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EFFECTS OF TEMPERATURE AND TIME ON COD AND BOD CHARACTERISTICS OF ANAEROBIC TREATMENT OF SULPHIDE/LIMED TANNERY WASTEWATER

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ABSTRACT

Anaerobic treatment was carried out as a simple method for handling effluent from sulphide/limed unhairing wastewater from a Beam house. Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) which are common parameters were used for assessing the quality of treated industrial wastewater. The sample wastewater was pre-treated by filtration, heating and maintaining the temperature to 70 ^{o}C for fifteen minutes, covered and left overnight. This was repeated for three consecutive days and then conditioning to pH 7.0, with dilute hydrochloric acid. The treatment was carried out using microorganisms isolated from aged sulphide/lime liquor, coded as T_{I}, T_{II}, T_{III}, T_{IV} and T_{V}. The process was carried out according to standard procedures at temperatures between 22 ^{o}C and 37 ^{o}C and treatment periods ranging from 5 to 9 days. The data obtained were analyzed with the general linear model (GLM). Means were obtained; the post hoc test on the means was obtained using Duncan Multiple Range Test (DMRT). For COD, the effects of all temperatures were significantly different ($P < 0.05$). Its reduction was significantly different between day 5 and 7 ($P < 0.05$), but there was no significant difference between Day 7 and 9. The highest percentage reduction of COD obtained was in Day 9 and the least in Day 5. BOD_5, reduction was observed throughout the treatment temperatures, though not significantly different ($P > 0.05$). However, the reduction of BOD was significantly different between day 7 and day 9 ($P < 0.05$). The anaerobic treatment of sulphide/liming unhairing wastewater was observed to have significantly reduced the pollutants determined by COD and BOD. Hence, this method may be use for the treatment of sulphide/limed unhairing wastewater before combining it with others from different sections of the Tannery.

KEYWORDS: Anaerobes, Tannery, Sulphide/lime wastewater, COD, BOD

INTRODUCTION

The treatment of wastewater generated from sulphide/limed unhairing process of leather manufacture is necessary if the environment is to be treated fairly. This is in view of the pollution load of tannery effluent particularly from the limed yard, which constitutes 65% -70% of pollutants in the whole tannery effluent [1]. This effluent, which had high values of COD, BOD and sulphide ions, poses serious environmental and health threats. TDS and TSS pollution values and other organic matter make the wastewater more complicated and difficult to treat. Several research efforts have been made and reported particularly on aerobic and anaerobic treatment of combined tannery wastewater [2], but, little have been reported specifically on sulphide/limed unhairing wastewater.

Aerobic treatment systems such as the conventional activated sludge (CAS) process are widely adopted for treating low strength wastewater (<1000 mg COD/L), like municipal wastewater. CAS process is energy intensive due to high aeration requirement. It also produces large quantity of sludge (about 0.4 g dry weight/g COD removed) that has to be treated and disposed [3]. Other methods like membrane filtration and ozone oxidation have been tried, yet biological method of treating tannery wastewater is most preferred as it requires less energy and generates less suspended solids [3]. This method has been reported to be cost effective [4, 5], particularly in the subtropical and tropical regions where the climate is consistent. Anaerobic wastewater treatment has an advantage of low sludge formation, removal of higher organic loading and high pathogenic removal [6], methane gas production and low energy consumption [7, 8]. It has also been reported to have low construction, operation, maintenance cost and small land requirement [8, 9].

Anaerobic digestion takes place in four phases which are as follows:

(i) Hydrolysis/liquefaction: $n (C_6H_{10}O_5 + n (H_2O) \rightarrow n(C_6H_{12}O_6)$,

(ii) Acidogenesis: $(C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2)$ and $C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2$.

(iii) Acetogenesis: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

(iv) Methanogens: $CH_3COOH \rightarrow CH_4 + CO_2$.

To ensure a balanced digestion process, it is important that the various biological conversion processes remain sufficiently coupled during the process so as to avoid accumulation of any intermediates in the system [10]. Majority of anaerobic digestion plants are operated under mesophilic conditions (approx. 35 ^oC), however, most wastewater released for treatment are at temperatures below 18 ^oC. Therefore, many wastewaters are heated prior to treatment, thus consuming up to 30% of energy produced. It has also been proven that many refractory difficult biodegradable organic compounds can be decomposed (to simpler substances) under anaerobic conditions [11]. Sulphide/limed wastewater with high pollution values of COD, BOD, sulphide ions and other organic matter, have potential of maintaining high biomass. These can be in form of granules, suspended solids and so on. Therefore, wastewater of this nature has little or no limitations in the application of anaerobic systems. This can be an advantage in the treatment of unhairing/limed liquor from a tanning industry.

This study is aimed at separate treatment of sulphide/limed unhairing wastewater because of its high pollutants level and to determine the extent of COD and BOD reduction, before combining other tannery wastewater, as it is presumed might ease the treatment of tannery wastewater.

MATERIALS AND METHODS

Isolation and characterization of anaerobic bacteria

An agar was prepared and kept overnight at control atmosphere and sterilized the next day. It was then inoculated with samples of sulphide/limed depilatory wastewater and incubated at 37 ^oC anaerobically for 48 hours [12] as follows: T_1 and T_2 – super latten sulphide depilatory/limed liquor while, T_3 and T_4 were taken from the same but stirred liquor and T_5 is a relimed liquor. These isolates were characterized and 0.5 and 1.0 McFarland standards were prepared for inoculation into the wastewater for the treatment.

Bioremediation of Tannery Effluent

The pH of filtered Tannery unhairing/limed effluent was adjusted to 7.0 using dil. HCL and heated to 70 ^oC. This temperature was maintained for fifteen minutes, covered and left overnight. The procedure was repeated for three consecutive days. Control sample was taken; the remaining was distributed into 120 ml sample rubber bottles each containing 100 ml of the effluent. The individual microorganisms were inoculated each into the sample effluent in triplicate according to standard procedures and incubated anaerobically at 22 ^oC, 27 ^oC and 37 ^oC temperatures. Then COD and BOD were determined at an interval of 5, 7 and 9 days, according to standard procedures to estimate the depletion of each parameter.

Degradation of organic matter is often an oxidation - reduction reactions, initiated by enzymes which causes organic substances to oxidized and the microorganisms abstract nutrients and energy to grow, as illustrated in the equation below:

$$\mathit{Oxidized\ Species} \quad < \frac{\mathit{Reduction}}{\mathit{Oxidation}} > \quad \mathit{Reduced\ Species}$$

RESULTS AND DISCUSSION

Table 1.0: Mean Reduction of the Parameters at Different Temperatures

Temp.	N	COD (mg/L)	BOD (mg/L)
23 ^oC	66	17014.4±5243.06^a	1064.5±109.80^a
27 ^oC	66	15395.6±4907.63^b	891.7±249.06^a
37 ^oC	66	14185.2±5405.02^c	866.2±815.12^a
Total	198	15531.7±5292.11	940.8±800.95

Notes: Means with the same letter are not significantly different at 0.05

Table 2.0.: Mean Reduction of Parameters at Different Period of Treatment

PERIOD	N	COD (mg/L)	BOD (mg/L)
DAY 5	66	17871.2±4003.14^a	1092.7±168.86^a
DAY 7	66	15845.5±5098.32^b	1135.0±1293.79^a
DAY 9	66	12878.5±5482.48^b	594.8±242.25^b
Total	198	15531.7±5292.11	940.8±800.95

Notes: Means with the same letter are not significantly different at 0.05

Percentage Reduction of COD and BOD of Sulphide/Lime Wastewater at Different Conditions of Temperatures, Periods of Treatment and McF Standard.

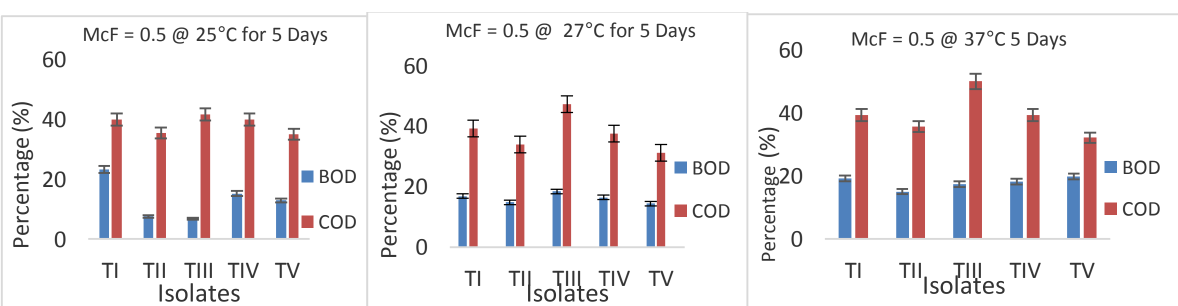

Fig. 1.0: Effects of Time and Temperature on Anaerobic Treatment with 0.5McF after 5 Days

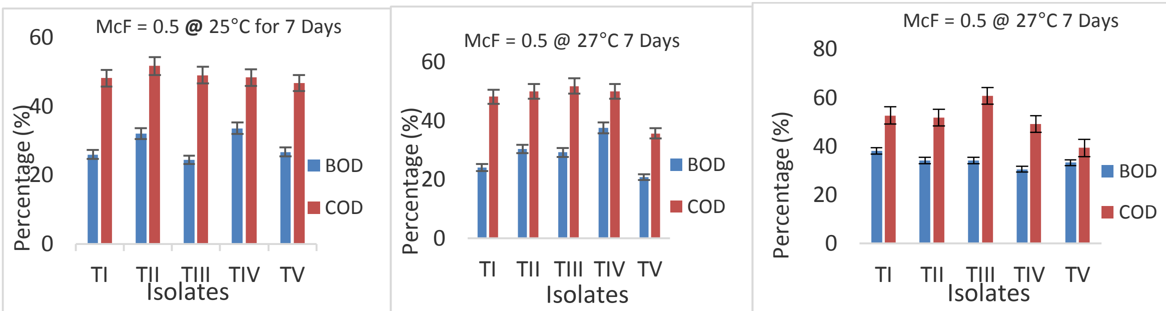

Fig. 2.0: Effects of Time and Temperature on Anaerobic Treatment with 0.5 McF after 7 Days

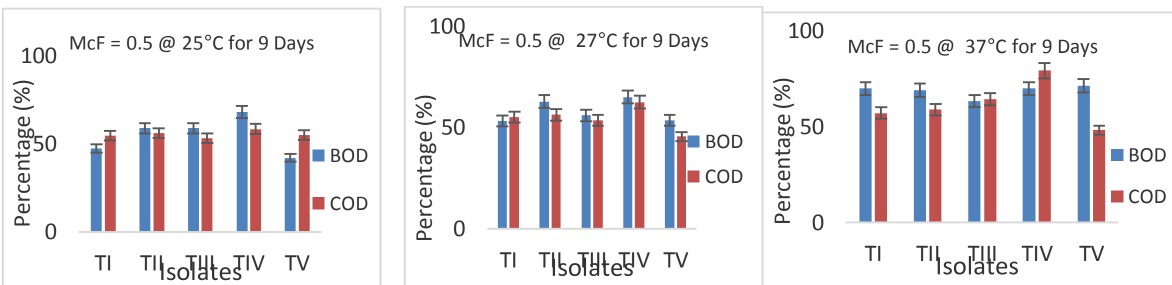

Fig. 3.0: Effects of Time and Temperature on Anaerobic Treatment with 0.5 McF after 9 Days

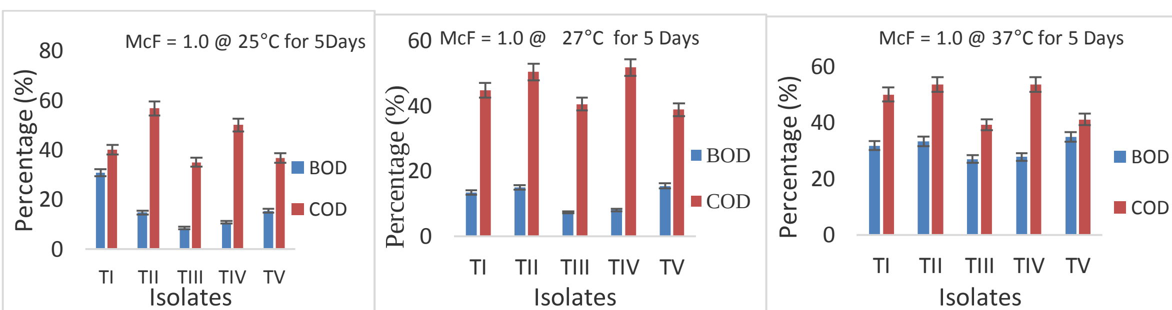

Fig. 4.0: Effects of Time and Temperature on Anaerobic Treatment with 1.0 McF after 5 Days

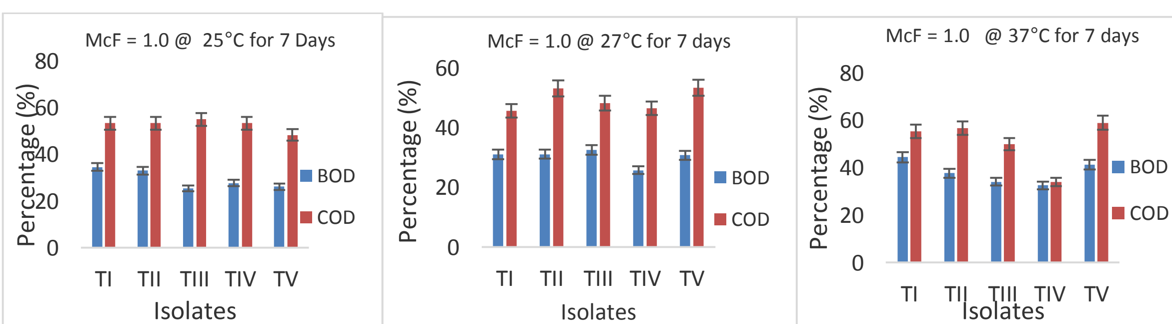

Fig. 5.0: Effects of Time and Temperature on Anaerobic Treatment with 1.0 McF after 7 Days

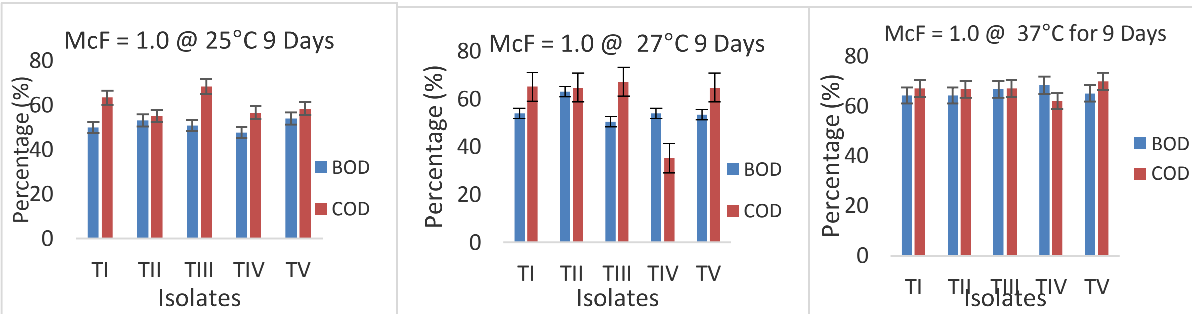

Fig. 6.0: Effects of Time and Temperature on Anaerobic Treatment with 1.0 McF after 9 Days

Chemical Oxygen Demand

The COD test is used to measure pollution of wastewater in terms of equivalence of oxygen required for oxidation of organic and inorganic matter to yield CO_2 and H_2O. COD is useful in pin-pointing toxic conditions and presence of biological resistance substances [13]. The permissible limit of discharge is at the range of 300-3000 mg/ L [14]. The result obtained in this study was higher than the set limit with the value of 6847 ± 1721 mg/L (Tables 1 and 2). This indicates that the effluent is unsuitable for the existence of aquatic organisms due to the reduction in the dissolved oxygen content, which is dependent upon the chemicals used in leather processing and their rate of biodegradability [1].

The data collected from the parameters determined after the anaerobic treatment were analyzed with the general linear model (GLM) to assess their level of reduction by the isolates at different temperatures, periods of treatment and McFarland standards. Means obtained from the ANOVA, along with the post hoc test on the means using Duncan Multiple Range Test (DMRT) is as shown in Tables 1.0 and 2.0. Classes of effectiveness in pollution reduction are indicated in alphabetic letters in descending order. The computation took into considerations all temperatures, different periods, different isolates and McFarland standards used for the treatment. For COD, the effects of temperature indicated significant difference for all the temperatures ($P < 0.05$). But was significant only between days 5 and 7as shown in Table 2.0.

The steady reduction of COD observed in Figures 1 - 6 could be attributed to the oxidation of carbon and other organic matter from the wastewater induced by the anaerobes. The process also led to the generation of hydrogen sulphide that was observed given off. This might have contributed to further reduction of COD from the wastewater as reported by Lofrano *et al* [15] and Muyzer and Stams [16]. The presence of hydrogen sulphide gas observed during the treatment proposes could be attributed to the isolates as sulphur reducing anaerobes [15]. This may account for the general increase observed in percentage reduction of COD from the wastewater, suggesting that the degradation that led to reduction of COD by the anaerobes is temperature dependent [4] (Figures 4 – 6). Results obtained show that COD had the highest percentage reduction compared to BOD from the treated wastewater. Sulphide concentration in the wastewater could not seriously deter the reduction of COD, possibly because it was observed to evolve in form of H_2S, hence, its presence in the wastewater as reported by other researchers [5, 17]. Another possible reason is that hydrogen sulphide could not seemly deter the degradation of COD from the wastewater is that it was not exclusively in a molecular form as reported by Lofrano *et al* [15]. For COD, its reduction was significantly different for the three different periods (Days 5, 7 and 9) of treatment ($P < 0.05$). For the period of treatment, the highest percentage reduction obtained was on Day 9 and least on Day 5.

Biological Oxygen Demand

BOD is a method of estimating the influence of effluent to reduce the oxygen content of water. The value obtained in this work is 2906 ± 115 mg/L. This is above the permissible limit of discharge of 125-1000 mg/L [14] as a result of high organic load. Over-application of high BOD effluents on land can create anaerobic conditions in the soil [18]. Prolonged oxygen depletion will reduce the soil microorganisms' capability to break down the organic matter in the effluent that may lead to obnoxious odour generation, surface and ground water pollution. BOD_5, reduction was observed throughout the treatment temperatures, though the difference was not significant ($P > 0.05$) (Table 1.0). This observation was as a result of the high amount of the organic matter in the wastewater whose degradation was slow, but with prolonged treatment the anaerobes are likely to degrade the wastewater significantly [19].

The anaerobic treatment of sulphide-liming unhairing wastewater has reduced the pollutants determined by COD and BOD significantly. However, the evolving of sulphide in form of hydrogen sulphide gas poses serious threats and could discourage the anaerobic method of treatment.

RECOMMENDATIONS

A technique for trapping H_2S gas generated during anaerobic treatment of sulphide-lime unhairing wastewater should be developed to reduce health threats posed by this poisonous gas. Its possible use as a raw material is recommended.

CONCLUSION

Anaerobic treatment of sulphide/lime unhairing tannery wastewater treated with microorganism isolated from a similar effluent, made a significant impact, as reasonable level of pollution load reduction has been achieved. The isolates as inoculum were more effective at higher temperatures, suggesting high probability of the isolates as mesophiles. The observed gas produced which has a rotten egg smell and turns lead acetate paper black indicates that the microorganism could be sulphide reducing bacteria. Increase in temperature led to increase of BOD pollution load of the sulphide/limed depilatory wastewater because biodegradation breaks down the matrices of organic component of the wastewater thereby requiring more oxygen for oxidation. Subsequently the oxidation of the tiny organic molecules will reduce the BOD pollution load of the sulphide/limed depilatory wastewater

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