ACCLIMITATION PROCESS OPERATION OF THE TWO STAGE ANAEROBIC BIOREACTOR FOR TREATING PHARMACEUTICAL WASTEWATER

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Abstract:

A laboratory-scale two-stage anaerobic bioreactor was operated at mesophilic temperature for treating pharmaceutical wastewater. The two-stage anaerobic bioreactor has innate advantages of selected process controls on the growth of microorganisms independently in acidogenic and methanogenic phases. A laboratory scale experimental model was fabricated with a total working volume of 36.92l capacity. The acidogenic reactor have an effective volume of 6.15l of an acidogenic reactor and 30.77l of the methanogenic reactor was used to treat pharmaceutical wastewater. The start-up stage of the process was began by continuous feeding of the reactor with an initial influent COD concentration of 890 mg/l with a HRT of 24 h with an organic loading rate of 0.520 Kg COD/m^3/day in acidogenic reactor and 0.418 kg COD/m^3/day in methanogenic reactor. This work was performed to emphasis an in depth understanding of a two stage reactor start up process inoculated with digested slurry from the treatment unit of Annamalai University. The reactor achieved at steady state conditions during the period of 18^{th} to 21^{st} day with a COD removal efficiency of 92% in the overall reactor performance. The acidogenic reactor was accomplished with suspended growth process and in the case of methanogenic reactor was with attached growth process.

Keywords:,Acetogenesis, Hydraulic loading rate, Methanogenesis, Pharmaceutical wastewater Organic loading rate.

I.INTRODUCTION:

Pharmaceutical wastewater contain a variety of organic and inorganic constituents including spent solvents, catalysts, additives, reactants and small amounts of intermediates and products, and may therefore be high in chemical oxygen demand.Pharmaceutical wastewater is a complex mixture of many compounds, solvents and salts (Mohanrao,1970). Wastewater is being generated during manufacturing process of bulk drugs and pharmaceuticals. Pharmaceutical wastewater contain a variety of organic and inorganic constituents including spent solvents, catalysts, additives, reactants and small amount of intermediates and products and may therefore be high in chemical oxygen demand.(Fent *et al ,2006*; Oktem *et al,2007*).Disposing of pharmaceutical wastewater has attracted much public and research attention, as around 80-100 pharmaceuticals and their metabolites have been measured in both effluent and surface water in numerous countries (Ashton et al., 2004; Chen et al., 2008). Moreover, uncontrolled and illegal drug disposal can supply to a load of pharmaceuticals in wastewater (Bottoni et al., 2010; Emke et al.,2014; Munoz et al 2010). Pharmaceutical wastewater treatment adopted dilution technique followed by Oxidation, coagulation and finally passing through the membranes. The constituents or complex compounds present in pharmaceutical waste water are oxidized using hydrogen peroxide . Oxidation is a part of secondary treatment.Most of the toxic organic compounds, those are present in the pharmaceutical effluents are oxidized using different oxidizing agents. Hydrogen peroxide is one of the most dependable and very effective oxidizing agents. It is suitable for the oxidation of pollutants particularly of pharmaceutical origin (Zwiner, 2000).

Anaerobic processes have become a viable option for the treatment of medium-high strength industrial wastewaters. The most important merits of anaerobic treatment are the ability to treat high strength wastes, low energy input, low sludge yield, low nutrient requirement, low operating cost, low space requirement and net benefit of energy generation in the form of biogas (Acharya *et al*, 2008 ; Mahmoud, 2008). Anaerobic process is applied to remove high concertrations of organic matter and decompose refractory substances (Liu et al. 2003; Minke and rott 1999) followed by an aerobic treatment to oxidize the residual organic matter in the wastewater .since influent COD is very high in most cases, effluent from the anerobic bioreactor can still have residue COD, which may be as high as several hundreds or even thousands of milligrams per litre, even if , organic matter removal efficiency is above 90%.Therefore, direct discharge of effluent from the anaerobic bioreactor is not permitted , and posttreatment of anerobic bioreactor anaerobic process effluent with an aerobic bioreactor is necessary. The introduction of an acidogenic phase should enable optimization of theconditions required for many of complex organic compounds present in the wastewater to be converted in to short - chain Volatile Fatty Acids (VFA) and other simple compounds. This, in turn, buffers the slow-growing methanogens, predominantly present in methanogenic reactor, from possible toxins or inhibitors and ensures a uniform feed stock for the methanogens (Asha.B and V.N.Kumar 2007).The two-stage biological system generally provides a better quality of effluent for the treatment of pharmaceutical wastewater. However, the two stages in the two-stage reactor are acidogenic and methanogenic. Such two-phase anaerobic digestion was proposed as a way to optimize for the growth of each type of bacteria in the separate reactors, specifically by growing the acetogenic bacteria at a lower pH and short hydraulic residence time (typically 1-2 days) in the first stage, while the slower growing methanogenic bacteria stage, requiring a more neutral pH, were preferentially cultured in the second stage with a much longer hydraulic residence time (typically 10-20 days),(Blonskaja et al., 2003; Demirel and Yenigun,2002; Pohland and Ghosh, 1971).

Anaerobic digestion involves a population comensal interaction of the two general types of bacteria populations, in which the methanogens feed on and efficiently remove, the waste products (H_2 and acetic acid) of the acidogenic bacteria. Thus separating these two basic processes will not generally significally accelerator or increase overall methane-production, although it can be of some advantages in making the process more resistant to shock loading. In earlier work on two-phase anaerobic digestion, the H_2 and CO_2, produced in the first stage was transferred to the second stage to be converted to CH_4 and indeed, few measurements on gas production from the first phase are reported in the literature (Das and Veziroglu,2001: Hallenback and Benemann,2002;Levin et al.,2004)which, essentially, corresponding to the first phase of such a two-phase anaerobic digestion process. However, as stated above, in all such studies, the overall H_2 yields are low ,only 10-20% of the substrate being converted to H_2 fuel with ythe remainder converted to organic acids, and other products.Hydrolysis and acidification processes stopped after about 100 days of solid-state fermentation due to end-product inhibition (E.R. Vieitez and S.Ghosh (1999)). Ince (1998) achieved good separation of acid and methane phases with low and high methane yields in the first and second phases. Solera et al. (2002) observed the variations in autofluorescent methanogens and non-methanogenic bacteria at differing rates of hydraulic retention time (HRT) and organic loading rate (OLR).

The phased anaerobic treatment process is in advance momentum in industrial wastewater treatment plants. The wastewater-specific design of a two-stage system is invariably important for the desired performance of the treatment plant. The Core aim of this research article is to present a detailed study of start-up phase of the two-stage anaerobic process for treating pharmaceutical wastewater accomplishing with both suspended as well as attached growth process.

II. MATERIALS AND METHOD:

The two-stage bioreactor configuration has been used to investigate treatability in terms of COD reduction in acidogenic and methanogenic reactors independently and collectively under different streams of pharmaceutical wastewater. The two reactors digesters are distinct in the recommended ratio of volume of 1:5 viz., acidogenic reactor (AR) and methanogenic reactor (MR). The experimental reactors setup was made up of Plexiglass and have a working volumes of 6.15 and 30.77 liters. The two reactors were hermetically potted to avoid any air setup. The acidogenic reactor was fed with diluted pharmaceutical wastewater from the influent tank by means of a peristaltic pump (PP-30). The methanogenic reactor is correspondingly and constantly fed with the acidogenic effluent. The % COD reduction and gas production are continuously measured for both the reactors. The schematics of the experimental setup of two stage bioreactor is shown in Fig. 1

2.1 Wastewater source and its characteristics:

Samples were collected from M/S Lifecare Formulations 2&3,91/5 Link Road Near ,Mettupalayam Industrial Estate, Sonia Gandhi Nagar, Extn, Mettupalayam, Puducherry 605009 and characteristics of the effluent were analyzed as per the procedure given in the Standard method for water and wastewater (APHA,2017).

2.3 Acclimatization and processes stability:

During start-up process, the digesters were seeded with anaerobic digesting sludge**,** which was collected from the treatment plant of Annamalai University. The granules were passed through a screening to remove debris. Establishment of the most suitable microbial population is the overall objective of the start-up of two stage anaerobic bioreactor.

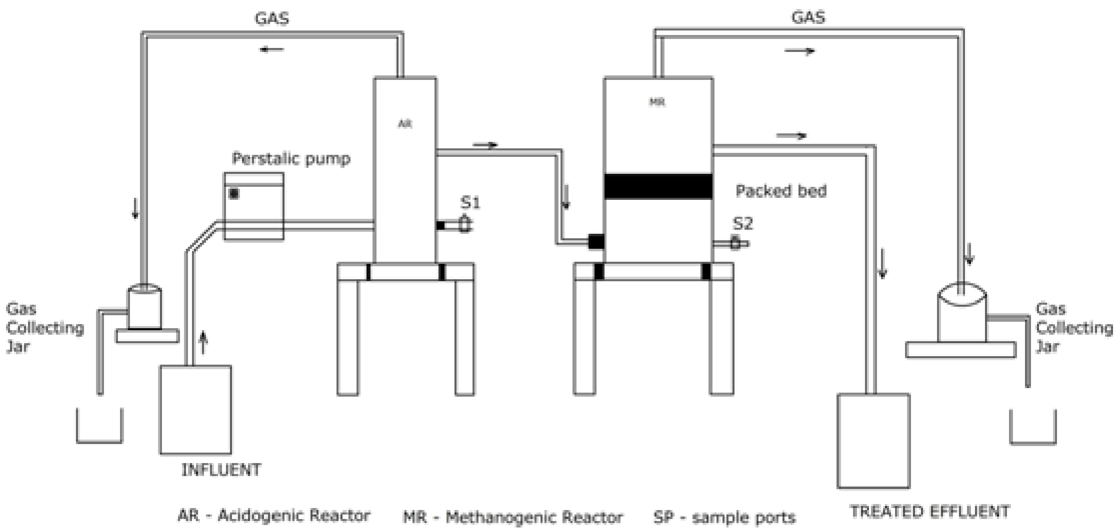

Figure 1 Schematic Diagram of the Experimental Set up of Two Stage Anaerobic Bioreactor

Table 1.1 Physical Features of Two Stage Anaerobic Bioreactor

Description	Measurements
Total working volume of the reactor, l	36.92
Working volume of the A.R reactor, l	6.15
working volume of the M.R reactor, l	30.77
Diameter of the A.R reactor, cm	14
Diameter of the M.R reactor , cm	30
Diameter of Influent & Effluent pipe, cm	1
Peristaltic pump	PP – 30 Model

Table 1.2 Physico-Chemical Characteristics of pharmaceutical wastewaters

S. No.	Parameter	Values
1.	pH	4.6
2.	Total solids, mg/l	7100mg/l
3.	Total suspended solids, mg/l	6,600mg/l
4.	Total dissolved solids, mg/l	500mg/l
5.	BOD_5@20^0C,mg/l	9240 mg/l
6.	COD, mg/l	16800mg/l
7.	Potassium, mg/l	190.8mg/l

8.	Oil and Grease, mg/l	45mg/l
9.	Phosphates, mg/l	120mg/l

2.4 Performance of the reactor:

The influent and effluent samples from the reactor were collected on the daily basis and were analyzed immediately. Initially the influent feed of wastewater which are collected from the Annamalai University. The low initial loading rate was recommended for the successful start-up of two stage bioreactor. A low initial organic loading rate was beneficial for the growth of anaerobic active sludge, due to low COD organic loading resulting in low production of gas rate and low waste water up-flow velocity. The start up process of two stage bioreactor have been well presented in the literature (Asha, B., & Kumar, V. N. (2007)). The start-up period is considered as the period taken for steady operation to be achieved. In addition, operating temperature is prominent during start-up. In this work, the treatment operation was carried out in the laboratory where the operating temperature varied from 25° C – 32° C (mesophilc range).

III. Result and Discussion:

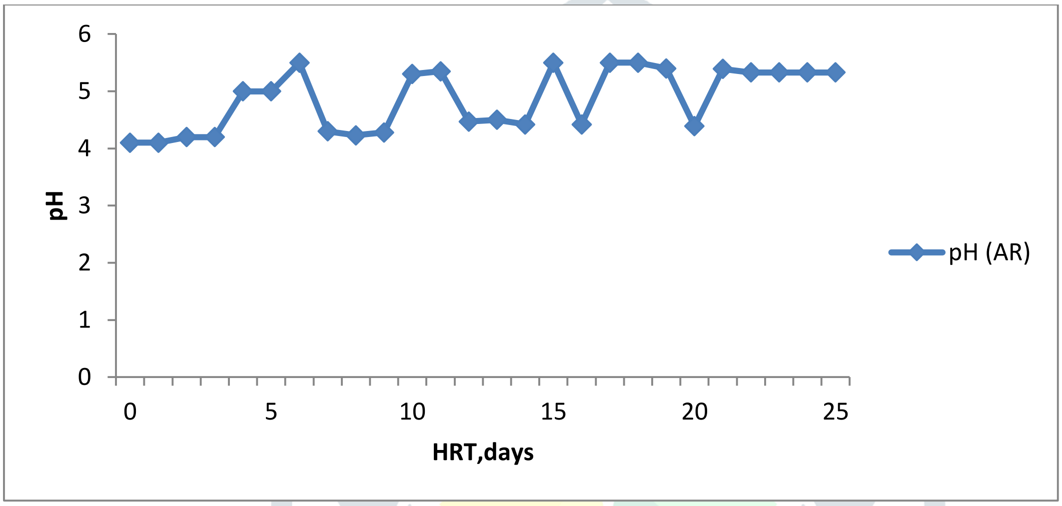

Figure.2 Characteristics Curve of HRT, days Vs pH in Acidogenic Reactor

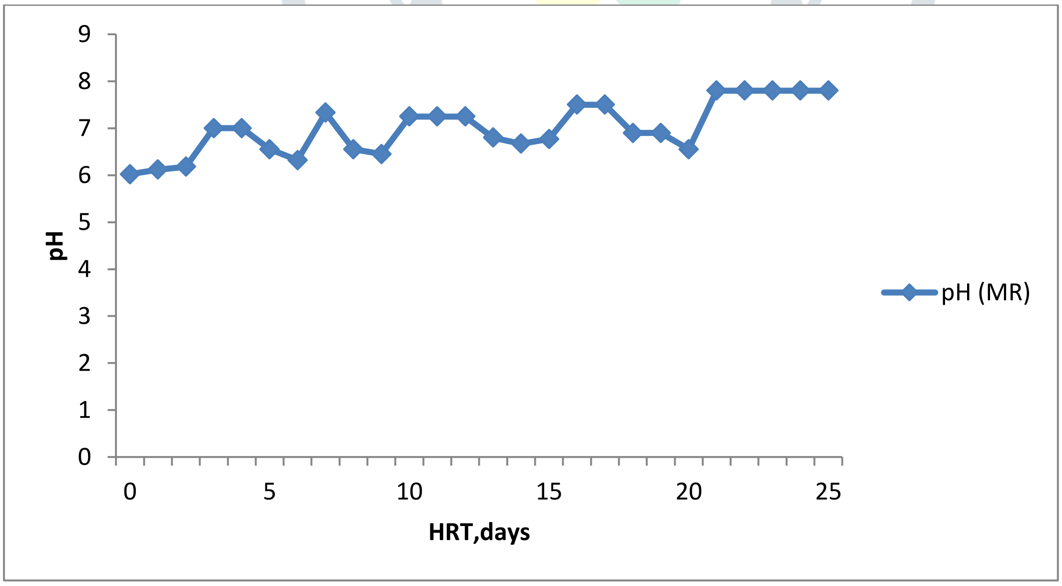

Figure.3 Characteristics Curve of HRT, days Vs pH in Methanogenic Reactor

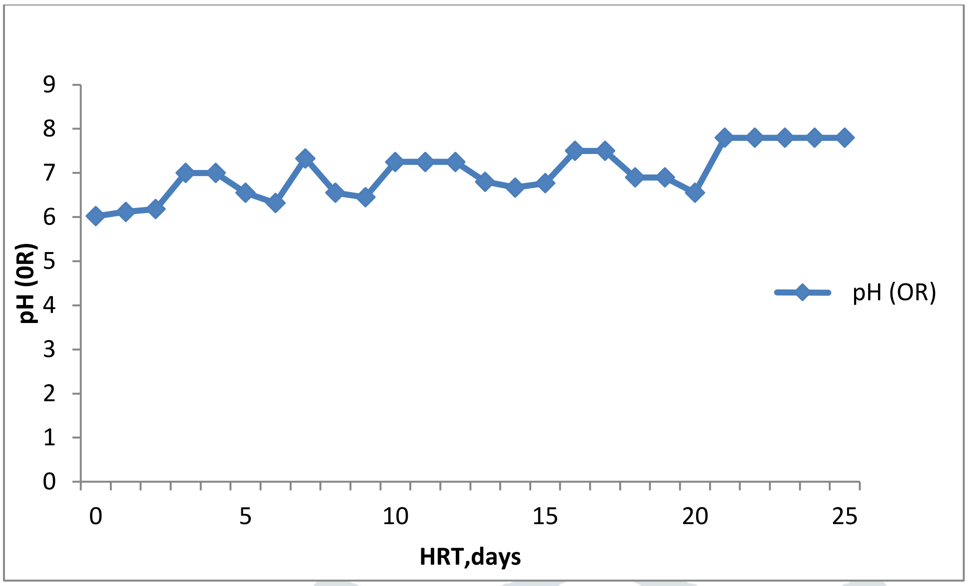

Figure.4 Characteristics Curve of HRT, days Vs pH in Overall Reactor

The pH is an important factor to control the digestion process in the anaerobic reactors. The acidogenic reactor itself act as a metabolic buffer, preventing pH shock to the methanogenic microorganisms and also increases the stability of the process by controlling the acidification phase in order to prevent over loading and the build up of toxic materials.The pH range of acidogenic is 4.1 to 5.5 (Figure 2) .The methanogenic organisms are very sensitive and can be active at an optimum pH of 6.8 to 7.65.The methane forming microorganisms can survive in a condition with pH values ranging between 6.6 and 7.6 (Ritmann and Mc cardy P.L 2001)., although stability may be achieved in the formation of methane over a range of 6.0 to 8.0. pH values below 6.0 and 8.3 should be avoided, as they can inhibit the methane forming microorganisms (Chernicharo C.A.L., 2007). Variations in pH of effluent from the reactor during the start up in acidogenic and methanogenic stages are shown in (Figure.3). Also the pH of the reactor was comparatively stable by varying from 6.02 to 7.8 (Figure 3) which are well suited for methanogenic activities. This range of pH indicates that the reactor had sufficient alkalinity to neutralize the organic acids delivered from the hydrolysis as well as the acidogenesis stages.In start up process pH rate gradually increasing by the changes , HRT reaching its in maximum value 7.8 at 25 days (Figure 4) in overall reactor.

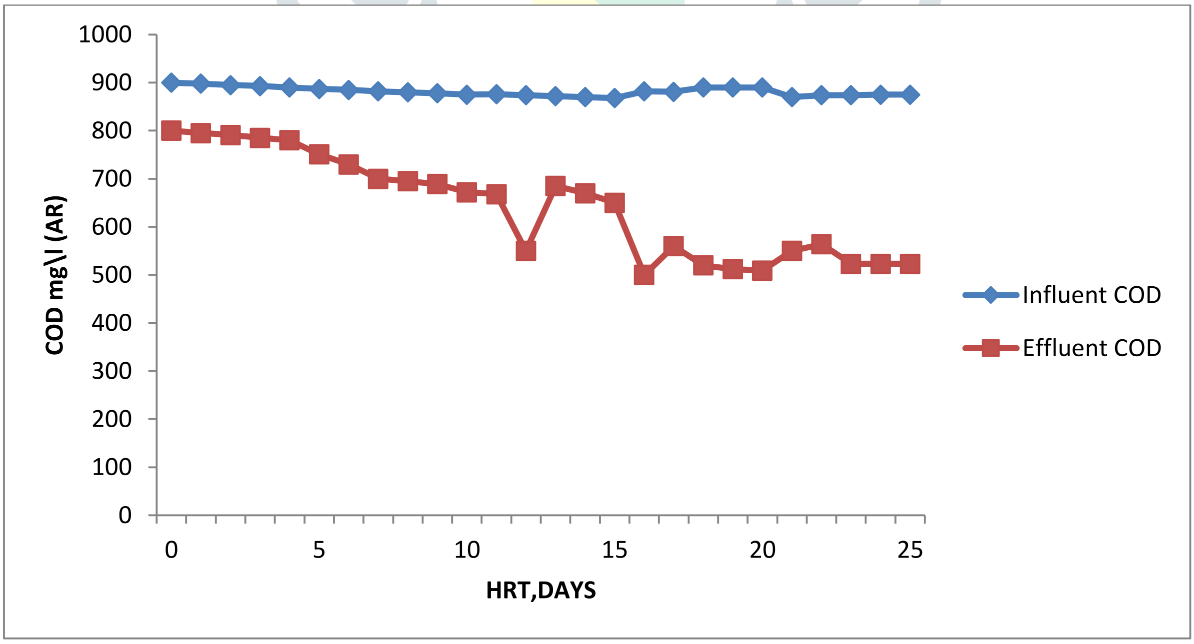

Figure.5 Characteristics Curve of HRT, days Vs COD in Acidogenic Reactor

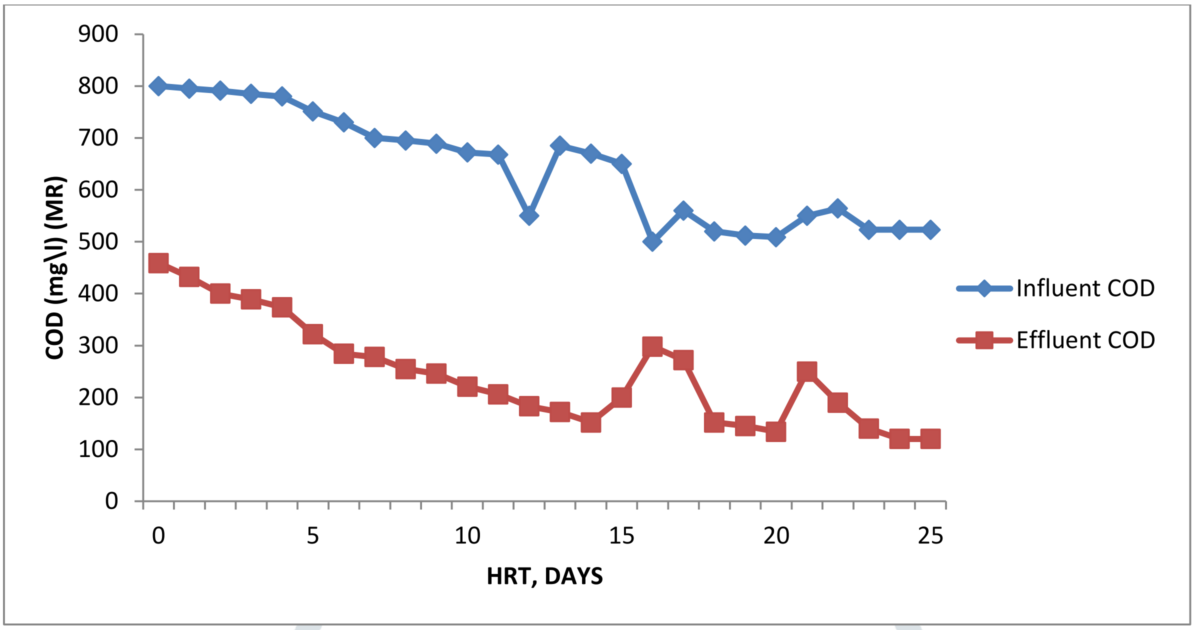

Figure.6 Characteristics Curve of HRT, days Vs COD in Methanogenic Reactor

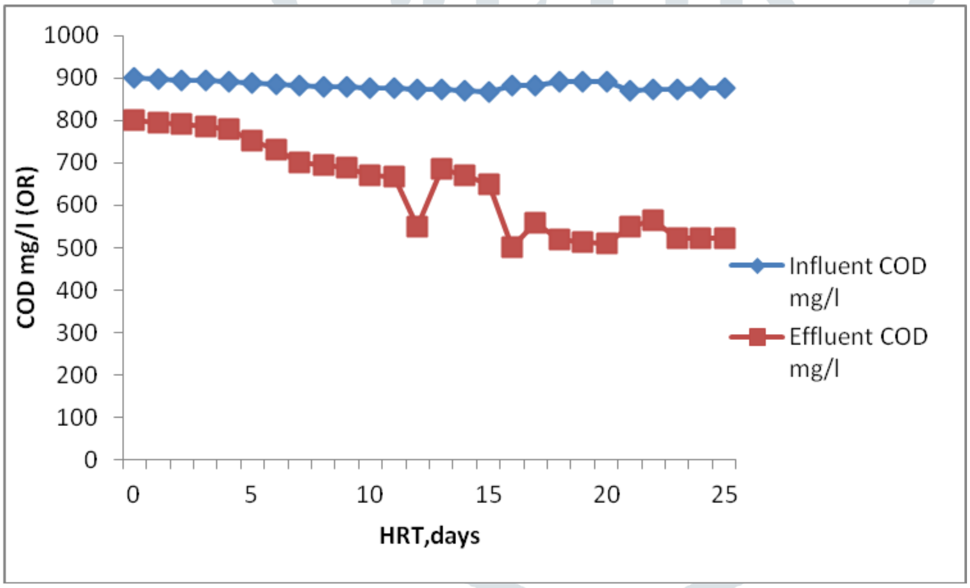

Figure.7 Characteristics Curve of HRT, days Vs COD in Overall Reactor

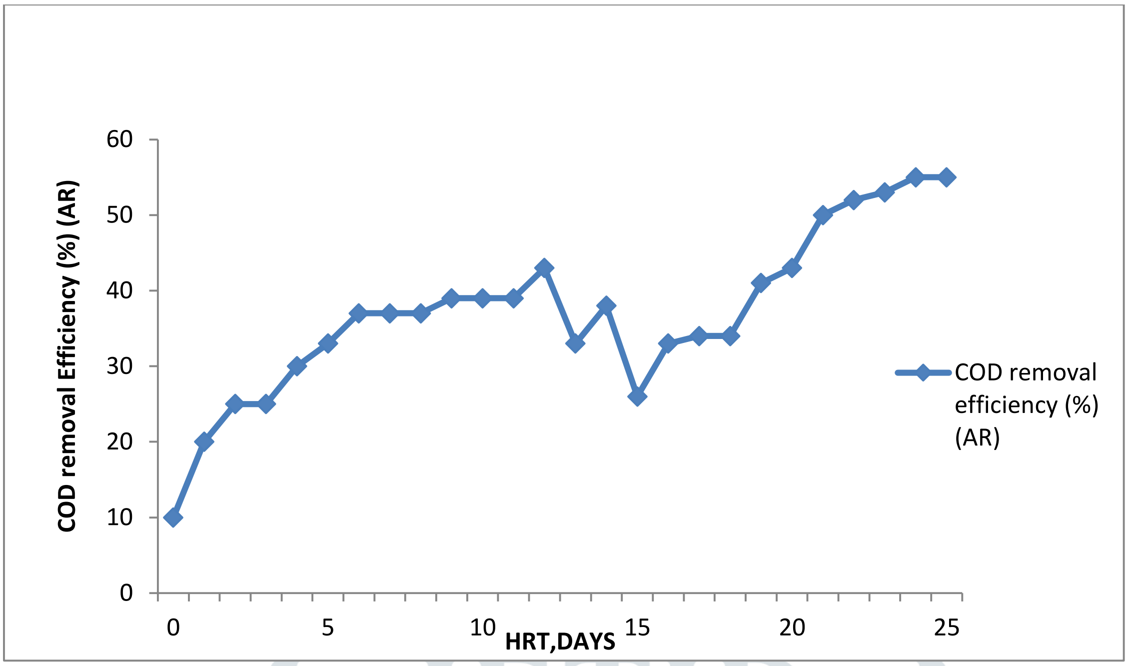

Figure.8 Characteristics Curve of HRT, days Vs COD removal efficiency in Acidogenic Reactor

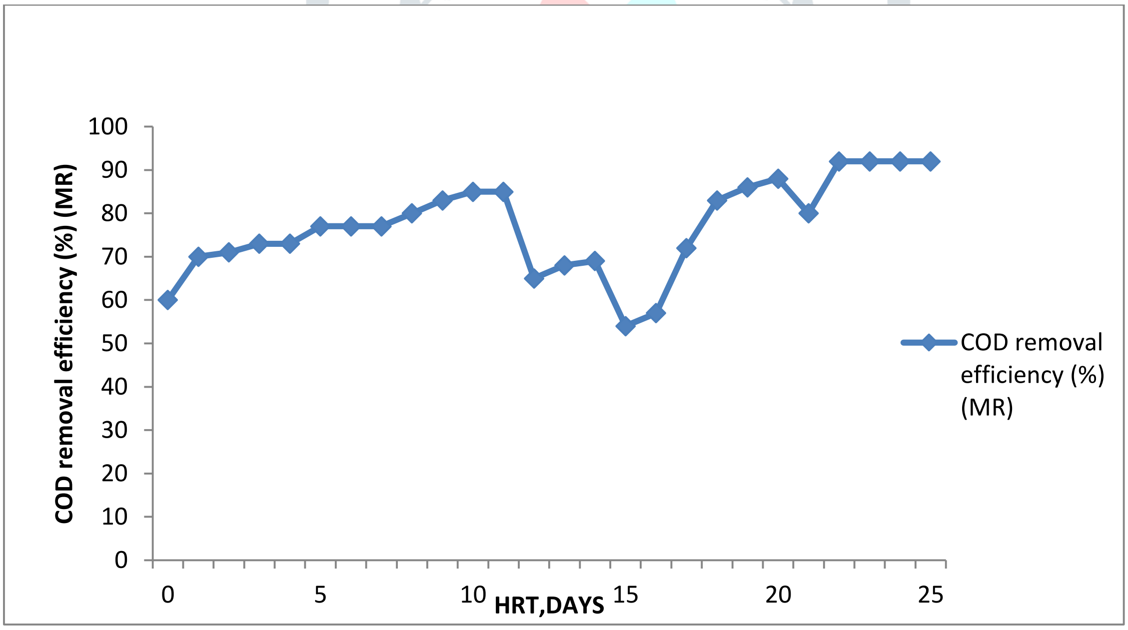

Figure.9 Characteristics Curve of HRT, days Vs COD removal efficiency in Methanogenic Reactor

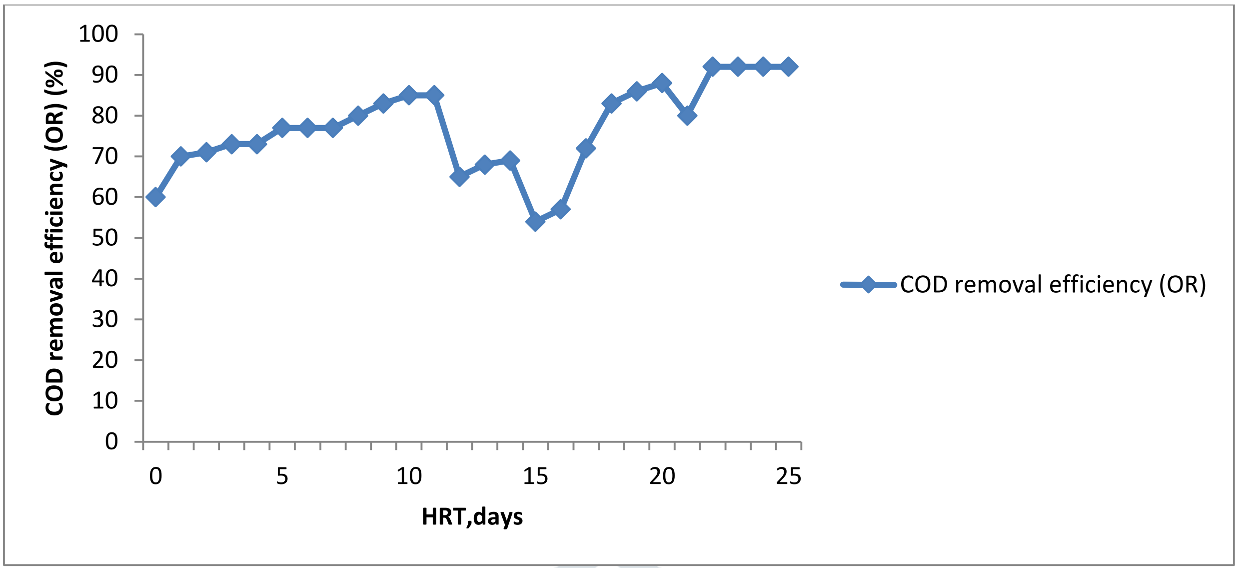

Figure.10 Characteristics Curve of HRT, days Vs COD removal efficiency in Overall Reactor

The start-up stage of the process was began by continuous feeding of the reactor with an initial influent COD concentration of 890 mg/l with a HRT of 24 h and consequently organic loading rate of 0.520 Kg COD/m^3/day (Figure 5) in acidogenic reactor and 0.418 kg COD/m^3/day (Figure 6) in methanogenic reactor and 0.938 Kg COD/m^3/day (Figure 7) which is remarkably a low value. The COD removal rate in acidogenic and methanogenic reactor during first two days was low in the range of 10% to 20% (Figure 8) and 50% to 60% (Figure 9). The low efficiency in removal at the beginning of the process is due to the biomass adaptation in the new environment. The reactor achieved at steady state conditions during the period of 18th day to 21st day with a COD removal efficiency of 92% in overall reactor (Figure 10). It is difficult to maintain the effective number of useful microorganisms in the system (BAL A.S et.al., 2001).

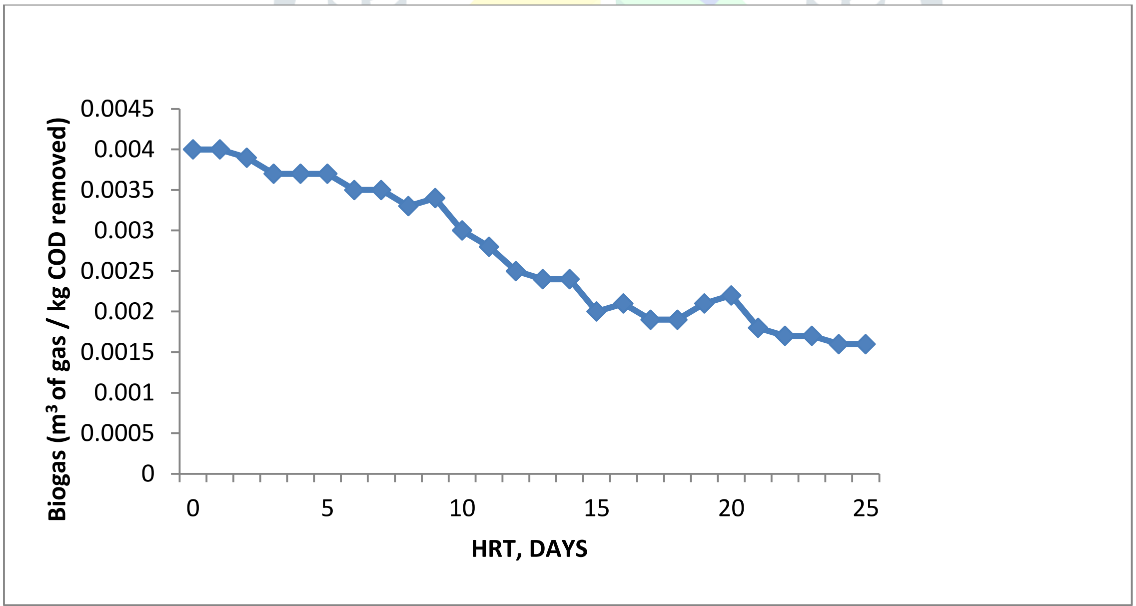

Figure.11 Characteristics Curve of HRT, days Vs Biogas production in Acidogenic Reactor

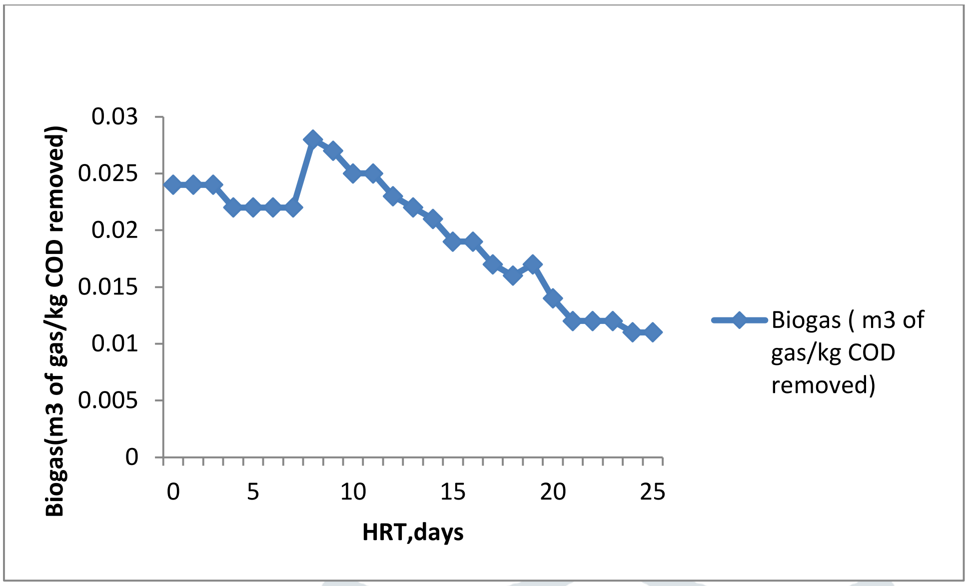

Figure.12 Characteristics Curve of HRT, days Vs Biogas production in Methanogenic Reactor

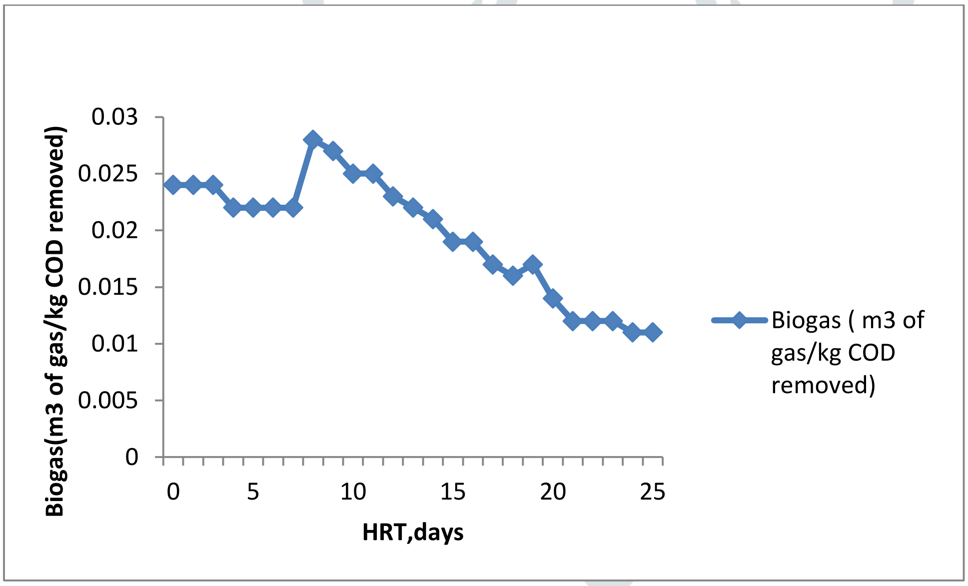

Figure.13 Characteristics Curve of HRT, days Vs Biogas production in Overall Reactor

During the start up process, acidogenic phase ,biogas production gradually decreases from 0.004 to 0.002 m^3 of gas/kg COD (Figure11) .Biogas rapidly decreases in the methanogenic phase ranging from 0.024 to 0.02 m^3 of gas/kg COD (Figure12).The biogas collection from the overall reactor is found to range from 0.024 to 0.02 m^3 of gas/kg COD (Figure13).Gas production was recorded daily after digester had reached a steady state it was run for 21 days at each organic loading rate.

IV. CONCLUSION

The start-up phase of the two-stage anaerobic bioreactor process was proved to be effective for the reduction of organic matter present in the pharmaceutical wastewater. The reactor was attained a steady state during the period of 18^{th} to 21^{st} days with a COD removal efficiency of 92% in the overall reactor by accomplishing the attached as well as suspended growth process.. The reactor was started up with an OLR of overall reactor, acidogenic and methanogenic reactor in 0.938 kg

COD/m3.day,0.252 kg COD/m3.day and 0.418kg COD/m^3.day.Maintaining a suitable and stable pH within the reactor should be a major priority for ensuring efficient methanogenic digestion .The pH of the wastewater plays an important role for acidification and methanization stages. The pH range of overall ,acidogenic and methanogenic reactor is 4.02 to 5.5,and 6.02 to 7.8. Proper pH and alkalinity are of key importance for the prompt startup Two stage reactor, when the reactor was operated efficiently, effluent pH was relatively stable.Biogas production in acidogenic and methanogenic reactor as well as overall reactor is0.004 to 0.002 m^3 of gas/kg COD , 0.024 to 0.02 m of gas/kg COD ^{3}.

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