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Degradation of diclofenac sodium using combined processes based on hydrodynamic cavitation and heterogeneous photocatalysis

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ABSTRACT

Diclofenac sodium, a widely detected pharmaceutical drug in wastewater samples, has been selected as a model pollutant for degradation using novel combined approach of hydrodynamic cavitation and heterogeneous photocatalysis. A slit venturi has been used as cavitating device in the hydrodynamic cavitation reactor. The effect of various operating parameters such as inlet fluid pressure (2–4 bar) and initial pH of the solution (4–7.5) on the extent of degradation have been studied. The maximum extent of degradation of diclofenac sodium was obtained at inlet fluid pressure of 3 bar and initial pH as 4 using hydrodynamic cavitation alone. The loadings of TiO_2 and H_2O_2 have been optimised to maximise the extent of degradation of diclofenac sodium. Kinetic study revealed that the degradation of diclofenac sodium fitted first order kinetics over the selected range of operating protocols. It has been observed that combination of hydrodynamic cavitation with UV, UV/TiO_2 and UV/TiO_2/H_2O_2 results in enhanced extents of degradation as compared to the individual schemes. The maximum extent of degradation as 95% with 76% reduction in TOC has been observed using hydrodynamic cavitation in conjunction with UV/TiO_2/H_2O_2 under the optimised operating conditions. The diclofenac sodium degradation byproducts have been identified using LC/MS analysis.

1. Introduction

Non-steroidal anti-inflammatory drugs (NSADs) are found to gain a special relevance from being the most frequently mentioned environmental contaminants due to the high consumption rate of these drugs [1,2]. Diclofenac (DCF) is one such synthetic non-steroidal anti-inflammatory drug (NSAD), mostly used as its sodium salt in medical care as ananalgesic, antiarthritic and antirheumatic [3]. The existence of diclofenac in the water is a consequence of direct disposal from households and possible effluent discharge from municipal/industrial wastewater treatment plants where proper treatment facilities are not existing [4,5]. Due to its limited biodegradation and/or natural attenuation, it is commonly detected at the outlets of domestic wastewater treatment plants and hence in the receiving aquatic bodies [6]. Thus, it becomes imperative to develop suitable treatment schemes as supplements to the conventional biological oxidation schemes which will ensure complete elimination of the pollutant from the water streams. Recently, many researchers have reported degradation of diclofenac sodium using advanced oxidation processes [7–15]. Vogna et al. [7] studied degradation of diclofenac using UV/H_2O_2 and ozone whereas Ravina et al. [8] have studied the Fenton chemistry in combination with a concentric photoreactor for the degradation of diclofenac. In another study [9], photo-Fenton degradation of diclofenac and identification of main intermediates and degradation pathway have been reported. Naddeo et al. [10] and Hartmann et al. [11] have reported ultrasonic degradation of diclofenac. Rizzo et al. [12] have studied the photocatalytic degradation of diclofenac using TiO_2 photocatalyst irradiated by black light fluorescent lamp whereas Mendez-Arriaga et al. [13] have studied diclofenac degradation using artificial solar irradiation. Achilleous et al. [14] investigated the factors affecting diclofenac decomposition in water by UV-A/TiO_2 photocatalysis with six different commercially available TiO_2 samples and Degussa P25 was found to be very efficient for diclofenac degradation. Madhavan et al. [15] have investigated the sonolytic, photocatalytic and sonophotocatalytic degradation of diclofenac using three photocatalysts (TiO_2, ZnO and Fe–ZnO) and reported that the sonophotocatalytic degradation using TiO_2 under UV–VIS radiations showed a synergistic enhancement in the degradation of the parent compound, whereas a detrimental effect was observed for the mineralisation process and in the case of Fe–ZnO, both degradation and mineralisation showed near additive effects.

Although there are many studies reported in the literature for the degradation of diclofenac using photocatalysis based treatment approaches, none of the studies to the best of our knowledge, have been reported in the literature using combination of hydrodynamic cavitation and photocatalysis. The cavitational effects, in terms of the intense turbulence with liquid circulation currents and local

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hot spots resulting into generation of hydroxyl radicals, generated due to the use of hydrodynamic cavitation are expected to intensify the efficacy of the heterogeneous photocatalysis operation. In all the earlier studies related to combination of cavitational reactors and photocatalytic oxidation, ultrasound based reactors have been used [15–17]. Hydrodynamic cavitation is an energy efficient alternative to the ultrasound based treatment approach that can be used for the destruction of organic pollutants [18]. Hydrodynamic cavitation can be generated when the liquid passes through the constriction such as orifice, venturi, etc., where the kinetic energy/velocity of the liquid increases at the expense of the pressure. If the throttling is sufficient to cause the pressure around the point of vena contracta to fall below the threshold pressure for cavitation, millions of cavities are generated. Subsequently as the liquid jet expands and the pressure recovers, the cavities collapse releasing large magnitudes of energy over a very small location resulting in very high energy densities [19]. The mechanisms for the degradation of pollutants using cavitation are the thermal decomposition/pyrolysis of the pollutant molecules entrapped inside the cavity during the collapse of the cavity and attack of hydroxyl radicals on the pollutant molecules at the cavity–water interface and in the bulk fluid medium [20]. In hydrodynamic cavitation different types of cavitating devices such as throttling valve, orifice plate, circular venturi or slit venturi can be used as constriction for the generation of cavitation. Bashir et al. [21] have carried out CFD based optimisation of the important geometrical parameters of a slit venturi and the dimensions of the slit venturi used in present work are based on the optimised parameters observed in the theoretical work.

The present work reports the combination of hydrodynamic cavitation and photocatalysis as a novel combination for treatment of diclofenac. TiO_2 has been used as the photocatalyst as it is inexpensive, non-toxic, photochemically stable and widely acceptable photocatalyst [22]. The illumination of an aqueous TiO_2 suspension using irradiation with energy greater than the band gap energy of the semiconductor generates valence band holes and conduction band electrons. Valence band holes can react with water and the hydroxide ion to generate hydroxyl radicals, while electrons can react with adsorbed molecular oxygen reducing it to superoxide radical anion which, in turn, reacts with protons to form the peroxide radicals [23–25]. The work also concentrates on optimisation of the hydrodynamic cavitation parameters and illustrates the synergism obtained due to the use of combination approach. The mechanistic details regarding the identification of the intermediates during the degradation process and the kinetic rate constants have also been presented.

2. Materials and methods

2.1. Materials

Diclofenac sodium was procured from Research Lab Fine Chemicals Ltd. The nanosize TiO_2 (mixture of anatase and rutile) was obtained from Sigma Aldrich. Analytical grade hydrogen peroxide (30% w/w) was obtained from S.D. Fine Chemicals. Distilled water was used for preparation of solutions, which was prepared in the laboratory using a distilled water plant. All the chemicals were used as received from the supplier.

2.2. Experimental setup and methodology

The experimental setup used for the combined process of hydrodynamic cavitation and photocatalysis is depicted in Fig. 1. The set up consist of holding tank, a pump of power rating 1.1 kW, flanges to accommodate the cavitating device (slit venturi),

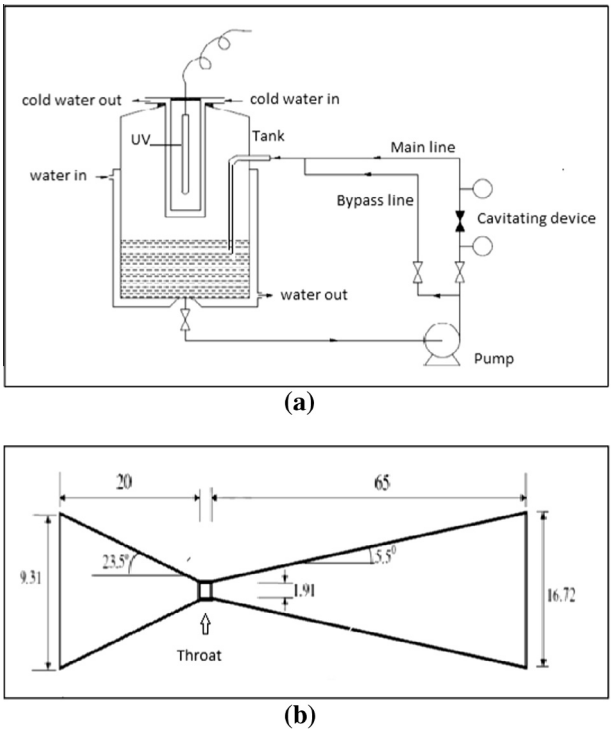

Fig. 1. (a) Schematic representation of hydrodynamic cavitation reactor with photocatalytic oxidation and (b) schematic of cavitating device (slit venturi).

control valves, a main line and a bypass line. It is important that the main line and bypass line terminate well inside the tank and below the liquid level so as to avoid any induction of air into the liquid. The dimensions of the slit venturi which are based on the optimised parameters investigated by Bashir et al. [21] are given in Table 1. UV lamp of 250 W placed inside a jacketed quartz cylinder was vertically immersed inside the liquid holding tank of hydrodynamic cavitational reactor.

The feed tank was filled with 5 L of aqueous solution of 20 ppm initial concentration of diclofenac sodium and the pump was started. The inlet pressures were adjusted by controlling the flow through the by-pass line. The effect of inlet pressure on the degradation of diclofenac sodium was investigated by varying the inlet pressure over the range of 2–4 bar pressure. The feed temperature was kept constant at 35 °C by circulating water through the jacket surrounding the holding tank. The initial pH of solution was varied over the range of 4–7.5 and the optimum pH has been selected for the remaining set of experiments.

In order to study the effect of combined HC/UV/TiO_2 process on the extent of degradation of diclofenac sodium, the loading of TiO_2 was varied over the range of 0.05–0.3 g/L. Hydrogen peroxide was also used as an process intensifying additive in HC/UV/TiO_2 process and loading of hydrogen peroxide was varied over the range of 0.05–0.3 g/L keeping TiO_2 loading constant at the optimised value. The total duration of each run was set to be 2 h and the samples were taken out at an interval of 20 min from the tank for an

Table 1
Dimensions of the slit venturi.

Dimensions of throat	W = 6 mm; H = 1.9 mm; L = 1.9 mm
Venturi length	87 mm
Length of convergent section	20 mm
Length of divergent section	65 mm
Half angle of convergent section	23.5°
Half angle of divergent section	5.5°