Chemical Engineering Journal 284 (2016) 841–849

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Comparison of coagulation efficiency of aluminium and ferric-based coagulants as pre-treatment for UVC/H_2O_2 treatment of wastewater RO concentrate

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HIGHLIGHTS

- Ferric-based coagulants removed a greater proportion of most of the DOC fractions.
- Ferric chloride was superior as pre-treatment for the UVC/H_2O_2 treatment of ROC.
- Coagulation led to lower rates of DOC reduction during UVC/H_2O_2 treatment.
- Biodegradability of ROC after UVC/H_2O_2 treatment was different for each coagulant.
- Marked reduction in energy demand obtained after pre- and biological post-treatment.

ARTICLE INFO

Article history:
Received 1 April 2015
Received in revised form 24 August 2015
Accepted 26 August 2015
Available online 1 September 2015

Keywords:
Coagulation
Reverse osmosis concentrate
UVC/H_2O_2
Dissolved organic matter
Biodegradability

ABSTRACT

Coagulation using two aluminium- (alum and aluminium chlorohydrate (ACH)) and two ferric-based coagulants (ferric chloride and ferric sulphate) was investigated as a pre-treatment for the UVC/H_2O_2 treatment of a high salinity municipal wastewater reverse osmosis concentrate (ROC). The ferric-based coagulants were generally better than alum, and ACH was the least efficient in removing dissolved organic carbon (DOC), colour, and A_{254} (and thus improving UV transmittance (UVT)). Ferric-based coagulants removed a greater proportion of most of the DOC fractions. However the reduction of DOC was comparable (46–49%) for alum and ferric chloride at a similar metal dosage (1 mM) for UV fluence of 32×10^3 mJ/cm^2, whereas ferric sulphate performed significantly better (58%). A similar trend was observed for colour and A_{254} reduction, and UVT improvement. The biodegradability almost doubled for UV fluence of 32×10^3 mJ/cm^2 without pre-treatment. The change in biodegradability of the pre-treated samples during UVC/H_2O_2 treatment was different for each coagulant, due to the difference in the content and type of organic matter removed. Ferric chloride was superior in terms of total DOC reduction and electrical energy dose (*EED*) for the treatment of the high salinity ROC to meet the target residual of 15 mg C/L.

1. Introduction

Membrane processes including reverse osmosis (RO) are widely used as a polishing treatment for secondary effluent in wastewater reclamation schemes. The global market for RO (wastewater recycling and seawater desalination) is growing continually and is predicted to reach \$8.1 billion by 2018 [1]. The RO process generates very high quality permeate but also generates reverse osmosis concentrate (ROC) which commonly comprises 15–20% of the volume of the feed stream. The ROC contains almost all the contaminants present in the original wastewater at elevated levels. Depending on the wastewater source, these contaminants may be toxic and/or bio-accumulative, and so disposal of untreated ROC presents a potential environmental risk. For example, emerging contaminants such as pharmaceuticals, personal care products (PPCPs) and endocrine disrupting compounds (EDCs) may be present in significantly greater concentration in ROC than feed water which necessitates

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Abbreviations: AOP, advanced oxidation process; ACH, aluminium chlorohydrate; DOC, dissolved organic carbon; AP, aromatic proteins; BDOC, biological dissolved organic carbon; *EED*, electrical energy dose; EDCs, endocrine disrupting compounds; EEM, excitation–emission matrix; FA, fulvic acid; HA, humic acid; FRI, fluorescence regional integration; IDEA, intermittently decanted extended aeration; LC–OCD, liquid chromatography–organic carbon detection; MW, molecular weight; PPCPs, pharmaceuticals and personal care products; ROC, reverse osmosis concentrate; SMPs, soluble microbial products; UVT, UV transmittance.

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http://dx.doi.org/10.1016/j.cej.2015.08.109

its treatment to avoid environmental impacts. As a result, on-site treatment of ROC prior to its discharge has been given significant attention due to the presence of high contents of recalcitrant organic compounds [2]. Given that the concentration and nature of contaminants significantly affect the efficiency of treatment methods, and given the potent toxicity and persistence of some of the contaminants, innovative and cost-effective treatment technologies are needed for the treatment of ROC [3].

The application of H_2O_2-assisted ultraviolet (UV) based advanced oxidation processes (AOPs) is increasingly reported for the oxidation of organic contaminants in water and wastewater [4–7]. During UVC/H_2O_2 treatment, oxidation occurs primarily by the hydroxyl radical ($HO^{\cdot}$), a strong oxidant (oxidation potential 2.80 V), which reacts non-selectively with a wide range of organic contaminants. UVC/H_2O_2 treatment is well known to destroy the parent toxicity of organic environmental toxicants [8]. Second order reaction rates of 10^8–10^9 M^{-1} s^{-1} have been reported for several organic compounds [9]. Like many other AOPs, UV-based AOPs are generally considered energy intensive and therefore it is desirable to integrate these processes with appropriate pre-treatment or post-treatment to improve cost efficiency. Since AOPs break down the high molecular weight organic matter to smaller more biodegradable molecules [10], the post-treatment is usually a biological process.

Treatment of ROC to remove organic content may differ from conventional wastewater due to high salinity, and the ROC in this investigation is particularly saline (electrical conductivity of 23 mS/cm). Coagulation is an effective pre-treatment as it not only can remove a portion of the organic matter but can also facilitate subsequent UVC/H_2O_2 treatment of the remaining organics, which may include PPCPs and EDCs, by improving UV transmittance (UVT) [11]. This reduces the irradiation requirements, making the combined coagulation-UVC/H_2O_2 process more energy efficient. High ion content means that coagulation for the removal of organic matter from water occurs in a different manner than in water of low salinity. The high ion content can affect chemical hydrolysis and metal stability and thus colloid destabilisation and removal [12–15]. Coagulation using alum has been proven effective for the removal of a significant fraction of the organic content of ROC in our previous work [16]. However no comparison of the efficiency of alum with other coagulants as a stand-alone process or followed by UVC/H_2O_2 and biotreatment for the treatment of high salinity ROC has been reported.

A range of aluminium-based coagulants has been used for the treatment of water, including polyaluminium chloride (PACl), aluminium chlorohydrate (ACH) and polyaluminium chlorohydrate. An important property of the pre-hydrolysed polyaluminium coagulants is their high basicity (ratio of hydroxyl to aluminium ions) which leads to low alkalinity consumption and so little impact on pH [17]. Although ACH is more hydrated, there is little difference between the performance of ACH and PACl in water treatment applications [17]. In this study, ACH was selected as an alternative coagulant. As the ferric-based coagulants are the second most commonly used coagulants, ferric sulphate and ferric chloride were selected to compare with alum and ACH for the removal of organic matter from a high salinity ROC and to determine the change in biodegradability with and without UVC/H_2O_2 treatment.

The objective of this study was to compare the four coagulants for the pre-treatment of the ROC with a view to reducing the UV fluence and hence energy consumption of the UVC/H_2O_2 process. As each coagulant has certain disadvantages (cost, corrosivity), the purpose was to investigate which coagulant is most advantageous for the treatment of the high salinity ROC. The most effective coagulant dosage and pH was established after taking the reductions of dissolved organic carbon (DOC), colour and A_{254}, and chemical use into account. The most effective conditions for each coagulant were then used to treat the ROC prior to the UVC/H_2O_2 process. The impact of UVC/H_2O_2 treatment with and without coagulation was characterised in terms of the reductions in organic content and corresponding changes in fluorescence excitation–emission matrix (EEM) spectra and biodegradability. Liquid chromatography–organic carbon detection (LC–OCD) was used to compare the removal of various fractions of the organic matter by the different coagulants. Biological treatment (as biological dissolved organic carbon (BDOC) assay) was used as post-treatment of the coagulated and UVC/H_2O_2-treated ROC in order to achieve a target residual DOC concentration of 15 mg/L. The energy requirement of each process was evaluated in terms of electrical energy dose (*E*ED).

2. Materials and methodology

2.1. Collection and characterisation of ROC

The ROC sample was collected from a wastewater reclamation facility at a local (Melbourne, Australia) municipal wastewater treatment plant (WWTP), and stored at 4 °C. In the treatment process at the WWTP, 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 effluent is then treated using a combination of ultrafiltration and RO. The characteristics of the ROC sample, which was high in alkalinity and salinity, are given in Table 1. The high salinity of the wastewater under investigation is due to groundwater infiltration of the sewer in the area. The intrusion of groundwater leads to increased salinity of the influent to RO and thus increased salinity of the ROC due to the rejection of salts by the membrane.

2.2. Coagulation

Aluminium stock solutions were prepared using alum ($Al_2(SO_4)_3 \cdot 18H_2O$) (Chem-Supply Pty Ltd, Australia) and ACH (Omega Chemicals, Australia), and the ferric stock solutions were prepared using ferric sulphate ($Fe_2(SO_4)_3$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) which were obtained from Chem-Supply Pty Ltd, Australia. Coagulation was carried out using a laboratory jar test apparatus (Phipps and Bird, PB-700) using 2 L 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 the supernatant for UVC/H_2O_2 treatment. The desired pH value was achieved using 1 M H_2SO_4 or 1 M NaOH. On determining that pH 5 was the most appropriate (Section 3.1), the pH of the sample was adjusted to 5 prior to coagulation for the subsequent work. A small increase in pH was noted after completing the jar test which was subsequently adjusted to 5 prior to the UVC/H_2O_2 treatment.

Table 1
Characteristics of ROC.

Parameter	Value
DOC (mg/L)	32
COD (mg/L)	101
pH	7.4
Colour (Pt.Co units)	157
Chloride (mg/L)	8520
TDS (mg/L)	16587
A_{254} (/cm)	0.63
SUVA (L/mg m)	1.97
Alkalinity (as $CaCO_3$, mg/L)	710
Conductivity (mS/cm)	23
BDOC (mg/L)	4