

MATHEMATICAL MODELING OF THE ANAEROBIC FILTER PROCESS

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ABSTRACT

A dilute synthetic waste water was anaerobically treated in a filter. A mathematical model of the anaerobic filter process was also developed and analyzed. Analysis showed that mathematical models are an efficient tool for system understanding and design.

KEYWORDS

Mathematical model; deamination; volatile acids; degradation; biological solids; anaerobic filter; biogas; methane; anaerobic treatment.

INTRODUCTION

For more than ten years anaerobic filters have been used to treat dilute industrial waste waters in laboratory scale and up to full scale plants. The lower concentration limit of treatability was assumed to be 1000 mg COD/l, but recent studies showed that low strength waste waters with COD-concentrations down to 200 mg COD l⁻¹ could be successfully treated in anaerobic fixed film reactors (Jewell and co-workers, 1981; Switzenbaum & Jewell, 1980). Together with the other fixed film reactors as the anaerobic expanded bed and the fluidized bed, anaerobic filters thereby appear as the most suitable anaerobic reactors for treatment of dilute waste waters.

Anaerobic decomposition of organic material to methane is a stepwise process. Extracellular enzymes solubilize the insoluble organic material. The soluble organics are then converted by acid forming bacteria into short-chain fatty acids, often called volatile acids, as well as carbon dioxide, hydrogen and other products. Finally, the volatile acids are converted into methane and carbon dioxide by methane-forming bacteria. Of the volatile acids only formic and acetic acid can directly be converted to methane. Other volatile acids must first be fermented to acetic acid.

MODEL DEVELOPMENT

A model describing the anaerobic digestion in two steps, acid formation and methane formation was developed. Liquifaction of complex insoluble organic compounds was assumed not to be rate-limiting and is therefore neglected in this model. Soluble

organic material was assumed to be converted to volatile acids and subsequently to methane and carbon dioxide.

The biological solids are assumed to consist of three fractions: acid formers, methane formers and an inert, inactive part of the total biological solids. Biological solids are assumed to decay to complex soluble COD and soluble organic nitrogen.

Due to the microbial growth a number of chemical reactions occur such as production of alkalinity during organic nitrogen deamination and ionization of volatile acids and carbon dioxide. The anaerobic filter was modeled as an infinite series of completely mixed reactors containing biological solids, liquid and gas phase. Substances are continuously interchanged between the three phases. At every point in the reactor the biological phase was assumed to be at steady state, i.e. no accumulation of biological solids occurred. The non-steady state differential equations for liquid and gas phase are (symbols in the Appendix):

$$\text{Liquid phase: } \frac{\partial C_i(x,t)}{\partial t} = -u_1 \frac{\partial C_i(x,t)}{\partial x} + D_i \frac{\partial^2 C_i(x,t)}{\partial x^2} + R_i^l(x,t) \quad (1)$$

$$\text{Gas phase: } \frac{\partial p_i(x,t)}{\partial t} = -\frac{1}{A_g} \frac{\partial (p_i(x,t) Q_g(x,t))}{\partial x} + \frac{\bar{R}T}{M_i} \frac{A_1 \eta}{A_g} R_i^g(x,t) \quad (2)$$

Neglecting the dispersion and considering the steady-state case, the two equations become:

$$\text{Liquid phase: } \frac{dC_i(x)}{dx} = \frac{1}{u_1} R_i^l(x) \quad (3)$$

$$\text{Gas phase: } \frac{d(p_i(x) Q_g(x))}{dx} = \frac{\bar{R}T}{M_i} A_1 \eta R_i^g(x) \quad (4)$$

These two equations were used on 11 state variables, 9 related to the liquid phase and 2 to the gas phase. The used state variables were; soluble complex COD, volatile acids, soluble organic nitrogen, volatile suspended solids produced in the reactor (2 fractions), dissolved carbon dioxide, dissolved methane, ammonia nitrogen, bicarbonate alkalinity, carbon dioxide and methane in the gas phase (Table 2).

The model was analyzed by two types of reaction kinetics (Table 1). Firstly, Monod-kinetics with an inhibition modification suggested by Andrews & Graef (1971) was analyzed. Subsequently, a simplified kinetic model based on zero and first order kinetics was developed and analyzed. Both models were based on separate biosolid fractions, acid and methane formers.

According to Andrews & Graef (1971) the nonionized volatile acids were assumed to be the substrate for the methane-forming bacteria. The Monod growth equation also contains an inhibition function I_2 , and consequently the nonionized fraction of volatile acids is both a rate-limiting and inhibiting substrate.

When $\text{pH} > 6$ the fraction nonionized volatile acids is small, i.e. most of the volatile acid molecules are ionized, or $|S_2^-| \approx |S_2|$. Consequently, the nonionized fraction of volatile acids was calculated as $HS_2 = S_2 \frac{K_{Ac}}{[H^+] + K_{Ac}} = S_2 f_2$ where $[H^+]$ was calculated from the bicarbonate equilibrium system. S_2 was measured in mg acetic acid/l and an average K_{Ac} of 4.75 was used. The bicarbonate alkalinity C_{HCO_3} was calculated as

$$C_{\text{HCO}_3} = \text{Total alkalinity} - \text{volatile acids alkalinity} - \text{organic nitrogen alkalinity.}$$

According to McCarty (1974) volatile acids alkalinity at pH = 4 was set to 0.71 S₂. Organic nitrogen alkalinity = 0.6 S₃ was used. This value was based on titration curves for nutrient broth.

TABLE 1. Kinetics.

Reaction	Monod kinetics	Simplified kinetics
R _A , removal rate of S ₁	$\epsilon C_A \frac{Y_{MA}}{Y_A} \frac{S_1}{K_1 + S_1}$	$\epsilon C_A \frac{Y_{MA}}{Y_A}$
R _M , removal rate of S ₂	$\epsilon C_M \frac{Y_{MA}}{Y_M} \frac{1}{1 + \frac{K_2}{HS_2} + \frac{1}{I_2}}$	$\epsilon C_M \frac{Y_{MA}}{Y_M} \frac{HS_2}{K_2}$
R _N , removal rate of S ₃	$\epsilon C_A k_N \frac{S_3}{K_3 + S_3}$	$\epsilon C_A k_N$

TABLE 2. Kinetic Terms in Equations 3 and 4.

Species	Designation	Bacterial growth and organic nitrogen hydrolysis	Bacterial decay	Gas-liquid transfer
<u>Liquid phase R_i^l</u>				
1 Soluble complex COD	S ₁	-R _A	+ u ₁ (b _A C _A + b _M C _M)	
2 Total volatile acids	S ₂	-R _M + u ₂ (1-u ₁ Y _A)R _A		
3 Soluble organic nitrogen	S ₃	-R _N	+ u ₃ (b _A C _A + b _M C _M)	
4 Acid formers	C _{S_A}	Y _A R _A	- b _A C _A	
5 Methane formers	C _{S_M}	Y _M R _M	- b _M C _M	
6 Total dissolved carbon dioxide	T _{CO2}	Y _{CO2} R _M		K _L ^a (H _{CO2} ^p CO ₂ /0.71 - T _{CO2})
7 Dissolved methane	T _{CH4}	Y _{CH4} R _M		K _L ^a (H _{CH4} ^p CH ₄ - T _{CH4})
8 Ammonia nitrogen	C _{NH3}	R _N - u ₃ (Y _A R _A + Y _M R _M)		
9 Bicarbonate alkalinity	C _{HCO3}	- 0.8333 R ₂ ^l + u ₄ R ₈ ^l		
<u>Gas phase R_i^g</u>				
10 Carbon dioxide	N _{CO2}			K _L ^a (T _{CO2} - H _{CO2} ^p CO ₂ /0.71)
11 Methane	N _{CH4}			K _L ^a (T _{CH4} - H _{CH4} ^p CH ₄)

LABORATORY STUDIES

The primary purpose of the laboratory studies was to find out whether anaerobic filters could be used to treat municipal sewage, i.e. waste waters with less than 400 mg COD l⁻¹. The second purpose was to analyze the kinetics of the anaerobic filter degradation process.

A 1.85 m high acrylic column with 0.111 m inner diameter was filled with a plastic material described by Frostell (1981) (polyurethane; density 40 kg m⁻³ with open pores; 2.5 mm/pore; porosity 0.95). The resulting void volume of the column was 17.0 l.

The column was fed with a synthetic waste water consisting of a ground dog food ("Doggy") mixed with appropriate amounts of tap water to obtain the desired concentration. No extra alkalinity was added.

During a period of 132 days the filter was fed with the described substrate at varying organic and hydraulic loads. The influent concentration was varied between 150 and 600 mg total COD l⁻¹ and the temperature between 20 and 35°C.

After that first experimental period the feeding was stopped and the reactor stood still for 96 days until it once again was started at an organic load of 1.0 kg COD m⁻³ d⁻¹ and an influent concentration of 300 mg total COD l⁻¹. After a period of 2 weeks the dog food substrate was changed to another synthetic waste water (4.0 g soluble starch, 4.96 g Nutrient Broth, No. 2, 0.1134 g K₂HPO₄ in 1 l deionized tap water) which was mixed with tap water to obtain the desired concentration. In contrast to the dog food substrate this water was almost free from suspended material, and consequently well suited for testing the mathematical models.

MODEL ANALYSIS

The model was analyzed on data from Young & McCarty's (1969) protein-carbohydrate run at an organic load of 212 lb ft⁻³ d⁻¹ (3.4 kg COD m⁻³ d⁻¹). Many coefficients and parameter values had to be estimated from the literature, laboratory studies or from stoichiometric relations. The values for cell yield coefficients Y_A and Y_M and for decay coefficients b_A and b_M were calculated from Young & McCarty's data as 0.11 and 0.015 and 0.0017 and 0.00083 h⁻¹ respectively.

The stoichiometric coefficients u₁, u₂ and u₃ were calculated as 1.42, 0.937 and 0.124 respectively, using the experimentally determined stoichiometric formula C₅H₇O₂N for biosolids (McCarty, 1974).

A K_{1a} value of 5.0 h⁻¹ was used to obtain near equilibrium conditions. Values for Henry's constant and pK values were taken from Chemical Engineer's Handbook (1969) and Handbook of Chemistry and Physics (1969) respectively. Due to the great variation of values for maximum growth rates μ_{MA} and μ_{MM} the values used were obtained from data fit. Values for Y_{CO2}, Y_{CH4}, K₁, K₂, l₂, K₃ and u₄ were also chosen to obtain data fit.

To calculate the biosolid fractions the total biosolid distribution measured by Young & McCarty (1969) was multiplied by the calculated fractional biomasses using Young & McCarty's removal data.

The model was analyzed on Young & McCarty's data. As shown in Fig. 1 a reasonable data fit was obtained with the Monod-model for both soluble complex COD and organic nitrogen. For the volatile acids the fit was poorer but due to the relative complexity of the model and the difficulty in measuring the biosolid fractions it was considered good enough and no further development was considered necessary. As illustrated in Fig. 1 adequate data fit could be obtained with over an order of magnitude change in

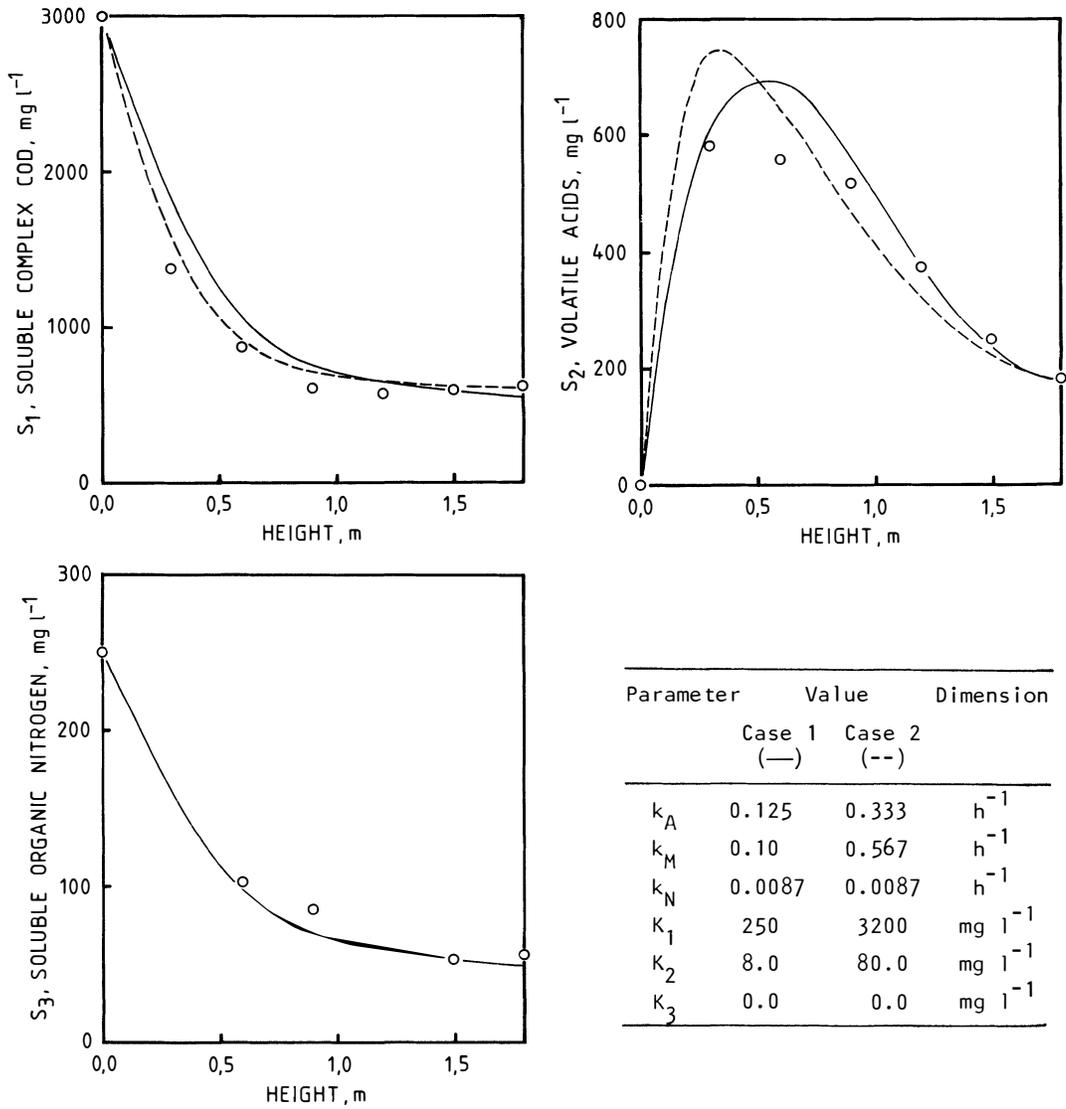


Fig. 1. Monod-model - Young & McCarty's data.

both the half velocity coefficients K_1 and K_2 . These variations were related to changes in the unit substrate removal rates k_A and k_M by more than 200 %.

After this run the same data and the same biosolid fractions were used to analyze a simplified model based on first and zero order kinetics. From the previous run, zero order kinetics for both soluble complex COD and soluble organic nitrogen, and first order kinetics for volatile acids were assumed to best describe the total decomposition. In this run a reasonable fit for both soluble complex COD and soluble organic nitrogen was obtained too (Fig. 2). For the volatile acids the fit was just as good as in the Monod-run.

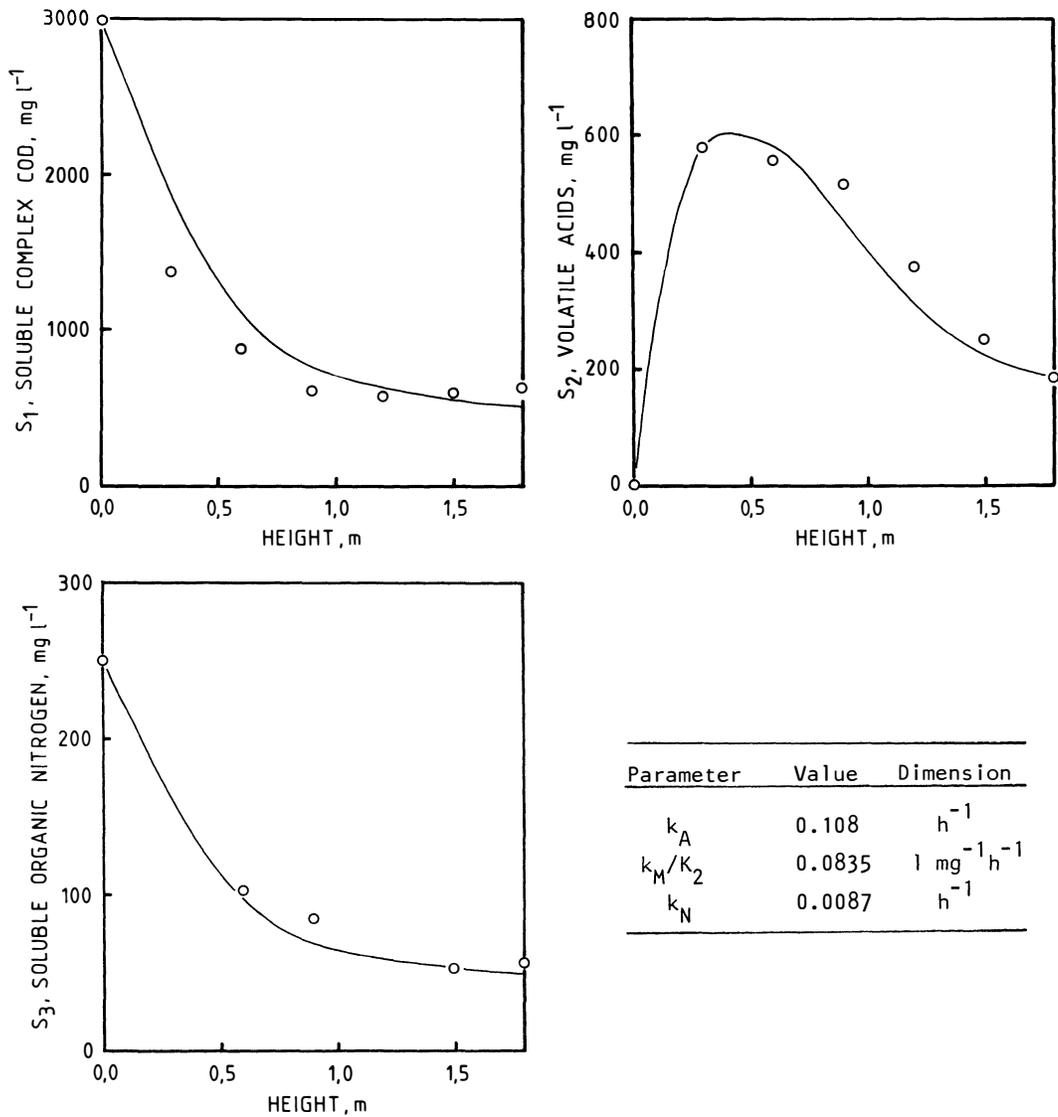
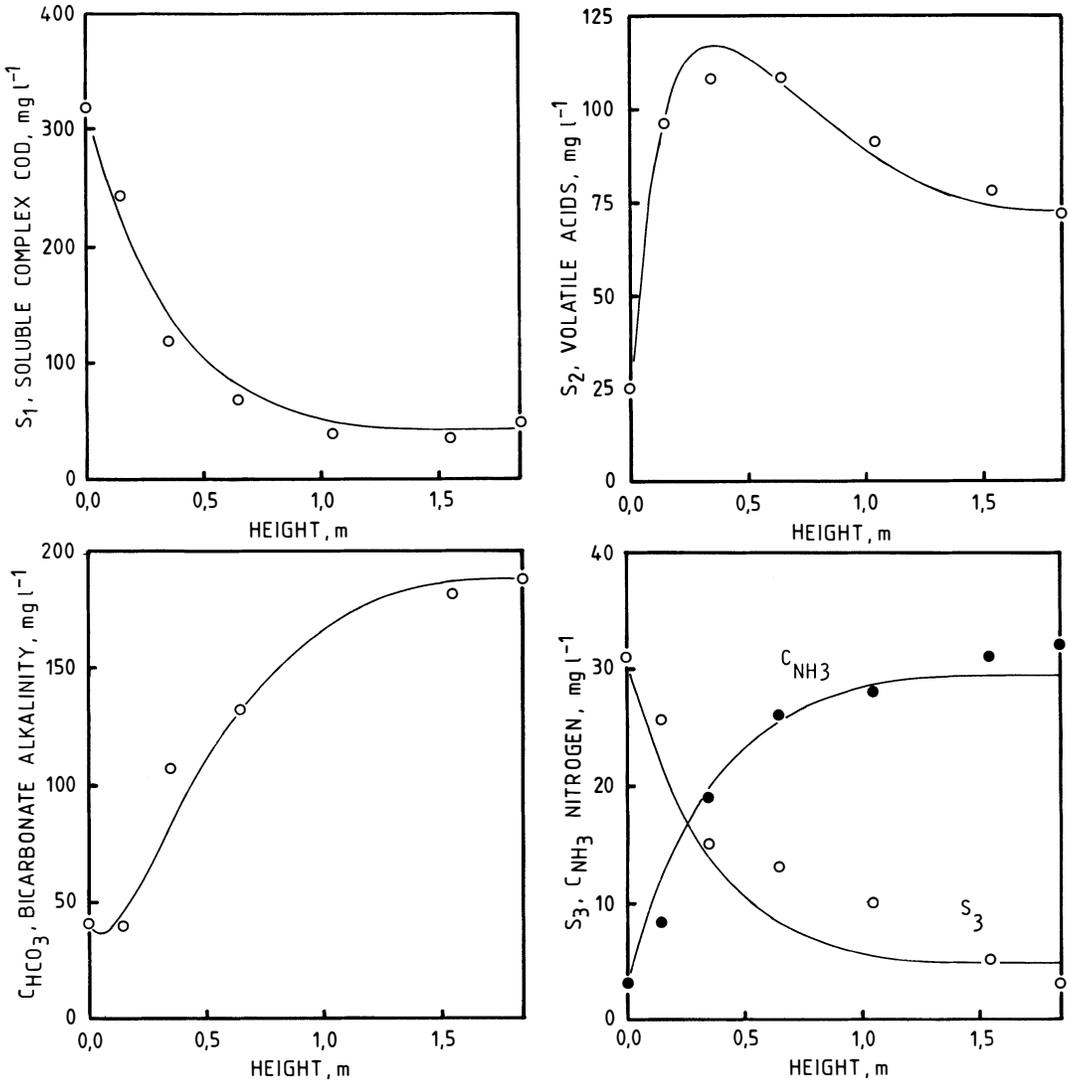


Fig. 2. Simplified model - Young & McCarty's data.

To obtain adequate gas data fit in the above mentioned runs, values for Y_{CO_2} and Y_{CH_4} of 0.45 and 0.23 were required when a u_3 value of 4.0 was used. Mueller & Mancini (1977) obtained Y_{CO_2} and Y_{CH_4} values of about 1.0 and 0.25 respectively, i.e. for Y_{CO_2} values twice as high as those obtained in this study. The substrate used by Young & McCarty has a TOC/COD ratio of about 0.34. Using $Y_A = 0.12$ and $Y_M = 0.015$ the formula $0.194 Y_{CO_2} + 0.75 Y_{CH_4} = 0.295$ can be calculated. This formula indicates that Mueller & Mancini's yield coefficients are about 25 % higher than those theoretically expected and that the coefficients calculated in this study are about 15 % lower than expected. The discrepancy might depend on the use of different values for Henry's constants, which in this study were expressed as functions of the temperature. Further investigation is necessary in this area.



Parameter	Value	Dimension
k_A	0.0365	h^{-1}
k_M/K_2	0.0070	$l\ mg^{-1}\ h^{-1}$
k_N	0.00343	h^{-1}

	Meas. Calc.	
Gas flow $l\ d^{-1}$	3.6	3.74
CH ₄ %	75	75.2
CO ₂ %	5	5.0
CH ₄ -flow $l\ d^{-1}$	2.74	2.81
Y_{CO_2}		0.45
Y_{CH_4}		0.20

Fig. 3. Simplified model - The experimental data obtained in this study.

The simplified model was then used on data from the present laboratory study. As illustrated in Fig. 3, a reasonable fit was obtained for all parameters measured; COD, volatile acids, bicarbonate alkalinity, organic and ammonia nitrogen and pH. The biosolid fractions used were based on measurements of volatile suspended solids at different levels in the anaerobic filter and calculated in the same way as in the Young & McCarty test.

To obtain adequate gas data and bicarbonate alkalinity data fit, values for Y_{CO_2} , Y_{CH_4} and u_3 of 0.45, 0.20 and 7.1 respectively were used.

As seen from Fig. 4 relatively high concentrations of biomass were found in the filter. These high concentrations, about 10 to 60 % of those found by Young & McCarty, would indicate high removal rates. However, as shown by Fig. 3, the maximum unit substrate removal rates k_A and k_N , and the first order coefficient k_M/K_2 are only 8 to 39 % of those obtained in the Young & McCarty test. This is probably an effect of the lower substrate concentrations, which probably results in higher cell yield coefficients. The high biomass concentrations and the low unit removal rates give moderate substrate removal rates. An interesting problem is to find out what would happen with the biomasses and the unit removal rates if the substrate concentrations were lowered further.

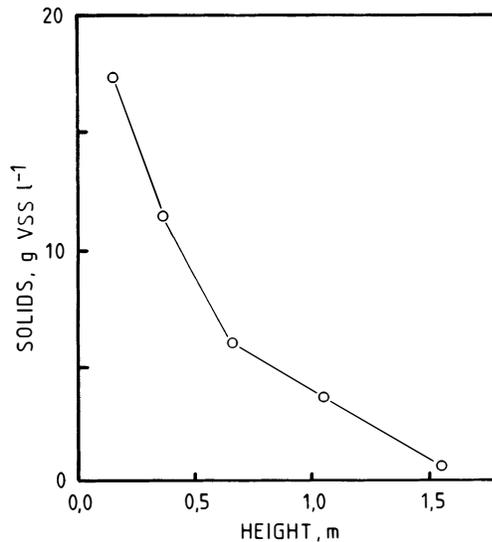


Fig.4. Solids distribution in the anaerobic filter.

DISCUSSION

A relatively complex mathematical model describing the anaerobic degradation of organic carbon and nitrogen in anaerobic filters, as a two-step process adequately simulates steady state data. The model is based on Monod-kinetics incorporating a pH-inhibition function but neglecting solids transport and biofilm diffusion.

The model adequately describes the chemical interactions occurring in the filter among nitrogen, volatile acids, carbon dioxide, alkalinity and pH and is very useful for system understanding.

A simplified model based on first and zero order kinetics and separate biosolid fractions also adequately simulates steady-state data. This model may be further simplified and is more readily usable for dynamic system analysis, optimization and design. Development work with the model continues.

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APPENDIX - NOMENCLATURE

State Variables and Biological Solids

S_1	Soluble complex COD	mg O_2 l^{-1}
S_2	Total volatile acids	mg acetic acid l^{-1}
HS_2	Nonionized volatile acids = $f_2 S_2$	mg acetic acid l^{-1}
S_3	Soluble organic nitrogen	mg N l^{-1}
T_{CO_2}	Total dissolved carbon dioxide	mg H_2CO_3 l^{-1}
T_{CH_4}	Dissolved methane	mg CH_4 l^{-1}
C_{NH_3}	Ammonia nitrogen	mg N l^{-1}
C_{HCO_3}	Bicarbonate alkalinity	mg $CaCO_3$ l^{-1}
N_{CO_2}	Carbon dioxide flow in gas phase = $P_{CO_2} Q_g$	Pa m^3 h^{-1}
N_{CH_4}	Methane flow in gas phase = $P_{CH_4} Q_g$	Pa m^3 h^{-1}

CS	Volatile suspended solids produced in the filter	mg VSS l ⁻¹
C	Initial volatile solids concentration	mg VSS l ⁻¹
A	Acid formers, total concentration	
M	Methane formers, total concentration	

Growth and Cell Yield Coefficients

μ_M	Maximum unit growth rate	h ⁻¹
Y	Cell yield coefficient	mg VSS produced/mg
b	Cell unit decay rate	h ⁻¹
k	Maximum unit substrate removal rate = μ_M/Y	h ⁻¹
A	Acid formers	
M	Methane formers	
N	Organic nitrogen	
K	Half velocity coefficient	mg l ⁻¹
I	Inhibition coefficient	mg l ⁻¹
1	Soluble complex COD	
2	Nonionized volatile acids	
3	Soluble organic nitrogen	
ϵ	Active part of total biological solids (VSS)	
R ^l	Kinetic term, liquid phase	mg h ⁻¹
R ^g	Kinetic term, gas phase	mg h ⁻¹

Stoichiometric Coefficients

u	Produced substrate per other substrate used	mg mg ⁻¹
1	S_1/C COD content of VSS = 1.42 for $C_5H_7O_2N$	
2	$S_2/S_1 = 0.937 (1 - u_1 Y_A)$	
3	S_3/C Organic nitrogen content of VSS = 0.124 for $C_5H_7O_2N$	
4	$-C_{HCO_3}/C_{NH_3} = 3.57$ if S_3 has no net charge	
Y_{CO_2}	$T_{CO_2}/S_2 = 3.88 Y_{CH_4}$ if equal moles produced from S_2 degradation	
Y_{CH_4}	$T_{CH_4}/S_2 = 0.267 (1 - 0.937 u_1 Y_M)$ from COD balance	

Chemistry, Gas and Liquid

pK_{Ac}	pK value for volatile acids equilibrium system
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H	Henry's constant	$\text{mg l}^{-1} \text{ Pa}^{-1}$
p	Partial pressure	Pa
C02	Carbon dioxide	
CH4	Methane	
M	Molecular weight	g mole^{-1}
$K_L a$	Liquid-gas transfer coefficient assumed = 5 to obtain near equilibrium conditions	h^{-1}
D_i	Dispersion coefficient for component i	$\text{m}^2 \text{ s}^{-1}$
\bar{R}	Gas constant = 8.13	$\text{m}^3 \text{ Pa mole}^{-1} \text{ K}^{-1}$
A_g	Cross section area for the gas phase in the filter	m^2
A_f	Cross section area of the filter	m^2
Q_g	Gas flow in the filter	$\text{m}^3 \text{ h}^{-1}$
u_l	Liquid velocity in the filter	m h^{-1}
η	The porosity of the carrier material	
x	Height coordinate in the filter	m
t	Time	h