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Optimization of Fenton Process for the Treatment of Mature Landfill Leachate from Vilappilsala Landfill Site

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Abstract— Mature leachate contains significant quantities of refractory organic materials that are impossible to get removed efficiently by biological processes. In the present study, for the treatment of mature landfill leachate from Vilappilsala site, Fenton process is adopted. 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). Thus Fenton process was an effective treatment option for mature landfill leachate. Biodegradability (BOD_5/COD ratio) enhanced from 0.3 to 0.65 and acute toxicity (96-hr LC_{50}) reduced to 6.3% from initial 3%. Thus Fenton process can be adopted as an excellent pretreatment option and a biological treatment can be adopted following the Fenton process in order to attain the quality for direct discharge.

Index Terms— Biodegradability, Chemical pretreatment, Fenton process, Landfill, Landfill leachate, Mature landfill leachate, Toxicity

1 INTRODUCTION

URBAN development, industrial and commercial growth together with increasing population is accompanied by ever increasing solid waste generation all over the world. According to Ministry of Urban Affairs, Govt. of India estimate, India is generating approximately 100,000 metric ton of solid waste everyday of which 90% is dumped in the open place. As per CPCB, municipal solid waste generation in Kerala was about 1298 T/day (1999-2000) and it has risen to 8338 T/day (2009-12). In Thiruvananthapuram 171 T/day of solid waste was generated in the year 2004-2005 and it has risen to 250 T/day in the year 2010-11. Due to economic advantages, landfilling is still the most commonly adopted solid waste disposal method. The inevitable drawback of landfilling is the generation of leachate produced by physico-chemical and biological decomposition of waste and percolation of rainwater through compacted waste. Its composition is site and time specific, based on the characteristics of deposited waste, physico-chemical conditions, volume of infiltrating water and landfill age. Untreated leachate can permeate ground water or mix with surface water and contribute to the pollution of soil, ground water and surface water consequently effecting human health. Therefore, there is a need to develop reliable and sustainable options to manage leachate generation and treatment effectively. Young leachate, usually formed within less than 2 years after waste deposition, contain more organic fraction of relatively low molecular weight and high biodegradability (BOD/COD>0.6) in comparison with old leachate, generated more than 10 years after deposition. In older leachate prevailing organics are humic and fulvic substances of relatively prevailing organics are humic and fulvic substances of relatively prevailing organics are humic and fulvic substances of high molecular weight with persistent character, resulting in lower biodegradability. It has been confirmed, that biological processes are effective in treating young leachate. But with increasing age, biodegradability of leachate decreases and biological treatment could become completely ineffective. To treat the old/refractory leachate, alternative treatment methods like physical and chemical methods are needed. Treatment options like reverse osmosis, adsorption etc. are nondestructive, changing the pollutant load from one phase to another. In such a case, advanced oxidation processes (AOPs) represent an attractive alternative to biological processes. Advanced oxidation processes remove organic load to high degree together with improving the biodegradability. Of the various AOPs, Fenton process is the easiest to setup and the most cost effective process. Under acidic conditions, Fenton reagent (ferrous ion combined with hydrogen peroxide) produces OH• (second highest powerful oxidant). The mechanism of the Fenton process:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \quad (1)$$
$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^- \quad (2)$$
$$HO^\bullet + RH \rightarrow H_2O + R^\bullet \quad (3)$$
$$R^\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \quad (4)$$

Several authors have studied the optimization of parameters influencing Fenton process and have achieved efficient removal of organics from landfill leachate - 68.1% COD removal, biodegradability improvement from 0.1 to 0.58 [1], 60% COD removal, biodegradability improvement from 0.2 to 0.5 [2], 50% COD removal, biodegradability improvement from 0.22 to 0.36 [3], 58.1 and 78.3% of COD and colour removal [4], 84% and 93% of COD and colour removal [5]. Fenton process has been applied successfully in a wide range of other type of wastewater also [6],[7],[8],[9]. Moreover, Fenton process has been successfully used as pretreatment method in order to reduce the concentrations of toxic/recalcitrant organic compounds, which will further favor biological wastewater treat-

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ment processes. Assessment of the biodegradability and toxicity during the oxidation process is necessary to determine the success of the process. BOD_5/COD ratio is the commonly used method for assessing biodegradability. Toxicity is a consequence of numerous contaminants in leachate, their interactive or opposing effects, and different physical-chemical properties. Toxicity tests may thus give more information about leachate quality when compared to chemical analysis. Toxicity testing of Okhla municipal landfill leachate using Poecilia reticulata revealed that leachate was highly toxic with 96-h LC_{50} less than 3% [10].

Thiruvananthapuram Corporation had a centralized solid waste management plant at Vilappilsala. The landfill at Vilappilsala was uncovered, and hence leachate from the landfills directly pollutes the nearby streams and Karamana River and also has adverse effect on inhabitants and their living environment as a whole. Biological processes could be ineffective for old leachate and other recalcitrant and/toxic wastewater. Optimal treatment in order to completely eliminate the associated environmental impact is still a challenge. This research was conducted to investigate the efficacy and feasibility of Fenton treatment in removing the organics, improving the biodegradability and reducing the toxicity of mature landfill leachate from Vilappilsala landfill site, Trivandrum.

2 METHODOLOGY

2.1 General

Mature leachate sample was collected from landfill site at Vilappilsala and characterization was done. As part of the treatability studies, analysis of COD and BOD_5 was carried out to investigate biodegradability of leachate. Acute toxicity of raw leachate and Fenton-treated leachate was checked using Poecilia reticulata as test species. Synthetic wastewater similar in characteristics to the collected leachate sample was prepared and its characterization was done. 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 Fenton process under the optimized conditions. Treatment efficiency including toxicity reduction and biodegradability improvement studied.

2.2 Materials and Method

2.2.1Mature 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 is not equipped with a leachate collection and treatment system. Leachate collected was stored in closed containers at 4^oC until use. 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. Synthetic wastewater characteristics were determined using standard methods.

2.2.4 Biodegradability and toxicity testing

Biodegradability was measured as BOD_5/COD ratio. Toxicity testing done as per IS 6582-1971. Acute toxicity (LC_{50}) of leachate determined using static 96h fish bioassay. LC_{50} is the lethal concentration that causes death for 50% of the test organisms. Test organism, Poecilia reticulata (guppy fish) was obtained from a commercial dealer. Test fishes acclimatized for 10 days to laboratory conditions in dilution water. Dilution water had DO content above 4mg/L. Fish were fed fairly during the acclimatization period. Fish not fed for about 48hrs before the 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. Full-scale bioassay was done and LC_{50} was estimated graphically for raw and Fenton 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 sulphate heptahydrate ($FeSO_4.7H_2O$) as source of Fe^{2+}, NaOH and H_2SO_4 solutions for pH adjustment.

2.2.6. Fenton process

Fenton process was carried out in batch mode in a glass beaker of 1L capacity. 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 adjusted to the required value with 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. The reaction was started by adding the required dose of 30% (w/w) hydrogen peroxide. The reaction solution stirred with a magnetic stirrer at a constant speed. After the required time, pH was neutralized to 7 to initiate coagulation. Stirrer turned off and the sludge allowed settling. 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 studied.

2.2.7. Experimental set up

Fig. 1. Experimental Setup for Fenton Process.

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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
VSS (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%

TABLE 2
SYNTHETIC LEACHATE CHARACTERISTICS

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 RESULTS AND DISCUSSION

3.1 Characterization of mature landfill leachate

3.2 Characterization of synthetic leachate

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. These optimized parameters were reaction time, pH, H_2O_2/COD ratio, H_2O_2 to Fe(II) molar ratio and sludge reuse.

i. Optimization of reaction time

The objective of the first set of test was to determine the time required for the treatment. Stoichiometric weight ratio H_2O_2/COD=2.125 calculated assuming complete oxidation of COD (1g COD =1g O_2 =0.03125 mol O_2 =0.0625 mol H_2O_2). Initial test conditions chosen were pH of 7.8, H_2O_2 /COD ratio 2, H_2O_2 to Fe (II) molar ratio 50. Keeping these conditions, Fenton oxidation reaction time was varied from 15 to 75 min. Results showed that organic materials were rapidly degraded by Fenton reagents. Most of the removal occurred in first 30 min after which only a minor reduction in removal was observed. Lower residence times will allow energy savings for stirring.

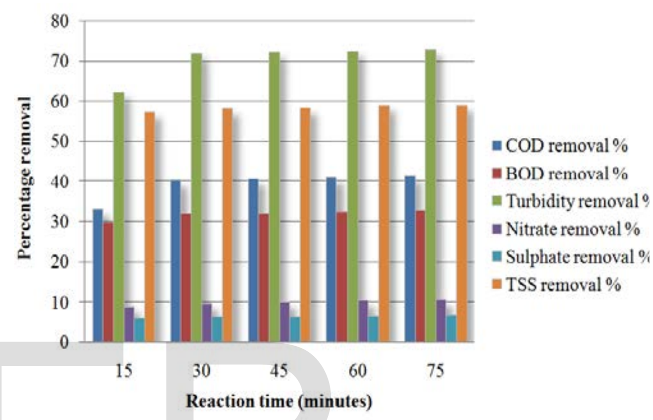

Fig. 2. Effect of reaction time on Fenton treatment (pH =7.8, T=30^{0}C, H_2O_2/COD=2, $[H_2O_2]/[Fe^{2+}]$ = 50).

ii. Optimization of pH

The tested pH range was 1 to 9 using a dosage of H_2O_2/COD ratio 2, H_2O_2 to Fe (II) molar ratio 50 and the reaction carried out for the optimized time period of 30 min. Results from the pH study showed that maximum removal occurred at pH levels below 5. This is because of the fact that OH• radical are effectively produced under acidic pH. Increasing the pH above 5 decreased the removal efficiencies and in the acidic range itself pH 3 produced slightly better results.

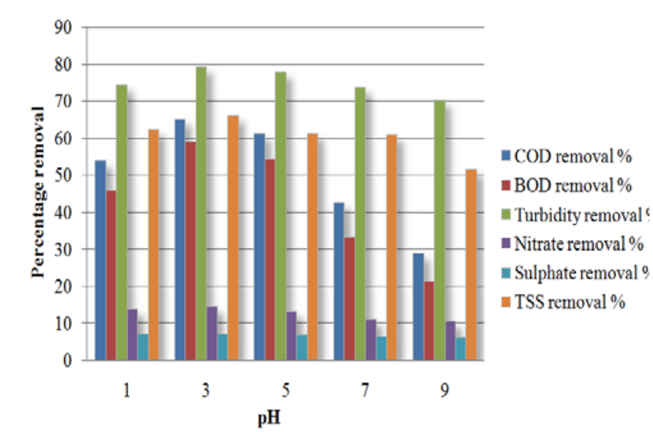

Fig. 3. Effect of pH on Fenton treatment (Reaction time =30 min, T=30^{0}C, H_2O_2/COD=2, $[H_2O_2]/[Fe^{2+}]$=50).

iii. Optimization of H_2O_2 dosage

In Fenton's reagent, hydrogen peroxide is catalyzed by ferrous iron to produce the active OH• radical; and hence it is important to optimize the dosage of both H_2O_2 and Fe^{2+}. When the peroxide dose was varied over a range of 1 to 5mg/L per mg/L of COD at a pH of 3 and an H_2O_2 to Fe (II) molar ratio of 50 and oxidized for a 30min reaction time, an increase in oxidation efficiency up to mass ratio 3 was observed, after which slight reduction in removal was observed due to the fact that excessive reagent produce the hydroxyl radical scavenging effect.

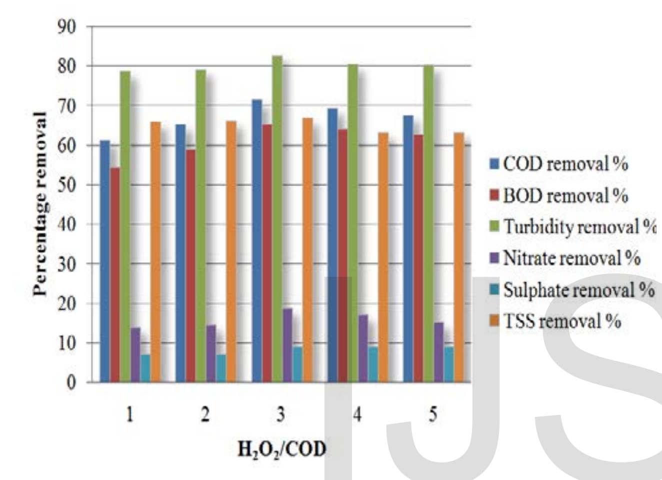

Fig. 4. Effect of H_2O_2 dosage on Fenton treatment (Reaction time =30min, pH=3, T=30^{0}C, $[H_2O_2]/[Fe^{2+}]$=50).

iv. Optimization of Fe^{2+} dosage

The molar ratio of H_2O_2:Fe^{2+} is important since too little iron will result in unutilized H_2O_2 and excessive Fe^{2+} will destroy produced OH• radical. When H_2O_2 to Fe (II) molar ratio was varied over a range of 1 to 100 at a pH of 3, reaction time 30 min and H_2O_2/COD ratio 3, an increase in the removal efficiency up to a molar ratio of 15 was observed, after which reduction in removal happened.

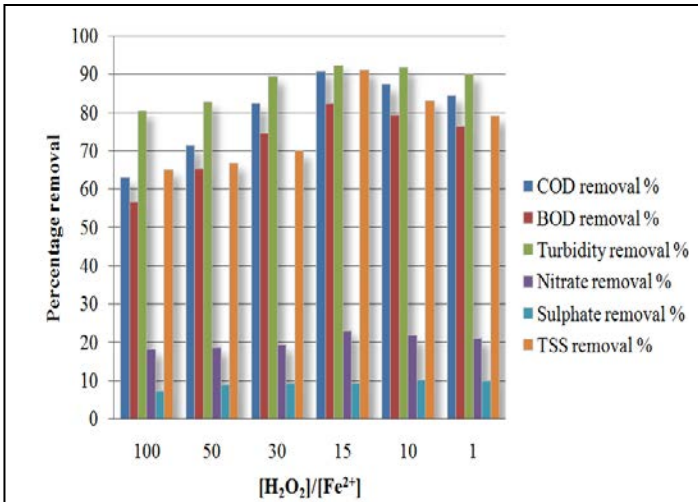

Fig. 5. Effect of Fe^{2+} dosage on Fenton treatment (Reaction time=30minutes, pH=3, T=30^{0}C, H_2O_2/COD=3).

v. Effect of sludge reuse

Sludge was recycled into the influent to find out the effect of sludge accumulation in Fenton treatment process. Recycling of 3g Fenton sludge per liter of influent enhanced the COD removal efficiency up to a significant level.

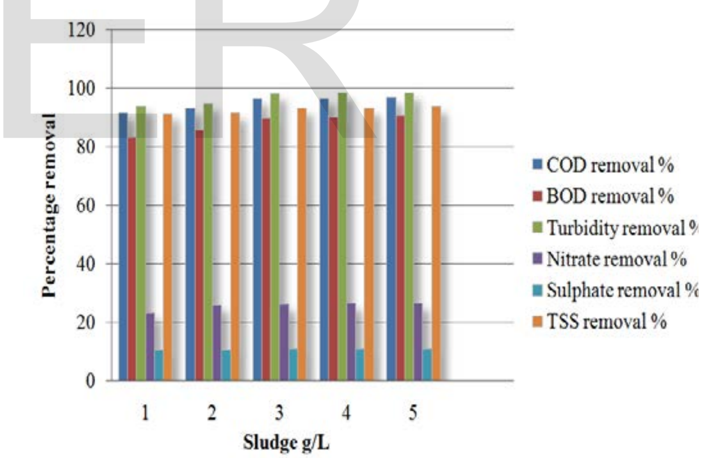

Fig. 6. Effect of sludge recycling on Fenton treatment (Reaction time=30min, pH=3, T=30^{0}C, H_2O_2/COD=3, $[H_2O_2]/[Fe^{2+}]$=15).

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 was applied to raw leachate. The Fenton treatment removed 92.1%, 83.5%, 94.2%, 18.86%, 11% and 96.6% removal of COD, BOD, turbidity, nitrate, sulphate and TSS respectively. Biodegradability of leachate improved to 0.65 and toxicity reduced to 6.3%.

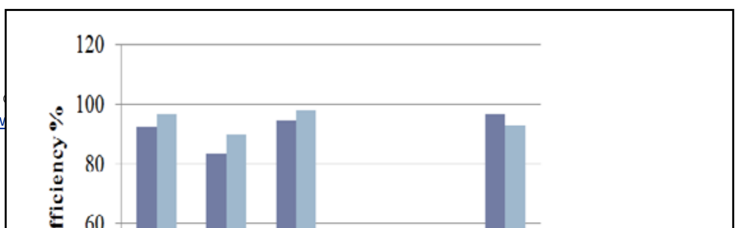

TABLE 3
CHARACTERISTICS OF RAW AND FENTON TREATED LEACHATE

Parameter	Raw leachate	Fenton treated leachate
COD(mg/L)	24000	1896
BOD (mg/L)	7500	1237.5
Turbidity(NTU)	280	16.24
Nitrates(mg/L)	200	162.28
Sulphate (mg/L)	320	284.8
TSS (mg/L)	9200	312.79

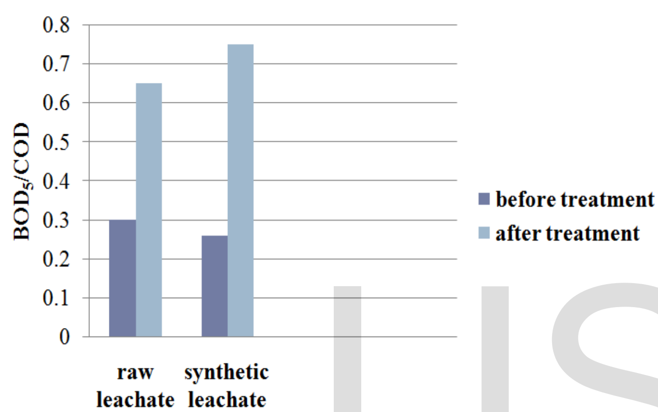

Fig. 8. Biodegradability of raw and synthetic leachate after Fenton.

Fig. 9. Raw and Fenton treated leachate.

4 CONCLUSION

Landfill leachate obtained from the Vilappilsala landfill site was treated using combined Fenton process. Based on the test results, optimal operating conditions identified. 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 improved biodegradability from 0.3 to 0.65 and reduced toxicity by 50% which will together favor biological post treatment. Fenton process was an efficient chemical pretreatment and a biological treatment can be adopted following Fenton treatment in order to improve the quality of leachate to discharge level. Cost in treating mature landfill leachate by Fenton treatment can be estimated.

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