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Investigation and Evaluation of Degradability of Ibuprofen from Wastewater by Using Fenton Process

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Abstract

Pharmaceutical residues are considered as emerging environmental problem because of their potential toxicology risk on living organisms. Environmental problem of pharmaceuticals are persistence to the aquatic ecosystem even at low concentrations (µg/L-ng/L). Conventional wastewater treatment plants are not enough to remove an emerging solution. Ibuprofen (IBF), a non-steroidalanti-inflammatory drug (NSAID), is a most widely used medicine in almost part of world. In present study, under laboratory conditions, coagulation followed by advance oxidation, using H_2O_2 and $FeSO_4$ (Fenton process) is used to degrade the concentrations of ibuprofen from water were conducted. Fenton process is known to be most effective and common methods for the treatment of such wastewaters. In the present study H_2O_2 was used with $FeSO_4$ for the treatment ibuprofen and effects of H_2O_2, $FeSO_4$ concentrations COD and TOC removals. Experiments with optimal concentrations of H_2O_2 and $FeSO_4$ were carried out by chancing pH, temperature, stirring and residence time of solution (2-6), room temperature, (10,20,30 min) and (30,60,90 min) respectively. Concentration of $FeSO_4$ and H_2O_2 were selected as (30,75,150 mg/L). After processing, 150 ml of samples taken out from the upper layers of sample COD and TOC tests were conducted.

Key words

Ibuprofen, Fenton Process, Pharmaceuticals, Water, Wastewater

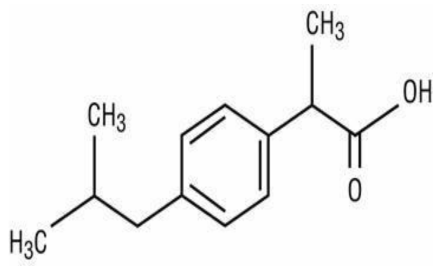
1. INTRODUCTION

Pharmaceuticals are used for treatment of diseases. Pharmaceutical compounds at aquatic environment are a great interest for researchers worldwide [1]. It has been observed the pharmaceutical residues on ground and surface water, wastewater where they have been found at very low concentrations like ng/L to µg/L [2]. Ibuprofen (2-(4-2-methylpropyl)phenyl) propanoic acid) is non-steroidal anti-inflammatory drug (NSAID), consuming often both for human and veterinary practices[3].Properties of Ibuprofen (IBF) are shown Table 1.IBF leaves the body in the shape of metabolized and non-metabolized after excretion [4]. Therefore the form links up with other substances on water, the regenerated form may cause hazard for aquatic environments. As a result of common use of IBF, there exists very high concentration of IBF in wastewater. To say more clearly, after using IBF by patients, the disused parts are removed out of body by urine [5]. In this way, the residue of IBF goes through canalization and arrives treatment plant. It is not only way to survive of the contamination but also the other way to survive is cumulating in sediments. The water from treatment plant and sediment can be used for agriculture which has access to reach soil and ground water [5] [6]. Conventional treatment plants are not advanced to refine the water, classic physical-chemical techniques and conventional microbiological techniques cannot effectively treat micropollutants. To purify them, Advanced Oxidation Process (AOP) is usually used. Many advanced treatment technologies have been used in removal of micropollutants. These methods include membrane technologies, ozonation, ultraviolet, ultrasound, hydrogen peroxide-ultraviolet, and Fenton [7]. Among them fenton process has been commonly studied because of cost effectiveness and good efficiency compared with other advanced oxidation process [8].Fenton Processes, a branch of AOP, are seen as a good process for micropollutant removal, and also it is easy to apply, works quickly [9]. The Fenton reaction iscomprised with highly reactive hydroxyl radicals (hydrogen peroxide) and ferrous ions in acidic [10], [11]. This reaction described by [12] in Eq (1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \quad (1)$$

With these qualifications, Fenton is most commonly used process for IBF removal. In this study the effectiveness of IBF degradation in drinking water uses Fenton process.

Table 1. Physico–chemical and pharmacological properties of IBF [13], [14].

Chemical structure	
Molecular formula,	$C_{13}H_{18}O_2$
Molecular weight	206,258 g mol−1
Water solubility	21 mg L−1 (20 °C)
Octanol-water partitioning	3,29-3,76
pKa	4,52
Usage	Analgesic, anti-inflammatory,antipyretic

2. MATERIALS AND METHODS

In the present study, under laboratory conditions, coagulation and advance oxidation, using H_2O_2 and $FeSO_4$ (Fenton process) is used to degrade the concentrations of ibuprofen from water were conducted. We have taken 25 mg/l ibuprofen synthetic solution. Biodegradability of the treated solutions (COD) and test with background constituents in the water matrix, like TOC will also observed. In the end of the experiments, to measure the efficiency of Fenton process, optimum pH, $FeSO_4$, H_2O_2, stirring time, residence time and temperature will be measured. Before starting our experiments we checked initial values of COD, TOC and amount of ibuprofen in untreated samples. Later, we selected different parameters like, pH values (2-6), $FeSO_4$ and H_2O_2 concentration (30-75-150 mg/l), stirring time (10, 20, 30 minutes), residence time (30, 60, 90 minutes) and room temperature that will be provided to our sample and optimal (high) values will be selected. After processing, 150 ml of samples was taken out from the upper layers of samples and COD and TOC tests were conducted.

A solution of IBF, obtained market was prepared in tap water to carry out advanced oxidation with Fenton process. In the experiments, Tablet was used to obtain 25 mg/L IBF content. For the preparation of sample, tablet containing 25 mg IBF tablet was first finely grinded to powdered form and then mixed with tap water in 1 liter flask to prepare 25 mg drug/liter solution.

We used in Fenton process 35% pure grade H_2O_2 hydrogen peroxide (Merck) , $FeSO_4.7H_2O$ iron sulphate (Sigma Aldrich), 98% pure grade H_2SO_4 sulfuric acid (Merck), NaOH sodium hydroxide (Merck). We used in COD process potassium dicromate K_2CrO_4 (Merck), Iron ammonium sulphate (Carlo Erba) 99% pure grade 1.10-phenanthroline and monohydrate (Sigma Aldich), mercury sulphate (Sigma Aldrich), silver sulphate (Sigma Aldrich), thermo reactor (Spectroquant TR 320).Physical measurements of synthetic wastewater are done by turbidimeter (Hach), TDS (Selectra), dissolved oxygen (Hach) and pH meter (Ohasus). We used in TOC analyze Apollo 9000 combustion TOC analyzer.The purpose of this study is to analyze the optimum degradation of IBF by using different parameters like pH, temperature, stirring time, waiting time, amount of Iron sulphate and hydrogen peroxide.

3. RESULTS AND DISCUSSION

Before starting the analysis, initial physicochemical properties of synthetic wastewater prepared from tap water were recorded and are given in Table 2.

Table 2. Physicochemical properties of synthetic wastewater with DFC.

Parameters	Units	Results
pH	pH birimi	6,85
TDS	µS/cm	402
Turbidity	NTU	1,3
Temperature	ºC	23,1
Dissolved oxygen	mg/L	6,99

In this context, first of all experiment with different pH like 2,3,4 and 6 was performed with concentrations: 75mg/l; $FeSO_4$, 75ml/l; H_2O_2 , stirring time;20 minutes, waiting time 60 minutes. After measuring COD and TOC optimum pH was observed to be in between 3 and 4. Because the value was closer to 3 and after consulting literature further experiments were decided to carry out by taking 3.5 pH as optimum [15], [16]. Values and results of TOC and COD can be cross checked from Figure 1.

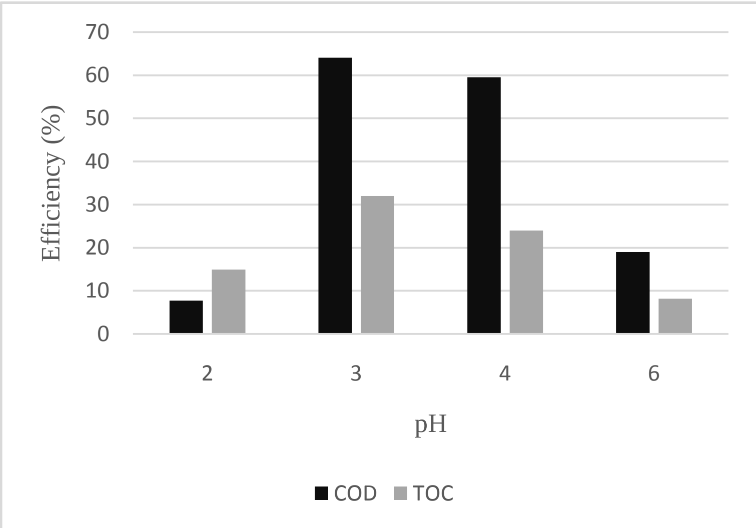


Figure 1. IBF removal with Fenton process. Efficiency with COD and TOC.

In the second step optimum concentration of $FeSO_4$ required for the degradation of drug was analyzed. For this purpose with optimum pH of <3.5, 75 mg/L; H_2O_2, stirring time;20 minute, waiting time 60 minute, different concentrations of $FeSO_4$ like, 30-75-150 mg/L were tried to select optimum amount to carry out further series of steps. As per the observed results of COD and TOC best value of $FeSO_4$ was 150 mg/L. Values and results of TOC and COD can be seen in Figure 2.

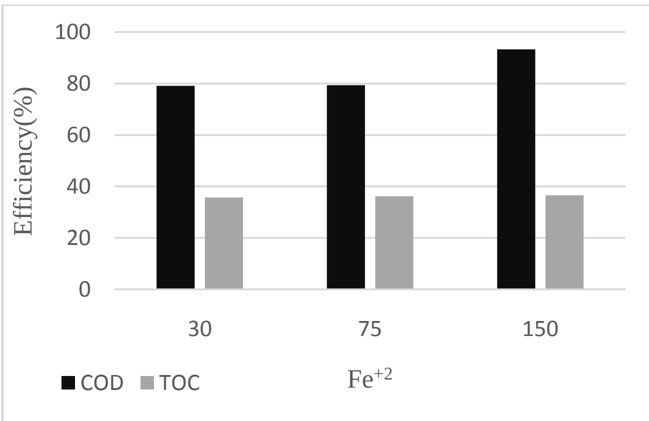


Figure 2.IBF removal with Fenton process.Efficiency with COD and TOC.

The purpose of third step was selection of optimum value of H_2O_2. In this step different concentrations of H_2O_2 like 30-75-150 mg/L were tried with optimum pH<3.5, optimum value of $FeSO_4$ 150 mg/L along with stirring time; 20 minute, waiting time 60 minute. According to the observed values of COD and TOC optimum value of H_2O_2 was selected as 150 mg/L. Published literature has shown that degradation of drugs increases with the increase amount of H_2O_2, hence increased amount of H_2O_2 means good degradation [16], [17]. After these results we assumed that our research is on right track. Observed TOC and COD values and results are shown in Figure 3.

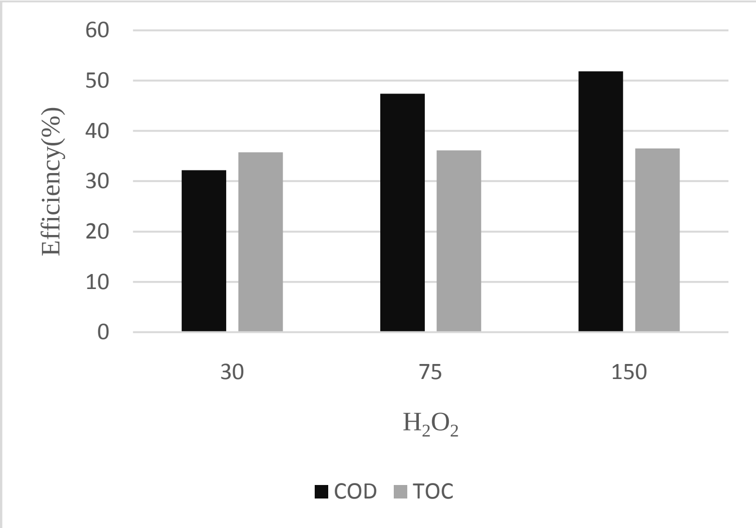


Figure 3.IBF removal with Fenton process.Efficiency with COD and TOC.

In the fourth step the optimum stirring time was figured out by applying different stirring times of 20-30-60 minutes to the solution under optimized parameters: pH<3.5, 150 mg/L; $FeSO_4$, 150 mg/L; H_2O_2, waiting time 60 minute. COD and TOC showed that 10 minute is the best optimum stirring time. Values of TOC and COD are showed in Figure 4.

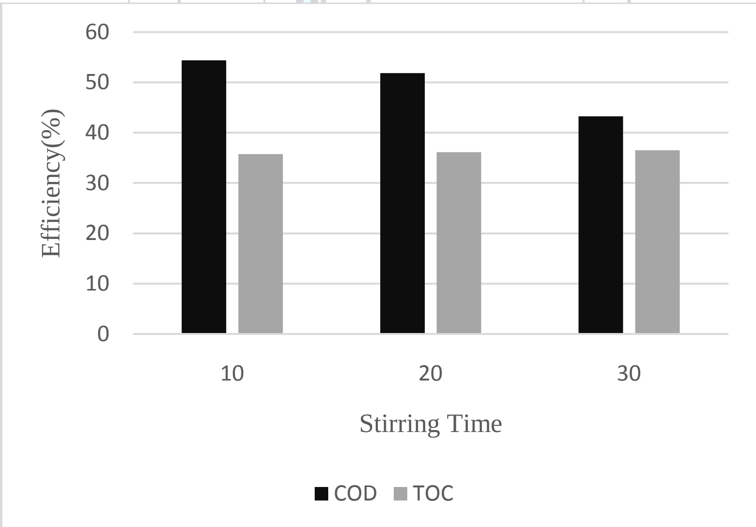


Figure 4.IBF removal with Fenton process.Efficiency with COD and TOC.

Fifth step was to optimize the waiting time, for this purpose time directions 30-60-90 minutes were provided to solution with other already optimized parameters as described above. Final optimized waiting time was cross checked by performing COD and TOC tests and it was finalized that waiting time of 90 minute was best optimum time. Observed TOC and COD values and results are shown in Figure5.

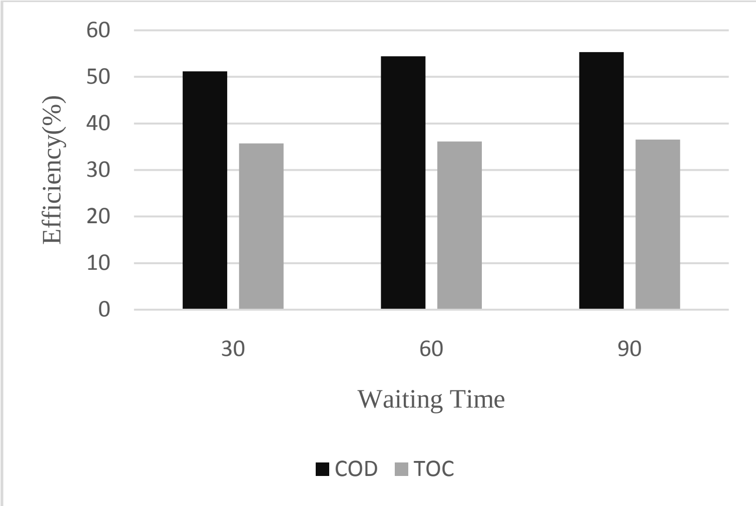


Figure 5.IBF removal with Fenton process.Efficiency with COD and TOC.

Total results were shown in Table 3.

Table 3.Results of total analysis.

		COD results (mg/l)	COD removal (%)	TOC results (mg/l)	TOC removal (%)
pH	**2**	262	7,74	66,57	14,95
	3	102	64,08	53,22	32,01
	<3,5	58,60	79,36	49,98	36,15
	4	115	59,50	59,23	23,95
	6	230	19,01	71,88	8,17
Fe^{+2} (mg/l)	**30**	59,43	79,07	50,30	35,74
	75	58,60	76,36	49,98	36,15
	150	19,20	93,23	49,68	36,53
H_2O_2 (mg/l)	**30**	48	83,09	53,04	32,20
	75	32	88,73	41,18	47,39
	150	16	94,36	37.70	51,83
Stirring Time (min)	**10**	6,4	97,74	35,69	54,40
	20	16	94,36	37,70	51,83
	30	20	92,95	44,70	43,28
Waiting Time (min)	**30**	7,0	97,53	38,18	51,22
	60	6,4	97,74	35,69	54,40
	90	6,1	97,85	34,98	53,31

*(Initial pH; 6,85, COD value; 284 mg/l, TOC value; 78,28 mg/l)

4. CONCULSION

All the results for investigated tap water sample containing drug (IBF) are precisely described below: pH<3.5, $FeSO_4$; 150 mg/L, H_2O_2; 150 mg/L, stirring time; 10 minute, waiting time; 90 minute were optimized. According to these results highest removal efficiencies for COD and TOC are 97,85 and 55,31 % respectively. Observed values of pH and H_2O_2 are in agreement with the published literature. With this research optimum figures for the degradation of IBF in the tap water by Fenton process were questioned. According to the results of the analysis, it can be decline that the best solution for the removal of pharmaceutical pollution from wastewater or freshwater resources is Fenton process which is compared with others.

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