Potential of UV/H₂O₂ oxidation for enhancing the biodegradability of municipal reverse osmosis concentrates
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ABSTRACT

UVC/H₂O₂ and VUV/H₂O₂ oxidation processes were evaluated for the degradation of organic pollutants in reverse osmosis concentrate (ROC) produced from a municipal secondary effluent. It was found that the oxidation by UVC/H₂O₂ and VUV/H₂O₂ processes could be described as a pseudo first-order reaction. For UVC increased oxidation occurred with increasing H₂O₂ dosage up to 2 mM above which improvement in oxidation performance decreased. At the same H₂O₂ dosage, VUV irradiation gave better overall oxidation performance. Compared with UVC/6 mM H₂O₂, VUV/2 mM H₂O₂ gave a greater rate of reduction of chemical oxygen demand, but a lower rate for reduction of dissolved organic carbon, suggesting that oxidation of organics by the two methods followed different pathways. The change of absorbance at 254 nm and fluorescence excitation emission matrix spectra of irradiated samples indicated that the large and complex compounds were fragmented rapidly by the *OH, resulting in rapid decolourisation. The biodegradability of the organics in the ROC was increased from 11% to 35% after 1 h treatment by UVC/3 mM H₂O₂ whereas a greater increase (41%) was obtained with VUV/2 mM H₂O₂. This increase in biodegradability indicates the potential for employing a subsequent biological treatment process.

Key words | biodegradability, organic pollutants, reverse osmosis concentrate, UVC/H₂O₂, VUV/H₂O₂

INTRODUCTION

UV-based advanced oxidation processes (AOPs) have potential for reducing the organic content of municipal reverse osmosis concentrates and so alleviate the negative impacts on the environment associated with the disposal of the organic pollutants. Recently Dialynas et al. (2008) reported that, compared with electrooxidation and ultrasound, UVA/TiO₂ was more effective and energy-efficient for treating municipal reverse osmosis concentrate (ROC). In a study by Westerhoff et al. (2009), the pharmaceuticals from municipal ROC were removed almost completely using UVC/TiO₂ and increased biodegradability of the remaining organic content was demonstrated.

UV irradiation leads to direct chemical bond breakage. The presence of TiO₂ or H₂O₂ enhances the efficacy of the UV irradiation due to the production of highly oxidising hydroxyl radicals (*OH) which result in non-selective and effectively instant degradation of complex organics (Gogate & Pandit 2004). Compared with TiO₂, H₂O₂ offers the advantages of homogeneous reaction and low cost. Buchanan et al. (2004) demonstrated that UV-based AOPs can break the conjugated bonds of natural organic matter and so enhance the biodegradability of resultant intermediates, suggesting the possibility of subsequent biological treatment.

Studies have demonstrated the advantages of VUV irradiation (254 + 185 nm) for degrading the natural organic matter in drinking water (Thomson et al. 2004; Buchanan et al. 2004). The 185 nm component photolyses water to produce *OH (Equations (1) and (2); Oppenlaender et al. 2005) and thus enhances the oxidation of organic contaminants. In addition, the presence of dissolved oxygen further facilitates the generation of several other reactive species such as O₂⁻ and HO₂* (Equations (3) and (4)) resulting in a highly oxidative environment (Alapi & Dombi 2007).

\[
\text{H}_2\text{O} \xrightarrow{\text{UV}} \cdot \text{H} + \cdot \text{OH}
\]

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{VUV}} \cdot \text{O}_2 + \cdot \text{OH}
\]

\[
\text{O}_2 \xrightarrow{\text{H}_2\text{O}_2} \cdot \text{O}_2 + \cdot \text{OH}
\]

\[
\text{HO}_2 \xrightarrow{\cdot \text{OH}} \cdot \text{H} + \text{O}_2
\]
H₂O $\xrightarrow{\text{VUV}}$ H⁺ + 'OH + $\text{e}^-$ \text{[aq]}

(2)

e$^{-}\text{[aq]}$ + 3O₂ $\rightarrow$ O₂$^-$

(3)

'H + O₂ $\rightarrow$ HO₂$^-$

(4)

As very limited research has been documented on the application of UV/H₂O₂ for the treatment of municipal wastewater ROC, UVC/H₂O₂ and VUV/H₂O₂ oxidation were evaluated to treat a ROC prepared from a municipal secondary effluent in this work. The biodegradability of the treated samples was determined (as biodegradable dissolved organic carbon, BDOC) to evaluate the potential for subsequent biological treatment. The change in water quality of the municipal ROC (i.e. chemical oxygen demand (COD), dissolved organic carbon (DOC), absorbance at 254 nm (A₂₅₄) and colour) during the treatment was investigated. The fate of some complex organic compounds such as humic substances, soluble microbial products and protein-like extracellular organic matter was tracked using fluorescence excitation emission matrix (EEM) spectra.

MATERIALS AND METHODS

Source of ROC

The municipal effluent was collected from Western Treatment Plant, Victoria, Australia. The ROC was prepared by feeding the effluent to a Sepa cell crossflow RO module (GE-Osmonics, Minnetonka, MN) with a polyamide membrane (AG; GE-Osmonics, Minnetonka, MN). The characteristics of the ROC were pH 8.3, DOC 21.4 mg/L, COD 67 mg/L, A₂₅₄ 0.43 cm⁻¹ and colour 55 mg Pt-Co units/L.

Irradiation experimental procedure

Irradiation was conducted using an annular reactor with a centrally mounted lamp. The ROC was dosed with H₂O₂ (Australian Chemical Reagents, 50% w/w) and aerated by humidified air during irradiation and sampled periodically. The average irradiated area was 464 cm² with a pathlength of 1.94 cm, other UV reactor conditions are reported elsewhere (Thomson et al. 2004).

The UV lamp (Australian Ultra Violet Services, G36T15NU, energy input 39 W) emitted at 254 nm, and the VUV lamp (Australian Ultraviolet Services, G36T15HU, energy input 46 W) emitted at both 254 nm and 185 nm.

Water quality analyses

All the samples were filtered through 0.45 µm membranes (cellulose acetate, ADVANTEC®) prior to the following analyses. The DOC was measured using a Sievers 5310 TOC analyser with an auto-sampler and an inorganic carbon removal module (Sievers 900 ICR; GE, Boulder, CO). The COD was determined using Hach Method 8000 using a Hach spectrophotometer (DR/4000U). The absorbance at 254 nm (A₂₅₄) was measured using a Unicam UV/vis spectrophotometer. The true colour of the samples was measured in Pt-Co units at 455 nm using a Hach spectrophotometer (DR/4000U). The pH was measured using a Hach Sension 156 pH/conductivity meter. The EEM spectra of the samples were obtained with a PerkinElmer LS55 fluorescence spectrometer. The concentration of hydrogen peroxide was measured using Merckoquant® peroxide test sticks.

Residual H₂O₂ decomposition

To remove the interference of residual H₂O₂ in COD measurement the enzyme catalase (from Aspergillus niger, Calbiochem®) was used to decompose the H₂O₂. To every 25 ml sample, 10 µl (activity of 20 units) of the catalase was added and the sample was shaken for 2 h at 100 rpm until H₂O₂ was less than 2 mg/L, which is considered negligible (Kang et al. 1999). The resultant increase in COD and DOC due to the added catalase was determined as <1 mg/L for COD and ~0.05 mg/L for DOC.

Biodegradable dissolved organic carbon

The BDOC method of Joret & Levi (1986) was used to estimate the potential of the variously treated samples for further biological treatment. Samples were exposed to cleaned biologically active sand over five days under aerobic conditions. The DOC was measured daily and the BDOC was calculated as the initial DOC minus the lowest DOC recorded over the five day period.
RESULTS AND DISCUSSION

H$_2$O$_2$ control experiment

The effect of H$_2$O$_2$ alone on the degradation of organic pollutants was evaluated by exposing the ROC containing 3 mM H$_2$O$_2$ in the UV reactor for 3 h without UV irradiation. There was no obvious change in the properties (DOC, COD, A$_{254}$ and colour) of the ROC (results not shown).

UVC/H$_2$O$_2$ oxidation method

UVC photolysis alone led to only 13% removal of COD after 3 h (Figure 1(a)). The addition of H$_2$O$_2$ greatly enhanced the degradation due to the formation of OH from the decomposition of H$_2$O$_2$ by the UVC irradiation. The kinetics of COD removal for the first 30 minutes could be modelled as a pseudo first-order reaction when the OH was assumed to remain constant until its significant depletion at the later phase of the reaction, this is in accordance with the observations of other researchers (Chin et al. 2009; Alhamedi et al. 2009). Thus, the reaction rate constants for the first 30 min of each UVC/H$_2$O$_2$ process were calculated using Equation (5):

$$\ln\left(\frac{\text{COD}_t}{\text{COD}_0}\right) = -kt$$

where COD$_0$ and COD$_t$ are the COD at irradiation time = 0 and t, respectively, and k is the apparent pseudo first-order reaction rate constant.

Plotting k against the dosage of H$_2$O$_2$ (Figure 1(b)) showed that the reaction rate constant increased proportionally with increasing H$_2$O$_2$ dosage up to 2 mM. Dosage at >2 mM did not lead to proportional increase in the COD removal rate, suggesting that self-quenching occurred at higher concentrations of H$_2$O$_2$ resulting in the formation of the less active HO$_2^-$ (Yonar et al. 2006), as described by Equation (6).

$$\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^-$$

The trends for DOC reduction were similar to those for COD reduction (Figure 2(a)). The decrease in COD and DOC tended to plateau after 1 h for all the UVC/H$_2$O$_2$ processes. This may be attributed to two factors: decrease in OH production due to the depletion of the H$_2$O$_2$ at that time (~0.3 mM H$_2$O$_2$ remained for the 6 mM system and less than ~0.2 mM for the other systems); and the rate of mineralisation of specific groups of compounds became limited because of the reduced concentration of such compounds (Buchanan et al. 2004).

The A$_{254}$ reflects the presence of conjugated bonds and aromatic rings in complex organic compounds which may be chromophoric. For UVC there was greater reduction (62%) of A$_{254}$ (Figure 2(b)) than in COD or DOC. The conjugated bonds and aromatic rings absorbed the UVC irradiation resulting in cleavage of these chemical bonds, but only little mineralisation of the resultant products. All UVC/H$_2$O$_2$ processes removed >80% of A$_{254}$ after 1 h, indicating the rapid breakdown of the chromophoric groups by the OH. These results were consistent with the large reduction in colour of the ROC (at least 87%, corresponding to 47 mg Pt-Co/L) after 1 h by all UVC/H$_2$O$_2$ processes (results not shown).

Comparison of UVC/H$_2$O$_2$ and VUV/H$_2$O$_2$ oxidation

As expected, VUV alone achieved markedly better overall treatment performance than UVC alone (Figures 1 and 2), which was mainly attributed to the formation of OH in situ via water photolysis (Equation (3)) by the 185 nm component.
of VUV irradiation. In addition, VUV irradiation can lead to the production of H$_2$O$_2$ through a pathway described in Equations (7)–(9) (Gonzalez & Braun 1998). The breakdown of DOC can also lead to the formation of peroxide precursor compounds that can include superoxide species from reactions of excited (triplet state) humic substances (HS) with triplet oxygen (Equation (10)) (Frimmel 1994), and hydrated electrons formed from excited humic substances (Equation (11)) (Cooper et al. 2013). Thus, the resultant H$_2$O$_2$ provided a further source for the production of $\cdot$OH at 254 nm. Nevertheless, the level of remaining organics after 3 h VUV irradiation treatment was still high (13.7 mg/L DOC and 45 mg/L COD). Hence H$_2$O$_2$ was added to improve treatment performance. The VUV/2 mM H$_2$O$_2$ process gave comparable COD removal but with a higher reaction rate than for the UVC/6 mM H$_2$O$_2$ process (Figure 1(a)). In contrast to COD reduction, the trend for DOC reduction by VUV/2 mM was slower and less than for UVC/6 mM, but still greater than for UVC/2 mM H$_2$O$_2$ (Figure 1(b)). A similar phenomenon occurred for the UVC/1 mM H$_2$O$_2$ and VUV alone processes. This strongly suggests that the oxidation of organic compounds in the ROC followed different pathways in the two UV-mediated processes.

$$\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^- \quad (7)$$

$$\text{O}_2^- + \text{HO}_2^- \rightarrow \text{HO}_2^- + \text{O}_2 \quad (8)$$

$$\text{HO}_2^- + \text{H}^+ \leftrightarrow \text{H}_2\text{O}_2 \quad (9)$$

$$3\text{HS}^+ + 3\text{O}_2 \rightarrow 3\text{HS}^{+\cdot} + \text{O}_2^- \quad (10)$$

$$\text{HS}^+ \text{ or } 3\text{HS}^+ \rightarrow \text{HS}^{+\cdot} + \text{e}^- \rightarrow \text{HS}^{+\cdot} + \text{e}^- (aq) \quad (11)$$

$$\text{R}_{\text{AromaticSpecies}} + \cdot\text{OH} \rightarrow \text{R}^- + \text{HO}_2^- \rightarrow \text{R'O}_2\text{OH} \quad (12)$$

The 185 nm component of VUV irradiation can initiate not only production of $\cdot$OH, but also some lower oxidation strength hydroperoxyl radicals (HO$_2$) (Equations (4) and (7)) which give additional oxidation of the aromatic species. The resultant extra $\cdot$OH led to faster and more extensive mineralisation of the organics resulting in better COD and DOC removal. In the meantime, HO$_2$ could convert the aromatic species into ring-open organic hydroperoxide via adding to the $\cdot$OH-initiated carbon-centred radicals (Equation (12)) (Alapi & Dombi 2007). In short, HO$_2$ produced intermediates with a higher degree of oxidation instead of mineralising the organic compounds. As a result, VUV irradiation achieved greater improvement in COD reduction than in DOC reduction.

**Tracking complex organics in the ROC**

EEMs are regarded as a highly sensitive and selective method for ‘fingerprinting’ the organic compounds in drinking and wastewater (Henderson et al. 2009). The five regions were defined according to Chen et al. (2005), as shown in Figure 3. The untreated municipal ROC contains two intense peaks which represent a large proportion of humic (region V) and fulvic acid-like (region III) species, these are complex with multifunctional aromatic components linked chemically and physically by a variety of aliphatic constituents (Shon et al. 2006). Their high degree of conjugation is associated with low biodegradability (Buchanan et al. 2004). Both UVC and VUV alone failed to completely degrade the fluorescence of the ROC after 3 h (Figure 3) whereas VUV gave greater reduction of the fluorescence due to the production of $\cdot$OH. The addition of H$_2$O$_2$ greatly accelerated the degradation of these compounds as after 20 min the processes with $>2$ mM H$_2$O$_2$ showed almost complete removal of the fluorescence in the ROC, which was consistent with the reduction in $A_{254}$ and decolourisation.
Biodegradability

The biodegradability of the remaining organics in selected samples after 3 h irradiation was determined using the BDOC method (Figure 4(a)). Only 11% of the DOC in the ROC was biodegradable, however, 22% of the remaining DOC was biodegradable after UVC irradiation and a slightly higher biodegradability of 26% was obtained after VUV irradiation. Nevertheless, there was still a high DOC loading after the sequence of UV irradiation and biological
treatment (12.8 mg/L for UVC-BDOC and 10.2 mg/L for VUV-BDOC). Increasing the H$_2$O$_2$ dosage to 2 mM improved both the biodegradability of the remaining organics and the total DOC removal. Higher H$_2$O$_2$ dosage up to 4 mM led to decreased biodegradability of the remaining organics and similar residual DOC level (∼4.5 mg/L). Further increasing H$_2$O$_2$ dosage to 6 mM led to no biodegradable products but the highest total DOC removal (83%), implying that approximately 4.5 mg/L of the remaining DOC cannot be transformed into biodegradable products or after formation they were mineralised by further UV/H$_2$O$_2$ treatment. The biodegradability of the VUV/2 mM H$_2$O$_2$ treated sample (32%) was comparable to that after UVC/2 mM H$_2$O$_2$ treatment (31%); however, there was greater mineralisation for the VUV/H$_2$O$_2$ process than for the UVC/H$_2$O$_2$ process with overall DOC removals of 79% compared with 74%.

As shown in Figure 2(a), UVC/3 mM and VUV/2 mM H$_2$O$_2$ processes led to similar DOC reduction profiles. The BDOC of treated samples after varying exposure periods for these two processes was measured to further investigate the change of biodegradability (Figure 4(b)). The biodegradability of the remaining organics after both treatments was maximal after 1 h after which it decreased. The VUV/2 mM H$_2$O$_2$ process gave the highest biodegradability (41%, with a BDOC of 3.7 mg/L) after 1 h and a residual DOC of 5.2 mg/L after biodegradation, corresponding to 76% removal of the total DOC, whereas after 1 h the UVC/3 mM H$_2$O$_2$ process gave lower biodegradability (35%, with a BDOC of 2.8 mg/L) and the same residual DOC after biodegradation, which indicates that VUV irradiation led to less mineralisation and greater formation of biodegradable products.

CONCLUSIONS

The ROC derived from a municipal biologically treated effluent was treated by UVC- and VUV-mediated processes. The addition of H$_2$O$_2$ enhanced the oxidation performance and increasing H$_2$O$_2$ dosage led to faster reaction rate and higher oxidation extent. However, self-quenching of H$_2$O$_2$ was observed at >2 mM H$_2$O$_2$. At a comparable dosage of H$_2$O$_2$, VUV irradiation was more efficient than UVC irradiation for mineralising the organics in the ROC which was attributed to the additional ·OH produced through water photolysis by the 185 nm component of the VUV irradiation.

The UV-mediated processes broke down the conjugated bonds and aromatic rings of humic and fulvic substances resulting in rapid decolourisation and some mineralisation of the organic compounds. The biodegradability of treated ROC increased from 11% to 35% after 1 h treatment with UVC/3 mM H$_2$O$_2$, whereas 41% biodegradability of the remaining organics was obtained with VUV/2 mM H$_2$O$_2$ which corresponded to a total DOC reduction of 76%. For both processes, there was a peak in the biodegradability of the remaining organics after which there was only a minor improvement in total DOC removal.

The potential of the application of UVC/H$_2$O$_2$ and VUV/H$_2$O$_2$ oxidation processes to treat municipal ROC was demonstrated. The coupling of biological treatment with these processes is recommended to reduce the energy consumption by taking advantage of the biodegradable intermediates formed during the oxidation processes. Complete mineralisation is possible but not practically viable due to the large energy consumption.

Since the biodegradability of the treated ROC depends on H$_2$O$_2$ dose, UV wavelength, and irradiation period, it would be necessary to determine the optimum conditions for each of these parameters to achieve an appropriate trade-off between energy use, reduction in DOC and maximum biodegradability and so determine the most economic conditions before this process could be applied in practice. Moreover, further investigation would be required to examine the effects of other parameters (e.g. pH and salinity) and H$_2$O$_2$ dosing regime (e.g. batch cf. fed-batch), with a view to enhancing the oxidation performance by reducing the self-quenching effect.

REFERENCES


