RESEARCH ARTICLE OPEN ACCESS

# Comparison of Fenton and Anaerobic Process in Treating Mature Landfill Leachate

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**ABSTRACT**
Mature landfill leachate from Vilapilsala site was subjected to both anaerobic and Fenton process separately. After Fenton treatment removal of COD, BOD, turbidity, nitrate, sulphate and TSS were 92.1%, 83.5%, 94.2%, 18.86%, 11% and 96.6% respectively (optimized treatment conditions pH 3, reaction time 30min, $H_2O_2$/COD ratio 3, $[H_2O_2]/[Fe^{2+}]$ ratio 15 and 3g/L sludge recycling). Biodegradability enhanced from 0.3 to 0.65 and acute toxicity reduced to 6.3% from initial 3.2%. Whereas by anaerobic treatment at an HRT of 11days and pH 7, removal of COD, BOD, turbidity, nitrate, sulphate and TSS were 40.5%, 50.0%, 23.5%, 46.2%, 35.3% and 37% respectively. Biodegradability reduced from 0.3 to 0.26 and acute toxicity remained almost the same. Economic analysis revealed that initial cost will come around 50,978/- for Fenton process and Rs.11,16,555/- for anaerobic process in batch mode. Operating cost was around 1,23,240/$m^3$ wastewater for Fenton process and it came only around 527/$m^3$ for anaerobic process.
*Keywords* – Acute Toxicity, Anaerobic Process, Biodegradability, Fenton Process, Mature landfill leachate

## I. INTRODUCTION

There has been a significant increase in waste generation in India and all over the world in the last few decades, largely due to rapid population growth, economic development, urbanization and changing lifestyles. Globally the estimated quantity of waste generation was 12 billion tonnes in the year 2002 of which 11 billion tonnes were industrial wastes and 1.6 billion tonnes were municipal solid wastes (MSW). According to Ministry of Urban Affairs, Govt. of India estimate, India is generating approximately100,000 metric ton of solid waste everyday of which 90% is dumped in the open place [1]. As per CPCB, municipal solid waste generation in Kerala was about 1298 T/day (1999-2000) and it raised to 8338 T/day (2009-12). In Thiruvanandapuram 171 Tonnes per day of solid waste was generated in the year 2004-2005 and it has raised to 250T/day in the year 2010-11. Due to its economic advantages, disposal on a landfill is still one of the most widely accepted and used method for ultimate disposal of solid waste. Up to 95% of solid waste generated worldwide is currently disposed in landfills. In developing countries, such land filling is common for example around 15% of municipal solid waste goes to landfill in India and 9% in Nepal, respectively. Unlike other Municipalities and Corporations in Kerala, the Thiruvananthapuram Corporation had a centralized solid waste management plant at Vilappilsala. Trivandrum city corporation on a daily basis collected an average of 200 tons of solid waste but the plant had the capacity to treat only 150 tons of waste/day. From the collected 200 tones of waste only 25-30% (50-60tons) of the waste was converted to manure through treatment. The rest of the solid waste (≈145tons) was piled up as open dumps. No proper capping was done [2]. Liquid seeping through the rotting organic waste called leachate pollutes underground water and poses a serious threat to health and environment. The environmental damage and the pollution caused by the leakage of leachate from the plant have been a cause of concern for the residents of Vilappilsala. Leachate management and treatment is a very important standard operation in landfilling process since its impact on environment is huge. The treatability of the leachate depends on its composition and characteristics, which are influenced by the type of waste and the age of the landfill. Young leachate, usually formed within less than 2 years after deposition of waste, contain more organic fraction of relatively low molecular weight in comparison with old leachate, generated during anaerobic phases of stabilization; more than 10 years after deposition. In older leachate prevailing organics are humic and fulvic substances of relatively high molecular weight with persistent character, resulting in lower biodegradability. The diversity of the leachate produced and the complexity of leachate composition make it very difficult to set up general recommendations. Biological processes are effective in treating young leachate, while they could be completely ineffective when old leachate are being considered. Even though it is said that chemical process which involves higher operation cost treats recalcitrant and/or toxic waste effectively than biological process, a comparison in treatment efficiency and cost involvement of both the processes need to be worked out. Among the chemical processes, advanced oxidation process (AOPs) has rapid reaction rates, creates only small foot print, and has potential to reduce toxicity, improve biodegradability and cause possibly complete mineralization of organics. Unlike the methods such as membranes, it does not concentrate waste for further treatment and does not produce materials that require further treatment such as "spent carbon" from activated carbon adsorption. Fenton process is the most cost effective and easy to set up AOP. Among the biological processes, anaerobic process is more suitable for concentrated waste. It requires only less energy and are net energy producers instead of energy users. It produces less sludge and less odour and end product of the process are saleable like biogas. Anaerobic treatment of landfill leachate was studied extensively [3, 4, 5]. Also Fenton process was adopted for the treatment of leachate by many authors [6, 7, 8, 9].

## II. METHODOLOGY

### 2.1 General

Mature leachate sample was collected from landfill sites at Vilappilsala and characterization was done. Synthetic waste water similar in characteristics to the collected leachate sample was prepared and its characterization was done. Operational conditions in the Fenton oxidation unit were optimized to achieve maximum treatment efficiency while minimizing the use of chemicals and hence minimizing operation costs of the treatment plant. Improved biodegradability after Fenton oxidation is as important as reduction in waste load. As part of the treatability studies, analysis of COD and $BOD_5$ was carried out to investigate biodegradability of leachate. Acute toxicity of leachate after each treatment scheme was checked using Poecilia reticulata as test species. In the first part of the study, Fenton treatment of synthetic leachate was done and optimization of treatment with respect to reaction time, pH, $H_2O_2$/COD ratio, $[H_2O_2]/[Fe^{2+}]$ ratio and sludge reuse done. Raw mature leachate was treated with the Fenton process under the optimized conditions. An anaerobic reactor was designed and then, organics in raw leachate was degraded using continuously mixed suspended growth anaerobic process, after optimization of pH using synthetic leachate. Treatment efficiency of both the processes including toxicity reduction and biodegradability improvement studied. A rough estimate of the initial and operating costs involved in both the process was also made to compare the economical feasibility.

### 2.2 Materials and methods

#### 2.2.1 Mature landfill leachate and its characterization

The mature landfill leachate was collected from Vilappilsala municipal landfill, Trivandrum. The centralized solid waste treatment plant at Vilappilsala started functioning in the year 2000. The treatment plant occupies an area of 43 acres. This landfill was not equipped with a leachate collection and treatment system. Leachate was collected in November and initial characterization was done immediately. It was then stored in closed containers at $4^oC$. The characteristics of the leachate used in the investigated period are listed in Table 1.

#### 2.2.2 Preparation and characterization of synthetic leachate

Proportion of components used for the preparation of synthetic wastewater was decided by trial and error so that a reasonable match with the chemical characteristics of actual leachate sample was achieved. The composition of the synthetic leachate similar in characteristics to raw leachate sample was obtained. Synthetic wastewater characteristics were determined using standard methods and are shown in Table 2.

#### 2.2.3 Analytical methods

The physical and chemical properties of the leachate were determined in accordance with standard methods (APHA, 2005). Standard physical and chemical parameters, including; Turbidity, Conductivity, Temperature, Chemical oxygen demand(COD), Biochemical oxygen demand(BOD), Chlorides, Sulphate, Nitrate, Total solids, Total dissolved solids and Total suspended solids were determined.

#### 2.2.4 Biodegradability and toxicity testing

Biodegradability was measured as $BOD_5$/COD ratio. Toxicity test was done as per IS 6582-1971. Acute toxicity ($LC_{50}$) of leachate determined using static 96hr fish bioassay. $LC_{50}$ is the lethal concentration that causes death for 50% of test organisms. Test organism, *Poeciliareticulata* (guppy fish) was obtained from a commercial dealer. Test fishes acclimatized for 10 days to laboratory conditions in dilution water. Dilution water had pH 7, DO content >4mg/L and temperature $31^0C$. Fish was fed fairly during the acclimatization period. Fish was not fed for about 48hrs before test and during the test. Preliminary test was done in order to find the desired range of concentration to be covered in the full scale test. For this two or more fish was put in 100, 10, 1 and 0.1% concentration of sample with diluent water and observed for 24hrs. Lowest concentration at which all fish survive for 24hrs and the highest concentration at which all or most fish die in 24hrs was taken as the range of concentration for full-scale bioassay test. For full-scale bioassay,10 fishes each were taken in five concentrations arranged at equal intervals within and including the limits of dilution got from preliminary test. A control test was run under similar conditions using diluent water alone. $LC_{50}$ was estimated graphically for raw, Fenton treated, anaerobically treated and Fenton-anaerobically treated leachate.

#### 2.2.5 Materials and reagents for Fenton process

Fenton process was carried out in a 1000 mL beaker, and constant stirring done with magnetic stirrer. Reagents used include Hydrogen peroxide as oxidant, Ferrous sulphateheptahydrate ($FeSO_4.7H_2O$) as source of $Fe^{2+}$, NaOH and $H_2SO_4$ solutions for pH adjustment. All the reagents used were of analytical grade.

**2.2.6 Materials and inoculum for anaerobic process**

A 7L laboratory scale anaerobic reactor of height 40cm and diameter 15cm was used. The reactor was a cylindrical column made of cast iron. The reactor was provided with suitable arrangements for feeding, gas collection and draining of residues. The reactor was operated at ambient temperature. Gas production was measured using water displacement method. Conc.$H_2SO_4$ and NaOH was used for pH adjustment. A mix of anaerobic sludge from biogas plant, Sreekaryam and cow dung slurry was used as inoculum.

**2.2.7 Fenton process**

Experiments on chemical oxidation of landfill leachate were conducted at laboratory scale, with 1L beaker as batch reactor. All experiments were conducted at room temperature. Fenton process is normally composed of four successive stages: pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. For oxidation to happen, pH of 500mL sample was adjusted to the required value using Conc.$H_2SO_4$ and NaOH. A weighed amount of $FeSO_4 \cdot 7H_2O$ was added and dissolved under stirring to achieve the scheduled ferrous ions. Reaction was started by adding the required dose of 30% (w/w) hydrogen peroxide. Reaction solution stirred with a magnetic stirrer at a constant speed. After the required time, pH was neutralized to 7 to initiate coagulation and stirring allowed at low speed. Stirrer turned off and the sludge was allowed to settle. Supernatant withdrawn from the reactor at pre-determined times and analyzed. A set of experiments was conducted and the optimum concentrations of $H_2O_2$ and $FeSO_4 \cdot 7H_2O$, optimal reaction time and pH found out. Effect of sludge reuse was also studied.

**2.2.8 Anaerobic process**

Preparation of inoculum was done by mixing cow dung with anaerobic sludge. Start up of reactor was done by adding cow dung slurry and anaerobic sludge in the ratio 1:1. Then it was left for stabilization for about 14 days. After stabilization, the reactor was fed with leachate and kept for the desired HRT. Leachate was allowed to stabilize under anaerobic condition. Optimization of pH was done. Biogas produced was measured by water displacement method.

**2.3Experimental set up**

**Fig. 1 Lab setup for Fenton Process**

**Fig. 2 Lab setup for anaerobic Process**

**a)Acclimatization of test bioassay test organism, *Poeciliareticulata* (guppy fish) to laboratory Conditions**

**b)Full scale raw of leachate**

**c)Full scale bioassay test test of**

**d)Full scale bioassay**

**of Fenton treated leachate** **anaerobically treated leachate**

**Fig.3 Acute toxicity testing of raw and treated leachate**

## III. RESULTS AND DISCUSSION

### 3.1 Collection and Characterization of Mature landfill Leachate Sample

The original mature leachate used in this study was obtained from VilappilsalaLandfill, Trivandrum.Samples of the leachatewere collected in high density polyethylene bottles(2L).Samples, with a blackcolour was immediately analyzed without any delay to assess the baseline toxicity and other characteristics. Characteristics of sample colected is given in Table 1.

**Table 1 Characteristics of collected leachate**

| Parameter | Value |
|---|---|
| pH | 8 |
| Temperature($^0$C) | 30 |
| Colour | Black |
| COD(mg/L) | 24000 |
| BOD (mg/L) | 7500 |
| $BOD_5$/COD | 0.3 |
| Total Solids (mg/L) | 17200 |
| Total dissolved solids(mg/L) | 8000 |
| Total suspended solids(mg/L) | 9200 |
| Volatile Suspended Solids (mg/L) | 5612 |
| Chlorides (mg/L) | 210 |
| Sulphide (mg/L) | 160 |
| Turbidity(NTU) | 280 |
| Sulphate (mg/L) | 320 |
| Nitrates(mg/L) | 200 |
| Conductivity(micromho/cm) | 17200 |
| Acute toxicity(96-hr $LC_{50}$) | 3.2% |

### 3.2 Preparation and Characterization of Synthetic Leachate

The study was conducted with synthetic leachate also. Characteristics of synthetic leachate was studied and is given in the table below.

**Table 2 Characteristics of Synthetic leachate**

| Parameter | Value |
|---|---|
| pH | 7.8 |
| COD(mg/L) | 24860 |
| BOD (mg/L) | 6464 |
| $BOD_5$/COD | 0.26 |
| Total Solids (mg/L) | 16400 |
| Total suspended solids(mg/L) | 8000 |
| Turbidity(NTU) | 286 |
| Sulphates (mg/L) | 355 |
| Nitrates(mg/L) | 298 |

### 3.3 Fenton Process

#### 3.3.1 Optimization of the Fenton reaction condition using synthetic leachate

The effect of major parameters on the Fenton process for treating mature landfill leachate was evaluated in this study by the traditional one-factor-at-a-time method using a bench-scale batch reactor. The optimized parameters were reaction time, pH, $H_2O_2$ /COD ratio, $H_2O_2$ to Fe (II) molar ratio and sludge reuse.

#### 3.3.2 Treatment of raw leachate using optimized reaction conditions

Optimized Fenton reaction conditions of reaction time 30 min, pH 3, $H_2O_2$/COD ratio 3, $H_2O_2$ to Fe (II) molar ratio 15 and 3g/L sludge reuse was applied to raw leachate. The Fenton treatment removed 92.1%, 83.5%, 94.2%, 18.86%, 11% and 96.6% of COD, BOD, turbidity, nitrate, sulphate and TSS respectively. Biodegradability of leachate improved to 0.65 and toxicity reduced to 6.3%.

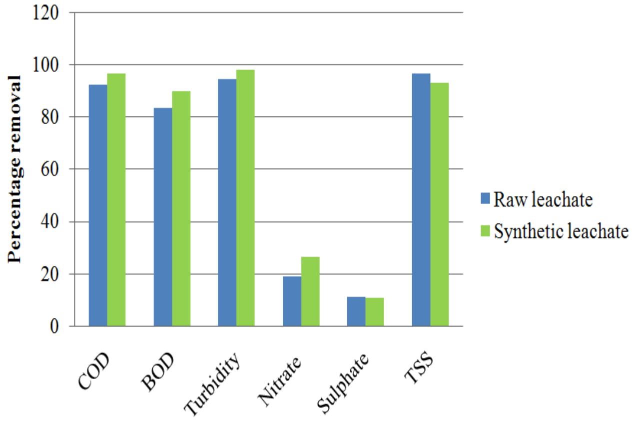


**Fig. 4 Removal efficiency of raw and synthetic leachate upon Fenton treatment**

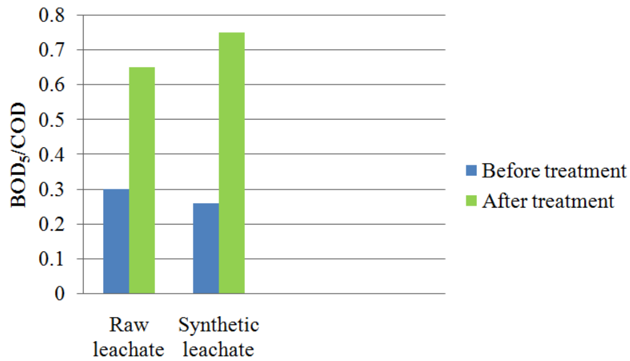


**Fig. 5 Biodegradability of raw and synthetic leachate after Fenton process**

**3.4 Treatment of Raw Leachate Using Anaerobic Process**

**3.4.1 Optimization of pH using synthetic leachate**

While treating the synthetic leachate by anaerobic process, pH variation of 6 to 8 was attempted in order to study the variation in treatment efficiency with pH and it was observed that slightly higher removal occurred at pH 7.

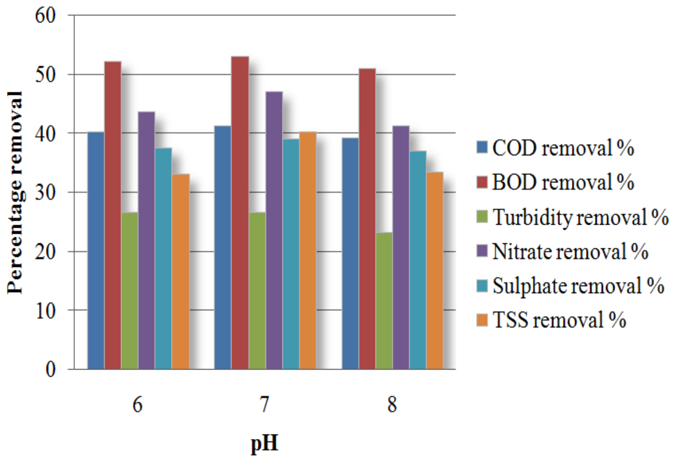


**Fig. 6 Effect of pH on anaerobic treatment efficiency of synthetic leachate**

**3.4.2 Anaerobic treatment of raw leachate**

Raw leachate was treated anaerobically at pH 7 for a period of 11days. Performance of anaerobic process in treating the mature leachate is shown in Fig. 7. Acute toxicity was 3.6% as revealed by full scale bioassay test.

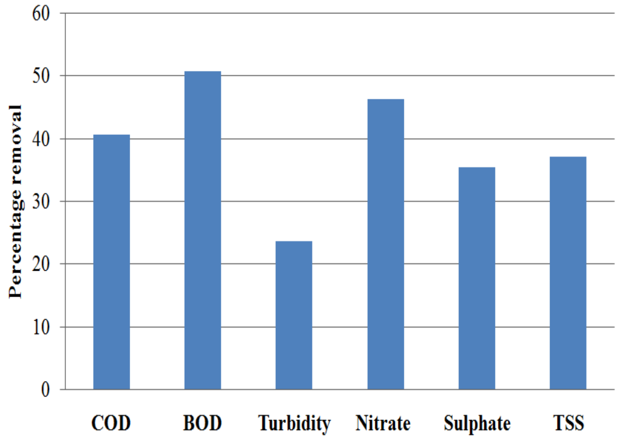


**Fig. 7 Anaerobic treatment efficiency of raw leachate at pH 7**

**3.5 Comparison of Fenton and Anaerobic Process in Treating Mature Landfill Leachate**

**3.5.1 Treatment efficiency of Fenton and anaerobic process**

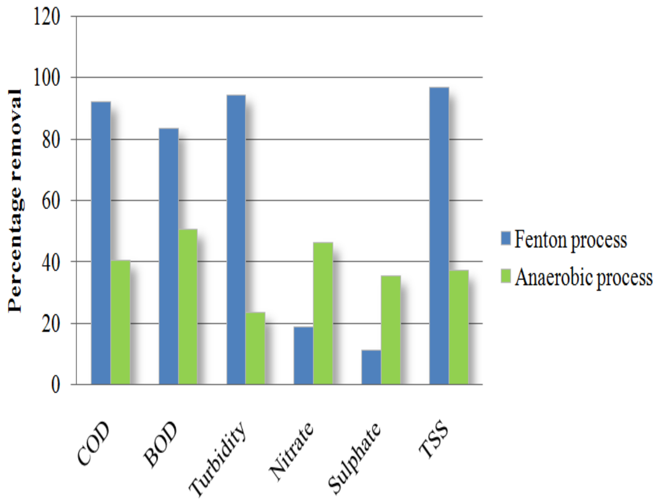


**Fig. 8 Efficiency of Fenton and anaerobic process in treating mature landfill leachate**

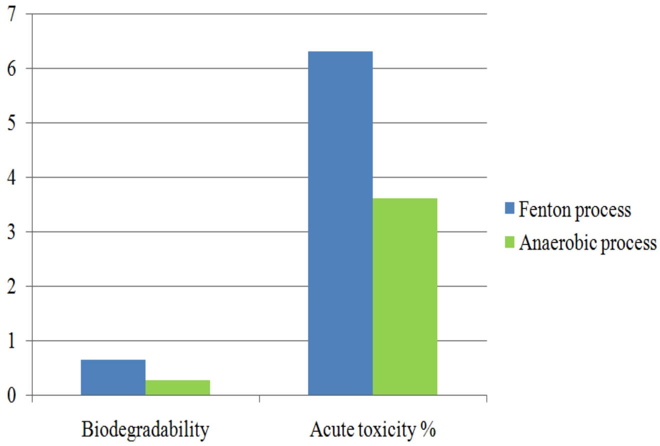


**Fig. 9 Biodegradability and acute toxicity of Fenton and anaerobic treated mature landfill leachate**

**3.5.2 Cost involvement in treating mature landfill leachate by Fenton and anaerobic process**

It might be beneficial to carry out a cost analysis of both the treatment processes, since economy is an important parameter. Economical analysis of the initial and operating costs associated with Fenton and anaerobic treatment of raw leachate was performed. The economic analysis was carried out based on Kerala PWD schedule of rates 2012. The construction costs normally depend on the influent quality and quantity and the capacity of the installation, while operation costs covered manpower, energy, chemicals etc. Initial cost for treating mature leachate by Fenton process was 50,978/- and that by anaerobic process, it was 11,16,555/-. Operating time was 30min and 11days for Fenton and anaerobic process respectively.The operating cost, which includes electricity cost, chemical cost and operator charge was around 1,23,240/m$^3$ wastewater for Fenton process and it came only around 527/m$^3$ for anaerobic process. Operating costs of conventional biological treatment are always lower than those employing

$H_2O_2$-based oxidation systems. $H_2O_2$ consumption is the most significant factor of the overall cost of the proposed treatment. These costs may be compensated to some extent by lower consumption of disinfecting agents.

## IV. CONCLUSION

- Biological(anaerobic)treatment of municipal landfill leachate was compared with Fenton process in terms of treatment efficiency and cost involvement. Fenton treatment at optimized conditions (pH 3, reaction time 30min, $H_2O_2$/COD ratio 3, $[H_2O_2]/[Fe^{2+}]$ ratio 15 and 3g/L sludge recycling) removed 92.1%, 83.5%, 94.2%, 18.86%, 11% and 96.6% of COD, BOD, turbidity, nitrate, sulphate and TSS respectively. Treatment with Fenton process was very fast. Biodegradability of effluent increased to 0.65 and toxicity reduced by about 50%.
- Anaerobic treatment of mature leachate at pH 7 and HRT 11 days removed 40.5%, 50%, 23.5%, 46.2%, 35.3% and 37% COD, BOD, turbidity, nitrate, sulphate and TSS respectively. Biodegradability of effluent was only 0.26 and toxicity remained almost the same.
- Initial cost for treating mature landfill leachate by Fenton process was Rs.50,978/- and that for anaerobic process was Rs.11,16,555/-.
- However with respect to operating cost, hydrogen peroxide/ferrous salts systems are much more expensive (1,23,240/$m^3$) than anaerobic treatment (527/$m^3$).
- However, provided that direct biological treatment cannot be used for refractory effluents, it is necessary to attempt such types of treatment.

## V. ACKNOWLEDGEMENT

The author would like to thank all the faculty members of College of Engineering, Trivandrum

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