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Ozonation combined with electrolysis of 1,4-dioxane using a two-compartment electrolytic flow cell with solid electrolyte

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ABSTRACT

Ozonation combined with electrolysis (ozone–electrolysis) is a new advanced oxidation process for water treatment. The advantages of ozone–electrolysis are (1) that reagents such as hydrogen peroxide or ferrous salts are unnecessary, (2) there is less influence from chromaticity, and (3) electric power is only required for operation. However, electrolysis has a serious limitation, in that it requires electrical conductivity (EC). This research is aimed at developing an ozone–electrolysis reactor that is applicable to wastewater with low EC using a cation exchange membrane as solid electrolyte. Moreover, experimental evidence of hydroxyl radical (·OH) generation via the cathodic reduction of ozone was obtained. Competitive kinetics analysis, based on the experimental data from the ozone–electrolysis of a mixed solution of 1,4-dioxane and *tert*-butyl alcohol, revealed that ·OH contributed to 1,4-dioxane degradation. The ozone–electrolysis reactor was successfully applicable to degradation of 1,4-dioxane in both 1,4-dioxane solution (EC: less than 0.30 μS/cm) and a landfill leachate treated by a low-pressure reverse osmosis membrane (EC: 0.06 mS/cm). The use of a solid electrolyte was also very effective in reducing the electric power required for electrolysis.

1. Introduction

Advanced oxidation processes (AOPs) have been defined by Glaze et al. (1987) as processes involving the generation of hydroxyl radicals (·OH) in sufficient quantity to effect water purification. AOPs are believed to be capable of mineralizing most organic contaminants into carbon dioxide due to the high oxidation potential of ·OH, which is 2.38 V vs. NHE in acid solution and 1.55 V vs. NHE in basic solution (Hoare, 1985). Many AOPs have been discussed and developed, such as combinations of ozone, hydrogen peroxide and/or UV irradiation, Fenton and Fenton-like processes, ultrasound processes, radiation processes, and so on (Andreozzi et al., 1999; Parsons, 2004).

Ozonation combined with electrolysis (ozone–electrolysis) is a new AOP. The advanced oxidation mechanism for ozone–electrolysis was estimated to be as follows (Kishimoto et al., 2005):

$$O_3 + e \rightarrow O_3^- \text{ at cathodes,} \quad (1)$$

$$O_3^- + H_2O \rightarrow \cdot OH + O_2 + OH^-. \quad (2)$$

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The above mechanism was proposed from a mathematical model analysis using 4-chlorobenzoic acid as a radical probe (Kishimoto et al., 2005). Previous work showing the degradation of 1,4-dioxane in the cathodic compartment of an ozone–electrolysis reactor also supports the above mechanism (Kishimoto et al., 2007). However, further evidence of the mechanism may be required, because the pH in the cathodic compartment in the reactor (Kishimoto et al., 2007) was alkaline, so that a different pathway for ·OH generation by chemical ozone decomposition is expected (Tomiyasu et al., 1985). Accordingly, the first objective of this research work was to obtain experimental evidence for the above mechanism.

The advantages of ozone–electrolysis compared with other AOPs are (1) that reagents such as hydrogen peroxide or ferrous salts are unnecessary, (2) there is less influence from chromaticity, and (3) electric power is required only for operation. However, electrolysis includes a serious limitation, the requirement of electrical conductivity (EC). When wastewater contains a high concentration of an electrolyte, electrolysis is applicable to wastewater treatment. However, electrolysis cannot be applied when wastewater contains no electrolyte. Accordingly, the second objective of this research work was to develop an ozone–electrolysis reactor applicable to wastewater with low EC.

1,4-Dioxane is one micro-organic contaminant that is often detected in natural and drinking water (Abe, 1999; Kawata et al., 2003; Suzuki et al., 2005). The International Agency for Research on Cancer (IARC) classifies it as a possible human carcinogen (2B). The tolerance limit for 1,4-dioxane in drinking water is low, at 50 μg/L, as given in the tentative guidelines of the World Health Organization (WHO). The potential sources of 1,4-dioxane loading are estimated to be chemical plants, sewage treatment plants, and waste landfill sites (Yasuhara, 1995; Yasuhara et al., 1997, 1999, 2003; Abe, 1999; Tanabe et al., 2006). In particular, the 1,4-dioxane concentration in waste landfill leachates is often much higher than the regulation for drinking water (Yasuhara, 1995; Yasuhara et al., 1997, 1999).

Some researchers have reported that the conventional activated sludge process is ineffective for the removal of 1,4-dioxane (Abe, 1999; Makino et al., 2005; Tanabe et al., 2006). Chemical oxidation processes, such as chlorination and ozonation under ambient temperature, are also ineffective (Hoigné and Bader, 1983; Klečka and Gonsior, 1986; Kishimoto et al., 2007). Furthermore, activated carbon adsorption is inefficient due to the high hydrophilicity of 1,4-dioxane. Thus, conventional leachate treatment processes, such as the combination of aerobic biological treatment, coagulation–sand filtration, and activated carbon adsorption, are unable to efficiently remove 1,4-dioxane. Nowadays, low-pressure reverse osmosis (RO) has been introduced for leachate treatment. RO membranes can generally retain ions and large molecules with a molecular weight of more than 100 (Baker, 2004). However, 1,4-dioxane may permeate a low-pressure RO membrane, because it is a neutral organic solute with a low molecular weight of 88. AOPs are effective for the removal of 1,4-dioxane from water (Klečka and Gonsior, 1986; Adams et al., 1994; Safarzadeh-Amiri et al., 1997; Beckett and Hua, 2003; Son et al., 2006; Yanagida et al., 2006; Kishimoto et al., 2007; Yamazaki et al., 2007), due to the high second-order reaction rate constant of ·OH and 1,4-dioxane (Thomas, 1966). Therefore, a synthetic 1,4-dioxane solution and an actual landfill leachate treated by low-pressure RO were used for evaluation of the process developed in this research.

2. Materials and methods

2.1. Materials

A 55 mg/L 1,4-dioxane solution was prepared by the dissolution of 1,4-dioxane (guaranteed grade, Nacalai Tesque, Kyoto, Japan) in distilled and ion exchanged water. No electrolyte was added into the solution to demonstrate the applicability of the developed ozone–electrolysis reactor to water treatment with extremely low EC. The EC of the solution was less than 0.30 μS/cm.

Mixtures of 1,4-dioxane and *tert*-butyl alcohol (guaranteed grade, Wako Pure Chemicals, Osaka, Japan) were also tested for confirmation of ·OH generation during ozone–electrolysis. One mixture contained 55 mg/L of 1,4-dioxane and 16 mg/L of *tert*-butyl alcohol and the other contained 24 mg/L of 1,4-dioxane and 134 mg/L of *tert*-butyl alcohol.

The landfill leachate was sampled from a waste landfill site in Saitama Prefecture, Japan. The leachate sample was filtered using a glass fiber filter (Whatman GF/D) and then electrodialysis was applied to remove salinity. A commercial electrodialyzer (ME-O, AMP Ionex, Tokyo, Japan) with 10 pairs of a strongly acidic cation permeable membrane (CMV, Asahi Glass, Tokyo, Japan) and a mono-anion permselective membrane (ASV, Asahi Glass, Tokyo, Japan) was used. The operating conditions were as follows: feed mode: continuous feeding at the flow rate of 50 mL/min (hydraulic retention time of 10 min); electrolysis: potentiostatic mode at 15.0 V; water recovery: 90%. The power consumption for electrodialysis amounted to 2.0 kWh/m^3. After the electrodialysis was completed, 1,4-dioxane and sodium hydroxide were added to the treated leachate at a final 1,4-dioxane concentration of 1.0 mg/L and a final pH of 10. Then the leachate was filtered with a low-pressure RO membrane. The operating conditions were as follows: membrane: cross-linked polyamide RO membrane (UTC-70B, Toray Industries, Japan); filtration mode: dead-end filtration; operating pressure: 1.5 MPa.

2.2. Apparatus

Fig. 1 depicts a schematic view of the experimental setup. The experimental apparatus consists of a ceramic plunger feed pump (VSP-1050, EYELA, Tokyo, Japan), a handmade electrolytic flow cell, a DC power supply (AD-8735, A&D, Tokyo, Japan), a mass flow controller (CMQ9200, Yamatake, Tokyo, Japan), an ozone generator (ED-OG-R3Lt, EcoDesign, Saitama, Japan), two ozone monitors (EG-600, Ebara Jitsugyou, Tokyo, Japan), two handmade gas separators, a gas dryer (DH-106-1, Komatsu Electronics, Hiratsuka, Japan), and an ozone decomposer (ED-MD9-500S, EcoDesign, Saitama, Japan).

The detailed structure of the electrolytic flow cell is illustrated in Fig. 2. The flow cell was divided into two