Degradation of Diclofenac Sodium Salt using Hydrodynamic Cavitation

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Abstract: Diclofenac sodium salt (DF) is a pharmaceutical product with a widespread occurrence in the aquatic environment. Most of advance oxidation techniques have been tested on the laboratory scale successfully but they are difficult to scale up on an industrial scale. In last few years, a new technology, hydrodynamic cavitation has been tested for the degradation of various organic pollutants such as pesticides, pharmaceutical drug, and textiles dyes by many researchers. In the present work, degradation of diclofenac sodium salt (DF) has been carried out using hydrodynamic cavitation (HC). Cavitation may be defined as the formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small interval of time (milliseconds) with releasing large magnitudes of energy at the time of collapse. In hydrodynamic cavitation, when the liquid is passed through the constriction/geometry (venturi has been used as cavitating devices in the present study), cavities are formed. The effect of inlet pressure on the degradation and the cavitational yield of acoustic and hydrodynamic cavitation was studied. All the experiments have been carried out using initial concentration of diclofenac sodium salt with a 100µM. The study reveals that the rate of degradation increases with an increase inlet pressure to the system up to 5 bar and then decreases. Around 70% degradation takes place in 1hr using hydrodynamic cavitation. Cavitational yield was obtained more in case of hydrodynamic cavitation as compared to that in acoustic cavitation.

Keywords: Diclofenac sodium salt (DF), Degradation, Hydrodynamic Cavitation, Wastewater treatment.

1. INTRODUCTION

Water pollution is a major problem for environment and human health due to industrial effluent discharged into the water body, which comes from various chemical industries such as pesticides, textile, pharmaceutical and petrochemical. These effluents contain large amounts of organic compounds, which are bio-refractory or very toxic to the microorganisms. Hence, conventional biological processes are not able to completely the degrade such compounds [1]. Treatment of industrial wastewater has always been a key aspect of research due to increasing awareness about the environment and more stringent environmental regulations [2]. Among many available treatment methods, the advanced oxidation processes (AOPs) are the most promising alternative to treat various types of industrial wastes because they involve the generation of hydroxyl radicals (OH•) that are nonselective and highly reactive oxidants [3]. Most of these AOP techniques have been studied on the laboratory scale successfully but difficult to scale up on an industrial scale. Among these techniques cavitational reactors are the simplest to design and operate. Cavitation may be defined as the formation, growth, and subsequent collapse of the microbubbles or cavities occurring in an extremely small interval of time (milliseconds) with releasing large magnitudes of energy. The cavity collapse affects the creation of hot spots with releasing highly reactive free radicals, and intensification in mass transfer rates. The collapse of bubbles creates localized ‘‘hot spots’’ with transient temperatures of about 10, 000 K and pressures of about 1000 atm [4]. Water molecules are separated into OH• and H radicals under the extreme conditions. Then these radical disperses into the bulk liquid medium where they react with organic pollutants and oxidize them. There are main two mechanisms for the destruction of organic pollutants by cavitation as firstly, the thermal decomposition/pyrolysis of the volatile pollutant molecule entrapped inside the cavity and secondly the reaction of OH• radicals with the pollutants.

Cavitation is classified into four types based on the method of cavities production as acoustic, hydrodynamic, optic, and particle. Out of these four techniques, only acoustic and hydrodynamic cavitation are most widely used, because they are more efficient for desired chemical changes. Acoustic Cavitation: The cavities are produced by passing the sound waves, usually ultrasound (>16 kHz), through the liquid medium. Hydrodynamic Cavitation: In hydrodynamic cavitation, when the liquid is passed through the cavitating device such as venturi, cavities are formed. When the pressure at the throat of the constriction falls below the vapor pressure of the liquid, the liquid flashes (generating number of vaporous cavities) that subsequently collapse when the pressure recovers downstream of the mechanical constriction [5].

In the last decade, a few researchers have studied hydrodynamic cavitation for carrying out chemical/physical transformations [6]. In this study, the degradation of Diclofenac sodium salt (DF) was investigated by hydrodynamic cavitation using a venturi as a cavitating device. The important operating parameter (inlet pressure to the system) for a cavitational device have been optimized in order to get maximum cavitational effects.

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2. MATERIALS AND METHODS

2.1 Materials

Diclofenac sodium salt (molecular weight: 318.13g/mol; molecular formula: $C_{14}H_{10}Cl_2NNaO_2$) was purchased from sigma aldrich. The solubility in water is 50 Mg/mL. The Molecular structure of DF is shown in Fig.1. The solution of DF was prepared in tap water for all the experiments. The pH of the solution was maintained using H_2SO_4.

2.2 Hydrodynamic Cavitation Setup

Schematic representation of experimental set-up used in this study is as shown in Fig.2. The setup includes a holding tank of 15 l volume, a positive displacement pump of power rating 1.1 kW, control valves (V1, V2, and V3), and flanges to accommodate the cavitating device in the main line and a bypass line to control the flow through the main line. The suction side of the pump is connected to the bottom of the tank and discharge from the pump branches into two lines; the main line and a bypass line. The main line consists of a flange which houses the cavitating device which can either be orifice or a venturi. The main line flow rate was adjusted by changing the number of piston strokes per unit time of the pump, which affects the total flow generated. Additionally, a valve is also provided in the bypass line to control the liquid flow through the main line. Venturi as a cavitating device has been used in this work. Fig. 3 shows cavitating device (venturi) used in this work. The dimensions of circular venturi are given in Table 1

2.3 Degradation Using Hydrodynamic Cavitation

Degradation of DF based Hydrodynamic cavitation was carried out at different conditions using a fixed solution volume of 5 L and for a constant circulation time of 1 h. The concentration of DF was 100 µM for the study of the degradation kinetics. The pressure study was done over a range of 3 to 8 bar (3, 4, 5, 6, 7, 8bar) and at pH of 4.0. The temperature of the solution during experiments was about 32 ± 4^0C maintained by circulating cooling water through the jacket provided to the holding tank.

2.4 Analytical Methods

UV-Spectrophotometer was used to determine the concentration of diclofenac sodium salt at regular interval of time in all the experiments. The absorbance of DF was monitored using UV-Spectrophotometer (Shimadzu-1800) and then the concentration of DF was calculated by analyzing the absorbance of DF solution at the wavelength of 276 nm.

3. RESULTS AND DISCUSSION

3.1 Hydraulic Characteristics

In this study, Venturi was used to investigate the hydraulic characteristics. At different inlet pressure, the main line flow rate and cavitation number were measured and then calculated. Table1 shows the value of mainline flow rate, the velocity and cavitation number at the throat of venturi. Appendix A shows one typical set of calculation, carried out to complete Table 2.

The cavitation number is a dimensionless number which is used to characterize the condition of cavitation in hydraulic devices[4][7]. The Cavitation number is given by

$$C_v = \frac{\text{pressure head}}{\text{Velocity head}} = \left(\frac{p_2 - p_v}{\frac{1}{2}\rho v_o^2}\right) \quad (1)$$

Where, p_2 is the fully recovered downstream pressure, p_v is the vapor pressure of the liquid, v_o is the velocity at the throat of the cavitating constriction, if the main line flow rate and diameter of the cavitating device is known then we can calculated velocity at the throat. cavities are generated (at a condition Cv ≤ 1) under ideal condition, but in many cases cavities are known to generated at which the value of Cv >1 due to the presence of some dissolved gases and suspended particles [7]. The cavitation number is called cavity inception number (C_{vi}) at which first cavity appears. It was found that the cavitation number decreases with increasing in inlet pressure to the venturi because the velocity (v_o) at the throat also increases with increasing in inlet pressure and the main line flow rate, which subsequently reduces the cavitation number. Cavitation number decreases beyond a certain value with an increase in the inlet pressure resulting in lower cavitational intensity (collapse pressure), but the number of cavities generated and collapsing per unit time increases at the same time [8].

3.2 Degradation Kinetics

Pseudo first order kinetics was assumed to correlate the observed data, and rate constants for the degradation/ mineralization process, which is calculated by using the following equation.

$$ln\left(\frac{C_o}{C}\right) = k\ x\ t \quad (2)$$

where C is the concentration of DF (in mol/l), k is the rate constant (min^{-1}) and t is the time (in minutes).

Fig.4 The plot of $\ln(C_O/C)$ vs time (t) is a straight line passing through the origin, which confirms that the degradation of DF using hydrodynamic cavitation showing a first order reaction kinetics. Y.G. Adewuyi [9] have observed that it follows the first order kinetics.

3.3 Effect of Inlet Pressure

The optimization of inlet pressure is necessary to get the maximum cavitational effects because the inlet fluid pressure and the velocity at the throat are dependent on each other, and it affects the cavitating condition inside the venturi. The experiments were carried out at different inlet pressure

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varying from 3 to 8 bar to investigate the effect of inlet pressure on the degradation rate. The solution pH and concentration of DF were kept constant in all the experiments at 4.0 and 100μM respectively. Fig.5 shows the effect of inlet pressure on the degradation rate of DF. It was found that rate of degradation increases with an increasing the inlet pressure reaching to the maximum at 5 bar and then decreases. As the pressure increases, the main line flow rate through the cavitating device increases, so the number of passes of the liquid through the venturi increases which increases the cavitational yield. Senthilkumar and Pandit [8] have shown that As the liquid flow rate and velocity increases, cavitation number decreases with an increase in the inlet pressure. A decrease in cavitation number results into lower cavitational intensity (collapse pressure), but at the same time the number of cavities generated and collapsing event per unit time, per unit volume increases. Gogate and Pandit [10] have showed that there is an optimum pressure at which cavitational intensity is maximum. Tullis [11] have also observed that as the cavitation number decreases, more number of cavities are formed and once the cavitation device is filled with a lot of cavities these cavities start coalescing to form a larger bubble. These larger bubbles escape the liquid without collapsing, thus reducing the cavitational yield (reduced degradation rate after 5 bar of operating fluid pressure).

3.4 Comparison between Hydrodynamic Cavitation and Acoustic Cavitation

Cavitational yield is calculated for the comparison between hydrodynamic cavitation and acoustic cavitation. The cavitational yield is the ratio of the moles of DF degraded to the total energy input to the system. The experiments were carried out at fixed initial concentration of DF (100μM) and at pH 4 for both types of reactor and the time of operation for hydrodynamic and acoustic cavitation reactor are 1hr. an ultrasonic horn having frequency of 20 kHz and power of 750W was used as an acoustic cavitational reactor. Experiments in the hydrodynamic cavitational reactor were carried out at an optimum operating fluid pressure of 5 bar. Fig. 6 shows the cavitational yield of both processes at pH 4. It was found that the cavitational yield in the case of hydrodynamic cavitation is higher than acoustic cavitation, almost 45 time's higher yield is obtained (detailed calculation is given in appendix B). Due to poor energy conversion efficiency, ultrasonic equipment have low cavitational yield. Sivakumar and Pandit [12] have also observed that the cavitational yield is higher in the hydrodynamic cavitation as compared ultrasonic equipment for the degradation of rhodamine B, water-soluble dye.

4. CONCLUSIONS

Hydrodynamic cavitation was evaluated for the degradation of DF in this study. It was found that the degradation of DF using the HC depends inlet pressure to the cavitating device, and cavitation number and it exhibits a maximum degradation rate at an inlet pressure of 5 bar. The degradation of DF using hydrodynamic cavitation followed first order reaction kinetics. Cavitational yield in case of hydrodynamic cavitation was obtained higher than acoustic cavitation.

5. FIGURES AND TABLES

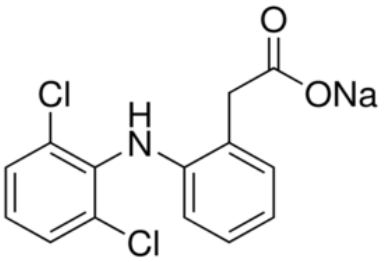
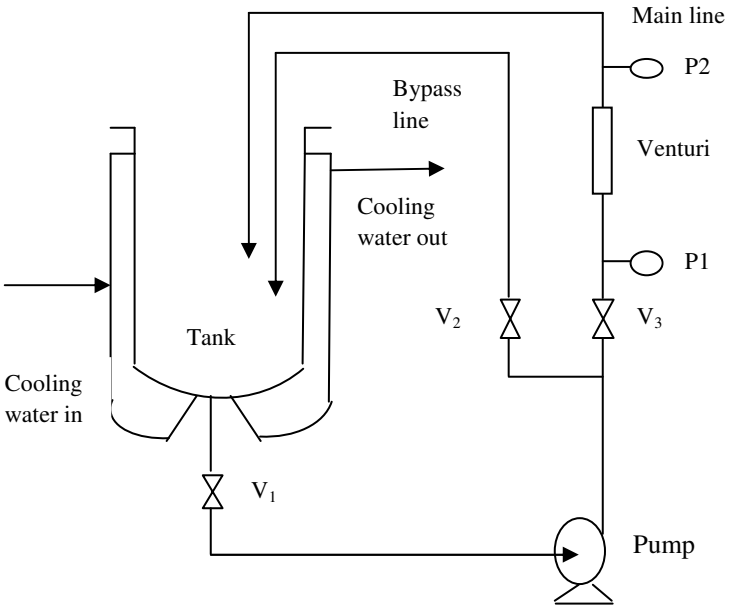
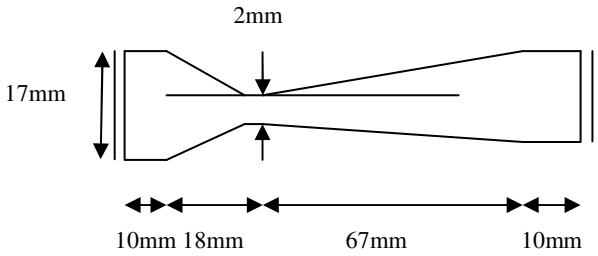


Fig. 1. Molecular structure of diclofenac sodium salt (DF)



P1, P2- Pressure gauges
$V_1V_2V_3$- Control valves

Fig. 2. Schematic representation of hydrodynamic cavitation reactor set-up



Half angle of convergent section= 22.61°
Half angle of divergent section= 6.4^0

Fig. 3. Geometric specifications of circular venturi

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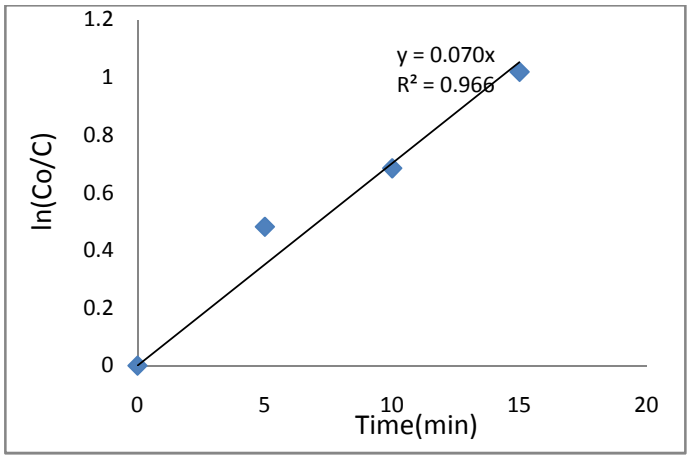

Fig.4 Pseudo First order degradation of DF (conditions: volume of solution: 5 l, inlet pressure: 4bar, initial concentration: 100µM, pH of solution: 4.0).

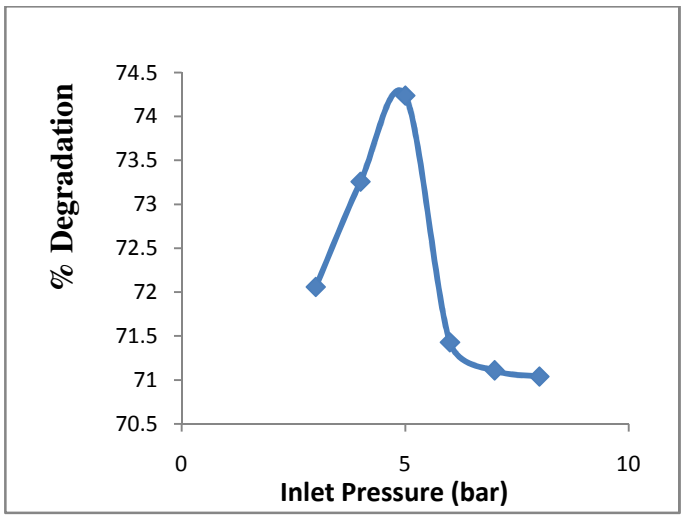

Fig. 5. Effect of inlet pressure on the degradation rate of DF. Conditions: volume of solution, 5L; initial concentration, 100µM; pH of solution, 4.

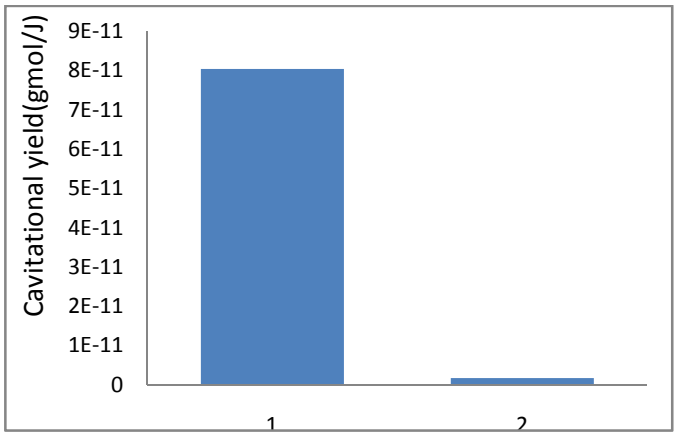

Fig. 6. Cavitational yield for hydrodynamic cavitation (1) and acoustic cavitation (2) (US: ultrasound/acoustic cavitation).

Table 1 Dimension of circular Venturi

Dimension	Circular Venturi
Dimension of throat	Circular hole of 2 mm diameter
Venturi length	87mm
Length of convergent section	18mm
Length of divergent section	67mm
Half angle of convergent section	22.6°
Half angle of divergent section	6.4 °

Table 2 Flow Characteristics of Venturi

S. No.	Inlet pressure (bar)	Flow rate (LPH)	Velocity (m/s)	Cavitation number (C_v)
1	3	340	30.06	0.21
2	4	375	33.16	0.18
3	5	410	36.30	0.15
4	6	445	39.35	0.13
5[a]	7	470	41.56	0.11
6	8	510	44.90	0.095

[a]***Sample calculation is given in appendix A***

APPENDIX A

Sample calculation for the estimation of hydraulic characteristics

Inlet fluid pressure = 601325 Pa
Downstream pressure (p_2) = 101325 Pa
Vapor pressure of water at 30^0C (p_v) = 4242.14 Pa
Volumetric flow rate (V) = 470 LPH = 1.31×10^{-4} m^3/s
Diameter of the throat of the Venturi (d_o) = 2mm
Flow area: $A_0 = 3.14 \times 10^{-6}$ m^2
Velocity at the throat of venture:

$V_0 = V/A_0 = 41.72$ m/s

And Cavitation number is calculated by equation (1)

$= 0.11$

APPENDIX B

Sample calculation for the estimation of cavitational yield *For Hydrodynamic Cavitation,*

Total energy delivered into the system in 1hr
= pump power x total treatment time
= 1.1×10^3(J/s) x 1x 3600(s)
= 3.96×10^6J
No. of moles of DF degraded,
= (C_0-C_t)/time x time x volume
= 63.79×10^{-6}(gmol/L) x 5L
= 3.19×10^{-4} gmol
Cavitational yield = No. of moles of DF degraded/ Total energy

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delivered
$= 3.19 \times 10^{-4}$(gmol)/3.96×10^{6}J
$= 8.05 \times 10^{-11}$ gmol/J

For Acoustic Cavitation,

Total energy delivered into the system in 1hr
= pump power x total treatment time
= 750(J/s) x 1x 3600(s)
$= 27 \times 10^{5}$J

No. of moles of DF degraded
$= (C_0-C_t)$/time x time x volume
$=23.96 \times 10^{-6}$(gmol/L) x 200 x 10^{-3}L
$= 47.92 \times 10^{-7}$gmol

Cavitational yield = No. of moles of DF degraded/ Total energy
delivered
$= 47.92 \times 10^{-7}$gmol/27×10^{5}J
$= 1.77 \times 10^{-12}$ gmol/J

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