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# Performance Characteristics of Anaerobic Biodegradation of Synthetic Phenolic Industrial Wastewater

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## ABSTRACT

The treatment of toxic and inhibitory phenolic compounds using biological techniques have been pursued vas a promising and widely accepted treatment process due to its easiness of handling, a greater level of stabilization of waste and properly operated to prevent the production of secondary pollutants. Up-flow Anaerobic Bio-Reactors (UAFB) has been widely applied for the handling of high organic load industrial wastewater. The treatment of synthetic phenolic wastewater by a single stage anaerobic fixed bed bioreactor with granite stones packing at four different temperatures was studied. The effect of hydraulic retention time on COD reduction and other steady state characteristics and kinetic parameters, which form these characteristics, was also studied. A recirculated single stage up-flow anaerobic bioreactor operated at all the above-given temperatures with initial BOD 1462 mg/l and initial COD 5720 mg/l for a digestion period of 25 days with a working volume of 1000 ml. The performance of the reactor was monitored after every five days and analyzed in terms of percentage (COD, BOD, TS, TDS, VS removal and biogas production). The removal efficiency of BOD, COD, TS, TDS and VS reached a maximum value of 63.20%, 61.24%, 44.88%, 47.67% and 53.12% respectively. With the change in HRT, the maximum COD reduction was 66.04% at 24 hrs HRT at 40$^0$C with initial COD of 5000 mg/l. Specific biogas yield increased up to 0.0162 ml/mg $COD_{r.}$

***Keywords*** **-** Phenol, anaerobic, fixed bed bioreactor, wastewater, up-flow anaerobic sludge blanket, experimental design, India

**Abbreviations**: BOD -Biochemical Oxygen Demand, COD - Chemical Oxygen Demand, TDS - Total Dissolved Solids, VS - Volatile Solids, UAFB - Up-Flow Anaerobic Fixed Bed Bioreactor

## INTRODUCTION

Aromatic compounds are abundant in the environment (Lettinga, Rebac, & Zeeman 2001; Colleran & Pender, 2002; Collins, 2005). One group of these products is phenolic compounds. Phenol is degraded under anaerobic conditions, methane and carbon dioxide as reviewed in several reports (Guieysse, Wickstro, Forsman & Mattiasson, 2001; Li & Fang, 1996). However, at some concentrations, phenol may promote inhibitory effects in methanogenic bacteria, diminishing methane production and carbon degradation (Rebecca & Gerbens, 1999). Therefore, phenolic compounds are problematic for the anaerobic treatment of effluent. One report (Hernandez, 2003) sets that various alternatives (dilution, ozonation, UV-H2O2) offer to eliminate the toxicity and improve phenol's anaerobic biodegradation. Previous works on phenol anaerobic biodegradation have been carried out in batch (Banks & Wang, 1999) and continuous operation: fluidized bed (Mc Hugh Carton, Collins & O'Flaherty, 2004), UASB (Chang, Nishio & Nagai, 1995) and expanded bed reactor (Collins, Foy, McHugh & O'Flaherty, 2004).

Veeresh, Kumar, and Mehrotra (2005) have reviewed treatment of phenol and cresols in up-flow anaerobic sludge blanket (UASBR). The anaerobic bacteria have the capability to degrade phenol as a sole substrate (Fang, Li, Chui, & Chen, 1996; Chang et al. 1995; Tay, He & Yan, 2000) and use of a co-substrate is not a prerequisite. However, the presence of a co-substrate retards/prevents the toxic effects of phenols during shocks helps in complete biodegradation of phenol (Tay *et al.,* 2001) and facilitates fast recovery of the process. Pure substrates such as glucose (Hwang and Cheng, 1991; Tay *et al.* 2001) and volatile fatty acids (VFA) (Kennes, Mendez & Lema, 1997) were used as co-substrates in the anaerobic treatment of phenols in UASBR. The use of pure substrates restricts the practical applicability of the process. Therefore, it has been deemed necessary to assess the potentials of a readily degradable wastewater as a co-substrate in the treatment of phenolic waste. The present technical note describes the performance of a (UAFB) up-flow anaerobic fixed bed bioreactor treating synthetic wastewater**.**

## OBJECTIVE OF THE STUDY

The work studied the anaerobic degradation of phenolic wastewater at four different temperatures 30$^0$C, 35$^0$C, 40$^0$C and 45$^0$C and with a change in hydraulic retention time from 2 to 24 hours. Chemical oxygen demand (COD), biochemical oxygen demand (BOD), total solids (TS), total dissolved solids (TDS), volatile solids (VS), biogas productivity and specific biogas yield, evaluated degradation of phenol.

## MATERIALS AND METHODS

Synthetic wastewater containing phenol with COD: N: P ratio of 100: 2.5: 0.5, using urea and potassium dihydrogen phosphate as a chief source of nitrogen and phosphorous, respectively was produced. The phenolic wastewater contained BOD (biochemical oxygen demand) of value 1278 mg/l and COD (chemical oxygen demand) of value 5000 mg/l. In this study, synthetic phenolic wastewater was prepared as and when required. Distilled water added maintained the composition of phenolic waste. To support the growth of microorganisms, nutrients like nitrogen and phosphorous were added in a ratio of COD: N: P of 50: 2.5: 1. Synthetic wastewater containing phenol is the sole carbon source. Urea and potassium dihydrogen phosphate are the chief source of N and P. Small quantities of Inorganic ions like $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+,}$ and $Fe^{3+}$ were added in wastewater.

An anaerobic mixed culture developed from cow dung in yeast extract media by digesting it up to two weeks at 35$^0$C temperature, was enriched in the synthetic medium of acetic acid. Acetic acid, added to inhibited the growth of acidogenic bacteria. The methanogenic culture was enriched in an acetic medium. This culture obtained was used as inoculums for the batch process. As phenol is toxic to microorganisms and is a good disinfectant, its higher concentration may prevent microbial growth in wastewater, may prevent microbial growth or, at least, make it difficult to sustain, so the mixed culture was thus, developed and was adapted to the phenolic wastewater. For adaptation, the concentration of phenol was gradually increased from 100 mg/l to 1000 mg/l. This experiment was carried out for 14 days at 35$^0$C temperature. The biogas production was measured each day to ensure the bacterial activity. Phenolic waste water and the developed adapted mixed culture was mixed in definite proportion and was introduced into the single stage attached film fixed bed bioreactor and was allowed to ferment anaerobically for 25 days at four different temperatures $30^0$C, $35^0$C, $40^0$C, and $45^0$C, respectively. One hundred (100) ml seed material was used in each digester while pH was adjusted by adding lime when required.

The single stage anaerobic attached film fixed bed reactor with a working volume of 1000 ml was packed with granite stones of size 1.0 cm to 1.5 cm in diameter. The reactor consists of a jacketed column was used to maintain the temperature by flowing water in the outside jacket using a thermostat water bath. The reactor was fed at a rate of 25 ml/hr to maintain the HRT of 24 hours. Continuous recycle of the treated effluent (phenolic wastewater) was done for the partial fluidization of the sludge by a peristaltic pump. These pumps were calibrated for different flow rates. COD, BOD, TS, TDS, VS and biogas production at four different temperatures (300C, 350C, 400C, and 450C), evaluated reactor performance.

In the experiment, the effect of a change in hydraulic retention time (HRT) on COD reduction and other steady state characteristics and kinetic parameters from these characteristics was studied. HRT varied from 02 to 24 hrs. The steady state reached between $9^{th}$ -13th days for different HRT in the reactor.

## RESULTS AND DISCUSSION

Phenols are highly toxic to microorganisms. After the development of methanogenic culture, 100 ml inoculum was mixed with wastewater having phenol concentration 100 mg/l. After two weeks, 100 ml inoculum from the experiment and wastewater with 200 mg/l phenol concentration was inoculated. In this manner, the highest concentration of phenol i.e. 1000 mg/l was digested and percentage COD removal of 59.33% was achieved (Table-1 & Figure-1).

Table 1. Percentage Phenol Removal during Adaptation of Phenolic Wastewater

| S. No | Initial Phenol Conc. (mg/l) | Initial COD (mg/l) | Final COD (mg/l) | % COD Removal |
|---|---|---|---|---|
| 1. | 100 | 804 | 699 | 13.05 |
| 2. | 200 | 1627 | 1363 | 16.22 |
| 3. | 300 | 2082 | 1620 | 22.19 |
| 4. | 400 | 2877 | 2047 | 28.84 |
| 5. | 500 | 3958 | 2493 | 37.01 |
| 6. | 700 | 4495 | 2425 | 46.05 |
| 7. | 800 | 5746 | 2722 | 52.62 |
| 8. | 1000 | 6728 | 2736 | 59.33 |

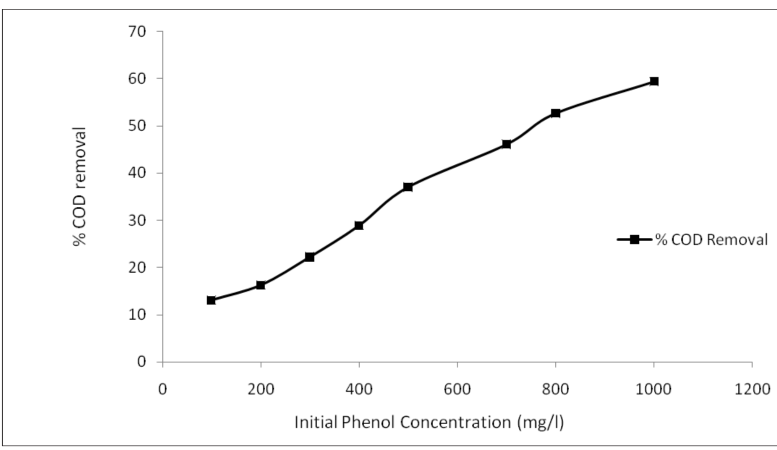


Figure 1. COD Percentage Removal during Adaptation of Phenolic Wastewater

**Effect of change in temperature**

Tables 2 to 5 show the characteristics of the treatment mixture viz. BOD, COD, TS, TDS and VS at different digestion time at four different temperatures $30^0C$, $35^0C$, $40^0C$, and $45^0C$, respectively. Figures 2 to 6 represent the effect of digestion time on % BOD, % COD, % TS, % TDS and % VS reduction, respectively.

Table 2. Percentage reduction of BOD at $30^0$C, $35^0$C, $40^0$C and $45^0$C temperature

| S.No. | Digestion Time(days) | % BOD Reduction | | | |
|---|---|---|---|---|---|
| | | At 30°C | At 35°C | At 40°C | At 45°C |
| 1. | 5 | 23.05 | 19.56 | 28.45 | 24.62 |
| 2. | 10 | 36.73 | 29.13 | 40.56 | 36.38 |
| 3. | 15 | 48.29 | 42.81 | 49.52 | 47.87 |
| 4. | 20 | 54.58 | 49.84 | 60.09 | 57.85 |
| 5. | 25 | 57.25 | 51.50 | 67.78 | 63.20 |

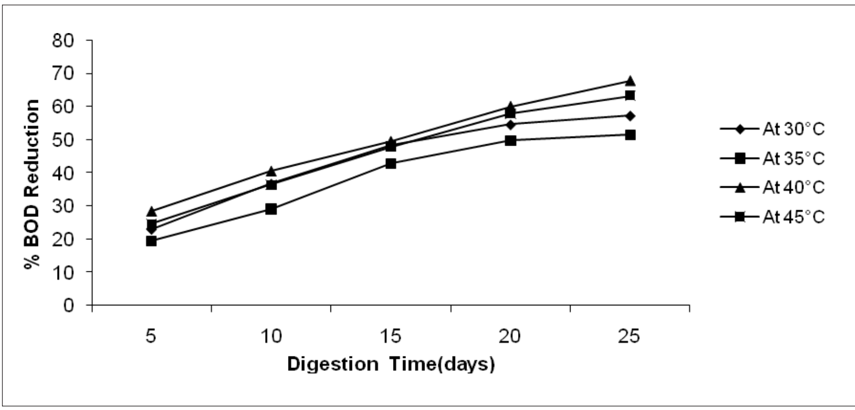


Figure 2. Effect of digestion time on percentage BOD Reduction at four different temperatures

Table 3. Percentage reduction of COD at $30^0$C, $35^0$C, $40^0$C and $45^0$C temperature

| S. No. | Digestion Time(days) | % COD Reduction | | | |
|---|---|---|---|---|---|
| | | At 30°C | At 35°C | At 40°C | At 45°C |
| 1. | 5 | 18.63 | 17.74 | 24.44 | 20.69 |
| 2. | 10 | 33.46 | 28.70 | 36.53 | 33.93 |
| 3. | 15 | 42.36 | 40.85 | 46.76 | 42.79 |
| 4. | 20 | 49.33 | 49.84 | 55.85 | 54.09 |
| 5. | 25 | 49.61 | 59.47 | 65.78 | 61.24 |

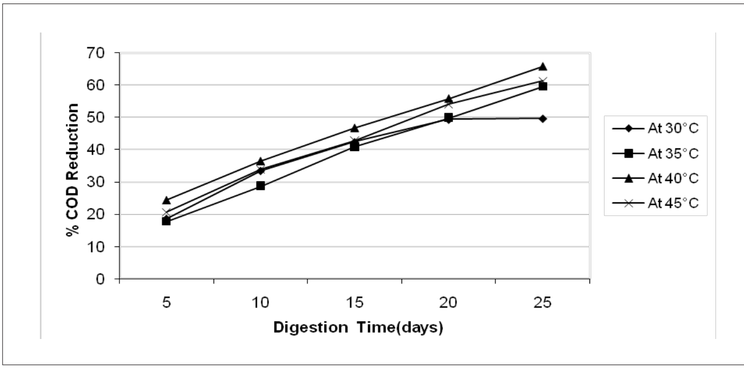


Figure 3. Effect of digestion time on percentage COD Reduction at four different temperatures

Table 4. Percentage Reduction of Total Solids at $30^0C$, $35^0C$, $40^0C$ and $45^0C$ Temperature

| S. No. | Digestion Time(days) | % TS Reduction | | | |
|---|---|---|---|---|---|
| | | At 30°C | At 35°C | At 40°C | At 45°C |
| 1. | 5 | 12.59 | 11.02 | 15.74 | 12.59 |
| 2. | 10 | 22.04 | 22.04 | 28.34 | 24.40 |
| 3. | 15 | 30.70 | 29.92 | 36.22 | 34.64 |
| 4. | 20 | 36.22 | 36.22 | 42.51 | 40.15 |
| 5. | 25 | 37.00 | 40.15 | 48.03 | 44.88 |

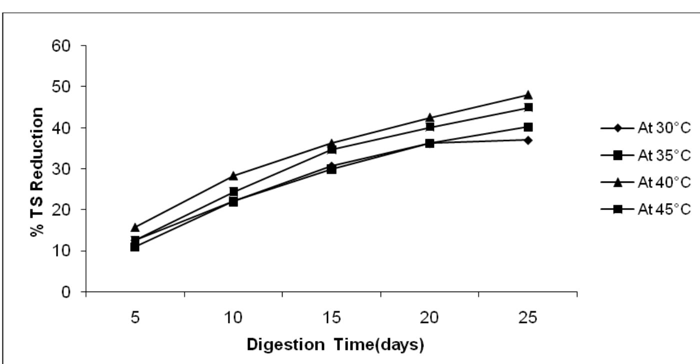


Figure 4. Effect of digestion time on percentage TS Reduction at four different temperatures

Table 5. Percentage Reduction of Total Dissolved Solids at 30⁰C, 35⁰C, 40⁰C and 45⁰C Temperature

| S.No. | Digestion Time(days) | percentage TDS Reduction | | | |
|---|---|---|---|---|---|
| | | At 30°C | At 35°C | At 40°C | At 45°C |
| 1. | 5 | 16.27 | 12.79 | 20.93 | 18.60 |
| 2. | 10 | 25.58 | 22.09 | 31.39 | 26.74 |
| 3. | 15 | 32.55 | 31.39 | 43.02 | 38.37 |
| 4. | 20 | 40.69 | 38.37 | 50.00 | 44.18 |
| 5. | 25 | 41.86 | 43.02 | 54.65 | 47.67 |

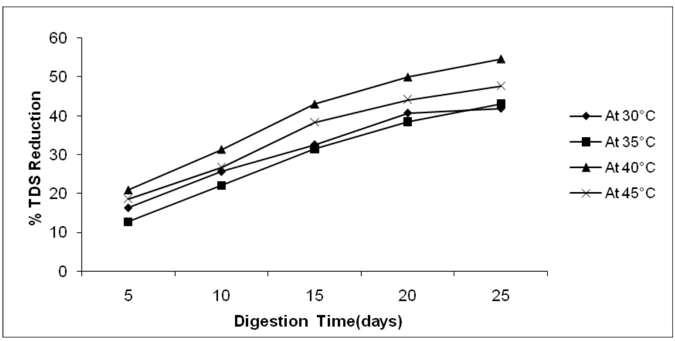


Figure 5. Effect of digestion time on percentage TDS Reduction at four different temperatures

Table 6. Percentage Reduction of Volatile Solids at 30⁰C, 35⁰C, 40⁰C and 45⁰C Temperature

| S.No. | Digestion Time(days) | percentage VS Reduction | | | |
|---|---|---|---|---|---|
| | | At 30°C | At 35°C | At 40°C | At 45°C |
| 1. | 5 | 21.87 | 18.75 | 26.56 | 20.31 |
| 2. | 10 | 29.68 | 29.68 | 35.93 | 32.81 |
| 3. | 15 | 35.93 | 43.75 | 46.87 | 42.18 |
| 4. | 20 | 43.75 | 48.43 | 56.25 | 51.56 |
| 5. | 25 | 46.87 | 51.56 | 60.93 | 53.12 |

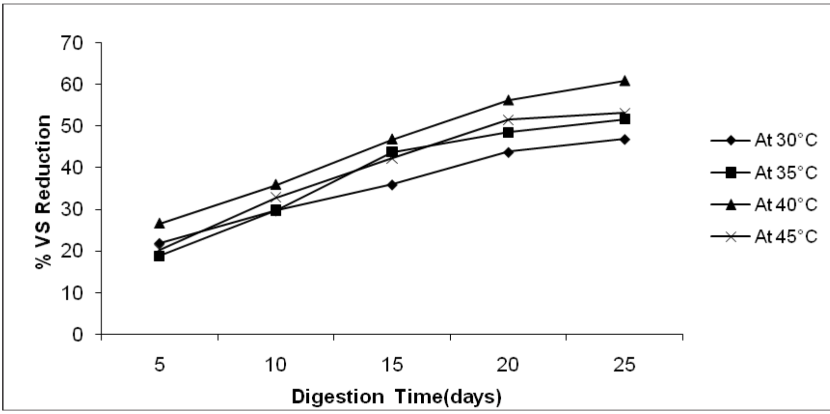


Figure 6. Effect of digestion time on percentage VS Reduction at four different temperatures

At $30^0$C BOD and COD of the treatment mixture ranged between 1462 mg/l to 625 mg/l and 5720 mg/l to 2882 mg/l respectively. The total dissolved solids ranged from 254 mg/l to 160 mg/l, total dissolved solids ranged from 172 mg/l to 100 mg/l and volatile solids ranged from 128 mg/l to 68 mg/l, with the increase in digestion time from 01 to 25 days. The value of BOD percentage reduction varied from 23.05 to 57.25% while COD percentage reduction varied from 18.63 % to 49.61%. The value of total solids, total dissolved solids, and volatile solids ranged between 12.59% to 37.00%, 16.27 % to 41.86 % and 21.87% to 46.87%, respectively.

At $35^0$C BOD and COD of the treatment mixture ranged between 1462 mg/l to 575 mg/l and 5720 mg/l to 2318 mg/l, respectively. The total dissolved solids ranged from 254 mg/l to 152 mg/l, total dissolved solids ranged from 172 mg/l to 98 mg/l and volatile solids ranged from 128 mg/l to 62 mg/l, with the increase in digestion time from 01 to 25 days. The value of BOD percentage reduction varied from 19.56% to 60.67% while COD percentage reduction varied from 17.74 % to 59.47%. The value of total solids, total dissolved solids, and volatile solids ranged between 11.02 % to40.15 %, 12.79 % to 43.02 % and 18.75% to 51.56%, respectively.

At $40^0$C BOD and COD of the treatment mixture ranged between 1462 mg/l to 481 mg/l and 5720 mg/l to 1957 mg/l respectively. The total dissolved solids ranged from 254 mg/l to 132 mg/l, total dissolved solids ranged from 172 mg/l to 78 mg/l and volatile solids ranged from 128 mg/l to 50 mg/l, with the increase in digestion time from 01 to 25 days. The value of BOD percentage reduction varied from 28.45% to 67.09 % while COD percentage reduction varied from 24.44 % to 65.78 %. The value of total solids, total dissolved solids, and volatile solids ranged between 15.57 % to 48.03 %, 20.93 % to 54.65 % and 26.56 % to 60.93% respectively.

At 45$^0$C BOD and COD of the treatment mixture ranged between 1462 mg/l to 538 mg/l and 5720 mg/l to 2217 mg/l respectively. The total dissolved solids ranged from 254 mg/l to 140 mg/l, total dissolved solids ranged from 172 mg/l to 90 mg/l and volatile solids ranged from 128 mg/l to 60 mg/l, with the increase in digestion time from 01 to 25 days. . The value of BOD percentage reduction varied from 24.62% to 63.20% while COD percentage reduction varied from 20.69 % to 61.24%. The value of total solids, total dissolved solids, and volatile solids ranged between 12.59% to 44.88%, 18.60 % to 47.67% and 20.31% to 53.12%, respectively.

**Effect of Hydraulic retention time on COD and biogas production:**

Table-7 shows the effect of change in the effect of a change in hydraulic retention time (HRT) on COD reduction and steady state characteristics and kinetic parameters from these characteristics for the reactor with granite stones as packing material. With variation in HRT from 2 -24 hrs, it was observed that the maximum COD reduction occurred at HRT 24 hrs and was found to be 66.04%. Figure 7 shows the corresponding graph. Biogas production value decreased with increase in HRT. Table 8 shows the effect of HRT on the biogas productivity and specific biogas yield respectively. The value of biogas productivity decreased from 0.0741 to 0.0535 ml/ml/day, while the specific biogas yield increased from 0.0036 to 0.0162 mg/ml $COD_r$ with an increase in HRT from 02 to 24 hours. Figures 8 and 9 show the change of kinetic parameters with change in HRT.

Table 7. Effect of hydraulic retention time on performance characteristics of the reactor at 40$^0$C

| S.No | Feed Rate ( ml/hr) | Hydraulic retention time (hrs) | COD of treated effluent (mg/l) | % COD removal |
|---|---|---|---|---|
| 1. | 300 | 2 | 3321 | 33.58 |
| 2. | 150 | 4 | 3133 | 37.34 |
| 3. | 75 | 8 | 1887 | 42.26 |
| 4. | 45 | 14 | 2444 | 51.12 |
| 5. | 25 | 24 | 1698 | 66.04 |

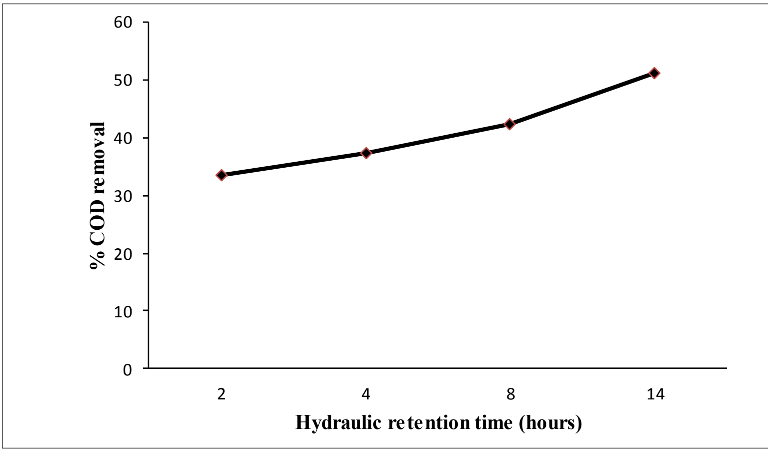


Figure 7. Effect of hydraulic retention time on percentage COD reduction

Table 8. Evaluation of kinetic parameters from Table 7

| S. No | Hydraulic retention time (hours) | % COD removal | Biogas productivity (ml/ml/day) | Specific biogas yield (mg/ml/ $COD_r$) |
|---|---|---|---|---|
| 1. | 2 | 33.58 | 0.0741 | 0.0036 |
| 2. | 4 | 37.34 | 0.0713 | 0.0063 |
| 3. | 8 | 42.26 | 0.0633 | 0.0099 |
| 4. | 14 | 51.12 | 0.0596 | 0.0129 |
| 5. | 24 | 66.04 | 0.0535 | 0.0162 |

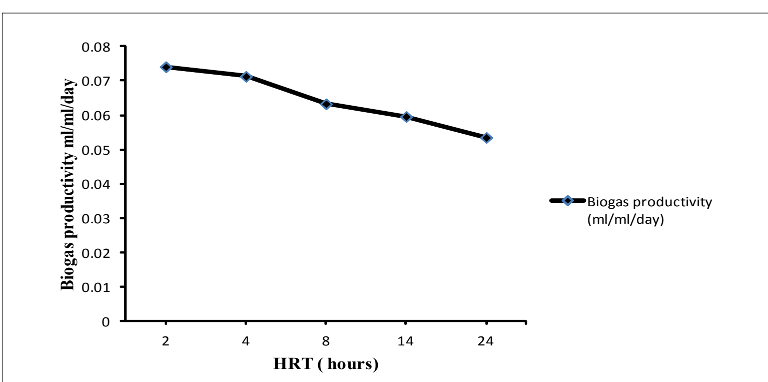


Figure 8. Effect of hydraulic retention time on biogas productivity

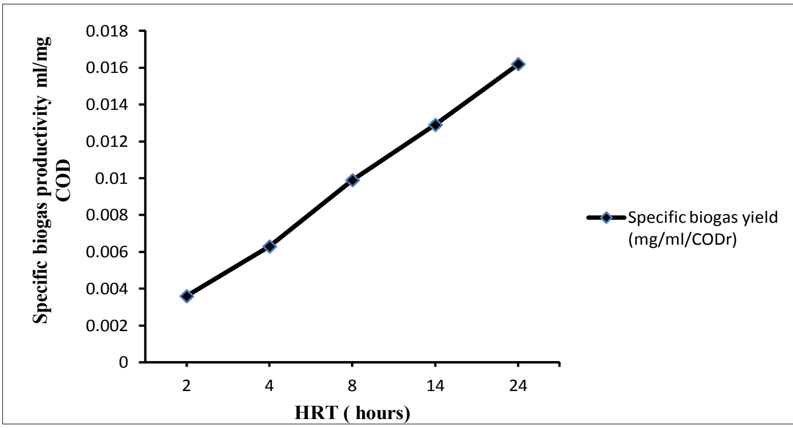


Figure 9. Effect of hydraulic retention time on specific biogas productivity

## CONCLUSIONS

The results indicate that there was a steady increase in the percentage reduction of BOD, COD, TS, TDS and VS from 05$^{th}$ to 20$^{th}$ day, but the rate of percentage reduction decreased after the 20$^{th}$ day at all the four different temperatures. Cumulative biogas production and rate of biogas production during the digestion process indicated that there was a steady increase in the yield of biogas from 7$^{th}$ day onwards and it attained a peak value on 20$^{th}$ treatment then after it started decreasing. The biogas production and reduction in effluent characteristics at various temperatures observed showed that optimum temperature for a reduction in effluent characteristics and biogas production was at 40$^0$C. The treatment efficiencies increased with the increase of retention time at 40$^0$C. Methane content in the biogas varied. The average composition of the biogas at the end of digestion with HRT 24 hrs at 40$^0$C was: $CH_4$ content varied from 62.2 to 64.1%, $CO_2$ varied from 34.0 – 36.5 %, $O_2$ varied from 0.3 – 0.5% and CO varied from 0.4- 0.7%.

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