the MF and RO permeate streams in conjunction with power input and peroxide dose using a Box-Behnken design (BBD) based on the levels indicated in Table 3. Regression analysis revealed UVT<sub>254</sub> and H<sub>2</sub>O<sub>2</sub> dose (C) to be the only significantly influential parameters on metaldehyde removal (p-value <0.05 for the linear coefficient in both cases), with power input having no significant impact (p-value 0.18) due to the limited range applied (1.66 - 2.82 kW). The overall relationship between %metaldehyde passage (P) and peroxide concentration and UV transmittance (Fig. 7) from multiple linear regression analysis (R<sup>2</sup> = 0.96):

$$P = 671 - 16.2 C - 11.44 UVT + 0.271 C^2 + 0.0497(UVT)^2 + 0.1056 C UVT \quad 3$$

The analysis indicates the extreme sensitivity of metaldehyde passage (1 - removal) to UVT, with passage at a dose of 8 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> ranging from 80% down to 8% on increasing the UVT from 65 to 90%. UV transmittance thus appears to be a significant parameter in determining the economic viability of AOP treatment for MA removal.

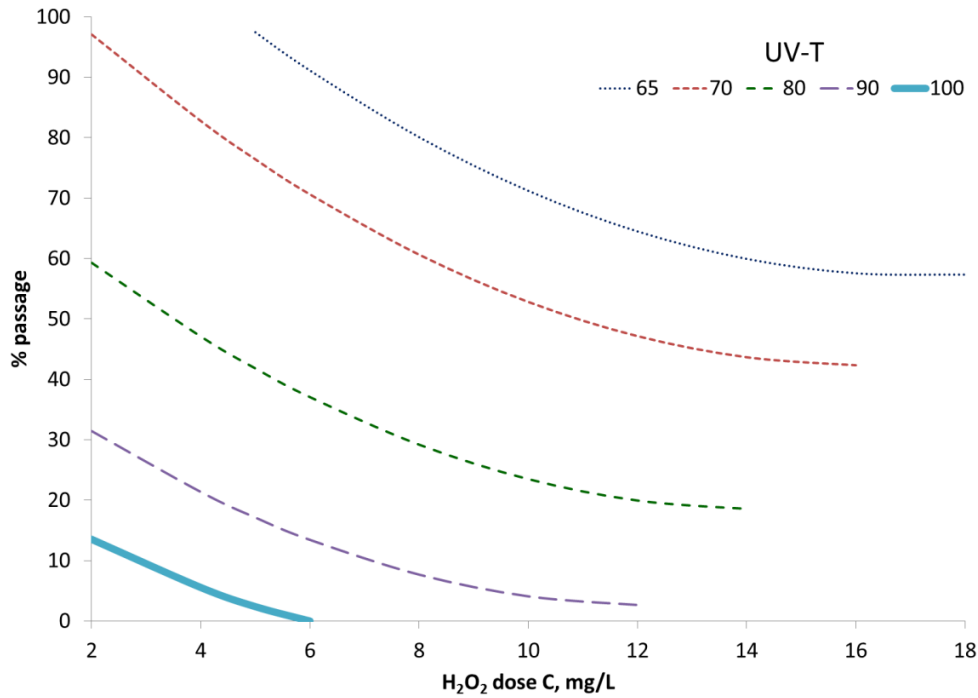


Figure 7. Effect of UVT on metaldehyde passage (100-%removal) as a function of UVT and H<sub>2</sub>O<sub>2</sub> concentration, according to BBD analysis, 1.68-2.98kW power input (from Equation 3)

### 3.5 Operating expenditure (OPEX)

The operating cost of applying a UV/H<sub>2</sub>O<sub>2</sub> AOP for MP removal is determined primarily by:

- the energy demand  $E_D$  of the UV device,
- the hydrogen peroxide demand, and
- the replacement frequency of critical, high-cost components.

The first two of these are defined by the outputs from Equation 3 (Figure 7), which permits computation of OPEX for water qualities pertaining to the MF and RO permeate based on the test conditions employed (Table 5). It is of interest to extend the OPEX calculation to include both other OPEX components and alternative treatment options for attaining a nominal target removal.

**Table 5:** AOP treatment conditions and associated OPEX relating to test conditions employed in the current study (MF and MF-RO pretreatment).

Parameter	MF-AOP	MF-RO-AOP
$E_D$ , kWh.m <sup>-3</sup>	2.17	0.50
UV dose, mJ cm <sup>2</sup>	2600	2181
% MA removal	77	80
H <sub>2</sub> O <sub>2</sub> dose, mg L <sup>-1</sup>	16	1
OPEX* £ m <sup>3</sup>		
Energy	0.241	0.072
Chemicals	0.033	0.002
Maintenance	0.099	0.099
TOTAL	0.373	0.173

\*Electricity cost 0.11 £ kWh<sup>-1</sup> (Energy EU, 2012); 35% w/v H<sub>2</sub>O<sub>2</sub> 0.59 £ L<sup>-1</sup> (Supplier); Pump rating 0.25 kW; H<sub>2</sub>O<sub>2</sub> pump rating, 0.015 kW; Lamp life 9000h; citric acid CIP frequency 26 y<sup>-1</sup>; citric acid CIP concentration 2.5 g L<sup>-1</sup>

A recent 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<sup>-3</sup> for the MF process and £0.19-0.23 m<sup>-3</sup> for the complete MF-RO process for flows of 25-100 MLD (Raffin, 2012). This compares with costs of £0.25-0.26 m<sup>-3</sup> 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 OPEX is primarily a function of the UVT, it is appropriate to consider the option of activated carbon (AC) for removing TOC which represents the main contributor to impaired UV transmittance. Recent trials, again based on the same plant (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<sub>254</sub> 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<sup>-3</sup> of water treated.

The AOP  $E_D$  and peroxide demand values computed from Equation 3 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 (Table 6). Combining the associated OPEX of these demand data (based on the assumptions listed in Table 5) allows the OPEX of the AOP stage to be determined for each of these streams. These can then be combined with the costs relating to the other unit operations (Table 7) to generate total OPEX values of the key candidate process treatment schemes (Figure 8), which exclude both labour and disposal costs but are otherwise based on similar conditions of feedwater quality (secondary municipal effluent).

**Table 6:** Calculated OPEX for AOP process within three treatment schemes for >75% metaldehyde removal.

Parameter	MF-AOP	MF-AC-AOP	MF-RO-AOP
$E_D$ , kWh.m <sup>-3</sup>	2.17	0.77	0.50
UV dose, mJ cm <sup>2</sup>	2600	2196	2181
% removal	77	82	80
H <sub>2</sub> O <sub>2</sub> dose, mg L <sup>-1</sup>	16	5	1

**Table 7:** Comparable unit process OPEX, £ m<sup>-3</sup>

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 <i>et al</i> (2013)
%RO of total	0.62	0.62	Raffin (2012)
AOP, post MF	0.373		James <i>et al</i> (this study)
AOP, post RO	0.176		James <i>et al</i> (this study)
AOP, post AC	0.199		James <i>et al</i> (this study)
GAC	0.09	0.16	Hatt <i>et al</i> (2013)

The OPEX data (Figure 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.

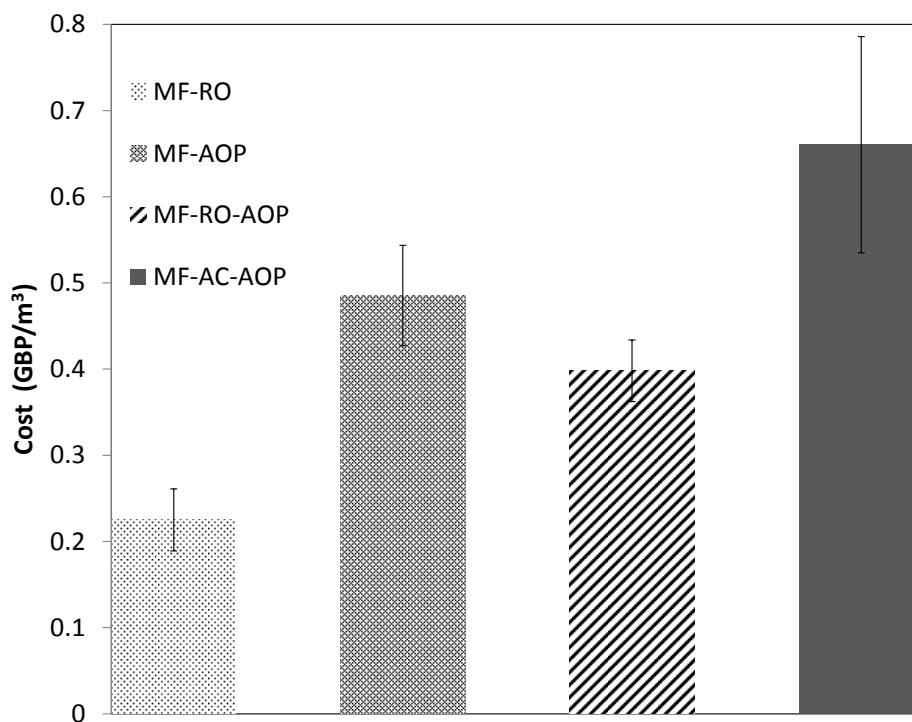


Figure 8. Projected OPEX values of four treatment schemes, based on 77-90% removal of metaldehyde from secondary municipal wastewater.

## 4 Conclusions

An extensive pilot-scale study of the efficacy of an advanced oxidation UV-H<sub>2</sub>O<sub>2</sub> process for micropollutant (MP) removal 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. Notwithstanding this, tests indicated all MPs other than metaldehyde and trihalomethanes to be removed by at least 85% by the AOP process when employed downstream of a microfilter (MF), with the estrogenic substances being more than 99% removed down to levels of ~1 ng L<sup>-1</sup>. Under the conditions employed to achieve such removal, the calculated OPEX of the MF-AOP process is in the range of £0.32-0.40 m<sup>-3</sup> – 50-70% higher than the MF-RO process but without the requirement for concentrate management.

Removal of the most recalcitrant MP metaldehyde (MA) by more than 75% demands improved transmittance of the wastewater using either a downstream reverse osmosis (RO) process or supplementary activated carbon (AC). Whilst 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, a significant waste stream volume is generated in the form of the concentrate

stream. The OPEX of the enhanced, three-stage processes can be up to 2.2 times that of the standard MF-RO process.

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