Treatability study of Pesticide Industry Effluent by Ozonation & Perexone process for the COD removal

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Abstract: Pesticides belong to the class of persistent chemicals in the environment which cause serious health hazard. The effluent 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. 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 are effective 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 Ozonation & Perexone treatment for the removal of Pesticide Industry Effluent in terms of Chemical Oxygen Demand (COD) at various pH with different contact time.

Keywords: Pesticide Industry Effluent, Ozonation, Advanced oxidation process.

Introduction

Pesticide manufacturing industry wastewater poses 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 wastewater is observed in agricultural areas and in surface waters that come from agricultural areas. Major quality of pesticide pollution is released during pesticide manufacturing. 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 fauna and flora. 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. 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 CO_2 and water or at least to degradable compounds.

Ozonation Treatment

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. AOP combine **ozone (O_3)**, ultraviolet (UV), **hydrogen peroxide (H_2O_2)** 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 Ozonation is one of them. Ozonation is a widely used technique for the removal of pollutants from water and wastewater. The degradation of compounds occurs through the action of ozone itself as well as through the radicals generated in aqueous medium. Ozone is use as an oxidizing gas which reacts with inorganic and organic compounds of wastewater, directly or indirectly, through the formation of hydroxyl radicals. It is poorly soluble in water, but once in contact with water, it becomes highly unstable and rapidly decomposes through a complex series of reactions, in accordance with the mechanism of hydroxide ions (HO-). The major reactions taking place are:

$$O_3 + HO^- \rightarrow HO_2^- + O_2$$

$$HO_2^- + O_3 \rightarrow O_3^{-\bullet} + HO_2^{\bullet}$$

$$HO_2^{\bullet} \rightarrow O_2^{\bullet} + H^+$$

$$O_3 + O_2^{\bullet} \rightarrow O_3^{-\bullet} + O_2$$

$$O_3^{-\bullet} + H^+ \rightarrow HO_3^{\bullet}$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2$$

$$O_3 + HO^{\bullet} \rightarrow O_2 + HO_2^{\bullet}$$

The chain reaction is sustained by the formation of the HO2• radical, which can use for then initiate further reactions. The hydroxyl radical (HO•) is the most important parameter formed during the ozone decomposition. pH, the nature and concentration of oxidizable organic compounds, ozone dose. 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. Removal of colour and COD has been favoured at pH higher than 9. The combination of Ozonation with biological treatment reduces biological regrowth potential, because biological treatment can remove biodegradable organic matter selectively. Ozonation transforms large molecules into smaller ones, thus increasing the biodegradability of the organic matter.

Perexone Treatment

Hydrogen peroxide is added in to ozone is initiating the ozone decomposition cycle, resulting in the formation of OH• radicals:

$$H_2O_2 \rightarrow HO_2^- + H^+$$

$$HO_2^- + O_3 \rightarrow HO_2\bullet + O_3\bullet^-$$

The reaction continues along the indirect pathway described above and OH• radicals are produced. The combination of different reaction steps shows that two ozone molecules produce two OH• radicals:

$$2O_3 + H_2O_2 \rightarrow 2OH\bullet + 3O_2$$

P.A.Fasnabi et.al using Ozonation process at pH 8.1 and Ozone dose 2g/h reduced COD about 53.9 %. A reduction of 8.7 % of TOC and 56.9 % of Pesticide (Acetamiprid) after 120 minutes of Ozonation have been reported for an industry that produces Acetamiprid Pesticide product. Ozonation is a viable process for acetamiprid removal and it does not produce sludge as in Fenton process. Combination of Ozone with other reagents like H_2O_2 and UV can be tried for improving the removal of pesticide.

Zhenglong et.al conclude that treatment of heterocyclic pesticide wastewater using Ultrasonic/ozone combined process. Using only ultrasonic process then COD removal efficiency is 5.8 % and increase BOD_5/COD ratio is 0.042 at pH 9.00, ultrasonic frequency 60 kHz & power 300 W. And using only Ozonation process with doses of 454.8 mg/(L·min) and pH 13.34 resulted in a COD removal of about 58.6 % and increase the biodegradability index about 0.33. Using Ultrasonic/ozone combined process COD removal efficiency is 61.1% and increase BOD_5/COD ratio is 0.41 at pH 9.00, ultrasonic frequency 60 kHz & power 300 W.

Post-ozonation, on the other hand, may have a polishing effect on effluent quality. It is therefore important to set the basis for the selection of the appropriate location for ozone application. The right choice between pre- or post-ozonation alternatives is significant for the optimum use of the chemical oxidation potential provided, both for overall COD and colour removal, and for reduction of soluble non-biodegradable COD fractions.

Kai Yang et.al conclude the advantages of pre- and post-Ozonation process at different ozone dose and contact time for the removal of atrazine pesticide. During pre-ozonation maximum atrazine removal achieved 65 % at ozone dose 3mg/l for 5 minutes only. And During post-ozonation maximum atrazine removal achieved 77 % at ozone dose 3mg/l for 15 minutes. post-ozonation generated approximately 6.0 µg/L bromate at an ozone dose of 3.0 mg/L, while pre-ozonation did not form bromate even at an ozone dose as high as 3.0 mg/L. Pre-ozonation exhibited slightly better odorant removal performance.

Materials & methods for O_3

Characterization of Pesticide wastewater

The pesticide wastewater was collected from a pesticide industry in Gujarat. The characteristics of the pesticide wastewater are present in Table 1.

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

Table 1: - Characterization of Effluent

Sr.No.	Parameter	Value
1.	pH	2
2.	COD	15,267 mg/l
3.	TDS	26,000 mg/l
4.	TSS	1100 mg/l
5.	Chlorides	5200 mg/l
6.	Colour	372 (Pt. Co. Scale)

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 (10,20,30,45,60). 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 (10,20,30,45,60,70). After the treatment effluent was analysed for COD concentration. COD was measured by standard methods.

Materials & methods for H_2O_2

The experiment was performed in 500ml conical flask. 200 ml samples were taken in each flask. Different quantity (1, 5, 10, 15, 20 ml) of hydrogen peroxide (H_2O_2) was added in each flask. The different pH value of effluent was taken for experiments. After addition of H_2O_2 solution the sample was stirrer for 60 minutes by magnetic stirrer and the sample were analysed for the measurement of COD value.

Materials & methods for $O_3 + H_2O_2$

The experiment was performed in 500 ml flask. 200 ml sample were taken in each flask. Different quantity of hydrogen peroxide (H_2O_2) was added in each beaker. After addition of H_2O_2 solution the sample was stirrer for 30 minutes by magnetic stirrer. As per above experiment value of pH and time period were taken for this process. After H_2O_2 dosing, passing of ozone in the sample for 60 minutes & then the sample were analyzed for the measurement of COD value.

Result & Discussion

The influence of different pH & time period on COD removal of the pesticide wastewater bu O_3 is illustrated in Figure. Higher COD removal e□ciencies were observed under alkaline conditions. Below chart indicate the removal efficiency of COD at different pH and different time period.

Figure 1 Ozonator Apparatus

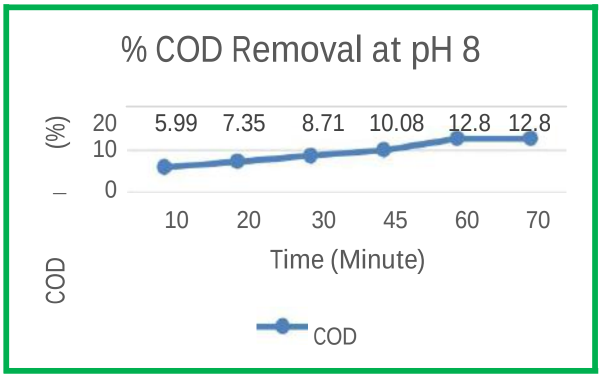

Figure 2 COD removal at pH 8

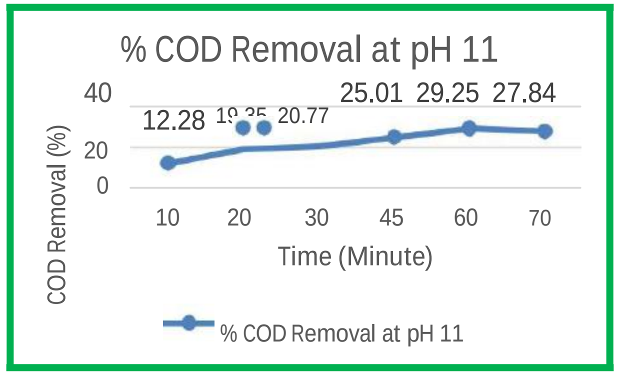

Figure 5 COD removal at pH 11

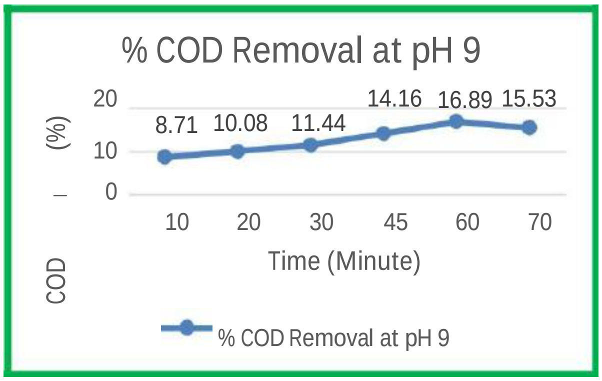

Figure 3 COD removal at pH 9

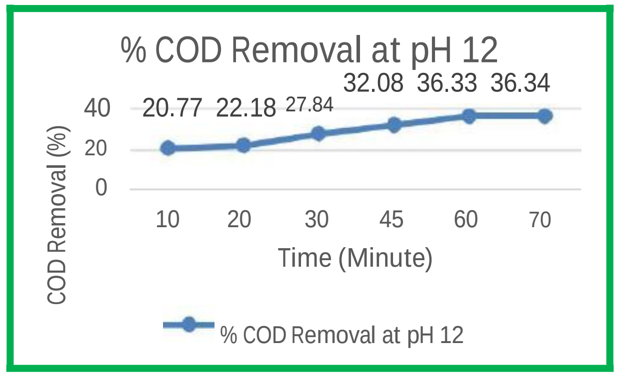

Figure 6 COD removal at pH 12

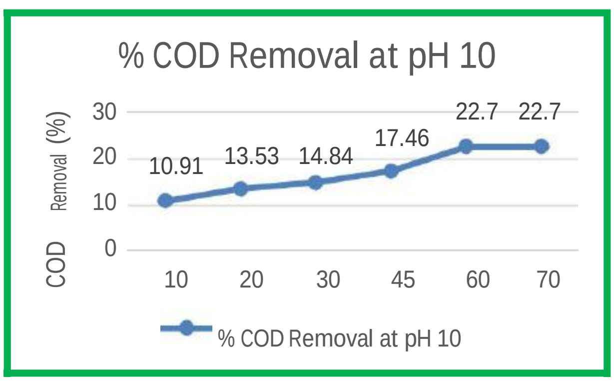

Figure 4 COD removal at pH 10

Fig.2,3,4,5 and Fig. 6 shows COD profile at pH 8,9,10,11 and 12 respectively. The influent COD concentration 15267 mg/l.

The influence of different pH & H_2O_2 dose on COD removal of the pesticide wastewater by H_2O_2 is illustrated in Figure. Below chart indicate the removal efficiency of COD at different pH with different H_2O_2 dose.

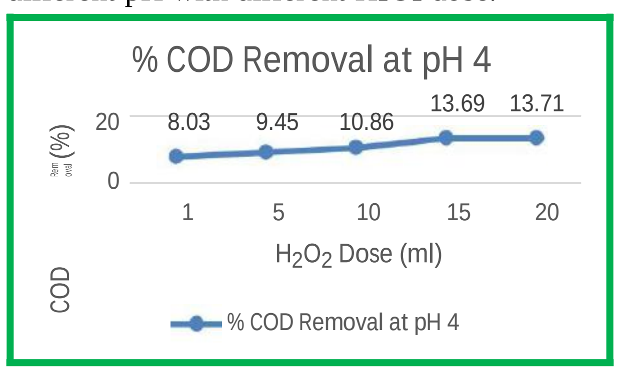

Figure 7 Different dosages of H_2O_2 at pH 4

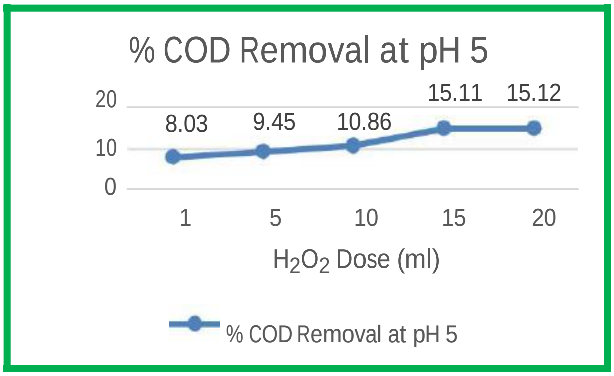

Figure 8 Different dosages of H_2O_2 at pH 5

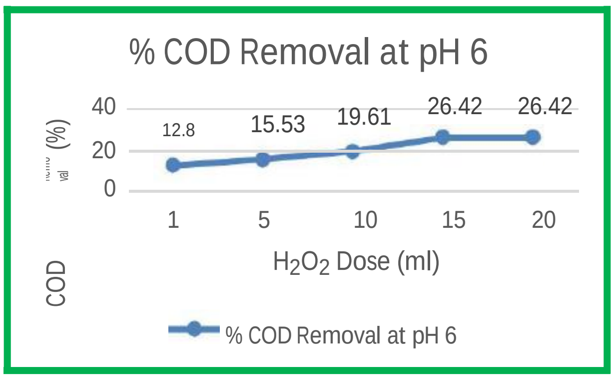

Figure 9 Different dosages of H_2O_2 at pH 6

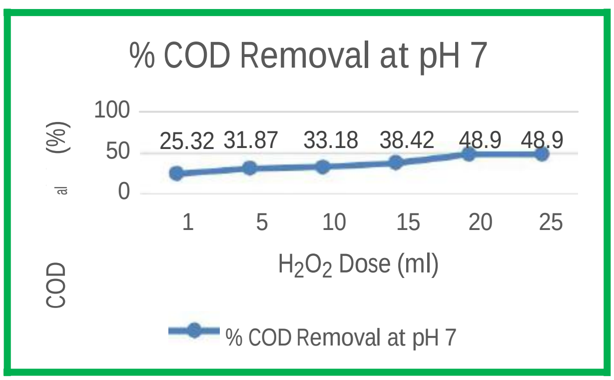

Figure 10 Different dosages of H_2O_2 at pH 7

Fig.7,8,9,10 and Fig. 11 shows COD profile at pH 4,5,6,7 and 8 respectively. The influent COD concentration 15267 mg/l.

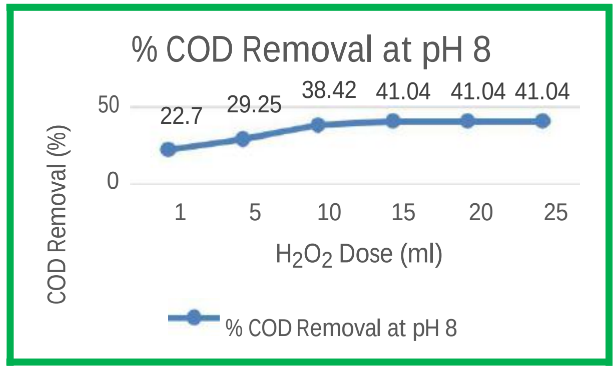

Figure 11 Different dosages of H_2O_2 at pH 8

The influence of selected pH, H_2O_2 dose & contact time based on above experiments, we have to carried out the Perexone process for COD removal of the pesticide wastewater is illustrated in Figure. Below chart indicate the removal efficiency of COD at selected pH 12 with 20ml H_2O_2 dose for 60 minutes time periode.

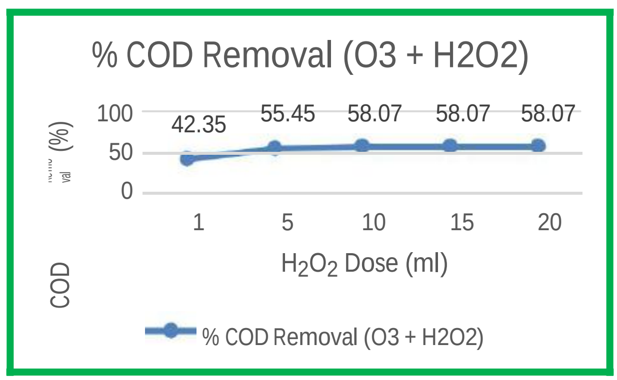

Figure 12 O_3 + H_2O_2 treatment

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, 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. And also, combination of Ozone with H_2O_2 can be tried for improving the removal of pesticide and concluded that 58 % of COD was removed by Perexone process.

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