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Technical Note

# Removing organic and nitrogen content from a highly saline municipal wastewater reverse osmosis concentrate by $UV/H_2O_2$–BAC treatment

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## HIGHLIGHTS

- $UV/H_2O_2$–BAC treatment of a highly saline wastewater ROC was investigated.
- Approximately 60% DOC and TN was removed from the ROC by the process.
- Residual $H_2O_2$ in BAC feed enhanced DOC removal but limited TN removal.

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## ABSTRACT

Reverse osmosis (RO) concentrate (ROC) streams generated from RO-based municipal wastewater reclamation processes pose potential health and environmental risks on their disposal to confined water bodies such as bays. A $UV/H_2O_2$ advanced oxidation process followed by a biological activated carbon (BAC) treatment was evaluated at lab-scale for the removal of organic and nutrient content from a highly saline ROC (TDS 16 g $L^{-1}$, EC 23.5 mS $cm^{-1}$) for its safe disposal to the receiving environment. Over the 230-day operation of the $UV/H_2O_2$–BAC process, the colour and UV absorbance (254 nm) of the ROC were reduced to well below those of the influent to the reclamation process. The concentrations of DOC and total nitrogen (TN) were reduced by approximately 60% at an empty bed contact time (EBCT) of 60 min. The reduction in ammonia nitrogen by the BAC remained high under all conditions tested (>90%). Further investigation confirmed that the presence of residual peroxide in the $UV/H_2O_2$ treated ROC was beneficial for DOC removal, but markedly inhibited the activities of the nitrifying bacteria (i.e., nitrite oxidising bacteria) in the BAC system and hence compromised total nitrogen removal. This work demonstrated that the BAC treatment could be acclimated to the very high salinity environment, and could be used as a robust method for the removal of organic matter and nitrogen from the pre-oxidised ROC under optimised conditions.



## 1. Introduction

Over the past decade, reverse osmosis (RO) technology has been used increasingly for full-scale municipal wastewater reclamation plants due to its ability to produce high quality effluent and increasing affordability (Shannon et al., 2008). However, management of the concentrate (also referred to as the brine) streams generated from the RO-based wastewater reclamation processes remains a major challenge for the water industry in applying the technology. The RO concentrate (ROC) contains almost all of the organic contaminants and nutrients from the secondary effluent at elevated levels (i.e., typically 4–6 times higher in concentration). The organic content of the ROC commonly includes pharmaceuticals, personal care products, pesticides, endocrine disruptors, disinfection by products and other organic species; many of these are toxic and bio-accumulative. Moreover, introduction of excess nutrients to the receiving environment can cause adverse effects such as blooms of harmful algae. The disposal of the untreated ROC to a confined water body (e.g., bays) consequently poses significant risks to the health of humans and ecosystems.

Due to the recalcitrant nature of the organic matter in the ROC, several oxidative treatment methods including advanced oxidation processes (AOPs) have been studied as a means of removing and/or enhancing the biodegradability of the organic content. In some recent studies, the homogeneous AOP utilising $UVC/H_2O_2$ has been demonstrated as an effective method for degrading the organic matter in the ROC and improving its biodegradability for subsequent biological treatment. One study showed the process (initial $H_2O_2$ concentration 11.5 mM, 120 min irradiation) could achieve

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complete decolourisation and 55% reduction in COD, 38% in DOC and 32% in dissolved organic nitrogen (DON) (Bagastyo et al., 2011). Liu et al. (2012) reported that more than 80% DOC removal could be achieved for a municipal wastewater ROC with UVC/$H_2O_2$ treatment (initial $H_2O_2$ concentration 4 mM, 30 min irradiation), followed by a biodegradable DOC (BDOC) determination as a surrogate biological treatment. The bench-scale study revealed that such treatment was effective for degrading the organic compounds over a wide range of salinity (EC 4.5–11.2 mS $cm^{-1}$). Based on these studies, low-energy requirement and small-footprint biological processes should be considered as the subsequent treatments to improve the total organic removal and hence the cost-effectiveness of the oxidative treatment processes.

Biological activated carbon (BAC) processes can provide simultaneous adsorption of non-biodegradable matter and oxidation of biodegradable matter in a single reactor with microbial activity in a granular activated carbon system (Walker and Weatherley, 1999). The use of BAC to treat pre-oxidised ROC has been reported in several studies. Lee et al. (2009) found that the coupling of a BAC column with ozone pre-oxidation enhanced the organic removal efficiency by 3 times that of BAC alone at an empty bed contact time (EBCT) of 60 min, with 70% TOC removed from the ROC (TDS 1.2 g $L^{-1}$, EC 2 mS $cm^{-1}$). In a more recent study, Lu et al. (2013) observed that the integrated treatment of UV/$H_2O_2$ followed by BAC removed 59% DOC, 64% colour and 78% UV absorbance at 254 nm ($UVA_{254}$) from a ROC (TDS 10 g $L^{-1}$, EC 13.5 mS $cm^{-1}$). However, the removal efficiencies for nutrients such as total nitrogen (TN) and total phosphate (TP) were fairly low, with only 24% of TN and 17% of TP removed. In an earlier study, Ng et al. (2008) found that BAC treatment following capacitive deionisation could achieve a higher TN removal (91%) from a ROC with relatively low salinity (EC 2 mS $cm^{-1}$). The low TN removal observed by Lu et al. (2013) may be related to the high salinity of the ROC, as it is well recognised that high salinity of wastewater can greatly affect biological activity, resulting in decreased nitrification and denitrification, thereby affecting overall TN removal (Kargi and Dinçer, 1997). The biological removal of nitrogen at elevated salt concentration can be challenging due to the sensitivity of nitrogen-removing microorganisms to high salt conditions, along with other environmental conditions including temperature, DO concentration, pH, ammonia concentration, heavy metals and C/N ratio (Okabe et al., 1996). However, it is possible for the microorganisms to be acclimated to high salinity environments. The ROC salinity level may be classified as low (TDS < 5 g $L^{-1}$), medium (5–10 g $L^{-1}$), high (10–15 g $L^{-1}$) and extremely high (>15 g $L^{-1}$). To date, most of the published work has been on ROC with low or medium salinity. Investigation of the removal of organic content and nutrients (particularly nitrogen) from ROC with extremely high level of salinity using UV/$H_2O_2$ followed by BAC has not been reported.

The aim of this study was to investigate the effectiveness and robustness of a UV/$H_2O_2$–BAC process for removing organic matter and nitrogen from a municipal wastewater ROC with extremely high salinity over an extended period of operation (230 days). The impact of the residual $H_2O_2$ in the BAC influent on the bio-treatment performance was also studied. The treatment effectiveness was characterised in terms of reductions in DOC, $UVA_{254}$, colour, COD, total nitrogen (TN), ammonium nitrogen ($NH_4$–N), nitrate nitrogen ($NO_3$–N) and nitrite nitrogen ($NO_2$–N).

## 2. Materials and methods

### 2.1. Source of ROC

The ROC samples were collected from a local wastewater reclamation facility in which the biologically treated secondary effluent was treated by a UF (0.04 µm)–RO system to remove salts and other contaminants to produce recycled wastewater. The water recovery of the RO system was approximately 75%. The general characteristics of the ROC samples collected during January to October, 2013 are given in Table 1. The secondary effluent had a high TDS level due to the infiltration of salty groundwater into the sewer system, leading to the extremely high salinity of the ROC. The collected samples were stored at 4 °C and brought to room temperature before use.

### 2.2. UV/$H_2O_2$ treatment of ROC

Irradiation was conducted in batch mode using an annular reactor with a centrally mounted lamp. The UVC lamp (254 nm) had an energy input of 39 W (Australian Ultra Violet Services, G36T15NU), and the average fluence was determined as 8.9 mJ $s^{-1}$ $cm^{-2}$. During irradiation, samples were mixed and aerated by humidified air. The average irradiation area was 464 $cm^2$ with a path length of 1.94 cm and other UV reactor conditions are reported elsewhere (Liu et al., 2012). The ROC sample (900 mL) was dosed with 3 mM $H_2O_2$ and then exposed to UV irradiation for 30 min (UV dose 16 J $cm^{-2}$) as suggested by Liu et al. (2012) as the optimum conditions for treating the ROC. The treated ROC was then fed to BAC columns under the defined experimental conditions.

The residual $H_2O_2$ in the UV/$H_2O_2$ treated ROC was measured using a photometric method at 551 nm (Bader et al., 1988). The enzyme catalase derived from bovine liver (Sigma, 3691 units per mg solids) was used to quench the residual $H_2O_2$ for examining the effect of residual peroxide on the efficiency of BAC treatment. For every 25 mL of the water sample, 10 µL (4000 U $mL^{-1}$) of catalase was added to remove the residual $H_2O_2$. Catalase was also used to decompose residual $H_2O_2$ to remove its interference in water quality analyses. The samples were shaken at 100 rpm at room temperature until the concentration of $H_2O_2$ was less than 0.5 mg $L^{-1}$.

### 2.3. BAC start-up and operation

Granular activated carbon (GAC) columns with an inner diameter of 1.5 cm and an effective packing height of 12 cm were set up. Coal-based activated carbon (Activated Carbon Technologies Pty Ltd, Australia) with effective size of 1.2–1.4 mm, density 0.20–0.30 g $cm^{-3}$ and surface area >1200 $m^2$ $g^{-1}$ was used. The carbon was sieved to remove the very fine particles, washed repeatedly with deionised water until the fine particles were removed, and then dried in an oven at 110 °C for 2 days. The carbon media (200 g) was then inoculated by mixing with activated sludge (1 L, MLSS 4000 mg $L^{-1}$) obtained from the wastewater treatment plant which supplied the secondary effluent to the reclamation facility for 4 days. Nutrients including N, P and C sources were added to the system to promote the growth of microorganisms during the inoculation period (glucose 0.78 g $L^{-1}$, ammonium chloride

**Table 1**
Characteristics of the ROC samples (January to October, 2013).

| Parameter | Value |
|---|---|
| pH | 7.7 ± 0.4 |
| DO (mg $L^{-1}$) | 10.2 ± 1.3 |
| DOC (mg $L^{-1}$) | 36.0 ± 4.0 |
| $UVA_{254}$ ($cm^{-1}$) | 0.62 ± 0.02 |
| Colour (mg Pt–Co $L^{-1}$) | 148 ± 10.0 |
| COD (mg $L^{-1}$) | 120 ± 19 |
| TN (mg $L^{-1}$) | 21.4 ± 4.5 |
| TP (mg $L^{-1}$) | 28.5 ± 1.1 |
| TDS (g $L^{-1}$) | 16.6 ± 0.8 |
| Chloride (mg $L^{-1}$) | 7,700 ± 1,800 |
| Conductivity (mS $cm^{-1}$) | 23.5 ± 1.3 |