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Treatability Study on COD Reduction using Advanced oxidation Process for Active pharmaceutical Ingredient Effluent

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Abstract *—Advanced Oxidation Process (AOP) is the emerging technology used for site remediation. two different oxidants are being used for this technology, i.e., Hydrogen peroxide, and sodium Persulfate. Mostly being used is catalyzed hydrogen peroxide among all because of its efficiency to remediate and is also less costly. The objective of this paper is Pharmaceutical API wastewater sample using Catalyzed Hydrogen Peroxide. Different concentrations of peroxide were tested.. The present study showed that catalysed hydrogen peroxide can be effective to decolorize and demineralize the groundwater and used for Wastewater treatment. The experimental results indicate that during Fenton's oxidation, COD reduction was faster than degradation .The rate of oxidation was influenced by dose of* Fe^{2+}*,* H_2O_2*,. The optimum conditions required for maximum degradation were 32.53g/L of* H_2O_2 *and accordingly Fe2+ dose. Fe2+ added is 5-25 parts wt/wt to hydrogen peroxide. This investigation has demonstrated the potential of applying Fenton's process for the treatment of Wastewater.*

Keywords-Advanced Oxidation Process, Wastewater treatment, Oxidation, COD degradation, Hydrogen peroxide and Sodium Persulfate

1. INTRODUCTION

Pharmaceutical compounds are being used for several beneficial purposes in modern society but simultaneously pharmacy industries are releasing very toxic contaminants in the environment directly or after chemical modifications. Moreover, pharmaceutical compounds may enter the environment by different routes such as discharge of treated wastewater, seepage from landfills sites, sewer lines, runoff from animal wastes etc. Even though various physical and biological processes occurring in aquatic ecosystem may cause reduction of many pharmaceutical compounds, trace concentrations of human and veterinary pharmaceutical compounds as well as their metabolites have been detected in different water bodies like surface water, groundwater and drinking water sources. The pharmaceutical industry in India is the world's third-largest in terms of volume and stands 14th rank in terms of value. It is growing at about 8 to 9 percent annually and is estimated to be worth 4.5 billion dollar. Different industries including pharmaceuticals, chemicals, paints etc. are speedily growing in India which disposes off their effluents into the streams either directly or after partial treatment. It has been found that the pharmaceutical compounds reach the environment and can be considered as environmental pollutants. The environmental exposure routes of pharmaceuticals into the environment are manufacturing units and hospital effluents, land applications (e.g., bio solids and water reuse) etc. However; sewage treatment services are not always successful in removing the active chemicals from waste-water. Consequently, pharmaceuticals find their way into the aquatic environment, where they directly affect aquatic organisms and can be incorporated into food chains. In a recent study, the extraordinarily high levels (mg/L) of several drugs were found in the effluents from local wastewater treatment plant.

SR. NO.	pH	COD (mg/L)	BOD (mg/L)	TDS (PPM)	CHLORIDES (mg/L)	SULFATE (mg/L)
1.	6.75	19520	5700	16325	8265	1045

Table no. 1: Characteristics of Wastewater Sample

Wastewater treatment technologies, each of these has limitations, which generally fall into two categories: (1) Reactivity with contaminants of concern and (2) mass transfer of contaminants from the sorbed phase and dense non-aqueous phase liquids (DNAPLs) to the medium in which the reactive species exists, usually water . AOP is the delivery of strong chemical oxidants to the subsurface for the purpose of treating organic contaminants. The first AOP process that was investigated in laboratory research and developed at full scale was catalyzed H2O2 propagations (CHP), commonly known as modified Fenton's reagent.Shortly following the initial use of Fenton's reagent, treatment came into widespread use alone or in combination with others.Recently, persulfate as a chemical oxidant has been found to be promising for in situ remediation of recalcitrant organic contaminants in groundwater and soil.
Most commonly used chemical oxidant is catalysed hydrogen peroxide (CHP), which works as shown in following reaction:

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

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^{+} + HO_2 \quad (2)$$

The process is based on the catalyzed decomposition of hydrogen peroxide by soluble iron, iron chelates, or iron minerals to generate the strong oxidant hydroxyl radical (OH·), as well as other reactive oxygen species.The nature of the catalyst used, the pH, and the hydrogen peroxide concentration are some of the important process parameters that are to be kept in mind while using peroxide in AOP. The iron oxide minerals naturally present in the subsurface serve as effective CHP catalysts. Soluble iron and iron minerals are most effective at acidic pH, and iron chelates are also effective at neutral pH regimes.
If iron minerals are used as the CHP catalyst, the pH must be maintained at less than 4.0.Hydrogen peroxide concentrations in the 2–12% (0.6–3.6 M) range are typically used for AOP applications.

The present study attempts to use Fenton's reagent to treat the Wastewater which has the characteristics shown in table no. 1.

2. MATERIALS AND METHODS

2.1. Reagents

Hydrogen peroxide, Sulfuric acid, Sodium Persulfate, Mercuric sulphate, Ferrous ammonium sulphate, silver sulphate, ferroin indicator , potassium dichromate, sodium hydroxide, hydrochloric acid, were used of analytical grade during experiments. All reagents and solutions employed for this work were prepared with deionised water.

2.2. Experimental setup

All the experiments were conducted in 100mL borosilicate. A known volume of wastewater sample was taken in the reactor.the sample was tested with different dosing of 30% hydrogen peroxide i.e. 0.25g/L, 0.5g/L and 0.75g/L, with ferrous sulfate addition and stirred using magnetic stirrer. All the experiments were carried out without any pH adjustment. Hydrogen peroxide and ferrous sulfate were added .Fe2+ added is 5-25 parts wt/wt to hydrogen peroxide. After reactions completed, samples were filtered through 0.45 lm filter paper and immediately analysed

2.3. Analysis

pH, chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS) and chlorides were measured using Standard Methods.
All the experiments were conducted in 100mL and 200mL borosilicate beakers. Two Oxidants were initially used i.e. Hydrogen peroxide and sodium persulfate to evaluate the efficiency of AOP technologies.
Activator Used- Acidic medium Sulfuric acid and alkaline medium Sodium hydroxide and No stabilizer needed for Sodium Persulfate and for Hydrogen peroxide Activator Used- Ferrous Sulfate (Fe2+) at different concentration and Acidic medium Hydrochloric Acid and No stabilizer needed. Activator used to increase the rate of reaction was sodium hydroxide for sodium Persulfate and ferrous sulfate for hydrogen peroxide.

3. RESULTS AND DISCUSSIONS

3.1 Experimental Trials With Sodium Persulfate

This trial run was started with the different ratio addition of sodium Persulfate concentration 1:05 to 1:10 for optimum dose found inefficient in removing COD. So, the concentration of different ratio sodium Persulfate is increased. Then first was in 1:05 ratio 12g/L sodium persulfate with NaOH used as an activator in 200ml sample. 0.1 N NaOH was added in wastewater sample to make sample's pH as 12. taken for contact time of 20 min on magnetic starrer Then Allow it to settle down and measured final characteristics at different time interval. The samples were timely drawn from the reactors for analysis. Some other ratio of sodium Persulfate and the results of the experiment are shown in table 3.1

FIGURE 3.1: Different ratio addition of sodium Persulfate concentration

Table 3.1: Treatment result with sodium Persulfate at different concentration

Sr.no	COD to Sodium Persulfate Ratio	Sodium Persulfate Concentration (g/l)	Initial COD	COD Reduction (g/l)			
				Day 1	Day 2	Day 4	Day 7
1.	1:0.5	12.09	19520	19000	15600	11200	14600
2.	1:1	24.19	19520	18400	17200	14200	17000
3.	1:2	48.39	19520	19200	15200	13400	17800
4.	1:3	72.59	19520	18600	16800	15600	21600
5.	1:4	96.78	19520	18000	17600	20000	22000
6.	1:5	120.98	19520	19200	18000	15600	16800
7.	1:6	145.18	19520	18800	17400	22800	24000
8.	1:7	169.37	19520	19200	17600	16200	23400
9.	1:8	193.57	19520	18000	14400	14000	15800
10	1:9	217.77	19520	18400	15600	19800	23200
11	1:10	241.96	19520	19200	17400	16200	15000

3.2 Experimental Trials With Hydrogen peroxide

When different concentrations of hydrogen peroxide were examined with different concentration of Fe2+ this concentration was tested on wastewater at different ratio of Hydrogen peroxide and Fe2+. Analysis was done in 30 min or 2 hr to check the COD. After 2 hr the oxidant concentration present in the reactor became zero. After that time span COD was analysed. At different concentration of Hydrogen peroxide and COD ratio is gave different result about COD reduction.COD reduction and different ratio of sodium Persulfate is shown in table 3.2

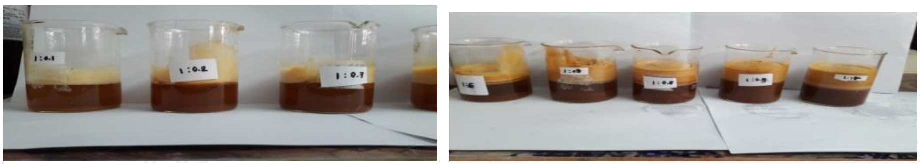

FIGURE 3.2: Different ratio addition of Hydrogen peroxide concentration

Table 3.2: Treatment result with Hydrogen peroxide at different concentration

Sr.no	COD to hydrogen Peroxide Ratio	Hydrogen Peroxide concentration (ml)	Feso4 Concentration (gm/l)	Initial COD(mg/l)	Final COD (mg/l)
1.	1:0.1	6.50	2.1666	19520	17600
2.	1:0.2	13.01	4.3666	19520	15600
3.	1:0.3	19.52	6.5066	19520	12800
4.	1:0.4	26.02	8.6733	19520	10200
5.	1:0.5	32.53	10.843	19520	9800
6.	1:0.6	39.04	13.013	19520	11400
7.	1:0.7	45.54	15.18	19520	14800
8.	1:0.8	52.04	17.35	19520	15600
9.	1:0.9	58.56	19.52	19520	18200
10.	1:1	65.06	21.68	19520	21800

4. CONCLUSION

Hydrogen peroxide based CHP has near-universal reactivity with all sorbed and soluble organic contaminants. The present study showed that catalysed hydrogen peroxide can be effective to decolorize and demineralise the wastewater and used as water treatment. The experimental results indicate that during Fenton's oxidation, COD reduction was faster than degradation. The rate of oxidation was influenced by dose of Fe^{2+}, H_2O_2, and sodium Hypochlorite. The optimum conditions required for maximum degradation were 32.53g/l of H_2O_2, and accordingly Fe2+ dose. Fe2+ added is 5-25 parts wt/wt to hydrogen peroxide. This investigation has demonstrated the potential of applying Fenton's process for the treatment of Wastewater.

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