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MODELLING OF COMPETITION BETWEEN SULPHATE REDUCTION AND METHANE PRODUCTION IN CONTINUOUS BIOREACTOR

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Abstract. The aim of the present paper was to develop a mathematical model of interaction between acetogenesis, sulphidogenesis and methanogenesis in anaerobic continuous reactor using chosen data from the literature. Kinetic equations and data published in the literature have been critically evaluated by introduction into the simulation program AQUASIM. The Michaelis – Menten equation was used for the preliminary calculations. Computer simulations by AQUASIM program were accomplished to illustrate the influence of hydraulic retention time, COD/SO_4 ratio, initial proportions of acetogenic bacteria, sulphate reducing and methane producing bacteria in seed sludge on the bacterial competition. The results obtained after simulation have been compared and the most appropriate of them have been chosen on the basis of the process selectivity to sulphide production. The main parameters affected sulphate-loading rates were found to be feeding flow rate, mole COD/SO_4 ratio in the feed as well as hydraulic retention time in the reactor. It has been shown that the AQUASIM program is useful for simulation of bacterial sulphate reduction of industrially polluted water.

Keywords: anaerobic continuous stirred tank reactor, AQUASIM program, mathematical modelling, methanogenesis, sulphate reduction.

AIMS AND BACKGROUND

Many industrial wastewaters contain sulphate at varying concentrations: the pulp and paper industry, the food processing industry, e.g., molasses-based fermentation, distillery wastes from wine industry, citric and tartaric acid production, edible oil refining, in seafood processing as well as the tanning industry, fixing of photographs, and trinitrotoluene manufacturing. Sulphates are used as raw materials in the manufacture of linear alkylbenzene sulphonate surfactants. Burning of fossil fuel releases SO_2 and SO_3 into atmosphere, where sulphur oxides can be converted into sulphate producing acid rain. The mining industry is responsible for the release of sulphate from spent mine tailings as acid mine drainage (Table 1)[1,2].

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Table 1. Biotechnological applications using SRB (after Hulshoff Pol[2])

Application	Reference
Biological sulphate removal	
Industrial wastewaters $[SO_4]$=2.9 – 50 g/l	Särner, 1990[3]; Colleran et al., 1995[4]
Acid mine drainage $[SO_4]$=1.5 – 7.2 g/l	Maree et al., 1991[5]
Spent sulphuric acid $[SO_4]$=5.0 – 46 g/l	Stucki et al., 1993[6]
Scrubbing waters SO_2-rich gasses $[SO_3]$ >2.0 g/l	Kaufman et al., 1996[7]
Heavy metal removal	
Extensive treatment (wetlands)	Hao et al., 1996[8]
High rate reactors	Tichy et al., 1998[9]
Process water	
Acid mine drainage $[SO_4]$=3.0– 30 g/l	
Ground water	
Microaerobic treatment	
Treatment domestic sewage $[SO_4]$=0.02– 0.5 g/l	Takahashi and Kyosai, 1991[10]
Reduction waste sludge production	Lens et al., 1995[11]

While sulphate itself is chemically inert, nonvolatile and relatively nontoxic, large inputs of sulphate can significantly alter the balance of the natural sulphur cycle. Upon release of sulphate-rich wasterwater into anaerobic environments, bacterial sulphate reduction converts sulphate into H_2S, which is toxic to living organisms and which causes corrosion problems to metal equipment.

The anaerobic degradation of complex, particulate organic materials occurs as a multistep process of reactions. Sub-processes involved in the degradation of organic matter in methanogenic and sulphate-reducing bioreactors consist of fermentative, acetogenic, methanogenic and sulphate-reducing reactions. An important component of the process is interspecies hydrogen transfer. In this syntrophy, several anaerobic microorganisms can share the energy available in the bioconversion of organic compound such as ethanol to acetic acid, methane and carbon dioxide.

The possibility of controlling the interaction between bacteria in anaerobic reactors is important for practical application of anaerobic treatment processes. Knowledge of the factors determining the outcome of the competition between sulphate reducing bacteria (SRB) and syntrophic and methanogenic (MPB) anaerobes at the intermediate (between 1 and 10) COD/ SO_4 ratios is limited and requires investigation if anaerobic treatment of these wastewaters is to be optimized[12]. So far, adequate practical methods to steer the competition between acetogenic SRB and acetogenic MPB are not available[1].

The mathematical modelling of anaerobic digestion of industrially polluted water includes dynamics of biological, chemical and physical subsystems with variety of interactions between them. Due to the complexity of the biological process it is difficult to develop a mathematical model reflecting the biological reality. Only few dynamic models of sulphate fed anaerobic reactors have been elaborated recently[13,14]. Multiple substrate competition between sulphidogenesis and methanogenesis received a substantial attention in the model of sulphate fed ideally mixed anaerobic reactor developed by Kalyuznyi and Fedorovich[15].

The aim of the present paper was to develop a mathematical model of interaction between acetogenesis, sulphidogenesis and methanogenesis in anaerobic reactor, calibrated with data from the literature. Computer simulations by AQUASIM program were accomplished to illustrate the influence of hydraulic retention time, COD/SO_4 ratio, initial proportions of acetogenic bacteria, sulphate reducing and methane producing bacteria in seed sludge on the bacterial competition.

Initially AQUASIM program was formulated for the simulation of aquatic systems and activated sludge models[16,17]. Later, it was used for the simulation of kinetic-based model for mixed weak acid/base systems[18]. The present paper shows application of the above program to anaerobic continuous stirred tank reactor (CSTR) fed with sulphate.

EXPERIMENTAL

In the preliminary work presented, ethanol was used as the organic electron donor. The use of relatively pure, fully degradable bulk chemicals as possible electron donors offers a number of substantial advantage[19]. Ethanol is cheaper for small scale applications (i.e., less than 5-10 kmol sulphate/h) and represents a substrate that supports growth of acetogenic bacteria. Ethanol rapidly oxidizes to acetate. Acetate is used as carbon source or is oxidized further to carbon dioxide. SRB and MPB compete for use of acetate and hydrogen as substrate.

The reactor was assumed to behave like an ideal continuous stirred tank reactor. In the case, when the system should treat an acid wastewater with pH-values down to 2.0 with sulphate content, a well mixed reactor liquid is necessary to prevent sulphite inhibition. SRB generally do not grow below pH 6.0 and therefore low pH in the reactor should be prevented.

The anaerobic reduction of sulphate was assumed to involve the following reactions:

Syntropic acetogenesis:	$C_2H_5OH + H_2O \rightarrow CH_3COOH + 2H_2$
Methanogenesis:	$CH_3COOH + H_2O \rightarrow CH_4 + H_2CO_3$
	$4H_2 + H_2CO_3 \rightarrow CH_4 + 3H_2O$
Sulphidogenesis:	$CH_3COOH + SO_4^{2-} + H^+ \rightarrow 2H_2CO_3 + HS^-$
	$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$

The rate equations for acetogenesis, methanogenesis and sulphidogenesis were assumed to be of the Michaelis – Menten form for the specific substrate utilization rate.

$$q = -\frac{r_s}{C_x} = \frac{q_{max}}{1+\frac{K_S}{C_S}}$$

The overall process kinetics can be determined by incorporating the rate of every step into the dynamic model. Experimental calibration of the model was performed, incorporating the set of kinetic data from (Ref. 15) into the Michaelis – Menten equations. AQUASIM was used to simultaneously integrate the system obtained.

In the initial investigation inhibition effects have been neglected. CH_3COOH and H_2CO_3 dissociation has been neglected as well as solubility of gases formed (CH_4 and H_2S).

RESULTS AND DISCUSSION

Simulations of bacterial sulphate reduction were carried out by AQUASIM program, evaluating different sets of kinetic parameters as well as varying mole ratios of COD/SO_4 (0.67, 1, 1.5 and 2)[20]. An anaerobic continuous stirred tank reactor with a volume of 10 l was used in order to reduce the concentration of sulphate ions presented in industrial wastewater. Preliminary simulations were accomplished using the kinetic data from Table 2 at the following initial conditions: mole ratio COD/SO_4=2, sulphate concentration C_{SO_4}=5.0 g/l, C_{ETOH}=4.80 g/l; concentrations of the bacteria in the mixed culture were $C_{XAc} = C_{XaSRB} = C_{XaMPB} = C_{XhMPB} = C_{XhSRB} = C_X$ = 1 g VSS/L, flow rate was 1 l/d. The results obtained are shown in the Figs 1 and 2. A variation of the concentrations of ethanol, sulphate, acetic acid, meth-

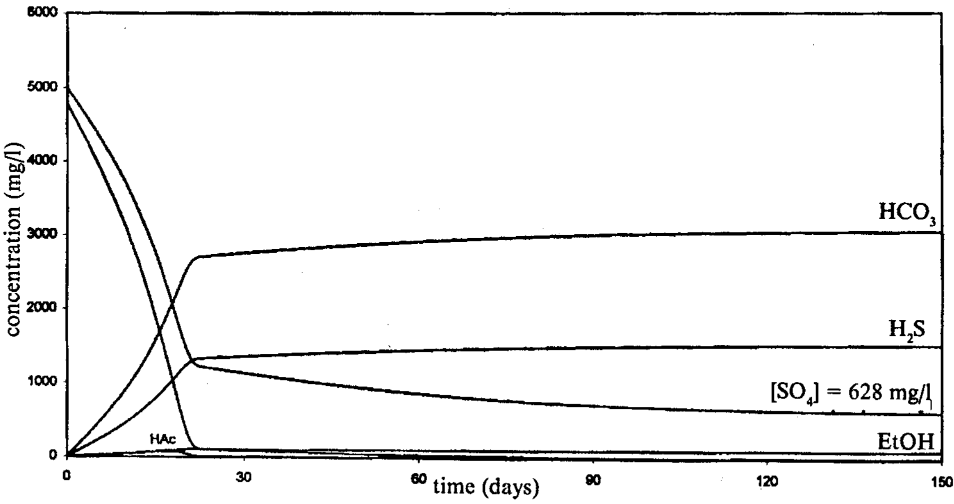

Fig.1. Variation of concentrations of chemicals (substrates) in time during simulation of CSTR with the initial data: COD/SO_4=2, F=1 l/d, $[SO_4]_0$= 5.0 g/l, $[EtOH]_0$= 4.79 g/l, Cx_0 = 24.6 g/l, V=10 l

ane, bicarbonate and H_2S versus time are shown in Fig.1. Dilution rate was 0.1 1/d and sulphate conversion was 87.8%. In this case, the lowest concentration of sulphate in effluent was 0.63 g/l. Bacterial concentrations versus time during the same experiment are shown in Fig. 2.The relative proportions of the acetogens, methanogens and sulphate reducers are also depicted. Acetotrophic SRB as well as hydrogenotrophic SRB are able to outcomplete MPB from the system described. Production of methane is not observed as hSRB outcompetes hMPB. The same was expected from the Gibbs free energy calculations.

Table 2. The set of kinetic data used for the preliminary simulation

Bacteria	K_s (g COD/l)	V_{max} (g COD/g VSS d)	Y (g VSS/g COD)	μ_{max} (1/d)	Reference
Acetogenic (XAc)	0.246	6.4	0.025	0.16	Gujer, Zehnder, 1983[21]
Acetotrophic MPB	0.409	4.70	0.051	0.024	Lawrence, Mc Carty, 1969[22]
Acetotrophic SRB	0.006	5.20	0.098	0.51	Middleton, Lawrence, 1977[23]
Hydrogenotrophic SRB	5.3×10^{-5}	12.5	0.053	1.37	Robinson, Tiedje, 1984[24]
Hydrogenotrophic MPB	1.1×10^{-4}	40	0.0125	1.20	Robinson, Tiedje, 1984[24]

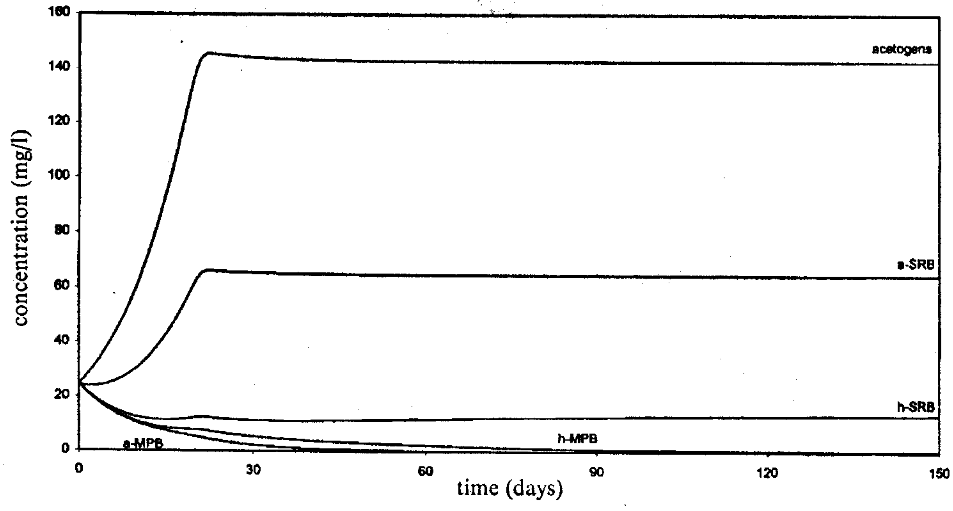

Fig.2. Variation of bacterial concentrations during the simulation of CSTR with the initial data: $COD/SO_4 = 2$, $F = 1$ l/d, $[SO_4]_0 = 5.0$ g/l, $[EtOH]_0 = 4.79$ g/l, $Cx_0 = 24.6$ g/l, $V = 10$ l

Influence of dilution rate on sulphate conversion at different COD/SO_4 was analyzed by the statistic methods. Maximum percentage of sulphate conversion was estimated at D average = 0.1 1/d. Also, statistic analysis of variation of sulphate loading rates versus mole COD/SO_4 feed ratios at different dilution rates (0.01, 0.05, 0.1 and 0.15 1/d) were accomplished. It showed that sulphate loading rates increase with increase of COD/SO_4 ratio as well as with higher dilution rates (0.15 1/d), when retention time was 10 days.

Comparison of the results from simulations with the different sets of kinetic data on the basis of selectivity of the process to sulphide production was demonstrated elsewhere[20]. It was proved that the set of kinetic data, shown in Table 2, is the most appropriate for the further calculations. Evaluating the results obtained as well as considering data from the literature, the following factors affecting the outcome of the competition between SRB and MPB in high-rate anaerobic reactors (shown in Table 3), have been recommended. Further work is been done on the incorporation of the above effects into model of the process.

Table 3. Factors affecting the outcome of the competition between SRB and MPB in high-rate anaerobic reactors (after Hulshoff Pol[2])

Factor	Reference
Kinetic considerations	
V_{max}/K_m; μ_{max}/K_s	Colleran et al., 1995[4]
Substrate thresholds	
Thermodynamics considerations	
$\Delta G°$ – minimum Gibbs free energy (kJ/mol)	Verstaete et al., 1996[25]
Inoculum composition	McCarty and Oleszkiewicz, 1993[26]
Type of the seed sludge	Harada et al., 1994[27]; Omil et al., 1998[28]
Bacterial composition	Isa et al., 1986[29]
Attachment properties of bacteria	Harada et al., 1994[27]; Omil et al., 1998[28]
Experimental run time	Omil et al., 1997[30]
Inoculation with new bacterial species	
Influent composition	
Type of COD	Polprasert and Haas, 1995[31]
Acetate concentration	Yoda et al., 1987[32]
Sulphate concentration	Overmeire et al., 1994[33]
Sulphide concentration	Omil et al., 1996[34]
COD/SO_4	Verstaete et al., 1996[25]
Differential sulphide toxicity	Kalyuznyi and Fedorovich, 1998[15]
Operational conditions	
pH	Visser et al., 1996[35]
Temperature	Visser et al., 1992[36]
Biomass retention time	

CONCLUSIONS

The successful application of the model is very much dependent on the right choice of kinetic coefficients. Kinetic data published in the literature were critically evaluated by a simulation program for the selectivity of the process to sulphide production. The Michaelis – Menten equation was chosen for the calculations. It has been shown that the AQUASIM program is useful for estimation of bacterial sulphate reduction in industrial wastewater. The simulation of an anaerobic continuous stirred tank bioreactor showed how concentrations of ethanol, sulphate and acetic acid varied at different COD/sulphate ratios and different dilution rates. The optimum flow rate estimated was about 1 l/d. The maximum conversion of sulphate obtained was about 90%, when a single CSTR with volume 10 l and initial sulphate concentration 5 g/l was simulated. The relative proportions of the acetogens, methanogens and sulphate reducers have been also depicted. Acetotrophic SRB as well as hydrogenotrophic SRB were able to outcompete MPB from the system described. The factors affecting modelling of the competition between SRB and MPB have been recommended.

APPENDIX

Glossary

aSRB — acetotrophic sulphate reducing bacteria
aMPB — acetotrophic methane producing bacteria
hSRB — hydrogenotrophic sulphate reducing bacteria
hMPB — hydrogenotrophic methane producing bacteria
COD — chemical oxygen demand
HRT — hydraulic retention time (d)
SLR — sulphate loading rate (g l^{-1}/d^{-1})
VSS — volatile suspended solids (biomass)

List of symbols

C_S — substrate concentration (g COD l^{-1} or mol l^{-1})
C_X — bacterial concentration (g VSS l^{-1} or mol l^{-1})
D — dilution rate (d^{-1})
F — flow rate (l d^{-1})
K_m - Michaelis-Menten constant (g COD l^{-1})
K_S —Monod half-saturation constant for organic substrates and hydrogen (g COD l^{-1})
Y — bacterial yield (g VSS g COD^{-1})
μ - specific growth rate (d^{-1})
r_S — substrate uptake rate (g COD(mol) l^{-1} d^{-1})
r_X - rate of biomass production (g VSS l^{-1} d^{-1})
q — specific substrate uptake rate (g COD(mol) l^{-1} d^{-1})
$q_{max} = V_{max}$ — maxium specific substrate uptake rate (g COD(mol) l^{-1} d^{-1})
V — volume of reactor (l)
τ - hydraulic retention time in the reactor (d)

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