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Efficiency of sequential ozone and UV-based treatments for the treatment of secondary effluent

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HIGHLIGHTS

- Compared ozonation and UV/H_2O_2 for decolourisation of secondary effluent.
- Sequential ozone (5 min) and UV/H_2O_2 (10 min) most effective re water quality.
- For this sequence, achieved colour target then 73% DOC removed after biodegradation.
- Synergistic UVA_{254}, COD and DOC, and faster colour removal demonstrated for sequence.

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ABSTRACT

Sequential ozone and UV-based processes (VUV irradiation and UV/H_2O_2) for the treatment of secondary effluent were investigated. The effectiveness of these sequential treatments was compared with the individual treatments in terms of reduction in DOC, COD, UV_{254} and colour and impact on BDOC. The greatest decrease in DOC, COD and UV_{254} was achieved for samples treated with ozone before UV/H_2O_2 (UVH), where a synergistic benefit was observed. By monitoring the formation of hydroxyl radicals ($HO^{\cdot}$) during UVH and ozonation it was demonstrated that UVH treatments generated more hydroxyl radicals than ozonation, which explained the greater extent of mineralisation attained during UVH treatment. Sequential O_3-UVH treatment (for 5 and 10 min, respectively) enhanced the formation of biodegradable compounds such that when followed by biological treatment up to 73% of the DOC could be removed from the secondary effluent. Furthermore, application of the O_3-UVH treatment achieved 2.5 times greater mineralisation than ozone alone. This improvement, however, required 4.5 times greater electrical energy input (EEI) for the same treatment time of 15 min.

1. Introduction

Increasing pressure for improved wastewater discharge quality, and the shortage of water resources, means that secondary treated effluent from wastewater treatment plants (WWTPs) is now considered by those in the water industry to be a valuable and sustainable source of recycled water. To ensure its acceptance by the wider community, any potential risks such as pathogenic, physical, chemical and environmental, need to be reduced to an acceptable level. In the present study, secondary effluent from a local WWTP was investigated. It contained a high concentration of brown coloured humic-like substances that not only caused aesthetic problems at the point of discharge, but also reduced its appeal to potential water reuse customers. Hence, in order to increase its potential for recycling, treatment was required to remove the coloured compounds. Colour and organic matter removal can be achieved through the use of a number of Advanced Oxidation Processes (AOPs). Among the AOPs used to treat water for drinking and recycling, UV-based and ozone-based processes are the most studied due to their ability to remove a wide range of pollutants [1–3].

UV-based AOPs generate highly reactive and non-selective hydroxyl radicals ($HO^{\cdot}$) for the destruction of pollutants. The $HO^{\cdot}$ can be produced from the photolysis of hydrogen peroxide (UV/H_2O_2), as well as through vacuum ultraviolet irradiation (VUV, 254 + 185 nm) which leads to the continuous production of $HO^{\cdot}$ from the photolysis of water via the 185 nm component. These technologies have been shown to be effective for the removal of organic matter and pollutants from water being processed for drinking water [2,4–6]. More recent studies have demonstrated the effectiveness of UV/H_2O_2 (UVH) for the removal of dissolved

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organic matter and micropollutants from secondary effluent [7–14]. The effluent organic matter (EfOM) is a complex mixture of natural organic matter from drinking water, soluble microbial products from the wastewater treatment process and refractory organic chemicals [15].

Ozone is a powerful oxidant due to its high redox potential (2.07 V, compared with 2.8 V for HO·), and it is often used in the treatment of water and wastewater. During ozonation, ozone may react via two possible mechanisms: direct oxidation of organic compounds having multiple bonds, or indirect oxidation through its decomposition to form HO· resulting in more rapid and less selective reactions [16]. Many studies have been conducted on the treatment of biologically treated wastewater by ozonation, e.g., [10,17–22]. In most cases, ozonation resulted in very little mineralisation of the organics as indicated by the low DOC removal. Higher dosages and thus greater energy consumption are required to achieve greater DOC removal.

Hydroxyl radicals are considered to be the main oxidants responsible for the degradation of organics in secondary effluent when using AOP treatments, hence the power of the AOPs can be compared by monitoring the formation of HO· during the treatments. Their reactivity towards the water matrix leads to a very low steady-state concentration, usually $<10^{-12}$ mol/L [23]. The use of para-chlorobenzoic acid (pCBA) as a probe compound for the indirect measurement of hydroxyl radical has been utilised widely in ozonation treatment [23–27]. It has a very low reactivity with ozone ($k_{O3} < 0.15$ L/mol/s), but reacts rapidly with hydroxyl radicals ($k_{HO} = 5 \times 10^9$ L/mol/s [23]. Therefore, by monitoring the disappearance of this compound, the HO· exposure can be determined to give an indication of the HO· production.

AOPs can also be used sequentially. The application of UV-based treatment following ozonation has been investigated by a number of researchers. Irradiation with UV was shown to reduce the required ozone dose, and so impede the formation of bromate in the disinfection of drinking water (a problem when ozonation alone is used) [28]. It was also observed that the transmittance of a water sample whilst undergoing ozone treatment increased, allowing for more efficient UV irradiation [28]. Kerc et al. [29] employed a pre-ozonation step for partial oxidation of humic acid which was followed by photocatalysis, achieving better oxidation efficiency. Arslan and Balcioglu [30] found that the sequential application of ozone then UVH significantly increased the degradation of the pollutants as well as the biodegradability of a textile effluent. Since the coloured effluent from the textile industry may have similar components to the coloured effluent from the local WWTP in the current study, a similar enhancement in degradation and biodegradability might be expected.

While VUV irradiation and UVH are able to achieve a high degree of mineralisation, they are energy intensive. In contrast, ozonation is a more energy efficient process for removing the colour from secondary effluent, but it is inefficient in terms of mineralisation. Hence the sequential use of these processes, and the order in which they are applied to a secondary effluent, was investigated to both improve the treatment performance and reduce the required energy consumption. Since partial mineralisation resulting from these processes generally leads to the formation of biodegradable compounds, there is potential for coupling the system with a biological process to achieve even better removal of DOC, and hence reduce the potential for biological regrowth in reclaimed water distribution systems.

The goal of the treatments under investigation was to reduce the colour of a brown-coloured, humic-containing secondary effluent to 20 mg/L Platinum–Cobalt (Pt–Co) units to comply with the requirement for Class A recycled water as regulated by EPA Victoria [31]. This study focused on the feasibility of using a sequential UV-based (UVH or VUV irradiation) and ozonation process to determine whether or not it resulted in a synergistic effect in terms of improved colour reduction and removal of organics, and to determine which combination of the sequential treatments worked best. The effectiveness of these sequential treatments was evaluated in terms of colour, UV_{254}, DOC, COD and biodegradability. Comparison of the efficiency in terms of electrical energy input was also conducted. In addition, experiments using the probe compound pCBA were conducted to compare the extent of formation of hydroxyl radicals for the UVC-based processes (UVC with and without H_2O_2), and the ozonation process.

2. Materials and methods

2.1. Sample collection

Secondary effluent samples were collected from a municipal WWTP in Victoria, Australia, and stored at 4 °C.

2.2. Irradiation conditions

Irradiation was conducted in an annular reactor fitted with a centrally mounted UV lamp. It had a working volume of 900 mL and an average irradiated area of 464 cm^2, with a path length of 1.95 cm. Two lamps of identical dimensions were employed: the UVC lamp (Australian Ultra Violet Services, G36T15NU) emitted monochromatic light at 254 nm, and the VUV lamp (Australian Ultra Violet Services, G36T15HU) emitted at 254 and 185 nm. The average fluence rate of the UVC lamp (electrical power input 39 W) was determined to be 13.1 mJ s^{-1} cm^{-2} by hydrogen peroxide actinometry according to the method of Bader et al. [32]. For the VUV lamp (electrical power input of 46 W), the intensity of the 185 nm component was determined by the methanol actinometry method of Heit et al. [33]. The average fluence rate of the 254 nm component of the VUV lamp was determined by the ratio of the electrical power inputs (46 W/39 W) times the intensity of the UVC lamp (vendor data indicated this assumption was valid). The average fluence rates were 15.28 and 2.53 mJ s^{-1} cm^{-2} at 254 and 185 nm, respectively. The samples were irradiated for various times with or without the addition of hydrogen peroxide (32 mg/L), as indicated, and then analysed. Fig. 1 displays the delivered dose for the UVC and VUV lamps over a range of irradiation times; these are much larger than the typical doses applied for UV disinfection and were required to achieve the colour target of 20 Pt–Co units for this secondary effluent.

2.3. Ozonation conditions

The laboratory scale ozonation experimental rig was operated in semi-batch mode and consisted of an ozone generator, ozone contactor, ozone gas inlet and outlet detector, and off-gas destructor. Ozone gas was produced on-site by an electrical discharge ozone generator (EDOG, Triogen Lab 2B) using compressed air as the feed gas. Concentration and flow rate of the output gas was manually adjusted and kept constant during the ozonation experiments at 8 mg/L and 30 L/h, respectively. These values were the most efficient based on preliminary tests of the effect of various ozone inlet concentrations (5–10 mg/L) [34]. Ozone gas was introduced continuously for various times into the glass contactor (working volume 2 L) through a fritted glass diffuser to the bottom of the contactor with continuous stirring at 250 rpm. The concentration of dissolved ozone was monitored by means of a dissolved ozone probe within the contactor, and routinely remained at zero for at least 15 min reaction time. The concentration of the ozone in the inlet and off-gas streams was continuously monitored with an ozone photometer (BMT 964BT) and an ozone off-gas analyser