

# Effect of Ozonation Pretreatment on Photo-Fenton Process for Landfill Leachate

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**Abstract:**-In this study the landfill leachate was treated with Photo-Fenton process with Ozonation as pre treatment. The leachate generated from landfill is a highly polluted wastewater containing organic pollutants, inorganic salts, nitrogen (N) and many other contaminants. The efficiency of the processes were analyzed by observing different parameters such as Chemical Oxygen demand (COD), Biological Oxygen demand (BOD), Total Solids (TS), Total Suspended solids (TSS), Total dissolved solids (TDS), Nitrogen, Turbidity and Alkalinity.

## I. INTRODUCTION

Waste is any substance which is discarded after primary use or it is worthless, defective and no use. The wastes can be classified into Household waste, Municipal waste (MSW), Commercial and non-hazardous industrial wastes, Hazardous (toxic) industrial wastes, Construction and demolition (C&D) waste, Health care wastes (Eg. hospitals, medical research facilities), Human and animal wastes. Generation of MSW has been increasing day by day.

Municipal solid waste disposal is the most common practice in developed and developing countries (Yang Denget al., 2006). Land filling is an alternative for Conventional incineration process. Incineration may cause serious pollution problems due to releasing toxic compounds such as polychlorinated dibenzodioxins and polychlorinated dibenzofurans.

The dumping yard for MSW generated in Tirunelveli city is Ramayanpatti landfill. Percolation of rainfall through landfill sites in combination with the decomposition of the solid wastes by simultaneous and interrelated biological, chemical and physical changes lead to the generation of a highly contaminated liquid called "leachate". The sanitary landfill leachate is a dark liquid, of highly variable composition. The composition of landfill leachate mainly depending upon landfill age the nature of the disposed wastes, climate, hydrological factors, rainfall patterns. The leachate generated from landfill is a highly polluted wastewater containing organic pollutants, inorganic salts, nitrogen (N) and many other contaminants. Ammonia has been considered as the most significant component in the leachate over the long term because Sometimes Leachate may contains Ammonia in concentrations up to 2000mg/L, which may be toxic to biological processes for leachate treatment (Kjeldsen et al., 2002).

There are many Laboratory studies of biological and chemical treatment processes since the early 1970s (Boyle and Ham, 1974; Ho et al., 1974). Photo-Fenton's oxidation, one of the 'oldest' Advanced oxidation process (AOPs) (Poblete R et al., 2012; Cho S.P et al., 2002; Poblete R et al., 2011), is relatively cheap, easily operated and maintained. It has the advantages of both coagulation and catalytic oxidation, as well as being enhanced by the Advanced oxidation processes (AOPs) (E.M.R. Rocha et al., 2011). Oxidation by Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) reactions is proven to be an economically feasible process for destruction of a variety of hazardous pollutants in wastewater. These processes have low reaction temperatures and thus require the presence of very active oxidation agents. In particular, the oxidation using Fenton's reagent has proved to be a promising and attractive treatment method for the effective destruction of a large number of hazardous and organic pollutants.

Pretreatments such as ultra-sonication and ozonation can be used to enhance the Fenton process. Ozonation is used as a pretreatment because of its high oxidation capacity and it has high reactivity and selectivity towards organic pollutants. This process is effective for the removal of the colour and also for disinfection. It is also helps to enhance the production of OH radicals in Fenton process due to its high Oxidation power (Bye, W.C., Ham et al., 1974; Huang S.S et al., 1993; Rice R. Jet et al., 1997). The combination of different pretreatment techniques have superiority over single pretreatment process.

This work aims the optimization Ozonation, Photo-Fenton process and combined ozonation-Photo-Fenton process on Leachate treatment by the simultaneous observation of specific parameters.

## II. MATERIALS AND METHODS

### 2.1 Leachate collection and characterization

Landfill leachates were collected from Ramayanpatti Compost Yard, Tirunelveli Corporation on 04-11-2015. Collected Leachate stored in laboratory at 4°C, for further analysis.

The initial characteristics of wastewater includes Total Solids (TS), Total Suspended Solids (TSS), Total dissolved solids (TDS), COD, BOD, Alkalinity, Turbidity, Nitrogen and pH, was determined using standard methods (APHA, 2005).

Table 1 Characteristics of Leachate

SL.NO	PARAMETERS	UNIT	VALUES
1	pH	-	8.57
2	Temperature	°C	33
3	Total solids	(mg/L)	16350
4	Total Suspended solids	(mg/L)	2580
5	Total Dissolved solids	(mg/L)	13196
6	Alkalinity	(mg/L)	10500
7	COD	(mg/L)	39333.33
8	BOD	(mg/L)	284.4
9	NITROGEN	(mg/L)	375.2
10	TURBIDITY	NTU	2778.7

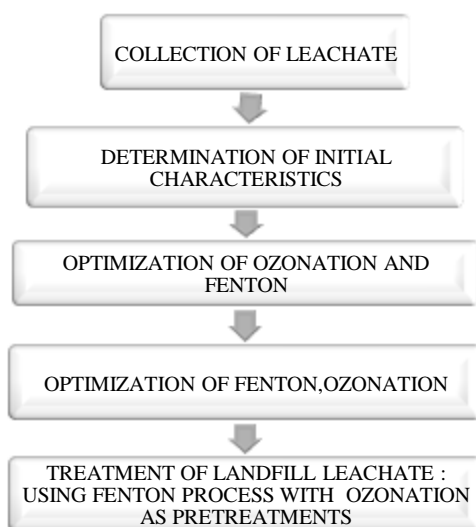


Fig 2.1 Schematic representation of process

### 2.2 Chemicals

The Photo-Fenton process were carried out by using Ferrous Sulphate (FeSO<sub>4</sub>.7H<sub>2</sub>O), Hydrogenperoxide (H<sub>2</sub>O<sub>2</sub>-50%), Hydrochloric Acid (HCl-33%) and Sodium Hydroxide (NaOH-30%)(for pH adjustment). All the chemicals were purchased from Merck ,Mumbai.

### 2.3 Experimental Procedure

Different pretreatments such as Ultra-sonication and Ozonation were used to enhance the Fenton process for the degradation of pollutants in Leachate.

Ozonation was used as a pretreatment because of its high oxidation capacity and it has high reactivity and selectivity towards organic pollutants. This process is effective for the removal of the colour and also for disinfection. It also helps to enhance the production of OH radicals in Fenton process. The ozonator with maximum input

voltage 230V is used for this study. Ozone flow rate, pH and time were the main variable for the Ozonation process. For the optimization of process the flow rate, pH and the time varied from 0.5 LPM to 4 LPM (0.5LPM,2LPM,3LPM and 4LPM) 6 to 9 (6,7,8 and 9) and 60 to 300 seconds (60 ,120,180,240 and 300 seconds) respectively. And the values with maximum COD removal efficiency was taken as the optimum values. The combination of two pretreatment techniques have superiority as compared to that of individual treatment.

The AOP procedure was useful for the reduction of the chemical contaminants and the toxicity to such an extent that the cleaned waste water may be reintroduced into receiving streams or, at least, into a conventional sewage treatment. In addition to that AOPs can be used to treat effluent of secondary treated wastewater which is then called tertiary treatment. The contaminant materials were converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts, i.e. they undergo mineralization.

The effect of H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup> and pH was determined by varying the individual parameters while keeping all other parameters constant. For the optimization process the concentration of H<sub>2</sub>O<sub>2</sub> was varied from 1 to 3 mL (1mL, 1.5mL, 2mL and 3mL ), concentration of Fe<sup>2+</sup> varied from .5 to 2g and the pH varies from 6 to 10 (6,7,8,9 and 10). Time optimization was done by taking the samples at different time intervals and analyze it to find the maximum removal efficiency. For that sample was taken at 15minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes and 90minutes. The time with maximum COD removal efficiency was taken as the optimum time. In combined Ozonation–Photo Fenton process the 1000 mL sample was treated by Ozonation (with suitable flowrate, pH and time) followed by the Photo-Fenton process.

## III. RESULTS AND DISCUSSIONS

**3.1 Optimization of Ozonation process:** The ozonator with maximum input voltage pretreatment for Photo-Fenton process. The ozonator with maximum input voltage 230 V was used for the study. In order to identify the optimum condition Ozone flow rate, pH and time were the main variables. For the optimization of process the flow rate, pH and the time varied from 0.5 LPM to 4 LPM (0.5LPM,2LPM,3LPM and 4LPM), 6 to 9 (6,7,8 and 9) and 60 to 300 seconds (60,120,180,240 and 300 seconds) respectively. The flow rate pH and time with maximum removal efficiency is considered as the optimum value for the Ozonation process. The maximum removal efficiency of 69.49 % were obtained at a flow rate of 0.5 LPM and at a time of 180 seconds.

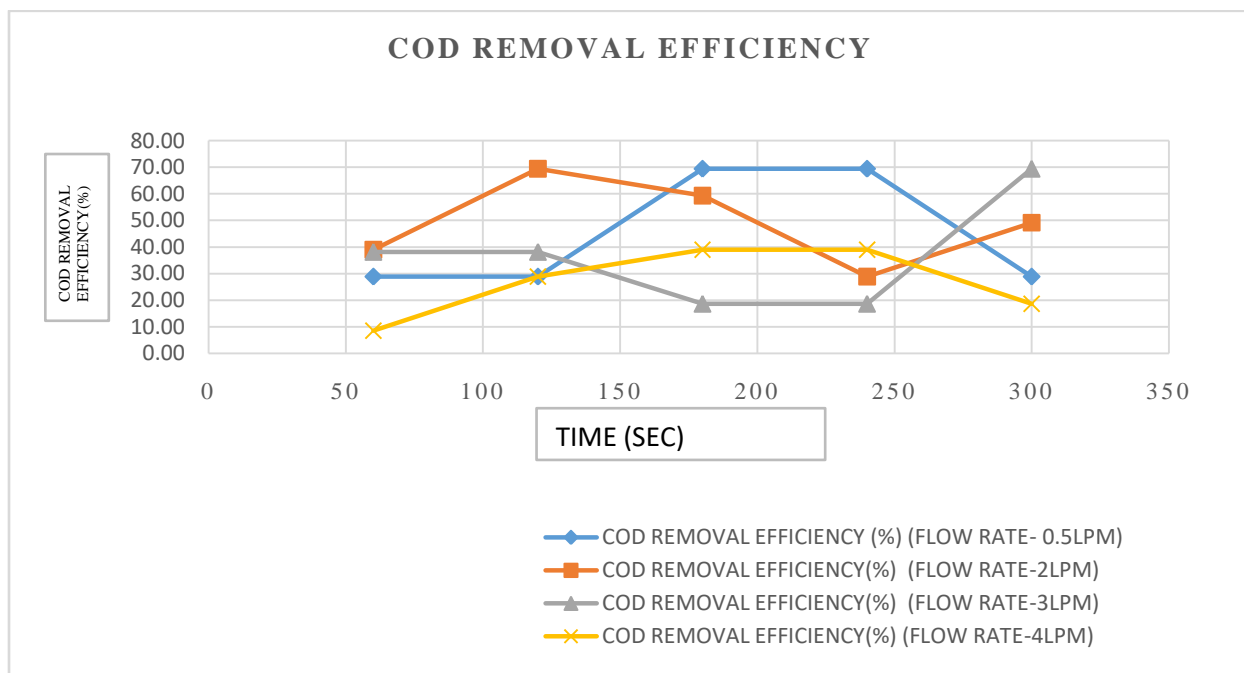


Fig 3.1 COD Removal efficiency (Ozonation pretreatment)

### 3.2 Optimization of Photo-Fenton process

The photo-Fenton process is an advanced oxidation process which oxidizes the contaminants in the leachate by producing active hydroxyl radicals and undergo a series of reactions with  $Fe^{2+}$  to oxidize the organic and inorganic contaminants. The process was carried out in a fenton glass tray of volume 1.5 L and by varying different parameters such as dosage of  $H_2O_2$ ,  $Fe^{2+}$ , pH and time. The  $H_2O_2$  dosage varied as 1.5ml, 1ml, 2ml and 3ml and  $Fe^{2+}$  dosage varied as 0.5gm, 1gm, 2gm. The experiments were conducted various pH such as 6, 7, 8, 9 and 10. The sample were collected at a

time interval of 15 minutes from 15 to 75 minutes. Each set of collected sample were analyzed .2 ml  $H_2O_2$  dosage, 2gm  $Fe^{2+}$  dosage with a reaction time of 60 minutes gave 100% COD removal efficiency. After conducting the experiments at optimum condition that sample were analyzed to identify the parameters such Total Solids (TS), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Biological Oxygen Demand (BOD), Nitrogen (N), Turbidity, Alkalinity. This helps to identify the effectiveness of photo-Fenton process in treatment of leachate.

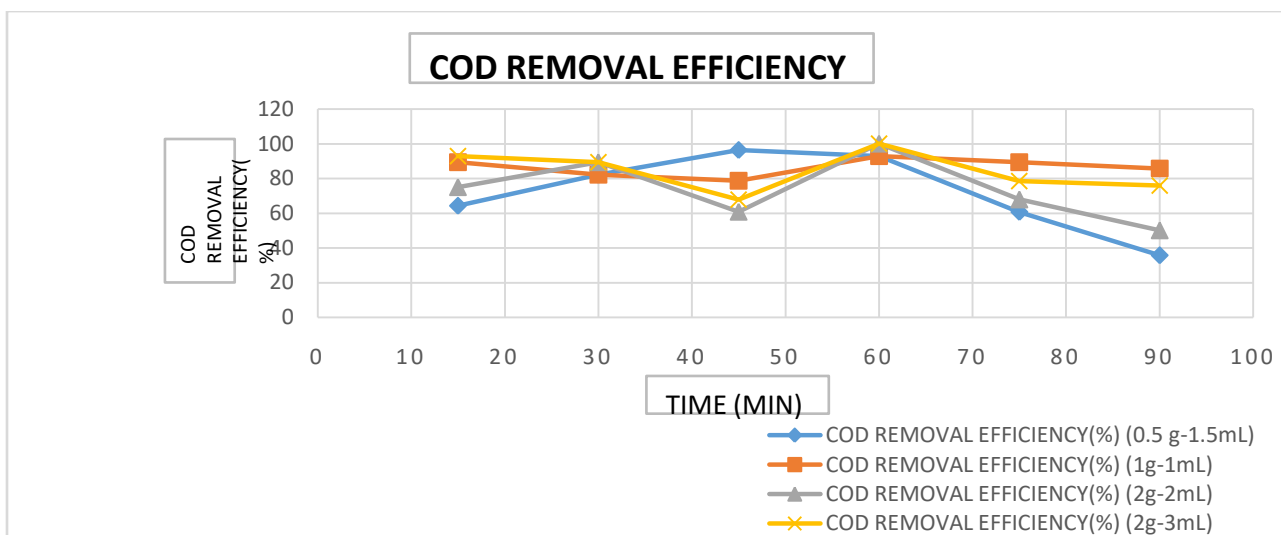


Fig 3.2 COD removal efficiency (Photo-Fenton process)

### 3.3 Optimization of ozonation/Photo-Fenton process

In this combined process the Ozonation process is followed by the Photo-Fenton process. Flow rate used for the experiment was 0.5 LPM (for 2 minutes) and the pH used was 9. The dosage of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> used for the Photo-Fenton process was 2g, 2 mL respectively. The samples were taken at an interval of 5 minutes. The collected samples were analyzed for the maximum COD removal efficiency.

100 % COD removal efficiency is obtained at a time of 15 minutes.

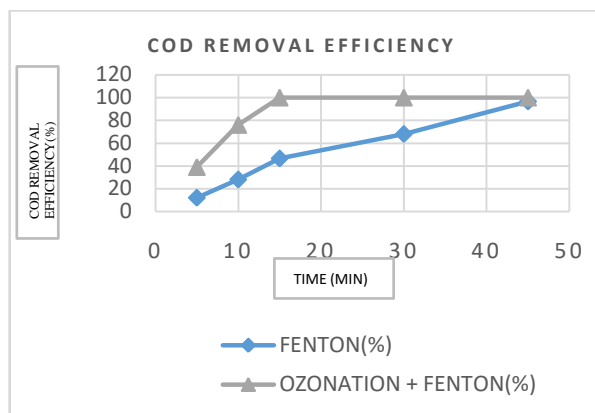


Fig 3.3 COD Removal efficiency

Table 2 Characteristics of leachate (initial and after the treatment processes)

PARAMETERS	INITIAL CHARACTERISTICS	CHARACTERISTICS (AFTER FENTON PROCESS)	CHARACTERISTICS (AFTER OZONATION / FENTON PROCESS)
pH	8.57	8	9
TEMPERATURE	33 C	34C	34 C
TURBIDITY	2778.7 NTU	2280 NTU	2187 NTU
T.S	1635.0 mg/L	1585.0 mg/L	1490.0 mg/L
T.S.S	258.0 mg/L	63.0 mg/L	223.0mg/L
T.D.S	1319.65 mg/L	1308.0 mg/L	1150.0 mg/L
ALKALINITY	1050.0 mg/L	975.0 mg/L	800.0mg/L
NH3-NITROGEN	375.2 mg/L	310 mg/L	246.4mg/L
COD	3933.33 mg/L	400.0 mg/L	0
BOD <sub>5</sub>	284.4 mg/L	151.5 mg/L	85 mg/L
TOC	1011.2568mg/L	106mg/L	0

### IV. CONCLUSION

The leachate generated from landfill is a highly polluted wastewater containing organic pollutants, inorganic salts, nitrogen (N) and many other contaminants. The AOP procedure was useful for the reduction of the chemical contaminants and the toxicity to such an extent that the cleaned waste water may be reintroduced into receiving streams or, at least, into a conventional sewage treatment. In addition to that AOPs can be used to treat effluent of secondary treated wastewater which is then called tertiary treatment. Pretreatments such as ultra-sonication and ozonation can be used to enhance the Fenton process. Ozonation is used as a pretreatment because of its high oxidation capacity and it has high reactivity and selectivity towards organic pollutants. From this study it is observed that the Ozonation pretreatment has a significant effect on Photo-Fenton treatment as it increases the removal efficiency of parameters such as COD, TSS, TDS, TOC, BOD, Nitrogen, Alkalinity, and Turbidity.

### REFERENCES

- [1]. Boyle, W.C., Ham, R.K.( 1974), ' Biological treatability of landfill leachate', *Journal of Water Pollution Control Fed.* 46 (5), pp.860–872.
- [2]. Cho S.P., Hong S.C., Hong S.(2002), 'Photocatalytic degradation of the landfill leachate containing refractory matters and nitrogen compounds', *Appl Catal B-Environ* ;39,pp.125-133.
- [3]. Ho, S., Boyle, W.C., Ham, R.K(1974), ' Chemical treatment of leachate from sanitary landfills', *Journal of Water Pollution Control Fed.* 46 (7), pp.1776–1791.
- [4]. Huang S.S, V. Diyamandoglu, J. Fillos(1993), 'Ozonation of leachates from aged domestic landfills', *Ozone:Sci.Eng.*15,pp. 433–444.
- [5]. Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., Christensen, T.H., (2002), ' Present and long-term composition of MSW landfill leachate: a review' *Crit. Rev. Environ. Sci.Technol.* 32 (4), pp.297–336.
- [6]. Poblete R.(2012), ' Solar photocatalytic treatment of landfill leachate using a solid mineral by-product as a catalyst', *Chemosphere*,pp.1090-1096.
- [7]. Poblete R., Otal E., Vilches L.F., Vale J., Fernández-Pereira C (2011), ' Photocatalytic degradation of humic acids and landfill leachate using a solid industrial by-product containing TiO<sub>2</sub> and F' *Appl Catal B-Environ*;102,pp.172-179.
- [8]. Rice R.J(1997), 'Applications of ozone for industrial wastewater treatment—a review', *Ozone: Sci. Eng.* 18, pp. 477–515.
- [9]. Rocha, V.J.P. Vilar, A. Fonseca, I. Saraiva, R.A.R. Boaventura (2011), 'Landfill leachate treatment by solar-driven AOPs', *Solar Energy* 85, pp46–56.
- [10]. Wu J.J, C.C. Wu, H.W. Ma, C.C. Chang, Treatment of landfill leachate by ozone-based advanced oxidation processes, *Chemosphere* 54 (2004) 997–1003.
- [11]. Yang Deng and James D. Englehardt (2006) , 'Treatment of landfill leachate by the Fenton process', *Water Research* 40,pp. 3683– 3694.
- [12]. Salem S.Abu Amr and Hmidi Abdul Aziz (2012), 'New treatment of stabilized leachate by Ozon/Fenton in the advanced oxidation process', *Waste Management* 32,pp.1693-1698.