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INTEGRATED CHEMICAL AND BIOLOGICAL TECHNIQUE FOR LANDFILL LEACHATE TREATMENT

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ABSTRACT

Landfilling although is a popular and economical method of solid waste disposal is associated with the risk of environmental degradation due to inherent problem of leachates. Leachate continues to be of concern especially when it comes into contact with ground water and surface water. Thus a proper treatment of leachate is essential prior to discharge of leachate into surface and subsurface environments. Advanced oxidation methods have proven to be one of the successful methods for treating the leachate. In the present study, the viability of sulphate radical based oxidation is used as a pretreatment to enhance biodegradability of matured leachate followed by biological treatment using Membrane bioreactor. The combined effect of chemical and biological treatment was found to be successful in removing 91.6 % COD and 99% ammonia nitrogen when the persulphate was temperature activated at 90^0C

Keywords : Leachate,Membrane Bioreactor,Persulphates, Sulphate Radical, Thermal Activation.

I INTRODUCTION

Sanitary landfilling is the most common way to eliminate solid urban wastes[1]. The most common solid waste is municipal solid waste which is known as garbage that mainly comes from residential and commercial complexes. Landfill leachate is a liquid that is mainly produced by the rain which falls on the top of the landfill. The rainwater infiltrates into the garbage and generates physical mixing and chemical reactions with the components existing in the waste.[2].Leachate usually contains high concentrations of ammonium, organic matter, toxic compounds and heavy metals [3].The quantity of leachate depend on rainwater percolation through wastes, biochemical processes in waste's cells, the inherent water content of wastes and its degree of compaction into the landfill tip. The production is generally greater whenever the waste is less compacted, since compaction reduces the filtration rate [4]. The major fraction of old or biologically treated leachate is large recalcitrant organic molecules that are not easily removed during biological treatment. So that, in order to meet strict quality standards for direct discharge of leachate into the surface water, a development of integrated methods of treatment, i.e. a combination of biological, chemical,

physical and membrane process steps, are required.AOPs remove the pollutants by the degradation process [5]. Advanced oxidation processes (AOPs) are one of technologies which involves the mechanism of highly reactive radicals generated such as hydroxyl radical and degradation of contaminants by the oxidants. The oxidation of organic compounds by persulphate (PS) ie $S_2O_8^{2-}$ has been studied as an alternative to conventional advanced oxidation processes (AOPs) which are based on highly reactive $HO^{\cdot-}$ (E^0= 2.7 V). PS decomposes to the sulphate radical anion ($SO4^{\cdot-}$) which is a strong oxidant with a redox potential of 2.5-3.1 V, depending on heat, UV and pH conditions of aqueous solution. [6]. Today, the use of membrane technologies either as a main step in a landfill leachate treatment or as a single post-treatment step has shown to be an indispensable means of achieving purification [7]. Membrane bioreactor (MBR) is the combination of membrane process like microfiltration or ultrafiltration with a suspended growth bioreactor. The Bioreactor provide controlled environment for the production of metabolites which can help to achieve the optimal growth of microbes[8].Zhong et al., (2016), conducted batch and column experiments to evaluate the feasibility of using persulfate oxidation to treat groundwater contaminated by landfill leachate (CGW).Persulfate was observed to be superior to H2O2 and permanganate for degradation of total organic carbon (TOC) in the CGW. Biodegradation could cause partial removal of TOC in CGW. In contrast, persulfate caused complete degradation of the TOC in the CGW or aged CGW, showing no selectivity to the contaminants. Deng et al., (2011) study to apply a sulfate radical based advanced oxidation process (SR-AOP) to treat a mature leachate, with an emphasis of concurrent removal of refractory organics and ammonia. In this study, all the experiments were run in a batch reactor with temperature control.The COD removal rates were 79% and 91% at pH 8.3 (no pH adjustment) and 4, respectively; and the ammonia nitrogen removal reached 100% at pH 8.3 or 4.Wang et al (2014) investigated the nitrogen removal pathways and nitrogen-related functional genes in on-site three-stage aged refuse bioreactor (ARB) treating landfill leachate. It was found that on average 90.0% of COD, 97.6% of BOD5, 99.3% of NH+4–N, and 81.0% of TN were removed with initial COD, BOD5, NH_4–N, and TN concentrations ranging from 2323 to 2754, 277 to 362, 1237 to 1506, and 1251 to 1580 mg/L, respectively.From the previous studies, sulphate radical based oxidation was found to be effective in removing organics and ammonia nitrogen and was also found to be effective in enhancing the biodegradability. In order to effectively treat a leachate a combination of physical, chemical and biological treatment are necessary. Membrane bioreactors are found to effective for biological treatment of waste compared to conventional biological processes. In the present study the effectiveness of advanced oxidation using sodium persulphate combined with biological treatment using membrane bioreactor was investigated.

II METHODOLOGY

2.1. Leachate Sampling and Characteristics

The landfill leachate sample was collected from Municipal Solid Waste Disposal Facility at Brahmapuram, Kochi. Samples were collected in plastic bottles and were stored in refrigerator at 4°C. Following parameters were investigated to ascertain the characteristics- BOD, COD, Ammonia nitrogen, BOD/COD ratio, pH, Turbidity,

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Chloride,TDS. Average values of these parameters were ascertained as shown in Table 1.

III EXPERIMENTAL PROCEDURES

3.1 Pretreatment by thermally activated persulphate

Optimizing parameters on synthetic sample bypreparing synthetic waste water having characteristics resembling original sample was done for use in further processes by trial and error. Composition of the synthetic leachate (SL) was determined based on literature data [9] with the objective of obtaining a leachate composition representative of sample leachate. The optimum conditions obtained were at pH of 3, contact time 75 minutes and $S_2O_8^{2-}/COD_i$dosage ratio of 2:1.

Since persulphate was found to show limited removal rates without activation, it was essential to enhance the performance using some activation mechanism. Persulphate on activation by heat, UV, trace metal ions etc is found to enhance the removal efficiency. Hence effect of temperature is also studied. At optimum pH, $S_2O_8^{2-}/COD_i$ ratios and contact time, effect of varying temperatures of 27, 40, 50, 60, 70, 80 and 90^oC was studied on original leachate. The best temperature was thus estimated. The sample was pretreated under optimal conditions of pH, contact time, dosage and temperature before biological treatment.

3.2 Biological Treatment Using Membrane Bioreactor

Bio sludge collected from a secondary sedimentation tank was used as inoculums for the bioreactor system after acclimatizing with leachate for 1 month. The MLSS concentrations are measured frequently and sludge is loaded such that MLSS concentration falls within the range 10000-20000 mg/l. The external membrane bioreactor consists of bioreactor and membrane filtration. The reactor is to be operated in batch mode which was filled with 0.5L sludge and 2.5L leachate. The optimum HRT was obtained by analyzing the COD removal obtained in each day. After the optimum HRT was obtained, mixed liquor was allowed to settle for 30 minutes. The supernatant from the bioreactor was passed through the hollow fibre membrane module using a pump of capacity 0.7 lpm. The treated effluent was collected and analyzed.

IV. RESULTS AND DISCUSSIONS

4.1 Initial Characteristics of Leachate

The collected sample was thawed to room temperature before the tests were conducted. The initial characteristics of the sample are given in Table 1. The main characteristics studied were COD, Ammonia nitrogen and BOD values. The parameters like pH, Turbidity, Chloride, TDS and TSS were also ascertained. The average values of BOD and COD were 12,408 mg/L and 88,000 mg/L which indicates that the sample was heavily polluted. BOD/COD ratio was 0.141 which indicates that leachate was mature and is not amenable to biological treatment. In order to improve the biodegradability, pretreatment was necessary.If the BOD/COD ratios are more than 0.3 sample is said to be

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young and amneble to biological treatment.

Parameter	Average characteristics of original sample
BOD mg/L	12,408
COD mg/L	88,000
BOD/COD	0.141
Ammonia Nitrogen mg/L	1780
Nitrate mg/L	1.4
pH	4.81
Turbidity	1328
TDS mg/L	18,590
TSS mg/L	8635

TABLE 1 CHARACTERISTICS OF LEACHATE SAMPLE FROM BRAHMAPURAM

4.2 Results of Pretreatment Using Sodium Persulphate on Original Sample

The original leachate sample was pretreated with conditions obtained optimal on synthetic leachate (Initial pH 3, dosage ratio of 2:1, 75 minute contact time at ambient temperature). The results showed a removal percentage of 36.36% COD and 56.5 % Ammonia nitrogen. The results are presented in Fig. 1. Limited removals may be attributed to the limited oxidation potential of persulfate alone against high organic concentration in leachate. Persulfate anion can act as a direct oxidant, its reaction rates are limited for more recalcitrant contaminants. Heating activate persulphate to produce sulphate free radical $SO_4^{\bullet-}$ so that the organics in landfill leachate are mineralized (Deng and Ezyske, 2011).

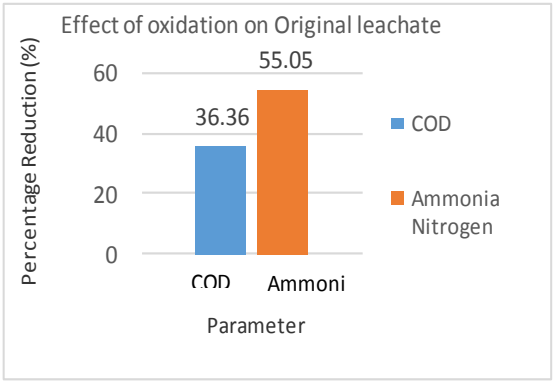

Fig. 1 Effect of oxidation on original leachate

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4.3. Effect of Temperature on Oxidation Reactions

Thermal activation is one of the activation methods widely used for the generation of sulfate radicals from persulfate anion. Under thermally enhanced conditions, the persulfate ion can be converted into sulfate radicals. Persulfate salts readily dissociate in water to form the persulfate anion ($S_2O_8^{2-}$), which has a strong oxidation potential (E^o= 2.01 V) but reacts slowly with most contaminants of concern. Therefore, the activation of persulphate is essential in improving the removal of the total organic load, specific phenolic micropollutants, and nitrogen compounds during landfill leachate treatment [10].

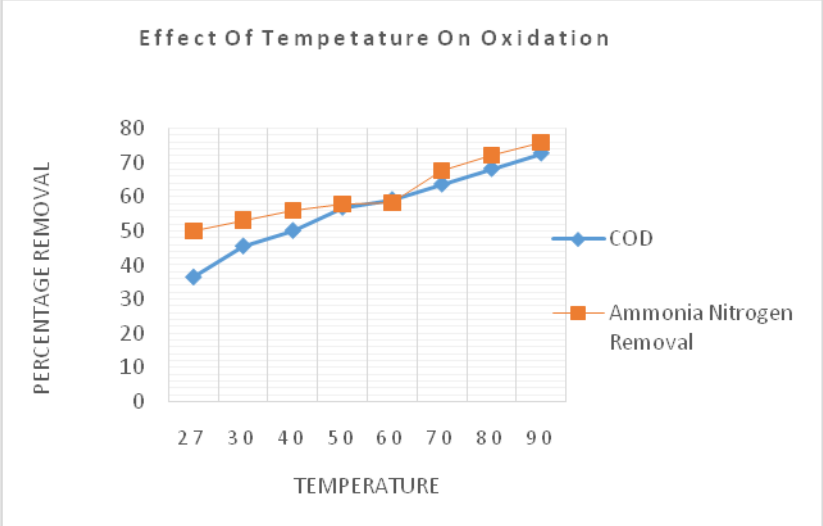

Fig. 2 Effect of temperature on oxidation

Persulfate is usually chemically or thermally activated to generate the reactive oxygen species sulfate radical ($SO_4^{\bullet-}$), a more effective oxidizing agent than persulfate (E^o = 2.6-3.5 V). Fig.2 shows effect of varying temperature on removing COD and Ammonia Nitrogen in original leachate sample.It was observed that with an increase in temperature, removal efficiencies also enhanced. This is because the persulfate anion was thermally activated according to eqn. 1[11]

$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$ (30°C < T < 99°C) (1)

$SO_4^{\bullet-}$ may initiate production of other intermediate highly reactive oxygen species (ROS) such as hydroxyl radicals (OH.) as shown in eq 2 and 3 respectively

$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$ (2)

$SO_4^{2-} + H_2O \rightarrow HSO_4^- + OH^-$ (3)

These ROS can initiate a series of radical propagation and termination chain reactions where organics are partially and even fully decomposed. To maintain a high treatment efficiency, heat was required. In fact, fresh landfill leachate has a high temperature due to the heat release from anaerobic digestion of solid wastes within landfills. Another potential energy source is biogas (e.g. CH_4) produced during land-filling, which may be utilized to sustainably support thermal for leachate treatment [10].

TABLE 2. CHARACTERISTICS OF PRETREATED ORIGINAL SAMPLE

Parameter	Value
BOD	9120 mg/L
COD	24000 mg/L
BOD/COD	0.38
NH3-N	430.56mg/L
Nitrate	4.9 mg/L
Turbidity	733NTU
TDS	19000mg/L
TSS	4000 mg/L

It was observed that significant reduction in COD, BOD, Ammonia nitrogen occurred BOD/COD ratio showed an increase from 0.141 to 0.38 indicating that the sample is now susceptible to biological treatment

4.4. Biological Treatment using Membrane Bioreactor

pH of the leachate sample pretreated under optimal conditions and temperature 90^0C and was adjusted to 7. It was then mixed with biosludge acclimatized for one month. MLVSS was adjusted to 20g/L. The mixed liquor was given aeration and COD removals were measured each day to ascertain the hydraulic retention time. Fig 3 shows the COD removals at different days.

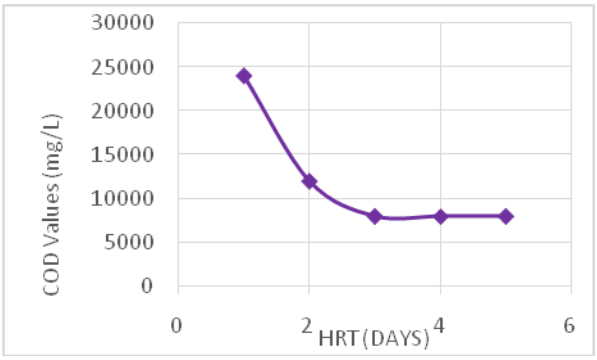

Fig.3 HRT of sample pretreated at 90^0C

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It was observed that COD values reached a steady state on 3rd day for the sample pretreated at 90^0C. Hence HRT for sample pretreated at 90^0C was taken as 3days

TABLE 3.CHARACTERISTICS OF SAMPLE AFTER PRETREATMENT AND AFTER BIOLOGICAL TREATMENT

Parameter	After Pretreatment	After Biological Treatment and Filtration	Percentage removal (%)
BOD mg/L	9120	440.4	95.17
COD mg/L	24000	2000	91.67
NH_3-N mg/L	430.56	2.15	99.50
Nitrate mg/L	4.9	2.19	55.3
Turbidity NTU	733	8	98.90
TDS ppm	19000	1570	98.7
TSS mg/L	6000	62.5	98.4
pH	7	5.6	-

The results indicated that almost 90% and more removal percentages was seen in most parameters ascertained. COD removals of about 91 % were seen while BOD removals of about 95% were observed. Overall removal percentage of treatment process was found to be more than 95% in removing almost all the parameters.

V CONCLUSION

The effect of sulphate radical based oxidation process combined with biological treatment process in treating highly polluted landfill leachate was studied. Based on the study it was observed that sodium persulphate was effective oxidant for removing COD and increasing the BOD/COD ratio of the matured leachate sample to make it suitable for biological process. Optimum parameters for application of oxidant was found to as pH of 3, $S_2O_8^{2-}$/CODi of 2:1, 75 minutes contact time.

However only limited removals were observed in the case of original leachate sample suggesting that activation of

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persulphate was necessary to generate sulphate radicals to degrade much recalcitrant contaminants. High temperature generally favoured higher removal rates. At about 90^0C about 72% of COD and 76% Ammonia nitrogen removals were observed in addition to a decrease in turbidity and TSS. An increase in TDS values were observed after pretreatment possibly due to Na^+ ions from sodium persulphate. However biological treatment could effectively remove organic fraction of TDS. The end product of oxidation, sulphate ion (SO_4^{2-}) is inert salt and not harmful to environment as it is not considered as pollutant [15].Thus advanced oxidation using activated persulphate can be combined with membrane bioreactor to effectively reduce the strength of leachate. The effluent of treatment was not allowed to discharge to the environment yet due to the inability to reach the discharge standard limits. So further post treatment is recommended for meeting the standards of disposal.

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