Scientific Journal of Impact Factor (SJIF): 5.71
e-ISSN (O): 2348-4470
p-ISSN (P): 2348-6406

International Journal of Advance Engineering and Research Development

Volume 5, Issue 03, March -2018

Application of Advance Oxidation Processes to Achieve Zero Liquid Discharge in Pharmaceutical Industry

Mr. Gaurav Agarwal[1], Dr. Vikas Gupta[2], Mrs. Reema Gupta[3]

[1]*Department of Civil Engineering, School of Engineering, RK University, Rajkot, Gujarat, India*
[2]*Director (Polytechnic), IFTM University, Moradabad, U.P, India*
[3]*Department of Humanities & Science, SLTIET, Rajkot, Gujarat, India*

Abstract - *Water is a scarce resource and essential for all the industries and human being. Due to anthropogenic activities, pollution problems of water are being critical today. To overcome water pollution problem, environmental regulatory requirements are becoming more stringent and enforcing water intensive industries like pharmaceutical industries to reuse of its treated effluent for various purposes which can be possible by adopting zero liquid discharge (ZLD) system in industries to minimizing water consumption. Pharmaceutical industries are generating highly colored, toxic and hazardous wastewater containing recalcitrant organic compounds which are highly hazardous, toxic, chemical stable and low biodegradable in nature which are not treatable by conventional treatment methods and pose serious human health and ecological risks. To achieve the zero liquid discharge in pharmaceutical industries, one of the most challenging issues is the removal of recalcitrant compounds in pharmaceutical wastewater. Therefore, treatment of pharmaceutical wastewater by using various advance oxidation processes (AOPs)are potential alternative solution to remove recalcitrant organic compounds, reduce chemical oxygen demand (COD) and improve biodegradability index of pharmaceutical wastewater which advantages to achieve zero liquid discharge in pharmaceutical industries. The objective of present study was to assess the possibility of UV, H_2O_2, UV/H_2O_2 and Fenton process in a laboratory-scale setup for the pretreatment of pharmaceutical wastewater and to determine the influences of various parameters on the pretreatment of pharmaceutical wastewater. The experimental results show UV, H_2O_2 and UV/H_2O_2 are not effective for the treatment of pharmaceutical wastewater except Fenton process. In the present study, the optimum conditions had been determined for Fenton process, and it was found that % COD removal efficiency obtained after 120 min of reaction, was about 68.2%. The optimal parameters were: initial pH=3; [H_2O_2] =600 mg/L; [Fe^{2+}] =200 mg/L and for 8640 mg/L initial COD of pharmaceutical wastewater. The results showed that COD removal efficiency first increased then decreased with the increase of solution pH, and the highest COD removal appeared as pH was about 3.0. The COD removal rose from 36.4 % to 68.2 % with H_2O_2 concentration from 50 mg/L to 1100 mg/L and from 4.1 % to 63.1 % with Fe^{+2} concentration from 25 mg/L to 250 mg/L. The COD removal first increased then decreased with the mole ratio of Fe^{+2} to H_2O_2. The maximum COD removal appeared as the mole ratio of Fe to H_2O_2 is 1:5. The COD removal increased with time and leveled off after 120 minutes. At optimum condition, improvement in biodegradability index was takes place from 0.95 to 0.27, which shows that the Fenton process is very suitable for the treatment of pharmaceutical wastewaters. After combination of Fenton process with conventional methods, it can possible to reuse the treated wastewater in the industry for various purpose or safely discharge into different streams or transfer into a sewage treatment by means of advanced oxidation processes.*

Keywords - *Advanced oxidation processes, Pharmaceutical wastewater, Chemical oxygen demand, Recalcitrant organic compounds, Zero liquid discharge*

I. INTRODUCTION

Clean water is the one of the essential requirement for the survival of the society on the earth. Water is a scarce resource and essential for all the industries and human being. Although our planet has a large amount of water, only 2.5 % of freshwater available to world [1]. Asia has 32% of global total freshwater resources but Asia is home to about 60% of the global population. It is projected that 2.4 billion people in Asia will suffer from water stress by 2025 and almost doubles the 1995 [2]. Fresh water is a scarce limited resource and polluting day by day due to anthropogenic activities which create water pollution issues and affect all living beings. Thus, it is necessary to adopt some water conservation alternatives or management strategies to overcome issues related with water pollution. Now, reuse of treated effluents in an industries for various purposes are getting attention as a prospective source under pressure of increasing fresh water scarcity. But, there are also certain limitations for the reuse of treated effluents. It can be carries pathogenic organism, high level of nitrogen and heavy metals which pose risk to the agriculture community, groundwater resources and wastewater irrigation respectively[3]. To overcome water pollution problem, environmental regulatory requirements are becoming more stringent and enforcing water intensive industries like pharmaceutical industries to reuse of its treated effluent for various purposes which can be possible by adopting zero liquid discharge (ZLD) system in industries to minimizing water consumption. Zero liquid discharge concepts is an innovation and an environmentally friendly approach to wisely and precisely use of water in their processes. A ZLD system ensure that there is no discharge of wastewater to the environment. Practically, zero liquid discharge term is not deal with the no generation of wastewater from industries but actual deal with no discharge of wastewater outside of their premises. In order to sustain in the real world competitive market and to conserve the natural resources, it has become essential for any industry to explore or investigate the possibility of zero liquid discharge by adopting 4R's i.e. Reduction, Reuse, Recycle and Recovery of resources. The theoretical concept regarding to achieve zero liquid discharge is the separation of waste impurities in the form of solids component from industrial wastewater, treated wastewater is reused and generated solids containing some moisture content are disposed as a waste or byproduct.

Pharmaceutical industries are using large amount of fresh water for their manufacturing processes and other purposes and generating highly colored, toxic and hazardous wastewater containing recalcitrant organic compounds which are highly hazardous, toxic, chemical stable and low biodegradable in nature which are not treatable by conventional treatment methods and pose serious human health and ecological risks. Therefore, it is necessary to degrade these toxic compounds in wastewaters prior to final discharge. Conventional wastewater treatment plants based on biological treatment are not efficient to remove these compounds to the desired level[4]. Therefore, there is a need of a combination of advance wastewater treatment methods to achieve zero liquid discharge system in pharmaceutical industry with an objective of minimizing water consumption by reusing effluents for production processes and various other purposes. Wastewater generated from the industries must be viewed not as a waste to be dispose-off but as a resource that must be used. The treated wastewater by using conventional methods cannot be used for landscape watering and other non-portable uses due to the presence of recalcitrant organic compounds even after the biological treatment.

To achieve the zero liquid discharge in pharmaceutical industries, one of the most challenging issues is the presence of recalcitrant compounds in pharmaceutical wastewater due to their toxicity on both human health and environment. Therefore, various treatment technologies have been developed over the last decades in order to meet these requirements. One such group of technologies is commonly referred to as Advanced Oxidation Processes (AOPs). AOPs could be considered as a pre-treatment step for making the pharmaceutical wastewater amenable to bio degradation by the conventional biological treatment process. Therefore, treatment of pharmaceutical wastewater by using various AOPs may be a promising treatment technology and potential alternative solution to remove recalcitrant organic compounds, reduce chemical oxygen demand (COD) and improve biodegradability index of pharmaceutical wastewater which advantages to achieve zero liquid discharge in pharmaceutical industries.

Advance oxidation processes are the processes based on the chemical oxidation through in situ generation of hydroxyl radicals ($^{\cdot}OH$), which are highly active strongest oxidants and mineralize recalcitrant compounds into biodegradable end products. After formation of hydroxyl radicals, these radicals continuously reacts with organic compound present in the wastewater and mineralize recalcitrant organic compounds into end products[5]. Advanced oxidation processes (AOPs) include techniques of degradation of recalcitrant or poorly biodegradable organics by oxidizing species such as hydroxyl ($^{\cdot}OH$) and hydroperoxyl ($^{\cdot}HO_2$) radicals [6]. Generation of hydroxyl radicals depends on the type and nature of primary oxidants, type of external energy sources and type of catalysts used separately or in combination under desired conditions. Generally ozone, hydrogen peroxide and oxygen are used as primary oxidants for the generation of hydroxyl radicals with or without using energy sources like ultraviolet light, solar light, ultrasounds and or catalysts used like metal oxides. For the mineralization of recalcitrant compounds require large amount of energy by means of electrical, solar or ultraviolet energy, so AOPs are highly energy intensive processes. So, advance oxidation processes are expensive than conventional wastewater treatment. To overcome this shortcoming, different combinations of AOPs with conventional methods can be used to obtained synergistic effects. AOPs techniques is an innovative and emerging best available processes that have better potential to achieve zero liquid discharge at plant level. Advanced oxidation involves several steps and explained as follows:

1. Formation of strong oxidants (e.g. hydroxyl radicals).
2. Reaction of these oxidants with organic compounds in the water producing biodegradable intermediates.
3. Reaction of biodegradable intermediates with oxidants referred to as mineralization (i.e. production of water, carbon dioxide and inorganic salts).

In recent years different combinations of these methods were used to obtain the complete mineralization of pollutants. Among these AOPS, Fenton's reagent is particularly interesting due to its low price, low toxicity of its reagents (Fe^{+2} and H_2O_2), and the simplicity of its technology. Several studies already conducted have shown that the reaction of Fenton's reagent is effective in the degradation of organic compounds. The active species can be generated from the reaction between hydrogen peroxide and ferrous and ferric ions depending on the reactions. The Fenton process is known as one of the most efficient advanced oxidation processes for the degradation of organic pollutants[7]. Fenton and related reactions encompass reactions of peroxides (usually H_2O_2) with iron ions to formactive oxygen species that oxidize organic or inorganic compounds when they are present. The history of Fenton chemistry dates to 1894, when Henry J. Fenton reported that H_2O_2 could be activated by Fe^{+2} salts to oxidize tartaric acid. In 1934 Haber and Weiss (1934) proposed that the active oxidant generated by the Fenton reaction is the hydroxyl radical ($^{\cdot}OH$), one of the most powerful oxidants known (E° = 2.73 V). Later, [8]. The Fenton and related reactions are viewed as potentially convenient and economical ways to generate oxidizing species for treating chemical wastes. Compared to other bulk oxidants, hydrogen peroxide is inexpensive, safe, and easy to handle, and poses no lasting environmental threat since it readily decomposes to water and oxygen. Likewise, iron is comparatively inexpensive, safe, and environmentally friendly. Research on applications of Fenton chemistry to waste treatment began in academic laboratories only around 1990. The number of scientific articles on applications of Fenton chemistry to waste treatment has increased exponentially over the years. Early on it was realized that Fenton reactions were markedly accelerated by light. The photo-assisted Fenton reaction ("photo-Fenton" reaction) typically gives faster rates and a higher degree of mineralization than the thermal ("dark") reaction and can take advantage of light in the solar spectral region.Treatment with Fenton's oxidation improved the biodegradability and reduced the toxicity of the pharmaceutical wastewaters. Fenton oxidation was an effective pretreatment method for the non-biodegradable portions of the pharmaceutical wastewater, which renders them more biodegradable for following biological processes.

II. Literature Review

Present study considered the pretreatment of pharmaceutical wastewater by UV, H_2O_2, UV/H_2O_2 and Fenton process to achieve zero liquid discharge in pharmaceutical industry. The effectiveness of the Fenton's reagent for the degradation of organic pollutants in wastewater has been reported in a large number of publications. The combination of hydrogen peroxide and ferrous salt is referred to as "Fenton's reagent". The primary oxidant in Fenton's reagent is the hydroxyl radical ($^{\cdot}OH$) generated by the reaction of hydrogen peroxide with ferrous ion (Fe^{2+}) [9]. In Fenton oxidation, the pH value has to be in the acidic range between 2 and 4 to generate the maximum amount of hydroxyl radicals to oxidize organic compounds. However, low pH has found effective for Fenton's reagent, and the best removal efficiency is obtained at a pH =3 [10]. Bensalah Nasr et.al (2004) was worked on olive oil mill wastewater and determined that 86% COD removal was taken place by using 5mole/L H_2O_2 and 0.4 mole/L Fe^{2+}. For high mass ratio of H_2O_2 to Fe^{+2}, hydroxyl radicals ($^{\cdot}OH$) formation becomes very slow and COD reduction increase is constant. The reaction was carried out under vigorous magnetic stirring and stopped by adding 10% aqueous solution of $Na_2S_2O_3$. He was plotted a graph in percentage removal of COD as function of time and showed a rapid decreases of COD in the first 5 minutes, a small variation on the time range of 5-15 minutes and a new decreases of COD after 20 minutes to reach 86% of removal COD[11]. Plakas K.V. and Karabelas A.J. (2016) was carried out Fenton reaction and residual H_2O_2 at the end of reaction was removed by adding a small quantity of sodium metabisulfite ($Na_2S_2O_5$), afterwards the solution pH was adjusted to ~7 [12]. Mohammad Bagher Miranzadeh et.al (2016) was investigated the effectiveness of Fenton and photo-Fenton processes by using 200 mg/L linear alkyl benzene Sulfonate (LAS) for removing anionic surfactants from aqueous solutions and conclude that the mean removal efficiency of LAS in Fenton and photo-Fenton at 20 minutes reaction time at 100 mg/L constant concentration of H_2O_2 and 20 mg/L Fe^{+2} were 20.16 and 22.47%, respectively. Meanwhile, LAS removal efficiency (at 80 minutes reaction time for constant concentration of 800 mg/L H_2O_2 and 120 mg/L Fe^{+2}) were 69.38 and 86.66%, respectively, which is consistent with the significant increase in the rate of LAS removal efficiency with reaction time [13]. Y. Segura (2013) was investigated the pre-treatment of a pharmaceutical wastewater (PWW) by Fenton Oxidation with zero-valent iron (ZVI) and H_2O_2 to improve the degradation of the complex-mixture of organic compounds present in the wastewater. This study shows that the Air/ZVI/ H_2O_2 system can be considered as an effective alternative solution for the removal of many organic pollutants present in wastewater generated from pharmaceutical industry. Moreover, the use of waste-metallic iron shavings instead of commercial ZVI powder, showed very promising results and further work on delineating the mechanisms are currently ongoing. The treatment of concentrated pharmaceutical wastewater by this Air/ZVI/ H_2O_2 system however, was less efficient than the use of more dilute effluents.[14] Ronak Shetty and Shweta Verma (2013) was studied the treatment of pharmaceutical wastewater by using Fe^{+2}/H_2O_2 molar ratio of 1:1, 1:2 and 1:3. 82% reduction of COD was observed at 3267 mg/L of Fe^{+2} and 800 mg/L of H_2O_2 for 1:1 ratio, 85% reduction of COD was observed at 3675 mg/L of Fe^{+2} and 900 mg/L of H_2O_2 for 1:2 ratio and maximum reduction of COD was observed at 2450 mg/L of Fe^{+2} and 900 mg/L of H_2O_2 for 1:3 ratio [15]. Ravi J. Acharya et.al (2016) was studied the treatability of Fenton activated carbon catalytically oxidation for pharmaceutical waste water treatment and investigated that FACCO as a treatment can be good option to increase biodegradability of pharmaceutical waste water. The oxidation of dissolved organics by Fenton's reagent resulted in the percentage removal of BOD, COD were 80.5 % , 70.83 % respectively[16]. Wei Li et.al (2011) was examined the effects of Fenton oxidation on trace level pharmaceuticals and personal care products (PPCPs) commonly occurring in wastewater. All tested PPCPs, except atrazine and iopromide, were completely removed by Fenton treatment carried out using a 20 mg/L Fe (II) concentration and a 2.5 H2O2/Fe (II) molar ratio[17]. Huseyin Tekin et.al (2006) was investigated applicability of Fenton's oxidation to improve the biodegradability of a pharmaceutical wastewater. Optimum pH was determined as 3.5 and 7.0 for the first (oxidation) and second stage (coagulation) of the Fenton process, respectively. For all chemicals, COD removal efficiency was highest when the molar ratio of $H_2O_2/Fe^{+2}$was 150–250. At H_2O_2/Fe^{+2} ratio of 155, 0.3M H_2O_2 and 0.002M Fe^{2+}, provided 45–65% COD removal. With an increase of

H_2O_2 doses from 0.8 to 5M, at constant Fe^{2+} dosage of 0.033M, average COD removal efficiency increased from about 40% to 85% [18]. Rajesh Nithyanandam and Raman Saravanane (2013) was used Fenton Oxidation to treat the pharmaceutical sludge having the COD value of 118, 400 mg/L for the safe disposal. For different ratio of Fe^{+2}/H_2O_2 (1:2, 1:4, 1:8, 1:10) in different molar ratio of Fenton's reagent (0.1M, 0.2M, 0.3M, 0.35M, 0.4M) the COD reduction was determined. It has been found that COD reduction is maximum in 1:10 ratio of Fe^{+2}/H_2O_2 at 0.3M of Fenton's reagent. In this ratio nearly 65% reduction in COD was achieved[19]. Yolanda Segura et.al (2014) was used waste metallic iron shavings as heterogeneous zero-valent iron (ZVI) catalyst and hydrogen peroxide to degrade pharmaceutical wastewater in Spain by Fenton Oxidation. This study shows that the ZVI/H_2O_2 system can be considered as an easy, economic and effective alternative solution as a pre-treatment step before biological treatments for the removal of many organic pollutants present in a wastewater generated by a drug manufacturing plant located in Madrid. The Higher mixing velocities as well as the use of smaller particle sizes of iron shavings were found to be more effective[20]. Yu Yang et.al (2009) was developed a novel microwave enhanced Fenton-like process for the treatment of pharmaceutical wastewater with high COD. Operating parameters were investigated and the optimal condition included as follows: microwave power was 300W, radiation time was 6min, initial pH was 4.42, H_2O_2 dosage was 1300mg/L and $Fe_2(SO_4)_3$ dosage was 4900mg/L, respectively. Within the present experimental condition used, the COD removal reached to 57.53%, and BOD5/COD was enhanced from 0.165 to 0.470. Microwave enhanced Fenton-like process is believed to be a promising treatment technology for high concentration and bio refractory wastewater [21]. Davor Dolar (2013) was studied the treatment of real pharmaceutical wastewater by combination of the Fenton process, sand filtration, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) was tested. The optimum concentrations of Fe^{2+} and H_2O_2 for Fenton process were 0.6 g/L and 32 g/L, respectively, and the pretreatment was found to be effective in the reduction of COD, TOC, total N, and total P. It can be considered as an effective pretreatment of this type of wastewater. The pretreatment (Fenton, sand filter, UF) decreased the above parameters for 62%, 56%, 10%, and 88%, respectively. Finally, and the most importantly, the combined methods of the pharmaceutical wastewater treatment resulted in high recovery of more than 90% [22]. Satyanarayana et.al (2015) was introduced dilution technique in primary treatment followed by hydrogen peroxide oxidation in secondary treatment and finally in tertiary treatment passed through R.O process. After secondary treatment the COD values are reduced to more than 90%. The results suggested that the treatment method is effective and more efficient for pharmaceutical industry effluent up to 25,000mg/l COD values[23]. Xiaoyu Cui (2015) et.al. was applied Fenton oxidation to treat the berberine finished mother liquor wastewater in pilot scale. The results showed that under the optimal conditions, pH 3, H_2O_2/COD molar ratio of 1.25, Fe^{2+}/H_2O_2 molar ratio of 0.1, Q 100 L/h with (HRT= 2.5 h), the COD and berberine removal efficiencies were 35.6 and 91.4 % at initial COD concentration of 4061 mg/L and berberine concentration of 709 mg/L, respectively. The (BOD5)/(COD) ratio (B/C) of the wastewater increased from 0 to 0.3, indicating significantly improved biodegradability of wastewater [24]. Tomas Mackulak (2015) et.al was analyzed 13 psychoactive pharmaceuticals, illicit drugs and their metabolites in wastewater treatment plant influent and effluent. Tramadol (413–853 ng/L) and methamphetamine (460–682 ng/L) were the most concentrated compounds in the wastewater in winter and summer, respectively. The lowest efficiency was observed for tramadol, venlafaxine, citalopram and oxazepam (∼10%) and the highest efficiency was observed for amphetamine and THC-COOH (∼80%) [25]. Hilla Shemer (2006) et.al was studied degradation of Metronidazole using UV, UV/H_2O_2, H_2O_2/Fe^{2+}, and UV/ H_2O_2/Fe^{2+}. It was found that the degradation of Metronidazole by UV and UV/H_2O_2 exhibited pseudo-first order reaction kinetics. By applying H_2O_2/Fe^{2+}, and UV/ H_2O_2/Fe^{2+} the degradation kinetics followed a second order behavior. Increasing the concentrations of H_2O_2 promoted the oxidation rate by UV/H_2O_2. Adding more Fe^{2+} enhanced the oxidation rate for the H_2O_2/Fe^{2+}. and UV/ H_2O_2/Fe^{2+} processes. An increase of 20% in the removal efficiency of Metronidazole occurred with the photo Fenton reaction as compared to the Fenton oxidation [26]. A. Vlyssides (2008) et.al was studied the chemical pretreatment of pharmaceutical wastewater using Fenton's reagent. The optimum experimental conditions for the oxidation of pharmaceutical wastewater were found to be the following: $FeSO_4{\cdot}7H_2O$ concentration 2 g/L, H_2O_2 concentration 2 mL/L. In all cases, the overall efficiency mounted over 70%, significantly higher than the untreated sample. Conclusively, Fenton oxidation could be a feasible method for the pretreatment of pharmaceutical wastewater [27]. Mousavi (2011) et.al was investigate the degradation of Linear Alkylbenzene Sulfonate (LAS) in aqueous solution using Fenton's process in a batch reactor (at pH = 3 and 25°C). Results shows that the oxidation capacities of H_2O_2 /Fe^{+2} were highly dependent on the concentration of H_2O_2 and Fe^{+2}. Satisfactory decay rates of LAS to lock up biodegradable concentration level were obtained, and in the case for oxidation of 200 mg /L LAS, the optimum values were achieved at 600 and 130 mg/L for H_2O_2 and Fe^{+2}, respectively [28]. The objective of this study was to assess the possibility of various AOPs process in a laboratory-scale setup for the treatment of pharmaceutical wastewater as a functionof operating parameters based on COD, BOD and improvement in biodegradability index.

The objective of present study was to assess the possibility of UV, H_2O_2, UV/H_2O_2 and Fenton process in a laboratory-scale setup for the pretreatment of pharmaceutical wastewater and to determine the influences of various parameters on the pretreatment of pharmaceutical wastewater. The effects of strength of pharmaceutical wastewater based on COD, Fe^{2+}/H_2O_2 molar ratio, H_2O_2 dose, Fe^{2+} dose, pH and oxidation time was investigated to determine the optimal operating conditions for a better performance of the treatment of pharmaceutical wastewater by Fenton Process. So that the treated wastewater may be reused in the industry or safely discharge into different streams or transfer into a sewage treatment by means of advanced oxidation processes.

III. Material and Methods

3.1. Material

All the chemicals used in the present study were analytical reagent grade and purchased from Molychem Company. Hydrogen peroxide (H2O2) was used as oxidant reagent, Ferrous Sulfate Heptahydrate ($FeSO_4.7H_2O$) as source of Fe^{2+} catalyst. Sulfuric acid and sodium hydroxides are used to adjust the pH of the solution. The double distilled water is used to prepare the entire solution.

3.2. Study Area

In present study, real untreated pharmaceutical wastewater samples were collected from Anlon Healthcare Pvt. Ltd industry located at village-Pipaliya, Gondal, Dist. Rajkot, Gujarat, India. All the sampling and analysis procedures were adopted from Standard Methods for the Examination of Water and Wastewater (APHA, 2000). The sampling bottle was cleaned and rinsed carefully with distilled water, filled and seal air tightly. The sample was stored at 4°C within one to two hours of sample collection.

The pharmaceutical industry is manufacturing various synthetic organic chemicals (pharmaceutical bulk drug & intermediates). Manufacturing of all the products are carried out in batch process, which involve various unit processes like chlorination, hydrolysis, neutralization, oxidation, reduction and various unit operations like filtration, drying, distillation, separation, extraction and evaporation etc. After collection, the samples were immediately transferred to the Environmental Engineering Laboratories, Department of Civil Engineering, School of Engineering, RK University, Rajkot, Gujarat, India for further analysis. Characterization of real pharmaceutical wastewater samples was performed (Table-1). After that, real pharmaceutical wastewater were treated by various advance oxidation processes UV, H_2O_2, UV/H_2O_2 and Fenton process and samples were collected and analyzed at predetermined time intervals for various parameters (Table-2).

Table1. Characteristics of Pharmaceutical Wastewater

S.No.	Parameters	Unit	Results (mg/L)	Desirable Limit (mg/L) (Inland Surface)
1	pH		5.0-5.5	5.5-9.0
2	BOD	mg/L	801	30
3	COD	mg/L	8430	250
4	BOD/COD ratio	------	0.95	-------

IV. EXPERIMENTAL PROCEDURE

To study the percentage reduction of COD ofreal pharmaceutical wastewater byUV, H_2O_2, UV/H_2O_2 and Fenton process batch experimental runs were performed in the laboratory in batches as per shown in Figure-1 & 2. In each experimental run of UV, H_2O_2, UV/H_2O_2 andFenton process, an effluent sample of 100 ml was taken and placed in a 250 mL borosilicate glass beaker as reactor at room temperature on magnetic stirrer for continuous stirring.For UV and UV/H_2O_2 method, five low pressure UV lamp each of 6W capacity were used at the top of the reactor as a source of radiation and arranged into the reactor in such a manner that one or more can be turned on as desired. A digital pH meter was used for monitoring pH of the reaction mixture. A thermometer was placed in the solution for measurement of the temperature of the reaction mixture. Initially pharmaceutical wastewater was rigorously stirred for few minutes by magnetic stirrer for homogenization of sample. Respective pH of the sample was adjusted by addition of sulfuric acid or sodium hydroxide according to the need of the method UV, H_2O_2, UV/H_2O_2used i.e. 6.5±0.2 for UV method alone, 4.0±0.2 for H_2O_2 method alone and for UV/H_2O_2& Fenton 3±0.2. The requested amount of reagents was added according to the need of the method UV, H_2O_2, UV/$H_2O_2$and Fenton process. In Fenton process, ferrous sulfate ($FeSO_4.7H_2O$) was added, which was followed by addition of a measured quantity of 30% H2O2. The effective oxidation time for Fenton process was 120 minutes..Allexperiments were carried out in batch mode. Several set of experiments were carriedout to determine the dose of reagents keeping the pH, and reaction time constant toobtain optimum results. Sample were withdrawn periodically to estimate the percentage reduction of COD and BOD. To stop the reaction prior to analysis was done by addition of 1 N NaOH solution to sample and to increase pH above 7. The precipitate was removed by filtration using Whatman40 filter paper of 0.45µm, and the COD, BOD and biodegradability Index of the sample was measured. The change of volume of the sample at different steps was taken into account for COD calculation.

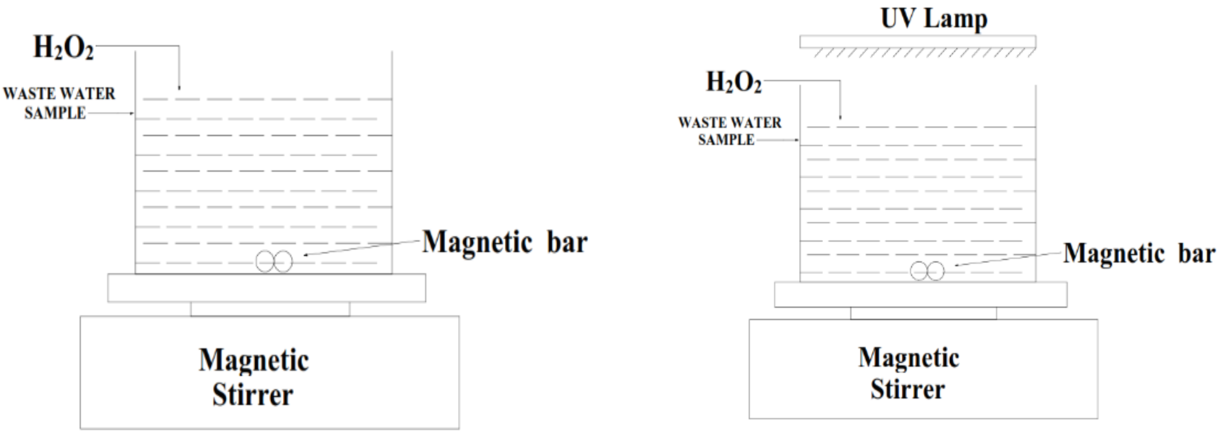

Figure 1. Experimental Setup a) H_2O_2 Method b) UV/H_2O_2 Method

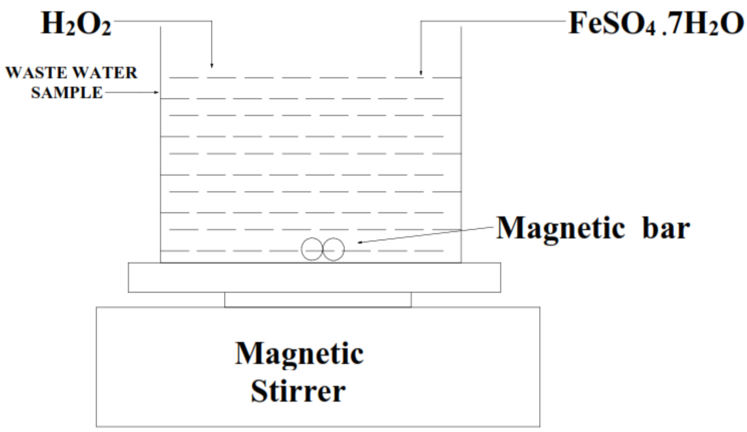

Figure 2. Experimental Setup Fenton Method

V. RESULTS AND DISCUSSION

5.1. UV Treatment

The effect of UV irradiation on the percentage COD, BOD and BOD/COD removal for the pharmaceutical effluent is shown in Figure-3 respectively. It can be noticed from the figure, UV irradiation increases from 1 to 8 hours, COD and BOD removal are increased from 2% to 8 % and 1% to 5 %, respectively. Improvement in biodegradability index of 0.98 from 0.95 was found after 8 hours UV irradiation.It was observed that the initial pH of the pharmaceutical wastewater was reduced from 6.5 to 5.9, after the UV radiation. The study conclude UV treatment alone need not much helpful for the biodegradability enhancement of pharmaceutical wastewater.

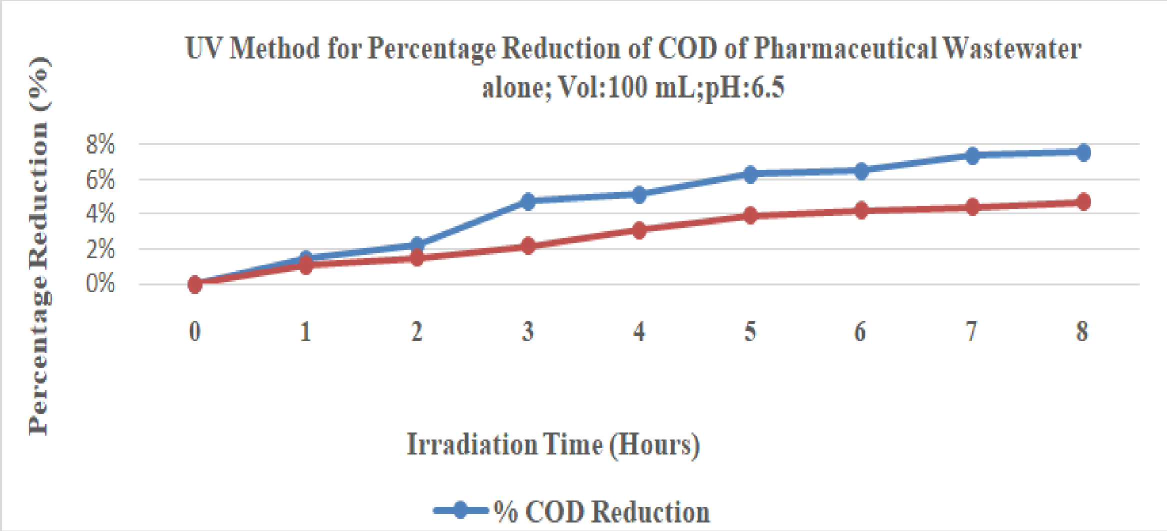

Figure3.UV Method for % Reduction of COD& BOD of Pharmaceutical Wastewater

5.2. H_2O_2 Treatment

The concentration of H_2O_2 is an important factor affecting the performance of the process, and the amount is directly connected to the generation of hydroxyl radicals. The effect of H_2O_2 concentration on the percentage COD, BOD and BOD/COD removal for the pharmaceutical effluent is shown in Figure- 4, 5respectively. It can be noticed from the figure, at optimum concentration of H_2O_2 of 1200 mg/L COD and BOD removal are increased from 3.4 % to 14.5 and 2.1 to 13.3 %, respectively. Minor variation in pH was observed after H_2O_2 treatment.Improvement in biodegradability index of 0.104 from 0.95 was found after treatment at 300 mg//L dose of H_2O_2.H_2O_2 treatment alone need not much helpful for the biodegradability enhancement of pharmaceutical wastewater.

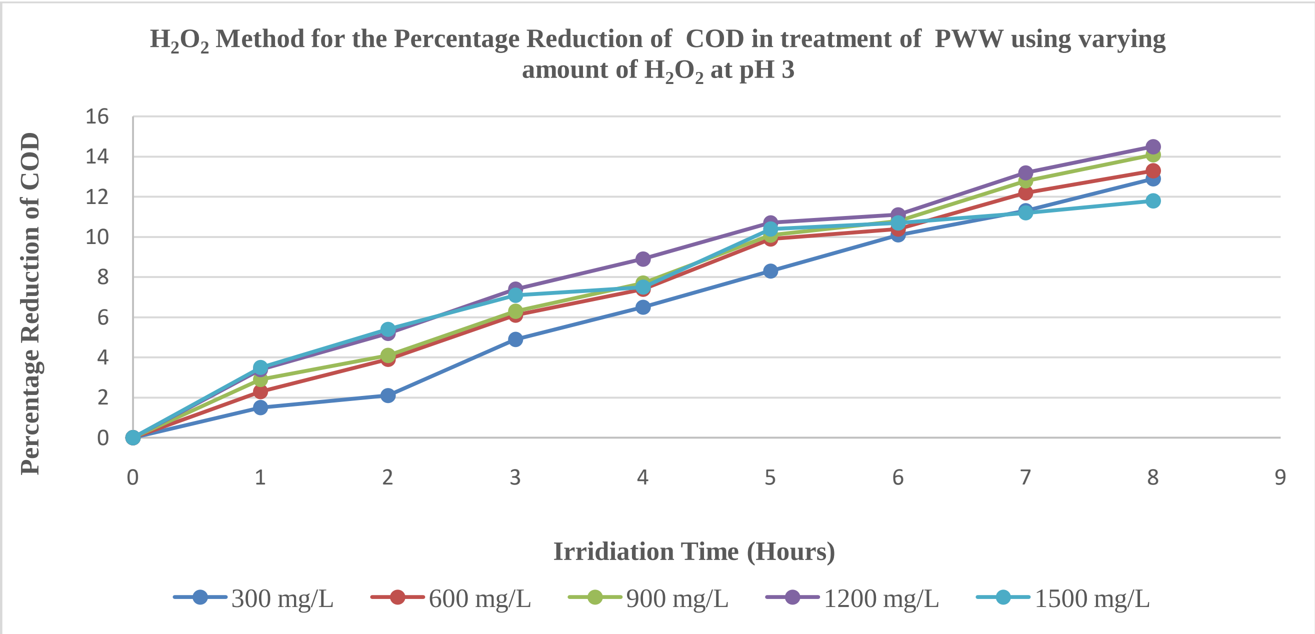

Figure4. H_2O_2 Method for % Reduction of COD of Pharmaceutical Wastewater

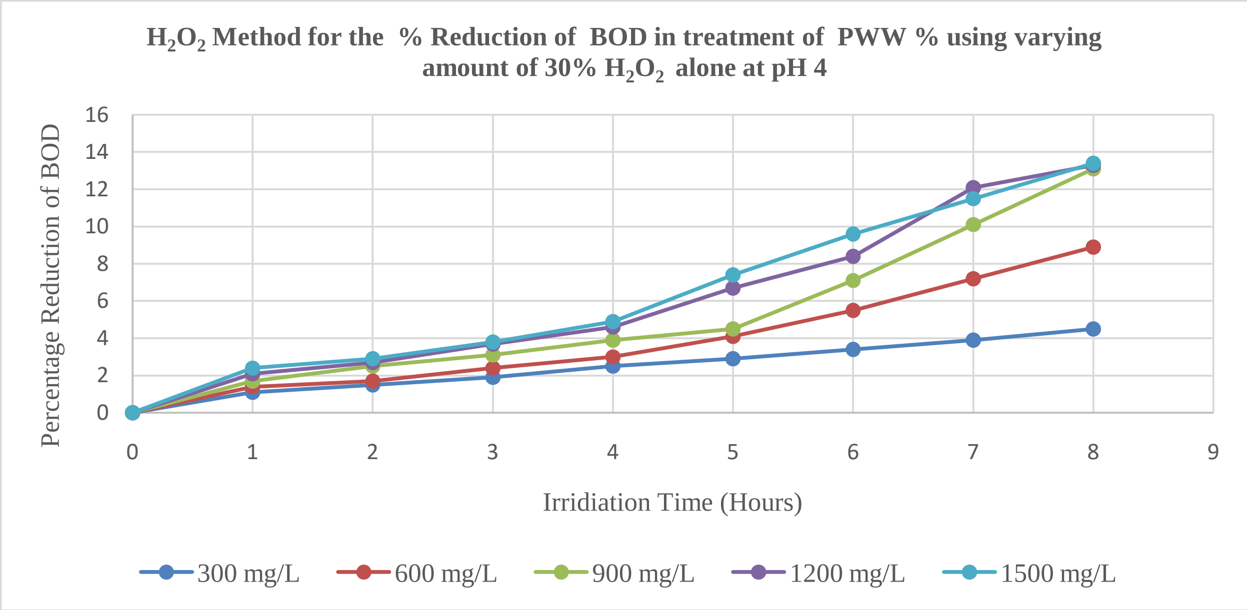

Figure5. H_2O_2 Method for % Reduction of BODof Pharmaceutical Wastewater

5. 3.UV/H_2O_2

The effect of H_2O_2 concentration and varying pH on the percentage COD, BOD and BOD/COD removal for the pharmaceutical effluent is shown in Figure-6, 7respectively. It can be noticed from the figure, at optimum concentration of H_2O_2 of 1200 mg/L COD and BOD removal are increased from 6.9to 20.5% and 3.1 to 16.2 %, respectively. UV/H_2O_2treatment methodis better than UV, H_2O_2 method, but not effective for the biodegradability enhancement of pharmaceutical wastewater.

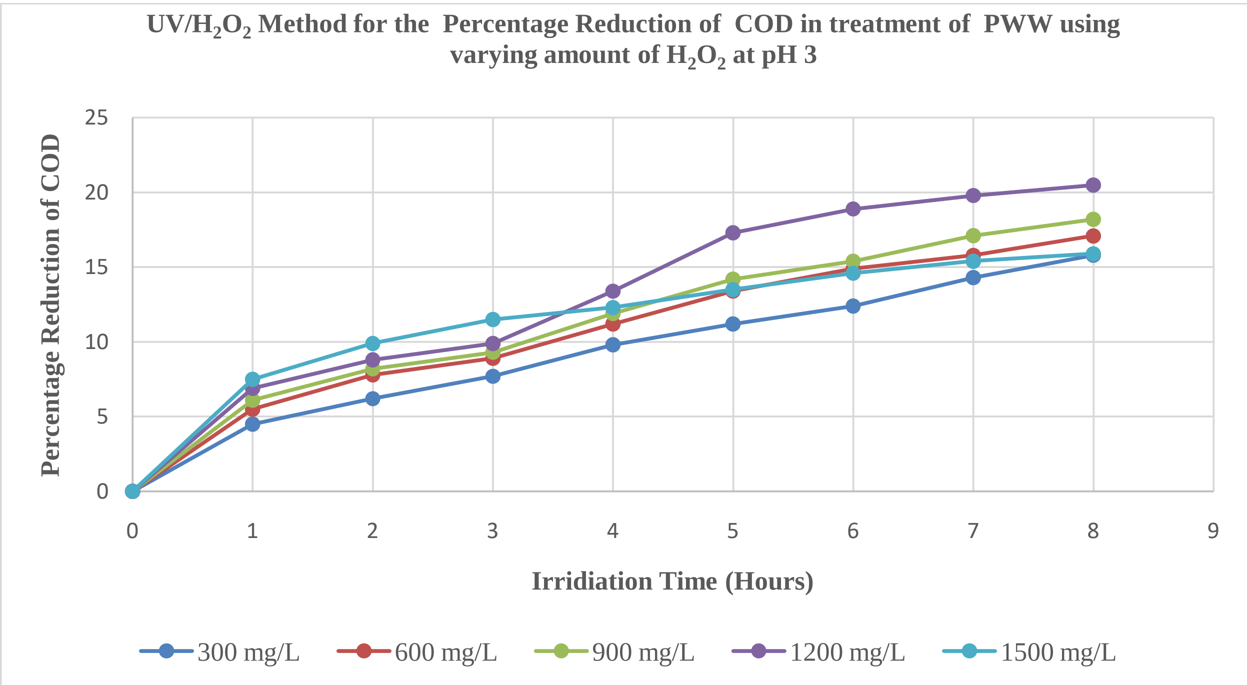

Figure6.UV/H_2O_2 Method for % Reduction of COD of Pharmaceutical Wastewater

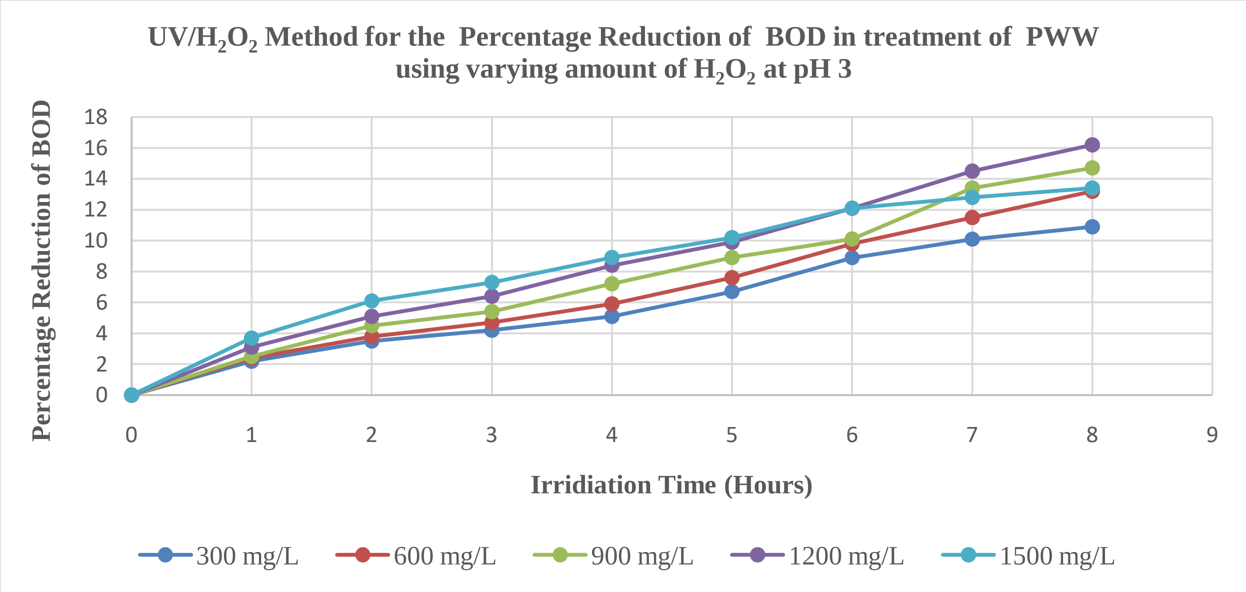

Figure7. UV/H_2O_2 Method for % Reduction of BOD of Pharmaceutical Wastewater

5.4. Fenton Method

The effects of strength of pharmaceutical wastewater based on COD, Fe^{2+}/H_2O_2 molar ratio, H_2O_2 dose, Fe^{2+} dose, pH and oxidation time was investigated to determine the optimal operating conditions for a better performance of the treatment of pharmaceutical wastewater by Fenton Process. The ranges of values of the variables used in the experiments are Fe^{+2}:H_2O_2 Molar ratio:1:1-1:20; Fe^{+2}: 8-1640 mg/L (0.147-29.4 mM); H_2O_2 (30% w/v): 100-1100 mg/L (1.47-32.34mM); pH: 1.5-6.5 and oxidation time:30-360 minutes.

5.4.1.Effect of H_2O_2 concentration

From the Figure-8, the concentration of H_2O_2 increases from 50 mg/L to 1100 mg/L with constant dose of 200 mg/L Fe^{+2} at pH 3, COD and BOD removal are increased from 36.4 to 68.2 % and 9.5 to 14.5 %, respectively. It is shown that the maximum COD removal of 68.2% was achieved at 800 mg/L H_2O_2 with 200 mg/LFe^{+2}. Improvement in BOD_3/COD of 0.235 from 0.95 was found after treatment at 200 mg/L dose of Fe^{+2}. Above 800 mg/L H_2O_2, no further increase of degradation could be observedin Figure-8. Even the decrease of COD removal observed at and above 800 mg/L H_2O_2can be ascribed to the scavenging of $OH^{\bullet}$by hydrogen peroxide.

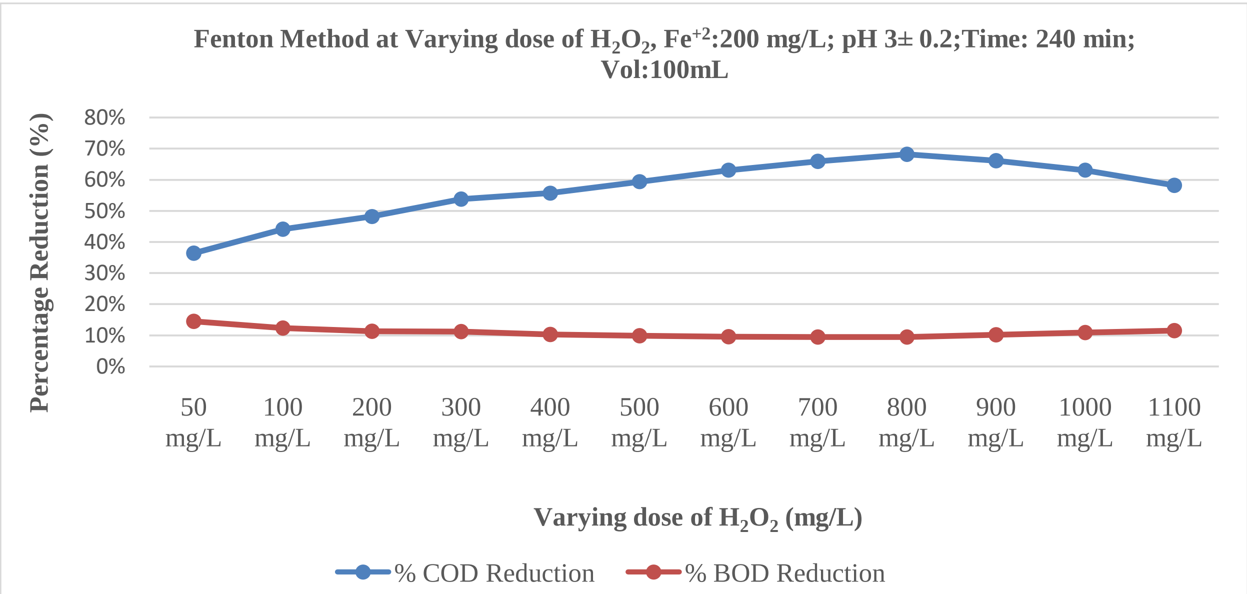

Figure 8. Fenton Method % Reduction of COD & BOD at varying dose of H_2O_2

5.4.2.Effect of Fe^{+2} concentration

It can be noticed from the Figure-9, the concentration of Fe^{2+} increases from 25 mg/L to 250mg/Lwith constant dose of 600 mg/L H_2O_2 at pH 3, COD and BOD removal are increased from 4.1 to 63.1 % and 2.1 to 19.9 %, respectively. Improvement in BOD_3/COD of 0.235 from 0.95 was found after treatment at 200 mg/L dose of Fe^{+2}. The results reported in Figure-9 suggest that the addition of Fe^{+2} above 200 mg/L would not help to increase the COD removal in the presence of 600 mg/L.

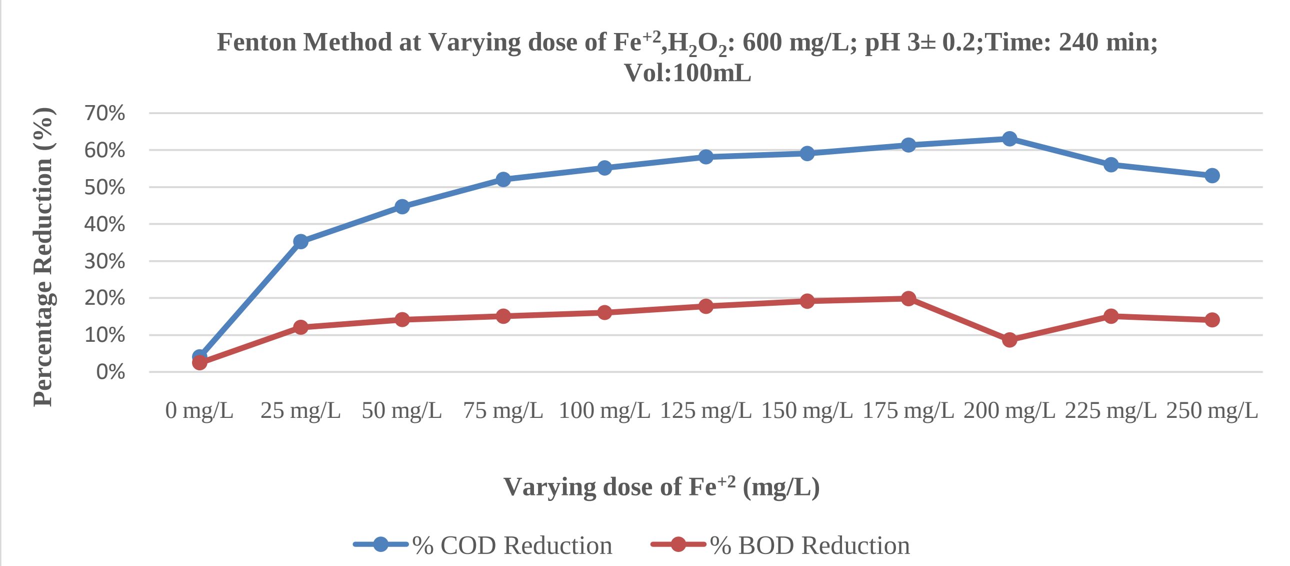

Figure9. Fenton Method % Reduction of COD & BOD at varying dose of Fe^{+2}

5.5. Effect ofpH

Experiments was conducted at varying pH from 1.5 to 6.5 with constant dose of 600 mg/L H_2O_2 and 200 mg/L of Fe^{+2},COD and BOD removal are increased from 5.4 to 8.2 % and 2.1 to 12.4 %, respectively. Improvement in BOD/COD of 0.270 from 0.95 was found after treatment at pH 3. The results shown in Figure-10 conclude that the Fe^{+2}/H_2O_2 system has its maximum activity at pH 3. A higher or lower pH sharply reduces the effectiveness of the Fenton's reaction. At low pH the complexation of Fe^{+3} with hydrogen peroxide is inhibited, therefore inhibiting the step of H_2O_2 reduction, while at a high pH ferric ions precipitate as ferric hydroxide, which catalyzes the decomposition of hydrogen peroxide.

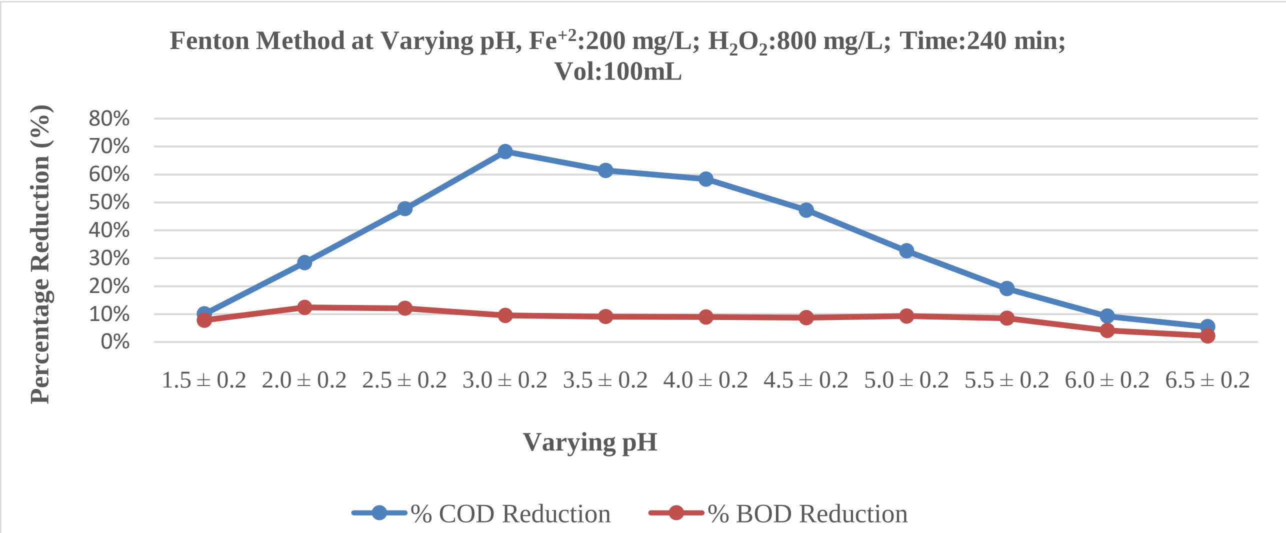

Figure10. Fenton Method % Reduction of COD & BOD at varying pH

5.6. Effect of Fe^{+2}/H_2O_2 Molar Ratio

Experiments was conducted at varying molar ratio from 1:1 to 1:20with constant dose of 600 mg/L H_2O_2, pH 3, oxidation time120 minutes. COD and BOD removal are increased from 37.1 to 59.2 % and 7.5 to 19.3 %, respectively.

Improvement in BOD/COD of 0.213 from 0.95 was found after treatment at pH 3. The results shown in Figure-11 conclude that the oxidation of pharmaceutical wastewater is strongly influenced by Fe^{+2}/H_2O_2 molar ratio. Maximum COD removal percentage was achieved at molar ratio 1:5 and 1:10.

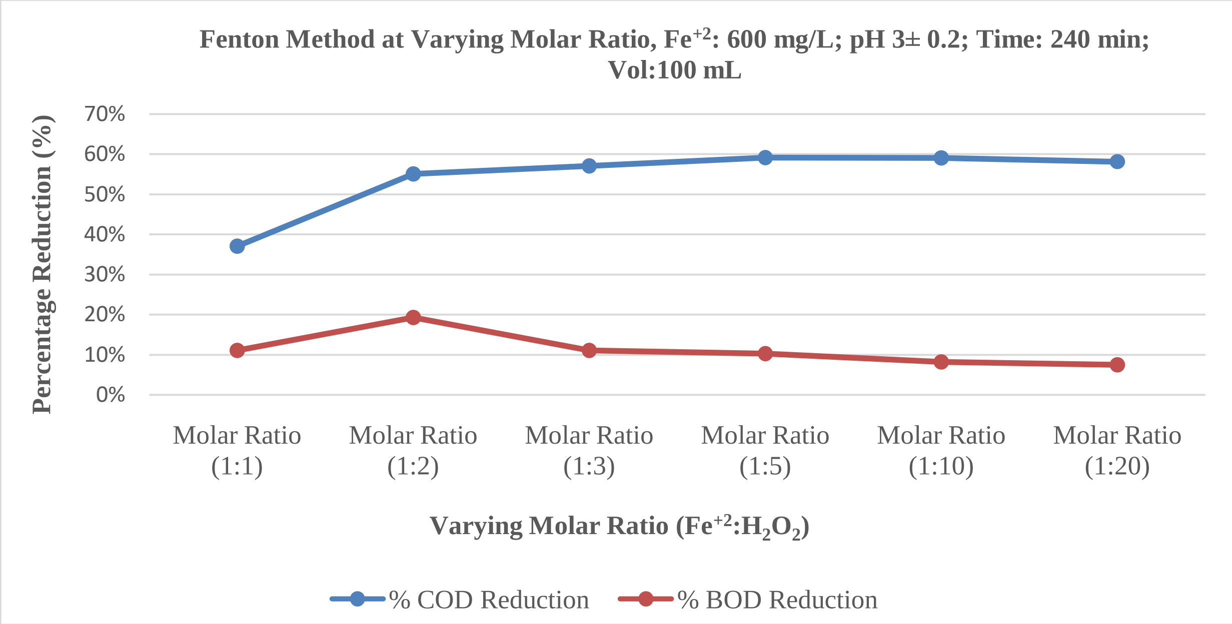

Figure-11: Fenton Method % Reduction of COD & BOD at varying molar ratio (Fe^{+2}:H_2O_2)

VI. CONCLUSION

The treatment of pharmaceutical wastewater by UV, H_2O_2, UV/H_2O_2 and Fentonprocess has been taken place at laboratory scale in batch process. The experimental results show UV, $H_2O_2$and UV/H_2O_2 are not effective for the treatment of pharmaceutical wastewater except Fenton process. The main objective of this study was to investigate the treatment of pharmaceutical wastewater for the removal of recalcitrant compound using Fenton process. Effects of various experimental parameters of the oxidation reaction of pharmaceutical wastewater were investigated. In the present study, it is concluded that that the initial pH, the initial concentration of H_2O_2, Fe^{+2} and molar ratio (Fe^{+2}:H_2O_2) had great influence on the treatment of pharmaceutical wastewater by the process of Fenton. The optimum conditions had been determined, and it was found that % COD removal efficiency obtained after 120 min of reaction, was about 68.2%. The optimal parameters were: initial pH=3; [H_2O_2] =600 mg/L; [Fe^{2+}]=200 mg/L and for a 8640 mg/L initial COD of pharmaceutical wastewater. The results showed that COD removal efficiency first increased then decreased with the increase of solution pH, and the highest COD removal appeared as pH was about 3.0. The COD removal rose from 36.4 % to 68.2 % with H_2O_2 concentration from 50 mg/L to 1100 mg/L and from 4.1 % to 63.1 % with Fe+2 concentration from 25 mg/L to 250 mg/L. The COD removal first increased then decreased with the mole ratio of Fe^{2+} to H_2O_2. The maximum COD removal appeared as the mole ratio of Fe to H_2O_2 is 1:5. The COD removal increased with time and leveled off after 120 minutes. At optimum condition, improvement in biodegradability index was takes place from 0.95 to 0.27, which shows that the Fenton process is very suitable for the treatment of pharmaceutical wastewaters. After combination of Fenton process with conventional methods, it can possible to reuse the treated wastewater in the industry for various purpose or safely discharge into different streams or transfer into a sewage treatment by means of advanced oxidation processes.

VII. REFERENCE

[1] G. NASA, "Precious Freshness : Water , the Way We Like It."
[2] Y. KATAOKA, Water resource management in Asia: Integration and interaction for a better future. 2005.
[3] S.M. Kanawade, "The Wastewater Treatment by Electrocoagulation & It ' s Reuse," Int. J. Chem. Phys. Sci., vol. 4, no. 1, pp. 93–104, 2015.
[4] S. G. Vrushali Pawar, "An overview of the Fenton Process for Industrial Wastewater," IOSR J. Mech. Civ. Eng., pp. 127–136, 2015.
[5] F. I. Chafia Bouasla, Mohamed El-Hadi Samar, "Degradation of methyl violet 6B dye by the Fenton process," Desalination, vol. 254, no. 1–3, pp. 35–41, 2010.
[6] S. C. Binay K Dutta, Sabtanti Harimurti , Idzham F. M. Ariff and D. Vione, "Degradation of diethanolamine by Fenton's reagent combined with biological post-treatment," Desalin. Water Treat., vol. 19, no. 1–3, pp. 286–293,

2010.
[7] M. S. Yalfani, S. Contreras, J. Llorca, M. Dominguez, J. E. Sueiras, and F. Medina, "Simultaneous in situ generation of hydrogen peroxide and Fenton reaction over Pd-Fe catalysts.," Phys. Chem. Chem. Phys., vol. 12, no. 44, pp. 14673–14676, 2010.
[8] J. J. Pignatello, E. Oliveros, and A. MacKay, "Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry," Crit. Rev. Environ. Sci. Technol., vol. 36, no. 1, pp. 1–84, 2006.
[9] J. Anotai, C. M. Chen, L. Bellotindos, and M. C. Lu, "Degradation of Ethanolamine by Fluidized-bed Fenton Process," pp. 1–11.
[10] V. Umadevi, "Fenton Process-A Pre Treatment Option for Hospital Waste water," Int. J. Innov. Eng. Technol., vol. 5, no. 2, pp. 306–312, 2015.
[11] G. A. Bensalah Nasr, Bedoui Ahmed, "Fenton Treatment of olive oil mill wastewater.pdf," J. Environ. Sci., vol. 16, no. 6, pp. 942–922, 2004.
[12] K. V. Plakas and A. J. Karabelas, "A study on heterogeneous fenton regeneration of powdered activated carbon impregnated with iron oxide nanoparticles," Glob. Nest J., vol. 18, no. 2, pp. 259–268, 2016.
[13] M. B. Miranzadeh et al., "Comparison of fenton and photo-fenton processes for removal of linear alkyle benzene sulfonate (LAS) from aqueous solutions," Polish J. Environ. Stud., vol. 25, no. 4, pp. 1639–1648, 2016.
[14] Y. Segura, F. Martinez, and J. A. Melero, "Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron," Appl. Catal. B Environ., vol. 136–137, pp. 64–69, 2013.
[15] R. Shetty and S. Verma, "Fenton ' s Reagent for the Treatment of Pharmaceutical Industry Wastewater," Int. J. Sci. Res., vol. 4, no. 7, pp. 3093–3096, 2015.
[16] R. J. Acharya, D. S. Vyas, and P. Shah, "Treatability study of fenton activated carbon catalytical oxidation for pharmaceutical waste water tratment," Int. J. Adv. Res. Innov. Ideas Educ., vol. 2, no. 3, pp. 2045–2057, 2016.
[17] W. Li, V. Nanaboina, Q. Zhou, and G. V. Korshin, "Effects of Fenton treatment on the properties of effluent organic matter and their relationships with the degradation of pharmaceuticals and personal care products," Water Res., vol. 46, no. 2, pp. 403–412, 2012.
[18] H. Tekin et al., "Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater," J. Hazard. Mater., vol. 136, no. 2, pp. 258–265, 2006.
[19] R. Nithyanandam and R. Saravanane, "Treatment of Pharmaceutical Sludge by Fenton Oxidation Process," Int. J. Chem. Eng. Appl., vol. 4, no. 6, pp. 359–364, 2013.
[20] S. Yolanda, M. Fernando, and J. A. Melero, "Pharmaceutical wastewater degradation: effective and economical treatment using waste-metallic iron shavings," Int. J. Environ. Stud., vol. 71, no. 2, pp. 200–208, 2014.
[21] Y. Yang, P. Wang, S. Shi, and Y. Liu, "Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater," J. Hazard. Mater., vol. 168, no. 1, pp. 238–245, 2009.
[22] D. Dolar, K. Kosutić, T. I. Zokic, L. Sipos, M. Markic, and M. Župan, "Combined methods of highly polluted pharmaceutical wastewater treatment - A case study of high recovery," Polish J. Environ. Stud., vol. 22, no. 6, pp. 1677–1683, 2013.
[23] S. V Satyanarayana, R. R. K, and N. Joodi, "Pharmaceutical waste water treatment using hydrogen peroxide oxidation method," Int. J. Appl. Res., vol. 1, no. 6, pp. 290–293, 2015.
[24] X. Cui et al., "Pilot-scale treatment of pharmaceutical berberine wastewater by Fenton oxidation," Environ. Earth Sci., vol. 73, no. 9, pp. 4967–4977, 2015.
[25] T. Mackulak, M. Mosny, R. Grabic, O. Golovko, O. Koba, and L. Birosova, "Fenton-like reaction: A possible way to efficiently remove illicit drugs and pharmaceuticals from wastewater," Environ. Toxicol. Pharmacol., vol. 39, no. 2, pp. 483–488, 2015.
[26] H. Shemer, Y. K. Kunukcu, and K. G. Linden, "Degradation of the pharmaceutical Metronidazole via UV, Fenton and photo-Fenton processes," Chemosphere, vol. 63, no. 2, pp. 269–276, 2006.
[27] A. Vlyssides, E. M. Barampouti, S. Mai, A. Stamatoglou, and D. Skouroumounis, "Fenton oxidation and biological treatment on pharmaceutical wastewater," WIT Trans. Ecol. Environ., vol. 109, pp. 771–780, 2008.
[28] S. A. R. Mousavi, A. H. Mahvi, and S. Nasseri, "Effect of fenton process (H2O2/Fe2+) on removal linear alkylbenzene sulfonate using central composite," Iranian J. Environ. Health Sci. Eng., vol. 8, no. 2, pp. 129–138, 2011.

