ADVANCED OXIDATION TECHNOLOGIES FOR WASTEWATER TREATMENT AND REUSE

Where to from here for decentralised systems?

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Abstract

This paper evaluates the technical, economical and environmental feasibilities for the application of advanced oxidation technologies (AOTs) for decentralised wastewater treatment systems. A comprehensive process selection and assessment framework for the application of AOTs in decentralised wastewater systems for water recycling and reuse purposes has been developed.

In this case study, different AOTs were assessed for their suitability as retrofit to a small decentralised wastewater plant in South-East Queensland (SEQ) as an advanced wastewater treatment option. Results showed that the H_2O_2 /UV treatment process was the best AOT treatment option in terms of the technical, economic and environmental benefits, as well as in the quality of treated wastewater for non-potable reuse. This study has also provided a new insight into the future application of AOTs for decentralised wastewater treatment, given the increased awareness of environmental protection coupled with strong legislation in final wastewater discharge requirements.

Introduction

With the increased awareness of environmental protection, coupled with strong legislation for the final discharge requirements for treated sewage effluent – together with the potential for nonpotable re-use – the need for green wastewater treatment technology is growing fast. The advanced oxidation technologies (AOTs) are considered an attractive eco-environmental wastewater treatment technology, considering their reported high destruction efficiency of toxic pollutants that are usually resistant to conventional biological wastewater treatments (Laera *et al*., 2011).

Previous studies have shown good removal efficiency by AOTs in degrading ubiquitous, refractory and recalcitrant chemical compounds such as aromatics, pesticides, pharmaceuticals, personal care products, endocrine disruptors and others (Synder *et al*., 2006; Suárez *et al*., 2008; Chong *et al*., 2010). In general, all these AOTs are characterised by a common chemical mechanism that involves the exploitation of in-situ generation of high reactivity OH radicals to react and degrade even the less reactive pollutants found in the targeted water sources to achieve a complete mineralisation state (Chong *et al*., 2009 and 2010).

The benefits of utilising AOTs for advanced wastewater treatment include: (i) reduction of the potential formation of disinfection by-products (DBPs); (ii) operating conditions at ambient temperature and pressure; (iii) complete mineralisation of refractory organic compounds to innocuous carbon dioxide, water or other harmless by-products (Chong *et al*., 2010).

This study was a case study to assess the feasibility of using different AOTs for a decentralised wastewater plant in SEQ. A process selection and assessment framework for the application of AOTs in decentralised wastewater treatment systems for water recycling and reuse purposes has been developed to guide the selection of the best AOT in terms of technical, economical and environmental criteria. It is anticipated that this study would also promote the future uptake of AOTs as an advanced treatment option for decentralised wastewater treatment for wastewater recycling and reuse, as well as meeting the strict discharge requirements to environment.

Types of Advanced Oxidation Technologies

Table 1 shows the different generic types of AOTs considered in this study, which are (1) Ozonation; (2) Fenton and photo-Fenton processes; (3) UV-based photolysis and chemical oxidation processes; and (4) Photocatalytic processes.

Decentralised Wastewater Treatment Plant – Case Study in SEQ

A decentralised wastewater treatment plant at Capo di Monte (CDM), 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 wastewater treatment option. Currently, the 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 an MBR (with submerged Kubota flat sheet membranes), alum dosing for phosphorus removal, UV disinfection and chlorination.

Figure 1 (overleaf) shows the schematic for the decentralised wastewater case study treatment plant. The treated Class A⁺ effluent is reticulated via a dual reticulation system and is used for toilet flushing at the households and for external irrigation. A vegetated buffer zone of $6,000m^2$ is available for land application of excess treated wastewater to prevent direct discharge into the local waterway.

The current feasibility study assessed the type of AOT suitable

Table 1: Generic types of AOTs used for advanced wastewater treatment.

Table 2: Summary of license requirements, measured influent wastewater qualities at CDM-STP and its comparison with common values from centralised WWTPs.

Figure 1. Schematic of decentralised wastewater system at Capo di Monte. RAS flow is the return activated sludge stream.

| Process Selection Criteria | Key Influencing Factors | Assessment Methodology & Approaches |
|-----------------------------------|--|---|
| Technical Suitability | Wastewater characteristics Operating conditions | \Rightarrow Wastewater samplings \Rightarrow In-situ sensory measurements |
| System Robustness | ← Hydraulic loadings perturbation Wastewater qualities perturbation | \Rightarrow Reaction kinetics estimation \Rightarrow Wastewater calibration, validation & modelling \Rightarrow Dynamic model simulation & optimisation |
| Economic Costing | Capital expenditures Operating & Maintenance (O&M) | \Rightarrow Engineering cost estimation using percentage of delivered equipments approach \Rightarrow Detailed costing (if data available) \Rightarrow Life cycle costing |
| Environmental Impacts | Sludge production Disinfection by-products (DBPs) Odour & Noise End-uses & Receiving environments | \Rightarrow System & environmental monitoring \Rightarrow Survey on end-users' satisfaction |
| Sustainability | Energy efficiency Indirect GHG emission (fossil fuel combustion) Direct GHG emission (fugitive GHG) | \Rightarrow Energy metering & monitoring \Rightarrow Mass & energy balances \Rightarrow Field measurements on fugitive GHG |
| Space Requirements | Physical footprint Accessibility Plant expansion | \Rightarrow Wastewater treatment process design \Rightarrow Land & site assessments |

Figure 2. A comprehensive process selection and assessment framework for the application of AOTs in decentralised wastewater systems for water recycling and reuse purposes.

to be used after MBR treatment to ensure and improve the quality of treated Class A+ effluent, reduce the DBPs' formation potential and minimise the associated public health and environmental risks. Table 2 shows the summary of license requirements, measured influent wastewater quality at CDM, and its comparison with the common values from centralised WWTPs.

Process Selection and Assessment Framework

Figure 2 shows the comprehensive process selection and assessment framework developed to assess the feasibility of using AOTs as an advanced treatment option in the decentralised wastewater case study treatment plant. Six major process selection criteria of technical suitability, system robustness, economic costing, environmental impacts, sustainability and space requirements were used to guide the selection process.

In this study, however, only the three main process selection criteria of technical, economic and environmental feasibility were targeted to give a preliminary overview on the best AOT suitable for the case study. Other process selection criteria will be assessed once the suitable AOT is selected, as well as the availability of all the relevant process inventory data sets that permit a comprehensive evaluation process.

For the technical suitability criterion, the AOTs were assessed based on their compatibility for wastewater characteristics and operating conditions if being applied downstream of the MBR process. The technical assessments include the evaluation of whether (i) the AOTs can handle the wastewater characteristics (i.e. COD, BOD, nitrogen, phosphorus and total suspended solids) after the MBR treatment; (ii) the use of additive chemicals (i.e. pHcorrection, alum dosing, chlorination and other oxidants); and (iii) the needs for alteration of process operating conditions (i.e. temperature and pressure).

The economic feasibility was assessed by using the engineering cost estimation method based on the available data in the literature. A recent review of the costs of all AOT processes, including those

Figure 3. Characteristics of the treated sewage effluent from the decentralised wastewater treatment plant.

involving ultrasonics, was published by Mahamuni and Adewuyi (2010) and extracts from their work has formed the basis of our estimates in economic feasibility. From their work, important information such as reaction rate constant $(k, min⁻¹)$, base reactor volume (L) and treatment cost (\$/1000 US gallon).

 The total reaction time required to achieve the anticipated final 10 mg/L COD concentration level was taken as the hydraulic retention time to size the AOT reactor for this feasibility study. The unit treatment cost (\$/L) was estimated by using available data in the literature, which has taken into account both the capital and operating and maintenance (O&M) costs (Mahamuni and Adewuyi, 2010). The total treatment cost for the AOTs was amortised 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 based on the literature data available on the base reactor volume and the corresponding unit treatment cost (\$/1000 US gallon). Similarly, the specific energy for different AOTs was estimated using the energy intensity data (kWh/kL) from literature with relation to the corresponding base reactor volume (Mahamuni and Adewuyi, 2010).

It should be stressed that the estimated treatment cost used to assess the economic feasibility of AOTs only serves as a preliminary guide towards the selection of the most appropriate AOT at this early stage. A detailed validation of the estimated treatment cost would be ascertained once the most feasible AOT is selected by quotations from the vendors. Such a validation would 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, where the cost database is currently scarce and incomplete.

Technical Evaluation

To assess the technical feasibility of retrofitting AOTs as an advanced wastewater treatment option for the existing case study, it is important to understand the quality of treated sewage effluent after MBR treatment. This is to ensure that the selected AOT can be retrofitted without much modification of either the effluent characteristics or process operating conditions or both. Figure 3 shows the quality characteristics of the treated sewage effluent, which was obtained by using grab sampling methodology (from *N = 6* events). From Figure 3, it can be observed that the statistics presented for the 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, their relevant mean, median 25th and 90th 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 \pm 0.17; BOD: 5.83 \pm 2.04 mg/L and COD: 21.50 \pm 3.27 mg/L). According to the Australian guidelines for water recycling, all the measured concentration values for these common wastewater parameters are deemed safe, acceptable and are within the current threshold limits for both the public health and environmental risks (NRMMC-EPHC-AHMC, 2006).

From the measured pH values, it was easy to determine which AOTs can be retrofitted without much use of additive chemical reagents (e.g. for pH correction) as well as the alterations of operating conditions of the wastewater treatment train. Since the measured pH values are in alkaline conditions, it would be more appropriate to retrofit AOTs that operate well within this alkaline pH regime. From all the reviewed AOTs, it can be concluded that only ozonation (O_3) , ozonation/ultraviolet irradiation (O₃/UV), hydrogen peroxide/ultraviolet irradiation (H₂O₂/UV) and TiO₂ photocatalysis would be suitable. Although the Fenton-based treatment processes have shown proven treatment efficiency, especially for the UV/Fe³⁺-Oxalate/H₂O₂ process with high quantum yield and lower operational energy, their application in this case study might still be hampered by their operating requirements of low acidic pH. Thus, only the assessed AOTs of O₃, O₃/UV, H₂O₂/UV and TiO₂ photocatalysis are considered technically feasible and, subsequently, their treatment cost was estimated.

Economic and Environmental Feasibility

The economics of treatment by the AOTs of O_3 , O_3 /UV, $\mathrm{H}_2\mathrm{O}_2$ /UV and TiO₂ photocatalytic processes was assessed based on the design hydraulic flow rate considered for this study, which was 11,000 L/day (i.e. the current flow rate of the decentralised wastewater treatment plant). Figure 4 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 was evident that the O_{3} treatment process was the most economically feasible AOT (\$0.03/L) at an average dosage of 6.8 mg/L and a residence time of 0.5 h. This was followed by the AOT options of H_2O_2 /UV and O_{g} /UV treatment processes with an estimated treatment cost of \$0.14/L and \$0.21/L respectively. The O_3 treatment process was a more economical AOT treatment option than the $\mathsf{O}_3 / \mathsf{UV}$ and H_2O_2 /UV treatment options, as the latter require higher O&M costs for the UV systems, which include higher energy intensity and constant bulb replacements for the UV systems involved (Mahamuni and Adewuyi, 2010).

Figure 4. Summary of estimated unit treatment cost (\$/L), specific energy (kWh/kL) and indirect GHG emission (kg CO₂-e/kL) for the **different AOTs considered in this study.**

From the economic analysis, the TiO₂ photocatalytic treatment appeared to be the most expensive AOT option for the current decentralised wastewater case study plant. This is due to the cost of TiO₂ particles used, part replacement cost of UV systems, catalyst holder replacements for the catalytic systems, as well as the issue with the postseparation of semiconductor TiO₂ particles after wastewater treatment.

In addition, the specific energy requirement (in kWh/kL) for each AOT was estimated. This information is important as it allows for determining the energy efficiency of various AOTs, as well as their indirect GHG emissions from fossil fuel combustion. Figure 4 shows that the H_2O_2 /UV treatment process was the least energy intensive AOT, with a specific energy requirement of 0.23 kWh/kL. This might be owing to the OH. radicals generation via the use of chemical reagents (i.e. H_2O_2). This was followed by the specific energy for $O_{\textit{3}}$ /UV and Ti $O_{\textit{2}}$ 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 the $O_{3}/$ UV treatment process than the \textsf{O}_3 treatment process is the shorter residence time required to achieve the final COD concentration requirement. The high specific requirement for $O₃$ treatment was also due to the low solubility level of O_3 in wastewater.

When the estimated specific energy was converted to indirect carbon footprints (i.e. 0.9 kg CO_2 -e/kWh), the indirect GHG emission was estimated to be in the range of 0.20 kg CO₂-e/kL (H₂O₂/UV treatment process) to 10.73 kg CO_{2} -e/kL $(O₃$ treatment process) (see Figure 4) (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, as well as the fugitive GHG emissions which add up to the overall carbon footprint for sustainability assessment of different AOTs. Further inventory data sets from different pilot or full-scale AOT plants are needed to allow for a more accurate and comprehensive multi-criteria assessment of AOTs for decentralised wastewater applications. However, the costs estimated in this study still present a useful quide on the selection of AOTs based on technical, economical and environmental criteria.

In conclusion, the H_2O_2 /UV treatment process was considered as 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, as well as minimising the potential public health and environmental risks.

Conclusion

This study has provided a new insight into the application of AOTs for decentralised wastewater treatment, in an attempt to improve the quality of treated sewage effluent for reuse purposes. The quality of treated sewage effluent is often impacted by the stability of the decentralised wastewater plant, which in turn might pose serious public health and environmental risks if the effluents were being reused.

From the outcomes of this feasibility study, it can be concluded that the $H₂O₂/UV$ treatment process is the best AOT option in terms of fulfilling the technical, economical and environmental criteria. The H_2O_2 /UV treatment process was assessed to be capable of meeting the quality requirements for treating the wastewater stream following the MBR process. At present, however, the overall GHG footprints are incomplete due to missing information on the fugitive GHG component.

 It is anticipated that more inventory data sets from different pilot or fullscale AOT plants are needed to allow for a more accurate and comprehensive assessment of AOTs for decentralised wastewater applications. However, the results presented in this study are still a useful guide for decentralised wastewater applications going forward.

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References

- Chong MN, Lei S, Jin B, Saint C, Chow CWK, 2009: 'Optimisation of an annular slurry photoreactor process for degradation of Congo red using a newly synthesized Titania impregnated Kaolinite nano-photocatalyst'. *Separation and Purification Technology*, Vol 67, pp 355–363.
- Chong MN, Jin B, Chow CWK, Saint C, 2010: 'Recent developments in photocatalytic water treatment technology: a review'. *Water Research*, Vol 44, pp 2997–3027.
- Hall M, West J, Lane J, de Haas D, Sherman B, 2009: 'Energy and greenhouse gas emissions for the SEQ water strategy'. *Urban Water Security Research Alliance Technical Report No. 14*, September 2009.
- Laera G, Chong MN, Jin B, Lopez A, 2011: 'An integrated MBR-TiO₂ photocatalysis process for the removal of Carbamazepine from simulated pharmaceutical industrial effluent'. *Bioresource Technology*, Vol 102, pp 7012–7015.
- Mahamuni NN, Adewuyi YG, 2010: 'Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation'. *Ultrasonics Sonochemistry*, Vol 17, pp 990–1003.
- NRMMC-EPHC-AHMC, 2006: 'Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 1)'. *National Water Quality Management Strategy*, November 2006.
- Peters MS, Timmerhaus KD, West RE, 2004: 'Plant Design and Economics for Chemical Engineers', International Eds. McGraw Hill, New York, NY.
- Snyder SA, Wert EC, Rexing DJ, Zegers RE, Drury DD, 2006: 'Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater'. *Ozone Science and Engineering*, Vol 28, pp 445–460.
- Suárez S, Carballa M, Omil F, Lema JM, 2008: 'How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters?'. Reviews in *Environmental Science and Biotechnology*, Vol 7, pp 125–138.

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