

Combination of Advanced Oxidation and Sonochemical Process for Treatment of Pharmaceutical Pollutant in Wastewater

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ABSTRACT: Wastewater release is a significant issue for ventures as administrative bodies mandate sufficient treatment before discharging it to the aquatic bodies. The nearness of different medications like Ibuprofen, Clofibric corrosive, Ketoprofen, Naproxen, Carbamazepine, and so on are noted in pharmaceutical industry wastewaters. In this work, we mean to target tranquilize, Ibuprofen (IBP) which is a non-steroidal mitigating drug. Literature review shows that activated sludge treatment, Fenton response, Membrane bioreactors, Photocatalysis, and so on are a portion of the common for the evacuation of Ibuprofen. In the current examination, we propose to work and look at chose Fenton, advanced oxidation forms/Photo Fenton, the sonochemical process for IBP evacuation. The operational boundaries like pH, temperature, ultrasound frequency and time are studied. Every one of these techniques is proposed to be joined for expanded adequacy of treatment. The investigation will be finished by HPLC (High-Performance Liquid Chromatography) and different boundaries as COD will be addressed.

KEYWORDS:Wastewater, Photo- Fenton, Pharmaceutical, Advanced Oxidation, Sonochemical.

I. INTRODUCTION

In the past few decades, many industries are found out in our country. These industries are being developed in several sectors because the processing work takes place, wastewater is generated from them. Different wastewaters have different contaminants supported the sort of industry generating it and that they have adverse effects on the environment. One of these issues is the treatment of pharmaceutical wastewater. This wastewater contains various sorts of drugs Ibuprofen, clofibric acid, ketoprofen, naproxen, diclofenac, carbamazepine in several amounts which have a nasty effect on the aquatic flora and fauna [2]. Environmental problems related to pharmaceuticals are mainly thanks to their persistence and important biological activity (i.e., high toxicity and alterations of biological key functions like reproduction). Generally, pharmaceuticals have high cell wall penetration, which favors their bioaccumulation and development of noxious effects. The wastewaters are a serious issue for the industries because it must be treated properly before releasing them into aquatic bodies [1].

There are various methods like activated sludge treatment, membrane bioreactors, Fenton reaction, Photocatalysis, sonochemical degradation, photo Fenton/ advanced oxidation process, etc. are prevalent for removal of Ibuprofen. The sonochemical degradation refers to the utilization of sound waves (energy) for the treatment. The ultrasonic waves are being irradiated in liquid causing high energy chemical reactions and are results of acoustic cavitation [1]. Advanced oxidation process and therefore the photochemically enhanced or assisted Fenton process, commonly called photo-Fenton, are considered to be among the foremost efficient for the oxidative degradation of an outsized sort of organic contaminants in aqueous systems. These processes have supported the generation of highly oxidizing species (hydroxyl radicals and possibly others) from peroxide and Fe ions. [4].

In this work, we shall target the degradation of Ibuprofen drug by Fenton, Photo Fenton, and sonochemical methods and therefore the combination of them.

II. MATERIALS AND METHODS

Ibuprofen (2-[4-(2-methyl propyl) phenyl] propionic acid) may be a common drug wont to treat fever, pain, inflammation, or minor injury, its annual consumption being about 200 tons/year. IBP can enter the environment through domestic, farming (intensive livestock production and aquaculture), and industry routes. Several studies have reported the presence of IBP in effluents from wastewater treatment plants whose concentration ranges from 0.002 to 95 µg/L, in surface water 0.01 to 0.4 µg/L and in beverage 0.0002 to 0.0013 µg/L, proving the lack of actual treatment processes to completely remove this compound, also as its accumulation within the environment. Ibuprofen (IBP, $C_{13}H_{18}O_2$) was purchased from Suvindhinath Laboratories, Vadodara. The compound was of high purity (> 97%) and a relative molecular mass of 206.28 g mol⁻¹. H₂O₂ (30% w/v) solution from FINAR chemicals ltd. Ahmedabad. Concentrated H₂SO₄ and NaOH (1 N) were also used. Fenton's reagent was prepared by adding 35 g of ferrous sulfate (FeSO₄.7H₂O) in 250 ml of water containing 2.5 ml of concentrated H₂SO₄. Synthetic wastewater containing IBP was prepared in 1000 ml of solution. The concentration of IBP was 0.3 g/l.

III. EXPERIMENTAL WORK

A. FENTON PROCESS

An aqueous solution of Ibuprofen was prepared. The concentration of Ibuprofen was kept 0.3 g/L. 500 ml of this solution was taken in a reactor. Fenton's reagent was prepared by adding 35 g of ferrous sulfate (FeSO₄.7H₂O) in 250 ml of water containing 2.5 ml of concentrated H₂SO₄. 5 ml of H₂O₂ solution (30% w/v) was added and magnetically stirred. To this, 5 ml of Fenton's Reagent was added to the Ibuprofen solution. The initial pH of the solution was 7- 8 and after that pH was maintained at 2 with the help of 1N H₂SO₄. The run time of the experiment was 2 hrs. The run time of the experiment was 2 hrs. Similar practicals were done for acidic, basic, and neutral pH all at room temperature. Also, one experiment was performed at a raised temperature at 50°C.

B. PHOTO FENTON PROCESS

An aqueous solution of Ibuprofen was prepared. The concentration of Ibuprofen was kept 0.3 g/L. 500 ml of Ibuprofen was taken in a reactor. Fenton's reagent was prepared. After that, the solution was kept for stirring on a magnetic stirrer for 1 hour. 5 ml of H₂O₂ solution (30% w/v) was added. To this solution, 0.5 ml of Fenton's reagent was added. The reaction takes place in acidic medium, hence the pH was checked and was maintained at 2 with the help of H₂SO₄. The photocatalytic reactor was set up and the solution was placed in it and was stirred for 1 hour. Two samples were collected from the reactor at the time interval of 30 mins each.

C. SONOCHEMICAL PROCESS

Synthetic wastewater containing Ibuprofen was prepared. After that, the pH adjustments were done using H₂SO₄ (1N). The pH was set to 2 (acidic). The wastewater sample was kept in the reactor and the probe was dipped in the beaker containing the wastewater solution. The power available was 250W and frequency was 23 ± 3 kHz. The experiment was carried at 35°C. The process is carried in batch for 30 minutes. Simultaneously the time was varied for various experiments and the degradation rate was compared.

D. COMBINATION OF PROCESSES

A combination of all these three strategies was utilized for the expanded proficiency of the corruption of Ibuprofen. The Fenton procedure was performed for 30 minutes and the Photo Fenton process was performed for 15 minutes. The technique was the equivalent for both of the strategies, for example by utilizing Fenton's reagent and H₂O₂. The pH was kept up at 2 as we get the proficient outcomes at acidic medium. Various analyses are performed by shifting the hour of Fenton and Photo Fenton forms. Later the blends including the sonochemical process were additionally done. The mixes are performed at room temperature.

Table 1.

Method	Time
Fenton Process	2 hrs.
Photo Fenton Process	30 min
Sonication	30 min
Sonication	1 hr
Fenton+ Photo Fenton	30 min + 15 min
Sonication + Fenton	10 min + 10 min
Photo +Sonication	10 min + 10 min
Fenton + Sonication	10 min + 20 min
Fenton + Photo Fenton + Sonication	10 min + 10 min + 10 min

E. ANALYTICAL METHODS

Synthetic oxygen request or all the examples were acquired by physically carrying out the COD test in the lab-scale and the % corruption of Ibuprofen was identified by HPLC (High-Performance Liquid Chromatography). For COD, various examples were taken and arranged. A clear example was set up by including 30ml H₂SO₄ (1N), 10ml K₂Cr₂O₇, and 20ml of distilled water were included. Globules were included the example to abstain from knocking. Tests readiness: 30ml H₂SO₄ (1N), 10ml K₂Cr₂O₇, and a spot of HgSO₄ were included step by step, at that point test water was added to this blend until green shading shows up. After the arrangement of tests, they were kept in COD digester for 2 hours at 145 °C. Following two hours, every one of the examples was taken out and was kept to be cooled. After that 10ml of the example was taken and hardly any drops of Ferroine marker were included and these examples were titrated against the FAS (Ferrous ammonium sulfate) arrangement. The shading change of the example was from green to somewhat blue-green to at long last tarnish shading.

IV. RESULTS AND DISCUSSION

A. EFFECT OF pH

Different arrangements of investigations have been performed with various degrees of pH. In the greater part of the procedures, the acidic pH was seen as the best for the corruption of the Ibuprofen. Subsequently, pH level 2 was kept up all through all the trials. The higher debasement was watched at an acidic (pH 2) because the higher [H⁺] benefits the development of ·OH and expands the yield of broke up ferrous complexes.

B. CHEMICAL OXYGEN DEMAND (COD)

From the results obtained COD, it was noticed that in the individual process the maximum COD degradation was found to be 71.42% in the Photo Fenton process followed by the sonochemical process at 70.23 %. When the combination of the processes was done it was found that the highest COD degradation was found in Fenton with the sonochemical process which again followed by the Fenton along with Photo Fenton process.

Table 2.

Process	% COD Rejection
Fenton (acidic)	66.66
Photo Fenton	71.42
Fenton (basic)	20.64
Fenton (neutral, temp 50°C)	32.14
Fenton + Photo Fenton	79.52
Sonication (30 mins)	68.57
Sonication (1 hr)	70.23
Sonication + Fenton (10 min + 10 min)	75.70
Photo +Sonication (10 min + 10 min)	64.28
Fenton + Sonication (10 min + 20 min)	79.61
Fenton + Photo Fenton + Sonication	75

C. EFFECT OF ULTRASOUND WAVES

The most essential boundaries for utilization of sonolysis are the force and recurrence utilized. Contingent upon the US corruption method of the natural compound, there is an ideal recurrence for each procedure. In this, the sonolysis of water happens, which produces $\text{OH}\cdot$, $\text{H}\cdot$, $\text{OOH}\cdot$, $\text{OH}_2\cdot$, and H_2O_2 utilizing the nucleation, development, and breakdown of cavitation rises in water because of the high temperature and weight coming about because of ultrasound waves. It was noticed that at a constant ultrasound frequency, time played a crucial role. As time was increased the amount of hydrogen peroxide also increases because the intensity of ultrasound was increased. The maximum degradation was found for the highest of times.

D. HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

All the samples collected from the experiments were analyzed by the means of High-Performance Liquid Chromatography (HPLC). High-performance liquid chromatography (HPLC; formerly referred to as high-pressure liquid chromatography) is a technique in analytical chemistry used to separate, identify, and quantify each component in a mixture. It relies on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material. Each component in the sample interacts slightly differently with the adsorbent material, causing different flow rates for the different components and leading to the separation of the components as they flow out of the column samples were sent to the Biochrome analytical Laboratories located at GIDC Ankleshwar. The column used was ultra techsphere ODS - 5 μ -(C-18) and the wavelength of detection was set at 214 to 233 nm. The schematic of the HPLC instrument typically includes a degasser, sampler, pumps, and a detector. The sampler brings the sample mixture into the mobile phase stream which carries it into the column. The pumps deliver the desired flow and composition of the mobile phase through the column. The detector generates a signal proportional to the amount of sample component emerging from the column, hence allowing for a quantitative analysis of the sample components. A digital microprocessor and user software control the HPLC instrument and provide data analysis. Some models of mechanical pumps in the HPLC instrument can mix multiple solvents in ratios changing in time, generating a composition gradient in the mobile phase.

The degradation of Ibuprofen drug for different processes is shown in the table below.

Table 3

Process	% Ibuprofen Degradation
Fenton (acidic)	80.2
Photo Fenton	94.5
Fenton (basic)	39.34
Fenton (neutral, temp 50°C)	55.99
Fenton + Photo Fenton	96.66
Sonication (30 mins)	86.77
Sonication (1 hr)	88.50
Sonication + Fenton (10 min + 10 min)	75.70
Photo +Sonication (10 min + 10 min)	69.21
Fenton + Sonication (10 min + 20 min)	79.61
Fenton + Photo Fenton + Sonication	78.77

V. CONCLUSION

This study evaluates the removal efficiency of the pharmaceutical drug Ibuprofen (IBP) by Fenton, Photo Fenton, and sonochemical process and their combination. The degradation of the IBP was found to be better at acidic pH value in AOPs. The IBP degradation for the raised temperature can be considered when the wastewater is having a neutral or basic pH. In the Photo Fenton process, the maximum degradation was found as with the incorporation of the UV light lead to more production of OH radicals. When the combination is to be incorporated it can be said that varying the parameters in one process can be balanced by the combination of the other. In photo Fenton to decrease the time of UV light addition of H_2O_2 is done so that the efficient results can be obtained by optimizing the parameters. Similarly when H_2O_2 is added along with the sonochemical process so that in less time a greater efficiency was obtained. The

maximum degradation in combination was found out in Fenton with Photo Fenton at 96.66%, followed by Fenton (10 mins) with the sonochemical process (20 mins) at 79.61%. COD % rejection was also found higher in combined processes.

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