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Removal of isopropyl alcohol and methanol in ultrapure water production system using a 185 nm ultraviolet and ion exchange system

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HIGHLIGHTS

- Low-molecular-weight (LMW) compounds was seldom removed in the production of UPW.
- Oxidative characteristics of LMW compounds in UV oxidation and ion exchange system.
- UV irradiation was effective to transform LMW compounds to more oxidative products.
- Ion exchange system removed organic acids as by-products of LMW from UV irradiation.
- Baffle in UV reactor enhanced solution turbidity and oxidation efficiency.

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ABSTRACT

The oxidation of low-molecular-weight (LMW) compounds, including isopropyl alcohol (IPA) and methanol in ultrapure water (UPW) production system was evaluated using the continuously operating 185 nm total organic carbon (TOC) reduction UV and ion exchange system. The initial concentration of compounds was in the range of tens of ppb which was the general feed condition of UV system located after 2 pass reverse osmosis (RO) in the UPW production system. UV irradiation transformed the compounds to less oxidative products that were ultimately converted to CO_2. The ion exchange system then removed carboxyl-containing organic acids generated by UV oxidation. It means that the oxidation efficiency of organic compounds by UV irradiation can be accurately measured by the summation of the final product (CO_2) and the by-product containing carboxyl functional group. The removal efficiency of LMW compounds decreased when either the initial TOC concentration increased or the UV intensity was reduced. Finally, the insertion of a baffle into the UV oxidation system was found to enhance solution turbulence and improve the oxidation efficiency.

1. Introduction

Ultrapure water is commonly used for wet cleaning/etching in semiconductor and display manufacturing processes. The ultrapure water is produced by refining the natural water to a high degree via adsorption, ion exchange, membrane filtration (reverse osmosis and ultra filtration), degasifier, and ultraviolet oxidation. Consequently, most of the contaminants (ion material, organic material, suspended solid, gas etc) in water are effectively removed. However, it is frequently observed that some of organic species contained in the natural water and reused water were not easily removed in the process of ultrapure water production. These organic compounds have the characteristic of low-molecular-weight (LMW), no surface charge (unionization of functional group) in natural pH, and low volatility. The representative compounds which are showing their features and are frequently detected in final ultrapure water are isopropyl alcohol (IPA), methanol, and trihalomethane (THMs) (Choi et al., 2013; Choi and Chung, 2014).

Activated carbon was widely utilized in water purification and the removal of dissolved or suspended organic compounds from wastewater (Lemus et al., 2013; Monica et al., 2012; Moussavi et al.,

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2013). However, granular activated carbon was effective in the removal of large non-polar molecules (e.g., certain surfactants), while a poor removal efficiency for compounds such as IPA by activated carbon was observed (Moussavi et al., 2013; Schmotzer et al., 2002; Summers et al., 2013; Sun and Chen, 2014). Furthermore, methanol has been easily removed with activated carbon when their concentration was in the hundreds ppb range (Al-Dawery, 2016; McCreary and Snoeyink, 1980). However, the lower level of methanol was significantly difficult to be removed from water because of the adsorption equilibrium and the nondestructive characteristics of the molecules (Tao et al., 2006).

Reverse osmosis (RO), which can also be utilized to remove organic LMW compounds, is one of the key treatment processes for ultrapure water production. Unfortunately, however, RO is seldom effective in the removal of low levels of non-polar IPA and THMs (Lee and Kim, 2015; Rajamohan et al., 2014). In addition, the removal of hydrophilic and uncharged molecules (e.g., methanol) via RO can be quite challenging, with rejection rates under 15% being reported (Yoon and Lueptow, 2005).

In the ultrapure water production facilities, UV (185 nm) oxidation process are normally located after RO for the removal of the residual organic compounds in the permeate of RO. Since 185 nm UV can produce OH radical by dissociating water molecule without any chemical injection, 185 nm UV is preferential to 254 nm UV. Previous research has shown that UV oxidation is more effective in terms of organic LMW compound degradation (Sun and Chen, 2014; Matilainen and Sillanpää, 2010; Morris et al., 2004). In particular, Sun and Chen (2014) demonstrated the 85% removal efficiency for IPA using a partial photocatalytic oxidation and adsorption system. The successful removal of methanol by UV oxidation has also been described in earlier reports (Hermann, 1999; Matilainen and Sillanpää, 2010). However, a few studies used the 185 and 254 nm UV lamp to oxidize organic compounds at a low concentration (the level of ppb). In general, the concentration of organic contaminant after 2 pass RO system in UPW production system is in the range of tens of ppb. In addition, there was little study showing the combination of UV and ion exchange to enhance the removal efficiency of total organic carbon (TOC). It is generally known that TOC-UV could oxidize the complex organic compounds to less oxidative compounds and CO_2.

Generally, the main role of ion exchange process after RO is to make 18.2 MΩ cm resistivity by removing residual anion and cation in solution. However, the role of ion exchange in the removal of organic carbon in water is not clearly verified even though the organic compounds containing the negatively charged functional groups could be easily removed by the ion exchange resin (Bornak, 2003).

The primary goal of this work was to evaluate the degradation efficiencies and mechanisms for IPA and methanol during UV oxidation and ion exchange reactions. The intermediates and final products generated from UV oxidation were measured to suggest the oxidative pathway of each compounds and to understand the role of ion exchange after UV irradiation. The effects of specific design and operational factors such as the irradiation intensity, the presence of a baffle, and initial concentration of contaminants were also investigated in order to improve the removal efficiency of LMW compounds in ultrapure water production system.

2. Materials and methods

2.1. Materials

The chemicals used in this study were isopropyl alcohol (99.5%, Junsei), methanol (99.8% Junsei), and acetone (99.5%, Junsei). Deionized water (DIW) was prepared with the ultrapure water production system operated in the authors' laboratory. The quality of the DIW was as follows: TOC <1 μg/L, resistivity >18.2 MΩ cm, metals (Na, K, Mg, Ca, Al, Fe, Cr, Mn, Co, Ni, Pb, and Zn) < 1 ng/L, ions (Cl^-, NO_3^-, Br^-, SO_4^{2-}, PO_4^{3-}, and NH_4^+) < 10 ng/L, dissolved oxygen < 1 μg/L, and dissolved CO_2 < 1 μg/L.

2.2. Apparatus and experimental condition

A schematic diagram of the test equipment is shown in Fig. 1. UV irradiation was carried out using a 4.8 L cylindrical SUS 316 reactor. One UV lamp (Aquafine, 41 W) and a synthetic quartz sleeve (25 mm in diameter and 90 mm in length) were installed in the center of the UV reactor. The transparency of the quartz sleeve to 185 nm UV irradiation, as measured at the sleeve surface with a UV power meter, was 80% (C8026, Hamamatsu Photonics, Japan).

DIW was supplied to the reactor by a magnetic pump, while chemical solutions were continuously injected into the line between the feed pump and the UV reactor using a piston pump; the flow ratio of DIW to injected chemical was 1000 to 1. The chemical concentration was adjusted from 20 to 100 μg/L by modifying the concentration of the chemical stock solution. An in-line mixer was employed to maintain homogeneity for both the chemicals and the DIW. The feed flow was varied from 1.4 to 4.0 L/min, resulting in electrical energy doses (EES) in the range of 294–783 mW s/cm^2. Especially, the change in IPA, acetone, acetic or formic acid, and CO_2 was investigated according to the change of EES. In this experiment, the initial IPA concentration was fixed at 50 μg/L. Also, a removable perforated baffle plate was installed symmetrically at the center of the reactor to evaluate the effect of baffle on the degradation of IPA. The diameter of the reactor and the baffle was 900 mm and 850 mm, respectively. There was a hole in the center of the baffle disk. The size of hole was 29 mm which was 4 mm larger than that of a sleeve. There were 12 holes (5 mm) on the baffle disk which were evenly located on the baffle disk to initiate the turbulences in the reactor. There were 5 disks at the constant interval in the reactor. This experiment was conducted when the initial IPA concentration and EES were 50 μg/L and 470 mW s/cm^2, respectively.

An ion exchange system was located after the UV reactor. The ion exchange resin used in this study was Amberjet UP6040 supplied by Dow Chemical; it consists of a mixture of strong acidic cations (40%) and strong basic anions (60%). The space velocity of the ion exchange system was 40 h^{-1}.

2.3. Sampling and analysis

The TOC and inorganic carbon (IC, CO_2) concentrations were measured with an online TOC meter (Sievers 900 On-line, GE, USA). Measurements of the IC content were conducted with the inorganic

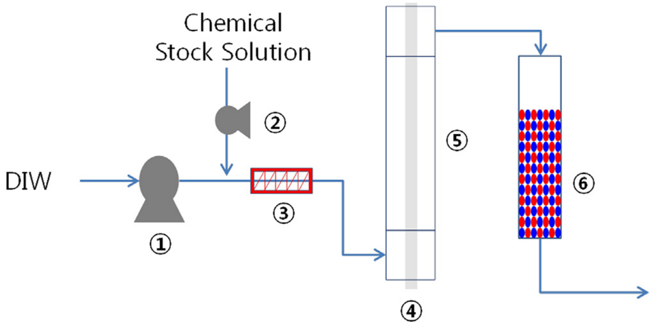

Fig. 1. Schematic of the TOC-UV oxidation and ion exchange system (1 and 2: pump, 3: in-line mixer, 4: UV lamp, 5: TOC-UV reactor, and 6: ion exchange tower).