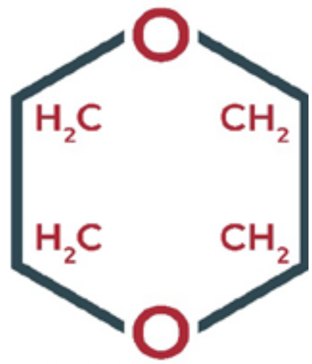
How ozone generators effectively remove 1,4-dioxane from water supplies

Abstract

The presence of 1,4-dioxane in water supplies has been a point of concern for a long time. This contaminant, considered a potential carcinogen, has been found in underground waters and supplies all over the world. In this paper, we show how ozone can be used for the safe, effective removal of 1,4-dioxane from water.

Problem Statement

The concentrations of 1,4-dioxane need to be reduced to acceptable levels in groundwater and drinking water.



Background

1,4-dioxane

1,4-dioxane is a highly water-soluble, non-biodegradable ether. It also has a high aqueous solubility, low vapor pressure, and a boiling point close to that of water. It may migrate rapidly in groundwater. It has been found in underground waters, industrial wastewaters, and water supplies. Chiang et al. (2016) give a discussion of the occurrence of 1,4-dioxane in water, including drinking water, and regulations applied in several countries. Stepien et al. (2014) studied the persistence and mobility in sewage, surface, and drinking water in the rivers Main, Rhine, and the Oder in Germany. Abe (1999) reported the presence of 1,4-dioxane in surface and groundwaters of the Kanagawa prefecture in Japan. Zenker et al. (2003) give a good revision of the sources and occurrence in drinking water, surface water, groundwater, and wastewater. It is often found as a trace contaminant in many goods, including consumer products and various chemicals.

1,4-dioxane has been classified as an emerging contaminant and as a priority hazardous pollutant. Manufacturers now tend to reduce the content of 1,4-dioxane in chemicals to low levels. Prolonged exposure has been linked to the central nervous system, liver, and kidney damage. It is classified by EPA as "likely to be carcinogenic to humans" by all routes of exposure, and by the European Union as having limited evidence of carcinogenic effect (EPA Technical Fact Sheet, 2017). Its primary use was as a stabilizer for industrial chlorinated solvents like 1,1,1-trichloroethane (TCA) and is found at some solvent release sites. This application was discontinued when TCA was discontinued in the 1990s when the Montreal Protocol banned it. In the U.S., several states have established guidelines for

Methods of analysis

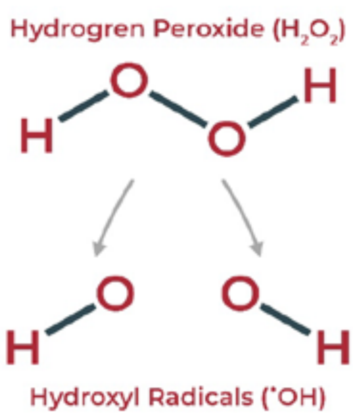
The reference methods of analysis are EPA Methods 522 ("Determination of 1,4-dioxane in drinking water by solid-phase extraction (SPE) and gas chromatography/ mass spectrometry (GC/MS) with selected ion monitoring (SIM)"), and 8270E ("Semivolatile organic compounds by gas chromatography/mass spectrometry"). The latter method also gives specific information about preparation techniques and includes 1,4-dioxane analysis.

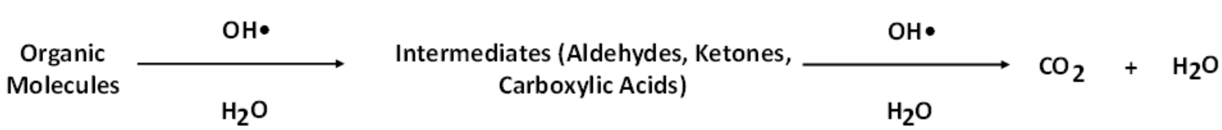
1,4-dioxane is resistant to separation or elimination by conventional methods

Its physical properties (high aqueous solubility, low vapor pressure, and a boiling point close to that of water) make it difficult to separate by conventional methods like activated carbon adsorption or air stripping. Also, it is rather stable and difficult to eliminate by chemical or biological degradation. The removal efficiency in wastewater treatment plants is very low. The same holds for domestic sewage and drinking water treatment processes (Tian et al., 2014; Tian et al., 2017).

Ozone for removal of 1,4-dioxane

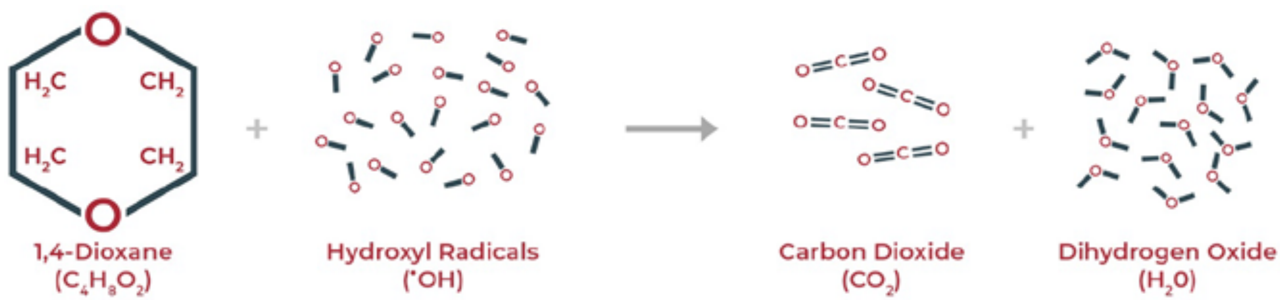
Ozone is a strong oxidant, with a standard redox potential of +2.07 V, and has been used for water and wastewater treatment because of its capacity for the organic matter removal, disinfection, and discoloration. Ozonation has the advantage of not producing toxic residues and is applied in many countries for water treatment (Barndock et al., 2018). Ozone can break organic molecules through direct reactions; however, attempts to degrade 1,4-dioxane did not give good results because of slow reaction rates. Also, the degradation of 1,4-dioxane with ozone in water at circumneutral (close to neutral) pH produces organic molecules that increase the toxicity of the water sample. Thus, so-called Advanced Oxidation Processes (AOPs) are available where ozone is used in combination with another chemical, for example, hydrogen peroxide (H2O2), to create hydroxyl radicals, OH▪. The OH▪ radicals are very reactive and capable of breaking down organic molecules, including dioxane.





However, some small organic fragments may remain in solution. Also, the presence of radical scavengers like the bicarbonate ion can trap the OH▪ radicals and interfere with the degradation of organic molecules. Other studies have shown that ozonation combined with other reagents and/or UV light can also remove 1,4-dioxane (Tian2014). If the conversion to CO2 and H2O (called mineralization) is not complete, the intermediates contribute to the dissolved organic carbon (DOC).

Ozone treatment with pH adjusted



Barndock et al. (2014) showed that the key for the 1,4-dioxane removal by ozone was to maintain the pH > 9 because the formation of the OH▪ radical is favored in alkaline media. The researchers found that the operational parameters should be carefully adjusted for the ozone treatment of wastewaters. Thus, the O3 process, which has formerly been considered inadequate as a sole treatment for such wastewaters, could be a viable treatment for the degradation of 1,4-dioxane at the adequate operation conditions.

The almost total removal of 1,4-dioxane and the isomer 2methyl-1,3-dioxolane (MDO) was demonstrated from both industrial wastewaters and a synthetic solution. Also, about 90% of chemical oxygen demand could be removed at optimal process conditions. Data from on-line Fourier transform infrared spectroscopy (FTIR) was used to get an insight into the different decomposition routes. They concluded that the degradation at pH > 9 occurs through the formation of ethylene glycol as a primary intermediate, whereas the decomposition in acidic conditions (pH < 5.7) consists in the formation and slower degradation of ethylene glycol diformate.

Ozonation combined with electrolysis

The applicability of ozonation combined with electrolysis was demonstrated by Kishimoto et al. (2007) for the removal of 1,4-dioxane from synthetic wastewater containing bicarbonate and chloride ions. One-compartment and two-compartment cells were used. The authors proposed that the OH▪ radical in these experiments was generated from the electrochemical reduction of ozone. The two-compartment cell was effective in reducing the scavenging effect of the bicarbonate ions, which tend to react with the hydroxyl radicals. The chemical oxygen demand (COD) was reduced in the two-compartment cell in relation to the one-compartment cell.

The two-compartment cell was useful for the treatment of wastewater containing bicarbonate and chloride ions. Bicarbonate is a known radical scavenger thus tends to react with the hydroxyl radical; however, the acidic conditions in the anodic compartment formed CO2 that was then stripped from the solution. Compartment formed CO2 that was then stripped from the solution.

Treatment with O3 and catalysts

Recent studies proved the effectiveness of the ozonation treatment with catalysts. Thus, a study by Scaratti et al. (2018) demonstrated the effective removal of 1,4-dioxane by ozonation using cupric oxide (CuO) as a catalyst. In the presence of the catalyst, ozone generated superoxide ions, which react with 1,4-dioxane to form ethylene glycol, which was further oxidized to formic acid. In addition to removing the dioxane, the toxicity of the treated water was reduced.

Activated carbon, which is a cheap and stable catalyst, exhibited positive effects in removing 1,4-dioxane by ozonation, as demonstrated by Tian et al. (2017). This method, with a high dose of O3, could also altogether remove the DOC (dissolved organic carbon) in a 1,4-dioxane solution.

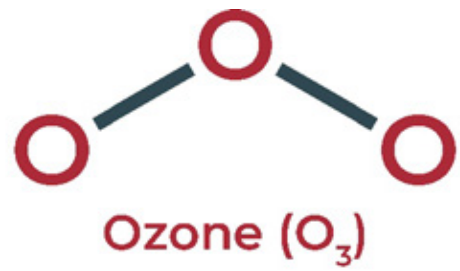
Ozone treatment with ultrasound

Dietrich et al. (2017) studied the synergistic removal of 1,4-dioxane using combined ozone/ultrasound. Ultrasonic irradiation of water produces cavitation generating high temperatures. Thus, degradation of the contaminant molecules can occur inside cavities, at the cavity interface, or in the bulk solution with the formed radicals. When ozone gas is subject to cavitation, a thermal process converts the ozone to molecular oxygen and an oxygen atom, which is then free to react with a water molecule to form the hydroxyl radical that reacts with organic molecules. It was found that the rate of removal by ozone/ultrasound exceeded the sum of the individual rates. Drinking water from a treatment plant was used. The effects of ozone concentration, ultrasonic intensity, retention time, pH, and bicarbonate ion were studied. Removal of 1,4-dioxane appeared to be driven primarily by the hydroxyl radical generation. It was concluded that ultrasound could be an attractive way to reduce retention time or reactor size, also as an alternative when pH adjustment is not practical. An empirical model was developed for this system.

Ozone combined with other chemicals and treatments

DiGuiseppi et al. (2016) discuss several methods and mention the successful ex-situ remediation of 1,4-dioxane in groundwater using O3 and H2O2.

Takahashi et al. (2013) compared the degradation of 1,4-dioxane by O3/UV and O3/H2O2 on a laboratory scale, with solutions of 1,4-dioxane prepared in distilled and deionized water. In both cases, the removal of dissolved organic carbon (DOC) needed additional O3. The authors suggested that O3/H2O2 should be more applicable than O3/UV for wastewater samples.



Ikehata et al. (2016) evaluated and optimized several AOPs (including O3 alone, O3 /OH–, /H2O2, O3/UV, O3/H2O2/UV, and H2O2/UV). For the reduction of the concentration of 1,4-dioxane and other organic contaminants for in situ chemical oxidation (ISCO) in groundwater. Based on the results, the O3/H2O2 AOP was found to be one of the best treatment alternatives for 1,4-dioxane removal in particular for the ISCO case. Vatankhah et al. (2019) studied the application of ozonation, followed by biologically active filtration. (O3-BAF) was evaluated for the treatment of potable wastewater for reuse. The reaction of O3 with granular activated carbon (GAC) (O3/GAC) to promote the formation of hydroxyl radicals (▪OH), was also studied.

Conclusion

Ozone offers many advantages for the treatment of 1,4-dioxane contaminated waters. Although O3 by itself is not reactive enough towards 1,4-dioxane, under adequate pH conditions, combined with other chemicals, ultrasound, catalysts, ultraviolet radiation, or electrolysis, it has been proven of being capable of degrading this molecule and even achieving total mineralization. Treatment with ozone does not leave residues. Also, our ozone generators are reliable and need very little maintenance.

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