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Degradation of vinyl chloride (VC) by the sulfite/UV advanced reduction process (ARP): Effects of process variables and a kinetic model

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HIGHLIGHTS

- VC degradation kinetics is studied in the sulfite/UV advanced reduction process.
- Rate constant is affected by pH, sulfite dose, light intensity, and VC concentration.
- A kinetic model explains the change in rate constant with various experimental factors.

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ABSTRACT

Vinyl chloride (VC) poses a threat to humans and environment due to its toxicity and carcinogenicity. In this study, an advanced reduction process (ARP) that combines sulfite with UV light was developed to destroy VC. The degradation of VC followed pseudo-first-order decay kinetics and the effects of several experimental factors on the degradation rate constant were investigated. The largest rate constant was observed at pH 9, but complete dechlorination was obtained at pH 11. Higher sulfite dose and light intensity were found to increase the rate constant linearly. The rate constant had a little drop when the initial VC concentration was below 1.5 mg/L and then was approximately constant between 1.5 mg/L and 3.1 mg/L. A degradation mechanism was proposed to describe reactions between VC and the reactive species that were produced by the photolysis of sulfite. A kinetic model that described major reactions in the system was developed and was able to explain the dependence of the rate constant on the experimental factors examined. This study may provide a new treatment technology for the removal of a variety of halogenated contaminants.

1. Introduction

Vinyl chloride (VC) is a chlorinated ethene that is of a concern due to its toxicity and carcinogenicity. VC is classified as a priority pollutant and has been found at many National Priority List sites established by US Environmental Protection Agency (ATSDR, 2006). The compound is produced at a large scale by the chemical industry in order to synthesize polyvinyl chloride (PVC) and the releases from those facilities are the major source of VC pollution in the atmosphere. VC contamination is also found in surface water and groundwater that were originally contaminated by chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE), because their biodegradation can result in accumulation of VC (Lee et al., 1998).

Some technologies have been developed to destroy VC. Biodegradation of VC has been reported under aerobic (Begley et al., 2012; Freedman and Herz, 1996; Tiehm et al., 2008; Zhao et al., 2011) and anaerobic conditions (Hata et al., 2004; Popat and Deshusses, 2011; Smits et al., 2011), with VC acting as sole carbon and energy source or being degraded through cometabolism. Zero-valent iron (ZVI) has been used to reduce chloroethenes including PCE, TCE and VC, both in lab scale (Andreas et al., 2009) and in field study (Wei et al., 2010). Abiotic degradation of VC by nanoscale ZVI has been reported to involve β-elimination and hydrogenolysis mechanisms with ethene, ethane and acetylene as major products (Elsner et al., 2008). VC can be absorbed from the gas phase by room-temperature ionic liquids (Cheng et al., 2009) and it can be degraded by direct photolysis at 185 nm producing both non-chlorinated and chlorinated organics (Gurtler et al., 1994). Other gas-phase VC degradation technologies involve the application of radio-frequency-powered plasma with a Pt/γ-Al_2O_3 catalyst (Yuan et al., 2011) and photocatalytic degradation by TiO_2 pellets (Sano et al., 2002; Yamazaki et al., 2004).

Sulfite species (SO_3^{2-} and HSO_3^-) have been used in the removal of chlorination byproducts but the dechlorination reactions are often slow and incomplete (Croue and Reckhow, 1989; MacCrehan et al., 1998; Yiin et al., 1987). However, sulfite has been reported to yield highly reactive species such as sulfite radical and hydrated electron when it is properly activated (Fischer and Warneck, 1996; Neta and Huie, 1985;

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Nomenclature

ARP	advanced reduction process
Sulfite/UV	the ARP that combines sulfite with UV irradiation
UV	ultraviolet
VC	vinyl chloride (CH_2CHCl)
R	reactive species that were produced when sulfite receives UV irradiation, including sulfite radical, hydrated electron and hydrogen atom
S	scavengers that could react with reactive species
P_1, P_2, P_3	products of reaction (b), (c) and (d) in Table 1
r_1, r_2, r_3, r_4	reaction rates of reactions (a)–(d) in Table 1
φ_1, φ_2	quantum yield of sulfite or VC
$\varepsilon_{ln,sulfite}$, $\varepsilon_{ln,VC}$	molar absorptivity of sulfite or VC ($M^{-1}\ cm^{-1}$, defined on natural logarithm basis, differs from molar absorptivity used with Beer–Lambert law for absorbance by factor of 2.303, $\varepsilon_{ln} = 2.303\ \varepsilon_{bl}$, where ε_{bl} is the decadic molar absorptivity used with the Beer–Lambert law, i.e. $I = I_0 10^{-\varepsilon Cx}$)
$C_{sulfite}$, C_{VC}, C_R, C_s	molar concentrations of sulfite, VC, reactive species and scavenger (mol/L)
I_{avg}	average light intensity in the solution ($\mu w/cm^2$)
I_0	light intensity entering the top surface of quartz reactor ($\mu w/cm^2$)
k_3, k_4	second order rate constant of reaction (c) and (d) in Table 1 ($M^{-1}\ s^{-1}$)
k_{obs}	the observed pseudo-first-order rate constant in VC degradation (min^{-1})

Zuo and Zhan, 2005; Zuo et al., 2005). Ultraviolet light (UV) at 253.7 nm has been widely applied in disinfection of drinking water and wastewater and it is also used as an activation method in advanced oxidation processes (AOPs) (Li et al., 2010; Zhao et al., 2010).

A new group of water and wastewater treatment technologies, called advanced reduction processes (ARPs), have been developed by combining activation methods and reducing reagents to produce reactive species which can destroy many contaminants. One recent article describes application of the sulfite/UV ARP to the degradation of monochloroacetic acid (Li et al., 2012). To the best of our knowledge, there has been no report on the degradation of chloroethenes with sulfite/UV treatment process. The objective of this study was to investigate the effects of solution pH, sulfite concentration, UV light intensity and initial VC concentration on the degradation kinetics of VC. A kinetic model that described the major photochemical reactions in the sulfite/UV ARP was developed to explain the influence of experimental factors on the degradation rate constants.

2. Materials and methods

2.1. Reagents

All reagents were purchased from commercial sources and used as received. Vinyl chloride gas (1000 ppm in nitrogen), and vinyl chloride standard solution (200 μg/mL in 2-propanol) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium sulfite (anhydrous, 98.6%) was supplied by Avantor Performance Materials (Center Valley, PA, USA). Potassium phosphate (anhydrous, 97%), potassium hydrogen phosphate (anhydrous, 98%), potassium dihydrogen phosphate (99%) and phosphoric acid (85%) were purchased from Alfa Aesar (Ward Hill, MA, USA). The vinyl chloride gas was used to prepare VC solution by sparging the gas into deoxygenated deionized water. Vinyl chloride standard solution (200 μg/mL in 2-propanol) was used for calibration.

2.2. Experimental procedure

All experiments were conducted in an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, MI, USA), which was filled by a gas mixture (95% nitrogen and 5% hydrogen) and equipped with an oxygen and hydrogen analyzer, fan boxes and palladium catalyst STAK-PAK (Coy Laboratory Products Inc., Grass Lake, MI, USA). The anaerobic chamber was flushed with the gas mixture periodically. All UV irradiation experiments were carried out in sealed, 17-mL, cylindrical, UV-transparent, quartz reactors purchased from Starna Cells, Inc. (Atascadero, CA, USA). The UV light source was a Phillips TUV PL-L36W/4P lamp, which emitted UV radiation with a monochromatic wavelength at 253.7 nm. The quartz reactor that contained samples was placed inside the anaerobic chamber and received UV irradiation perpendicular to its top surface (19.6 cm^2). The light path (reactor thickness) was 1 cm. The light intensity that entered the top surface of quartz reactor was adjusted by changing the distance between the reactor and the UV lamp and its value was recorded as I_0. Temperature was controlled around 34 ± 2 °C by an air circulation fan box. Phosphate buffers were used to control a constant pH during all experiments.

Batch experiments were conducted as a blank control (VC only), reagent control (VC and sulfite) and irradiation control (direct photolysis of VC by UV) in order to compare with the results obtained with the sulfite/UV ARP. Batch experiments also were conducted to investigate several experimental factors that affected the degradation kinetics of VC with the sulfite/UV ARP. These factors included pH value, light intensity, sulfite dose and initial concentration of VC. During each experiment, 10 to 12 samples were taken to measure the concentration of VC by gas chromatography. Since there was little reaction between sulfite and VC (less than 5% of initial VC depletion in 9 h), VC samples were directly measured after irradiation without quenching the residual sulfite in solution.

2.3. Analytical methods

The light intensity was measured by a UVC 512 light meter (Professional Equipment, Janesville, WI, USA), which was calibrated by the modified ferrioxalate actinometer (Murov et al., 1993). The primary modification was to use the ferrozine method for the colorimetric analysis of iron (Stookey, 1970) using an Agilent 8453 UV-visible spectroscopy system (Agilent, Santa Clara, CA, USA). To analyze VC, a 5-mL sample was taken from the quartz reactor and injected into a O.I. Analytical Eclipse 4660 purge and trap sample concentrator (O.I. Analytical, College Station, TX, USA). The sample was purged for 11 min at 30 °C and then desorbed for 2 min before injection into a HP 6890 gas chromatograph (GC) (Agilent, Santa Clara, CA, USA). During the GC analysis, the trap was baked at 210 °C for 10 min. The GC equipped with a FID detector and a DB-5 column (30 m ∗ 0.25 mm ∗ 1 μm). The GC inlet temperature was set at 225 °C. Helium was used as carrier gas with a constant flow at 1.3 mL/min and the spilt ratio was 50:1. The oven temperature started at an initial temperature of 35 °C for 3 min, followed by a ramp of 20 °C/min to 80 °C, followed by another ramp of 40 °C/min to 200 °C and held for 2 min. Chloride ion was detected by ion chromatography (Dionex 500) equipped with a AS-19 column and a AS40 automated sampler following Standard Method 4110. The volatile degradation products were analyzed using static head space gas chromatography–mass spectrometry (SHGC–MS). SHGC–MS was performed on Ultra GC/DSQ (ThermoElectron, Waltham, MA, USA). First, a 5-mL sample was transferred to a 10-mL vial and immediately capped with silicone rubber Teflon cap. This sample was equilibrated at 80 °C for 10 min in the static headspace sampler. A Rxi-5 ms column was used with dimensions of 60 m length, 0.25 mm i.d., and 0.25 μm film thickness (Restek; Bellefonte, PA, USA). A split (1:20) injection was used with helium as the carrier gas at constant flow of 1.5 mL/min. The transfer line and ion source were held at 250 °C. The column temperature was maintained at 30 °C for 3 min; raised to 80 °C at 10 °C/min;