

Anaerobic Digestion of CHLORphenolic Wastes

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ABSTRACT: Feasibility of methanolic wastes treatment containing chlorophenol in experimental UASB reactors i.e. R-I and R-II working side by side constantly for a couple of almost 32 weeks were studied. UASB reactor R-I was initiated by utilizing the digested sludge alone, whereas, the UASB reactor R-II was started-up by adding an activated carbon of an effective size 1.5-2.5mm to the digested sludge with the volume-volume ratio of 3:2. At low loading rates of 0.5g-TOC/L-d for R-I and 2.6g-TOC/L-d for R-II, it was observed that the effect of HRT on the TOC reduction was not prominent, and in both the reactors the TOC reduction effectiveness was noticed to be above 80%. An optimum OLR to accomplish 80-85% TOC and chlorophenol reduction effectiveness (at HRT of 12hours) was observed to be 2.6g-TOC/L-day and 10.8g-TOC/L-day for reactor R-I and R-II, respectively. It was also observed that to attain more than 80% TOC removal efficiency at a constant OLR of 6.5g-TOC/L-day and at a HRT of 18-20hours, the maximum influent chlorophenol concentration should stay below 21mg/L and 29mg/L for reactor R-I and R-II, respectively. The average VFAs effluent concentration observed was 357mg/L and 230mg/L for the reactor R-I and R-II, respectively. Comparatively the production of biogas in reactor R-II was less. The overall gas conversion rate observed at greater than 80% TOC removal efficiency for R-I and R-II was found to be 0.28L/g-COD_{removed} and 0.17L/g-COD_{removed}, respectively, with 60-62% of methane content for both the reactors. The results of this study suggested that the use of methanol as a medium to biodegrade chlorophenol in the presence of an activated carbon in a UASB reactor is an effective and feasible method at mesophilic temperature and neutral pH.

Key words : UASB reactor, Methanol, Activated carbon, TOC, COD

INTRODUCTION

In terms of fresh water extraction, the pulp and paper industry is a water intensive industry and stands third in number over all after the primary metals and the chemical industries. It is also considered to be the sixth major polluter releasing a jumble of gaseous, liquid and solid wastes (Ali *et al.*, 2001, Khallas *et al.*, 1994). In Pakistan, there are more than sixty pulps and paper mills in operation and majority of the mills do not have wastewater treatment facilities to treat their effluent and hence discharge the entire major effluent stream into environment thus poses a great threat to the entire ecosystem (Draft Report Pak-EPA, 1999). The bleaching effluent of the paper industry contains high amount of toxic and persistent pollutants, which are created as a product of reaction among remaining lignin from the pulping step and chlorine and chlorine mix utilized in the bleaching practice (Draft Report Pak-EPA, 1999, Savant *et al.*, 2005). Up to now, 500 diverse chlorinated organic compounds have been recognized in the bleaching waste of pulp and paper mills. In wastewater, these compounds are knowable jointly as “absorbable or-

ganic halides” (AOX). Quantity of these compounds is completely relative to utilization of chlorine in the bleaching practice of pulp and paper manufacturing (Yan *et al.*, 1994). Most of these compounds are hydrophobic, persistent, bio-accumulative and carcinogenic in nature and causes a variety of harms to human health (Savant *et al.*, 2005). A variety of techniques have been developed for the reduction of AOX concentration, categorized as physical, chemical, electrochemical and biological. Amongst them the physical, chemical and electrochemical techniques for the elimination of AOX compounds are too costly when practical used in field. As the contamination crisis in the third world countries are quite serious and since, these countries cannot maintain wastes handling scheme with high working costs, therefore, fairly low-cost and uncomplicated technologies should be developed for its proper control. Aerobic technologies burden huge input of energy, creating it costly for the third world countries. Applying of anaerobic technology, which is technically simple, fairly economical and uses very little energy, is considered to be one of the most en-

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couraging choice for the treatment of different industrial effluents along with the pulp and paper industrial wastes (Lettinga *et al.* 1980, Bhatti *et al.* 1996, Mtethiwa *et al.*, 2008). The employing of anaerobic treatment in pulp and paper industry initiated in early seventies (Savant 2005). The initial anaerobic digestion process launched was anaerobic lagoon. Contact reactor and upflow anaerobic sludge blanket reactor (UASB) technology was started nearly in eighties. Nowadays, above 50 complete anaerobic treatment systems, treating pulp and paper mills waste matter are working in the world (Bajpai, 2000). Recently the implementation of anaerobic processes for wastewater handling has received a rising interest since they stand as a substitute economical approach for the elimination of a variety of contaminants. Anaerobic processes have turned into extensively recognized treatment systems after the information added in the functioning of numerous anaerobic systems in the world (Schellinkhout, 1993). The best choice in anaerobic digestion is the UASB reactor, which perform as a compact structure for the treatment of high strength sewage. Complete UASB reactors are functioning now in various parts of the world like Japan, India, Colombia, Brazil etc. for the handling of multiple type of wastes material (Driessen *et al.*, 1994, Vieira *et al.*, 1988; Chernicharo 2001, Wiegant *et al.*, 2001). The available informations regarding the use of single-step UASB reactor to biodegrade AOX are very little. A first system introduced was the combination of anaerobic fluidized bed and trickling filter and that system was able to remove 64-94% of the chlorophenol (Hakulien 1982, Savant 2005). Anaerobic process in arrangement with aerobic treatment, membrane filtration and chemical treatment has been capable to eliminate about 42-65% of AOX (Lee *et al.*, 1993, Hall *et al.*, 1995, Francis *et al.*, 1997, Tezel *et al.*, 2001), while the anaerobic processes unaccompanied was merely able to eliminate 42-45% of AOX at hydraulic retention time of 36hours (Fitzsimons *et al.* 1990). It was noticed 40-65% elimination of AOX while working on the anaerobic digestion of bleaching effluent of pulp and paper mill Ferguson and Dalentoft (1991). It was concluded from a study that the chlorophenol can be removed up to 60% by using an activated carbon (Daifullah 1998) and as was also observed that by adding an additional source of easily biodegradable substance to UASB reactor, its treatment efficiency for the chlorophenolic wastes could be improved (Scholz *et al.*, 1995), therefore, this work was carried out in order to observe the viability of UASB reactor for the handling of chlorophenolic wastes by means of methanol as an easily biodegradable agent (Bhatti 1995). The key objective of this work was to examine the treatability of UASB reactor of methanolic waste having chlorophenol in the presence

of activated carbon added with the digested sludge during the start-up phase.

MATERIAL & METHODS

Two UASB reactors, namely R-I and R-II made up of acryl resin material, each of 7.84liters were used in this study. Water jackets were provided to the reactors to maintain their temperature around 32°C. The reactors were also equipped with gas solid separators (GSS) and mixing devices. Both of these reactors were run parallel with same type of waste, under same operating conditions. Methanol and 2-Chlorophenol, diluted with tap water to the desired concentration, were used as the carbon provider in the supply (influent) for both the reactors, R-I and R-II. Methanol to chlorophenol ratio was kept constant at 500:1, throughout the study. Nitrogen and Phosphorous were added to them in the form of $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 in accordance with the C:N:P ratio of 350:5:1, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was added in concentration of 0.1 g/L and the trace nutrients were added at concentrations shown in Table 1.0 to both the reactors (Bhatti *et al.*, 1996, Yaochatchaval *et al.*, 2008).

Table 1. Trace nutrients concentration

Trace Nutrient	Concentration (mg/L)
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	4.9
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.3
ZnSO_4	0.35
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.35
CuSO_4	0.09

A seeded sludge was prepared by mixing fully digested sludge obtained from a local wastewater treatment plant and the digested sludge acclimatized with methanolic waste containing chlorophenol in the laboratory for few weeks in the ratio of 5:1 The seeded sludge obtained had mixed-liquid suspended solids (MLSS) content of 76.8g/L and VSS content of 68.2g/L. This sludge was than added to both the reactors R-I and R-II for their start-up. The R-I was totally filled with this sludge, whereas, for R-II this sludge was further mixed with granular activated carbon in the ratio of 3:2. The effective size of granular activated carbon used was ranging from 1.5-2.5mm.

The UASB reactors were continuously operated for approximately 32 weeks according to the sequence as mentioned in the Table 2.

pH, temperature, influent and effluent total organic carbon (TOC), chemical oxygen demand (COD) and chlorophenol concentration, mixed-liquid suspended solids (MLVSS) of the reactor, effluent volatile fatty acids (VFAs), total gas production and methane content of the gas were monitored regularly; 2-3 times

Table 2. UASB reactors operation strategy

Weeks of operation	Phase of study	Organic loading rate	Major objectives
01-22	Phase-I	From; OLR = 0.13g-TOC/L-d To OLR = 24g-TOC/L-d (HRT: from 48-6.0hrs)	Start-up and study on the effects of HRT and OLR
22-23		Constant OLR 4.5-6.5g-TOC/L-d HRT: 18 hrs Influent chlorophenol 11 mg/L	Normalization period
24-32	Phase-II	Constant OLR ? 6.50g-TOC/L-d Constant HRT = 18-20hrs Chlorophenol conc.: 13-45mg/L	Determination of maximum influent chlorophenol concentration for the given OLR and HRT.

weekly. TOC was analyzed by Multi N/C 3100 Analytik Jena AG, using "differential method". Gas was collected over a tap water saturated with NaCl. All the analysis was carried out according to the Standard Methods (AWWA 1995).

RESULTS & DISCUSSION

The reactors were operated according to the as per the given guidelines of renowned scientist "Lettinga" (Lettinga *et al.*, 1984). Since, pH is the most important and principle operational parameter of an anaerobic digestion, therefore, an extreme care was taken for its control during the study period. The optimal pH required for acidogenic bacteria is between 5.9 and 6.5, whereas, that for methanogenesis is reported to be above 6.5. Therefore, the pH of the methane bioreactor is usually controlled to set-point within the range of 6.5-7.5 (Bryant, 1979), but the neutral pH is considered to be the most suitable range for the optimum growth of methanogenic bacteria. In addition to this, low bioreactor pH can increase the toxicity or inhibitory characteristics of a number of organic and inorganic inhibitors (Bhatti *et al.*, 1995). Therefore, in this study the pH of the reactors were maintained around neutral by adding an external buffer in the form of 0.03M NaHCO₃ to the feed solution after 3rd week of operation when the pH of both the reactors, R-I and R-II dropped drastically to 4.72 and 5.01, respectively. The initial pH of both the reactors was observed to be neutral, 7.0±3.0 during the two weeks of the study. Due to the addition of an external buffer to the reactors, the average pH of the bioreactors observed during the rest of the period was almost neutral.

Temperature of a bioreactor is also an important influencing factor on biomass activity. The temperature optima identified for anaerobic fermentation lies between 30-40°C (Henze *et al.*, 1983). Although, methanogenic bacteria appear to be active at temperature of 8-10°C, but the biomass activities and anaerobic treatment capacities may be significantly reduced at lower temperature (Switzenbaum *et al.*, 1980,

Kennedy *et al.*, 1982, Grin *et al.*, 1985). The biomass activity at thermophilic operation at 50-60°C is reported to be generally 25-50% higher than mesophilic temperature (Henze *et al.*, 1983, Zinder, 1998), but there are number of potential problems associated with the thermophilic operations, like low bacterial growth yields and high endogenous death rate (Henze *et al.*, 1983, Buhr *et al.*, 1977), leaving higher residual level of volatile acids (Bryant 1979). Moreover, anaerobic bacteria are most sensitive to rapid alteration in temperature (Henze *et al.* 1983, Stronach *et al.*, 1986). Therefore, in this study the temperature of the bioreactors were kept constant at about 32-35°C, by using an external heating device.

Both the reactors were started-up simultaneously, running parallel, each with a synthetic wastewater having TOC of 250mg/L, containing 0.5mg/L chlorophenol at a hydraulic retention time (HRT) of 48hours. This corresponds to an organic loading rate (OLR) of 0.13g-TOC/L-d. The TOC and chlorophenol concentrations were increased stepwise in order to avoid the methanolic and chlorophenolic shocks to the reactors.

HRT and OLR are the significant design parameters that decide the capital cost, and set up the engineering and financial viability of a particular method. The connection among HRT and OLR with respect to TOC and chlorophenol elimination competency is illustrated in Fig 1-4 and 5-8, respectively.

These figures are generated from the experimental work conducted during phase I. During the start weeks, at low loading rates ≤0.5g-TOC/L-d for R-I and ≤2.6g-TOC/L-d for R-II, it was observed that the effect of HRT on the TOC elimination efficiency was not prominent, as in both the reactors the TOC elimination efficiency was noticed to be above 80%. Similarly, at low loading rate, ≤2.6g-TOC/L-d (at HRT ≥12 hrs) the effect of HRT on the chlorophenol removal efficiency was also not marked in reactor R-1. In this range the chlorophenol removal efficiency varied between 80-85%. But in reactor R-II, the organic loading rate could

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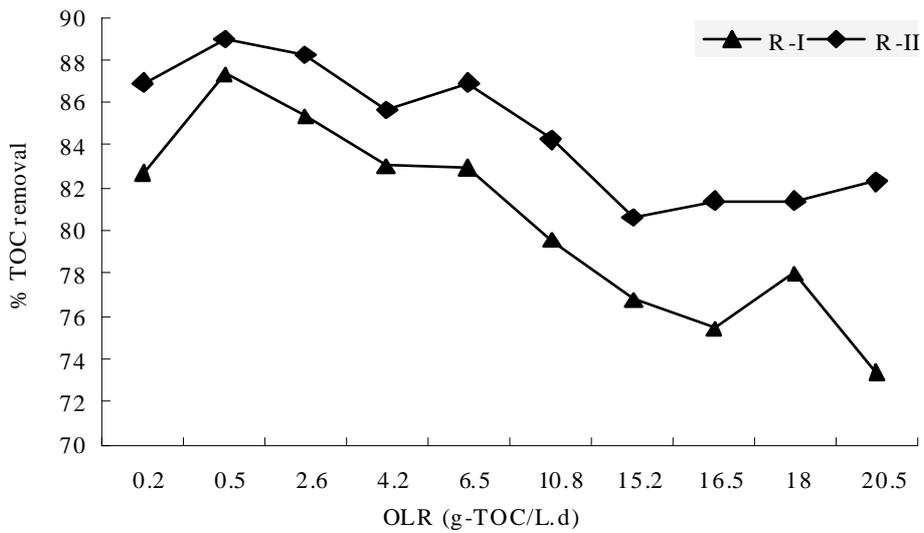


Fig. 1. Relationship b/w OLR and TOC removal at HRT of 36 hrs

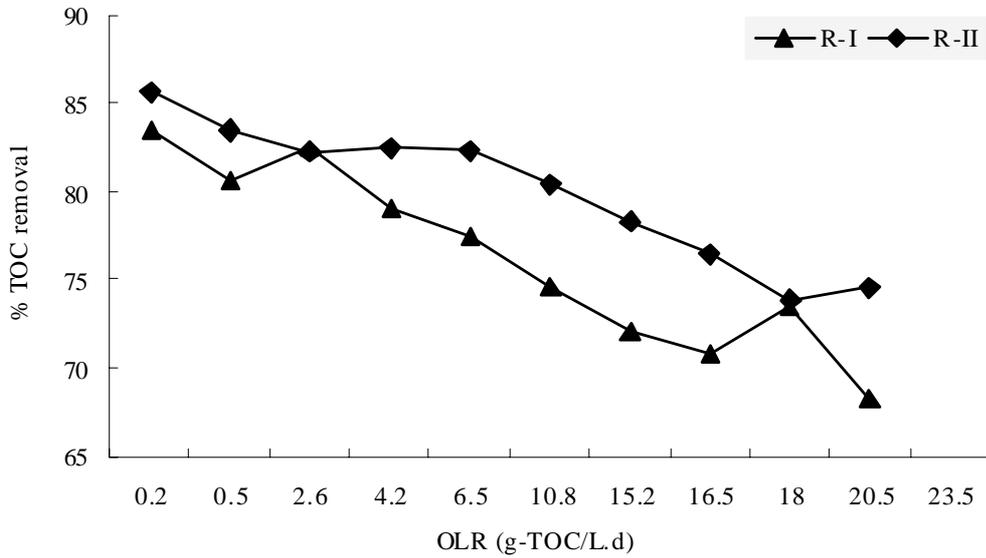


Fig. 2. Relationship b/w OLR and TOC removal at HRT of 24 hrs

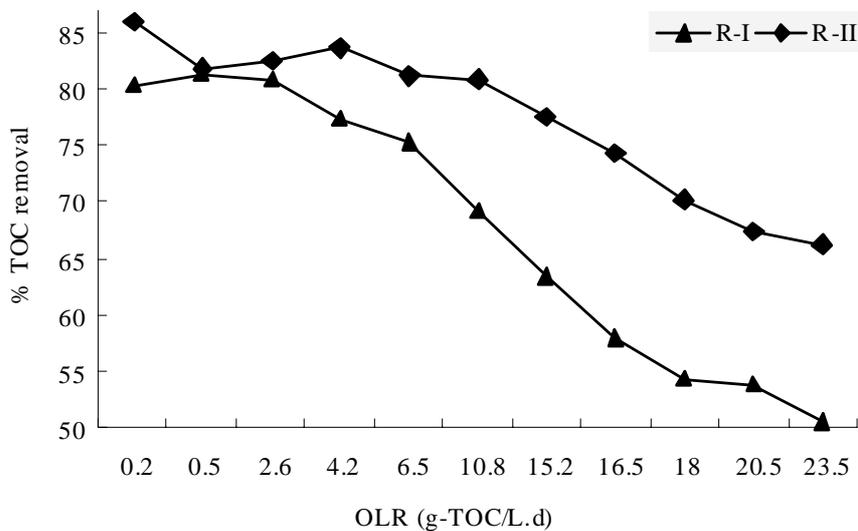


Fig. 3. Relationship b/w OLR and TOC removal at HRT of 12 hrs

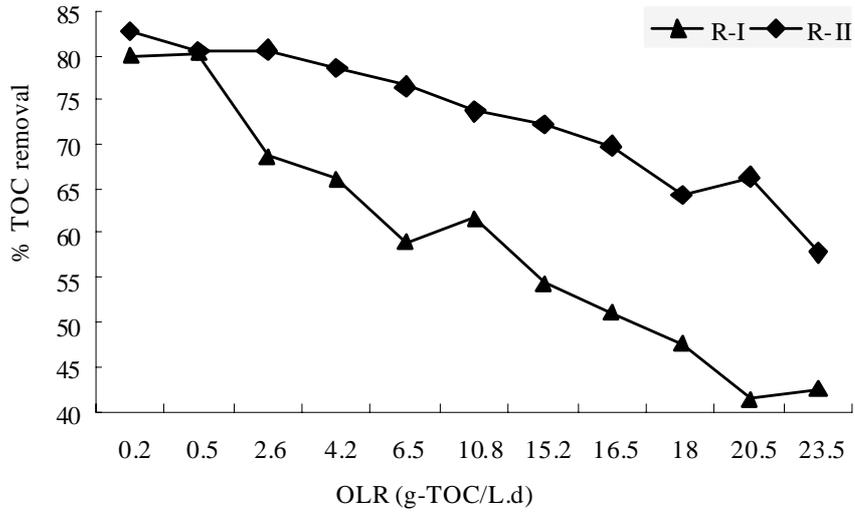


Fig. 4. Relationship b/w OLR and TOC removal at HRT of 06 hrs

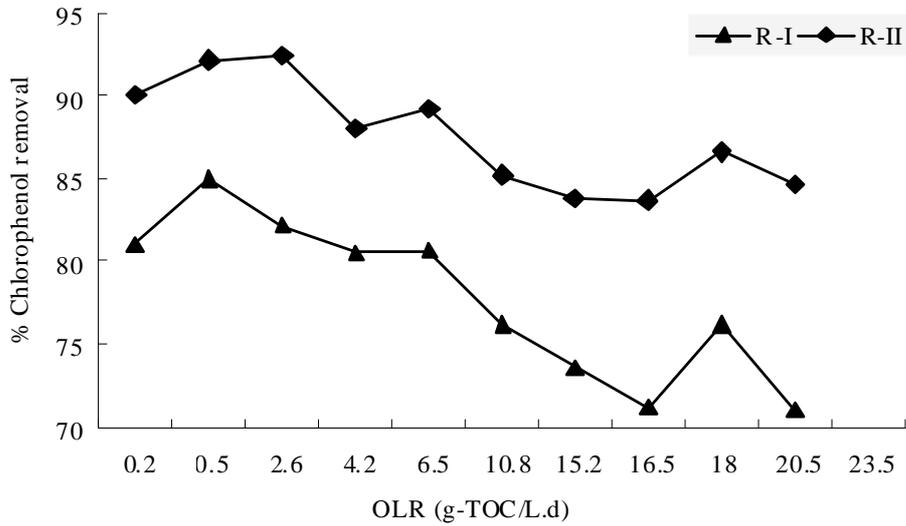


Fig. 5. Relationship b/w OLR and Chlorophenol at HRT of 36 hrs

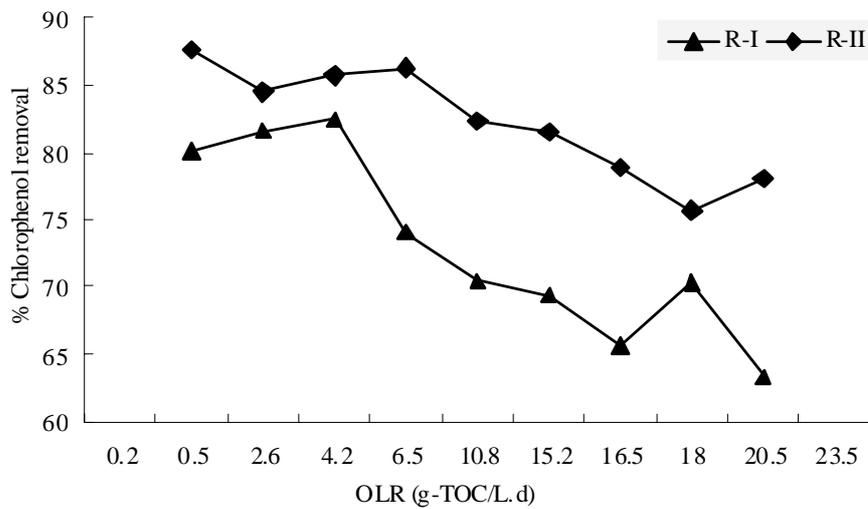


Fig. 6. Relationship b/w OLR and Chlorophenol at HRT of 24 hrs

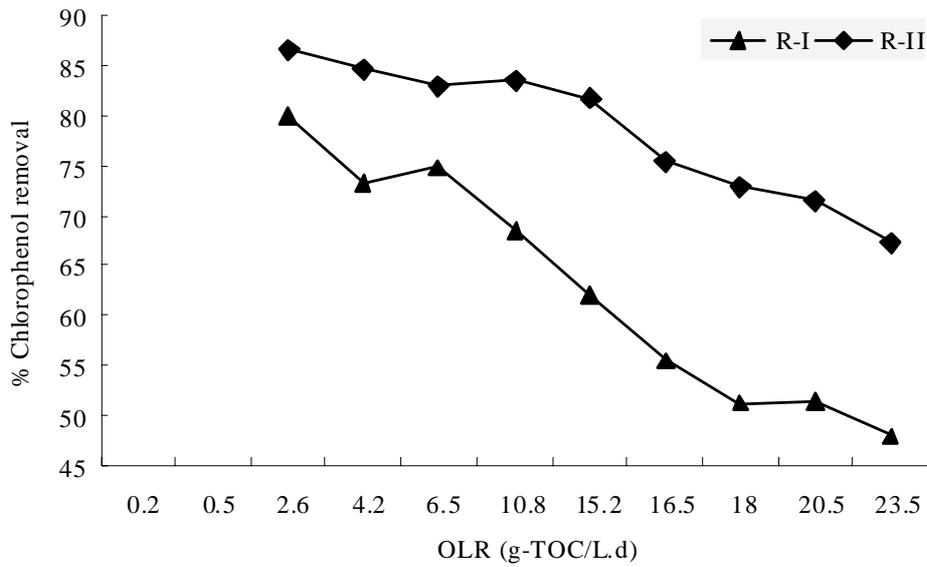


Fig. 7. Relationship b/w OLR and Chlorophenol at HRT of 12 hrs

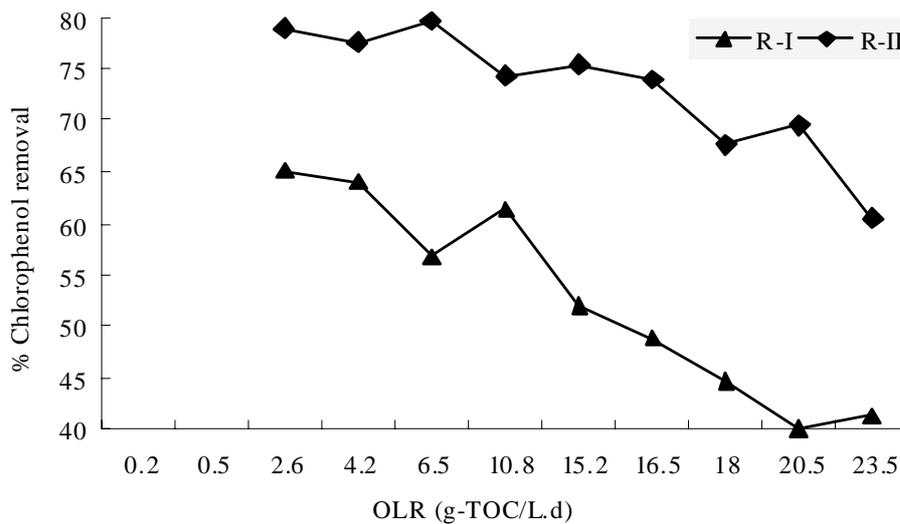


Fig. 8. Relationship b/w OLR and Chlorophenol at HRT of 06 hrs

be increased up to 15.2g-TOC/L-d at HRT \geq 12 hours to achieve more than 80% chlorophenol removal under anaerobic conditions. Comparatively greater treatability achievement of R-II indicates that the presence of an activated carbon with the digested sludge is facilitating the treatability performance of the UASB reactor.

However, beyond these points of inflection at higher organic loading rate, the effect of HRT became increasingly prominent on the TOC and chlorophenol removal efficiencies in both the reactors. For instance, at an OLR of 18g-TOC/L-d, varying HRT from 36 to 6 hour the decrease in TOC and chlorophenol removal efficiencies for reactor R-I was observed from 78% to 47% and 76% to 44%, respectively. Whereas, in the

reactor R-II, with an OLR 18g-TOC/L-d, varying HRT from 36 to 6 hour the decrease in TOC and chlorophenol removal efficiency was observed from 83% to 64% and 86% to 67%, respectively. Similarly, in these ranges, varying OLR for a given HRT had a major effect on TOC and chlorophenol elimination efficiency in both the reactors. But the treatability performance of R-II observed was comparatively more than that of R-I.

As of the field viewpoint, even if the reactor is to be designed to function at greater than 80-85% TOC and chlorophenol removal efficiencies the allowable OLR should be maintained less than 2.6g-TOC/L-d for R-I and 10.8g-TOC/L-d for R-II at HRT \geq 12 hours. Thus, HRT will have to be related in combination with TOC

and chlorophenol concentration to stay in the range. Fig. 1. and 2. provide useful guidelines for selecting an appropriate HRT and OLR for the design of UASB reactor, with or without using an activated carbon along with the digested sludge.

The fallout of this study shows that allowable OLR to get 80% TOC and chlorophenol elimination efficiencies for methanolic waste containing chlorophenol is about 2.6g/TOC/L-d and 10.8g-TOC/L-d for reactor R-I and R-II, respectively. These values are theoretically equal to 7.04g-COD/L-d and 29.27g-COD/L-d, respectively.

Comparison of this study with the similar work on same type of wastes, conducted (Fitzsimons 1990, Bhatti 1995, Scholz 1995, Daifullah 1998, Rajakumar and Meenambal 2008) indicates that using a source of an easily biodegradable substance, like methanol, the chlorophenol could be easily treated in a UASB reactor. Although the presence of chlorophenol in methanol can affect the treatability performance of the UASB reactor to a certain extent but by adding an activated carbon, its treatability performance could be improved even for more toxic wastes like chlorophenol. Thus this study suggests that the technique of using an activated carbon with an easily biodegradable substance in a UASB reactor is a feasible and effective approach for the treatment of chlorophenol.

Fig. 9. illustrates the relationship between the biogas production and influent of TOC concentration. This data were collected during phase-I of the study at TOC removal efficiencies of greater than 80% at various different HRT.

Since, the lower detention time promotes the wash-out of sludge from the reactor, therefore by decreasing the HRT from 30hrs to 6.0hrs, there was a significant decrease in the biogas production in both the reactors. In reactor R-I the decrease observed was from 0.29L/g-COD_{removed} to 0.09L/g-COD_{removed}, whereas in reactor R-II it was from 0.23L/g-COD_{removed} to 0.07L/g-COD_{removed}.

Although the use of an activated carbon as in R-II facilitates the system treatability but the gas production remain lower than R-I throughout the study period. This might be due to the reason that the organic acids formed during the process get adsorbed on the activated carbon, thus decreasing the biogas production. The average gas production in reactor R-I and in reactor R-II was 0.28L/g-COD_{removed} and 0.17L/g-COD_{removed}, respectively. Both of these values are lower than the theoretical value of 0.35L/g-COD_{removed} that might be due to the reason of low mixing between the biomass and the substrate, especially in reactor R-II the mixing could not be done properly due to the presence of much denser sludge particles. Moreover, the presence of recalcitrant material in such wastes also effects the biogas production. The biogas collected from both the reactors throughout this study was composed of 60-62% methane and the rest was carbon dioxide.

To check the shock absorption of both the reactors for the influent chlorophenol concentration, the concentration of chlorophenol in the influent feed to both the reactors was increased step-wise from 13mg/L to 47mg/L, at a constant OLR of 6.50g-TOC/L-d and

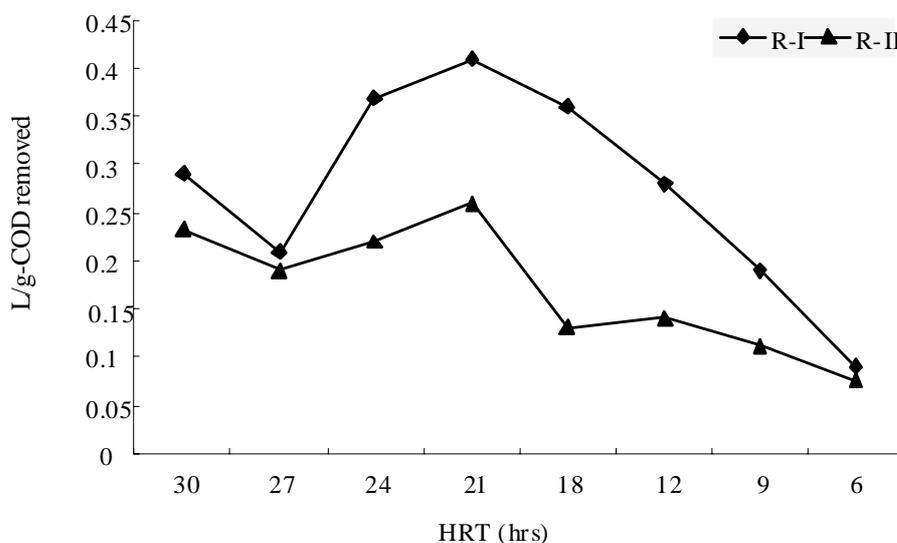


Fig. 9. Relationship b/w HRT and Gas Production

constant HRT of 18-20hrs. As shown in the Fig. 10. by increasing the concentration of chlorophenol in the influent to the reactors R-I and R-II, their treatability performance gradually decreased. At constant OLR and constant HRT the TOC removal efficiencies were decreased from 89% to 55% and from 95% to 71% in reactor R-I and R-II, respectively. Comparatively the reactor R-II gives better results in terms of treatability. In order to obtain more than 80% TOC removal efficiency from the UASB reactor, the influent chlorophenol concentration observed was 21mg/L and 29 mg/L, for reactor R-I and reactor R-II, respectively. The re-

sults obtained indicate that the reactor R-II can absorb comparatively more shocks of high concentration of influent chlorophenol than the reactor R-I operating at same conditions. It might be because of the reason that the reactor R-II not only treats the wastes by the process of biodegradation but it also facilitates the adsorption of chlorophenol on activated carbon used within the UASB reactor.

It was early reported that the effluent concentration of VFAs decreases with the increase in the treatability performance of the UASB reactor (Mahadevaswamy, 2004), the same phenomenon is also

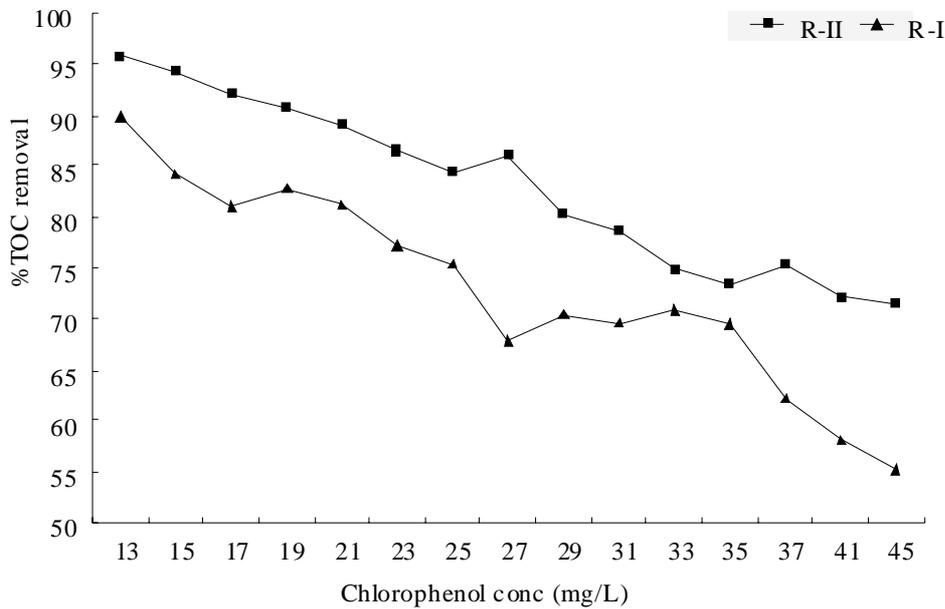


Fig. 10. Impacts of chlorophenols on the treatability performance of R-I and R-II

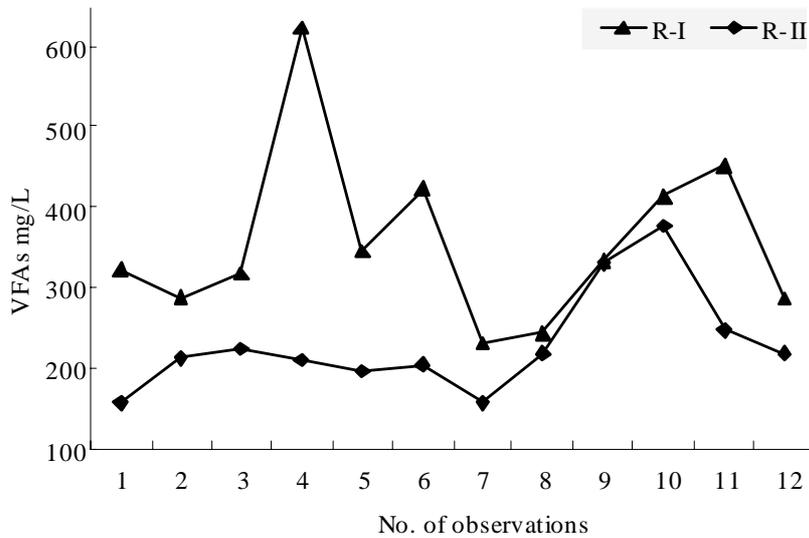


Fig. 11. Concentration of VFAs during the study period

observed in this study. But the reactor R-I comparatively gives more effluent VFAs than the reactor R-II for same level of operating conditions as shown in the Fig. 11.

The overall inhibitory effect of the VFAs is related to the pH establishment by prevailing the buffering system (Andrews 1969, Pohland 1969), and the unbalance anaerobic treatment operations generally is indicated by the increase in the effluent concentration of VFAs, therefore, it is very essential to keep the concentration of VFAs at optimum by maintaining a balance operating conditions. As in the present study the average pH maintained was neutral, therefore the overall effluent VFAs concentration observed was at the optimum. During the study period the effluent VFAs concentration remained below 600mg/L for both the reactors. The average effluent concentration observed was 357mg/L and 230mg/L for the reactor R-I and R-II, respectively. The results indicate that both the reactors were working at normal required condition for the anaerobic digestion.

CONCLUSION

From the results of this study, the following conclusions can be drawn:

1. The presence of chlorophenol can affect the treatability performance of UASB reactor to a certain extent. Whereas, methanol can be used a source of an easily biodegradable substance to facilitate the treatment of chlorophenol using the UASB reactor.
2. The presence of an activated carbon in UASB reactor increases its treatability efficiency and facilitates it to absorb high shocks of the influent chlorophenol concentration. It also gives more polishing results in terms of effluent VFAs concentration.
3. Applicable volumetric loading rate to achieve 80-85% TOC and chlorophenol removal efficiency (at HRT \geq 12hours) is 2.6g-TOC/L-day and 10.8g-TOC/L-day for reactor R-I and R-II, respectively.
4. In order to achieve more than 80% TOC removal efficiency from the UASB reactor working at an OLR of \leq 6.5g-TOC/L-day and at a HRT of 18-20hours, the maximum influent chlorophenol concentration should remain below 21mg/L and 29mg/L for reactor R-I and R-II, respectively.
5. Gas production in reactor R-II is comparatively less due to low mixing facility. The gas conversion rate corresponding to 80-85% removal efficiencies is 0.28L/g-COD_{removed} and 0.17L/g-COD_{removed} for the reactor R-I and R-II, respectively. The gas produced in both the reactors was composed of 60-62% methane.

Treatability of chlorophenol in a single-step UASB reactor in the presence of methanol, as an easily biodegradable substance, is a highly feasible technique at mesophilic temperature and neutral pH, and if an activated carbon is added to the system that will further enhances its treatability performance. But more advance studies are required to evaluate and investigate the exhaust and regeneration time of an activated carbon, when used during such processes. The bio-kinetic behavior of such reactors also needs further investigations.

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