Feasibility study on the application of advanced oxidation technologies for decentralised wastewater treatment

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Abstract

Advanced oxidation technologies (AOTs) have been widely investigated for their potential application in post-tertiary sewage treatment due to their ease of operation, high efficiency in organic mineralisation, inactivation of pathogens and low formation of disinfection by-products. This study aimed to evaluate the technical, economical and environmental feasibility for applying AOTs at decentralised wastewater treatment. A comprehensive process selection and assessment framework for the application of AOTs in decentralised wastewater systems for wastewater recycling and reuse purposes was developed in this study. Different AOTs were assessed for their suitability to retrofit as an advanced wastewater treatment option to a decentralised wastewater case study plant in South East Queensland, Australia to produce Class A+ recycled water. Among the different AOTs assessed, it was assessed that the H2O2/UV process was the best AOT treatment option, in terms of technical, economic and environmental benefits for treating sewage effluent from the decentralised wastewater system analysed in this case study. It is anticipated that additional data sets from different pilot or full scale AOT plants will allow the performance predictions of AOTs for a wide range of decentralised wastewater treatment applications. Through this study, it is anticipated that the potential future uptake of AOTs as an advanced treatment option will be enhanced, given the comprehensive and detailed technical, economic and environmental analysis presented in the paper.

Key words: Small-scale wastewater systems; water recycling and reuse; techno-economic assessment and advanced oxidation processes.
1. Introduction

Water scarcity has become an issue worldwide due to various factors such as rapid population growth, booming industrialisation activities and climate change issues (Tjandraatmadja et al., 2009). With growing demand on clean water resources, the traditional methods of supplying water supply for day-to-day non-potable activities has to be re-examined to consider alternative water sources such as rainwater, stormwater and treated wastewater effluent (Sharma et al., 2010). A strategy utilising various alternative water sources for non-potable household application, could contribute to a reduction in the reliance on traditional mains water supplied from the grid. This would allow alternative water sources to be used on a “fit-for-purpose” basis which could possibly also reduce the costs associated with centralised water treatment, long-water transport distances, pumping from centralised water treatment plants, pumping energy as well as construction and maintenance of water pipeline infrastructure (Chong et al., 2011). In this context, there are several examples in Australia where water recycling and reuse have been successfully demonstrated on a large-scale to supply alternative water sources for non-potable household application (i.e. toilet flushing, cold tap washing machine and external garden irrigation) (Cook et al., 2009).

In a push to achieve a more sustainable urban water environment through Integrated Urban Water Management (IUWM), the decentralisation of water sources has gained importance for new greenfield urban residential developments (Sharma et al., 2012). These approaches are considered to be beneficial in reducing the stress and loadings on existing water transport infrastructure and treatment systems, as well as the previously mentioned benefits obtained from water recycling and reuse. Reuse of treated sewage effluent might be more promising because it is not hampered by the temporal and spatial availability of rainwater and stormwater sources. Historically, decentralised wastewater systems were mostly used in semi-urban, rural and remote areas where the provision of centralised sanitation technology is not technically, economically and environmentally feasible (Cook et al., 2009). For example, septic tanks and absorption trenches have been used at a decentralised scale to treat wastewater to meet the necessary environmental discharge obligations. With the advancement of water/wastewater treatment technologies, a suite of water treatment technologies is now available to provide a higher standard of wastewater treatment to enable better end-use application of the treated sewage effluents in an urban environment (Ho et al., 2010). These include technologies such as sand and media filtration, adsorption using granular activated carbon, zeolite or other clay materials, membrane bioreactor, biological nutrient removal processes, chlorination and an emerging suite of oxidation processes, which can be applied based on the treated sewage quality requirements and matching specific end-uses (Ho et al., 2010).

Advanced oxidation technologies (AOTs) have been widely investigated for their potential application in post-tertiary treatment of sewage, particularly where the source waters contain high concentration of ambiguous, refractory and recalcitrant chemical compounds such as aromatics, pesticides, pharmaceuticals and personal care products, drugs and endocrine disruptors and others (Suárez et al., 2008; Snyder et al., 2006; Chong et al., 2010a). The principles of AOTs are based on the in situ generation of reactive oxygen species such as hydroxyl radicals, superoxide anions, ozone and hydrogen peroxide for the oxidation of organic compounds that lead to a complete mineralisation (Chong et al., 2009 & 2010a). The AOTs include ultrasound, photocatalysis, ozonation, Fenton’s chemistry, hydrogen peroxide and others (Choi et al., 2002). The main objectives of utilising AOTs for advanced wastewater treatment include: (1) reduction in the formation potential of disinfection by-products (DBPs); (2) operating condition at ambient temperature and pressure; (3) complete oxidation of organics to innocuous carbon dioxide, water or other harmless by-products, rather than phase transferred via conventional adsorption, absorption or stripping treatment options (Chong et al., 2010a). The targeted compounds are usually mineralised when treated with AOTs rather than transferred to other phases, making AOTs a rather interesting suite of treatment technologies for water recycling where (1) high water quality obligations have to be met or (2) the wastewater sources are highly contaminated with recalcitrant compounds. Most of the previous studies have prescribed that the AOTs are ease to operate, highly efficient in organics oxidation and potentially adaptable to a range of wastewater treatment scales and final treated effluent requirements (Chong et al., 2009 & 2010a). To date, however; examples of AOTs for decentralised wastewater treatment are scarce and a proper process selection and assessment framework does not currently exist.
In this study, a comprehensive process selection and assessment framework for the application of AOTs in decentralised wastewater treatment systems for water recycling and reuse purposes been developed. A preliminary feasibility evaluation of different AOTs for decentralised wastewater treatment was conducted using the data and information from the open literature. The focus was on AOTs using (1) Ozonation; (2) Fenton and photo-Fenton processes; (3) UV-based photolysis and chemical oxidation processes; and (4) Photocatalytic processes. The technical, economic and environmental feasibility criteria for applying AOTs at decentralised wastewater treatment scale have been assessed for a case study plant in South East Queensland (SEQ). The technical feasibility and suitability of utilising different AOTs for advanced treatment, after membrane bioreactor (MBRs) treatment is justified. Other key processes and applicability constraints such as operation and maintenance, environmental impacts (i.e. sludge production, discharge of treated effluent to environmentally sensitive areas) and physical footprints are also discussed. Additionally, the economics of using different AOTs as advanced wastewater treatment options for decentralised systems have been quantified. Kinetic data on organic degradation using AOTs available in the open literature is used to estimate the treatment cost ($/L) together with a simple engineering cost estimation. Through this study, it is anticipated that the potential future uptake of AOTs as an advanced treatment option will be enhanced, given the comprehensive and detailed technical, economic and environmental analysis presented in the paper.
2. Background Information

2.1. Advanced oxidation technologies (AOTs)

With the increased awareness of environmental protection coupled with strong wastewater discharge legislation, the need for green wastewater treatment technology is growing fast. AOTs are considered as an advanced technology for wastewater treatment, considering their reported high destruction efficiency for toxic pollutants that are usually resistant to conventional biological wastewater treatment processes (Laera et al., 2011). Previous studies have reported that the pollutants that are amenable to biological treatments can be oxidised by integrating a post-treatment AOT stage (Fedorak and Hrudey, 1984; Barreiro and Pratt, 1992; Reemtsma and Jekel, 1997). Although the mechanism of AOTs rely on the formation of OH radicals, the formation pathways might be different under various operating conditions and this may have a strong implication on the respective operating and maintenance issues. Table 1 shows the different AOTs, which are commonly used for wastewater treatment, along with their dominant chemicals or equipment used.

2.2. Case study of decentralised wastewater treatment in SEQ

In Australia, there are a number of well-known cases where local wastewater is collected, treated and reticulated for non-potable reuse within the household. This is usually achieved through the operation of a small decentralised wastewater treatment plant that serves the particular area or urban development of interest. In this study, a decentralised wastewater treatment plant at Capo di Monte, Mount Tamborine (SEQ) that serves 46 detached and semi-detached residential dwellings and a large community centre was used as a case study for assessing the feasibility of using AOTs as an advanced treatment option. Currently, the decentralised wastewater treatment plant is operating with a hydraulic capacity of 11,000 L/d, and is comprised of a raw sewage primary holding wet well followed by a MBR (with submerged Kubota flat sheet membranes), alum dosing for phosphorus removal, UV disinfection and chlorination. Figure 1 shows the schematic for the decentralised wastewater treatment plant at Capo di Monte. The treated Class A+ effluent is reticulated via a dual reticulation system and is used for toilet flushing and external irrigation at each household. A vegetated buffer zone of 6,000 m² is available for land application of excess treated wastewater to prevent direct discharge into the local waterway. This feasibility study assessed the type of AOT to be used after MBR treatment to minimise the potential public health and environmental risks in treated effluent.

An automatic sampler (ISCO 6700 series) was used in parallel with grab sampling (every 4 h) for wastewater samples up to 3 day. The sampler was programmed to fill 1 L high-density polyethylene containers for individual and daily composite samples. Subsequently, these samples were analysed for suspended solids (SS), total nitrogen (TN), pH, biological oxygen demand (BOD) and chemical oxygen demand (COD) in water qualities.

2.3. Methodology - Process selection and assessment framework

In order to assess the feasibility of using AOTs as an advanced treatment option in a decentralised wastewater treatment plant, a comprehensive process selection and assessment framework was developed (Nakakubo et al., 2012). Figure 2 shows the assessment framework, which contains 6 major process selection criteria of (1) technical suitability, (2) system robustness, (3) economic, (4) environmental impacts, (5) sustainability and (6) space requirements. This framework was developed based on the scenario that AOTs will be retrofitted as an advanced treatment option for existing wastewater treatment plants (WWTPs). In this instance, this framework was used to guide the process selection for the selected case study.

In this study, three process selection criteria of technical, economic and environmental feasibility were targeted to give a preliminary review on the AOTs considered for the case study. Other process selection criteria assessed once the suitable AOTs are selected, based on the availability of relevant process inventory data sets to permit a comprehensive evaluation process. For the technical suitability criterion, the AOTs was assessed based on their compatibility to the wastewater characteristics and operating conditions if applied downstream of the wastewater treatment processes. These technical assessments include the evaluation of whether (1) the AOTs can handle the wastewater characteristics (i.e. COD, BOD, nitrogen, phosphorus and
total suspended solids) after the MBR treatment; (2) cope with the use of additive chemicals (i.e. pH correction, alum dosing, chlorination and other oxidants) and (3) meet the process needs for different operating conditions (i.e. temperature and pressure).

The economic feasibility was assessed by using the first principle engineering cost estimation methods based on the literature data available for the reaction rate constant \( k \), base reactor volume (L), unit treatment cost ($/1000 US galloon) and specific energy (kWh/kL) (Mahamuni and Adewuyi, 2010). In this instance, the rate constants for degradation of COD by different AOTs were assumed to be the average value comprised of three common pollutants of phenol, trichloroethylene (TCE) and reactive azo dyes.

\[
k_{\text{COD}}(\text{min}^{-1}) = \frac{k_{\text{phenol}}(\text{min}^{-1}) + k_{\text{TCE}}(\text{min}^{-1}) + k_{\text{dye}}(\text{min}^{-1})}{3}
\]  

By assuming a first-order rate equation, the total reaction time required to achieve the anticipated final COD concentration was taken as the hydraulic retention time to size the AOT reactors for this feasibility study.

\[
\ln\left(\frac{C_{\text{AO}}}{C_A}\right) = k_{\text{COD}}t
\]

\[
t(\text{min}) = \frac{\ln\left(\frac{C_{\text{AO}}}{C_A}\right)}{k_{\text{COD}}}
\]

where \( k \) is the first order rate constant (min\(^{-1}\)), \( C_{\text{AO}} \) is the initial COD concentration (mg/L) and \( C_A \) is the final COD concentration (mg/L), and \( t \) is the total reaction time or residence time (min). Subsequently, the AOT reactor size required was estimated based on Eq. (4).

\[
V(\text{AOT volume})[\text{L}] = \tau(\text{Residence time})[\text{min}] \times \nu(\text{Hydraulic flow rate})[\text{L/min}]
\]

where \( \tau \) is the residence time (min), \( V \) is the AOT reactor volume (L) and \( \nu \) is the hydraulic flow rate (L/min). The unit treatment cost ($/L) was estimated by using available literature data, taken into account both the capital, operating and maintenance (O&M) costs. The total treatment cost for the AOTs was amortized at a rate of 7% over an effective plant life of 30 years. In this instance, the power relationship known as the six-tenths factor rule was used to estimate the unit treatment costs for each AOT assessed in this study (Peters et al., 2004). This is to make use of the literature available data on the base reactor volume and the corresponding unit treatment cost ($/1000 US galloon) (Mahamuni and Adewuyi, 2010).

\[
\text{Unit treatment cost}($/L) = \left(\frac{V_{\text{estimated}}}{V_{\text{base}}}\right)^{0.6} \times \left(\frac{\text{Base treatment cost}($)}{1000 \text{ US galloon}}\right) \times \frac{1000 \text{ US galloon}}{3785.412L}
\]

It should be stressed that the treatment costs estimated and used to assess the economic feasibility of AOTs serves as a preliminary guide towards the selection of the most appropriate AOTs. A detailed validation for the treatment cost should be ascertained once the most feasible AOTs are selected by quotations from the
vendors. Such a validation will enable the development of a cost function that can be used to accurately predict the economic feasibility for the application of AOTs in decentralised wastewater systems. Unfortunately at the moment the cost database for such systems is scarce and incomplete.

The specific energy for different AOTs was assessed in a similar way to the unit treatment cost estimation as presented in Eq. (6). The available energy intensity data (kWh/kL) in literature with the relevant information on base reactor volume was used for this estimation (Mahamuni and Adewuyi, 2010).

\[
\text{Specific energy (kWh/kL)} = \left( \frac{V_{\text{estimated}}}{V_{\text{base}}} \right)^{0.6} \times \left( \frac{\text{Energy intensity [kWh]}}{kL} \right) \tag{6}
\]
3. Results and Discussion

3.1. Comparison between different AOTs for decentralised system

The integration or retrofitting of AOTs as an advanced wastewater treatment option for existing WWTPs requires the development of proper assessment guidelines, such as the one shown in Figure 2. In this instance, the suggested technical assessments such as the evaluation of whether the AOTs can (1) handle the wastewater characteristics (i.e. COD, BOD, nitrogen, phosphorus and total suspended solids); (2) cope with the use of additive chemicals (i.e. pH correction, alum dosing, chlorination and other oxidants) and (3) meet the process needs for different operating conditions (i.e. temperature and pressure) should be considered and assessed thoroughly.

The basic understanding of the reaction mechanisms, operating conditions and requirements and any other process application constraints for the four AOTs of interest needs to be reviewed prior to the technical assessments. Table 2 shows a brief overview summary and comparison of the formation mechanisms of OH radicals in common AOTs, as well as a comparison of their operating conditions, requirements and constraints. From Table 2, it can be observed that ozonation processes operate at ambient temperature and pressure but require strict pH control at alkaline conditions to avoid the formation of conjugate base HO₂⁻ which can strongly affect the concentration of reactive radicals formed (Hoigné, 1998). The presence of such conjugate bases might affect the short lifetime of ozone in alkaline solution (Hoigné, 1998). Although the side formation of H₂O₂ can also play an enhancement role during the decomposition of O₃ to form OH-, the detrimental effect of pH on its formation has yet to be ascertained, as H₂O₂ in nature is a weak acid. The pH for pure H₂O₂ was reported to be 6.2, but this pH can go as low as 4.5 when diluted at approximately 60% (i.e. volume/volume %) (US Peroxide, 2011). Also, if the ozonation is to be retrofitted as an advanced wastewater treatment option for the case study presented, additional equipment such as a reactor vessel and special gas-liquid contactor for ozone sparging and distribution needs to be taken into account (Gogate and Pandit, 2004).

As for the Fenton or photo–Fenton processes that include the UV/Fe³⁺-Oxalate/H₂O₂ process in this instance, their basic mechanism relies strongly upon the formation of OH radicals via the reaction with the iron species found in wastewater (Neyens and Baeyens, 2003). The benefits of the Fenton based process are that iron is usually present in abundance in wastewater and the H₂O₂ is easy to handle and is environmental friendly (Andreozzi et al., 1999). The only difference between the three Fenton based processes is that the UV/Fe³⁺-Oxalate/H₂O₂ system has the highest quantum efficiency of 1.0 – 1.2, followed by the photo–Fenton process with a low quantum yield of 0.14 (at 313 nm) to 0.017 (at 360 nm) and lastly, the Fenton process (Andreozzi et al., 1999). Other distinction between the Fenton based processes and other AOTs is that the mechanism for the formation of reactive hydroxyl radicals is preferred at a low acidic pH of 2.6 – 2.8. Andreozzi et al. (1999) reported that the use of the UV/Fe³⁺-Oxalate/H₂O₂ process provides a higher quantum efficiency due to accessibility to the wider UV spectrum of 200-400 nm, which can generate a continuous Fenton’s reagent at only about 20% the energy required by typical photo-Fenton system. Similarly to other AOTs, the downside for the Fenton based processes might be due to competition between the different hydroxyl derivatives, organic and inorganic substrates found in wastewater.

The UV–based photolysis and chemical oxidation processes utilise similar reactions but enhance the formation of OH radicals via the presence of a UV irradiation source. The presence of UV source induces cleavage and formation of OH radicals from its precursors (i.e. H₂O₂ or O₃). A few examples for AOTs that belong to this class are shown in Table 2. Among the different processes shown, it was interesting to note that the reactivity for O₃ decomposition under UV irradiation is much higher than H₂O₂, where the molar extinction coefficient for O₃ is 3600 M⁻¹cm⁻¹ (254 nm) and that of H₂O₂ is 240 M⁻¹cm⁻¹ (Andreozzi et al., 1999). Moreover, it should be noted that the O₃/UV process possesses the combined chemical behaviour of H₂O₂/UV and O₃/UV as H₂O₂ is produced during the reaction. Other than this, the AOTs were found to follow the standard operating conditions and requirements except for the additional UV irradiation needs. Similarly, the UV–based photolysis and chemical oxidation processes might get competition from other
organic substrates, which might act as inner filters to attenuate the intensity of UV lights used.

Among the AOTs detailed in Table 2, photocatalysis is an emerging type of heterogeneous AOT process where the mechanism for OH$^-$ radicals generation occurs on the solid-liquid interface of the semiconductor particles (Chong et al., 2010a). Usually the solid semiconductor particles such as TiO$_2$ are suspended in the targeted effluent for treatment with the co-presence of UV irradiation with wavelengths below 385 nm. The operating conditions are at ambient temperature and pressure. However, the current application of TiO$_2$ photocatalytic technology still faces the challenges of (1) post-separation of semiconductor after water treatment; (2) rapid electron-hole recombination that warrants low quantum efficiency; (3) mass transfer problems with oxygen, light and water pollutants at the solid-liquid interface and (4) the semiconductor catalytic surface might get fouled by different organic pollutants and inorganic ions in wastewater (Chong et al., 2010a & 2010b). A comprehensive review of these issues was discussed previously in Chong et al. (2010). After considering all these operating conditions, requirements and constraints for the different AOTs of interest, it is necessary to assess their technical suitability and applicability to the current case study decentralised wastewater plant in SEQ.
3.2. Technical Feasibility

To assess the technical feasibility of retrofitting AOTs as an advanced wastewater treatment option for the case study, it is important to understand the quality of treated sewage effluent that is supplied to the AOT. This ensures that the AOTs can be retrofitted with minimal modification of both the effluent characteristics and process operating conditions. Figure 3 shows the quality characteristics of the treated sewage effluent from the decentralised wastewater treatment plant in SEQ, obtained by using grab sampling methodology (from \( N = 6 \) events). From Figure 3, it can be observed that the statistics presented for five common wastewater parameters of suspended solids (SS), total nitrogen (TN), pH, biological oxygen demand (BOD) and chemical oxygen demand (COD) are quite constant. For each wastewater parameter, the relevant mean, median 25\(^{th}\) and 90\(^{th}\) percentile concentrations are given. The corresponding concentrations (± S.D.) for the measured wastewater parameters are; suspended solids: 4.5 ±0.5 mg/L; total nitrogen: 11.68 ±1.70 mg/L; pH: 7.78 ±0.17; BOD: 5.83 ±2.04 mg/L and COD: 21.50 ±3.27 mg/L. According to the Australian guidelines for water recycling (NRMCC-EPHC-AHMC, 2006), all of the measured concentrations for these common wastewater parameters are deemed safe, acceptable and are within the current threshold limits for both public health and environmental risks. In the guidelines however, no guideline limit was recommended for COD concentrations. In this instance, the presence of a relatively high COD concentration might present public health and environmental risks owing to the potential presence of effluent organic matters, recalcitrant organic compounds, un-degraded reactive azo dye compounds, pharmaceutical parent compounds or metabolites which are hazardous and might further react with chlorine to form DBPs (Chong et al., 2010c). Detailed monitoring of the individual chemical compounds needs to be undertaken to determine the DBPs formation potential. The real public health risks of using treated sewage effluent to augment mains water demand from a decentralised wastewater plant comes from the potential cross connection of piping between the mains water supply and the third pipe supplying treated sewage effluent. Thus, a final COD concentration limit of 10 mg/L was set in this instance to minimise the potential risks, as well as serving as a treatment target for the subsequent economic evaluation of the different AOTs under consideration.

From the measured pH values, it was easy to assess which AOTs can be retrofitted without the vast use of additive chemical reagents (for pH correction) as well as alteration of the operating conditions for the existing wastewater treatment train. Since the measured pH values are marginally alkaline, it would be more appropriate to retrofit AOTs that operate well within this alkaline pH regime. From Table 2, from all the reviewed AOTs, it can be observed that only ozonation (O\(_3\)), ozonation/ultraviolet irradiation (O\(_3\)/UV), hydrogen peroxide/ultraviolet irradiation (H\(_2\)O\(_2\)/UV) and TiO\(_2\) photocatalysis would be suitable. Although the Fenton–based treatment processes have been shown to be relatively superior in treatment efficacy, especially for the UV/Fe\(^{3+}\)/Oxalate/H\(_2\)O\(_2\) process with high quantum yield and lower operational energy, their application in this case study might be hampered by their low acidity operating requirements. Thus, only the assessed AOTs of ozonation (O\(_3\)), ozonation/ultraviolet irradiation (O\(_3\)/UV), hydrogen peroxide/ultraviolet irradiation (H\(_2\)O\(_2\)/UV) and TiO\(_2\) photocatalysis are considered technically feasible and their treatment cost are estimated in the following section.

Although the results shown in Figure 3 indicted that as the other parameters (i.e. SS, TN and BOD) are close to the threshold limit of 10 mg/L, there might be some chance of exceeding this licensed concentration. Figure 4 shows the probability of exceedances for the respective wastewater parameters, which was estimated using the measured average (± S.D.) in Monte Carlo simulations. Results showed that there is an 84% chance for the TN to exceed the 10 mg/L concentration limit, with a maximum simulated concentration of 17.36 mg/L. This is followed by a 4% chance for BOD to exceed the license concentration of 10 mg/L, with a maximum simulated concentration of 12.60 mg/L. It was found that the decentralised wastewater system is quite efficient in the removal of suspended solids, with little chance of the wastewater parameter exceeding the 10 mg/L concentration threshold. Previously, it has been shown that apart from the removal of organic carbon compounds (i.e. TOC and COD), AOTs are also capable of simultaneously degrading BOD and other nitrogenous compounds (Gogate and Pandit, 2004). Thus, given the stochastic variations in the treated sewage effluent, it is anticipated that the integration of the proposed AOTs can not only minimise the public health and environmental risks but also improve the stability of the system to produce treated sewage effluent with the quality needed by the license requirements.
### 3.3. Economic and Environmental Feasibility

The treatment economics of AOTs using O$_3$, O$_3$/UV, H$_2$O$_2$/UV and TiO$_2$ photocatalytic processes was assessed based on the methodology described in Section 2.3. The design hydraulic flow rate considered for this study was 11,000 L/day (i.e. the current flow rate of the decentralised wastewater treatment plant). Table 3 shows the summary of estimated treatment cost ($/L) of various AOTs assessed for the current decentralised wastewater treatment plant case study in SEQ. From the estimated treatment costs, it is evident that the O$_3$ treatment process was the most economically feasible AOT ($ 0.03/L) for minimising the potential health and environmental risks and in ensuring the quality of the treated sewage effluent for reuse purposes. This was followed by the AOTs of H$_2$O$_2$/UV and O$_3$/UV treatment with estimated treatment costs of $ 0.14/L and $ 0.21/L, respectively. From the economic analysis, the TiO$_2$ photocatalytic treatment appeared to be most expensive AOT option. Similarly, Mahamuni and Adewuyi (2010) also estimated the AOTs treatment costs for O$_3$, O$_3$/UV, H$_2$O$_2$/UV and TiO$_2$ photocatalytic treatment processes based on a much higher design hydraulic flow rate of 1000 L/min (i.e. 1,440,000 L/day). They also found a similar trend of treatment costs in the order of O$_3$ < O$_3$/UV < H$_2$O$_2$/UV < TiO$_2$ photocatalytic processes.

The O$_3$ treatment process was the more economical AOT treatment option for similar level of COD reduction from 21.5 mg/L to 10.0 mg/L compared with the O$_3$/UV and H$_2$O$_2$/UV treatment options, as the later require higher O&M costs for UV system. This includes higher energy intensity and constant bulb replacement for the UV systems involved (Mahamuni and Adewuyi, 2010). It has been reported that the part replacement costs for UV systems are as high as 45% of the annual electrical power consumption costs (USEPA, 2006). Although the O$_3$ treatment process also involves parts replacement costs for the ozone generator, the total O&M costs is still relatively lower than the AOTs, which combine chemical and UV photolysis systems. For example, the H$_2$O$_2$/UV treatment process requires a metering pump, reservoir storage, the use of H$_2$O$_2$ and part replacement for the UV system. For the TiO$_2$ photocatalytic treatment process, the relatively high treatment costs are incurred because of the cost of TiO$_2$ particles used, parts replacement costs for the UV system, catalyst holder replacements for the catalytic system, as well as issues with the post-separation of semiconductor TiO$_2$ particles after wastewater treatment (Mahamuni and Adewuyi, 2010).

The specific energy requirement (in kWh/kL) for each AOT was also estimated. This was assessed in accordance with the sustainability criterion detailed in Figure 2. This information is important as it allows the determination of the energy efficiency of the AOTs; as well as their indirect GHG emissions from fossil fuel combustion. Figure 5 shows the estimated specific energy for the different AOTs considered in this study. Results showed that the H$_2$O$_2$/UV treatment process is the most efficient technology with a specific energy of 0.23 kWh/kL, owing to the OH$^-$ radicals generation via the use of chemical reagents. This was followed by the specific energy for O$_3$/UV and TiO$_2$ photocatalytic treatment processes of 6.15 kWh/kL and 7.09 kWh/kL, respectively. The O$_3$ treatment process was the most energy intensive process with a specific energy of 11.93 kWh/kL. The reason for the lower specific energy in O$_3$/UV treatment process compared to the O$_3$ treatment process is due to the higher turnover rate or shorter residence time in the former required to achieve the final COD concentration requirement. When the estimated specific energy was converted to an indirect carbon footprint (i.e.0.9 kg CO$_2$-e/kWh), the indirect GHG emission was estimated to be in the range of 0.20 kg CO$_2$-e/kL (H$_2$O$_2$/UV treatment process) to 10.73 kg CO$_2$-e/kL (O$_3$ treatment process) (Hall et al., 2009). It is apparent, however; from Figure 2 that a comprehensive sustainability assessment cannot be made as these estimations were not validated through energy system monitoring, nor did they include fugitive GHG emissions (i.e. methane and nitrous oxide) which add to the overall carbon footprint for different AOTs (Blottnitz and Curran, 2007). Further inventory data sets from different pilot or full scale AOTs are needed to allow for a more accurate and comprehensive sustainability assessment of AOTs for decentralised wastewater applications. However, the costs estimated in this study still present a useful guide on the selection of AOTs based on the technical, economical and environmental criteria. Based on this, the H$_2$O$_2$/UV treatment process was considered to be the best AOT treatment option that can be retrofitted to the current decentralised wastewater case study plant in an effort to improve the quality of treated sewage effluent for non-potable reuse.
4. Conclusion

This study provided new insight into the application of AOTs for decentralised wastewater treatment, in an attempt to improve the quality of treated sewage effluent. From this feasibility study, it can be concluded that the $\text{H}_2\text{O}_2$/UV treatment process is the best AOT in terms of fulfilling the technical, economical and environmental constraints for advanced wastewater treatment for the water quality existing in the case study. The $\text{H}_2\text{O}_2$/UV treatment process was assessed to be capable of treating the connecting wastewater stream after the MBR process to the quality of licensed requirements. The estimated unit treatment cost for the $\text{H}_2\text{O}_2$/UV option was estimated to be $0.14/L. The $\text{H}_2\text{O}_2$/UV treatment process was the most energy efficient technology with a specific energy of 0.23 kWh/kL, which corresponded to a low indirect GHG emission of 0.20 kg CO$_2$-e/kL. At present, the overall GHG footprints are incomplete due to missing information on the fugitive GHG emissions. In this context more inventory data sets from different pilot or full scale AOTs plants are needed to allow accurate and comprehensive assessment of AOTs for decentralised wastewater applications. Until this data can be obtained the costs estimated in this study still present a useful guide on the selection of AOTs based on technical, economical and environmental criteria. In conclusion, the $\text{H}_2\text{O}_2$/UV treatment process was found to be the best AOT treatment option that can be retrofitted to the current decentralised wastewater case study plant in an effort to improve the quality of treated sewage effluent for non-potable reuse.

Acknowledgement

The authors would like to thank Ms Shivanita Umapathi for the collection of wastewater samples, and the Urban Water Security Research Alliance’s SEQ Decentralised Systems project for the information on wastewater characteristics. This work was funded by the CSIRO’s Land and Water Divisions Capability Development Theme.

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TABLES

**Table 1**: Different types of AOTs used in wastewater treatment, along with their dominant chemicals or equipment used (Choi et al., 2010).

<table>
<thead>
<tr>
<th>Process</th>
<th>Chemicals or equipment used</th>
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<tr>
<td>Ozonation</td>
<td>O$_3$</td>
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<tr>
<td>Fenton and photo-Fenton processes</td>
<td>Fe$^{2+}$+H$_2$O$_2$, Fe$^{2+}$+H$_2$O$_2$+UV</td>
</tr>
<tr>
<td>UV-based photolysis &amp; chemical oxidation</td>
<td>UV+O$_3$, UV+H$_2$O$_2$, UV+O$_3$+H$_2$O$_2$</td>
</tr>
<tr>
<td>processes</td>
<td></td>
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<tr>
<td>Photocatalytic processes</td>
<td>Semiconductor (TiO$_2$, ZnO)/UV</td>
</tr>
</tbody>
</table>
Table 2: A brief overview summary and comparison on the formation mechanisms of HO radicals for common AOTs, as well as their common operating conditions, requirements and constraints.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction Mechanism</th>
<th>Operating Conditions &amp; Requirements</th>
<th>Remarks</th>
<th>Constraints</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozonation (Hoigné, 1998)</td>
<td>HO(^+) + O(_3) \rightarrow O(_2) + HO(_2)</td>
<td>Requires high pH conditions (alkaline solutions).</td>
<td>The reaction fundamentals are based on the ozone chemistry in aqueous alkaline solutions.</td>
<td>Usually the reaction extent is limited by the short life time of ozone in alkaline solutions.</td>
</tr>
<tr>
<td></td>
<td>HO(_2) + O(_3) \rightarrow HO(_2)(^+) + O(_3)</td>
<td>Requires special contactor for ozone sparging and distribution.</td>
<td>The side H(_2)O(_2) formed during ozonation also plays a role in the treatment process. Addition of H(_2)O(_2) will enhance O(_3) decomposition with formation of OH(^-).</td>
<td>Influence of pH is evident as the active species from ozonation is the conjugate base HO(_2)(^-) whose concentration is strictly dependent upon pH.</td>
</tr>
<tr>
<td></td>
<td>HO(_2)(^-) \leftrightarrow H(^+) + O(_2)(^-)</td>
<td>Ambient temperature and pressure.</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>O(_2)(^-) + O(_3) \rightarrow O(_2) + O(_3)(^-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(_3)(^-) + H(^+) \rightarrow HO(_3)(^-)</td>
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<tr>
<td></td>
<td>HO(_2)(^-) \rightarrow HO(^-) + O(_2)(^-)</td>
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<tr>
<td></td>
<td>HO(^+) + O(_2) \rightarrow HO(_2)(^+) + O(_2)</td>
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</tr>
<tr>
<td>Fenton (Andreozzi et al., 1999)</td>
<td>Fe(^{2+}) + H(_2)O(_2) \rightarrow Fe(^{3+}) + OH(^-) + OH(^\cdot)</td>
<td>Fenton process: Low pH (pH 2.7 – 2.8).</td>
<td>Fenton process: Iron is very abundant in wastewater and hydrogen peroxide is easy to handle and environmentally safe.</td>
<td>Requires strict pH control and sludge can be formed with related disposal problems.</td>
</tr>
<tr>
<td></td>
<td>Fe(OH)(^{2+}) + hv \leftrightarrow H(^+) + FeOOH(^{2+})</td>
<td>Photo-Fenton process: Low pH, UV-Vis wavelength of higher than 300 nm.</td>
<td>Photo-Fenton process: Allows the photolysis of Fe(^{3+}) complexes allows Fe(^{2+}) regeneration. Low quantum of 0.14 (at 313 nm) to 0.017 (at 360 nm).</td>
<td>Might compete with hydroxyl derivatives of aromatic pollutants as these absorb the same UV range as H(_2)O(_2) and Fe(^{3+}).</td>
</tr>
<tr>
<td></td>
<td>FeOOH(^{2+}) \rightarrow HO(^{-}) + Fe(^{2+})</td>
<td>UV/Fe(^{3+})-Oxalate/H(_2)O(_2): Low pH, UV-Vis wavelength of higher than 200-400 nm and addition of H(_2)O(_2).</td>
<td>UV/Fe(^{3+})-Oxalate/H(_2)O(_2): Can provide a continuous source of Fenton’s reagent and uses about only 20% of the energy required by typical photo-Fenton system. Quantum yield is 1.0-1.2.</td>
<td></td>
</tr>
</tbody>
</table>
UV-based photolysis & chemical oxidation processes (Andreozzi et al., 1999)

**Mn^{2+}/Oxalic acid/Ozone**

Mn(III) (AO^2-) + O_3 + H^+ → Mn(II) + (n-1)(AO^2-) + 2SO_2 + O_2 + OH^-  

The radical formation mechanism is at pH 4.0.

**H_2O_2/UV**

H_2O_2 + hv → 2OH^-  

Requires UV wavelength of smaller than 280 nm to induce the homolytic cleavage of H_2O_2.

**O_3/UV**

O_3 + hv → O_1(D) + O_2  

The cage effect of water molecules might lower the primary quantum yield to 0.5.

**TiO_2 Photocatalysis**

TiO_2 + hv → e^- + h^+  

e^-_{CB} → e^-_{TR}  

h^+_{VB} → h^+_{TR}  

e^-_{TR} + h^+_{VB}(h^+_{TR}) → e^-_{CB} + heat  

(O_2)_{ab} + e^- → O_2^-  

OH^- + h^+ → OH^-  

R-H + OH^- → R^- + H_2O  

R + h^+ → R^+ → Intermediate(s)/ Final Degradation Products  

O_2^- + OH^- → HOO^-  

HOO^- + e^- → HO_2  

HOO^- + H^+ → H_2O_2  

Continuous irradiation and aeration to provide agitation for catalysts suspension and electron scavengers (for slurry reactor) and electron scavengers only (for fixed bed reactor).

Ambient temperature and pressure.

Operates well at pH > PZC (semiconductor).

UV irradiation in the wavelength <385 nm.

Can be used to recover some noble metals found in wastewater.

Low quantum efficiency as caused by the rapid electron-hole recombination.

Treatment efficiency usually limited by mass transfer problems between the catalyst particles and pollutants found in wastewater.

Difficulty in post-separation of catalyst particles after wastewater treatment.

Catalytic surfaces might get fouled from different organic pollutants and inorganic ions.

**H_2O_2/UV:**

Requires alkaline pH.

**O_3/UV:**

Requires UV light of 254 nm.

Operates efficiently under alkaline pH.

Posses the combined chemical behaviour of H_2O_2/UV and O_3/UV, as H_2O_2 was produced during the reaction.

**H_2O_2/UV:**

Small molar extinction of H_2O_2 of 18.6 M^-1 cm^-1 at 254 nm, and thus only a relatively small fraction of light is exploited.

Might get competition from other organic substrates, which might act as inner filters to attenuate the UV light.

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Small molar extinction of H_2O_2 of 18.6 M^-1 cm^-1 at 254 nm, and thus only a relatively small fraction of light is exploited.

Might get competition from other organic substrates, which might act as inner filters to attenuate the UV light.

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Table 3: Summary of estimated treatment cost ($/L) of various AOPs for the decentralised wastewater case study plant in SEQ.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Rate Constant (k)</th>
<th>Estimated Residence Time (min)</th>
<th>Estimated Residence Time (sec)</th>
<th>Base reactor volume (L)</th>
<th>Estimated reactor volume (L)</th>
<th>Base Cost $ (1000 galloon)</th>
<th>Cost $/US gallon</th>
<th>Estimated Cost ($/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>For phenol</strong></td>
<td></td>
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<tr>
<td>O₃ (2 mg/L)</td>
<td>Kidak and Ince (2007)</td>
<td>0.0279 min⁻¹</td>
<td>27.4</td>
<td>0.10</td>
<td>209.58</td>
<td>1.20</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>O₃/UV</td>
<td>Kidak and Ince (2007)</td>
<td>0.0869 min⁻¹</td>
<td>8.8</td>
<td>0.10</td>
<td>67.29</td>
<td>38.65</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>Primo et al. (2007)</td>
<td>0.0524 min⁻¹</td>
<td>14.6</td>
<td>0.75</td>
<td>111.59</td>
<td>308.48</td>
<td>1.64</td>
<td></td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>Chen and Smirniotis (2002)</td>
<td>0.433 ppm min⁻¹</td>
<td>1.8</td>
<td>0.10</td>
<td>13.50</td>
<td>8648.79</td>
<td>43.36</td>
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</tr>
<tr>
<td><strong>For reactive azo dye</strong></td>
<td></td>
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<tr>
<td>O₃ (12.4 mg/L)</td>
<td>Tezcanli-Guyer and Ince (2004)</td>
<td>0.01108 min⁻¹</td>
<td>69.1</td>
<td>1.20</td>
<td>527.74</td>
<td>4.08</td>
<td>0.04</td>
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<tr>
<td>O₃/UV</td>
<td>Tezcanli-Guyer and Ince (2004)</td>
<td>0.02064 min⁻¹</td>
<td>37.1</td>
<td>1.20</td>
<td>283.30</td>
<td>34.02</td>
<td>0.24</td>
<td></td>
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<tr>
<td>H₂O₂/UV</td>
<td>Fung et al. (2000)</td>
<td>0.0124 min⁻¹</td>
<td>61.7</td>
<td>4.50</td>
<td>471.56</td>
<td>74.61</td>
<td>0.32</td>
<td></td>
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<tr>
<td>Photocatalysis</td>
<td>Taicheng et al. (2003)</td>
<td>0.0207 ppm min⁻¹</td>
<td>37.0</td>
<td>0.70</td>
<td>282.48</td>
<td>739.85</td>
<td>7.15</td>
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<tr>
<td><strong>For TCE</strong></td>
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<tr>
<td>O₃ (6 mg/L)</td>
<td>Nakano et al. (2003)</td>
<td>0.0209 min⁻¹</td>
<td>36.6</td>
<td>0.10</td>
<td>279.78</td>
<td>2.35</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>Hirnoven et al. (1996)</td>
<td>0.4418 min⁻¹</td>
<td>1.7</td>
<td>5.00</td>
<td>13.24</td>
<td>3.33</td>
<td>0.01</td>
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<tr>
<td><strong>For COD</strong></td>
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<td></td>
</tr>
<tr>
<td>O₃</td>
<td>This study*</td>
<td>0.01996 min⁻¹</td>
<td>38.4</td>
<td>0.47</td>
<td>292.95</td>
<td>2.55</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>O₃/UV</td>
<td>This study*</td>
<td>0.05377 min⁻¹</td>
<td>14.2</td>
<td>0.65</td>
<td>108.75</td>
<td>36.34</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>This study*</td>
<td>0.1689 min⁻¹</td>
<td>4.5</td>
<td>3.42</td>
<td>34.63</td>
<td>128.81</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>This study*</td>
<td>0.2269 ppm min⁻¹</td>
<td>3.4</td>
<td>0.40</td>
<td>25.78</td>
<td>4694.32</td>
<td>15.10</td>
<td></td>
</tr>
</tbody>
</table>
FIGURES

Figure 1: Schematic of decentralised wastewater system at Capo di Monte. RAS flow is the return activated sludge stream.
Figure 2: A comprehensive process selection and assessment framework for the application of AOTs in decentralised wastewater system for water recycling and reuse purposes.
Figure 3: Characteristics of the treated sewage effluent from the decentralised wastewater treatment plant in SEQ.
Figure 4: Monte Carlo simulations on the probability of exceedances for the respective measured treated wastewater parameters.
Figure 5: Estimated specific energy for the different AOTs considered in this study.