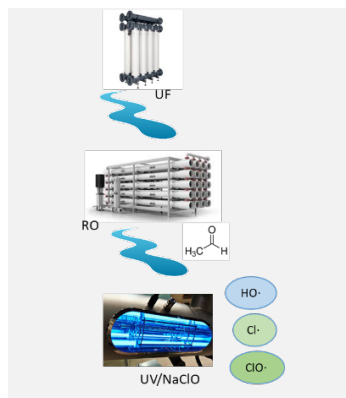


Application of the UV/chlorine process in the treatment train for water reuse: impact on aldehydes removal

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Potable water reuse is gaining interest, especially in urban communities, due to the limited availability of water resources. In most of the treatment trains, a RO stage is included. Although the efficiency of RO in removing organic compounds is very high, some low molecular weight organic compounds can be found in the permeate. Carbonyl compounds, such as saturated and unsaturated aldehydes, have been identified among the remaining DOC. Carbonyl compounds, such as acetaldehyde, have been identified in RO permeate of reclaimed municipal water. In this study, the feasibility of applying a UV/chlorine process after an RO stage for the removal of saturated aldehydes (e.g. acetaldehyde) has been explored. Under the tested NaClO concentrations and pH range, it was observed that acetaldehyde can be properly degraded. No regulated chlorinated DBP was identified among byproducts formed. A kinetic study in presence of probe molecules has been performed.

Introduction

In the current and future scenarios with an increase in water demand and the effects of climate change with the associated water stress and scarcity, the need for alternative sources of water, like water reuse, appears as an urgent need, especially in urban environments. Even though reused water has been preferentially applied in non-potable applications, the reclamation of water for potable uses is increasingly gaining interest and awareness due to the limited freshwater resources. With reference regions, like Southern California, Singapore or Namibia, providing successful examples of treatment trains for potable water reuse systems, a reverse osmosis (RO) stage is commonly included due to its high efficiency in removing chemicals and pathogens. However, some low molecular weight compounds can pass through RO membranes, and it has been pointed out the necessity to address the effect of subsequent processes (such as an advanced oxidation process (AOP) on such compounds present in RO permeate [1]. After RO treatment, recycled water typically contains between 20 and 200 $\mu\text{g C/L}$ of dissolved organic carbon (DOC). Saturated carbonyl compounds (e.g. formaldehyde, acetone) and α,β -unsaturated aldehydes (e.g. acrolein, crotonaldehyde) can account for between 19% and 38% of this remaining DOC. Among them, acetaldehyde and formaldehyde have been identified as the main contributors [2]. In California, legislation has defined a notification level of 100 $\mu\text{g/L}$ for formaldehyde. $\text{UV}/\text{H}_2\text{O}_2$ is the AOP that is more commonly applied as final stage on water reclamation systems. However, UV/chlorine system can offer an interesting alternative, because of the higher UV absorbance and quantum yield of chlorine, no need to quench residual chlorine, and both (UV and chlorine) have been applied in water treatment for more than a century. In the UV/chlorine system, different active species are involved ($\text{HO}\cdot$, $\text{Cl}\cdot$, $\text{ClO}\cdot$) [3]. However, the kinetic parameters for the reaction of many organic compounds

with those active species, especially $\text{Cl}\cdot$ and $\text{ClO}\cdot$, are still unknown.

The aim of this study was to assess the feasibility of using UV/chlorine as AOP after RO stage in a potable water reuse treatment train, evaluating its efficiency on acetaldehyde removal, assessing possible chlorinated by-products that can be eventually formed, and perform a kinetic study in presence of probe molecules.

Material and Methods

A lab-scale UV chamber with a UV LED lamp (4W 254/365 nm, Analytic Jena) operated in the UVC range (254 nm) inside of a metal box with a circular aperture to produce a semicollimated beam, described in [4]. UV lamp fluence was quantified with iodide/iodate actinometry as 0.14 $\text{mJ}/(\text{cm}^2\cdot\text{s})$. To minimize evaporation losses, the crystallization dish was covered by a UV-transparent quartz disk during experiments. For residual chlorine determination, the DPD method was used (Standard Methods 4500-Cl G. DPD Colorimetric method). Ascorbic acid was used as quencher of residual chlorine. Identification and quantification of acetaldehyde was performed by HPLC after derivatization with DNPH (2,4-dinitrophenylhydrazine), on an Agilent 1260 equipment provided with DAD detector, Kinetex Biphenyl column; mobile phase A (50:50 methanol:ethanol) and B (Milli Q water), starting from 60% A/ 40% B increasing to 69% over 5 min at a constant flowrate of 1.3 mL/min at 40°C, and absorbance at 360 nm.

Results and Discussion

Acetaldehyde (AcA) is a very volatile molecule. In the blank tests performed with only UV or only NaClO , it was observed that it is not photolyzed and only slightly removed by dark chlorination (ca 10%). UV/NaClO tests of a synthetic 100 μM AcA solution

under pH 7 (phosphate buffer) using different initial NaClO concentrations (250-1500 μM), revealed that maximum removal of acetaldehyde achieved was ca 65% with highest chlorine dose (1500 μM) (Fig. 1a). Similar percentage of removal was achieved by the UV/H₂O₂ process under equal concentration of oxidant. Regarding the effect of pH, in tests performed with a 100 μM AcA solution and 500 μM NaClO in the range 5-9, best removal was achieved at pH 7 (Fig. 1b). Tests performed with real RO permeate effluent with spiked AcA presented a lower AcA removal, probably due to the lower pH of the permeate. To unveil the role of radical species, tests with HO· scavengers (t-BuOH and bicarbonate) were performed, which showed that removal of AcA was diminished,

especially in presence of t-BuOH.

To the best of our knowledge, there is no previous work on the literature that has experimentally determined the reaction constants for the reaction of acetaldehyde with HO·, Cl· and other radical species that are produced in the UV/chlorine system. To determine the second order kinetic constants for the reaction of acetaldehyde and HO· and Cl· radicals, competition kinetic tests were performed in presence of nitrobenzene (HO· probe) and benzoate (Cl· probe).

By-products formed during UV/chlorine process were identified by LC-MS. Among the possible by-products formed, formaldehyde, glyoxal and monochloroacetic acid were identified.

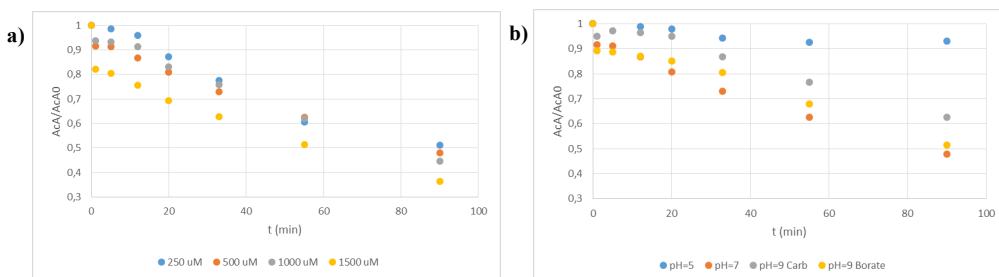


Figure 1. Effect of NaClO dose (a, left) and pH (b, right) on the removal of AcA (100 μM) by the UV/chlorine process.

Conclusions

Carbonyl compounds, such as acetaldehyde, have been identified in RO permeate of reclaimed municipal water. In order to evaluate the feasibility of applying UV/chlorine process in the final stage of a potable reuse system, the performance of this AOP process on acetaldehyde removal has been explored. Under the tested NaClO concentrations and pH range, acetaldehyde can be properly degraded. No regulated chlorinated DBP was identified among byproducts formed. A kinetic study in presence of probe molecules was performed.

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