

KINETIC STUDIES ON A UASB REACTOR SUBJECTED TO INCREASING COD CONCENTRATION

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ABSTRACT

This paper shows the response of a UASB reactor subjected to increasing influent COD concentrations.

The study was carried out using a 10.5 l UASB reactor continuously operated during ten months, and fed with synthetic wastes prepared daily using glucose, ammonium acetate, methanol and nutrient solution. The flow rate of 16 l.d⁻¹ was held constant throughout the experiment, corresponding to a hydraulic retention time (θ) of 15.6 h. Four intermediate sampling ports besides the influent and effluent ones allowed a study of the reactor behaviour along its vertical profile.

For average values of the initial COD concentrations ranging from 1780 to 9700 mg.l⁻¹, corresponding to volumetric loading rates (B_V) of 2.7 to 14.8 kg COD.m⁻³.d⁻¹, COD removal efficiencies varying from 98 to 80% were achieved.

It could be concluded that the step-increase of the influent COD affected the reactor performance in two different ways. First, the reactor could assimilate the shock loads due to the step-increase of the influent COD and B_V , beyond the transient periods following changes in the operation parameters. Second, the overall efficiency decreased gradually with the step-increase of the initial COD and B_V .

Kinetic studies indicate that the overall kinetic parameters are probably affected by the step-increase of influent COD concentrations.

KEYWORDS

Anaerobic process; UASB reactor; glucose synthetic substrate; step-increasing COD concentrations; kinetic.

INTRODUCTION

Among the several anaerobic reactor configurations developed in the last two decades, up-flow reactors have exhibited superior performance compared to the others when submitted to high values of volumetric loading rates (B_V). They also have shown better assimilatory capacity of toxic and organic shock loads. This is particularly true for reactors in which granular sludge is formed and maintained (Young and Yang, 1988).

There are several hypotheses for explaining the granulation phenomenon; but actually no simple reasons seem to exist for it to occur, nor procedures to guarantee the formation

of granules. Notwithstanding this, the phenomenon seems to be closely related to the reactor flow pattern.

Attempts to describe the flow pattern of UASB reactor were first made by Heertjes and Van Der Meer (1978) using Li as tracer in stimulus-response experiments. The 30 m³ reactor tested was described as composed of three distinct zones - the sludge bed, the sludge blanket and the gas/solid/liquid separation zone. While the sludge bed and the blanket zone were assumed to be completely mixed regions with flow bypass and back-flow, the settling zone was characterized as a plug-flow region. This structure has been used to formulate mathematical models; further studies on UASB reactor modelling have maintained most of these main assumptions. (Heertjes and Kuijvenhoven, 1982; Bolle et al. 1986 a,b). However, data of COD (Chemical Oxygen Demand) and VSS (Volatile Suspended Solids) reactor profiles have indicated that a significant fraction of the organic matter is removed in the first layer of the reactors near the bottom, where the VSS concentrations are normally higher than in other regions (Foresti, 1990). Moreover, visual observations of UASB bench-scale reactors do not confirm the hypothesis of completely mixed zones, since the granulated sludge seems to behave not as a suspended biomass in the bulk liquid, but rather as a fixed biomass mainly in the lower regions of the reactor.

On the other hand, kinetic parameters determined from completely mixed batch reactors have been proposed to be used for modelling anaerobic reactors of different configurations, including up-flow. It is possible that kinetic parameters may not be the same for different reactor configurations.

The main objective of this paper is to present data obtained from a UASB reactor subjected to increasing synthetic substrate COD concentrations in order to evaluate the process kinetic parameters.

MATERIALS AND METHODS

The study was carried out using the apparatus schematically shown in Fig. 1.

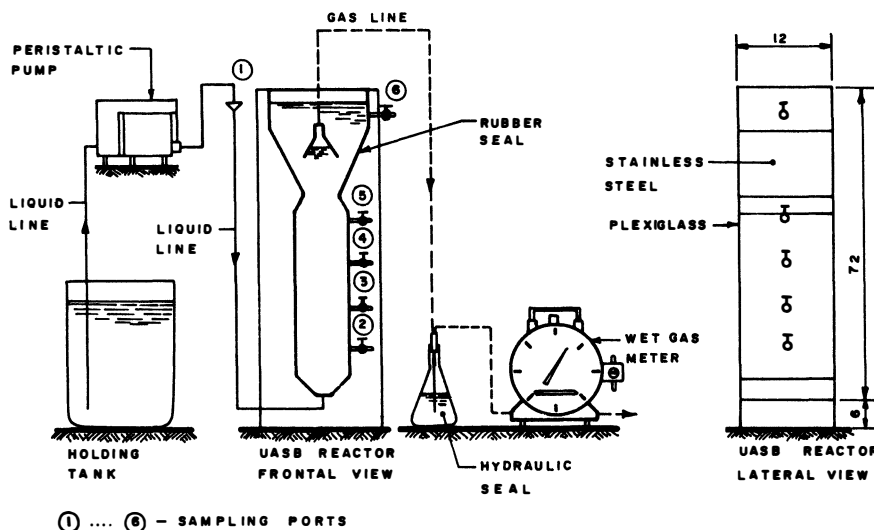


Fig. 1. Scheme of the apparatus used during the experiment.

The 10.5 litre reactor was built with a 2 - dimensional flow geometry, as seen in Fig. 1. The reactor is defined by two 30 cm x 78 cm parallel Plexiglass plates 12 cm apart, and by a variable contour made of stainless steel. The plates are tightened together by bolts against the stainless steel contour separated from the plates by rubber seals. The system, thus built, permitted the visualization of the interior of the reactor. Four intermediate sampling ports were provided along its height, besides the influent and effluent ones (1 and 6 in Fig. 1).

The hydraulic retention time (θ) of 15.6 h was kept constant throughout the experiment by controlling the flow rate of the peristaltic pump (Watson Marlow - 502 S). Gas production was measured by means of a wet gas meter (Alexander Wright - DM 3A).

The substrate was prepared daily at desired COD concentrations in a 25 litre plastic holding tank from which the liquid was pumped to the reactor inlet. The composition of the substrate corresponding to a COD concentration of $2 \times 10^3 \text{ mg.l}^{-1}$ is shown in Table 1. Other values (4×10^3 , 6×10^3 , 8×10^3 , 12×10^3) were obtained by increasing the substrate constituent concentrations accordingly.

TABLE 1 Substrate Composition for COD of $2 \times 10^3 \text{ mg.l}^{-1}$

Constituent	Concentration (mg.l^{-1})	Constituent	Concentration (mg.l^{-1})
$\text{C}_6\text{H}_{12}\text{O}_6$	1,500.00	KH_2PO_4	8.50
$\text{CH}_3\text{COONH}_4$	400.00	K_2HPO_4	21.75
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	5.00	$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$	33.40
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.25	NaHCO_3	2,000.00
CaCl_2	44.50	NiSO_4	1.00
CoCl_2	0.08	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	22.50
SeO_2	8.50	CH_3OH (99.8%)	0.50 (ml.l^{-1})

Actual initial COD concentrations were lower than the expected values due to fermentation in the holding tank which could not be completely avoided.

Digested anaerobic sludge from a conventional sewage treatment plant was used to inoculate the reactor, and the start-up period lasted two months. Since the reactor was used also as a control reactor for toxicity studies, the initial COD concentration of $2,000 \text{ mg.l}^{-1}$ was maintained for five months. Thereafter, another five-month period was used for evaluating the response of the reactor to step-increasing COD concentrations, including the analyses of samples from intermediate ports.

The reactor was monitored daily in respect to pH, temperature, flow rate, gas production and sludge height, which was maintained at the level corresponding to port 5 (see Fig. 1). The excess sludge discharged from this port was always analyzed in relation to the VSS concentration in order to allow the evaluation of VSS losses.

At least twice a week, samples from the influent and effluent, and from intermediate ports were centrifuged at $3,500 \text{ g}$ for 20 min for COD analyses while raw samples were

used for total alkalinity (TA), and VSS determinations. All these analyses were carried out according to the "Standard Methods for the Examination of Water and Wastewater" (1985). Volatile acids (VA) concentrations were measured by direct titration (DiLallo and Albertson, 1961) twice a week, while gas compositions were determined once a week using a CG - 04 model 3537 gas chromatograph equipped with a flame ionization detector.

Kinetic parameters were estimated by using the equations:

$$\frac{1}{\theta_x} = Yq - b \quad (1)$$

$$q = q_{\max} \cdot \frac{S}{K_S + S} \quad (2)$$

$$\mu_{\max} = Yq_{\max} \quad (3)$$

where θ_x = mean solid residence time, d
 Y = biomass yield coefficient, mg VSS.mg S⁻¹
 q = specific rate of substrate utilization, mg S . mg VSS⁻¹ . d⁻¹
 q_{\max} = maximum specific rate of substrate utilization, mg S.mg VSS⁻¹ . d⁻¹
 b = VSS decay rate, d⁻¹
 K_S = half-velocity coefficient, mg S.l⁻¹
 μ_{\max} = maximum specific biomass growth rate, d⁻¹
 S = substrate COD concentration, mg.l⁻¹

The mean solid residence time, θ_x , was estimated for each phase using the equation:

$$\theta_x = \frac{\bar{X}_V V_R}{X_e^* Q} \quad (4)$$

where \bar{X}_V = average concentration of VSS, mg.l⁻¹;
 X_e^* = average concentration of VSS losses, mg.l⁻¹;
 V_R = 5.3 l = volume of the reaction zone;
 Q = 16.0 l.d⁻¹ = liquid volumetric flow rate.

The values of X_e^* include the average concentration of VSS in the effluent, X_e , and VSS losses due to periodic reactor profile sampling and non-periodic discharges from the sampling port 5, distributed along each phase.

RESULTS AND DISCUSSION

Performance of the Reactor

The results obtained during the last five-month operation of the reactor were grouped according to the initial influent COD concentration, thus resulting in six distinct sets with common periods, hereafter referred to as phases. The average value (A) and the standard deviation (sd) of the parameters calculated for each phase are shown in Table 2.

TABLE 2 Data Obtained During the Operation of the UASB Reactor
 Subjected to Influent COD Step-Increase

Parameter	T(°C)	S(mg.l ⁻¹)		ε (%)	Qg(l.d ⁻¹)	CH ₄ (%)	
		i	e			(273°K)	
I	A	25.9	1780	46	97.4	16.2	69.3
	sd	1.4	248	22	1.0	2.1	0.8
II	A	25.0	3100	90	97.1	23.2	62.5
	sd	1.5	141	25	0.7	2.9	6.1
III	A	24.6	3950	67	98.4	28.5	59.5
	sd	2.5	353	38	0.8	4.4	3.5
IV	A	23.7	5510	394	93.0	38.5	56.5
	sd	2.5	325	174	4.0	3.3	2.1
V	A	21.7	6975	413	94.4	47.8	55.0
	sd	1.7	1288	230	2.3	6.0	1.4
VI	A	20.0	9700	1910	80.4	59.5	42.0
	sd	2.3	2127	730	5.8	5.1	2.8

Parameter	pH	TA(mg.l ⁻¹)		VA(mg.l ⁻¹)		VSS(mg.l ⁻¹)		
		(as CaCO ₃)		(as Acetic Acid)				
		i	e	i	e	X _e		
I	A	7.7	7.4	636	760	198	24	30
	sd	0.1	0.2	192	164	69	7	9
II	A	7.8	7.3	893	1150	320	48	88
	sd	0.1	0.3	48	156	156	39	24
III	A	8.0	7.2	1043	1550	479	308	104
	sd	0.1	0.2	172	120	236	210	16
IV	A	8.0	7.3	2433	2633	902	714	205
	sd	0.1	0.2	90	372	93	358	19
V	A	8.0	7.6	3500	2783	1149	905	275
	sd	0.1	0.4	409	305	41	134	88
VI	A	8.0	7.0	5470	2943	2567	1602	490
	sd	0.1	0.4	394	343	95	144	217

Here indices i and e refer to influent and effluent parameters, ε is the percent removal efficiency for COD, and Qg is the gas flow rate at 273°K.

From the results obtained it can be concluded that this step-increasing influent COD concentration caused a gradual deterioration in the performance of the reactor. This is clearly shown by the decreasing percentage of methane in the off-gas with the increase of the influent COD concentration, indicating that the methanogenic activity was gradually affected. It can be also verified that the increase of effluent volatile acids (VA) was not proportional to the initial COD applied. For phase I, the ratio VAe/Si was 0.015 while for phase VI this ratio reached 0.165. The same trend was

observed for the effluent volatile suspended solids (VSS), which increased disproportionately from phase I to VI, giving ratios (X_e/S_i) ranging from 0.018 to 0.051.

The results of influent and effluent COD show two apparent discrepancies in relation to the general trend in the behaviour of the reactor, viz., the removal efficiencies in phases III and V were 1.3% and 1.4% higher than the values obtained for their respective precedent phases.

In order to formulate hypotheses for this behaviour other parameters were calculated as shown in Table 3.

TABLE 3 Values of Volumetric Loading Rate (B_V), Organic Load Applied (F_A), Organic Load Removed (F_R), and Methanogenic Activity (F_M)

Parameter	B_V (kg COD.m ⁻³ .d ⁻¹)	F_A (g COD.d ⁻¹)	F_R (g COD.d ⁻¹)	F_M (g COD-CH ₄ .d ⁻¹)	$F_M \times 100/F_R$ (%)
I	2.7	28.5	27.7	32.1	116*
II	4.7	49.7	48.2	41.4	86
III	6.0	63.1	62.1	48.5	78
IV	8.4	88.2	82.7	62.1	75
V	10.6	116.6	105.0	75.1	72
VI	14.8	155.1	124.6	71.4	57

The last column of Table 3 indicates the percentage of the COD removed due to methanogenic metabolism. It clearly shows that increasing fractions of the COD removed were shifted from the methanogenic metabolism to other processes, presumably for the production of non-methanogenic biomass. The visual observation of the sludge in the reactor confirmed a progressive change in its colour from black-grey to grey-white.

This changing of colour started at the bottom, and reached the top of the reactor by the end of the experiment. Although no microbiological studies have been done, the hypothesis of a change in the metabolic pathways due to the step-increasing of the influent COD seems to offer a reasonable explanation for the discrepancies observed in the COD removal efficiency parameters which were calculated from centrifuged samples.

Finally, the first value of the last column in Table 3 was higher than the maximum value theoretically possible to be achieved. The most probable explanation would be the lack of precision of the wet gas meter for low flows of gas, since the overestimation of gas production had been verified before in similar circumstances.

Kinetic Parameters

Kinetic parameters were determined by using the data of substrate removal presented in Table 2, and the data of \bar{X}_V and X_e^* shown in Table 4 in which the calculated values for θ_x are also presented.

The values of the overall kinetic parameters obtained by linear regression of the kinetic equations were: $Y = 0.23$; $b = 0.04 \text{ d}^{-1}$; $\mu_{\max} = 0.12 \text{ d}^{-1}$; $K_S = 82 \text{ mg.l}^{-1}$, $q_{\max} = 0.53 \text{ d}^{-1}$. Except for K_S which was lower than the values determined by other authors, the kinetic parameters are close to those found in the literature for glucose-based substrate obtained for the mesophilic range of temperature (Henze and Harremoës, 1983). However, factors other than the reactor configuration in different experiments (e.g. substrate composition) may have important influences on the kinetic parameters; therefore the comparison based on the reactor configuration cannot be conclusive.

TABLE 4 Value of \bar{X}_V , X_e^* and θ_x Used for theDetermination of the Kinetic Parameters

Parameter	Phase					
	I	II	III	IV	V	VI
$\bar{X}_V \times 1000$ (mg.l ⁻¹)	28.90	36.00	38.25	39.40	40.70	43.90
X_e^* (mg.l ⁻¹)	137	176	214	414	555	1654
θ_x (d)	70	68	59	32	24	9

As presented before in this text, evidence of shifting in the anaerobic metabolism of the biomass due to the step-increase influent COD concentration was detected. In order to verify if this shift would be reflected in the overall kinetic parameters, representative data of Si and Se from each phase were used to compose two sub-sets of data. The first one includes data from phases I, II and III, and the second one data from phases IV, V and VI. The choice was made according to the results shown in the last column of Table 3. Table 5 shows the data used for the determination of q_{max} and K_S for each set, and the results obtained by linear regression of the kinetic equations.

TABLE 5 Values of Si, Se, X_V , q_{max} , and K_S for Different Range of Influent COD Concentrations

Set of Data	Si (mg.l ⁻¹)	Se (mg.l ⁻¹)	$\bar{X}_V \times 1000$ (mg.l ⁻¹)	
1	1643	29	29,25	$q_{max1} = 0,40 \text{ d}^{-1}$ $K_{S1} = 36 \text{ mg.l}^{-1}$
	1650	32	28,60	
	3200	108	36,25	
	3000	72	35,75	
	4200	94	39,00	
	3700	40	37,50	
2	5740	568	39,00	$q_{max2} = 0,52 \text{ d}^{-1}$ $K_{S2} = 64 \text{ mg.l}^{-1}$
	5280	220	39,75	
	5860	214	39,75	
	8090	612	41,65	
	8580	1120	46,25	
	8360	2048	41,25	
12150	2560	44,15		

The results indicate that q_{max} and K_S were affected by the step-increase of the influent COD concentrations. For the lower range of Si, q_{max1} was $0,40 \text{ d}^{-1}$, 25% lower than the overall q_{max} previously determined, while q_{max2} resulted similar to q_{max} for the upper range of Si. K_{S1} and K_{S2} were respectively 36 mg.l^{-1} and 64 mg.l^{-1} , while the overall K_S was 82 mg.l^{-1} .

It can be concluded that operating at the upper range of Si had a strong effect on the value of q_{max} , as could have been expected. However, the same situation did not influence K_S in the same proportion.

Assuming that K_S can be used to compare the affinity of the biomass for the substrate, the results seem to confirm the hypothesis made on the effect of changing the biomass composition along the experiment, since K_{S2} was lower than K_S .

All the kinetic parameters were determined assuming a completely mixed flow pattern in

the reaction zone. However, the results of COD and VSS from samples taken along the reactor height (Fig. 2), and visual observations of the reactor behaviour recommend further studies for the improvement of this assumption. On-going experiments on toxicity response of UASB reactors will give better information on the rate of substrate

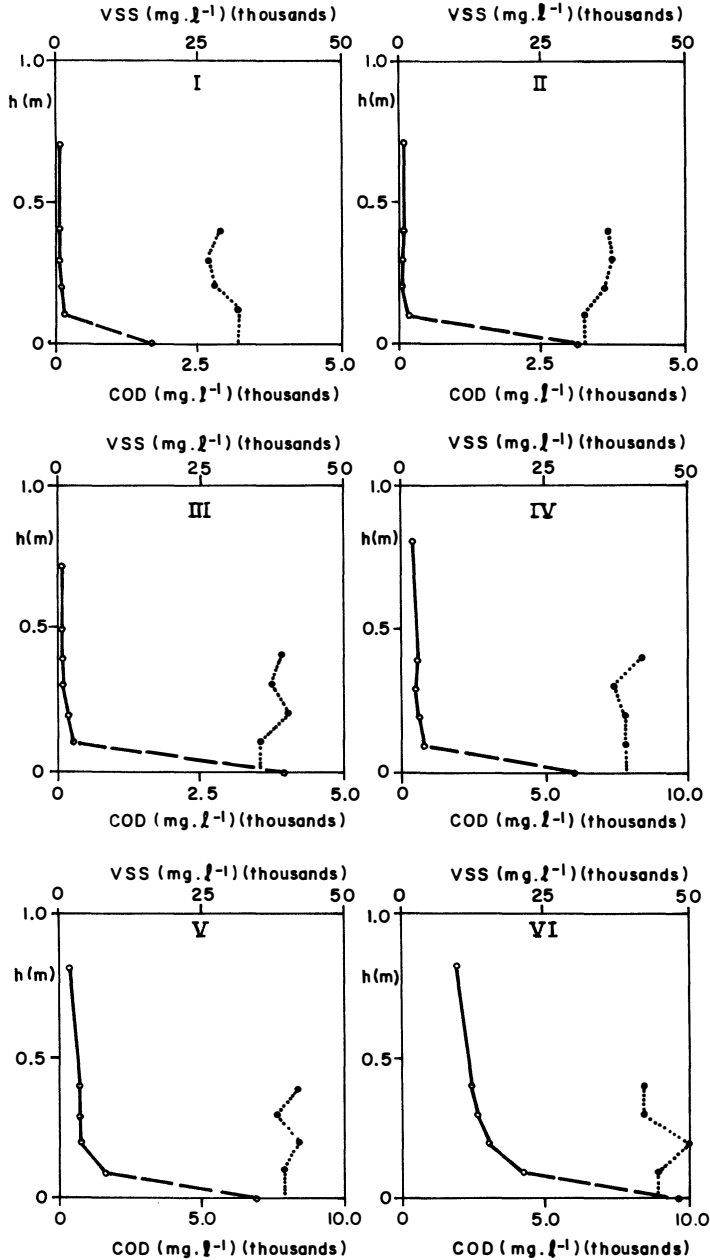


Fig. 2. Average values of COD (o) and VSS (●) of each phase along the reactor height. COD dashed line speculates on zone of sharp transition.

utilization by the biomass along the reactor height, possibly allowing the improvement of the knowledge on the kinetic parameters for up-flow reactors.

CONCLUSIONS

1. For average values of the initial COD concentrations ranging from 1780 to 9700 mg.l⁻¹, corresponding to volumetric loading rates (B_V) of 2.7 to 14.8 kg COD.m⁻³.d⁻¹, COD removal efficiencies varying from 98% to 80% were achieved.
2. The reactor could assimilate the shock loads due to the step-increase of influent COD concentration beyond the transient periods following changes in the operation.
3. A gradual deterioration of the overall performance of the reactor with the step-increase of the influent COD concentration was observed. Changes in the monitored parameters indicated that increasing fractions of the removed COD were used for non-methanogenic biomass production along the experiment.
4. Considering the reaction zone as being a completely mixed reactor, the following kinetic parameters were determined: $Y = 0.23$; $b = 0.04 \text{ d}^{-1}$; $\mu_{\max} = 0.12 \text{ d}^{-1}$; $K_S = 82 \text{ mg.l}^{-1}$, $q_{\max} = 0.53 \text{ d}^{-1}$.
5. Different results of q_{\max} and K_S obtained from the lower and the upper range of influent COD concentration indicated that the kinetic parameters were affected by the step-increase of the influent COD concentrations.

REFERENCES

- Bolle, W.L., Van Breugel, J., Van Eybergen, G.C., Kossen, N.W.F., Van Gils, W. (1986a). An integral dynamic model for UASB reactor. *Biotech. and Bioeng.*, 21 (11), 1615-1620.
- Bolle, W.L., Van Breugel, J., Van Eybergen, G.C., Kossen, N.W.F., Zoetemeyer, R.S. (1986b). Modelling the liquid-flow anaerobic sludge blanket reactors. *Biotech. and Bioeng.*, 21 (11), 1621-1636.
- DiLallo, R. and Albertson, O.E. (1961). Volatile acids by direct titration. *J. Wat. Pollut. Control Fed.*, 33, 356-365.
- Foresti, E. (1990). Anaerobic treatment of cannery industry wastewaters. Paper presented at the 45th Purdue Industrial Waste Conference Purdue University, Lafayette, Indiana.
- Heertjes, P.M. and Van Der Meer, R.R. (1978). Dynamics of liquid flow in an up-flow reactor used for anaerobic treatment of wastewater. *Biotech. and Bioeng.*, 20, 1577-1594.
- Heertjes, P.M. and Kuijvenhoven, L.J. (1982). Fluid flow patterns in anaerobic reactors for anaerobic treatment of beet sugar factory wastewater. *Biotech. and Bioeng.*, 24, 443-459.
- Henze, M. and Harremoës, P. (1983). Anaerobic treatment of wastewater in fixed film reactors - A literature review. *Wat. Sci. Tech.*, 15 (8/9), 1-101.
- Standard Methods for the Examination of Water and Wastewater (1985). American Public Health Association, New York, N.Y.
- Young, J.C. and Yang, B.S. (1988). Design considerations for full-scale anaerobic filters. University of Arkansas, Fayetteville, Arkansas, USA.