

Degradation Kinetics of Diclofenac in Water by Fenton's Oxidation

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Abstract: An extensively used non-steroidal anti-inflammatory drug (NAID) diclofenac (DCF) is reported to be present in the environment. Several adverse effects have been reported due to presence of DCF and hence it should be removed from the environment. Among several treatment methods, classic Fenton oxidation is found to be an effective process for the removal of organic contaminants. In the present study, the effect of initial DCF concentration and pseudo second order rate constants of DCF degradation are evaluated by Fenton oxidation process. Percent DCF reduction and percent Chemical Oxygen Demand (COD) removal are measured as the objective parameters to be maximized. At the optimum conditions, for 31.43×10^{-3} mM of initial DCF concentration, 74.25 percent DCF reduction and 72.80 percent COD removal are observed in 240 minutes reaction time. The pseudo second order rate constants are $206.95 \text{ M}^{-1}\text{S}^{-1}$ for 31.43×10^{-3} mM and $75.55 \text{ M}^{-1}\text{S}^{-1}$ for 157.17×10^{-3} mM initial concentration of DCF. The Fenton oxidation process is the most effective in degradation of DCF in water.

Keywords: AOPs; COD removal; Diclofenac degradation; Fenton oxidation; Kinetic studies.

1. Introduction

Diclofenac (DCF) is a non-steroidal anti-inflammatory drug (NAID) most prevalently used as analgesic, anti-arthritis and anti-rheumatic and about 15% is excreted unchanged after human consumption [1]. Though it has been confirmed that diclofenac is rapidly degraded by direct photolysis under normal environmental conditions [2-4], it is still one of the most frequently detected pharmaceuticals in the water environment [5]. The diclofenac is found to be present in sewage treatment plant (STP) effluent and surface water in the range of 0.14-1.48 $\mu\text{g/L}$ [6], up to 0.59 $\mu\text{g/L}$ in groundwater [7], up to 15 $\mu\text{g/L}$ in surface water [8] and up to 28.4 $\mu\text{g/L}$ in aquatic environment [9]. In India and Pakistan, a catastrophic decline of *Gyps vultures* is reported due to an analgesic and anti-inflammatory drug, diclofenac [10]. The drug has been regularly used for veterinary medication and residues entered the vultures as they fed on dead domestic livestock, causing renal failure and resulting in an over 95% decline in some populations since early 1990s [11]. Another study found the diclofenac to cause vitellogenin induction in male Japanese medaka (*Oryzias latipes*) at environmentally relevant concentrations of just 1 $\mu\text{g/L}$ [12]. Cytopathology occurs in livers, kidneys and gills of rainbow trout at 1 $\mu\text{g/L}$ [13-14].

Considering the potential adverse effects of DCF, it should be removed from the environment. Among several chemical treatment techniques that have been emerged in the last few decades, the advanced oxidation processes (AOPs) appear to be promising and reported to be effective for the degradation of pharmaceuticals in water. AOPs have proved capable of completely degrading the pharmaceuticals from aqueous solutions [15]. These processes are based on the generation of hydroxyl radical (OH^\bullet), which is a more powerful oxidant than most of the other chemical oxidants. Among AOPs, Fenton oxidation process has emerged as the most promising methods, in terms of cost effectiveness, ease of operation and effective degradation of organic non-biodegradable pollutants [16].

Recently, degradation of DCF in aqueous solutions by O_3 [17-18], UV/ H_2O_2 [17], Solar UV-Fenton [19], Solar/ TiO_2 [20], UV/ TiO_2 [21], Sonolysis, Sonolysis+ O_3 [18], Electro-oxidation [22], Solar/ $\text{TiO}_2/\text{SiO}_2$ [23], UV-A/ TiO_2 [24] and Homogeneous/heterogeneous Sonolysis [25] has been reported. However, the classic Fenton oxidation of DCF has not been reported in the literature. The present study is to investigate the

efficacy of Fenton oxidation process by kinetic studies to degrade and mineralize diclofenac in aqueous solution. The effect initial drug concentration and pseudo second order rate constants are evaluated.

2. Experimental

2.1 Chemicals

Diclofenac sodium salt (99.5% purity) is purchased from Sigma-Aldrich and is used as obtained. Hydrogen peroxide (H_2O_2) (50% w/w) and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) are purchased from Merck (India). All other chemicals - hydrochloric acid (HCl, Merck, India, 35% purity), sulfuric acid (H_2SO_4 , Merck, India, 98% purity), sodium hydroxide (NaOH, Merck, India, 98% purity), are used in the experiments. The simulated diclofenac aqueous stock solution of 1000 mg/L concentration has been prepared every week with Millipore Elix-3 demineralized water and stored in the dark at 4°C .

2.2 Experimental Procedure

The experiments are conducted at ambient temperature ($27 \pm 3^\circ\text{C}$) in batch reactors for a reaction time of 240 minutes. A 1000 mL solution of required DCF concentration is prepared from the stock DCF solution and is taken in a 2-liter reactor. The intrinsic pH of the synthetic DCF solution is 6.1. The initial pH 3.5 of the solution is maintained using 0.1 N H_2SO_4 and 0.1N NaOH. Appropriate amount of Fe^{2+} concentration is added to the reactor bath and stirred with magnetic stirrer. Required amount of H_2O_2 is added to the reactor bath to initiate the reaction. The mixture of DCF solution and Fenton's reagent is stirred with magnetic stirrer during treatment. The DCF solution sample is taken out from reactor at pre-defined time intervals and filtered through 0.45- μm Millipore filter membrane for COD analysis. For determination of DCF concentration by using UV-VIS spectrophotometer, sample is collected after mixing the solution in reactor thoroughly and acetonitrile is added to the collected sample for redissolution of DCF in solution and then filtered through a 0.45- μm Millipore Syringe.

2.3 Analytical Methods

The UV-VIS spectrum of DCF is recorded from 190 to 450 nm using UV-VIS spectrophotometer and the absorbance peak for DCF is observed to be at wavelength 276 nm (Figure 1). To establish a calibration curve between sample absorbance and concentration, solutions at 5 different DCF concentrations from

31.43×10^{-3} to 157.17×10^{-3} mM are prepared and measured. For the range of concentrations considered, a linear relationship between absorbance and concentration is established. The concentration of DCF in water samples is measured immediately after removal of samples from the reactor using the calibration curve. The pH is measured with a digital pH meter (Lovibond – pH 100). So as to determine extent of mineralization, the COD of the samples is determined by closed reflux titrimetric method as per the procedure outlined in the Standard Methods [26]. Final COD is quantitatively corrected for hydrogen peroxide interference according to the correlation equation given by Kang et al. (1999) [27]. The Iron concentration is measured using Spectrocolorimeter (PC Spectroll, Lovibond) by Thiocyanate-colorimetric Method. The H_2O_2 concentration is determined by iodometric titration method [28].

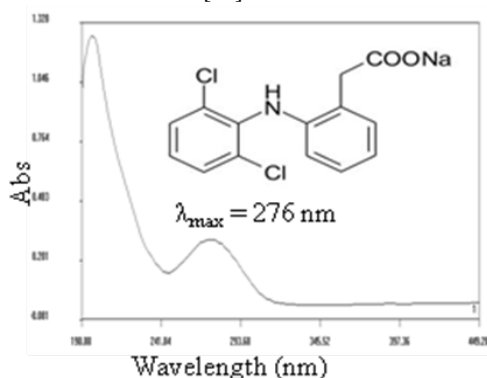


Figure 1 UV-VIS spectrum of DCF with chemical structure

3. Results and Discussion

The optimum experimental conditions like pH = 3.5, $[DCF]_0/[H_2O_2]_0 = 1:32.75$ (molar) and $[H_2O_2]_0/[Fe^{2+}]_0 = 57.49:1$ (molar) at which degradation and mineralization is the maximum, are optimized by Fenton oxidation (results not shown) and are considered in the kinetic experiments.

3.1 Effect of Initial DCF Concentration

The oxidation experiments are carried out at the optimum conditions for 24 hours; however, the DCF degradation and COD removal are very slow and not appreciable after 240 minutes of reaction time. Hence, further experiments are carried out for a reaction time of 240 minutes. The variations in percent DCF reduction and percent COD removals at optimum conditions for 240 minutes of reaction time are shown in Figure 2. The percent DCF reduction and percent COD removal are observed as 66.39 and 52.00 respectively in 5 minutes, whereas 74.25 percent DCF reduction and 72.80 of percent COD removal are observed in 240 minutes for 31.43×10^{-3} mM initial concentration of DCF. With the increase in DCF concentration from 31.43×10^{-3} to 157.17×10^{-3} mM, the percent drug removal increased from 74.25 to 82.28 and the percent COD removal decreased to 50.93 from 72.80. The degradation of DCF increases and the mineralization decreases with increase in initial DCF concentration. At the optimum $[H_2O_2]_0/[Fe^{2+}]_0$ ratio of 57.49:1 (molar), degradation of the drug increases with increase in its initial concentration is due to the higher probability of availability of the drug molecules to the highly reactive OH radicals that involve in the oxidation process. The reduction in COD removal at high pollutant concentrations may be due to the formation of intermediate oxidation products, which trap the OH radicals. This result is comparable with the literature, where COD removal of pharmaceutical wastewater by Fenton's oxidation is more for the lower initial concentrations of drugs [29].

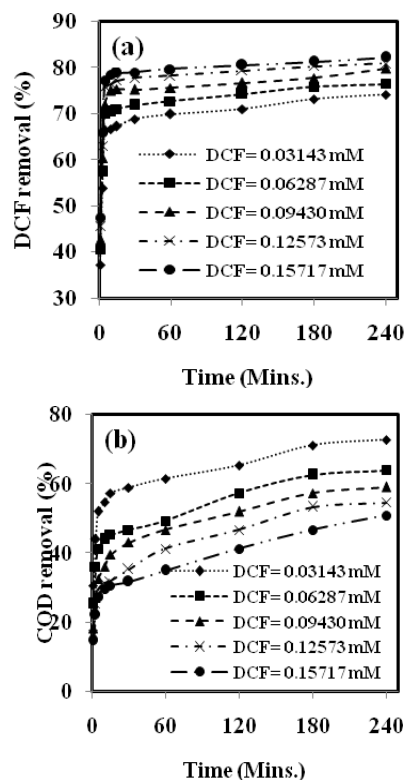


Figure 2 Variations in (a) percent DCF reduction and (b) percent COD removal; [Reaction conditions; pH 3.5, $[DCF]_0/[H_2O_2]_0 = 1:32.75$ (molar) and $[H_2O_2]_0/[Fe^{2+}]_0 = 57.49:1$ (molar), reaction time 240 minutes].

3.2 Kinetic Studies on DCF Oxidation

In the present investigation, kinetic studies are conducted at the optimum conditions for 240 minutes of reaction time. The oxidation is fast in the beginning for reaction time up to 5 minutes and therefore, the second-order kinetic equation has been fit up to the reaction time of 5 minutes [30]. In this study, the degradation rates of drug are described with pseudo-second order kinetics equation (Eq. (1)).

$$-r_2 = k_d C_d^2 \quad (1)$$

The Figure 3 shows the trend of a second-order reaction kinetic model (Eq. (1)) for initial DCF concentrations from 31.43×10^{-3} to 157.17×10^{-3} mM at optimum conditions in the 5 minutes.

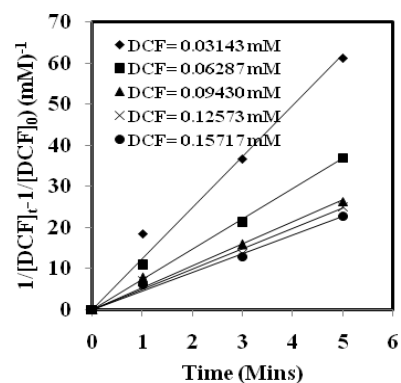


Figure 3 Trend of pseudo-second order reaction kinetics for degradation of DCF in 5 minutes by Fenton oxidation process; [Reaction conditions; pH 3, $[DCF]_0/[H_2O_2]_0 = 1:32.75$ (molar), $[H_2O_2]_0/[Fe^{2+}]_0 = 57.49:1$ (molar) and $[DCF]_0 = 31.43 \times 10^{-3}$ to 157.17×10^{-3} mM].

The values obtained for the pseudo second-order kinetic constants at ambient temperature ($27\pm 3^\circ\text{C}$) are summarized in Table 1. When other conditions like nature of the reactants, temperature, light, catalysts and solvent used etc are constant; the reaction rate depends up on the concentration of the drug, concentration of OH radicals for all reaction rates [31]. It is observed from the results that the rate of degradation decreased with the increase in initial DCF concentration. The rate constant decreased with increase in concentration of DCF and it is because the rate constant in a second-order reaction is inversely proportional to the initial concentration of the reactant.

Table 1. Pseudo second order kinetic rate constants for degradation of DCF by Fenton oxidation.

Initial conditions			Pseudo second order kinetic constants	
[DCF] ₀ mM	[Fe ²⁺] ₀ mM	[H ₂ O ₂] ₀ mM	M ⁻¹ S ⁻¹	R ²
31.43×10^{-3}	17.91×10^{-3}	1.03	206.95	0.981
62.87×10^{-3}	35.82×10^{-3}	2.06	123.13	0.983
94.30×10^{-3}	53.73×10^{-3}	3.09	88.90	0.985
125.73×10^{-3}	71.64×10^{-3}	4.12	82.13	0.986
157.17×10^{-3}	89.55×10^{-3}	5.15	75.55	0.991

4. Conclusions

The efficacy of Fenton oxidation process to degrade and mineralize diclofenac in aqueous solution is investigated. At the optimum conditions, for the initial concentration of DCF 31.43×10^{-3} mM with a reaction time of 240 minutes, the percent DCF reduction is 74.25 and the percent COD removal is 72.80. The DCF removal efficiencies increased and COD removal efficiency decreased with the increase in initial DCF concentration from 31.43×10^{-3} to 31.43×10^{-3} mM. The pseudo second order rate constants are inversely proportional to the initial concentration of the drug. The rate constants are $206.95\text{ M}^{-1}\text{S}^{-1}$ for 31.43×10^{-3} mM and $75.55\text{ M}^{-1}\text{S}^{-1}$ for 157.17×10^{-3} mM initial concentration of DCF. The Fenton Oxidation is an efficient treatment method for the effective removal of DCF.

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