European Water 58: 41-46, 2017.

Removal of diclofenac in drinking water with fenton process

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Abstract: Pharmaceutical residues are found in low concentrations (µg/L-ng/L) in aquatic environment. Pharmaceuticals are used to treat human and animal diseases. These drugs and their metabolites are excreted unchanged and they are continuously mixed in wastewaters. The residues of these compounds can be involved in environment in different ways: for example, expired drugs, hospital wastewater, human and animal excretion, pharmaceutical industry. Diclofenac sodium salt is a non-steroidal anti-inflammatory drug (NSAID) and is used commonly in worldwide. Conventional wastewater treatment plants are not sufficient to remove micropollutants, therefore advanced oxidation process have become an emerging solution. Fenton process is a branch of advanced oxidation process. Therefore, fenton process is used to clear out the effectiveness of diclofenac degradation in drinking water. In the present study, under laboratory conditions, coagulation and advance oxidation, with H_2O_2 and $FeSO_4$ (Fenton process) are used to degrade the concentrations of diclofenac from water conducted. To find out, biodegradability of the treated solutions the COD and TOC values of the background constituents in the water matrix are planned to measure. For this purpose, we used 10 mg/l diclofenac sodium salt synthetic solution with selected different parameters as, pH (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) all in room temperature. These selected parameter are the determined optimal values. After processing, 150 ml of sample is taken out from the upper layers of the solutions to make COD and TOC tests.

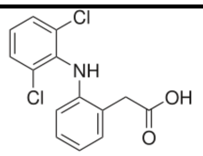
Key words: Diclofenac, Fenton Process, Pharmaceuticals, Water, Wastewater

1. INTRODUCTION

Diclofenac (DFC) is a non-steroidal anti-inflammatory drug (NSAID) mostly used to treat inflammatory and painful diseases (Basavaraju, 2012; Vogna et al., 2004). This pharmaceutical is excreted about %15 unchanged after human consumption (Basavaraju, 2012). Diclofenac, other name is [2-[(2,6-Dichlorophenyl)amino]phenyl]acetic acid, is shown in Table 1. Pharmaceutical residues are transported to water body. DFC leaves the body in the shape of metabolized and non-metabolized after excretion (Lishman et al., 2006). To say more clearly, after using DFC by patients, the disused parts are removed out of body by urine. In this way, the residue of DFC goes through canalization and reaches the treatment plant. It is a way to survive not only for contamination but also cumulating in sediments. The water from treatment plant and sediment can be used for agriculture which has access to reach soil and ground water (Kummerer, 2001; Heberer, 2002). The wastewater treatment plants are not capable to remove of micropollutant. Furthermore, micropollutants can be introduced to drinking water. For example, DFC was detected at less than 10 ng/L in drinking water sample taken from a private water tap in Berlin (Heberer, 2002). Therefore, it is recommended to use advanced oxidation processes in micropollutant removal. The studies show that classic fenton, fenton like process, ozonation, ultraviolet system are good for micropollutant removal. Fenton process is suitable for the degradation of diclofenac because of cheap, efficient and fast. The classic fenton process to degrade and mineralize diclofenac in synthetic solution is investigated (Jianlong et al., 2016).

In this paper, DFC is chosen as the target contaminant to investigate the oxidation performance with different parameters including the oxidant dosage, pH, stirring time and waiting time (Fenton process).

Table 1. Physico-chemical and pharmacological properties of DFC (Zhang et al., 2008)

Chemical structure	
Molecular formula	$C_{14}H_{11}C_{12}NO_2$
Molecular weight	269,16 g mol^{-1}
Water solubility	23,73 mg L^{-1} (25 °C)
Octanol-water partitioning	-
pKa	4,15
Usage	Analgesic, anti-inflammatory
Excretion	Biliary excretion: 65 % of oral dosage excreted in urine.

2. MATERIAL 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 diclofenac from water are conducted. In the experiments, Tablet is used to obtain diclofenac content. We used 10 mg/l diclofenac synthetic solution. To find out, biodegradability of the treated solutions the COD and TOC values of the background constituents in the water matrix are planned to measure. In the end of the experiments, to determine the efficiency of Fenton process, optimum pH, $FeSO_4$, H_2O_2, stirring time and waiting time is measured. Before starting our experiments we checked initial values of COD, TOC and amount of diclofenac in untreated samples. Later, we used 10 mg/l diclofenac sodium salt synthetic solution with selected different parameters as, pH (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) all in room temperature. After processing, 150 ml of sample is taken out from the upper layers of the solutions to make COD and TOC tests.

Chemicals used were 35% pure grade Hydrogen Peroxide (Merck); 99.5% pure grade Iron Sulphate (Sigma Aldrich); 98% pure grade Sulfuric Acid (Merck); >99 % Sodium Hydroxide (Merck) for Fenton processes. Potassium Dicromate >99.9 (Merck); Iron Ammonium Sulphate (Carlo Erba) 99% pure grade; 1.10-phenanthroline and monohydrate (Sigma Aldich) >99.9%; Mercury Sulphate (Sigma Aldrich) >98%; Silver Sulphate (Sigma Aldrich) >99% for COD analysis. All chemicals are used as received without further purification. All aqueous solutions are prepared with distilled water. Total organic carbon (TOC) are measured using Apollo 9000 combustion TOC analyzer. The COD tests are analyzed according to standard method (Methods: 5220 C. Closed Reflux Titrimetric Method). The pH of all the samples are measured using pH meter (Ohasus).

3. RESULTS AND DISCUSSION

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

Table 2. Physicochemical properties of synthetic wastewater

Parameters	Units	Results
pH	pH	6,92
TDS	µS/cm	403
Turbidity	NTU	1,4
Temperature	ºC	21,9
Dissolved oxygen	mg/L	6,98

Firstly, all experiment with different pH like 2, 3, 4 and 6 is performed with concentrations: 75

mg/l, $FeSO_4$; 75 mg/l, H_2O_2; stirring time, 20 minutes and waiting time, 60 minutes, at room temperature. After measuring COD and TOC, pH < 3,5 is decided as also optimum as discussed in different studies (Sonmez, 2016; Ustun Odabasi et al., 2016). Results of TOC are described in Figure 1.

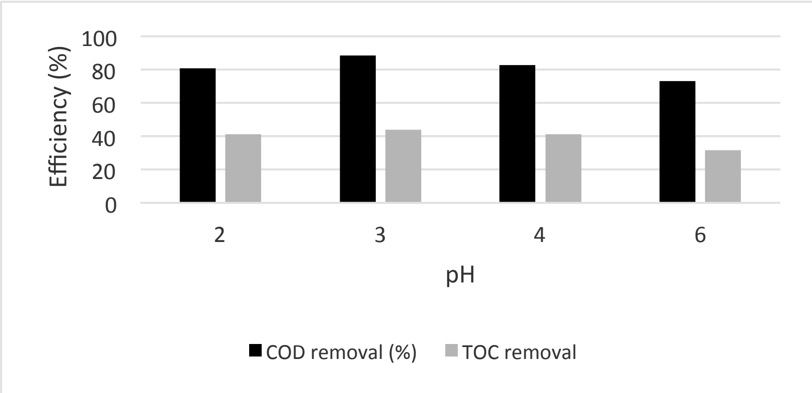


Figure 1. DFC removal with Fenton process (pH<3,5 effect)

In the second step, optimum concentration of $FeSO_4$ for the degradation of drug is determined. 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 are applied. For every observed results of COD and TOC, the best value of $FeSO_4$ is found to be 75 mg/L. Results of TOC and COD are provided in Figure 2.

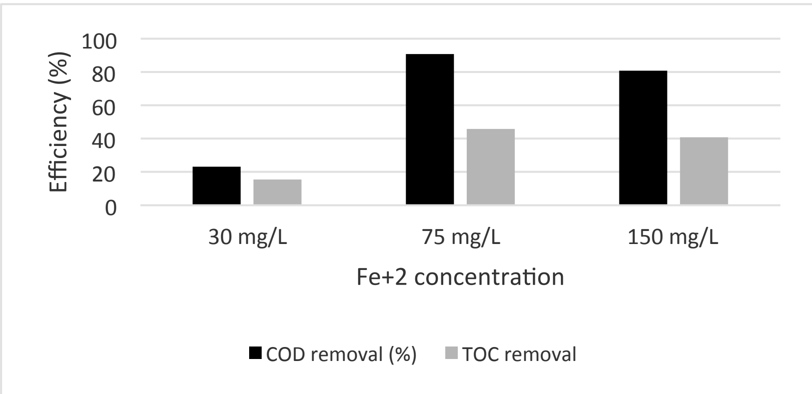


Figure 2. DFC removal with Fenton process (Fe^{+2} effect)

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 are selected with optimum pH<3.5, optimum value of $FeSO_4$ 75 mg/L along with stirring time, 20 minute and waiting time, 60 minute. According to the observed values of COD and TOC, optimum value of H_2O_2 is selected as 75 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 (Kang et al., 2000; Ustun Odabasi and Buyukgungor, 2016). H_2O_2 is not a sustainable chemical because of its harmful impact on environment. For this reason, it should not be used in large quantities. 150 mg/l and 75 mg/l H_2O_2 of dosage results were close to each other. Therefore, 75 mg/l of H_2O_2 dosage is chosen in this study. Observed TOC and COD results are shown in Figure 3.

In the fourth step, the optimum stirring time is figured out by applying different stirring times of 10-20-30 minutes with selected optimum pH<3.5, optimum value of $FeSO_4$ 75 mg/L, H_2O_2 75 mg/l along with waiting time; 60 minute. COD and TOC results showed that 20 minute is the best optimum stirring time. Values of TOC and COD are showed in Figure 4.

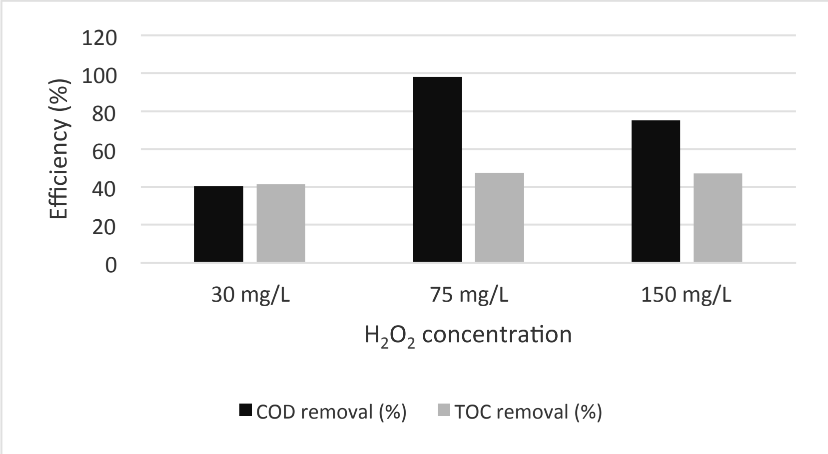


Figure 3. DFC removal with Fenton process (H_2O_2 effect)

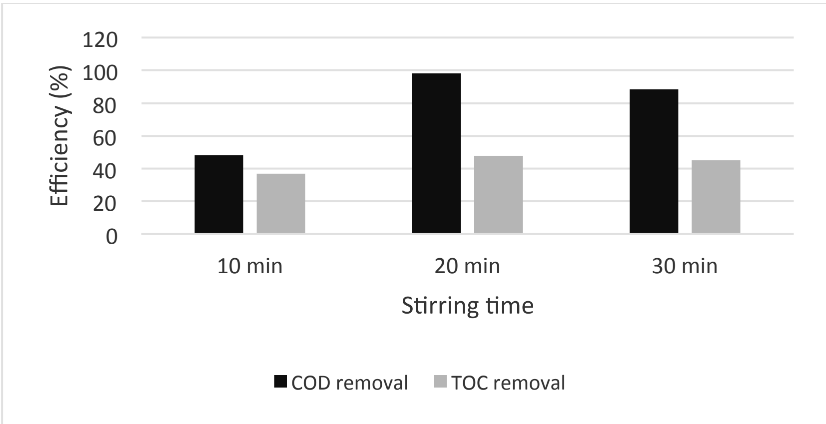


Figure 4. DFC removal with Fenton process (stirring time)

In the fifth step, the waiting time is figured out by applying different waiting times of 30-60-90 minutes to the solution under optimized parameters: pH<3.5, optimum value of $FeSO_4$ 75 mg/L, H_2O_2 75 mg/l, 20 minute stirring time. COD and TOC results showed that 90 minute is the best optimum waiting time. Values of COD and TOC are showed in Figure 5.

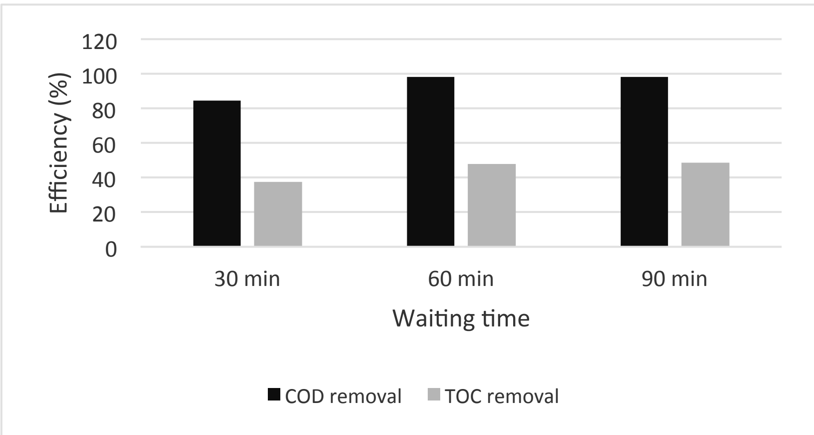


Figure 5. DFC removal with Fenton process (waiting time)

Total results are shown in Table 3.

Table 3. Results of total analysis

		COD results (mg/l)	COD removal (%)	TOC results (mg/l)	TOC removal (%)
pH	**2**	32	80,76	36,56	41,25
	3	19,2	88,46	34,83	44,03
	3,5	15	90,98	33,70	45,85
	4	28,8	82,69	36,68	41,06
	6	44,8	73,08	42,61	31,53
Fe^{+2} (mg/l)	**30**	128	23	52,68	15,35
	75	15	90,98	33,70	45,85
	150	32	80,76	36,92	40,68
H_2O_2 (ml)	**30**	99,2	40,38	36,52	41,32
	75	3,2	98,07	32,60	47,62
	150	41,6	75	32,81	47,28
Stirring Time (min)	**10**	86,4	48,07	39,39	36,71
	20	3,2	98,07	32,60	47,62
	30	19,2	88,46	34,18	45,08
Waiting Time (min)	**30**	25,6	86,41	38,84	37,59
	60	3,2	98,07	32,40	47,94
	90	3,1	98,13	32,08	48,45

*(Initial pH; 6,92, COD value; 166,4 mg/l, TOC value; 62,24 mg/l)

4. CONCULSION

There is a limited number of studies to determine the presence of micropollutant in drinking water. Most of the studies, report very low concentration or below detection concentration in drinking water treatment plants (Yunlong et al. 2014). Diclofenac is widely present in wastewaters and ultimately in water bodies. Therefore, it is necessary to evaluate and address their impact on the ecosystems by applying degradation techniques.

In the present study, all the results and best working conditions for the degradation of DFC are precisely described as: pH<3,5, $FeSO_4$; 75 mg/l, H_2O_2; 75 mg/l, stirring time; 20 minutes and waiting time; 90 minutes. According to these results, highest removal efficiencies for COD and TOC are 98,13 and 48,45% respectively at room temperature. Results suggested that DFC degradation enhanced as the H_2O_2 dosage increased. But, excessive usage of H_2O_2 should be avoided because of its harmful impacts. Although DFC degradation is difficult with conventional and biological treatments but still fenton process is a compromising technique. We suggest further experiments at different conditions.

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