



Mineralization of dichloromethane using solar-oxidation and activated TiO₂: Pilot scale study

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ABSTRACT

The oxidation of gaseous dichloromethane (DCM) by advanced oxidation technology, advanced solar oxidation technology, biological treatment, and the combination of solar advanced oxidation technology and biological treatment were investigated in a pilot study. The effects of the inlet concentration of DCM, flow rate, and relative humidity on the percentage DCM removal were recorded. Photolysis and photocatalytic oxidation using TiO₂ does not result in the complete removal of DCM, while ozone, ozone/solar- $h\nu$ and TiO₂/ozone/solar- $h\nu$ can completely remove DCM from the gas stream. Combined photocatalytic oxidation processes enhance the process efficiency and reduce both ozone demand and the energy requirements needed to completely remove DCM. Through a combination of processes, ozone, solar photons, and hydroxyl radicals oxidize DCM, generating by-products that are water soluble and more biodegradable than the original DCM, providing the possibility for it to be combined with subsequent biological treatment. The decomposition of DCM was affected by the inlet flow rate, gas relative humidity, and gas flow rate with high percentage DCM removal achieved at low flow rate, DCM initial concentration up to 200 mg/m³, and humidity around 40%. The kinetics of DCM oxidation in different processes were successfully modeled to pseudo-first order or second-order kinetics. The kinetic analysis showed that the choice of oxidation process greatly affected the kinetic constants of DCM conversion, and RH 40% could cause faster oxidation. The results support the use of solar oxidation, not only for the mineralization of DCM, but also as a pretreatment before biodegradation.

1. Introduction

In recent years, a large volume of literature has focused on the treatment of micropollutants, given their various adverse effects on the environment and on human health (Ribeiro et al., 2015). Such pollutants may be naturally occurring or anthropogenic, resulting from various industries, such as those producing pharmaceuticals, personal care products, pesticides, chemicals, and others. (Al Momani et al., 2010; Jurado et al., 2012; Lemus et al., 2012; Almomani et al., 2016a). The pollutants enter the environment via industrial and domestic wastewaters, hospital effluents, landfill leachates, and other runoff sources (Khan et al., 2010; Jurado et al., 2012). Although there has not been any discharge limit for most micropollutants, a strategy was defined in 2000 (Directive, 2000/60/EC), listing priority compounds with high risk to the environment. In 2013, the water framework policy was updated, and a list of new priority substances was identified in Directive, 2013/39/EU (Directive, 2000/60/EC; Directive, 2013/39/

EU). Dichloromethane (DCM) is one of the newly added substances listed in the solvent category, alongside substances such as benzene, trichloromethane, and tetrachlorides. In addition, DCM is listed by the US EPA and China as a priority controlled pollutant. DCM (CH₂Cl₂), a solvent used in many industries, is a typical chlorinated volatile organic compound (VOC) with an estimated emission of 15 million tons a year (Janda et al., 2004; Joo et al., 2013). Finding cost effective treatments has been considered a focus area of research in recent years. Oxidative and nonoxidative treatment technologies have been employed to treat it. Shestakova and Sillanpa (2013) offered a recent review into the removal of DCM from ground waters and wastewaters, reporting on the most common water treatment methods used for DCM, including adsorption, biological, chemical degradation, photodegradation, and catalytic treatments. (De Best et al., 2000; Muller et al., 2011). Advanced treatments, such as electrocatalysis, radiolysis, and acoustic cavitation were also reviewed (Alfassi et al., 1989; Truszkowski and Szymaski, 1994; Rondinini and Vertova, 2004; Chakinala et al., 2008;

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Khan et al., 2010). The authors reported that GAC adsorption and biological treatments are most widely used in treating DCM, on account of their availability, low cost, and ease of implementation (Diks and Ottengraf, 1991; Flanagan, 1998; Bailan et al., 2009; Ravi et al., 2010; Zeinali et al., 2011). They stated that, although adsorption may offer upwards of 90% removal are many problems associated with the disposal of spent absorbents, whether partial (GACs) or complete (agricultural and municipal waste materials), which come to cause secondary environmental pollution. Aerobic biological treatment, on other hand, is considered the simplest and cheapest treatment technology that can provide the potential for DCM removal. However, the low solubility of DCM in water and gas–liquid mass transfer resistance affect the process performance and limit the practical application of this treatment option. In addition, according to our literature review, most reported treatment techniques for DCM were only applicable on the small laboratory scale, with the exception of one works dealing with a pilot plant tested using photodegradation of DCM assisted with H_2O_2 (Mak et al., 1997). Thus, pilot plant studies are necessary to extrapolate studies to the industrial scale.

In a 2015 study, Ribeiro et al. offered an overview of advanced oxidation processes (AOP), reporting that AOP can be considered a form of clean technology that can be used to treat polluted water by producing hydroxyl radicals ($\text{HO}^\bullet$). Hydroxyl radicals, which are the most potent after fluorine, can be produced in a number of pathways using different AOPS (Al Momani and Jarrah, 2010; Souza et al., 2013; Souza and Faris, 2015). They offer flexibility depending on the specific characteristics of the target water or wastewater pollutant (Espejo et al., 2014a). The process, with full mineralization, degrades organic pollutants into less complex forms, yielding CO_2 , H_2O , and ultimately inorganic ions as the final products (Al Momani, 2007a; Hinojosa-Reyes et al., 2012; Liu et al., 2017). In the best case scenario of full mineralization, critical secondary waste is not generated and the process hence has the advantage of needing no extra treatment or final disposal. However, it is reported that, in most cases, complete mineralization is not achieved, and occasionally the products are less biodegradable and more toxic than the parent compounds (Deng and Zhao, 2015). Therefore, the integration of more than one AOP may be required to achieve biodegradable effluent that can be effectively treated by conventional wastewater treatment works (Espejo et al., 2014b; Almomani et al., 2016b).

This study thus investigates the use of AOPs, biological process, and solar-driven AOPs on the treatment of DCM. The oxidation experiments were carried out in a pilot plant setup using two irradiation sources; (1) an artificial UV light and (2) natural solar irradiation. Different combinations of AOP, including photolysis and ozonation were studied and investigated for catalytic oxidation of DCM using one of the irradiation sources. The impact of the key experimental parameters was studied—including relative humidity (RH), reaction time, concentrations, and intermediate byproducts. Furthermore, the kinetic parameters best representing the system were described, and the photodegradation pathway for DCM was proposed based on detected intermediates.

2. Material and methods

2.1. Experimental setups

2.1.1. Solar installation

Solar oxidation experiments were performed in a pilot plant solar reactor whose scheme is shown in Fig. 1A. The Pilot plant is equipped with: (1) a pure air tank (21% O_2 and 79% N_2) used to prepare a specific concentration of DCM in the gas stream; (2) a flow meter used to measure gas flow rate through the reactor; (3) a humidifier; (4) a DCM evaporation vessel used to evaporate DCM using air bubbles; (5) a gas mixer to mix air with the evaporated DCM; (6) an Anseros COM-AD-01 ozone generator to generate ozone from high-purity oxygen; (7) a two-way valve; (8) a solar photo-reactor consists of eight low-iron quartz

tubes ($L = 80$ cm and $ID = 1.6$ cm), and with the solar reactor surface at 45° to the horizontal. The photo-reactor was designed around a compound parabolic collector (CPC) that allows almost solar radiation arriving at the reactor (direct and reflected) to be available for reaction. In order to optimize solar irradiation (400–1000 nm); the TiO_2 photocatalyst was attached to the solar elements as per the procedure outlined in our previous work (Almomani et al., 2016c). During the solar oxidation experiment, the sun's movement was tracked manually; (9) a radiometer (Macam Q102 PAR) to measure solar light intensity during the oxidation reactions; (10) an Ozomat GM-60000-OEM ozone analyzer to measure the reactor's inlet and outlet ozone concentrations, calibrated using the indigo method and with an ozone detection limit of $\pm 0.02 \text{ mg L}^{-1}$; (11) an ozone scrubber; (12) a humidity meter to measure the gas stream's relative humidity; (13) a two-way valve; (14) water impingers to collect DCM oxidation byproducts; (15) a TOC analyzer; and (16) a gas chromatograph (GC). A thermocouple was used to measure the gas temperature during operation.

2.1.2. Stirred tank bioreactor (STBR)

The stirred tank bioreactor (STBR) used to biodegrade DCM is shown in Fig. 1B. The STBR is a suspended-culture biological reactor with a working volume of 2 L. The reactor is equipped with dissolved oxygen electrode and pH meter. A water jacket maintains a constant reactor temperature. The reactor was filled with 2 L mineral medium with suspended biomass and mixed at a speed of 300 rpm; the oxygen saturation was kept at 80% w/w. The reactor medium pH was maintained at 7.0 ± 0.5 by automatically adding 1 N NaOH solution to neutralize the HCl formed during DCM biooxidation. To avoid inhibiting microbial activity, the accumulation of NaCl inside the reactor was controlled by replacing part of the medium when needed. The conductivity of the media inside the reactor was kept below 20 mS/cm^2 . Where required, the biomass recovered from the mineral medium was recycled to the reactor to maintain a constant biomass concentration. An air stream polluted with DCM was produced by mixing stream containing evaporated DCM with humidified air stream in a mixing chamber. The gas flow rates were adjusted by means of a flow meter. Air samples were regularly taken from the inlet and outlet gas streams to determine the inlet and outlet DCM concentrations.

2.2. Experimental procedure

2.2.1. Oxidation processes

Solar oxidation experiments were carried out in the open air at Qatar University campus, Doha, Qatar, (25.2854°N , 51.5310°E). The DCM-contaminated air stream was generated by splitting high-purity clean air ($\text{N}_2:\text{O}_2 = 8:2$) into two portions, with the major portion passing through a humidifier to bring the air to the desired relative humidity. The minor air stream was passed through a porous flask containing DCM to evaporate the DCM and to generate the contaminated air stream. The inlet concentration of DCM and the gas stream humidity were controlled by varying the degree of mixing between the streams. At the beginning of each experiment, the solar elements were covered and the gas stream was circulated through the solar reactor for 15 min. This time was determined to be sufficient to reach steady-state DMC concentration. The solar elements were then uncovered and the oxidation reaction started. For the experiments involving ozone, the ozone generator was turned on. Then ozone, DCM, and air stream were mixed together using a two-way valve, and entered the photo-reactor. The steady state was usually reached after 30 s. For further analysis, the outlet of the solar photo-reactor was connected to an ozone analyzer (UVAD-1000, Shimadzu) to continuously monitor the outlet concentration of gaseous ozone, a humidity meter to measure the outlet stream humidity, a gas chromatograph to measure the outlet DCM concentration. All gaseous ozone in the effluent gas was removed selectively using a potassium iodide (KI)-coated annular denuder prior to GC analysis to prevent GC damage and to eliminate the experimental

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