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Effect of coagulation on treatment of municipal wastewater reverse osmosis concentrate by UVC/H_2O_2

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HIGHLIGHTS

- Alum coagulation is an effective pre-treatment for UVC/H_2O_2 treatment of high salinity ROC.
- Comparable DOC in samples but different coagulation success due to different nature of organics.
- Comparable mineralization obtained for two different ROCs with UVC/H_2O_2 only treatment.
- UVC/H_2O_2 treatment led to increased biodegradability with and without coagulation.
- Significant reduction in energy consumption obtained after pre- and biological post-treatment.

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ABSTRACT

Disposal of reverse osmosis concentrate (ROC) is a growing concern due to potential health and ecological risks. Alum coagulation was investigated as pre-treatment for the UVC/H_2O_2 treatment of two high salinity ROC samples (ROC A and B) of comparable organic and inorganic content. Coagulation removed a greater fraction of the organic content for ROC B (29%) than ROC A (16%) which correlated well with the reductions of colour and A_{254}. Although the total reductions after 60 min UVC/H_2O_2 treatment with and without coagulation were comparable, large differences in the trends of reduction were observed which were attributed to the different nature of the organic content (humic-like) of the samples as indicated by the LC-OCD analyses and different initial (5% and 16%) biodegradability. Coagulation and UVC/H_2O_2 treatment preferentially removed humic-like compounds which resulted in low reaction rates after UVC/H_2O_2 treatment of the coagulated samples. The improvement in biodegradability was greater (2–3-fold) during UVC/H_2O_2 treatment of the pre-treated samples than without pre-treatment. The target DOC residual ($\leq$15 mg/L) was obtained after 30 and 20 min irradiation of pre-treated ROC A and ROC B with downstream biological treatment, corresponding to reductions of 55% and 62%, respectively.

1. Introduction

Increasing use of reverse osmosis (RO)-based processes in water and wastewater treatment has led to significant attention being paid to the treatment of the resultant RO concentrate (ROC). The successful rejection of various inorganic and organic contaminants by RO membranes results in their elevated (3–4-fold) concentrations in ROC. The addition of chemicals (antiscalants, biocides and acids) further complicates the situation as they can change the character of the organic and inorganic pollutants and can influence the chemical equilibrium of the dissolved constituents [1]. The genotoxicity of a ROC was investigated in a recent study by Tang et al. [2] using the SOS *umu* method and found that it ranged between 500 and 559 μg 4-NQO (4-nitroquinoline-1-oxide)/L, which was much higher than for the RO influent (105–160 μg 4-NQO/L). Therefore, discharging the ROC to the environment can pose serious toxicological and environmental risks. Some facilities have made treatment of ROC mandatory prior to its discharge. For example, in Brisbane (Australia), the Bundamba advanced wastewater treatment plant which contributes purified recycled water to the Western Corridor Recycled Water Scheme, the largest recycled water scheme in Australia and the third largest advanced water treatment project in the world, is required to treat ROC and monitor nutrients and metal concentration prior to its discharge to the Brisbane river [3]. In addition to minimizing the environmental impacts, economically profitable reuse applications can help to offset the costs of treatment processes [4].

Due to the successful application of UVC/H_2O_2 process in drinking water treatment and wastewater polishing after advanced treatment (e.g., RO permeate), its use in the treatment of ROC has recently been investigated [5–7]. The process has been reported to reduce the concentration of organic matter as well as improve

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Table 1
Characteristics of ROC samples.

Parameter	ROC A[a]	ROC B[b]
DOC (mg/L)	32.5	37.5
COD (mg/L)	155	105
pH	7.4	8.3
Colour (Pt.Co)	137	158
Chloride (mg/L)	8875	8060
TDS (mg/L)	17,400	16,140
A_{254} (/cm)	0.6	0.68
SUVA (L/mg/m)	1.9	2
Alkalinity (as $CaCO_3$, mg/L)	450	410
Conductivity (mS/cm)	27.5	22.3

[a] Collected on 17 April, 2012.
[b] Collected on 26 June, 2012.

the biodegradability. In addition, UVC/H_2O_2 treatment caused no toxicity (Microtox assay) and slightly reduced the trihalomethane formation potential when combined with biological treatment [6]. However the process is considered energy intensive. Pre-treatment can potentially reduce irradiation time and thus energy requirements, and can facilitate the subsequent UVC/H_2O_2 treatment by improving UV transmittance (UVT).

Some studies [8–10] have reported coagulation as an individual process for the treatment of ROC but none of these investigated sequential coagulation-UVC/H_2O_2 treatment. Furthermore, the ROC samples used in those studies were of markedly different characteristics, particularly in terms of salinity. The ROC in the present investigation was high in salinity (22–27 mS/cm). Coagulation for the removal of humic substances in saline (marine) water conditions [11–14] has been suggested to occur differently than in low salinity water in terms of colloid destabilization and removal as the high ion content can affect chemical hydrolysis and metal-hydroxide solubility reactions.

The present study was carried out to investigate the effect of sequential coagulation using alum and UVC/H_2O_2 treatment on a high salinity ROC with a view to reducing the irradiation time to produce a target residual DOC concentration of ≤15 mg/L. Alum was chosen due to its wide use in water treatment, less impact on pH and lower cost than iron-based coagulants. The most appropriate coagulant dosage (as Al^{3+}) and pH were established to enable comparison of the efficiency of the UVC/H_2O_2 process with and without pre-treatment. The change in biodegradability was investigated by determining the biological dissolved organic carbon (BDOC) concentration, and fluorescence excitation–emission (EEM) spectra and liquid chromatography-organic carbon detection (LC-OCD) were used to track the changes in the organic components of the ROC. A preliminary estimate of the energy requirements was made to find appropriate conditions in terms of process efficiency and cost effectiveness.

2. Materials and methodology

2.1. Collection and characterization of ROC

Two grab samples of ROC (Table 1) were collected from a wastewater reclamation facility at a local municipal wastewater treatment plant (WWTP), and analyzed according to standard methods [15]. In the treatment process at the WWTP, the raw sewage is screened and de-gritted and sent to intermittently decanted extended aeration (IDEA) bioreactors where it is treated in a cycle of aeration, settling, and decant. The IDEA reactor effluent is then treated using a combination of ultrafiltration and RO. Both samples were high in salinity and total dissolved solids (TDS) concentration, and overall, the bulk characteristics of both ROC samples were comparable except for pH, COD and conductivity which were higher for ROC A. All experiments were carried out in duplicate and average results are reported.

2.2. Alum coagulation

Alum stock solution was prepared using $Al_2(SO_4)_3{\cdot}18H_2O$ (Chem-Supply, Pty Ltd., Australia). A range of alum concentrations (1–6 mM as Al^{3+}) was tested to find the best coagulant dosage. Coagulation was conducted with a laboratory jar test apparatus (Phipps and Bird, PB-700) using 2 L ROC samples. The samples were rapidly mixed for 2 min at 250 rpm followed by slow mixing for 30 min at 30 rpm and subsequent settling for 2 h before taking supernatant for analyses. Desired pH value was adjusted using 1 M H_2SO_4 or 1 M NaOH.

2.3. Irradiation conditions

Irradiation was conducted using an annular reactor (working volume 900 mL) with a centrally mounted UV lamp [16]. The average irradiated area was 464 cm^2, and the path length was 1.94 cm. UVC irradiation (λ = 254 nm) was provided by a 39 W UV lamp (Australian Ultra Violet Services, G36T15NU). The average fluence rate of the lamp was 8.91 mW/cm^2. After the addition of H_2O_2 (3 mM), the samples were mixed and aerated by humidified air in the reactor and irradiated for various contact times. The H_2O_2 dosage was selected based on initial tests conducted using a range of dosages (1–6 mM). For comparison, the pH of the ROC samples subjected to UVC/H_2O_2 only treatment was adjusted to 5.

2.4. Analytical methods

DOC was determined using a TOC analyser (Sievers model 5310C) in in-line mode to purge inorganic carbon. Absorbance was determined 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 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 [17] and modified by Volk et al. [18].

The concentration of residual H_2O_2 was estimated using Merckoquant® peroxide test strips. To avoid the interference of H_2O_2 in COD and DOC measurement, the residual H_2O_2 was quenched by using the enzyme catalase (from *Aspergillus niger*, Calbiochem®) as described elsewhere [19]. 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.

3. Results and discussion

3.1. Effect of pH and dosage on coagulation

Alum is generally considered effective at pH 5–6 [20] and the effect of these values on ROC A and B was investigated using 1.5 mM Al^{3+} to confirm the best pH. Coagulation efficiency was significantly greater at pH 5 than at pH 6 (Table 2) for both samples and therefore pH 5 was chosen for further investigation.

A range of concentrations (1–6 mM as Al^{3+}) was then tested for ROC A to find the best dosage at pH 5. The reduction of DOC increased with increasing coagulant dosage up to 3 mM (22%) whereas COD reduction remained fairly similar above 1 mM (Fig. 1a). The reduction of colour and A_{254} increased with increasing