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Pharmaceutical waste water treatment using hydrogen peroxide oxidation method

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Abstract

Pharmaceutical drugs are manufactured in many ways either by chemical synthesis or biological derivatives or fermented compounds. The waste water generated from pharmaceutical industry is a complex mixture of many organic compounds, solvents and inorganic salts. The wastewater is colored, turbid with high BOD, COD and contains highly toxic water pollutants. In the present study dilution technique is introduced in primary treatment followed by hydrogen peroxide oxidation in secondary treatment and finally in tertiary treatment passed through R.O process. The results suggested that the treatment method is effective and more efficient for pharmaceutical industry effluent up to 25,000mg/l COD values.

Keywords: Dilution, Hydrogen peroxide, Oxidation, Wastewater

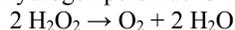
1. Introduction

Pharmaceutical industry waste water is a complex mixture of many compounds, solvents and salts (Mohanrao, 1970) [4]. Waste water is being generated during manufacturing process of bulk drugs and pharmaceuticals. The effluent contains high level of organic material, numerous nutrients, toxic compounds and high COD values varying from 5000 mg/l to 50,000 mg/l. The COD is non-biodegradable (Abu Safa, 2012) [1]. Moreover the sludge generated from Pharma industry effluent treatment is highly toxic and hazardous. Very few industries have their own treatment facilities with zero liquid effluent discharge. Most of the industries are treating their effluents partially and then sending the waste water to the common effluent treatment plant by tankers. These common effluent treatment plants process cannot accept COD values more than 25,000 mg/l. Besides COD and BOD content, the waste water contains nearly 30- 40% suspended and settle able solids. The pollution load of waste water depends on the process and type of drug that was going to be manufactured. Oil and Grease is another toxic pollutant that is contributing for water pollution and has an impact on aquatic life. As Common Effluent Treatment Plants cannot treat waste water containing COD values more than 25,000ppm. (Shreeshivasan Chaliapin, 2010) [10]. Effluents from manufacturing operations in the pharmaceutical industry, such as antibiotic formulation, usually contain recalcitrant compounds. An approach towards appropriate technology for the treatment of pharmaceutical wastewaters has become imperative due to strict water quality legislation for environmental protection. Deegan, Eegam Dr. *et al.* (2011) [3] Traditional wastewater treatment methods, such as activated sludge, are not sufficient for the complete removal of active pharmaceutical ingredients and other wastewater constituents from these waters (Mudri, 1968) [5]. As a result, complementary treatment methods such as membrane filtration, reverse osmosis and activated carbon are often used in conjunction with the traditional methods for treatment of industrial wastewater.

In the present study, Pharmaceutical waste water treatment adopted dilution technique followed by Oxidation, coagulation and finally passing through the membranes. The constituents or complex compounds present in pharmaceutical waste water are oxidized using hydrogen peroxide (Zwiner, 2000) [11]. Oxidation is a part of secondary treatment. Most of the toxic organic compounds, those are present in the pharmaceutical effluents are oxidized using different oxidizing agents. Hydrogen peroxide has been used to oxidize high levels of compounds that are toxic and complex. Hydrogen peroxide is one of the most dependable and very effective oxidizing agents. It is suitable for the oxidation of pollutants particularly of pharmaceutical origin.

1.1 Enhanced Reduction of COD with Hydrogen peroxide.

Dilution technique and hydrogen peroxide are separating the COD contributing compounds. Free oxygen molecule from hydrogen peroxide is initiating the COD reduction process.



Mechanism: It is a two-step mechanism.

Step 1: $\text{COD} + \text{H}_2\text{O}_2 \rightarrow \text{oxidized species} + \text{reduced species}$.

Step 2: $\text{Oxidized species} + \text{H}_2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Salts}$.

2. Literature Review

Miranda. N 1989 [6] developed a new biological treatment process to treat low COD values up to 3000ppm pharmaceutical effluents. This treatment process consists of introduction of certain bacteria followed by extended aeration.

Rosen. M *et al.* 1998 [9] developed a new process for treatment of Pharmaceutical Waste Water. This process involves different methods including activated sludge process both aerobic and anaerobic processes and chemical treatment methods like flocculation and clarification methods.

Raj. D.S.S and Anjaneyulum. Y [7], developed a method to treat palm oil mill effluent using aerobic oxidation integrated

with chemical treatment in 2005. Most of the industries are following this method for treatment of their effluents. This method is best suitable for COD values up to 25,000mg/l.

3. Material and Methods

Outline of Study:

The study is carried out in two different steps. The first step involved the collection of samples from a pharmaceutical industry and qualitative analysis of the samples for different parameters using standard methods of analysis. The second step involves the treatment of the samples in 3 different stages.

3.1 Sample Collection

Physicochemical Analysis of Samples

Five pharmaceutical waste water samples are collected from local pharmaceutical industry from Hyderabad. The collected pharmaceutical waste water samples were analyzed using standard methods for analysis of water, wastewater and Vogel's Quantitative Inorganic Analysis. These samples were analyzed for pH, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and Oil & Grease and the results are shown in Table 1.

Table 1: Physicochemical characterisation of untreated effluents

S.NO	Parameter	Units	Sample No:1	Sample No:2	Sample No:3	Sample No:4	Sample No:5
1	pH	---	3.54	2.9	4.1	5.26	4.55
2	TDS	mg/l	19400	21900	17400	17250	19630
3	TSS	mg/l	2040	2170	1990	1560	1685
4	C.O.D	mg/l	15920	16860	15400	13800	14760
5	O & G	mg/l	1550	1360	1650	1080	1290

A graph was drawn keeping TSS values in X-axis and COD values in Y-axis and shown in Fig 1.

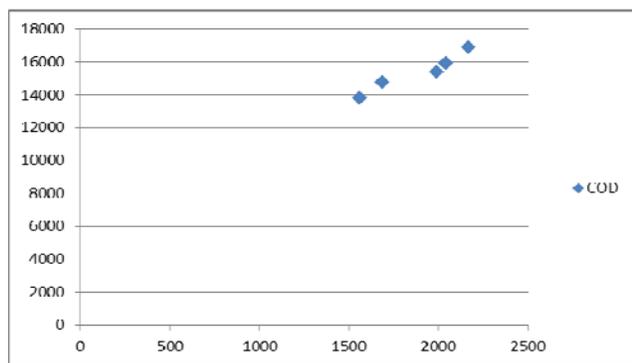


Fig 1: TSS vs. COD.

Treatment Process

The treatment of pharmaceutical waste water is divided into three stages. They are primary treatment, secondary treatment and tertiary treatment.

3.2 Primary treatment

In the Primary treatment dilution tank is introduced before the bar screens. All the five samples were diluted so that to bring down the COD concentration to less than 3000mg/l. Dilution played a major role in treating high COD pharmaceutical waste water. Dilution technique will reduce the concentration of pollutants. Initially fresh water is drawn for dilution, thereafter the treated water from ETP can be

reused as dilution water. The effluent is passed through Bar Screens to remove all suspended Solids. Then the Oil & Grease content of the effluent is removed completely by passing through a specially designed Oil separation tank followed by sedimentation tank, where all the suspended solids are settled down by gravity. A detention period of 4-5 hours is provided in the sedimentation tank (Bhaskaran T.R, 1971) [2].

Waste water → Dilution → bar screens → Oil & Grease → equalization → clarification →

3.3 Secondary Treatment

Secondary treatment consists of four stages. They are oxidation, aeration, coagulation and clarification.

→ Oxidation → Aeration → Coagulation → Clarification.

In secondary treatment process, the effluent is exposed to chemical treatment. In this present project study, the effluent from the primary sedimentation tank is allowed to enter into an oxidation tank where 10% Hydrogen peroxide is added at a rate of 4-5 mg/l with a retention time of 30 minutes followed by aeration for two hours to oxidize the complex compounds. 2HP blower is sufficient up to 6 cubic meters of effluent. After aeration 50-100 mg/l poly aluminum chloride coagulant is added till the pH is reached to 7.5. The oxidation tank overflow is collected in a clarifier where all sludge is settled at the bottom and clear water overflow from clarifier.

3.4 Tertiary treatment process

Finally in the tertiary treatment the effluent is passed through a sand bed to remove all fine suspended particles if any. In

tertiary treatment the water from clarifier out let enters the Rapid Sand Filter followed by Activated Carbon Filter and finally passes through the membrane filter. Activated carbon filter (ACF) is used for final filtration. ACF will remove

color, odor and organic matter in the effluent. The treated effluent collected from sand bed is analyzed and the results are tabulated in Table 2.

Table 2: Physicochemical characterisation of treated effluents

S. No	Parameter	Units	Sample No:1	Sample No:2	Sample No:3	Sample No:4	Sample No:5
1	pH	---	6.5	6.5	6.5	6.5	6.5
2	TDS	mg/l	430	485	360	290	440
3	TSS	mg/l	< 10	< 10	< 10	< 10	< 10
4	C.O.D	mg/l	220	240	190	130	180
5	O & G	mg/l	10	8	10	6	8

4. Results and Discussion

4.1 pH

It was observed that all the samples pH is acidic in nature and varied between 2.9 to 5.26 before treatment pH values generally depend on nature of chemicals used in synthesis and other compounds and their reaction mechanism. Some drugs release neutral or highly alkaline effluents. The pH was fixed at 6.5 for all the samples to reach 98% efficiency of treatment.

4.2 Oil & Grease

The source of oil and grease in effluents is due to fatty acids and esters. Oil and Grease varied from 1080mg/L to 1650mg/L before treatment. After the treatment the O & G values varied from 6mg/L to 10mg/l.

4.3 TDS

Total Dissolved Solids are very high and varied from 17250mg/L to 21900mg/L.TDS before treatment. After treatment the TDS values varied from 190mg/L to 135mg/l. There is enough scope to increase or to decrease the TDS values by operating bypass valve of R.O. Process.

4.4 TSS

Total suspended solids (TSS) were more prominent in all the samples. TSS varied between 1560mg/L to 2170 mg/L before treatment. After treatment the TSS values are less than 10mg/L. This is due to R.O. Process in tertiary treatment.

4.5 COD

Chemical oxygen demand is mainly due to organic matter present in the effluent. Organic matter is two types, one is bio-degradable and the other is non bio-degradable. In pharmaceutical industry the effluent contains non-biodegradable chemical oxygen demand. COD values varied from 13800mg/L to 16860 mg/L before treatment. After treatment the COD values varied from 130mg/L to 240 mg/L.

Table 3: COD values before and after treatment

Sample No	COD in mg/L Before Treatment	COD in mg/L After Treatment
1	15920	220
2	16860	240
3	15400	190
4	13800	130
5	14760	180

5. Conclusions

The following conclusions are drawn from the present study of "Waste Water Treatment Technologies using Membranes" with reference to Pharmaceutical industry.

- Dilution method is yielding better results. There are two advantages, one is we can reduce COD values 10 times lower, and the second one is the kinetics of oxidation reactions are highly influenced.
- It was established that Total Suspended Solids (TSS) are directly proportional to COD values.
- In this present study Bar Screens are fixed after dilution tank. This method enhances the reduction of TSS.
- In Secondary Treatment, Hydrogen Peroxide oxidized complex organic compounds and facilitated to precipitate these complex compounds. After secondary treatment the COD values are reduced to more than 90%.

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