Abstract: Pesticides belong to the class of persistent chemicals in the environment which cause serious health hazards. The wastewater generated from the Pesticide industry are potentially pollutant, because of their large volume and their refractory nature. Biological treatment generally is not capable to remove these compounds. Advanced Oxidation Processes (AOPs) represent the fast-developing area in water and wastewater treatment by which non-biodegradable and difficult to biodegradable compounds can be removed. Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of Pesticide Industry Effluent containing non-biodegradable compounds. All AOP are designed to produce hydroxyl radicals HO•. It is the hydroxyl radicals that act with high efficiency to destroy organic compounds. Generation of HO• is commonly accelerated by combining oxidizing agents. This paper discusses the use of Advanced Oxidation using Ozone and Hydrogen Peroxide for the removal of Pesticide Industry Effluent.

Keywords: Pesticide Industry Effluent, Ozonation, Ozone + Hydrogen Peroxide, Advanced oxidation process, AOPs.

I. INTRODUCTION

India is the fourth largest producer of agrochemicals globally, after United States, Japan and China. The agrochemicals industry is a significant industry for the Indian economy. India’s agrochemicals consumption is one of the lowest in the world with per hectare consumption of just 381 g only compared to US, Japan and China [1].

Pesticides have become an unavoidable commodity in our modern life. The introduction of pesticides in the environment cause serious issues of which water pollution is of primary importance. Removal of these compounds from water is a challenge to the environmental engineers because most of them are nonbiodegradable. Most of the chemical treatment methods utilized for pesticides degradation cause the formation of secondary pollutants. Advanced oxidation processes employ different methods for generation of the hydroxyl radicals. Hydroxyl radicals are very reactive and not highly selective. They can convert the pollutants to CO₂ and water or at least to degradable compounds [3].

Agrochemical manufacturing industry effluent causes pollution problems due to the toxic components, high chemical oxygen demand (COD), high Total dissolved solids (TDS) and high acidic pH. The most important portion of contamination due to this effluent is observed in agricultural areas and in surface waters that come from agricultural areas. Major quality of pesticide pollution is released during pesticide manufacturing process. Pesticide, usually have direct adverse effects on the living organisms. Pesticides are highly toxic and carcinogenic in nature even at picogram loads. Moreover, it persists in nature for long period of time. The process of pesticide removal from the industrial wastewater is of great importance because of well-known pesticide resistance to microbial degradation and has tendency to bio-accumulate in the soil flora and fauna. Pesticides are carcinogenic and mutagenic in nature. Hence biological treatment processes have their own limitations like toxicity and inefficiency in performance. Acclimatized microbial culture can be used for the treatment of this wastewater [2].

For treatment of effluent from the pesticides industry, there are many options depending on the type of waste. Best practice may include segregation of streams, characteristics-wise individual treatment and common treatment subsequently i.e., separation of toxic and highly organic streams for incineration; detoxification of moderate streams; directly sending the easily biological streams to secondary treatment; separation of inorganic streams for separate treatment [1].

II. ADVANCED OXIDATION USING OZONE

All AOP are designed to produce hydroxyl radicals HO•. It is the hydroxyl radicals that act with high efficiency to destroy organic compounds. Generation of HO• is commonly accelerated by combining oxidizing agents. AOP combine ozone (O₃), ultraviolet (UV), hydrogen peroxide (H₂O₂) and/or catalyst to offer a powerful wastewater treatment solution for the reduction and/or removal of residual organic compounds as measured by COD. Out of this all, Ozonation is one of them [4]. Ozonation is a widely used technique for the removal and reduction of pollutants from effluent. The reduction of compounds occurs through the action of ozone itself as well as through the radicals generated in aqueous medium. Ozone is used as an oxidizing gas which reacts with inorganic and organic compounds of effluent, directly or indirectly through the free formation of hydroxyl radicals. It is badly soluble in water, but once in contact with water, it becomes highly unstable and rapidly degrade through a complex series of reactions, in accordance with the
The mechanism of hydroxide ions (HO\text{-}). The major reactions taking place are:

\begin{align*}
\text{O}_3 + \text{HO}^- & \rightarrow \text{HO}_2^- + \text{O}_2 \\
\text{HO}_2^- + \text{O}_3 & \rightarrow \text{O}_3^- + \text{HO}_2^- \\
\text{HO}_2^- & \rightarrow \text{O}_2^- + \text{H}^+ \\
\text{O}_3 + \text{O}_2^- & \rightarrow \text{O}_3^- + \text{O}_2 \\
\text{O}_3^- + \text{H}^+ & \rightarrow \text{HO}_2^-, \\
\text{HO}_2^- & \rightarrow \text{HO}^- + \text{O}_2, \\
\text{O}_3 + \text{HO}^- & \rightarrow \text{O}_2 + \text{HO}_2^- \\
\end{align*}

The reaction is sustained by the formation of the \text{HO}_2^- radical, which can use for then initiate further reactions. The hydroxyl radical is the most important parameter formed during the ozone process. Ozonation process give best result at alkaline pH, and it is due to the reaction between all organic and inorganic compounds with the molecular ozone and the oxygen radicals, including the hydroxyl radical. These hydroxyl radicals have an oxidation potential (E° = 2.80) higher than O3 (E° = 2.07) in the direct reaction under acidic conditions. Greater than 9 pH has been favoured for removal of Colour & COD. The combination of Ozonation with biological treatment reduces biological regrowth potential, because biological treatment can remove biodegradable organic matter selectively. Biodegradability of the organic matter is increased because the Ozonation process have a capability to transforms large molecules into smaller ones.

### III. MATERIALS & METHODS

**Characterization of Pesticide wastewater**

The pesticide wastewater was collected from a pesticide industry in Gujarat. The characteristics of the pesticide wastewater are followed as:

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>pH</td>
<td>2</td>
</tr>
<tr>
<td>2.</td>
<td>COD</td>
<td>15,267 mg/l</td>
</tr>
<tr>
<td>3.</td>
<td>TDS</td>
<td>26,000 mg/l</td>
</tr>
<tr>
<td>4.</td>
<td>TSS</td>
<td>1100 mg/l</td>
</tr>
<tr>
<td>5.</td>
<td>Chlorides</td>
<td>5200 mg/l</td>
</tr>
</tbody>
</table>

### IV. EXPERIMENTAL SETUP & PROCEDURE

Ozonator used in the whole experimental process is shown in the figure 1. Ozone generation capacity of Ozonator is 3 g/hour and Oxygen flowrate 1 LPM (litre per minute) is fixed. Also based on literature survey Ozonation process gives higher reduction in alkaline pH 8 to > 10. In this research paper ozonation process applied for the Chemical oxygen demand (COD) reduction at different pH (8,9,10,11,12) with different time period (10,20,40,60). Sodium hydroxide (6M NaOH) were used for adjusting the pH. 200ml of the pesticide effluent was taken and pH (8,9,10,11,12) was adjusted using 6M NaOH. The flow rate of ozone was adjusted to the desired level and it was passed through diffusers in to the solution for different time periods (10,20,40,60). After the treatment effluent was analysed for COD concentration. COD was measured by standard methods.

### V. RESULT & DISCUSSION

The influence of different pH & time period on COD removal of the pesticide wastewater is illustrated in Figure. Higher COD removal efficiencies were observed under alkaline conditions. Below chart indicate the removal efficiency of COD at different pH and different time period.
VI. CONCLUSION

The Ozonation process for the removal of pesticide was investigated. As Ozonation is normally used for disinfection, the removal of pesticide is an added advantage. Even though the degradation is not complete, a removal efficiency of 36% was obtained which shows that Ozonation can be used as a first step in the treatment process. The optimum pH obtained was 12 and time period is 60 minute, which shows that the process is more effective in alkaline medium. Ozonation is a viable process for pesticide removal and it does not produce sludge as in Fenton process. Combination of Ozone with other reagents like H$_2$O$_2$ and UV can be tried for improving the removal of pesticide.
REFERENCES


