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Mathematical approach towards non-stepwise performance assessment in HUASB reactor for wastewater treatment from pulp and paper mills

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A lab-scale Hybrid Upflow Anaerobic Sludge Blanket (HUASB) reactor with a working volume of 6.5 litres has been taken for the performance analysis, in the treatability study of pulp and paper mill wastewater. In order to analyze the performance of the reactor, operational parameter like hydraulic retention time (HRT) was varied from 10, 20, 30 and 40 h. In addition to that, performance parameters like chemical oxygen demand (COD), pH, volatile fatty acids (VFA), alkalinity, gas production and VFA/alkalinity ratio are analyzed to check the reactor efficacy. The maximum COD removal efficiency of 81.3% is obtained at 40 h HRT, with gas production (methane content of 58%). Also, the obtained results are fitted to the kinetic models like the standard first order, first order and second order to evaluate the performance of the HUASB reactor.

Keywords: Anaerobic digestion, HUASB reactor, Pulp and Paper mill wastewater, Kinetic modelling

Pulp and paper mill is one of the industries that require more amount of water for the production process. Based on the raw materials used and the manufacturing process adopted, Pulp and Paper Industry (PPI) produce relatively large amounts of both wastewater and solid wastes[1]. According to the studies[2-5] pertained by, the wastewater produced from each unit of PPI constitutes various organic and inorganic substances in it and are considered as a significant threat in affecting the water resources. Hence, there is a need for advanced treatment to treat pulp and paper wastewater (PPW), which in turn will reduce the organic and inorganic substances under standard levels. Instead of treatment, on-site reuse and recycling, and also modifications in the production process technology are some of most efficient economic and environmental options which may result in the reduction of the scarce amount of pollutants in PPW[6]. But in many cases, the process modifications are economically not feasible due to unavailability and cost of raw materials; in such circumstances, the treatment option is the only approach to reduce the pollutants levels in PPW. Even though several treatment techniques are available, adopting the integrated methods like a combination of biological (e.g. Anaerobic digestion) and physiochemical (e.g. Novel Fenton reactions) can be environmentally and economically preferable to minimize environmental contaminant[1]. Among many treatments, anaerobic treatment plays a significant role due to its efficiency in the removal of organic and inorganic substances. In anaerobic treatment, particularly Upflow Anaerobic Sludge Blanket (UASB) has been commonly adopted because of its advantages like low investment requirements, less sludge production and energy recovery[7,8] reached 80% average removal of COD when treating diluted black liquor from a kraft pulp (KP) mill by using a UASB reactor. The performance of a bench-scale UASB was also investigated by[9] for the treatment of simulated bleached and unbleached cellulose pulp mill wastewater[10]. Advancement of UASB leads to HUASB reactor, which has the advantage of both anaerobic filter and UASB[11]. Moreover, most of the studies about the performances of various HUASB reactors indicate the “stepwise” mode of operation, in treating varieties of industrial wastewaters[12-14]. Hence in this present research, a novel effort was made to

assess the non-stepwise performance of HUASB reactor in treatment of PPW originated from Hardwood/Bagasse unit, under various HRTs, 10, 20, 30 and 40 h. The reactor performance was assessed in a non-stepwise mode, i.e. separate start-up process for each Hydraulic Retention Time (HRT), to compare the performance of stepwise way, i.e. one-time start-up process for all HRTs. In addition to above, an attempt was made to fit the performance data through mathematical approach.

Experimental Section

A HUASB reactor was fabricated of glass with an overall capacity of 7.8 l and a working volume of 6.5 l (Fig. 1). The hood provided at the top and bottom of the reactor was used for gas venting and sludge accumulation. The polypropylene polyhedral spherical media was used as the packing media inside the reactor. Also the rumen liquid of goat and cow dung was taken as the inoculum mixture. The physicochemical characteristics of the raw wastewater originating from the Hardwood/Bagasse unit of PPI was presented in Table 1. The reactor was started up by sending the inoculum mixture and wastewater with an influent COD of 8042 mgL^{-1} (with a variation between 6 and 10%) into the reactor periodically. One litre of inoculum mixture containing 750 mL rumen liquid and 250 ml cow-dung was pumped through a peristaltic pump (RH-P100VS-100, Ravel Hiteks Pvt, Ltd, India), at a rate of 0.5 mL min^{-1}. Subsequently, at the second and third days of the start-up, about 1l solution of inoculum mixture and wastewater at ratios of 1:1 and 1:3 (v/v), were respectively pumped at a rate of 0.5 mL min^{-1}. Also, from the fourth day onwards, about 1l wastewater was introduced into the reactor at a constant speed of 0.5 mL min^{-1}, till the level of liquid reaches the top outlet port of the reactor. Finally, the entire reactor kept undisturbed for the start-up process. Based on influent COD value of 8,042 mgL^{-1} and a working volume of 6.5 L, the non-stepwise performance was undertaken in the reactor at different influent flow rates of 10.8, 5.4, 3.6 and 2.7 mL min^{-1}, to arrive the respective HRTs of 10, 20, 30 and 40 h. The OLR was maintained as

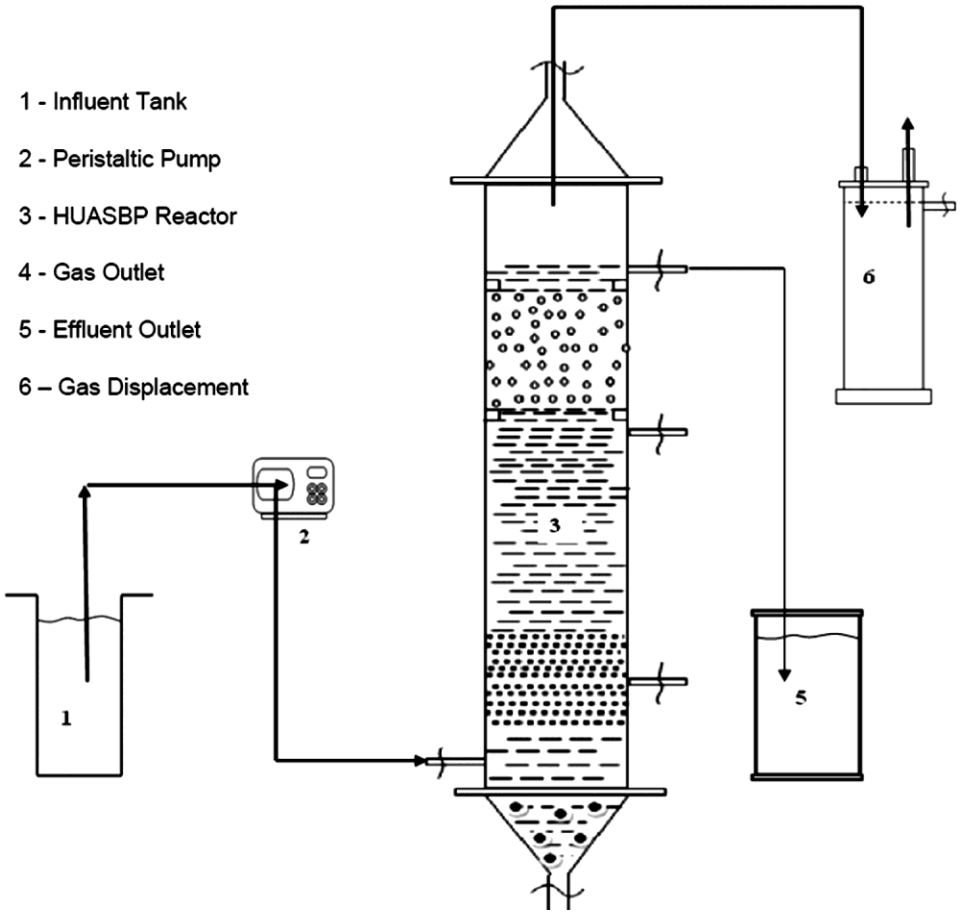

Fig. 1 — Schematic diagram of the laboratory HUASB reactor

Table 1 — Physico- chemical characteristics of raw wastewater from hardwood/ bagasse unit.

Sl. No.	Characteristics	Result*
	Physical	
1	Colour	Light brown[1]
2	Odour	Pungent smell[1]
3	Temperature (at site), ^oC	23 – 30
	Chemical	
1	*p*H	3.38
2	Acidity, mgL^{-1} as $CaCO_3$	1480
3	Alkalinity, mgL^{-1} as $CaCO_3$	Nil
4	Solids	
A	Total solids (TS), mgL^{-1}	7200
B	Total non-volatile solids (TNVS), mgL^{-1}	5200
C	Total volatile solids (TVS), mgL^{-1} (by difference)	2000
D	Total dissolved solids(TDS), mgL^{-1}	5000
i	Total dissolved inorganic solids (TDIS), mgL^{-1}	2750
ii	Total dissolved volatile solids (TDVS), mgL^{-1} (by difference)	2250
E	Total suspended solids (TSS), mgL^{-1}	2200
F	Settleable solids, mgL^{-1}	80
5	Calcium, mgL^{-1} as Ca^{2+}	240
6	Magnesium, mgL^{-1} as Mg^{2+}	165
7	Chlorides, mgL^{-1} as Cl^-	760
8	Sulphates, mgL^{-1} as SO_4^{2-}	490
9	Nitrate, mgL^{-1} as NO_3^-	48
10	Nitrite, mgL^{-1} as NO_2^-	2.8
11	Phosphate, mgL^{-1} as PO_4^{3-}	4.7
12	Ammonium ion, mgL^{-1}	2.2
13	Iron, mgL^{-1} as Fe^{2+}	1.2
14	Manganese, mgL^{-1} as Mn^{2+}	0.3
15	Fluorides, mgL^{-1} as F^-	0.5
	Biological	
1	BOD	
A	Total BOD_5@ 20^0C, mgL^{-1}	6000
B	Soluble BOD_5 @ 20^0C, mgL^{-1}	4600
2	COD	
A	Total COD, mgL^{-1}	8042
B	Soluble COD, mgL^{-1}	5616

(* -average of five periodical values with 9% variation and 1-qualitative basis)

3 $kgCODm^{-3}day^{-1}$ for all HRTs. Further, the influent raw wastewater was buffered with 120mL of 1M $NaHCO_3$ solution per litre of wastewater, to maintain *p*H at the neutral condition. Also, at the end of each day, 100 mL of sample volume was collected from the top port and analyzed for COD, VFA, Alkalinity, *p*H. However, the influent COD was also investigated daily. The gas production was monitored daily by the standard procedure of downward displacement of water.

Effective performance of any anaerobic reactor (either lab-scale or real size reactor), chiefly depends on the efficient start-up of the reactor. HRT, OLR, alkalinity, VFA, Alkalinity/VFA ratio and gas production are some main operating conditions which influence the reactor performance. In the present work, the non-stepwise performance of the reactor was assessed based on *p*H, COD, alkalinity, VFA, and gas production.

Results and Discussion

In the current research, the experimental observation of the reactor system is illustrated in Fig. 2. It is seen from the figure that about 50% removal of initial COD was noticed at the end of 24^{th}, 20^{th}, 16^{th} and 14^{th} d for 10, 20, 30 and 40 h HRTs. The steady states were attained in the reactor at the end of 27^{th}, 25^{th}, 24^{th} and 23^{rd} d, for 10 to 40 h HRTs. Moreover, the respective maximum removals of COD were about 55, 63.8, 74 and 81.3%, for 10 to 40 h HRTs. Under various HRTs, the respective removals of COD per d of operating time of the reactor were about 2.2, 2.77, 3.34 and 3.87%. In UASB reactors type, at high HRTs, the upflow velocity decreases and as a result the efficiency of the reactor for the removal of the suspended solids increases [15].

It appears that the alkalinity variations at different HRTs were significantly higher. The respective average alkalinity values at the end of steady-state were about 7900, 6685, 6400 and 5180 mgL^{-1} as $CaCO_3$, for 10 to 40 h HRT. Further, from Fig. 2, the maximum removals of COD (i.e. 55, 63.8, 74 and 81.3%) was due to the moderate conversion of biodegradable matter to VFA, and further gas production is substantiated through the significant *p*H changes. However, at the end of respective steady states, the maximum alkalinity values were about 7900, 6685, 6400 and 5180 mgL^{-1} as $CaCO_3$ could be seen.

Unlike the build-up of alkalinity in the reactor the VFA was drastically reduced between 4889 and 2834 mgL^{-1} as $CaCO_3$ (for 10 h HRT), 4710 and 1800 mgL^{-1} as $CaCO_3$ (for 20 h HRT), 4390 and 1325 mgL^{-1} as $CaCO_3$ (for 30 h HRT) and between 4157 and 625 mgL^{-1} (for 40 h HRT). Also, the respective VFA values remain the same beyond 27^{th} and 23^{rd} days. Therefore, this decreasing trend of VFA indicates the conversion of VFA to gas from 6^{th} day onwards. Hence, it can be understood that the methanogenic phase of anaerobic digestion is not significantly affected.

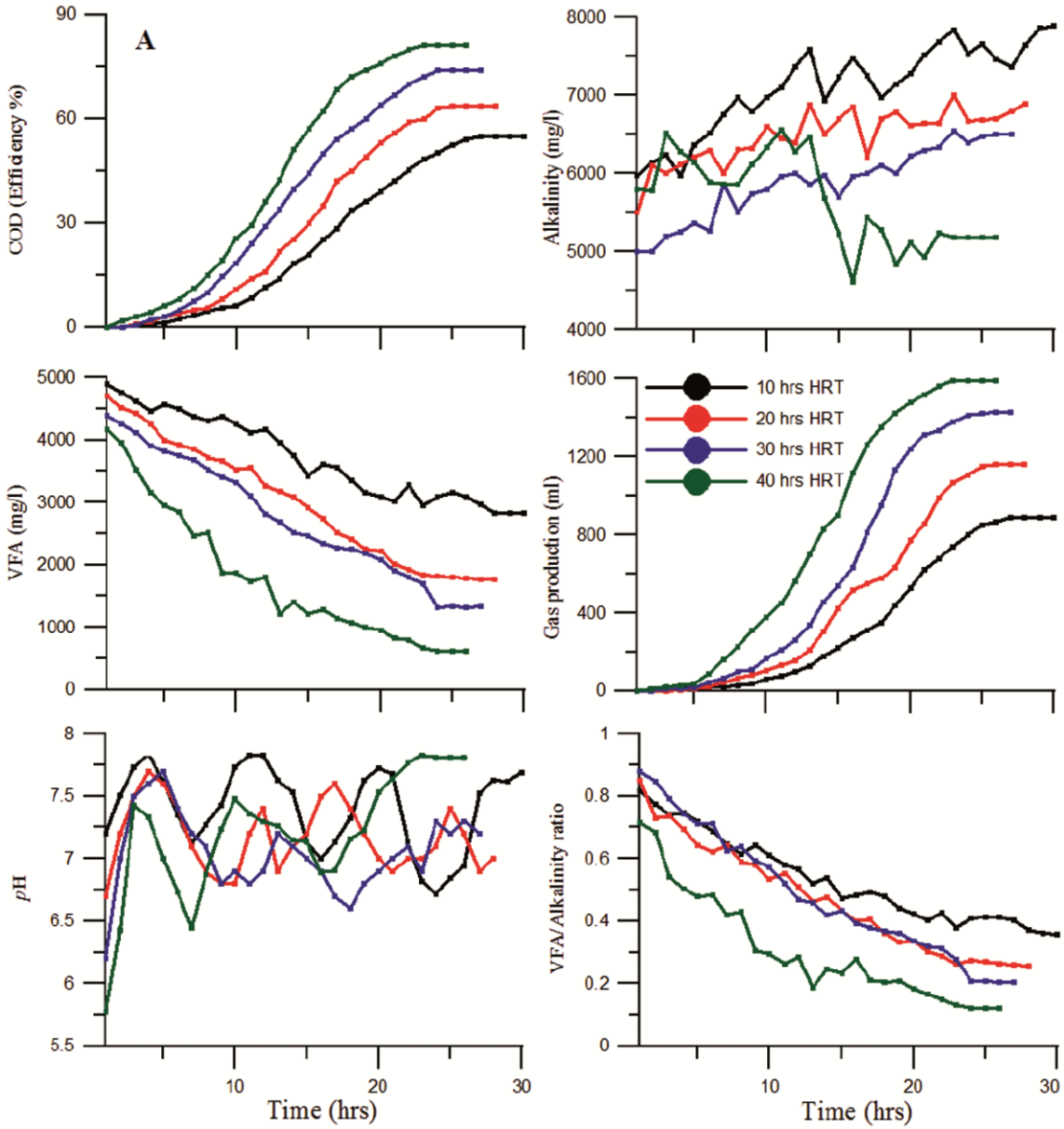

Fig. 2 — Non-stepwise performance curves of HUASB reactor for variations in COD removals, alkalinity, VFA, gas production, *p*H and VFA/Alkalinity ratio

Since the stability of any anaerobic system (i.e. including HUASB) chiefly depends on VFA/Alkalinity ratio, the present study values were significantly varied between 0.1 and 0.8. But, the experimental VFA/Alkalinity ratios are in accordance with the studies undertaken by[16,17]. In this context, several pieces of research had proposed different optimum values for VFA/Alkalinity ratio. For example, this ratio should be less than 0.3 or 0.4 according to[18,19] and less than 0.4[20]. Comparing the VFA/Alkalinity ratios, it is evident that the system had sufficient buffering capacity and the conditions were significantly favourable for the anaerobes. The variations in *p*H of the study were almost gradual, and the overall *p*H values have fluctuated between 5.78 and 7.84. It is understood that the little variations in *p*H, could not impede the build-up of VFA within the reactor. Hence, it supports the biochemical activity of methanogenic bacterial cultures. It was previously reported that the reactor fed with feed *p*H above 10, leads to failure of the system[20]. Therefore, *p*H of the feed should be taken care of to avoid the unfavourable circumstances inside the reactor.

Till 4 d of operation of the reactor, no significant gas production was noticed, except the accumulation of tiny air bubbles within the reactor. But, from the 5th d onwards, gas production was seen. Moreover, at the respective terminal days 27th and 23rd d, the maximum cumulative gas productions of 890 and 1590 mL were noticed. Further, the rate of gas production is in accordance with the variations in COD removal, alkalinity, VFA, and pH values. Since the calorific value of the gas chiefly depends upon the methane to carbon dioxide composition of the gas produced in the reactor, it is highly necessary to assess their concentrations appropriately. Methane content of 58% was measured in gas chromatography using porapak-Q column.

Biomass accumulation within the reactor

Under each HRT, at the end of operation of HUASB reactor, the accumulated biomass was assessed (volatile and non-volatile matter) within the reactor. Table 2 shows the necessary data collected at the end of each HRT. From the observation, the following parameter like total sludge (including sludge blanket) accumulated at the bottom was about 910 ml/l and the approximate sludge blanket thickness was about 5.4 cm (above 10 cm from the influent port). Moreover, the biomass accumulation on the polypropylene spherical inert media (about 72 numbers) was also observed and shown in Fig. 3.

Fig. 3 — Photograph of the biomass accumulation on polypropylene spherical inert media.

From this, about <1 mm thick biofilm accumulation was observed on each piece of the packing material. Also, about 1.36 g of dry biomass was noticed on each part of the packing material.

Mathematical modelling of model HUASB reactor

Process modelling is an acceptable protocol for appropriately describing the performance of biological treatment systems and predicting their returns. To verify optimum reactor performance, the kinetic coefficients rate should be taken into consideration at the process of engineering design instead of using only empirical methods. Moreover, the types of substrates and microorganisms surrounding the environment in a bioreactor are associated with the value of the kinetic coefficients[21]. Several models have appeared in the wastewater treatment literature,[22,23]. First-order substrate removal model[24,25] and second order model often known as Optaken- Grau model are some of those which are used to test the kinetics of organic matter and nitrogen removals in a bioreactor[26,27]. However, first-order[21], and second-order[27], substrate removal models have been adopted together with classical first-order rate kinetics models.

As per the classical first, enjoin rate kinetics model, the efficient COD leaving the HUASB reactor can be written as

$$\frac{dS}{dt} = -kt \quad \text{... (1)}$$

Also, the linearized form of the solution to the equation 4.1 is given by

$$lnS_t = lnS_0 - kt \quad \text{... (2)}$$

where, S_t , S_0 are the COD values leaving the reactor at any time t (i.e. operating time, d) and average influent COD of wastewater in mgL^{-1}; and k is the first-order rate constant in d^{-1}.

As per as the first order substrate removal model is concerned[21] the rate of change in substrate concentration within the system by assuming the first-order rate for substrate removal can be expressed as follows:

$$-\frac{dS}{dt} = \frac{S_0}{\theta} - \frac{S}{\theta} - k_1 s \quad \text{... (3)}$$

Table 2 — Essential data pertaining to biomass accumulation in the reactor

Parameter HRT	Total sludge, mL L^{-1}	Sludge blanket thickness, cm	Total biomass accumulation on the media, g	Thickness of bio film, mm
10 h	390	3	72.89	<1
20 h	470	3	86.45	<1
30 h	580	3.5	100.81	<1
40 h	640	4	122.42	<1

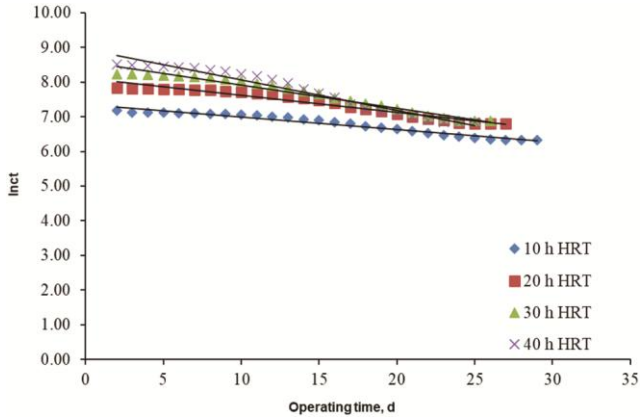

Fig. 4 — Linearized form of classical first order model

Under pseudo steady state conditions, the rate of change in substrate concentration is negligible and equation 3 can be written as:

$$\frac{S_0 - S}{\theta} = k_1 s \qquad \ldots (4)$$

where θ is HRT which is given by $\frac{V}{Q}$

According to *Grau et al.* (1975), the general second-order model is given by

$$-\frac{dS}{dt} = k_2 \left(\frac{S_0}{S}\right)^2 \qquad \ldots (5)$$

The linearized form of the integrated equation 5 is given by

$$\frac{S_0\theta}{S_0 - S} = \theta + \frac{S_0}{k_2 x} \qquad \ldots (6)$$

where k_2 and X are second-order rate constant and biomass concentration mgl^{-1}. The second term of the right-hand side of equation 4.6 is accepted as constant then equation 6 becomes

$$\frac{S_0\theta}{S_0 - S} = a + b\theta \qquad \ldots (7)$$

Further, if $\frac{S_0 - S}{S_0}$ expresses the substrate removal fraction (i.e. F) then equation 7 can be written as

$$\frac{\theta}{F} = a + b\theta \qquad \ldots (8)$$

Based on the data of the eq. 2, 4 and 8, Figures 4 - 6 are drawn. The respective first-order kinetic model constants of various models are shown in Table 3. As per Fig. 6, the individual model constants, along with correlation coefficients were a=9.25, b=1.02, and r=0.989.

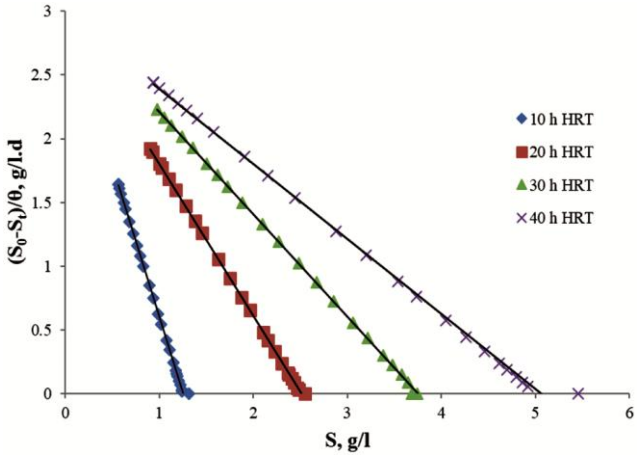

Fig. 5 — Linearized form of first order removal kinetics model

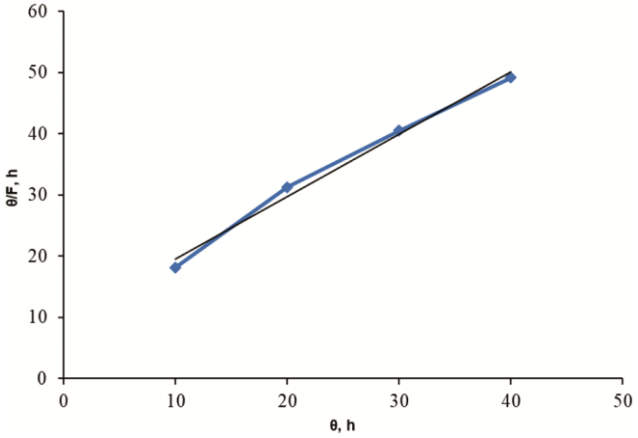

Fig. 6 — Linearized form of second order removal kinetics model

Table 3 — First order kinetic model constants

Sl. No	HRT, h	Classical first order kinetics		First order removal kinetics	
		$K_{1,d}^{-1}$	Correlation coefficient r	$K_{2,d}^{-1}$	Correlation coefficient r
1	10	7.356	0.946	2.975	0.997
2	20	8.11	0.944	2.890	0.994
3	30	8.66	0.979	3.020	0.999
4	40	8.955	0.957	2.975	0.996

Conclusion

Based on the studies of the non- stepwise treatment of the Pulp and paper mill wastewater, by HUASB reactor, the following conclusions were drawn.

1. The HUASB reactor is highly suitable in treating pulp and paper mill effluent.
2. The polypropylene spherical inert media is suitable for HUASB reactor.
3. A high correlation is found between COD removals with those of variations in VFA and Alkalinity.

4. The biomass attachment and accumulation is moderate over the surfaces of the polypropylene spherical balls inert media.
5. VFA/Alkalinity ratio is varied between 0.1 and 0.8, which shows the stability of the HUASB reactor.
6. Among the three process model kinetics were concerned, the first-order removal kinetics model is appeared to be appropriate in thoroughly describing the removal kinetics of COD.

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