

Comparison of UVC Lamp and UVC-light Emitting Diodes for Treating Municipal Wastewater Reverse Osmosis Concentrate

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Abstract—The potential of a prototype UVC light emitting diode (UVC-LED) reactor was investigated for the degradation of organic matter in a highly saline (electrical conductivity ~22 mS/cm) municipal wastewater reverse osmosis concentrate by comparing with a conventional UVC lamp reactor at comparable UV fluences. Reducing the pH of ROC to 5 (initial value 8.3) led to greater reduction of DOC, A_{254} and colour for both systems. The reduction of DOC was greater (25%) using the UVC lamp than the UVC-LED system (21%) at pH 5 whereas it was comparable at original pH (13-14%). A similar trend was observed for A_{254} with little difference (4%) between the two systems at pH 5, whereas the reduction of colour was comparable (85-86%). Fluorescence excitation-emission matrix spectra and liquid chromatography-organic carbon detection revealed greater breakdown of humics by the UVC lamp system resulting in greater increase in biodegradability (~4 fold) than the UVC-LED system (<2 fold). Preliminary evaluation of energy consumption using electrical energy per order (EE/O) suggested the UVC-LED system utilised 4 to 9 fold less energy than UVC lamp system for sequential coagulation, UVC/H₂O₂ and BDOC assay.

Keywords—Organic matter, reverse osmosis concentrate, UVC lamp, UV-LED

I. INTRODUCTION

THE application of UV radiation in drinking water treatment has been documented for almost 100 years [1] and conventional UV lamps (low or medium pressure) remain the most common source of UV irradiation worldwide. However, the sustainability of UV technology continues to be an issue due to inherent disadvantages of UV arc lamps such as the use of mercury, low mechanical stability and high energy consumption. Ultraviolet light emitting diodes (UV-LEDs) are emerging as alternatives to conventional UV lamps as they offer several advantages such as small size, durability, energy efficiency and long life. The UV-LEDs are mercury free sources of monochromatic UV radiation and are regarded as the most promising new UV light sources [1].

Significant interest has recently been paid to the application of UV-LEDs for disinfection [2] and, in the presence of H₂O₂, degradation of single organic compounds [3]. UVC radiation

in the presence of H₂O₂ leads to the production of highly oxidising hydroxyl radicals (HO[•]) which can break down organic molecules to simpler more biodegradable molecules and eventually lead to their mineralization. In this study we have investigated the potential of UVC-LEDs for the degradation of the organic content of a highly saline municipal wastewater reverse osmosis concentrate (ROC) to destroy potentially toxic micropollutants and reduce the organic content to enable its safe disposal or reuse. The efficiency of a UVC-LED reactor was investigated with regard to the reduction in dissolved organic carbon (DOC), colour and A_{254} and change in biodegradability, and compared with a conventional UVC lamp reactor at comparable UV fluence values. Fluorescence excitation-emission (EEM) spectra and liquid chromatography-organic carbon detection (LC-OCD) were used to characterise the changes in the organic components of the ROC. A preliminary estimate of the energy requirements was made with a view to achieving a residual DOC of 20 mg/L.

II. MATERIALS AND METHODS

A. Collection and characterisation of ROC

The ROC sample was collected from a wastewater reclamation facility at a local municipal wastewater treatment plant, and stored at 4°C. The sample was characterised (Table 1) according to Standard Methods [4]. The sample was fairly high in alkalinity and total dissolved solids (TDS).

TABLE I
CHARACTERISTICS OF ROC

Parameter	Value
DOC (mg/L)	37.5
COD (mg/L)	105
pH	8.3
Colour (Pt.Co units)	158
Chlorides (mg/L)	8,060
TDS (mg/L)	16,140
A_{254} (/cm)	0.68
SUVA (L/mg-m)	1.8
Alkalinity (as CaCO ₃ , mg/L)	410
Conductivity (mS/cm)	22.3

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B. UVC lamp reactor

An annular reactor (working volume 900 mL) with a centrally mounted UVC lamp was used [5]. The average irradiated area was 464 cm², and the path length was 1.94 cm. UVC irradiation ($\lambda = 254$ nm) was provided by a 39 W UV lamp (Australian Ultra Violet Services, G36T15NU). After the addition of H₂O₂ (3 mM), the samples were mixed and aerated by humidified air in the reactor and irradiated for various contact times. The fluence rate was 8.95 mW/cm² and the UV fluence after 60 min irradiation was 33000 mJ/cm².

C. UVC-LED reactor

UV-LEDs which emit UV light at 255 nm were purchased from Sensor Electronic Technology (Columbia, South Carolina, USA). The LEDs were soldered to a plate and connected to a DC power supply (INSTEK GPR-6030 D, 0-60 V, 0-3 A). Tests were performed using 50 mL of ROC sample which was continuously stirred using a magnetic stirrer. The fluence rate was 0.14 mW/cm² and the UV fluence after 72 h irradiation was 36000 mJ/cm².

D. Analytical methods

DOC was determined using a total organic carbon analyser (Sievers model 5310C) in in-line mode to purge inorganic carbon. Absorbance was measured using a double beam scanning UV/vis spectrophotometer (Unicam UV2). Colour was measured with a Hach DR 4000 spectrophotometer at 455 nm in Platinum Cobalt (Pt.Co) units. Fluorescence excitation-emission matrix (EEM) spectra were determined with a Perkin Elmer LS-50B luminescence spectrometer. The biodegradability of the organics was evaluated as BDOC using the assay introduced by Joret and Levi [6] and modified by Volk et al. [7]. Molecular size distribution was determined using liquid chromatography with organic carbon detection (LC-OCD) at the Water Research Centre of the University of New South Wales (Sydney, Australia) with a DOC-Labor LC-OCD Model 8, with a Toyopearl TSK HW-50S column, using a phosphate buffer of pH 6.4 as the mobile phase. All analyses except LC-OCD were carried out in duplicate and average results are reported.

III. RESULTS AND DISCUSSION

The reduction of DOC of ROC was greater at pH 5 than at pH 8.3 (Figure 1) for both systems. At pH 5, the reduction of DOC was greater for the UVC lamp reactor (25%) after 60 min of irradiation than after 72 h of irradiation using the UVC-LED reactor (20%) (Figure 1a). The reduction of DOC was low and comparable (13-14%) at pH 8.3 for both systems (Figure 1b). As the ROC had a high HCO₃⁻/CO₃²⁻ content as indicated by the high alkalinity (Table 1), the greater reduction in DOC at low pH was attributed to the reduced concentration of HO[•] scavengers such as HCO₃⁻ and CO₃²⁻. The reduction of colour was fairly similar for both systems and was a little greater at pH 5 (85-86%) (Figure 1a) than at pH 8.3 (76-77%) (Figure 1b). Similarly, the reduction of A₂₅₄ was greater at pH 5 (65-69%) than at pH 8.3 (55-57%) (Figure 1). The reductions in colour and A₂₅₄ represent the breakdown of chromophore bonds and aromatic structure of the organic matter. Therefore, large reductions in colour and A₂₅₄, but a

low reduction in DOC, indicates partial degradation of the organic matter.

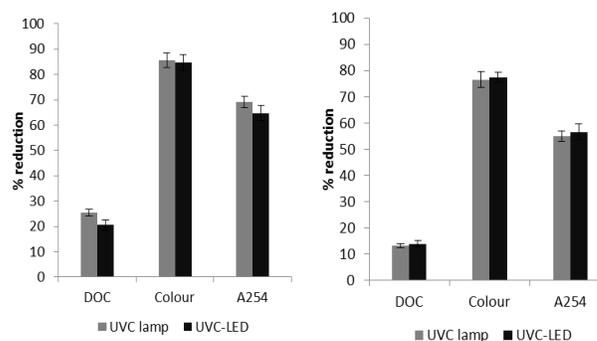


Fig 1 Comparison of the reduction of DOC, colour and A₂₅₄ after treatment at (a) pH 5 and (b) pH 8.3

A. Fluorescence excitation-emission matrix spectra

Fluorescence excitation-emission matrix (EEM) spectra provide a “fingerprint” of the types of fluorescent organics in water and wastewater [8]. The EEM spectra of the raw sample showed humic matter as two large peaks as humic acid-like (HA-like) matter and fulvic acid-like (FA-like) followed by soluble microbial products (SMPs) and aromatic proteins (AP I and AP II) (Figure 2). The EEM spectra demonstrated the loss of fluorescence and thus breakdown of humic-like matter after irradiation which corresponded to the removal of colour and A₂₅₄, demonstrating that the humic-like matter was responsible for the colour of the ROC. A similar pattern of reduction was observed for SMPs and API and APII with increasing time. Some difference in the shape of the peaks of HA-like acid was observed after treatment which can possibly be due to the difference in the irradiation intensity of the two systems. However further investigation is needed to confirm this effect. Furthermore, the UVC-LEDs have a broader bandwidth than the monochromatic 253.7 nm LP lamps [9]. According to the manufacturer, the guaranteed minimum wavelength is 255 nm with 260 nm being the typical peak. The different impact on the organic compounds was therefore likely due to the difference in the wavelength and bandwidth of the two systems.

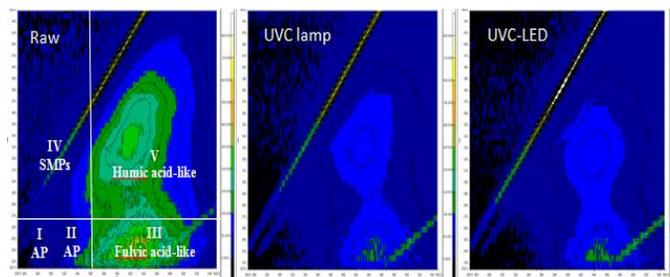


Fig 2 Excitation-emission matrix spectra of (a) raw, (b) UVC lamp and (c) UV-LED treated ROC

B. Change in molecular weight

The impact on the apparent molecular weight of the organic components of ROC was investigated using LC-OCD which separates DOC into five different chromatographic fractions:

biopolymers ($>>20,000$ Da), high MW humic substances (1,000-20,000 Da), building blocks (300-500 Da), low MW (LMW) acids and humic substances (<350 Da) and LMW neutrals (<350 Da) [10]. The LC-OCD chromatograms showed a greater reduction in humics from irradiation by the UVC lamp compared with the UVC-LEDs (Figure 3). There was a corresponding increase in the concentrations of building blocks, LMW acids and HS; these concentrations were greater for the UVC-LED treated ROC and were attributed to their lower mineralization. An interval of approximately 8 min was noted between the LMW neutrals peak for the two treated samples, the shorter retention time occurred for the UVC-LED treated sample. The smaller decrease in the humics, building blocks and LMW acids and HS peaks, compared with the higher apparent MW of the LMW neutrals demonstrated that there was less breakdown of the organic molecules for the UVC-LED system.

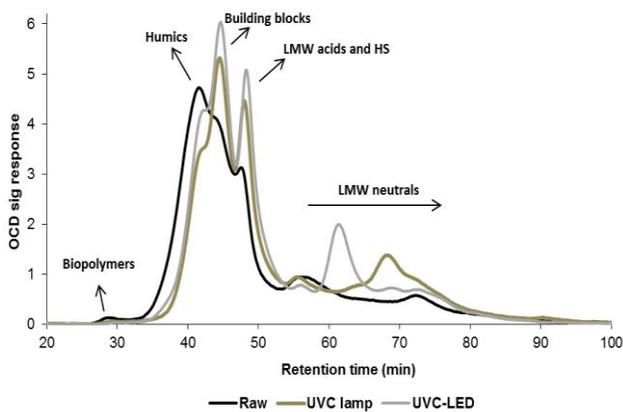


Fig 3 Comparison of LC-OCD chromatograms before and after treatment

C. Change in biodegradability

As the UVC/H₂O₂ process partially mineralizes and breaks down large MW compounds to LMW compounds, downstream biological treatment can significantly improve the overall removal of organic content. Raw ROC had a biodegradability of 8% which increased 3.7-fold after UVC lamp irradiation (Figure 4a) whereas the corresponding increase for the UVC-LEDs was 1.5-fold (Figure 4b). These results, in combination with the EEMs and LC-OCD analyses, confirmed that the UVC lamp led to greater breakdown of the large MW organic (humic-like) compounds to small organic molecules, which were more biodegradable.

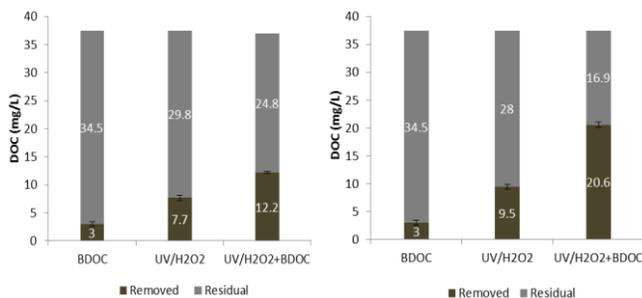


Fig 4 DOC after treatment by (a) UVC lamp, (b) UVC-LED

D. Electrical Energy Requirement

Electrical energy per order (EE/O), the electrical energy (in kilowatt hours) required to reduce the concentration of a pollutant by one order of magnitude in 1000 L of water, was calculated for both systems. The EE/O values were calculated based on the rate constants obtained for both systems. As UVC/H₂O₂ leads to partial mineralization of the organic content, downstream biological treatment is generally useful for improving the effectiveness of the process because the smaller intermediate products (aldehydes, carboxylic acids) generated from the breakdown of the humic-like compounds are more biodegradable than the parent compounds [11]. As the energy required for biological treatment is negligible compared with the AOPs, only the energy required for UVC/H₂O₂ treatment was considered [12].

TABLE II
ENERGY REQUIRED FOR TARGET RESIDUAL DOC OF 20 mg/L

	UVC lamp	UVC-LED
UVC/H ₂ O ₂	313	34
UVC/H ₂ O ₂ +BDOC	80	19

The energy consumption for the UVC lamp system was 9 times greater than for the UVC-LED system without biological treatment (Table 2). The energy requirement for both systems was markedly reduced when UVC/H₂O₂ treated ROC was subjected to the downstream biological treatment (i.e., BDOC assay), but the UVC-LED system was still more than 4 times more energy efficient than the UVC lamp system. Although the reduction of DOC was low for the UVC-LED system, it was several times more energy efficient than the UVC lamp system, demonstrating its potential in wastewater treatment.

IV. CONCLUSIONS

This study demonstrated the potential of the UVC/H₂O₂ process using UVC-LEDs as UV source for the degradation of the organic content of high salinity municipal wastewater reverse osmosis concentrate (ROC). UVC/H₂O₂ treatment with a conventional UVC lamp was compared with a novel source, UVC-LEDs. Longer irradiation time (72 h) was needed using the reactor to achieve UV fluence comparable with that of the UVC lamp reactor (60 min) due to the low output power and fluence rate of the UVC-LED system. Both treatments performed better at pH 5 than at pH 8.3. At pH 5, the reduction of DOC and A₂₅₄ was a little greater (4-5%) using the UVC lamp than the UVC-LEDs, whereas colour reduction was comparable. The fluorescence excitation emission matrix spectra revealed large and comparable reduction of fluorophores, although some difference in the shape of the peaks was observed. The LC-OCD data demonstrated greater breakdown and mineralization of humic-like substances by conventional UVC lamp irradiation resulting in greater increase of biodegradability (3.7-fold) than the UVC-LED treated sample (1.5-fold). Preliminary analysis of energy efficiency suggested that UVC-LED system was several times (4-9) more energy efficient than the UVC lamp system.

Although high capital cost and low fluence are the major limitations for the application of UV-LEDs, ongoing developments are expected to significantly improve their output power and reduce costs making this technology a competitive alternative to the conventional UV lamps.

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