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Impact of salinity and pH on the UVC/H_2O_2 treatment of reverse osmosis concentrate produced from municipal wastewater reclamation

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ABSTRACT

While reverse osmosis (RO) technology is playing an increasingly important role in the reclamation of municipal wastewater, safe disposal of the resulting RO concentrate (ROC), which can have high levels of effluent organic pollutants, remains a challenge to the water industry. The potential of UVC/H_2O_2 treatment for degrading the organic pollutants and increasing their biodegradability has been demonstrated in several studies, and in this work the impact of the water quality variables pH, salinity and initial organic concentration on the UVC/H_2O_2 (3 mM) treatment of a municipal ROC was investigated. The reduction in chemical oxygen demand and dissolved organic carbon was markedly faster and greater under acidic conditions, and the treatment performance was apparently not affected by salinity as increasing the ROC salinity 4-fold had only minimal impact on organics reduction. The biodegradability of the ROC (as indicated by biodegradable dissolved organic carbon (BDOC) level) was at least doubled after 2 h UVC/H_2O_2 treatment under various reaction conditions. However, the production of biodegradable intermediates was limited after 30 min treatment, which was associated with the depletion of the conjugated compounds. Overall, more than 80% of the DOC was removed after 2 h UVC/3 mM H_2O_2 treatment followed by biological treatment (BDOC test) for the ROC at pH 4–8.5 and electrical conductivity up to 11.16 mS/cm. However, shorter UV irradiation time gave markedly higher energy efficiency (e.g., EE/O 50 kWh/m^3 at 30 min (63% DOC removal) cf. 112 kWh/m^3 at 2 h). No toxicity was detected for the treated ROC using Microtox® tests. Although the trihalomethane formation potential increased after the UVC/H_2O_2 treatment, it was reduced to below that of the raw ROC after the biological treatment.

1. Introduction

Reverse osmosis (RO) technology has been used increasingly in municipal wastewater reclamation over the past decade to address freshwater shortages in many regions. Due to the excellent performance of RO membranes in rejecting organic and inorganic pollutants present in biologically treated secondary effluent, RO-based tertiary/advanced wastewater treatment processes can produce very high quality water which is suitable for a wide range of reuse purposes. However, the brine streams (also referred to as reverse osmosis concentrate (ROC) streams) generated from the RO systems may pose major health and environmental risks if they are discharged to the receiving environment without appropriate treatment. The

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risks are due to the ROC containing almost all of the pollutants in the original secondary effluent at elevated levels (i.e., commonly 4–6 times higher concentration). Depending on the wastewater source, the organic pollutants in the ROC may be toxic and/or bioaccumulative (Shon et al., 2006).

Advanced oxidation processes (AOPs) are regarded as an effective means for degrading the organic matter in ROC. In general, AOPs utilise the highly oxidising hydroxyl radical (•OH) to break down organic matter into smaller (often more biodegradable) molecules, and eventually to CO_2. Several AOPs, including UV/TiO_2 (Westerhoff et al., 2009; Zhou et al., 2010), UV/H_2O_2 (Liu et al., 2011; Bagastyo et al., 2011), ozone (Zhou et al., 2010; Lee et al., 2009) and electrochemical oxidation (Pérez et al., 2010), have been demonstrated to be effective for treating the ROC produced from the reclamation of municipal secondary effluent. As H_2O_2 is very soluble in water, it can be used as an effective source for •OH production in the presence of UV irradiation. Moreover, UV/H_2O_2 processes are simple to design and operate (Buchanan et al., 2004). In most cases, the partially oxidised intermediates have less inherent environmental and human health risk (Westerhoff et al., 2009). Although Zhou et al. (2010) reported that UV/H_2O_2 treatment was not very effective, they used UVA (365 nm) at which wavelength H_2O_2 has a very low molecular extinction coefficient (approximately 0.01 L mol^{-1} cm^{-1}) compared with at the more commonly used UVC (254 nm, 19.6 L mol^{-1} cm^{-1}) (H2O2.com, 2009). In our recent study using a UVC/H_2O_2 system to treat an ROC produced from a municipal secondary effluent, the potential for decreasing the concentration of organic contaminants and increasing the biodegradability of the ROC was demonstrated (Liu et al., 2011). Furthermore, Bagastyo et al. (2011) reported that compared with other treatments including alum and ferric coagulation, and ion exchange, UVC/H_2O_2 was the most efficient treatment for the organic content of a municipal ROC.

As the pH, salinity and organic pollutant level of municipal ROC can vary with source, season or treatment method, the aim of this work was to investigate the effects of these water quality variables on the efficiency of UVC/H_2O_2 treatment. The treatment performance was characterised using COD, DOC, A_{254}, colour and fluorescence excitation–emission matrix (EEM) spectroscopy. Size exclusion chromatography using liquid chromatography with organic carbon detection (LC-OCD) was employed to determine the molecular size changes during the treatment. The biodegradability of the ROC before and after the treatment was determined as biodegradable dissolved organic carbon (BDOC). An indication of the potential toxicity of the treated ROC was obtained through Microtox® assay and trihalomethane formation potential (THMFP) measurement.

2. Materials and methods

2.1. Source of wastewater and preparation of ROC

A biologically treated municipal wastewater from a local wastewater treatment plant was used for the preparation of the ROC. To prepare the ROC, the wastewater was subjected to microfiltration (Microza®, Part No. UMP-153, PALL) followed by reverse osmosis using a Sepa cell crossflow RO module (GE-Osmonics, Minnetonka, MN) with a commercial polyamide membrane (AG; GE-Osmonics, Minnetonka, MN). The characteristics of the resultant ROC are presented in Table 1. H_2SO_4 (1 M) and NaOH (1 M) were used for adjusting the pH of the ROC; NaCl (Analytical Reagent Grade) and $MgSO_4$ (BDH Chemicals, General Purpose Reagent) were used for the adjustment of its salinity.

2.2. UV irradiation experiments

Irradiation was conducted using an annular reactor with a centrally mounted lamp. The ROC was dosed with 3 mM H_2O_2 (Australian Chemical Reagents, 50% w/w) which was found to be the optimum dosage in our previous study (Liu et al., 2011), aerated by humidified air during irradiation and sampled periodically. The average irradiated area was 464 cm^2 with a pathlength of 1.94 cm, other UV reactor conditions are reported elsewhere (Thomson et al., 2004). The UVC lamp emitted at 254 nm, and was manufactured by Australian Ultra Violet Services (G36T15NU, energy input 39 W). H_2O_2 actinometry (Beltran et al., 1995) was used for measuring the intensity of the UVC lamp, and the average fluence rate of the lamp was determined as 12.89 mJ/s/cm^2. Duplicate experiments were undertaken and average results reported. The enzyme catalase (from *Aspergillus niger*, Calbiochem®) was used to decompose the residual H_2O_2 and so remove its interference in water quality measurement. To every 20 mL sample, 8 μL (activity of 16 units) of the catalase was added and the sample was shaken at 100 rpm until H_2O_2 was less than 0.5 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.

2.3. Analytical methods

Samples were filtered (0.45 μm cellulose acetate, ADVANTEC®) prior to the following analyses. A Sievers 5310 TOC analyser with an auto-sampler and an inorganic carbon removal module (Sievers 900 ICR; GE, Boulder, Co) was used for DOC measurement. Inorganic carbon was measured by the same TOC analyser without utilising the inorganic carbon removal module. The COD was determined with Hach Method 8000

Table 1 – Characteristics of the ROC.

Parameter	Value	Ions	mg/L
DOC (mg/L)	21	Cl^-	780
COD (mg/L)	65	PO_4^{3-}	38
A_{254} (/cm)	0.41	SO_4^{2-}	233
Colour (Pt–Co mg/L)	88	NO_3^-	35
pH	8.5	Na^+	529
TDS (mg/L)	1685	Mg^{2+}	56
Electrical Conductivity (mS/cm)	2.82	K^+	66
BDOC (mg/L)	3.2	Ca^{2+}	68
Alkalinity (as $CaCO_3$, mg/L)	295	Fe^{3+}	8
		Zn^{2+}	20