Journal of Water Process Engineering 23 (2018) 20–26

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Improvement in biological oxidation process for the removal of dichlorvos from aqueous solutions using pretreatment based on Hydrodynamic Cavitation

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ARTICLE INFO

Keywords:
Dichlorvos
Hydrodynamic cavitation
Slit venturi
Biodegradation
OECD 301 E protocol

ABSTRACT

In the present work, the removal of Dichlorvos (DDVP) from aqueous solution was investigated using combined approach of Hydrodynamic cavitation (HC) as pretreatment followed by the biodegradation operated as per the OECD protocol, 301E. Initially, the efficiency of HC reactor based on slit venturi was optimized by varying the inlet pressure (range of 4–7 bar) and pH (range of 4–9). Under optimized conditions established as inlet pressure of 5 bar and pH of 4, subsequent studies for the degradation of DDVP using combined approaches of HC with Ozone (HC + O_3) as intensified pretreatment were performed. It was established that the combined approach significantly enhanced the degradation to 84.8% with TOC reduction of 39.4%. Further, biodegradation analysis of HC and HC + O_3 pretreated DDVP aqueous solution was performed. A maximum kinetic rate constant as 64.2×10^{-3} day^{-1} was obtained for pretreated DDVP solution using the HC + O_3 combination, which was about 10 times higher as compared to the case where untreated solution of DDVP (kinetic rate constant as 5.3×10^{-3} day^{-1}) was directly used for biological oxidation. Integral method of analysis revealed that the reduction follows the first order kinetics with maximum oxidation rate constant as 64.2×10^{-3} day^{-1} for the combined approach involving HC + O_3 as the pretreatemnt followed by biological oxidation. Overall, it has been demonstrated that HC combined with ozone can be effectively used as pretreatment for improving the biodegradability of DDVP.

1. Introduction

The use of synthetic pesticides in India started in 1948–49 with an objective to increase food production for meeting the demand of rapidly growing population [1]. As primary occupation in India is agriculture, there is a large demand for use of pesticides to increase crop productivity which leads to the significant occurrence of pesticides in the industrial wastewater from manufacturing plants as well as processed water from field making it a key environmental concern [2]. For protection of the plants, different types of pesticides are used and among these types, organochlorophosphate compounds are the most widely used. Significant use of pesticides, especially in the agriculturally dominated countries like India, results in contamination of water (both natural sources and ground water) due to their incomplete utilization which means that residual pesticides will be further mixed with run off waters. A majority of these pesticides are recalcitrant or bio-refractory, in that they cannot be degraded using any kind of conventional techniques and can remain in the environment for longer time [3,4]. Human exposure to pesticides via inhalation, ingestion and dermal contact may also cause severe acute and chronic health issues [1]. So, in agricultural countries like India, there is necessity to develop an efficient treatment process for the removal of pesticides and their toxic residues [5].

The target pesticide considered in the present work is 2, 2-dichlorovinyl dimethyl phosphate (commonly known as Dichlorvos or DDVP), which belongs to organophosphate class of pesticides. DDVP is used to control insects in greenhouses and food storage areas as well as for parasite control. DDVP in its pure form is a dense colorless liquid having sweetish smell [6]. High level exposure of DDVP may cause hazardous effects like nausea, vomiting, headache, excessive sweating, and tightness in chest and muscle tremors to humans and animals. Also, long-term exposure of certain pesticides, including DDVP may lead to increased risk of diabetes [7]. Thus there is need for development of efficient treatment and/or pretreatment method to conventional methods such as biological oxidation for complete removal of such type of pollutant (DDVP) from effluent.

Traditional biological treatment typically only removes the highly biodegradable compounds [8]. Similar limitations also exist with the chemical oxidation methods. Hence, it can be said that these treatment

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https://doi.org/10.1016/j.jwpe.2018.03.004
Received 28 December 2017; Received in revised form 7 February 2018; Accepted 3 March 2018
2214-7144/

methods cannot be used for complete removal or degradation of toxic emerging pollutants including most pesticides due to the significant stability toward oxidation by chemicals or microorganisms [9,10]. Based on literature analysis, it can be said that advanced oxidation techniques (AOPs) have proven effective in degradation of such type of pollutants to a certain extent. However, complete mineralization of pollutant requires large amount of energy along with chemicals like catalysts, oxidizers etc. which increases treatment cost. Furthermore, oxidation intermediates may be more resistant to degradation which increases further treatment time and hence overall costs. In order to overcome these drawbacks AOPs could be combined with biological processes to yield an efficient hybrid process with considerably low treatment cost [10,11]. AOPs such as cavitation, ozonation combined with hydrogen peroxide or individual operation of ozone at specific pH conditions etc. can be used as a pretreatment for improvement in biological oxidation processes. Cavitation typically generates highly reactive free radicals as well as intense liquid circulation currents and local turbulence. All these effects in the cavitational reactors are extremely suitable for degradation of complex compounds. Hydrodynamic cavitation (HC) has been found to be a more efficient technique as compared to the more commonly used ultrasound based cavitation for the removal of toxic pollutants. In HC, cavitation is produced by pressure variations induced in the fluid flow based on the constrictions such as orifice plates, slit venturi etc. [12]. A literature analysis revealed that degradation of DDVP using advanced oxidation techniques such as ultrasound [13], photo catalytic oxidation [14], HC and combined oxidation techniques [15] etc. has been reported demonstrating limited degree of mineralization. The analysis also revealed that there has been no study based on the use of HC or ozone as pretreatment for biological oxidation of DDVP containing wastewater and hence the present work investigates the combined use of HC and ozonation as pretreatment followed by biodegradation as per OECD protocol. Slit venturi has been used as the cavitating device in the hydrodynamic cavitation reactor.

To establish the novelty of the current work, the earlier work related to DDVP degradation using HC based approaches has been elaborated. Joshi et al. investigated the degradation of DDVP using HC reactor and reported the effect of addition of hydrogen peroxide, carbon tetrachloride, and Fenton's reagent. Maximum degradation as 91.5% was reported in 1 h treatment time using a combination of HC and Fenton's reagent [15]. The work of Joshi et al. did not investigate any changes in the biodegradability or subsequent treatment using biological oxidation protocols and also no quantification of the extent of mineralization was reported. Another study of Golash et al. was related to the application of sonochemical reactors (ultrasonic horn with frequency 20 kHz with a power rating of 270 W) for degradation of DDVP [13]. It was reported that complete removal of DDVP was obtained using combination of ultrasound and Fenton chemistry, although no investigations related to mineralization were reported. In general it can be said that all the previous investigations based on degradation of DDVP established that cavitation combined with other oxidizing agents could degrade DDVP to some degree though the mineralization was limited. It is important to note that degradation intermediates formed also requires high load of oxidants for their complete mineralization which further increases cost. Also, sometimes the formed intermediates may increase chemical oxidation demand (COD) load or create inhibitory conditions for subsequent oxidation [8]. Hence, AOPs as pretreatment need to be optimized such that the subsequent biological treatment processes can be effectively operated. A literature analysis revealed that there have been very little information on combined operation of AOPs and biological treatment processes especially for the case of pesticides. Some studies available for pesticides or pesticide intermediates have now been discussed.

Ramteke et al. studied the treatment of wastewater containing ethylbenzene and *p*-nitrophenol using combined operation of ultrasound assisted Fenton process and the conventional biological oxidation process. It was reported that under optimized conditions about 55–70% COD reduction was obtained after pretreatment. Also, the biodegradability index value increased from 0.15 to 0.36 in 40 min treatment which shows the enhanced degradable nature of the constituent [16]. Parra et al. studied the application of the photo-Fenton system applied in different approaches as pre-treatment followed by a biological treatment. In this work, the destruction of two bio-recalcitrant herbicides viz. metobromuron and isoproturon was investigated using different approaches as UV/TiO_2, $UV/TiO_2/H_2O_2$, Fe^{3+}/H_2O_2, and $UV/Fe^{3+}/H_2O_2$ as pretreatment. It was reported that in coupled photo Fenton system followed by biological treatment, 100% degradation of Isoproturon and Total organic carbon (TOC) reduction of 95% was obtained [17].

Considering that not many studies were reported for the application of combined operation of HC with biological treatment for treatment of wastewaters containing pesticides and emerging contaminants, the present work aims at establishing the best treatment strategies for the implementation of one of the most efficient AOPs, hydrodynamic cavitation (HC) (individually and in combination with ozone) as pretreatment method followed by biological oxidation for degradation of DDVP and mineralization of the effluent stream. Overall, the novelty of the work lies in the fact that first detailed study of biological oxidation has been performed as per the internationally accepted OECD guidelines for the case of DDVP mineralization with combination studies based on the use of hydrodynamic cavitation and ozone as pretreatment to the biological oxidation.

2. Materials and methodology

2.1. Materials

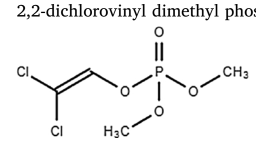
The chemical structure of dichlorvos (DDVP) has been given in Table 1. The commercial grade DDVP was obtained from local supplier in Mumbai, India. Activated sludge was obtained from sewage treatment plant (STP), Mumbai, India. The characteristics of the activated sludge have been depicted in Table 2. All the other chemicals (AR grade) were obtained from S.D. Fine Chemicals Ltd. Mumbai and used without any further purification. Freshly prepared deionized water (DI) was used for making solutions of desired concentrations.

2.2. Methodology

2.2.1. Degradation using HC

The HC reactor used in present work has already been described in our earlier work [12]. The experiments related to the optimization of operating parameters (initial concentration, inlet pressure and pH) were performed using 4 L of aqueous solution of specific DDVP concentration for a total treatment time of 120 min. Initially, the variation in extent of degradation with initial concentration of pollutant has been studied at five different initial concentration of DDVP as 10, 20, 30, 40 and 50 ppm at an inlet pressure of 5 bar and pH of 4. The effect of inlet pressure on the extent of degradation was subsequently studied over the inlet pressure range of 4 bar to 7 bar at fixed pH of 4. The pressure was controlled by closing the valves provided in the circulation loop. The feed temperature was maintained constant at 30 ± 5 °C with the use of

Table 1
Chemical structure of DDVP.

Pesticide common name	Dichlorvos; abbreviated as DDVP
IUPAC name	2,2-dichlorovinyl dimethyl phosphate
Chemical Structure	
Mol. mass (g/mol)	220.98