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Effect of process intensifying parameters on the hydrodynamic cavitation based degradation of commercial pesticide (methomyl) in the aqueous solution

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ABSTRACT

Methomyl, a carbamate pesticide, is classified as a pesticide of category-1 toxicity and hence shows harmful effects on both human and aquatic life. In the present work, the degradation of methomyl has been studied by using hydrodynamic cavitation reactor (HC) and its combination with intensifying agents such as H_2O_2, fenton reagent and ozone (hybrid processes). Initially, the optimization of operating parameters such pH and inlet pressure to the cavitating device (circular venturi) has been carried out for maximizing the efficacy of hydrodynamic cavitation. Further degradation study of methomyl by the application of hybrid processes was carried out at an optimal pH of 2.5 and the optimal inlet pressure of 5 bar. Significant synergetic effect has been observed in case of all the hybrid processes studied. Synergetic coefficient of 5.8, 13.41 and 47.6 has been obtained by combining hydrodynamic cavitation with H_2O_2, fenton process and ozone respectively. Efficacy of individual and hybrid processes has also been obtained in terms of energy efficiency and extent of mineralization. HC + Ozone process has proved to be the most effective process having highest synergetic coefficient, energy efficiency and the extent of mineralization. The study has also encompassed the identification of intermediate by-products generated during the degradation and has proposed the probable degradation pathway. It has been conclusively established that hydrodynamic cavitation in the presence of intensifying agents can effectively be used for complete degradation of methomyl.

1. Introduction

Large amounts of pesticides have been used across the globe for the purpose of increased cultivation; however their residues have posed serious threats to the environment and mankind [1]. Methomyl, $C_5H_{10}O_2N_2S$, is a broad spectrum insecticide which belongs to the family of oxime carbamate pesticides. It has been classified as a very toxic and hazardous pesticide by many agencies such as World Health Organization (WHO), Environment Protection Agency (EPA), European Chemical Classification (ECC), etc. It can easily cause contamination of both ground and surface water resources, due to its high solubility in water (57.9 g/L, 20 °C) and a low-sorption affinity to soils [2].

Application of Advanced Oxidation Processes (AOPs) has found to be a promising technology for the degradation of various insecticides and pesticides. AOPs are based primarily on the formation and subsequent attack of the highly reactive hydroxyl radicals, leading to the destruction/oxidation of the target pesticide compound [3]. Cavitation is an emerging AOP and not many studies have been reported for its application in the degradation of pesticides. It is the phenomena of formation, growth and collapse of large number of cavities in the liquid medium [4]. Two most important ways of generating cavitating conditions are acoustic cavitation (US) and hydrodynamic cavitation (HC). If the cavitation occurs by a passage of high frequency sound wave it is called as an acoustic cavitation and if it occurs by pressure variation in the flowing liquid due to the presence of throttling devices such as venturi, orifice etc., it is called as hydrodynamic cavitation [5]. It

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is reported in the literature that hydrodynamic cavitation is more energy efficient and can easily be scaled up to industrial scale as compared to acoustic cavitation [6,7]. The principle of hydrodynamic cavitation can be described by using Bernoulli's theorem.

$$P_{static} + P_{dynamic} = \text{Constant} = P_{static} + \frac{1}{2}\rho v^2$$

where P_{static} and $P_{dynamic}$ are static and dynamic pressures, ρ and v are the density and velocity of the liquid at the throat of the cavitating device. When the liquid passes through a cavitating device, the fluid velocity increases due to a decrease in the flow area and hence increases the dynamic pressure. Since, the sum of dynamic and static pressure is constant according to the Bernoulli's equation; increase in dynamic pressure subsequently reduces the static pressure. If the static pressure falls below the cavitation threshold of the solvent (i.e. the vapor pressure of the solvent) millions of cavities are generated. Recovery of static pressure in the downstream section of the cavitating device causes violent collapse of these cavities resulting into the formation of localized hot spots and highly reactive $OH^{\cdot}$ and $H^{\cdot}$ radicals [8]. The two key mechanisms responsible for the degradation of organic pollutants using hydrodynamic cavitation are, the thermal decomposition/pyrolysis of organic pollutant entrapped in the cavities due to the generation of transient temperature pressure conditions (localized hot spots) and secondly, the reaction of free radicals with the organic pollutant occurring at the cavity–water interface [9].

Some of the AOPs which have been applied in the past for the degradation of methomyl include fenton process [4], photofenton process [4,10] and photocatalytic oxidation process [11,12]. However, to the best of our knowledge, degradation study of methomyl by employing hydrodynamic cavitation reactors and their combination with other AOPs is not yet reported in the literature.

In the current work, the degradation of methomyl has been studied by using hydrodynamic cavitation reactors and the two important operating parameters, pH and inlet pressure to the cavitating device have been optimized in order to maximize the cavitational effect. An attempt has also been made to enhance the rate of degradation of methomyl by using hydrodynamic cavitation in combination with the intensifying agents such as H_2O_2, ozone and fenton reagent. The main focus of the work is to compare the rates of degradation, energy efficiency and the extent of mineralization of methomyl that can be obtained by using individual hydrodynamic cavitation reactor and its combination with intensifying agents (hybrid processes) to determine the synergetic effect of combined processes. In addition to this, current work also proposes a probable degradation pathway of methomyl by identifying the oxidation by-products and intermediates generated during the degradation process of methomyl. In short, the present work deals with the application of hydrodynamic cavitation (HC) and hydrodynamic cavitation based hybrid techniques such as HC + H_2O_2, HC + Fenton, HC + Ozone for the effective degradation carbamate pesticide, methomyl in aqueous solutions.

2. Materials and methods

2.1. Materials

Commercial grade methomyl (Dupont) was used as a model organic pollutant without further purification. Hydrogen peroxide (30% w/v), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sodium sulfite (Na_2SO_3) and sulfuric acid (H_2SO_4) all of AR grade were obtained from S D Fine Chemicals Ltd., Mumbai, India. Acetonitrile and water used for HPLC analysis were purchased from S D Fine Chemicals Ltd., Mumbai, India of HPLC grade. All chemicals were used as received from the supplier.

2.2. Experimental set-up

Hydrodynamic cavitation setup used in the present work is as shown in the Fig. 1. The setup primarily consists of a holding tank, a positive displacement pump (capacity 1.1 KW), pressure gauges (P_1, P_2 and P_3), valves (V_1, V_2 and V_3), flanges, main line and a bypass line. Holding tank was surrounded by a cooling jacket to control the temperature, as it likely to increases due to the heat liberated during cavitation. The suction line from the pump is connected to the bottom of the holding tank and discharge line from the pump is branched into two lines; main line and bypass line. The main line houses the flanges which are used to accommodate the cavitating device and a valve is provided in the bypass line to control the flow through the main line. Pressure gauges are provided at appropriate places to measure the inlet pressure to the

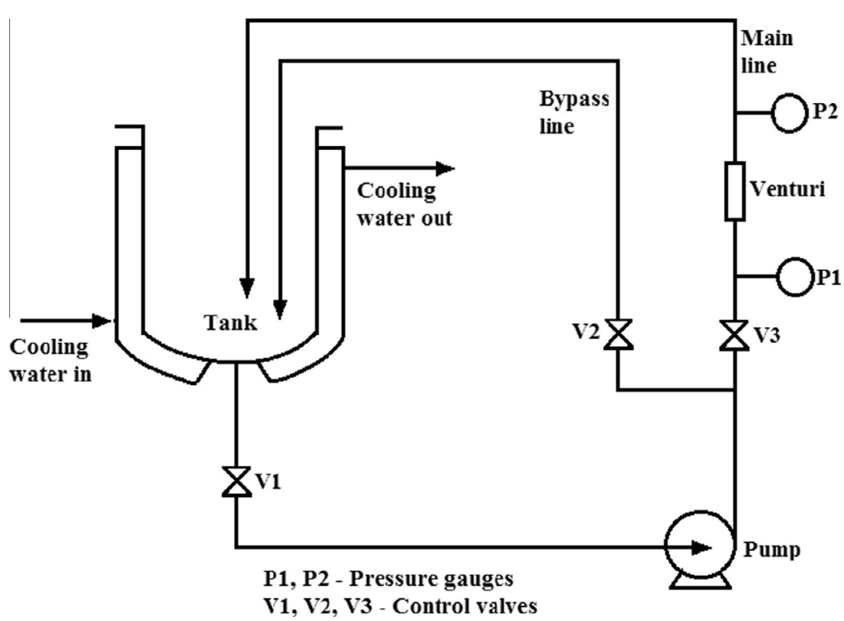

Fig. 1. Schematic representation of hydrodynamic cavitation set-up.