

BIOLOGICAL SULFATE REDUCTION OF REVERSE OSMOSIS BRINE
CONCENTRATE: PROCESS MODELING AND DESIGN

by

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DEDICATION

To my parents...

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ABBREVIATIONS

a	mass transfer area to bed volume ratio, (L^2/L^3)
A	cross section area of bed, (L^2)
A_{tp}	total surface area of the adsorbent particle, (L^2)
C_o	influent concentration of substrate in chemostat, (M/L^3)
C_o	initial substrate concentration, (M/L^3)
C	concentration of substrate in chemostat, (M/L^3)
C	bulk substrate concentration at any time, (M/L^3)
C_b	biofilm substrate concentration, (M/L^3)
$C_{b,avg}$	average biofilm substrate concentration, (M/L^3)
$C_{b,max}$	maximum biofilm substrate concentration, (M/L^3)
C_{bl}	substrate concentration at bulk liquid-biofilm interface, (M/L^3)
C_{bp}	substrate concentration at biofilm-adsorbent interface, (M/L^3)
C_e	effluent substrate concentration, (M/L^3)
D	dilution rate, ($1/T$)
Da_f	Damköhler number for film transfer, (dimensionless)
Da_{ov}	Damköhler number for overall transport, (dimensionless)
Da_s	Damköhler number for surface diffusivity, (dimensionless)
D_b	biofilm substrate diffusion coefficient, (L^2/T)
D_l	free liquid diffusivity of the substrate, (L^2/T)
D_z	axial (hydrodynamic) substrate dispersion coefficient, (L^2/T)
d_l	density of the fluid, (M/L^3)

d_p	carbon particle density, (M/L ³)
dC/dt	rate of change of substrate in chemostat reactor, (M/TL ³)
dX/dt	rate of change of biomass in chemostat reactor, (M/TL ³)
Ga	Galileo number for the adsorber bed, (dimensionless)
H	length of the FBBR column, (L)
k	rate constant in the CMBR, (M/TL ³)
k	maximum rate of substrate utilization per unit mass of microorganism, (M/MT), μ_m/Y
k_d	endogenous decay coefficient, (T ⁻¹)
k_{fc}	external mass transfer coefficient, (L/T)
K_s	half-velocity constant, (M/L ³)
M	concentration of biomass in chemostat, (M/L ³)
M_b	biomass density in the biofilm, (M/L ³)
M_l	concentration of biomass in the liquid bulk phase, (M/L ³)
M_{lo}	initial biomass concentration in the bulk liquid phase at time zero, (M/L ³)
M_o	concentration of biomass in influent, (M/L ³)
N	Freundlich intensity constant, (dimensionless)
N_p	number of adsorbent particles, (dimensionless)
Q	fluid flowrate, (L ³ /T)
Q_r	recycled fluid flowrate, (L ³ /T)
r_g'	net rate of biomass growth, (M/TL ³)
r_{su}	substrate utilization rate, (M/TL ³)

Re	Reynolds number for the adsorber column, (dimensionless)
Re_{mod}	modified Reynolds number for the adsorber column, (dimensionless)
R_p	GAC particle radius, (L)
Sh	Sherwood number for the adsorber, (dimensionless)
Sc	Schmidt number for the adsorber, (dimensionless)
t	time coordinate, (T)
t_{max}	time at which biofilm thickness is maximum, (T)
T_b	biofilm thickness at any time, (L)
T_{bo}	initial biofilm thickness, (L)
$T_{b,max}$	maximum biofilm thickness, (L)
v_s	superficial fluid velocity in the axial direction, (L/T)
v_z	interstitial fluid velocity in the axial direction, (L/T)
V	volume of chemostat, (L ³)
V_b	total bed volume, (L ³)
V_c	total dry volume of adsorbent (carbon), (L ³)
ΔV	volume of the bed expansion due to biological growth, (L ³)
W_b	mass of dry biomass obtained from the biofilm, (M)
W_{tp}	total dry weight of activated carbon, (M)
Y	yield coefficient, (M/M)
z	axial coordinate, (L)
z_b	radial coordinate in biofilm, (L)
ε	bed porosity, (dimensionless)

μ	fluid viscosity, (M/TL)
μ_m	maximum specific growth rate, (1/T)

ACRONYMS

BSR	Biological Sulfate Reduction
C/S	Carbon-to-Sulfur ratio
CMBR	Completely Mixed Batch Reactor
CSTR	Continuous Stirred Tank Reactor
DO	Dissolved Oxygen
EPA	Environmental Protection Agency
FBBR	Fluidized Bed Bioadsorber Reactor
GAC	Granular Activated Carbon
HRT	Hydraulic Retention Time
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
ORP	Oxidation-Reduction Potential
RO	Reverse Osmosis
SRB	Sulfate Reducing Bacteria
TDS	Total Dissolved Solids

ABSTRACT

The Colorado River is the most important source of water in southern California which typically contains high total dissolved solids (TDS) of more than 700 mg/L. The Metropolitan Water District of Southern California (MWDSC) identified reverse osmosis as the best available technology for desalination of the water for reducing the TDS level. One of the major problems associated with reverse osmosis process under a high-recovery of over 95%, is the precipitation of sparingly soluble inorganic salts present in the brine concentrate. These salts include barium sulfate, calcium sulfate, strontium sulfate, and calcium carbonate, and they have the potential to cause precipitation fouling of reverse osmosis membranes resulting in lowering of membrane permeate fluxes. Sulfate removal from the brine concentrate is the only solution to overcome the problem of membrane scaling. This research evaluated a biological process to recover reverse osmosis concentrate produced from desalting high-sulfate waters. The process employed biological sulfate reduction (BSR) using fluidized bed bioadsorber reactor (FBBR) and to concomitantly reduce the saturation levels of sparingly soluble salts. This research also focused on evaluating biological kinetics and pertinent operating variables in the BSR reactor and modeling of the process.

In the first phase of the study, a series of completely mixed batch reactor (CMBR) studies were conducted to determine the effect of various environmental parameters including pH, temperature, and carbon-to-sulfur (C/S) on the desulfurization process.

Subsequently, a series of chemostat experiments were carried out to determine the biokinetic parameters. These parameters further used as input for the mathematical model developed for the desulfurization process. Furthermore, fluidized bed bioadsorber reactor studies were conducted to evaluate the process performance as a function of several variables including the influent sulfate concentration, C/S ratio, and pH. The process performance was evaluated at different influent sulfate concentrations of 600, 700, 800, 900, 1000, and 1100 mg/L, different pHs of 6.5, 7.0, and 7.5, and different C/S ratios of 0.8, 1.0, and 1.2. Sulfate reduction and removal efficiencies as high as 86-91% were achieved at an influent sulfate concentration of 1100 mg/L. Later, the FBBR-sand process performance was investigated and compared with those using granular activated carbon (GAC). The general observation was that GAC performed significantly better than sand. Nonetheless, the superiority of GAC would even be more apparent, should the brine concentrate contain heavy metals and organic constituents that would potentially inhibit microbial activity.

The next phase of the research included the simulation of the chemostat process dynamics and performance of model sensitivity analyses to identify the various key parameters that have a significant influence on the system operation and subsequently on the FBBR process, and to evaluate the biokinetic parameters that would eventually be employed as input parameters in the FBBR model. The chemostat simulation studies demonstrated good agreement between the

experimental data and the chemostat model predictions. Sensitivity analyses of the chemostat model indicated that maximum specific growth rate, μ_m and half-velocity constant, K_s had the greatest influence on chemostat dynamics with reference to sulfate reduction and carbon source (ethanol) utilization.

The next phase involved the development of a mathematical model for predicting the FBBR process dynamics. Model calibration was based on biological and transport parameters determined from independent laboratory experiments and/or correlation techniques. The model was verified and validated for different process variables.

In the last phase of this study, process design and upscaling strategies were developed, and the significance of the relevant non-dimensional groups identified besides their relative contribution to the overall process dynamics. Model simulation studies were performed to predict the FBBR dynamics under different process and operating conditions, and to determine the sensitivity of process dynamics to various biokinetic parameters. Sensitivity analyses demonstrated that the maximum specific growth rate, μ_m and half-velocity constant, K_s had the most profound influence on the process dynamics with reference to sulfate reduction and ethanol utilization.

The results of this study demonstrated that the FBBR system represents a reliable, efficient, and cost effective technology for removing sulfate from the reverse osmosis brine concentrate. It was found that the FBBR system using GAC was

significantly more efficient than the FBBR-sand system. However, the latter process required lower hydraulic retention time, and therefore, entails smaller reactor and lower energy costs. The FBBR model successfully predicted the process dynamics with reference to sulfate removal and carbon source utilization. Furthermore, it was found useful in the performance prediction of laboratory-scale FBBR systems and provided the means for process upscaling using dimensional analysis and similitude. The results of biofiltration of hydrogen sulfide demonstrated that the anaerobic biofiltration would be a preferred treatment method for H_2S gas stream. Additionally, the anaerobic biofiltration of H_2S and its subsequent conversion to elemental sulfur is important from the economic perspective of sulfate recovery.

CHAPTER 1

INTRODUCTION

Colorado River Water (CRW) is the main source of water in California and Metropolitan Water District (MWD). The CRW typically contains total dissolved solids of over 700 mg/L. The MWD developed large-scale and cost-effective desalination technologies for the treatment of CRW and other water sources containing high levels of TDS. Reverse osmosis was chosen and proven to be reliable for large-scale applications. A major problem associated with large-scale reverse osmosis is the minimization and disposal of brine or concentrate from the process that is a concentrated mixture of inorganic salts and organic matter. A full-scale desalination plant would necessarily incorporate conventional pretreatment followed by split-flow treatment, wherein one third of the flow would be subjected to reverse osmosis.

There are no established regulations related to the handling of brine reject. Depending on the disposal alternatives selected, proper permits must be obtained from the appropriate regulatory agencies. For example, discharge of brine rejects to a receiving water body requires a National Pollutant Discharge Elimination System (NPDES) permit, which authorized under the Clean Water Act (CWA). The reverse osmosis brine reject which was studied in this research has high sulfate, chloride, total dissolved solid and heavy metals. Since the agency has great concern about the

disposal due to the characteristics of the brine reject, it was concluded that the brine should be treated before discharge.

During the large-scale operations of conventional treatment plants by the MWD at 320-750 million gallons per day (MGD), the resulting desalination plants would require operation at capacities greater than 150 MGD, with the objective of reducing the overall total dissolved solids (TDS) from 750 mg/L to 500 mg/L. Prior estimates showed that at least a typical 150 MGD desalination plant, at a low recovery of 85%, would generate 22 MGD of brine. The disposal of brine in inland facilities presents a major problem owing to the large volume generated, marine disposal not being considered as a viable option due to poor access to the ocean. High recoveries of over 95% in the reverse osmosis plants are therefore desirable for reducing the intensity of the brine disposal problem. Reduction in brine volumes using secondary brine-concentration processes would result in lower area requirements for drying beds in inland facilities that do not have access to the brine disposal line. A number of technologies were considered and reviewed with reference to concentrating the brine, including several thermal and non-thermal processes. Thermal processes involving phase change such as distillation processes and crystallizer processes employed by the paper-pulp and oil industry were considered very energy intensive.

Reverse osmosis appeared to be the most economically viable technology for this purpose. A major obstacle to operating reverse osmosis process under a high-

recovery scenario is the precipitation of sparingly soluble inorganic salts present in the brine such as barium sulfate, calcium sulfate, strontium sulfate, and calcium carbonate. Hence, removal of sulfate from the brine is required for reducing membrane fouling and maintaining high permeate fluxes during reverse osmosis. Biological sulfate reduction (BSR) appears to be a viable option that requires investigation. The proposed research was directed towards the application of the BSR process for lowering sulfate concentrations in the aqueous phase, and simultaneously removing other organic components associated with membrane fouling problems.

The present research evaluated a novel technology for recovering reverse osmosis brine. Recovering brine is a key to the viability of large-scale reverse osmosis plants treating surface water, or reverse osmosis plants operating at inland locations with restricted access to ocean discharge. A major obstacle to operation of reverse osmosis process at higher recoveries is the precipitation of sparingly soluble inorganic salts. In Colorado River water, a major water source for the southwestern United States, precipitation of carbonate and sulfate salts limits water recovery to 85 percent when using reverse osmosis. In the biological sulfate reduction process, the sulfate is biochemically reduced to sulfide, and the sulfides and carbonates are subsequently air-stripped from solution under acidic conditions. By removing anions that promote membrane scale formation, very high concentration factors and water

recoveries could be accomplished by further concentrating the treated brine using the reverse osmosis process (Figure 1-1).

The reduction of sulfates by BSR system and the treatment of the resultant hydrogen sulfide by a suitable technique will effectively lower the potential for the precipitation of sodium sulfate and other inorganic scalants and reducing the fouling potential of reverse osmosis membranes during brine concentration. Biological conversion of sulfate to sulfide in aqueous medium using the BSR technology would be an efficient and cost-effective strategy. The operational variables shall include the reactor configuration, type of solid media employed, reactor hydraulic residence time, and organic electron donors such as methanol, ethanol, acetate, etc., for sustaining the microbial population. This will minimize the extent of pilot-scale studies required for validating the applicability of the treatment strategy, and facilitating the design and cost estimation of full-scale BSR reactor system. In the present treatment strategy, the brine concentrate is treated in a bioreactor system for reduction of sulfates to prevent the occurrence of precipitation scaling on the reverse osmosis membrane. The gas from the bioreactor system will be sent to a treatment system such as a biofiltration unit for the removal of hydrogen sulfide.

There are very few scientific reports describing the health effects of exposure to sulfate in water, and the concerns regarding sensitive populations are based on case studies and anecdotal reports. One such potentially sensitive population are infants

receiving their first bottles containing tap water. Another group of people who could potentially be adversely affected by water with high sulfate concentrations are transient populations (i.e., tourists, hunters, students, and other temporary visitors) and people moving into areas with high sulfate concentrations in the drinking water from areas with low sulfate concentrations in drinking water. The US EPA proposed the Secondary Maximum Contaminant Level (SMCL) of 250 mg/L based on taste (the World Health Organization (WHO) guideline for sulfate is 400 mg/L, based on taste; people's threshold for tasting sulfate ranges from 250-350 mg/L). This standard is recommended to make the water more desirable for use and it is not related to health risks and is not enforceable by the US EPA.

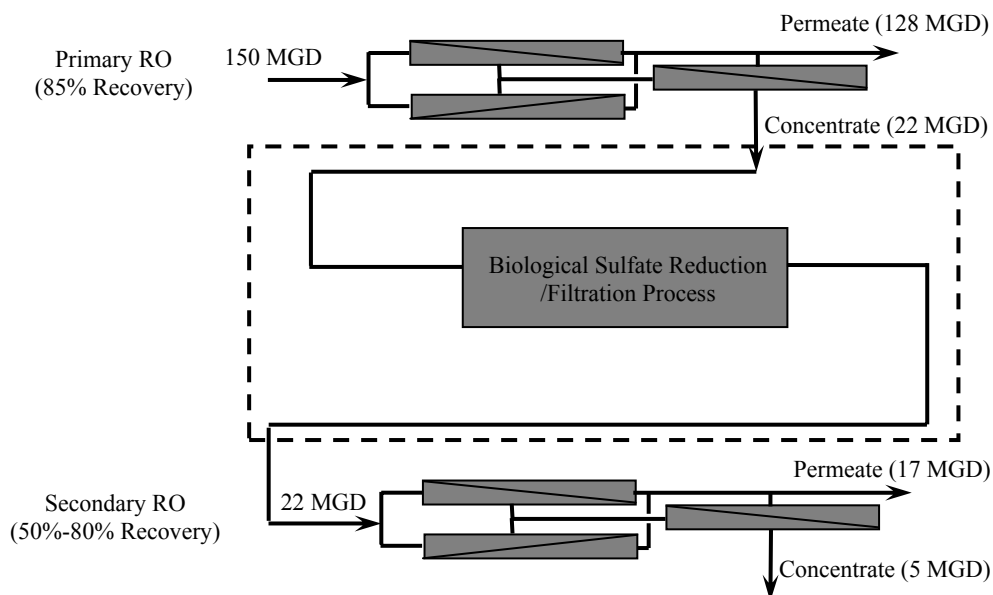


Figure 1-1 Schematic Flow Diagram for Treatment of Reverse Osmosis Brine Concentrate Prepared by the Metropolitan Water District of Southern California

CHAPTER 2

THEORETICAL BACKGROUND

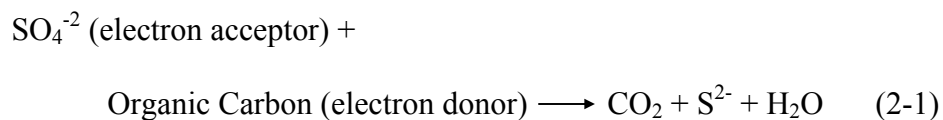
2.1 Principles of Biological Sulfate Reduction (BSR) Process

Discharge of large quantities of wastewater to the receiving water which usually contain high levels of sulfate and dissolved metals are the major sources of pollution in receiving waters. High sulfate concentrations in water cause many environmental problems including taste, odor and laxative effect that can lead to dehydration. Sulfate reducing bacteria (SRB) are facultative anaerobes that use sulfate ions as the terminal electron acceptor for metabolism of organic substrates (Pfennig et al., 1981). They chemically convert natural sulfates in water to hydrogen sulfide, and are the primary producers of large quantities of odorous gas. They often live in anaerobic environments such as deep wells, plumbing systems, water softeners and water heaters, and usually grow in water distribution systems. Sulfur reducing bacteria are more common than the sulfur-oxidizing bacteria whose environmental effects are similar to those of iron bacteria. Sulfur oxidizing bacteria convert sulfide into sulfate, producing a dark slime that can clog plumbing. Although they pose no known human health risk, they blacken most waters or form a dark slime coating inside toilet tanks.

Past and current treatment technologies are based on biological and physicochemical processes such as oxidation, reduction, adsorption and precipitation which are not desirable due to by-product generation and unfavorable economics. Consequently,

biological sulfate reduction (BSR) processes have a wider popularity due to their high efficiency and low initial and operational cost. Under anaerobic conditions, sulfate can be used as a terminal electron acceptor by sulfate reducing bacteria (SRB) that couple the oxidation of the substrate (organic or inorganic compounds) to the reduction of sulfate and use the energy produced for growth and maintenance (Moosa et al., 2002).

Dissimilatory sulfate reduction or “sulfate respiration” is the process in which the sulfate ion acts as an oxidizing agent and a terminal electron acceptor for dissimilation of an organic compound (electron donor) by sulfate-reducing microorganisms. Microbial sulfate reduction processes generally produce hydrogen sulfide gas as a hydrolysis product of sulfide ion, primarily responsible for inhibition of most anaerobic biological processes for organic removal. However, only a small fraction of the reduced sulfur is assimilated by sulfate-reducing bacteria (SRB), as most of the sulfur content is released into the environment as sulfide ion. A general equation for sulfate reduction is expressed by Postgate (1979) as follows:



2.2 BSR Processes

Zitomer and Shrout (2000) used aerated methanogenic fluidized beds for the treatment of wastewaters with high-sulfate, and high-chemical oxygen demand. Many industrial wastewaters have both high organic pollution and sulfate (SO_4^{2-}) concentrations. Although biological conversion of organics to methane may be an economical chemical oxygen demand (COD) removal option, significant inhibition of methane production results from reduction of SO_4^{2-} to hydrogen sulfide (H_2S), which is inhibitory to methanogenic microorganisms. Therefore, sulfate-containing wastewater is often not amenable to conventional anaerobic treatment. Recently, Zitomer and Strout (2000) conducted limited study on the aeration of recycle flow to hybrid and baffled reactors for the above wastewater.

Steed et al. (2000) developed a sulfate-reducing biological process to study the removal of heavy metals from acid mine drainage. The feasibility of using sulfate-reducing bacteria to remove heavy metals from aqueous streams such as acid mine drainage (AMD) was evaluated using three anaerobic reactors: an upflow anaerobic sludge blanket (UASB) reactor, a packed filter reactor, and a filter reactor that was partially packed with floating plastic pall rings.

Kolmert and Johnson (2001) used immobilized acidophilic sulfate-reducing bacteria to study remediation of acidic wastewaters. In this study by Kolmert, they have evaluated the potential use of novel acidophilic SRB for remediating acidic

wastewaters, in comparison with, and in conjunction with, neutrophilic SRB. Three SRB-populations (a mixed population of acidophilic isolates, a neutrophilic culture and a mixed acidophilic/neutrophilic consortium) were immobilized on porous glass beads, packed into Perspex® columns and percolated with synthetic medium for several months. Energy and carbon source utilization, and tolerance to acid stress of the different consortia were evaluated. They noted that acidophilic SRB were more efficient than the neutrophilic culture in coupling ethanol oxidation to sulfate reduction and all of the substrates tested were oxidized to acetic acid. The bioreactors containing acidophilic SRB reduced sulfate and generated alkalinity challenged with influent at pH 3 and above; indicating that such bacteria have potential for bioremediation of highly acidic wastewaters. In these studies, average reduction rates of $0.25\text{--}0.30 \text{ g SO}_4^{2-}/\text{m}^3\cdot\text{day}$ were achieved with bioreactors containing acidophilic SRB percolated with a pH 4 liquid medium.

Nagpal et al. (2000) operated a liquid–solid fluidized bed reactor to carry out sulfate reduction with a mixed culture of sulfate reducing bacteria. The bacteria were immobilized on porous glass beads. The low specific gravity of the hydrated beads allowed operation at low liquid recirculation rates. H_2S level in the reactor was controlled by N_2 purging, which also served as the location for liquid feed and removal. Ethanol was used as the electron donor/carbon source for the bacteria. Sulfate reduction rates up to $6.33 \text{ g sulfate/L}\cdot\text{day}$ were attained in the reactor at a hydraulic retention time of 5.1 hr. They examined the effect of hydraulic retention

time and biomass loading on the beads, on reactor performance, and efficiency and notified that the efficiency of sulfate reduction increased considerably as the hydraulic retention increased, until the bacteria became very strongly substrate-limited at 55 hr HRT. They further studied the effect of bead biomass loading on bed expansion at various liquid superficial velocities. Nagpal et al. also developed a model for the reactor. Simulations of the continuous flow experiments indicated that the model can describe the system well, and thus could be used in the design/scale-up of such reactors. Their model suggested that a significant increase in the sulfate reduction capacity of the system was possible by increasing the bed volume relative to the total liquid volume of the system. The results indicated that the fluidized bed reactor can be used to achieve high rates of sulfate reduction at high liquid throughputs. Significant improvement in the system capacity was estimated as possible by the use of systems with higher ratio of bed volume to system liquid volume. They notified that the advantage of a fluidized bed reactor as compared to a packed bed or UASB type reactor was enhanced mass transfer rates for both substrates and the toxic product H_2S . It might be concluded that the overall sulfate reduction capacity of the system depended on the feed sulfate concentration, HRT, and efficiency of reduction. The main drawback of their system was the production of acetate, resulting in an effluent with significant residual COD.

Nagpal et al. (2000) investigated the sulfate-reduction stoichiometry and associated kinetics using ethanol as the carbon source by a mixed culture of SRB containing the

species *Desulfovibrio desulfuricans*. Growth yield was lower, and kinetics was slower for ethanol compared to lactate. Ethanol was converted into acetate and no significant carbon dioxide production was observed. A mathematical model for growth of sulfate-reducing bacteria on ethanol was developed, and simulations of the growth experiments on ethanol were carried out using the model. The pH variation due to sulfate reduction, and hydrogen sulfide production and removal by nitrogen purging, were examined. The modeling study was distinct from earlier models using sulfate-reducing bacteria in that it considered growth on ethanol, and analyzed pH variations due to the product-formation reactions. The maximum specific growth rate for SRB utilization of ethanol was estimated to be in the range of 0.012–0.013 hr⁻¹. Monod saturation constant for ethanol and sulfate were estimated to be around 0.2 g/L, and 0.8 g/L, respectively. The model for sulfate-reducing bacteria growth using ethanol allowed satisfactory simulation of the completely mixed batch reactor (CMBR) growth experiments.

Weijma et al. (2000) investigated thermophilic sulfate and sulfite reduction in laboratory-scale expanded granular sludge bed (EGSB) reactors operated at 65°C and pH 7.5 with methanol as the sole carbon and energy. At a hydraulic retention time (HRT) of 10 hr, maximum sulfite and sulfate elimination rates of 5.5 g SO₃²⁻/L.day (100% elimination) and 5.7 g SO₄²⁻/L.day (55% elimination) were achieved, resulting in an effluent sulfide concentration of approximately 1800 mg S²⁻/L. Sulfate elimination was limited by the sulfide concentration, as stripping of H₂S from

the reactor with nitrogen gas was found to increase the sulfate elimination rate to 9.9 g SO₄²⁻/L.day (100% elimination).

Weijma et al. observed that at a HRT of 3 hr, maximum achievable sulfite and sulfate elimination rates were 18 g SO₃²⁻/L.day (100% elimination) and 11 g SO₄²⁻/L.day (50% elimination). However, at a HRT of 3 hr, the elimination rate was limited by the biomass retention of the system, and 5.5 ± 1.8% of the consumed methanol was converted to acetate, which was not further degraded by sulfate reducing bacteria present in the sludge. Sulfate degradation in the reactor was described by zero order kinetics down to a threshold concentration of 0.05 g/L, while methanol degradation followed Michaelis-Menten kinetics with Michaelis-Menten constant, K_m of 0.037 g COD/L. A disadvantage of using methanol was the formation of acetate as undesired by-products. Their results indicated that formation of acetate is an intrinsic feature of sulfite reducing conditions. Therefore, for application of methanol in biological desulfurization of flue-gases, a compromise must be found between the formation of sulfide and acetate.

The kinetics of anaerobic reduction of sulfate was studied by Moosa (2002) in continuous bioreactors. The effects of initial sulfate concentration and its volumetric loading on the kinetics of reaction and activity of sulfate-reducing bacteria were investigated. The increase in initial concentration of sulfate in the range 1.0-10.0 kg/m³ enhanced the reaction rate from 0.007-0.17 kg/m³.hr. The results of this study

indicated that the growth of SRB and the kinetics of anaerobic reduction of sulfate were influenced by initial concentration of sulfate in enhancing the reaction rate. The kinetic expression derived in this work describes the effects of initial and residual concentrations of sulfate, as well as bacterial concentration on the kinetics of sulfate bio-reduction and is able to predict the experimental data with a reasonable accuracy.

Feasibility and engineering aspects of biological sulfate reduction in gas-lift reactors were studied by Van Houten et al. (1994). Hydrogen and carbon dioxide were used as energy and carbon source, respectively. In this study, attention was paid to biofilm formation, sulfide toxicity, sulfate conversion rate optimization, and gas liquid mass transfer limitations. The results clearly demonstrated that sulfate reducing bacteria were able to form stable biofilms under turbulent flow conditions, as observed from microbial growth on pumice particles. It was observed that the use of basalt particles led to the formation of granules of sulfate reducing biomass. Also, growth of sulfate reducing bacteria was still possible at H_2S concentrations of up to 450 mg/L without problems due to toxic inhibition. It was found that high H_2S concentrations caused reversible inhibition rather than acute toxicity. When free H_2S concentrations were maintained 450 mg/L, a maximum sulfate conversion rate of 30 g SO_4^{2-} /L.day could be achieved after 10 days of operation.

Annachhatre et al. (2001) demonstrated the feasibility of using a laboratory-scale upflow anaerobic sludge blanket process for sulfate reduction with molasses as a carbon source. These investigators observed that competition between methane-producing bacteria (MPB) and sulfate-reducing bacteria (SRB) was influenced by the chemical oxygen demand-to-sulfur (COD/S) ratio in the feed. Furthermore, sulfate removal greater than 80% was achieved at COD/S greater than 10 when MPB predominated. Also, they noted that activity of MPB and SRB was inhibited at a dissolved sulfide concentration of approximately 200 mg/L. These researchers further observed that competition between MPB and SRB was intense as the COD/S was reduced from 5 to 2. Further reduction in the COD/S to 0.7 led to the formation of sulfidogenic granules. Their investigations showed that satisfactory biological sulfate removal could be achieved in a UASB process with molasses as a carbon source.

2.3 Effects of Various Factors on BSR Processes

Mixed cultures containing SRB were often employed in treatment of wastewaters with high sulfate concentrations requiring an organic energy and carbon source for extensive growth and higher sulfate reduction activity. Low molecular weight organic compounds, such as acetate, propionate, ethanol, glucose, glycerol, malate, lactate, sucrose, hydrogen etc., are well known electron donors for sulfate reduction (Middleton, 1975). Okabe et al. (1992) studied the specific growth rate and cell yield for *Desulfovibrio desulfuricans* under sulfate-limiting and lactate-limiting (carbon

source) conditions. The specific growth rate and yield coefficient under sulfate-limiting conditions were lower than those obtained under lactate-limiting conditions, mainly due to the increase in the maintenance energy requirement.

Dovark et al. (1992) reported that rates of sulfate reduction and metal retention increased by a factor of 10 when lactate was added to the nickel-contaminated influent to a reactor filled with spent mushroom compost. They suggested that the type and quantity of organic compound released by the decomposition of compost substantially limited the maximum sulfate reduction rate. Matsui et al. (1993) conducted fluidized bioreactor experiments with mixed culture of sulfate-reducing bacteria on glucose decomposition with and without sulfate reduction. Glucose in the reactor was mainly decomposed into lactate and ethanol, which, in turn, were decomposed into acetate and propionate. Sulfate reduction occurred with propionate and acetate decomposition. With sulfate reduction, propionate was decomposed into acetate, while accumulation of propionate was observed without sulfate reduction. Later, Nagpal et al. (2000) stated that some species of sulfate-reducing bacteria are capable of complete oxidation of the organic compound molecules into carbon dioxide, while others can oxidize the C2-C4 compounds to only acetate.

Among various carbon sources mentioned above, although ethanol permits poor bacterial growth, its yield of sulfide is relatively high (Postgate, 1979). Barnes et al. (1991) employed upflow anaerobic sludge blanket (UASB) process called “Pacques

Process” for sulfate reduction utilizing ethanol as the electron donor. A mixed culture of anaerobic sulfate reducers and methanogens obtained from various natural sites and industrial waste effluents was used in the start-up stage of the process. The laboratory-scale reactor was able to achieve sulfate reduction rates of 7.8 g/L.day at a 4 hours hydraulic retention time, while the pilot-scale reactor achieved 10 g/L.day at a hydraulic retention time of 5 hours. The overall stoichiometry of sulfate reduction in their system for the growth on ethanol can be written as follows:



Temperature and nutrients are the other important factors affecting the sulfate reduction process. Postgate (1979) reported that bacterial rates of sulfide production decreased substantially at temperatures of 7°C to 15°C. Therefore, most of the sulfate reduction studies were conducted between 30°C and 37°C. Dovark et al. (1992) suggested for their simple anaerobic reactors installed to achieve sulfate reduction coupled with heavy metal removal, that sulfate reduction rates could be increased by raising the reactor temperature to 25-35°C for stimulating bacterial activity. In another study conducted by Okabe and Characklis (1992), it was reported that the maximum substrate utilization rate of *Desulfovibrio desulfuricans* was relatively constant between 25°C and 43°C, and dramatically decreased outside this temperature range. However, the stoichiometry of microbial sulfate reduction was not temperature dependent.

In addition to strains described above, *Desulfovibrio*, the most predominant sulfate-reducing bacteria, showed an exceptionally high requirement for inorganic iron to be used as cell constituent. For instance, addition of metallic iron to a growing *Desulfovibrio vulgaris* culture in a medium containing organic carbon causes more extensive hydrogen sulfide production than its omission (Somlev and Tishkov, 1994). Since soluble iron was fairly common in soil and aquatic environments, blackening due to ferric sulfide (FeS) formation was a characteristic of activity of such sulfate-reducing bacteria (Postgate, 1979). The precipitation of FeS also aids in detoxifying the growth environment of the sulfate-reducing bacteria. However, they did not require any addition of excess iron to the system when grown in wastewater or sewage sludge, as reported by Middleton (1975).

Chen et al. (1994) employed an anaerobic upflow porous media biofilm reactor with sand as the support medium, lactate as the carbon source and *Desulfovibrio desulfuricans* as the sulfate-reducing strain for sulfate removal. The appearance of well-separated black spots was the initial indication of sulfate reduction and hydrogen sulfide generation (souring). These black spots were attributed to the precipitation of iron in the medium as ferrous sulfide (FeS). After seven days, the blackened zones radially expanded indicating bacterial growth. Chen and coworkers (1994) also reported that biofilm accumulation in porous media was the net result of these phenomena: microbial cell adsorption, desorption, growth on media surfaces, detachment and filtration. The sulfate-reducing bacteria attached to a solid surface

were entrapped in polysaccharide gels produced by themselves or slime-forming bacteria, and were well protected in the microenvironment confined to the biofilm. They together observed that, in such biofilm reactors, bacterial cells attached to the entry part of the column grew faster than those attached to the upper parts of the reactors because most of the substrate was depleted at the inlet part of the reactor. This observation was well supported by an earlier work of Taylor et al. (1990) who reported high permeability reduction and much thicker biofilm formation at the inlet of their reactor attributable to high substrate utilization and biofilm growth in this part.

In a more recent study, Muthumbi et al. (2001) investigated the extent of biological sulfate reduction (BSR) using acetate as the carbon source in an upflow anaerobic sludge blanket (UASB) reactor depended on the level of salinity. They found that an important factor influencing the performance of SRB was the overall salt content of the treated wastewater. They further investigated whether the composition of the microbial communities in the reactor was related to the process performance at various salinity levels. They noted that the salinity level in the influent had a strong influence on the reactor performance, which was indicated by the sulfate conversion rate and efficiency. An optimal sulfate reduction of about 14 g S/L.day by acetate utilizing sulfate-reducing bacteria was achieved after raising the salinity level to between 1.26% and 1.39%, and this reflected conversion efficiency exceeding 90%. Raising the concentration of chloride, potassium and magnesium ions only helped to

enhance the sulfate removal rate and efficiency. Muthumbi et al. (2001) observed initial increase in reactor performance due to the enhanced biological activity of acetate-utilizing sulfate reducers as a result of increased concentrations of potassium, magnesium and chloride ions in the influent. They further concluded that salinity levels had direct impact on the composition of microbial communities within the UASB reactor. Their findings were in agreement with Postgate (1979) who stated that salinity determined the composition of microbial populations, and that above 2% salinity levels, the population predominantly consisted of *Desulfovibrio* bacterium.

Dvorak et al. (1992) used two pilot-scale anaerobic continuous flow reactor systems in series for biological sulfate reduction and removal of heavy metals in a US Bureau of Mines facility in Pennsylvania. They identified that hydraulic flow rate or the hydraulic residence time (HRT) strongly affected the performance of SRB. Short HRTs might not allow sufficient time for the microbial activity to remove sulfate, precipitate metals and neutralize acidity formed during the process. The use of very short HRTs could also overcome the problem of generate alkalinity, often resulting in acidification of the reactor interior to the point of severely inhibiting bacteria activity. On the other hand, excessively long HRTs might subject a reactor to such small influent loads of acidity and metals so that much of the hydrogen sulfide and alkalinity produced would exit the reactor without having been used.

Stucki et al. (1993) employed fixed-bed reactors with recycling for sulfate removal, and these reactors used glass beads, porous lava beads or polyurethane foam as packing media. Acetic acid was their preferred carbon source for the pure cultures of *Desulfotomaculum acetooxidans*, *Desulfobacter postgatei*, and mixed biomass from a digester that had been loaded with sulfate. A medium containing high salt concentration was used. Sulfate reduction rates up to 60 g/L.day were reported at conversion efficiencies equal to approximately 60 to 75%. However, the process was reported to be unstable at high sulfate loading rates.

Van Houten et al. (1994) employed gas-lift reactors to conduct sulfate reduction studies using hydrogen/carbon dioxide as the electron donor. These investigators used pumice and basalt as reactor particle media for microbial immobilization, and the media were inoculated with anaerobic granular sludge biomass that had been previously grown on volatile fatty acids and sulfate. They paid special attention to the following aspects, namely, biofilm formation, sulfide toxicity, sulfate conversion rate optimization, and gas liquid mass transfer limitations. They reported biofilm formation on pumice particles, but not on basalt particles. Sulfate reduction rates up to 30 g/L.day were observed corresponding to conversion efficiencies of 50% at a hydraulic retention time of 2.25 hours. However, higher sulfate conversion efficiencies (> 95 percent) were reported at loading rates of 18 g/L.day. The sulfate reducing bacteria, grown on pumice, easily adapted to free H₂S concentrations up to 450 mg/L. Biofilm growth rate then equilibrated biomass loss rate. The Gas-to-

liquid hydrogen mass transfer capacity of the reactor determined the maximum sulfate conversion rate.

Subsequently, Nagpal et al. (2000) employed a fluidized bed reactor to carry out sulfate reduction using ethanol as the carbon source. The mixed culture of sulfate-reducing bacteria was immobilized on porous glass beads. The process achieved sulfate reduction rates up to 6.33 g/L.day at a hydraulic retention time of 5.1 hours. They emphasized the advantage of using fluidized bed reactors over packed bed or upflow anaerobic sludge blanket reactors. They stated that fluidization enhanced mass transfer rates for both substrates (sulfate and carbon source) and product gas (hydrogen sulfide), and improved process efficiencies. They compared the peak capacities reported by Stucki et al. (1993) at 18 hours to those reported by Van Houten et al. (1994) at 4.5 hours and their own study at 5.1 hours, and concluded that fluidized bed process could be used to achieve high rates of sulfate reduction at high liquid throughputs, and that the overall sulfate reduction capacity of the system depends on the feed sulfate concentration, hydraulic retention time and efficiency of the reduction capacity.

2.4 Sulfate Reducing Bacteria Species

The sulfate-reducing bacteria (SRB) are anaerobic microorganisms that respire using sulfate as the oxidizing agent, or electron acceptor. The SRB species are obligate anaerobic heterotrophs, although they can adapt themselves and survive remarkably

well in aerobic terrestrial and aquatic environments by remaining dormant, and become active when the local conditions become anaerobic. These strains grow more slowly than other soil or water microorganisms partly because the growth of cultures exhibits a non-exponential trend (Postgate, 1979). Initially, all SRB were classified according to salt tolerance and ability to use different organic carbon substrates. However, fresh water strains have been adapted to saline environments, and organic carbon classifications did not hold for all strains. Therefore, recent classification schemes use two main groups: spore formers and non-spore formers. Among all bacteria, due to the ease of isolation, the genus *Desulfovibrio* is the most commonly encountered sulfate-reducing bacteria. They are known to be mesophilic, and at the same time, can be halophilic (salt-tolerant up to 6 to 10 percent of total dissolved solids) or non-halophilic (Postgate, 1979). The ensuing section discusses the classification criteria for SRB species.

Brock and Madigan (1988) have listed 10 genera of dissimilatory sulfate-reducing bacteria placed into two broad physiological subgroups as presented in Table 2-1. The genera in the first group, *Desulfovibrio*, *Desulfomonas*, *Desulfotomaculum*, and *Desulfobulbus*, utilize lactate, pyruvate, ethanol, and certain fatty acids as carbon and energy sources reducing sulfate to hydrogen sulfide. Many species of this group can utilize malate, sulfonates, and certain primary alcohols and oxidize their electron donors to the level of acetate and excrete these fatty acids as an end product.

Table 2-1 Characteristics of Some Key Genera of Sulfate Reducing Bacteria

Group I Species	Electron donor	End Product	DNA (mol% GC)
<i>Desulfovibrio</i>	ethanol	H ₂ S	46-61
<i>Desulfomonas</i>	lactate, pyruvate, ethanol, glucose	H ₂ S	NA
<i>Desulfotomaculum</i>	lactate, pyruvate, ethanol	H ₂ S	37-46
<i>Desulfobacula</i>	Various aromatic compound, aromatic hydrocarbon toluene	H ₂ S, CO ₂	42
<i>Desulfobulbus</i>	propionate	acetate, CO ₂ , H ₂ S	59-60
<i>Desulforhopalus</i>	Propionate, lactate, alcohols	H ₂ S	48
Group II Species	Electron donor	End Product	DNA (mol% GC)
<i>Desulfobacter</i>	acetate	oxidation to CO ₂ via citric acid cycle, S ²⁻	45-46
<i>Desulfococcus</i>	C ₁ to C ₁₄ fatty acids	complete oxidation to CO ₂ , S ²⁻	57
<i>Desulfonema</i>	C ₂ to C ₁₂ fatty acids	complete oxidation to CO ₂ , S ²⁻	35-42
<i>Desulfosarcina</i>	C ₂ to C ₁₄ fatty acids	complete oxidation to CO ₂ , S ²⁻	51

The genera in the second group differs from those in group I by their ability to oxidize fatty acids (including acetate), lactate, succinate, and even bezonate in some species, completely to CO₂ and to reduce sulfate to sulfide. *Desulfococcus*, *Desulfosarcina*, *Desulfobacterium*, *Desulfotomaculum*, and *Desulfonema*, and certain species of *Desulfovibrio*, are unique among sulfate-reducers in their ability to grow chemolithotrophically and autotrophically with H₂ as electron donor, sulfate as electron acceptor, and CO₂ as sole carbon source (Brock and Madigan, 1988). The characteristics of both groups are well summarized in Table 2-1. The ability of both the incomplete and completely oxidizing sulfate reducers to grow with ethanol as

electron donor had been widely reported (Widdel, 1988). Mechalias and Rittenburg (1960) reported that ethanol was converted to acetate by *Desulfovibrio desulfuricans*. Bryant et al. (1977) indicated that a strain called EC1, belonging to the genus *Desulfovibrio*, utilized ethanol as electron donor to produce acetate.

2.5 Fluidized Bed Bioadsorber Reactor Processes

In this session the theory of fluidized bed bioadsorber reactor, their advantages, working principles and design criteria briefly will be discussed. The FBBR concept and its advantages over other conventional technologies have been realized for quite a long time since 1974, and studies extensively until 1980s (Heijnen et al., 1989). After overcoming the operational problems, the fluidized bed reactors have become more common in full-scale systems in the last two decades (Godia and Sola, 1995). The results of these studies and operations have shown that FBBR technology have a great potential in a wide range of processes, due to their intrinsic advantages and also to the possibilities they offer to the engineers for design changes to achieve greater performance efficiency.

The fluidized bed bioreactor with recycle can provide 5 to 10 times the microorganism concentrations as compared to suspended growth processes (Sadick et al., 1996). The microorganisms in the fluidized bed bioadsorber reactor appear to readily recover in case of shutdowns and capable of handling shock loadings (Heijnen et al., 1989). FBBR system has a relatively smaller reactor size (Sutton and

Mishra, 1991) compared to conventional fixed film or suspended growth technologies (Sadick et al., 1996) and also easy to operate and maintain and brings up lower operational problems in regard to clogging or head loss (Mulcahy et al., 1980).

Yoder et al. (1995) summarized the most important parameters in the modeling and design of FBBRs as follows: (1) The size of the bioreactor, (2) the quantity of biomass and biofilm thickness, (3) the bed expansion due to hydraulic flow and biofilm growth, (4) the expansion index and expanded bed height, (5) the type, size and density of the support media used, and (6) the superficial fluid velocity through the reactor. According to Safferman and Bishop (1997), the two most important design parameters for fluidized bioreactors were the substrate per unit of biomass and the biomass per unit of support medium. The greater the biomass concentration, the greater was the rate of substrate removal up to the point where diffusion into the biofilm layer becomes limiting; the higher the reactor loading, the more the biomass produced. Then, the biomass control of the fluidized bed bioadsorber reactors could be governed by the control of the substrate loading into the system or vice versa.

2.6 H₂S Production and Mass Balance

In the FBBR process sulfate is reduced to sulfide which is distributed between H₂S in the gas phase and H₂S, HS⁻, and S²⁻ in the aqueous phase, and insoluble metallic

sulfides. The following equation shows the biochemical reaction of sulfate with ethanol which leads to the production of hydrogen sulfide and acetate.



$$\Delta G_{\text{rxn}} = -15.9 \text{ kcal/mole ethanol}$$

Inhibition of SRB metabolism by the products of sulfate respiration, $\text{HS}^-/\text{H}_2\text{S}$, has been reported in several studies. This inhibition has been ascribed to the general toxic nature of undissociated H_2S to living organisms, as well as its removal of trace nutrients which precipitate as metal sulfides (Nagpal et al., 2000). Van Houten et al. (1997) reported that H_2S concentration of 250 mg/L inhibited SRB growth. Reis et al. (1996) reported that H_2S at 547 mg/L completely inhibited growth in a culture of *Desulfovibrio*. Van Houten et al. (1994) observed that SRB growth was possible at H_2S concentrations up to 450 mg/L, and noted that H_2S inhibition was reversible, so that upon the removal of H_2S from the reactor, the bacteria recovered their metabolic activity to normal levels.

Okabe, and Nielsen (1992) indicated that sulfide inhibition of SRB probably occurs when sulfide species (H_2S , HS^- , and S^{2-}) combine with the iron of any essential iron-containing compounds in the cell, causing electron transport systems to cease activity. Their experimental results also indicated that under pre-existing high sulfide concentration in the formation, biological sulfide production was not a favorable

process. Although other nutritional and physical conditions were suitable for SRB growth, their activity was strongly inhibited by high sulfide concentration.

Effect of H₂S stripping with nitrogen gas in the laboratory-scale expanded granular sludge bed (EGSB) reactors was studied by Weijma et al. (2000); and 100% sulfate elimination achieved. H₂S level was also controlled in a liquid-solid fluidized bed reactor by N₂ sparging (Nagpal et al., 2000). Total inhibition of growth of SRB generally occurs at concentrations of undissociated H₂S below 550 mg S /L. Strong inhibition of SRB bacterial group is usually observed at concentrations of undissociated H₂S of 180-200 mg S /L (Stucki et al., 1996).

Hydrogen sulfide is a toxic and odorous compound present in biogas produced by the anaerobic biological reduction of sulfate. In addition to its unpleasant odor, hydrogen sulfide gas is highly toxic (Roth, 1993). Upon inhalation, hydrogen sulfide reacts with enzymes in the bloodstream and inhibits cellular respiration resulting in pulmonary paralysis, sudden collapse, and death. Continuous exposure to low concentrations of 15-50 mg/L will generally lead to irritation to mucous membranes and may also cause headaches, dizziness, and nausea. Higher concentrations such as 200-300 mg/L might result in respiratory arrest leading to coma and unconsciousness. Exposures for more than 30 minutes at concentrations greater than 700 mg/L have been fatal (MSDS, 1996).

Hydrogen sulfide is a corrosive and toxic air pollutant that causes odor problems in trace levels and in excess amounts can cause irritation of the human eyes or injury to the central nervous system (Roth et al., 1995; Wani et al., 1999). The human threshold exposure limit to hydrogen sulfide is 10 mg/L for 7-8 hour periods, and the contaminant must therefore be removed from the effluent gas stream for health and safety reasons (Chung et al., 1996). Other organo-sulfur compounds exemplified by mercaptans, dimethyl sulfide and dimethyl disulfide that are formed along with hydrogen sulfide do not necessarily pose health hazards at the levels produced in anaerobic biological sulfate reduction processes, but can cause serious odor problems and skin irritation (Wani et al., 1999). The physical and chemical processes employed for hydrogen sulfide removal from contaminated or waste gas include activated carbon adsorption, ozone oxidation, incineration, and chemical scrubbing. As the concentrations of hydrogen sulfide and organo-sulfur species are relatively dilute in contaminated gas streams, conventional air pollution control technologies have major drawbacks including high energy requirements, treatment costs, and disposal expenses, besides pollution problems. The continued demand for economy and efficiency in processes has led to investigating microbiological alternatives to conventional technologies.

2.6.1 Biofiltration for H₂S Removal

Biofiltration refers to the biological transformation or treatment of contaminants present in the gas phase, usually air. In this process, microorganisms fixed to a

porous medium break down pollutants present in an air stream. As the air passes through the media bed, the contaminants in the air phase adsorb onto the biofilm and the medium particles. The contaminants are degraded into end product through a series of oxidative and reductive reactions.

The configurations of biofilters have changed over time; according to Leson and Winer (1991), biofilters may be built using conventional open single-bed systems, open multiple-story systems, or totally enclosed systems. Enclosed types, or modular biofilter systems, usually operate slightly above atmospheric pressure with the contaminated gas being pumped into the reactor. Air humidification and nutrient addition is usually done with digital pumps. Enclosed systems have been designed in many shapes, including cylindrical and rectangular, and are available from different vendors for application to various industries (Togna et al., 1994, Torres et al., 1994). These systems typically contain a proprietary support medium inoculated with specific microbial populations to achieve reduction of target compound concentrations.

Biofiltration studies for the removal of mixtures of reduced sulfur compounds including hydrogen sulfide and organo-sulfur compounds from the gas phase in laboratory-scale and pilot-scale are well documented (Wani et al., 1999, Ng et al., 2004). Biofiltration is devoid of cross-media transfer problems because it utilizes microorganisms immobilized on a solid packing medium to aerobically degrade or

metabolize the target pollutants; it is catalyzed enzymatically and functions under ambient conditions, and its energy requirements for operation and maintenance are minimal; and furthermore, it can be potentially used for long-term operations without media replacement. The technology can be made more efficient and cost-effective for the purification of gas streams containing hydrogen sulfide and organo-sulfur compounds by employing specific packing materials as carriers, and breeding appropriate microbial strains. The packing could be made of media such as soil, peat, compost, wood bark, wood chips, anthracite, activated carbon, or synthetic materials including plastics and polymers. Soils as biofilter media are prone to short-circuiting and clogging. Compost is inexpensive and purifies waste gases containing hydrogen sulfide well over short-term periods; nevertheless, it suffers from aging effects, short-circuiting problems, and reduced effectiveness on long-term operations. Fibrous peat has been considered preferable to soil or compost; however peat biofilters experience significant pressure losses, and require large installation spaces due to their high air permeability. An adsorbing media such as activated carbon does not only constitute support for microorganisms, but also acts as a shield or buffer in protecting the microbial populations from inhibitory or toxic substances, and further, sorbs high concentrations of substrates, gradually releasing them for microbial degradation (Den and Pirbazari, 2003). A study by Ng et al. (2004) demonstrated that biofiltration systems employing bacteria immobilized on activated carbon exhibited superior performance for the removal of hydrogen sulfide and other reduced sulfur compounds. Activated carbons perform reliably and efficiently, and

withstand shock loading from toxically inhibitive but adsorbable components; nevertheless, they are considered more expensive than other media.

2.6.2 Type of Microorganisms Capable of Oxidizing Hydrogen Sulfide

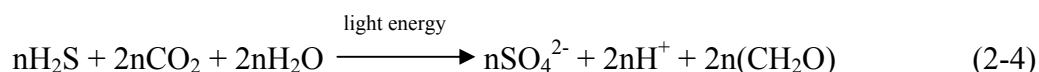
In the application of biofiltration processes, besides selection of appropriate packing materials, screening of effective microbial species is also important to achieve optimal process efficiencies. Autotrophic and heterotrophic microorganisms have both been used for the treatment of hydrogen sulfide and organo-sulfur compounds, despite their inherent differences in nutrient requirements and ability to catalyze specific reactions. Some chemolithoautotrophic bacteria such as members of the *Thiobacillus* species have been seeded into different packing media for metabolizing hydrogen sulfide. The products of H₂S oxidation are dependent on the strain of *Thiobacillus* employed. Some chemolithoheterotrophic bacteria such as *Thiotrix*, *Beggiatoa*, and *Hyphomicrobium* genera can oxidize hydrogen sulfide into elemental sulfur and store it in their cells. This elemental sulfur will undergo further oxidation to sulfate and the resulting acidity can have adverse effects on microbial activity, especially at low H₂S concentrations. Photoautotrophic bacteria including *Chlorobium*, *Chroamtium*, *ctothiorhodospira*, and *Rhodobacter* have been employed for converting hydrogen sulfide to elemental sulfur under anaerobic conditions. The major disadvantages of these strains lie in their anaerobic characteristics and their need for radiant energy. Chemorganotrophic bacteria such as *Streptomyces* species, *Pseudomonas auriginosa*, *Bacillus brevis*, *Micrococcus* species, *Xanthamonas*

species, and *Arthrobacter* species have also been reported to oxidize H_2S . However, little information on the desired mechanisms as well as proper design, operation and maintenance of biofilter is available.

The desirable bacteria in biofilter for converting H_2S to S^0 are certain chemotrophs and photoautotrophs which have a reliable capability to convert H_2S to S^0 , minimum nutrient input, and easy separation of S^0 from the biomass (Syed, 2006). In a pond in autumn where fallen leaves are the source of organic matter, different bacteria tend to live in areas of the pond where their particular capabilities provide them with an ecological niche (Postgate, 1968). Near the water surface, chemotrophic bacteria dominate where they can obtain their energy from the aerobic oxidation of H_2S and S^0 to form SO_4^{2-} . In the deep anaerobic zone, anaerobic decomposition of organic matter occurs and H_2S is produced. In the upper anaerobic zone where light can still penetrate and H_2S is available, growth of phototrophic bacteria occurs. These bacteria find suitable conditions for growth only in a narrow zone of overlap since sulfide and light occur in opposite gradients. In these narrow layers, they obtain reducing electrons from either H_2S or S^0 (Overmann, 2001).

Studies on microbial ecology associated with phototrophic bacteria showed that a species of green sulfur bacteria (GSB) *Cholorobium limicola*, which was originally called *Cholorobium limicola* forma *thiosulfatophilum* was the most suitable for sulfide removal and satisfied the criteria for a desirable bacterium (Syed and

Henshaw, 2003). *Cholorobium limicola*, a strict anaerobe, is capable of oxidizing sulfide to elemental sulfur and requires only light, CO₂, and inorganic nutrients for growth. GSB are nonmotile and deposit elemental sulfur extracellularly. This feature makes them suitable where the recovery of elemental sulfur from sulfide-containing water is desired. The overall photochemical reaction by which GSB oxidizes S²⁻ to S⁰ while reducing CO₂ to carbohydrates is (Van Niel, 1931):



Phototrophic *C. limicola* is considered an ideal bacterium in anaerobic biological processes for treatment of gaseous hydrogen sulfide owing to its ability to grow under anaerobic conditions using only inorganic substrates and a light source and its efficient extracellular production of elemental sulfur from H₂S. Phototrophic biofilters are an interesting concept for cost-effective H₂S removal from biogas due to their ability to operate for long periods of time without requiring a biomass separation step and their ability to operate under higher and variable loadings. However, a light source is one of the key constraints for this process (Syed, 2006).

CHAPTER 3

RESEARCH OBJECTIVES AND SCOPE

3.1 Research Objectives

The overall objectives of this research included the removal of sulfate from the reverse osmosis brine concentrate utilizing ethanol as carbon source, evaluation of the biological brine treatment by fluidized bed bioadsorber reactor process for further concentrating reverse osmosis brine generated from surface water desalination, and development and application of a mathematical model to simulate/predict, up scale, and enhance the efficiency of the FBBR process. These objectives were accomplished by conducting a series of laboratory investigations including completely mixed batch reactor (CMBR) biokinetic studies, chemostat biokinetic studies and FBBR processes to evaluate biological sulfate removal with ethanol as carbon source from the brine and evaluate the effect of biological sulfate process variables including different influent sulfate concentrations, C/S ratios, and pHs. The simulation of chemostat dynamics and development of a mathematical model for the FBBR processes were further performed using the biokinetic parameters obtained from the laboratory experiments as input into the chemostat and the FBBR models. These studies were followed by sensitivity analyses to identify the parameters that have a significant influence on the chemostat dynamics and subsequently on the FBBR system. Process upscaling was further investigated for the FBBR system using dimensional analysis and similitude.

3.2 Scope of the Research

The scope of the research intended to achieve the objectives mentioned above can be briefly outlined as follows:

- 1) Conduct completely mixed batch reactor (CMBR) biokinetic studies and evaluate the effect of various environmental parameters such as temperature, pH and C/S ratio on the desulfurization and ethanol utilization of RO brine through a series of CMBR experiments.
- 2) Perform chemostat studies under carbon-limiting condition with respect to sulfate in different carbon to sulfur ratios to determine the biokinetic parameters which include the Monod maximum substrate utilization rate, k half-saturation constant, K_s the yield coefficient, Y , and decay coefficient, k_d .
- 3) Conduct column studies and evaluate the FBBR – GAC and FBBR – sand processes with respect to the removal efficiencies of sulfate and ethanol.
- 4) Determine the effect of hydrogen sulfide stripping on removal efficiency in the FBBR.
- 5) Develop a model for continuous flow chemostat studies and model sensitivity analysis based on the proposed chemostat model.
- 6) Develop and apply a predictive mathematical model for forecasting the performance of the FBBR-GAC and FBBR-sand processes and techniques for process scaling.
- 7) Conduct laboratory-scale FBBR experiment to determine the treatment efficiency of the system with respect to sulfate removal and ethanol utilization

by employing different initial sulfate concentration and different hydraulic retention time. The results of these experiments provide the feedback for model verification.

- 8) Perform model simulation studies to evaluate the behavior of FBBR process under different operating conditions, and to conduct sensitivity studies to determine the FBBR model parameters most influential on the FBBR process dynamics.
- 9) Develop process upscaling procedures by dimensional analysis and similitude techniques to effect a smooth transition from laboratory scale to pilot scale, and eventually to full scale design.

CHAPTER 4

CHEMOSTAT REACTOR DYNAMICS AND MODELING

4.1 Significance of Chemostat Studies

Chemostat studies are used to determine biological sulfate reduction rates and associated biokinetic parameters including the specific growth rate, μ_m Monod half saturation coefficient, K_s yield coefficient, Y , and decay coefficient, k_d . These parameters are difficult to determine in batch biokinetic studies. Batch reactors are generally not capable of coping with fluctuations in environmental parameters such as pH, temperature, nutrient, and substrate concentrations because the cells undergo “phenotypic variations” through rapid mechanisms. Chemostats also have certain inherent advantages because they are well-mixed continuous systems appropriate for measuring microbial growth rates and substrate utilization rates under steady-state conditions. Additionally, chemostats provide better understanding of microbial cell cycles, metabolic regulations, and product formations; and offer useful information for design and optimization of continuous flow reactor systems. This information includes biokinetic parameters and design parameters such as specific microbial growth rate, specific desulfurization rate, organic loadings, and carbon-to-sulfur ratio. Furthermore, chemostats provide information on the best carbon source or electron donor, and optimal combination of microbial strains, besides biomass concentrations, sludge age, solids detention time, hydraulic retention time, and limits for biomass washout or enzyme inactivity. Certain phenomenological aspects of chemostat

biokinetics and dynamics could play an important role in the development of models for performance simulation/forecasting towards efficient and economical design, optimization and upscaling of various types of continuous-flow systems such as packed-bed or fluidized-bed bioreactors. A caveat must however be added that chemostats may not always reflect the fluid dynamics, mass transfer, and media-sorption characteristics in bioreactors or biofilm processes.

4.2 Theory of Chemostat Modeling

The mathematical model and simulation of chemostat process can be a helpful method to evaluate the effect of various biokinetic parameters that have a significant influence on the process dynamics of sulfate reduction. The modeling of the process can be further used to estimate the accuracy of the chemostat results in order to verify the model parameters for developing FBBR model. Shimizu et al. (1978) investigated both batch and chemostat studies that were employed to evaluate a model and kinetic parameters for denitrification-associated cell growth of *paracoccus denitrificans*. Their objective was to develop a model which satisfactorily describes denitrification reaction and to determine the important kinetic parameters by using continuous culture of a specific denitrifier, *p. denitrificans* in a defined medium. Shimizu et al. examined their kinetic model with the denitrification data obtained in batch and chemostat systems. The equations were solved by a fourth-order Runge-Kutta technique and the kinetic parameters obtained experimentally from chemostat were used as input into the chemostat model. Their

model appeared to predict that the buildup of nitrite out as an intermediate product would reach a peak in batch culture, but that nitrite concentration in continuous culture would be very low even at high dilution rate. Herrea et al. (1993) featured description of model for SRB growth alone in a continuous stirred tank reactor (CSTR). They used batch-growth data of *Desulfovibrio desulfuricans* utilization of lactate to verify their model. Van Houten et al. (1994) developed a model for CSTR without experimental verification. Gupta et al. (1994) have presented a detailed dynamic CSTR model for reactors containing both methanogens and SRBs. The proposed model in this work applies to the continuous flow CSTR and is distinct from the other modeling. Table 4-1 summarizes the salient features of the four CSTR models mentioned above.

Table 4-1 CSTR Models for SRB Growth

CSTR Models for SRBs	Carbon source	Metabolic products	Gas phase composition	Growth rate dependence
Herrera et al. (1993) • Gas-liquid mass transfer considered • pH kept constant	Lactate	acetate, CO ₂ and sulfide	N ₂ and H ₂ S	$\mu = \mu(\text{SO}_4^{2-}, \text{HS}^-)$
van Houten et al. (1994) • Gas-liquid mass transfer considered • pH kept constant	H ₂ /CO ₂	acetate and sulfide	H ₂ , CO ₂ , and H ₂ S	$\mu = \mu(\text{H}_2\text{S})$
Gupta et al. (1994) (methanogens and SRB's) • Gas-liquid mass transfer considered • pH variation calculated • metal precipitation considered	Acetate and formate	CH ₄ , CO ₂ , and sulfide	N ₂ , CH ₄ , CO ₂ , NH ₃ , H ₂ S, and H ₂ O	$\mu = \mu(\text{CH}_3\text{COOH}, \text{HCOOH})$

Table 4-1: Continued CSTR Models for SRB growth

CSTR Models for SRBs	Carbon source	Metabolic products	Gas phase composition	Growth rate dependence
This work (Chemostat) • liquid mass transfer considered • pH kept constant • Effect of biokinetic parameter variation calculated	Ethanol	acetate and sulfide	CO ₂ and H ₂ S	$\mu = \mu(\text{SO}_4^{2-}, \text{C}_2\text{H}_5\text{OH})$

4.3 Biokinetic Parameters

The biokinetic parameters including maximum specific growth rate, μ_m half saturation constant, K_s yield coefficient, Y , and decay constant, k_d were determined by running a series of continuous flow chemostat experiments. The objectives for chemostat study were as follows: (1) to determine the Monod biokinetic constants, (2) to develop a biokinetic model, and (3) to determine the Monod biokinetic parameters for FBBR model to predict and simulate the process performance under various condition.

For carbon source limiting continuous culture, a mass balance for the biomass and substrate can be expressed as follows (Shimizu et al., 1978):

$$V \frac{dM}{dt} = QM_o - QM + Vr_g' \quad (4-1)$$

$$V \frac{dC}{dt} = QC_o - QC + Vr_{su} \quad (4-2)$$

If reaction rate r_g' and r_{su} are limited by carbon source, the Monod Equation can be applied and r_g' and r_{su} can be expressed as follows;

$$r_g' = \frac{\mu_m M C}{K_s + C} - k_d M \quad (4-3)$$

$$r_{su} = -\frac{\mu_m M C}{Y(K_s + C)} = -\frac{k M C}{K_s + C} \quad (4-4)$$

Equation 4-1 can be expressed by substituting r_g' from Equation 4-3;

$$V \frac{dM}{dt} = QM_o - QM + V \left(\frac{\mu_m M C}{K_s + C} - k_d M \right) \quad (4-5)$$

In the above equation, the influent concentration of biomass can be assumed negligible and since at steady state, $dM/dt=0$, Equation 4-5 may be expressed as:

$$\frac{Q}{V} = \frac{\mu_m C}{K_s + C} - k_d \quad (4-6)$$

By applying the hydraulic retention time, $\theta = \frac{V}{Q} = \frac{1}{D}$, the above equation can be expressed as Equation 4-7:

$$\frac{1}{\theta} = \frac{\mu_m C}{K_s + C} - k_d \quad (4-7)$$

r_{su} from Equation 4-4 is determined using the following expression:

$$r_{su} = -\frac{Q}{V}(C_o - C) = -\frac{C_o - C}{\theta} \quad (4-8)$$

The above equations can be combined with Equation 4-4:

$$\frac{1}{\theta} = -Y \frac{r_{su}}{M} - k_d$$

or

$$\frac{1}{\theta} = Y \frac{C_o - C}{M\theta} - k_d \quad (4-9)$$

Equation 4-2 can be expressed by substituting r_{su} from Equation 4-4:

$$V \frac{dC}{dt} = QC_o - QC + V \left(-\frac{\mu_m M C}{Y(K_s + C)} \right) \quad (4-10)$$

At steady state $\frac{dC}{dt} = 0$, so that Equation 4-10 can be expressed as follows:

$$\frac{(C_o - C)}{M\theta} = \frac{k C}{K_s + C}$$

or

$$\frac{M\theta}{(C_o - C)} = \left(\frac{K_s}{k} \right) \frac{1}{C} + \frac{1}{k} \quad (4-11)$$

The biokinetic parameters K_s and k can be determined by plotting the term $\frac{M\theta}{(C_o - C)}$ versus $\frac{1}{C}$ from Equation 4-11. Also, parameters Y and k_d can be estimated by plotting $\frac{1}{\theta}$ versus $\frac{(C_o - C)}{M\theta}$ from Equation 4-9.

4.4 Numerical Solution

Equations 4-5 and 4-10 can be rearranged as below. Traditionally, these differential equations are solved using the finite difference method (FDM). However, the Runge-Kutta method using Matlab software is more efficient and accurate in handling the ordinary differential equations (ODE).

Sulfate or ethanol as substrate:

$$\frac{dC}{dt} = F(C, M, t) \quad (4-12)$$

$$\frac{dC}{dt} = D(C_o - C) - \frac{\mu_m M C}{Y(K_s + C)} \quad (4-13)$$

Biomass:

$$\frac{dM}{dt} = F(M, C, t) \quad (4-14)$$

$$\frac{dM}{dt} = -DM + \frac{\mu_m M C}{K_s + C} - k_d M \quad (4-15)$$

The initial and boundary conditions for the above equations are as follows:

$$C(M = 0, t = 0) = C_o \quad (4-16)$$

$$C(M, t) = C \quad (4-17)$$

$$M(t = 0, C_o) = 0 \quad (4-18)$$

The ODE solver functions implement numerical integration methods for solving initial-value problems (IVPs) for ODEs. Beginning at the initial time with initial conditions, they step through the time interval, computing a solution at each time step. If the solution for a time step satisfies the solver's error tolerance criteria, it is a successful step. Otherwise, it is a failed attempt; the solver shrinks the step size and tries again. The ode23 Matlab function was used successfully to solve the above model equations. The function is an implementation of an explicit Runge-Kutta (2, 3) pair of Bogacki and Shampine, (1994). Ode23 is a one-step solver and offer an efficient function at crude tolerances and in the presence of moderate stiffness. It is especially effective at crude tolerances, when a one-step method has advantages over methods with memory, and when Jacobians have eigen values near the imaginary axis (Shampine L.F., 1994).

4.5 Simulation and Sensitivity Analyses

The aim of model sensitivity analysis is to identify the various model parameters that have a significant influence on the chemostat operation. The chemostat modeling

was discussed in the previous section. The key system parameters are the kinetic parameters including K_s , k , Y , and μ_m . The developed model is dependent on the kinetic parameters and initial substrate concentrations. The results of sensitivity analysis are illustrated in Section 8.1.6. The sensitivity evaluation of this model with reference to biokinetic parameters is important from several viewpoints:

- Evaluate the process variables affecting the FBBR process such as influent contaminant concentration, biological parameters, and biomass concentration.
- Determine the parameters which have significance influence on the process dynamics which further provide relevant information on the parameters that can be adjusted, changed, or tuned to alter process conditions and improve the FBBR process efficiency.
- Estimate the accuracy and precision required for determination of each parameter for modeling and designing the process.
- Simplify the FBBR model to eliminate certain insignificant parameters or to incorporate other parameters for modifying or refining models.

CHAPTER 5

FLUIDIZED BED BIOADSORBER REACTOR DYNAMICS AND MODELING APPROACH

5.1 Significance of Mathematical Modeling

In order to obtain an optimal design of FBBR with GAC and sand for biological sulfate reduction process, modeling of the process is a necessary step to control and estimate the efficiency of system in pilot-scale and full-scale design. A mathematical model incorporates the estimation of overall biodegradation of sulfate in a FBBR process and predicts the effect of different parameters and operating conditions on the reactor performance. Moreover; a good mathematical model can be attributed to the estimation of the size of process reactor of interest, also a helpful tool for design engineers in order to up-scale the process. These phenomenological models economize time and effort involved in the design of process systems for water and wastewater treatment. Determination of model parameters and verification of model validity can be accomplished by well designed laboratory-scale experiments. The treatment process can be subsequently scaled up using dimensional analysis and similitude techniques to pilot-scale and eventually to full-scale. This approach would reduce the costs of full-scale design by several orders of magnitude. In the absence of such models, expensive and time consuming pilot-scale experiments are needed to establish the process feasibility. Thus, the philosophy of mathematical modeling is to

reduce the scope and magnitude of pilot-scale studies and to design full-scale processes economically and efficiently.

The formulation and implementation of mathematical models involves several important considerations. Firstly, the model must adequately represent the various phenomena that occur in the subprocesses. Secondly, determination of model parameters from experimental or theoretical methods must be possible. Thirdly, model verification or model refinement must be possible with the help of laboratory-scale experiments. Lastly, the model must be supported by reliable numerical computation techniques and adaptive softwares so that it is capable of providing good performance predictions/simulations of the process under a variety of operating conditions. This requirement emphasizes the importance of computationally efficient numerical techniques from the standpoints of consistency, stability, and convergence rates (Ravindran et al., 1996).

5.2 Process Bioadsorber Models

Ying and Weber (1979) developed a model including liquid film transfer, Monod kinetics for substrate utilization, intraparticle diffusion; and biomass buildup. The biofilm thickness was considered to be a function of both time and distance into the bed, and it kept growing until it reached a certain thickness that was maintained same by washing the media and air scouring. Their model was applicable to both

completely mixed and plug flow fluidized beds, and had good predictive capability for glucose and sucrose as the substrate.

Andrews and Tien (1981) proposed a model for the biological activity in fluidized beds based on completely mixed reactor assumption. The model included the following phenomenological assumptions: (i) Mass transfer resistance of the liquid film and diffusion resistance of the solid phase were negligible; (ii) organic material was assumed to be present in low concentrations to limit the biomass growth; and (iii) organic material consumption by biofilm was assumed to follow first-order kinetics. Their model exhibited satisfactory predictive capability with respect to the organic material they used at dilute concentrations. Nonetheless, due to the restrictive nature of the assumptions the applicability of the developed model to desulfurization process is limited. Subsequently, Speitel et al. (1987) and Chang and Rittmann (1987) proposed similar models as Andrews and Tien (1981). The Chang and Rittmann (1987) model was for a completely mixed reactor while the model of Speitel et al. (1987) was for plug-flow fixed reactor configuration. Both models were efficient in predicting the effluent concentration of a single substrate (phenol) in low concentrations.

Pirbazari and coworkers (Kim and Pirbazari, 1989; Ravindran et al., 1997) developed models for the recycle fluidized bed (RFB) adsorber as well as plug-flow

configurations. Their model incorporated additional features such as maximum biofilm thickness, will constitute the framework for the proposed model.

5.3 Proposed Model and Assumptions

The design of FBBR-GAC process necessitates prior modeling efforts in order to predict the performance, feasibility and cost of the process. In other words, the cost-effective design and economic performance evaluation of FBBR-GACs are essentially predicated upon the application of phenomenological models. A mathematical model that combines the estimation of overall removal of sulfate and biodegradation would be a useful tool for the design engineers in up-scaling the process from bench scale to pilot scale, and eventually full scale. A good model makes it possible to determine the size of the reactor of interest, and to predict the influence of changing the operating conditions on the reactor performance. The input parameters required by these predictive models are obtained from well-designed bench scale experiments, a technique that reduces the need for expensive and time-consuming pilot scale investigations. A mathematical model that has been proven to be successful facilitates pilot-scale investigations and a better understanding of various phenomena and associated interaction mechanisms among microorganisms, substrate and support particles.

The first step in developing a conceptual model involves understanding its essential components. Figure 5-1 presents a segment of a fluidized bed biofilm column

formulation for the model. As demonstrated, microorganisms attach themselves onto the activated carbon surface and begin to grow. The model described herein is distinct from earlier models and considers adsorption and biodegradation phenomena in biofilms, also the role of suspended biomass sheared off the bioparticles in the bulk liquid solution on the biodegradation of the contaminant(s) (Kim, 1987; Kim and Pirbazari, 1989; Ravindran et al., 1997). However, since sulfate is very weakly adsorbed onto the GAC, a modification of the current model by excluding the adsorption phenomenon is necessary.

The model discussed here incorporates the following fundamental mechanisms:

- Substrate transport from bulk liquid to biofilm through an external liquid film,
- Mass transfer and degradation within the biofilm,
- Growth of biofilm, and
- Suspended biofilm in bulk liquid solution

The important assumptions made for the development of the model are as follows:

1. The activated carbon particles are spherical and uniformly distributed
2. The FBBR has a uniform cross sectional area
3. The biofilm is homogeneous (its composition, density, porosity, and thickness do not vary as the biofilm gets thicker), and it grows with time
4. The biodegradation and substrate utilization as well as biomass growth and development can be represented by Monod kinetics

5. Biodegradation occurs in both the biofilm layer and bulk liquid phase, no biodegradation occurs in the activated carbon particle
6. The substrate concentration profile across the biofilm can be considered to be in pseudo-state even though the biofilm thickness varies as a function of time
7. The biofilm growth does not substantially affect the porosity of the fluidized bed, nor does it significantly affect the flow pattern of the liquid. Especially during early stages of FBBR run, change in bed porosity due to bacterial growth is negligible (this assumption is essential for model development)
8. The biomass loss due to fluid shear from high superficial velocities in the bed is negligible during the initial stages when the biofilm is still thin. However, the loss of biomass due to shear and decay balances the new biomass so that a steady-state maximum biomass concentration is reached within the bed
9. The mixing and fluidization in the FBBR is achieved by high recycle ratios and upflow velocities
10. The uptake of substrate by the activated carbon particle involves a one-step mass transport mechanism of liquid film mass transfer followed by biofilm diffusion.
11. The model accounts for the effect of substrate diffusion through the biofilm and an important aspect of the associated mass-transfer resistance.

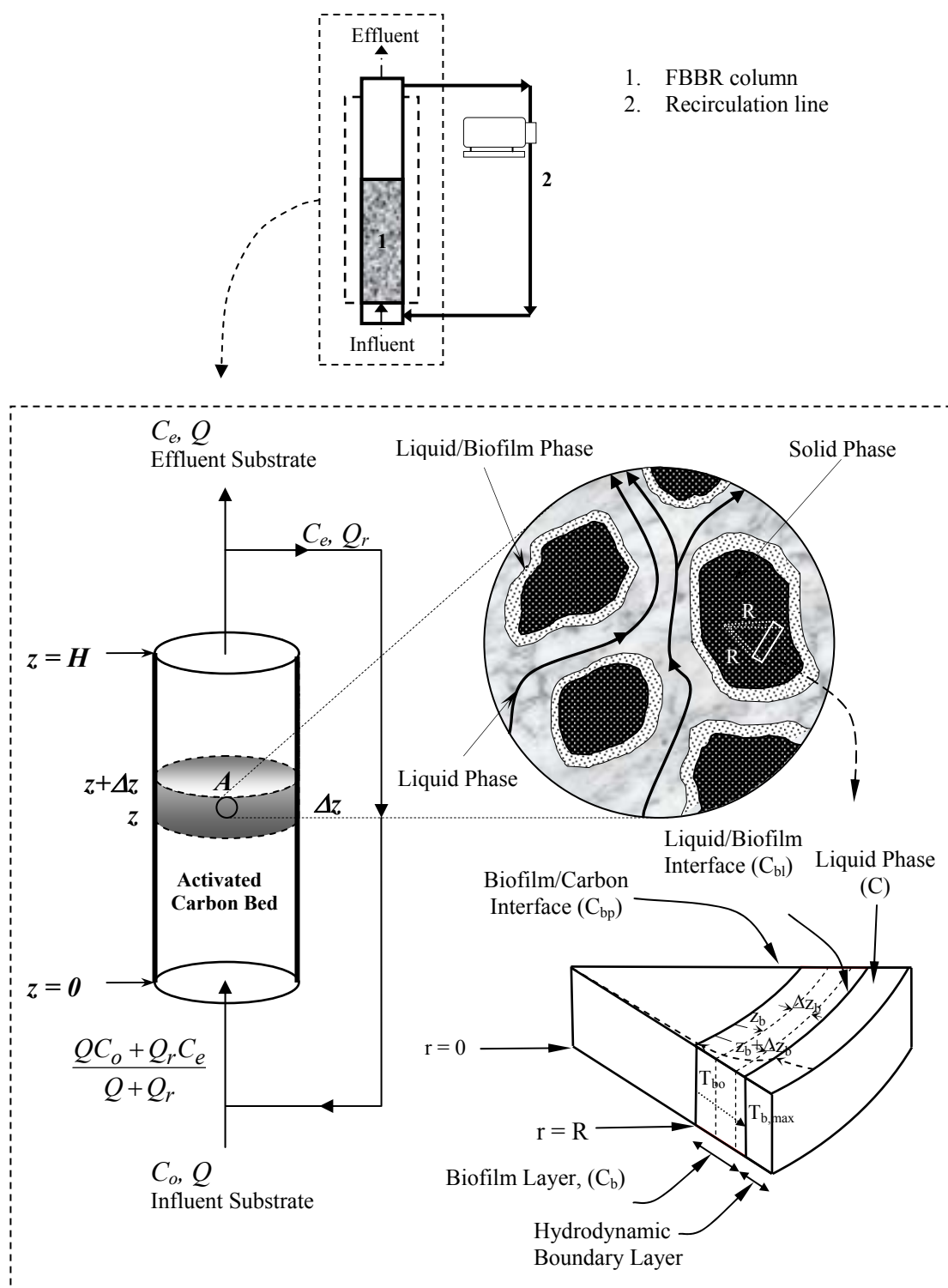


Figure 5-1 Schematic of a Fluidized Bed Bioadsorber Reactor (FBBR) Used in the Formulation of the Model

12. The following parameters regarded as constants:

D_z : axial substrate dispersion coefficient, (m^2/hr)

v_z : axial interstitial fluid velocity, (m/sec)

ε : fraction of volumetric space unoccupied by the adsorbent, (dimensionless)

V_{ip} : total carbon particle section volume, (m^3)

D_l : molecular liquid diffusivity, (m^2/hr)

D_b : diffusion coefficient in the biofilm, (m^2/hr)

M_b : biofilm density or biomass concentration in biofilm, (g/m^3)

T_{bo} : initial biofilm tickness, (m)

5.4 Model Formulation for the FBBR with Recycling

In the process of substrate uptake by a biofilm in media-supported reactors, substrate must first be transported from the bulk fluid into the biofilm. This process may occur in three steps:

1. Transport of substrate from the bulk liquid to the liquid-biofilm interface (external mass transfer).
2. Transport of substrate within the biofilm (internal mass transfer).
3. Substrate consumption reaction (biodegradation) within the biofilm and in the bulk liquid phase

The ensuing section describes each of these three steps with respect to their phases. Figure 5-1 depicts the schematic of the components that will be used for the formulation of the FBBR, and Figure 5-2 represents the schematic of a bioparticle.

1) Liquid Phase Material Balance

The material balance of the substrate (sulfate, ethanol) for any differential segment of the bed is represented by the following equation:

(Net rate of accumulation of substrate) = (Flux in) – (Flux out) – (Rate of substrate degradation)

$$\begin{aligned} \varepsilon A \Delta z \frac{\partial C(z,t)}{\partial t} = \varepsilon A [U(c)|_z - U(c)|_{z+\Delta z}] - k_{fc} a A \Delta z [C(z,t) - C_{bl}(z_b,t)] \\ - \frac{k M_l(z,t) C(z,t)}{K_s + C(z,t)} \varepsilon A \Delta z \end{aligned} \quad (5-1)$$

where

$$U(c) = -D_z \frac{\partial C}{\partial z} + v_z C \quad (5-2)$$

$$v_z = \frac{Q}{\varepsilon A} \quad (5-3)$$

k_{fc} = external substrate mass transfer coefficient, (m/hr)

A_{tp} = total surface area available for mass transfer, (m²)

A = cross section area of bed, (m²)

V_b = total bed volume, (m³)

a = ratio of total mass transfer area to bed volume, (m²/m³) = A_{tp}/V_b

Dividing Equation 5-1 by $\varepsilon A \Delta z$, and taking the limit as $\Delta z \rightarrow 0$:

$$\begin{aligned} \frac{\partial C(z,t)}{\partial t} = D_z \frac{\partial^2 C(z,t)}{\partial z^2} - v_z \frac{\partial C(z,t)}{\partial z} \\ - \frac{k_{fc} A_{tp}}{\varepsilon V_b} (C(z,t) - C_{bl}(z_b,t)) - \frac{k M_l(z,t) C(z,t)}{K_s + C(z,t)} \end{aligned} \quad (5-4)$$

where

A_{tp} = (total number of activated carbon) $\times$ (surface area of bioparticle)

$$A_{tp} = \left(\frac{3 W_{tp}}{4 \pi R^3 d_p} \right) [4 \pi (R + T_b)^2] \quad (5-5)$$

$$\frac{W_{tp}}{V_b d_p} = 1 - \varepsilon \quad (5-6)$$

where

W_{tp} = total dry weight of activated carbon, (g)

M_l = concentration of biomass in the liquid bulk phase, (g/m³)

R = activated carbon radius, (m)

d_p = dry density of activated carbon, (kg/m³)

T_b = biofilm thickness, (m)

by substituting the above equations into Equation 5-4:

$$\begin{aligned} \frac{\partial C(z,t)}{\partial t} = D_z \frac{\partial^2 C(z,t)}{\partial z^2} - v_z \frac{\partial C(z,t)}{\partial z} - \frac{3 k_{fc} (1 - \varepsilon) (R + T_b)^2}{\varepsilon R^3} (C(z,t) - C_{bl}(z_b,t)) \\ - \frac{k M_l(z,t) C(z,t)}{K_s + C(z,t)} \end{aligned} \quad (5-7)$$

The boundary conditions for this equation are as follows:

$$C(z, t=0) = 0 \quad (5-8)$$

$$\left. \frac{\partial C(z, t)}{\partial z} \right|_{z=H} = 0 \quad (5-9)$$

Equation 5-7 assumes there is no substrate in the liquid phase within the fluidized bed reactor at the time zero, and Equation 5-10 assumes that the substrate concentration at the reactor entrance is non-zero due to the recycled flow.

$$C(z = 0, t) = \frac{QC_o + Q_r C(z = H, t)}{Q + Q_r} \quad (5-10)$$

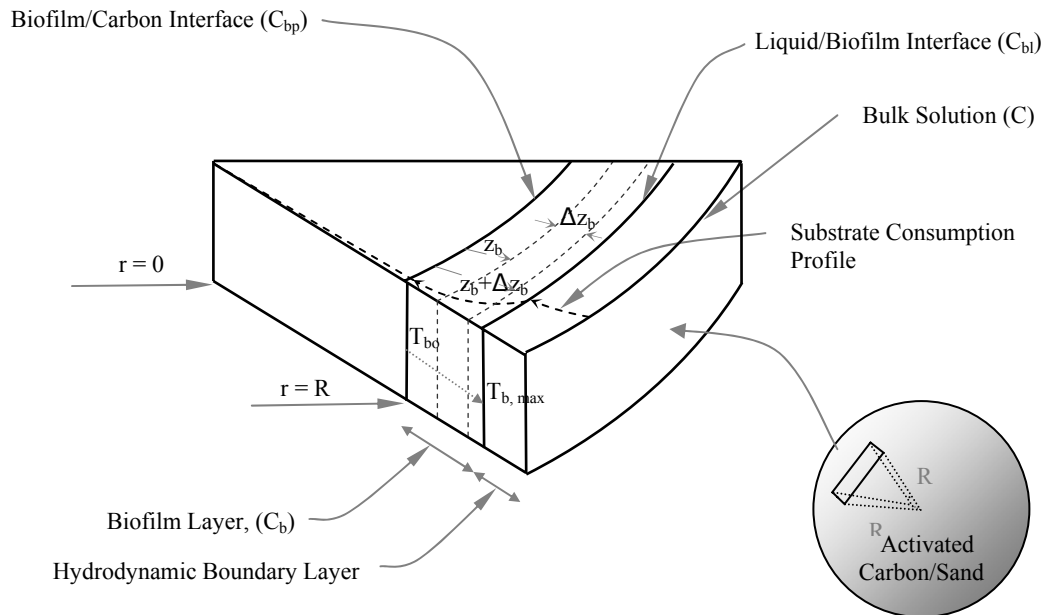


Figure 5-2 Substrate Transport into the Activated Carbon or Sand Bioparticle

2) Substrate Diffusion and Degradation in Biofilm

The substrate degradation within the biofilm layer was assumed to occur in the direction normal to the surface of the biofilm (z -direction, represented by z_b). Moreover, the substrate concentration gradient across the biofilm was assumed to

have reached pseudo steady state, consequently $\frac{\partial C_b(z, z_b, t)}{\partial t} = 0$:

$$\frac{\partial C_b(z, z_b, t)}{\partial t} = \frac{kM_b C_b(z, z_b, t)}{K_s + C_b(z, z_b, t)} - D_b \frac{\partial^2 C_b(z, z_b, t)}{\partial z_b^2} = 0 \quad (5-11)$$

where

D_b = biofilm substrate diffusion coefficient, (m²/hr)

C_b = substrate concentration in the biofilm, (g/m³)

M_b = Biomass concentration within the biofilm, (g/m³)

k = maximum rate of substrate utilization per unit mass of microorganism, (1/hr)

K_s = half saturation constant, (g/m³)

The boundary conditions are:

$$C_b(z, z_b = 0, t) = C_{bp}(z, t) \quad (5-12)$$

$$C_b(z, z_b = T_b, t) = C_{bl}(z, t) \quad (5-13)$$

$$C_b(z, z_b, t = 0) = C_{bo} \quad (5-14)$$

$$k_{jc}[C(z, t) - C_{bl}(z_b, t)] = D_b \frac{\partial C_b(z, z_b, t)}{\partial z_b} \Big|_{z_b=T_b} \quad (5-15)$$

$$\frac{\partial C_b(z, z_b = 0, t)}{\partial z_b} = 0 \quad (5-16)$$

where

C_{bo} = Initial biofilm concentration, (g/m³)

3) Biofilm Growth

The variation of the biofilm thickness with time and position could be represented by the following equation, wherein biofilm growth and decay are governed by Monod kinetics.

$$\frac{\partial T_b(z, t)}{\partial t} = \int_{z_b=0}^{z_b=T_b} \left(\frac{k C_{b,avg}(z, z_b, t)}{K_s + C_{b,avg}(z, z_b, t)} - k_d \right) dz_b \quad (5-17)$$

The initial and boundary conditions are as follows:

$$T(z, t = 0) = T_{bo} \quad (5-18)$$

$$T(z, t = t_{\max}) = T_{b, \max} \quad (5-19)$$

where

T_{bo} = initial biofilm thickness, (m)

$T_{b, \max}$ = maximum biofilm thickness, (m)

k_d = endogenous decay coefficient, (1/hr)

4) Suspended Biomass in Bulk Liquid Phase

A portion of the biomass which sloughed off the biofilm will become suspended and leave the bioadsorber with the effluent.

$$\begin{aligned} \frac{\partial M_l(z,t)}{\partial t} = D_z \frac{\partial^2 M_l(z,t)}{\partial z^2} - v_z \frac{\partial M_l(z,t)}{\partial z} \\ + \left(\frac{\mu_m C(z,t)}{K_s + C(z,t)} - k_d \right) (M_l(z,t) - M_b(z,t)) \end{aligned} \quad (5-20)$$

The initial and boundary conditions are as follows:

$$M_l(z, t = 0) = M_{lo} \quad (5-21)$$

$$M_l(z = 0, t) = \frac{Q M_o + Q_r M_l(z = H, t)}{Q + Q_r} \quad (5-22)$$

$$\left. \frac{\partial M_l(z,t)}{\partial z} \right|_{z=L} = 0 \quad (5-23)$$

where

M_{lo} = Initial biomass concentration in the bulk liquid phase
at time zero, (g/m³)

M_o = Influent biomass concentration, (g/m³)

The biomass lost to the bulk liquid phase can be expressed by the following equation:

$$M_{l,b}(z, t \geq t_{\max}) = \left(\frac{3(1-\varepsilon)}{\varepsilon} \right) \frac{M_b(T_b(z,t) - T_{b,\max})(R_p + T_{b,\max})^2}{R_p^3} \quad (5-24)$$

$$T_b(z, t = t_{\max}) = T_{b, \max} \quad (5-25)$$

where

$M_{l,b}$ = Biomass concentration that is lost from biofilm to liquid bulk phase, (g/m³)

For recycle fluidized beds, the superficial flow velocity, $v_s = v_z - v_r$ where $v_s = \frac{Q}{A}$,

$v_r = \frac{Q_r}{A}$, and A is the cross sectional area of fluidized bed and Q is the influent

flowrate. Furthermore, C_{in} is different from the influent concentration, C_o , since

the feed is diluted with recycled effluent; $C_{in} = \frac{(v_s C_o + v_r C_e)}{v_z} = \frac{(Q C_o + Q_r C_e)}{(Q + Q_r)}$ in

which C_{in} is the substrate concentration at entrance $z=0$ of fluidized bed and C_e

is the effluent substrate concentration at exit $z=H$. Therefore, in all equations it

should be assumed that $v_z = \frac{Q + Q_r}{A}$ and $C_{in} = \frac{Q C_o + Q_r C_e}{Q + Q_r}$.

5.5 Numerical Solution for the Model

The Equations 5-7, 5-11, and 5-17 used in this work to describe the biodegradation of FBBR process and biofilm growth can not be solved analytically, and numerical solutions are therefore employed. Traditionally, the differential equations are solved using the finite difference method (FDM). However, the Runge-Kutta (RK) method is reported to be more efficient in handling differential equations governing momentum, heat, and mass transfer. The Runge-Kutta method is now a popular

method for numerical solution of ordinary differential equations (ODEs). The method is relatively stable and hence particularly suitable for the simulation of long-period evolution in FBBR system. MATLAB partial differential equation (PDE) solvers and RK method were used successfully to solve the model equations. For brevity, a short discussion about the PDE solver and the Runge-Kutta method is provided below.

The PDE solvers can solve the systems of partial differential equations (Equation 5-7) in one spatial variable z and time t , of the following form where $t_0 \leq t \leq t_f$, and $a \leq z \leq b$, and $a \geq 0$ (Skeel et al., 1990):

$$r\left(z, t, f, \frac{\partial f}{\partial t}\right) \frac{\partial f}{\partial t} = z^{-n} \frac{\partial}{\partial z} \left(z^n g\left(z, t, f, \frac{\partial f}{\partial t}\right) + h\left(z, t, f, \frac{\partial f}{\partial t}\right) \right) \quad (5-26)$$

where n can be 0, 1, or 2, corresponding to slab, cylindrical, or spherical symmetry, respectively, and consequently n was considered 2 for this study due to the spherical symmetry of the adsorber particle. In Equation 5-26, $g(z, t, f, \partial f/\partial z)$ is a flux term, and $h(z, t, f, \partial f/\partial z)$ is a source term. The coupling of the partial derivatives with respect to time was restricted to multiplication by a diagonal matrix $r(z, t, f, \partial f/\partial z)$, and at least one parabolic equation was maintained for this equation. The diagonal elements of this matrix were either identically zero or positive. An element of r that

corresponded to a parabolic equation could vanish at isolated values of z if they were mesh points.

At the initial time $t = t_0$, for all z the solution components should satisfy initial conditions of the following form.

$$f(z, t_0) = f_0(z) \quad (5-27)$$

At the boundary of $z = a$, or $z = b$, for all t the solution components should satisfy the boundary condition of the following form:

$$h(z, t, f) + k(z, t)g\left(z, t, f, \frac{\partial f}{\partial z}\right) = 0 \quad (5-28)$$

Where $k(z, t)$ is a diagonal matrix with elements that are either identically zero or never zero. It should be noted that the boundary conditions were expressed in terms of the flux g rather than $\partial f / \partial z$, additionally, of the two coefficients, only h could depend on f (Skeel et al., 1990).

Butcher's (1964) fifth-order Runge-Kutta method was used to solve the substrate diffusion and degradation equation in the biofilm (Equation 5-11). This method is briefly described as follows:

The Runge-Kutta algorithm solves a differential equation numerically, and is known to be very accurate and well-behaved for a wide range of problems. This method achieves the accuracy of a Taylor series approach without requiring the calculation of higher derivatives. Many variations exist but all can be cast in the generalized form of the following equation.

$$y_{i+1} = y_i + \phi(x_i, y_i, h)h \quad (5-29)$$

where $\phi(x_i, y_i, h)h$ is called an increment function, which can be interpreted as a representative slope over the interval. The increment function can be written in general form as:

$$\phi = a_1 k_1 + a_2 k_2 + a_3 k_3 + \cdots + a_n k_n \quad (5-30)$$

where the a 's are constants and the k 's are

$$k_1 = f(x_i, y_i) \quad (5-31)$$

$$k_2 = f(x_i + p_1 h, y_i + q_{11} k_1 h) \quad (5-32)$$

$$k_3 = f(x_i + p_2 h, y_i + q_{21} k_1 h + q_{22} k_2 h) \quad (5-33)$$

·
·
·

$$k_n = f(x_i + p_{n-1} h, y_i + q_{n-1,1} k_1 h + q_{n-1,2} k_2 h + \cdots + q_{n-1,n-1} k_{n-1} h) \quad (5-34)$$

where the p 's and q 's are constants, and the k 's are recurrence relationships. Because each k is a functional evaluation, this recurrence makes RK methods efficient for computer calculations. Various types of RK methods can be devised by employing different numbers of terms in the increment function as specified by n . For this study the Butcher's (1964) fifth-order RK method was used ($n=5$) to solve the differential equations. For the present case, the following fifth-order formula (Equation 5-35) was used to solve the differential equations:

$$y_{i+1} = y_i + \frac{1}{90}(7k_1 + 32k_3 + 12k_4 + 32k_5 + 7k_6)h \quad (5-35)$$

where

$$k_1 = f(x_i, y_i) \quad (5-36)$$

$$k_2 = f(x_i + \frac{1}{4}h, y_i + \frac{1}{4}k_1h) \quad (5-37)$$

$$k_3 = f(x_i + \frac{1}{4}h, y_i + \frac{1}{8}k_1h + \frac{1}{8}k_2h) \quad (5-38)$$

$$k_4 = f(x_i + \frac{1}{2}h, y_i - \frac{1}{2}k_2h + k_3h) \quad (5-39)$$

$$k_5 = f(x_i + \frac{3}{4}h, y_i + \frac{3}{16}k_1h + \frac{9}{16}k_4h) \quad (5-40)$$

$$k_6 = f(x_i + h, y_i - \frac{3}{7}k_1h + \frac{2}{7}k_2h + \frac{12}{7}k_3h - \frac{12}{7}k_4h + \frac{8}{7}k_5h) \quad (5-41)$$

In this method, first slopes for all variables at the initial value are developed. These slopes (a set of k_i 's) are then used to make predictions of the dependent variable at

the mid point of the interval. These midpoint values are in turn used to compute a set of slopes at the midpoint (the k_2 's). These new slopes are then taken back to the starting point to make another set of midpoint predictions that lead to new slope predictions at the midpoint (the k_3 's). These are then employed to make predictions for the next mid point and finally the last set of k 's are used for predictions at the end of the interval that are used to develop slopes at the end of the interval. Finally, the k 's are combined into a set of increment functions and brought back to the beginning to make the final prediction.

5.6 Model Parameters

5.6.1 Biokinetic Parameters

Biokinetic parameters were determined by the linear regression of Equations 4-9, and 4-11 as elaborately described in Section 4.3. Half-velocity constant, K_s , and maximum substrate utilization rate, k parameters were determined by plotting the

term $\frac{M\theta}{(C_o - C)}$ versus $\frac{1}{C}$ from Equation 4-11. While, yield coefficient, Y and

endogenous decay coefficient, k_d parameters were further obtained by plotting $\frac{1}{\theta}$

versus $\frac{(C_o - C)}{M\theta}$ from Equation 4-9.

5.6.2 External Film Transfer Coefficient and Liquid Diffusivity

The external film transfer coefficient or reactor substrate mass transfer coefficient, k_{fc} , can be evaluated from the hydrodynamic characteristics of the fluid-particle system using the following correlation proposed by Wakao and Funazkri (1978):

$$Sh = 2 + 1.1 Re^{1/2} Sc^{1/3} \quad (5-42)$$

where

Sh = Sherwood number for the activated carbon, (dimensionless)

Re = Reynolds number for the activated carbon, (dimensionless)

Sc = Schmidt number for the activated carbon, (dimensionless)

In this correlation, the Sherwood number is a dimensionless number used in mass transfer operation. It represents the ratio of mass diffusivity to molecular diffusivity. The Raynolds number is the ratio of inertial forces to viscous forces and it provides a criterion for determining dynamic similitude (Rott, 1990). The Schmidt number is the ratio of momentum diffusivity to mass diffusivity, and is used to characterize fluid flows in where processes of momentum and mass diffusion convection simultaneously exist.

These dimensionless groups Re , Sc , and Sh are defined by the equations:

$$Sh = \frac{2R_p}{D_l} k_{fc} \quad (5-43)$$

$$\text{Re} = \left(\frac{2R_p}{D_l Sc} \right) v_z \quad \text{or} \quad \text{Re} = \left(\frac{2R_p d_l}{\mu} \right) v_s \quad (5-44)$$

$$Sc = \frac{\mu}{d_l D_l} \quad (5-45)$$

where

D_l = Free liquid diffusivity, (m²/sec)

d_l = Fluid density, (kg/m³)

μ = fluid viscosity, (kg/m.sec)

v_s = superficial fluid velocity in the axial direction, (m/sec)

v_z = interstitial fluid velocity in the axial direction, (m/sec)

The external film transfer coefficient, k_{fc} can be expressed as Equation 5-46 by substituting Equations 5-43, 5-44 and 5-45 into the correlation proposed by Wakao and Funazkri, 1978 (Equation 5-42):

$$k_{fc} = \frac{D_l}{R_p} + 0.778 \left(\frac{v_s}{R_p} \right)^{1/2} \left(\frac{d_l}{\mu} \right)^{1/6} D_l^{2/3} \quad (5-46)$$

5.6.3 Biofilm parameters

The important biofilm parameters for bioadsorber modeling are the maximum biofilm thickness, $T_{b,max}$, and the biofilm density, M_b . Estimates of $T_{b,max}$ were

obtained during the steady-state stages of bioadsorber studies, according to the relation:

$$T_{b,\max} = \frac{\Delta V}{4\pi R_p^2 N_p} \quad (5-47)$$

where

ΔV = volume of bed expansion due to growth of biomass, (m³)

R_p = activated carbon particle radius, (m)

N_p = Number of activated carbon particles, (dimensionless)

The parameter M_b was determined from the mass of the dry biomass, W_b , and the estimated value of $T_{b\max}$, using the relation:

$$M_b = \frac{W_b}{A_{tp} T_{b,\max}} \quad (5-48)$$

where

A_{tp} = total surface area of carbon particles, $N_p A_p$, (m²)

W_b = activated carbon weight with biofilm before drying, (weight of virgin GAC)

5.6.4 Biofilm Diffusion Coefficient

The biofilm diffusion coefficient D_b for the brine concentrate was determined from the free liquid diffusivity D_l by using the ratio $D_b/D_l = 0.8$, as suggested by Williamson and McCarty (1976). The value of D_l was estimated from the correlation adapted from Perry and Green (1984):

$$D_l = \frac{RT}{F^2 Z_l} \left(\frac{\nu_1 + \nu_2}{\nu_1} \right) \left(\frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} \right) \quad (5-49)$$

where

F = Faraday's constant, 96489 coul. (g.equiv.)⁻¹

R = gas constant, 8.3145 J/mol.K

T = absolute temperature, K

Z_l = valency of metal ion

ν_l, ν_l = numbers of the metal ions and the corresponding anions, respectively

λ_l, λ_2 = limiting equivalent conductances of the metal ion and the corresponding anions, respectively, mho.equiv⁻¹

5.6.5 Axial Substrate Dispersion Coefficient

Axial substrate dispersion coefficient D_z was determined using the correlation of Chung and Wen (1968), as shown in the following equations:

$$Ga = \frac{8R_p^3 d_l g (d_p - d_l)}{\mu^2} \quad (5-50)$$

$$Re_{mod} = (33.7^2 + 0.0408Ga)^{1/2} - 33.7 \quad (5-51)$$

Galileo number (Ga) is a dimensionless number proportional to ratio of gravity and buoyant forces to viscous forces.

The parameter D_z was finally estimated from the relation;

$$\frac{D_z d_l P_a}{\mu} = \frac{Re}{0.20 + 0.011 Re^{0.48}} \quad (5-52)$$

where

$$P_a = \frac{Re_{mod}}{Re} \quad (5-53)$$

P_a = adsorber parameter based on hydrodynamic regime, (dimensionless)

D_z = hydrodynamic axial substrate dispersion coefficient, (m²/sec)

Re = Reynolds number for fluid flow around the activated carbon particle, (dimensionless)

Re_{mod} = modified Reynolds number for activated carbon column, (dimensionless)

Ga = Galileo number for activated carbon bed, (dimensionless)

g = gravitational acceleration, (m²/sec)

5.7 Dimensional Analysis, Similitude, and Up-Scaling Process

Scaling of processes can be accomplished by dimensional analysis and similitude techniques. Dimensional analysis is a powerful tool for dealing with complex physical, chemical and biological systems, and can describe the phenomenological aspects of scaling in relatively simple relationships. Similitude, on the other hand, refers to similarities between two systems from geometric, phenomenological, or dynamic points of view, so that characteristics of a small-scale system can be related to those of a large-scale system by conversion factors. Similitude is generally more powerful a tool than dimensional analysis because it can handle more than one unit, and can also account for dimensionless quantities (Den and Pirbazari, 2002; Badriyha and Ravindran, 2003).

In biological processes employing microporous adsorbents as media such as GAC, the kinetics of film transfer, biodegradation, and adsorption (excluded for this study) must be considered. Monod biokinetic coefficients (k and K_s) are intrinsic properties of microbial culture and are therefore independent of geometric and dynamic properties; therefore, following properties have identical values regardless of scale: (i) influent concentration; (ii) particle density and packing porosity; and (iii) Monod kinetic constants.

Assuming that the bioadsorber model provides satisfactory predictions for the small-scale process, a reliable performance evaluation and design for the large-scale

process can be obtained by comparing the five dimensionless groups described below. Setting the values of some of these groups equal for small-scale and large-scale bioadsorbers, certain scaling relationships among major design variables can be established. The important design and operation parameters for scaling relate to the following aspects: (i) particle size, (ii) reactor dimensions, and (iii) biodegradation kinetics.

Badriyha et al. (2003) indicated that the dimensionless parameters recognized from their model equations ofalachor removal process suggest that the bioadsorber reactor dynamics can be characterized by the following dimensionless groups defined as below: Sherwood number, Sh Peclet number, Pe Stanton number, St Damköhler number, Da , and biochemical reactivity modulus, Er .

$$\text{Sherwood number, } Sh = \frac{k_{fc} R_p}{D_b} \quad (5-54)$$

$$\text{Stanton number, } St = \frac{k_{fc} H}{R_p v_z} \quad (5-55)$$

$$\text{Peclet number, } Pe = \frac{H v_z}{D_z} \quad (5-56)$$

$$\text{Biochemical reactivity modulus, } Er = \frac{D_b Da_{ov} t_c}{R_p^2} \quad (5-57)$$

where

$$Da = \frac{\delta R_p^2}{D_b} \quad (5-58)$$

$$\delta = \frac{M_b k}{K_s} \quad (5-59)$$

$$\frac{1}{Da_{ov}} = \frac{1}{Da_s} + \frac{1}{Da_f} \quad (5-60)$$

Da_s = Damköhler number for surface diffusivity, (dimensionless)

Da_f = Damköhler number for film transfer, (dimensionless)

Da_{ov} = Damköhler number for overall transport, (dimensionless)

In the definition of biochemical reactivity modulus, E_r the term t_c is referred to the critical time of contact for the occurrence of biochemical reaction and mass transfer. It represents the ratio of the extent of biochemical reaction to the mass-transfer rate in the bioactive adsorber. The Damköhler numbers (Da_s , and Da_f) generally denote the ratios of reaction rates to the mass transport rates for contaminants, and each specific Damköhler number represents the ratio of rate of biochemical reaction to the rate of the corresponding transport mechanism. The Damköhler number is used as design parameter for many chemical and biological processes. A high Damköhler number signifies that the reaction rate corresponding to a certain component exceeds the mass-transfer rate, and that mass-transfer might be a rate-limiting factor. A low Damköhler number has exactly the reverse connotation, when reaction rate might be the limiting factor (Badriyha et al., 2003).

The relationship between particle size and biodegradation kinetics is established by comparisons of reactivity modulus and overall Damköhler numbers corresponding to

small-scale and large-scale processes. It is indeed an important premise that all the five dimensionless groups cannot be held simultaneously constant for developing scaling criteria because a few of them might possibly control the ultimate design. Nevertheless, certain minimum or maximum values of dimensionless groups must be maintained to accomplish a feasible, practical, and near-optimal design. As large-scale processes are usually designed from experimental results corresponding to small-scale versions, incorporation of appropriate safety criteria to guarantee desired performance levels in large-scale systems is an important consideration. In order to meet this objective, the following equality or inequality criteria must be satisfied:

$$St_L > St_S, Pe_L < Pe_S, Er_L > Er_S, \text{ and } Da_{ov,L} = Da_{ov,S}$$

In the scaling relationships, the subscripts S and L represent the small-scale and large-scale systems, respectively. The Stanton number criterion will ensure that the large-scale bioadsorber does not undergo channeling without adequate film transfer. The Peclet number criterion may be significant only when axial dispersion effects cannot be neglected. The biochemical reactivity modulus criterion will insure sufficient biodegradation in the large-scale reactor to accomplish the desired level of contaminant removal (Badriyha et al., 2003). The important scaling variables are bioadsorber dimensions (length and diameter), packing medium particle sizes, and hydraulic retention time (HRT).

This research study represents biodegradation of a non-adsorbing contaminant (sulfate) with very low surface diffusivity; therefore, biodegradation is the predominant mechanism and the removal process is biokinetically rate-limiting. The scale-up relationship for this case can be developed by equating the biochemical reactivity modulus

$$\frac{HRT_L}{HRT_S} = \left(\frac{R_{p,L}}{R_{p,S}} \right)^2 \left(\frac{Da_{ov,S}}{Da_{ov,L}} \right) \quad (5-61)$$

If the Damköhler number is held constant for upscaling, then the HRT is proportional to the square of the particle size. However, the variation in the particle sizes may also reflect on the values of Da_{ov} ; since the film transfer rate, k_{fc} and the biofilm density, M_b could sometimes be particle size-dependent. If the Damköhler number and surface diffusivity are both independent of particle size, the scale-up relationship reduces to (Den and Pirbazari, 2002):

$$\frac{HRT_L}{HRT_S} = \left(\frac{R_{p,L}}{R_{p,S}} \right)^2 \quad (5-62)$$

5.8 FBBR Process Modeling and Protocol

The following protocol outline, presented in Figure 5-3 illustrates the procedures that were taken to model and design a FBBR process and expand it to the pilot- and full-scale fluidized bed bioadsorber reactor model.

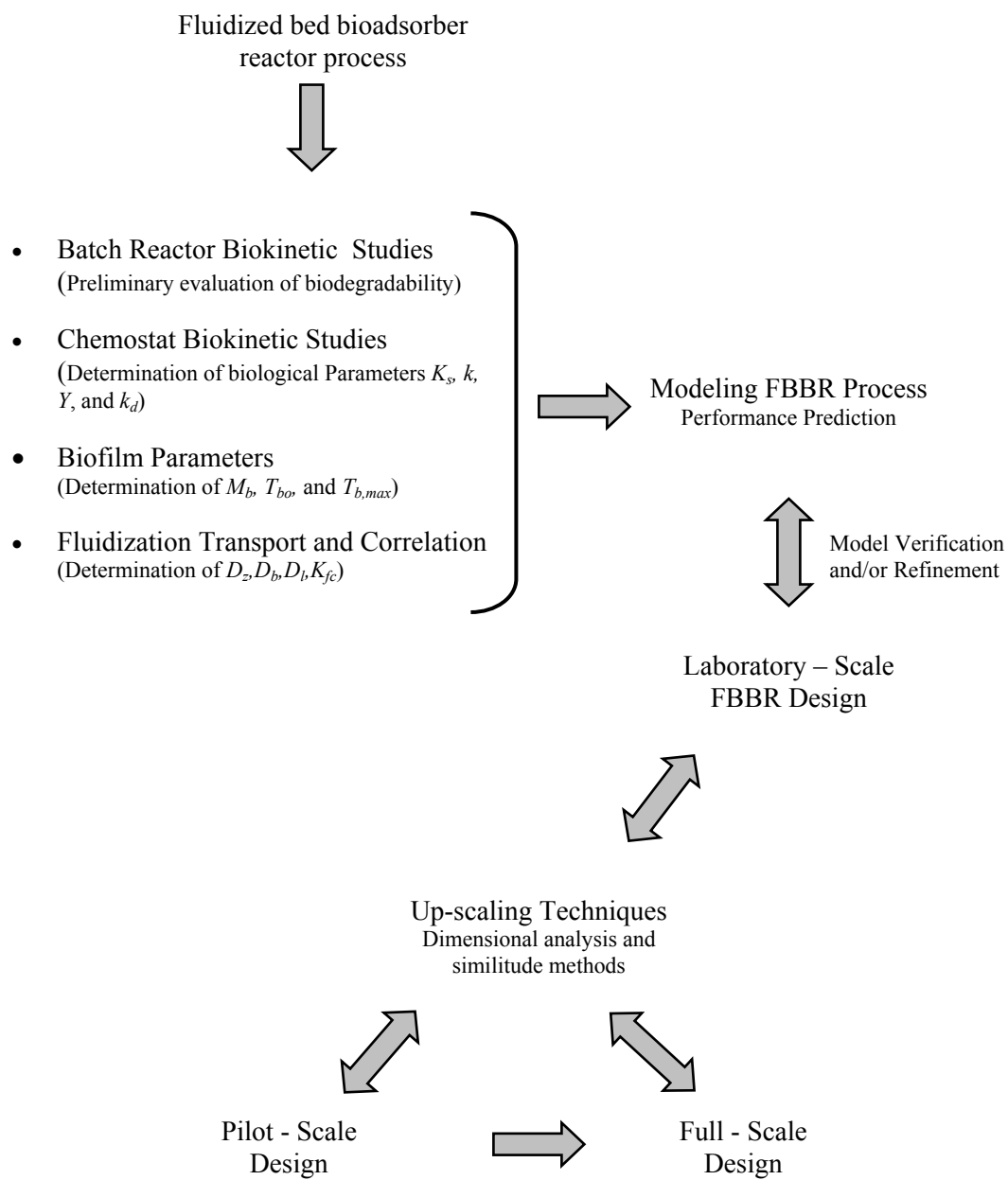


Figure 5-3 Protocol for Modeling, Design, and Scale-up of the Fluidized Bed Bioadsorber Reactor with Recycle

5.9 Model Sensitivity Analysis

Sensitivity studies can be conducted to predict the overall performance of fluidized bed bioadsorber reactor. The model developed for predicting and simulating the dynamics of fluidized bed bioadsorber reactor is dependent on several parameters, including those representing biofilm transport, and biodegradation in the microbial film. Some parameters have a profound influence on the performance dynamics of FBBR system, while others may have relatively insignificant effects. Evaluating the sensitivity of the model to each of these parameters is important from several points of view as follows: Firstly, the analysis can provide an estimate of accuracy and precision required for the determination of each parameter for modeling and designing the process. The parameters that have a significant influence on the FBBR dynamics must be determined with greater accuracy, while those that do not affect the dynamics to a large extent maybe estimated by simpler experimental methods or correlation techniques. Secondly, the technique is useful in model simplification to eliminate certain insignificant parameters or to incorporate other parameters for modifying or refining the model. However, these procedures must be carefully performed to avoid oversimplification or complication of the existing model. Lastly, the method provides more information on the behavioral patterns of process dynamics under variety of operating conditions. The parameters which were investigated are biokinetic parameters K_s , μ_m , Y , and k_d . These parameters were increased or decreased separately 30% in the simulation to investigate the influence

of each parameter on the effluent substrate concentration profile and system performance.

CHAPTER 6

MATERIALS AND METHODS

6.1 Materials

6.1.1 Brine Specification and Chemicals

The waste product of reverse osmosis process referred to as brine reject or concentrate is comprised of materials rejected by the membrane filter. The synthetic brine concentrate made for this research comprised of compounds specified in Table 6-3. Alkalinity in the form of sodium bicarbonate was added as needed to buffer the reactor.

The mixed microbial culture used for this study was obtained from the activated sludge tank of wastewater treatment plant. The GAC employed in the fluidized bed reactor studies and biofilter was coconut-shell-based activated carbon manufactured by Carbon Activated Corporation (Compton, CA). The effective particle size was 8-10 U.S. mesh, corresponding to mean geometric diameter of 1.85 mm.

The sand media employed in the fluidized bed reactor studies was Ottawa sand (Silicon Dioxide; Silica, Quartz) with 20-30 U.S. mesh size from VWR Scientific Products (San Diego, CA).

6.2 Experimental Methods

6.2.1 Completely Mixed Batch Biokinetic Reactor (CMBR)

The completely mixed batch system was specially designed for biokinetic studies. The schematic of the designed system is illustrated in Figure 6-1. The experimental setup consisted of a glass reactor of capacity 2.5 liters, fitted with two glass tubes, one of which was used for sampling purposes and the other employed to vent the produced biogas of the reactor. All the glassware were sterilized with an autoclave prior to use. The liquid phase in the reactor was of volume 1.2 liters, consisting of the feed mixed with nutrient solution and with acclimated microorganisms obtained from the wastewater treatment plant. After the addition of the nutrient solution to the feed (synthesized brine), 25 mL concentrated biomass was added to each CMBR system. Feed solution, nutrients, and microbial population were similar to those employed in the fluidized bed reactor studies.

The initial biomass concentration, mixed liquor suspended solids (MLSS), for all reactors was maintained at 95-100 mg/L with mixed liquor volatile suspended solids (MLVSS) of 90-95 mg/L. The reactor contents were purged with nitrogen gas to eliminate dissolved oxygen and sealed air-tight with rubber stoppers to maintain anaerobic conditions. The reactor temperature was controlled by a water bath made of a Plexiglas tank of dimensions 15" × 10" × 10" equipped with a submersible heater, thermometer and a recirculation pump, as shown in Figures 6-1 and 6-2. The contents of the reactor were constantly agitated and mixed by means of a magnetic

stirrer. The biogas from the reactor was passed through zinc acetate solution in a glass reservoir for scrubbing out the generated hydrogen sulfide. Samples were periodically taken every six hours from the reactor and refrigerated at 10°C prior to analysis for sulfate, acetate, and ethanol concentrations.

Figure 6-2 depicts a photograph of the CMBR system operated to study the kinetics of sulfate reduction. The nutrient composition used in these CMBR biokinetic studies are summarized in Table 6-1.

Table 6-1 Nutrient Composition Used in the CMBR Biokinetic Studies

Constituent	Concentration (mg/L)	Chemical form
Na ⁺	530	Na ₂ SO ₄ , NaHCO ₃ , NaNO ₃
Ca ²⁺	350	CaCl ₂ 2H ₂ O
Mg ²⁺	140	MgCl ₂ 6H ₂ O
PO ₄ ³⁻	12	NaHCO ₃
NO ₃ ⁻	5	KH ₂ PO ₄
Ba ²⁺	0.5	BaCl ₂
SO ₄ ²⁻	700	NaNO ₃
Fe ²⁺	1	Na ₂ SO ₄
Alkalinity	430	FeSO ₄ 7H ₂ O
Ethanol (C/S = 0.8)	358.74	C ₂ H ₅ OH
Ethanol (C/S = 1.0)	448.42	C ₂ H ₅ OH
Ethanol (C/S = 1.2)	538.1	C ₂ H ₅ OH
Ethanol (C/S = 1.4)	627.79	C ₂ H ₅ OH
Amino Acid	14.16	
Micro nutrients	2.2	

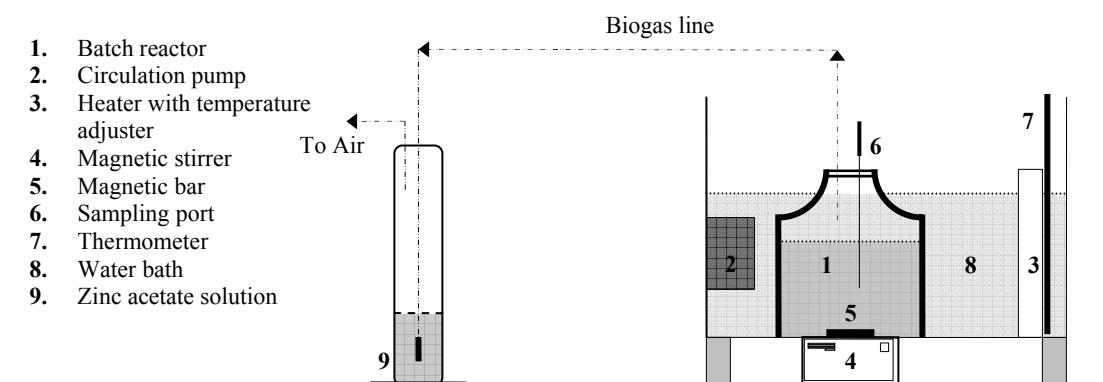


Figure 6-1 Schematic of the Experimental CMBR System for Biokinetic Studies

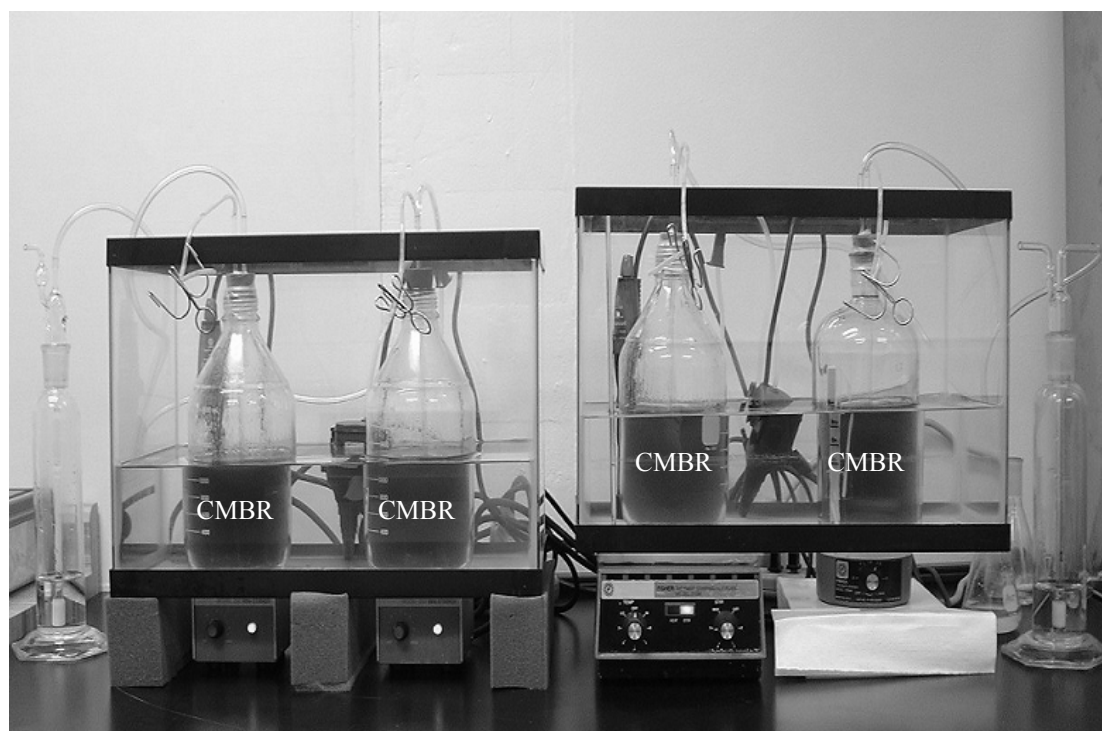


Figure 6-2 Photograph of the Experimental CMBR System for Biokinetic Studies

6.2.2 Chemostat System

The chemostat system operated for this study consisted of a 4-liter Pyrex® cylindrical beaker with an operating volume of 2 liters, a glass lid sealed with an O-ring and a water jacket to maintain the temperature as illustrated in Figure 6-3. The feed solution containing the simulated brine concentrate and ethanol as carbon source was injected into the reactor through diaphragm pump. The chemostat system was equipped with ORP and DO meter as well. The pH was maintained at 7.5 ± 0.1 by a pH controller which automatically added sterile, oxygen-free, 0.5N NaOH solutions. The temperature was maintained at 30°C by means of a waterbath system.

The reactor was fed with acclimated mixed culture of SRBs obtained from the fluidized bed reactor operated for process evaluation study. Dissolved oxygen (DO) concentration, and the oxidation-reduction potential (ORP) were continuously monitored. DO was maintained zero and ORP varied from -280 to -430 mv throughout the study. The chemostat was also equipped with a speed-control stirrer in order to mix the chemostat content and enhance the biochemical reactions. Figure 6-3 illustrates a schematic of the chemostat system employed for the estimation of biokinetic parameters.

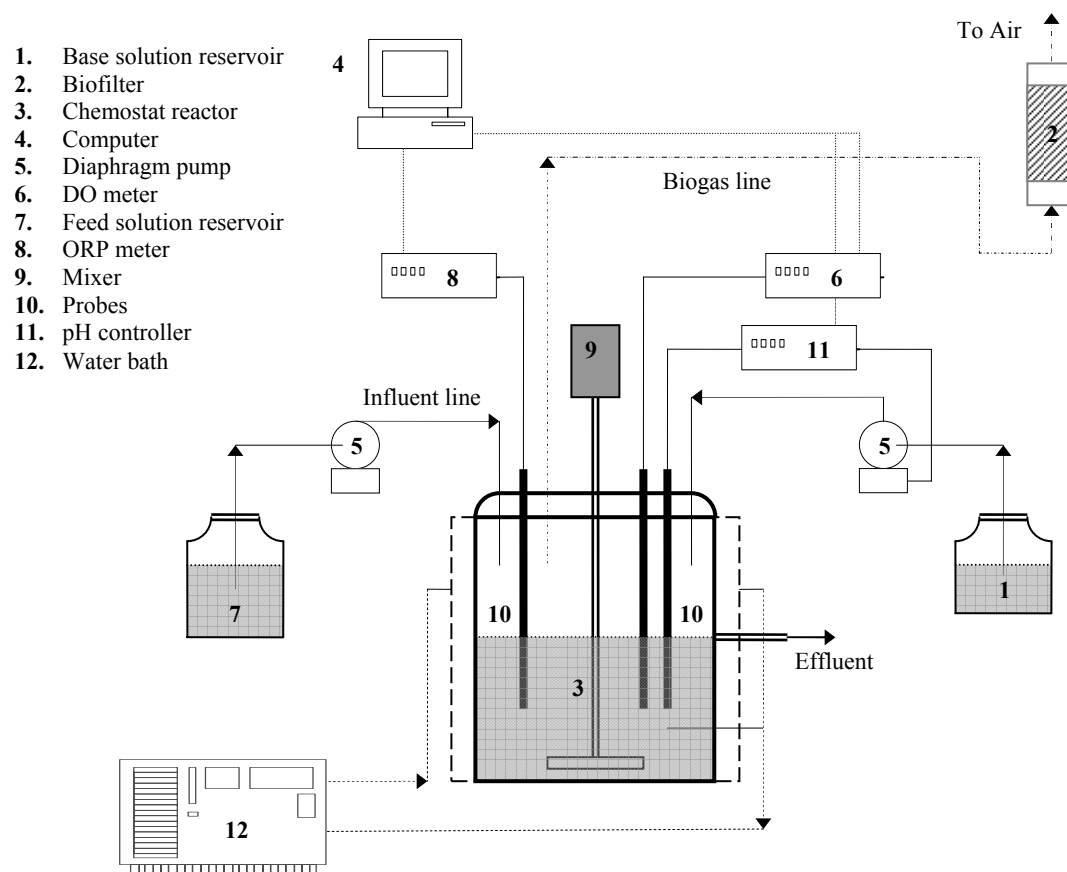


Figure 6-3 Schematic of Experimental Chemostat System for Continuous Flow Biokinetic Studies

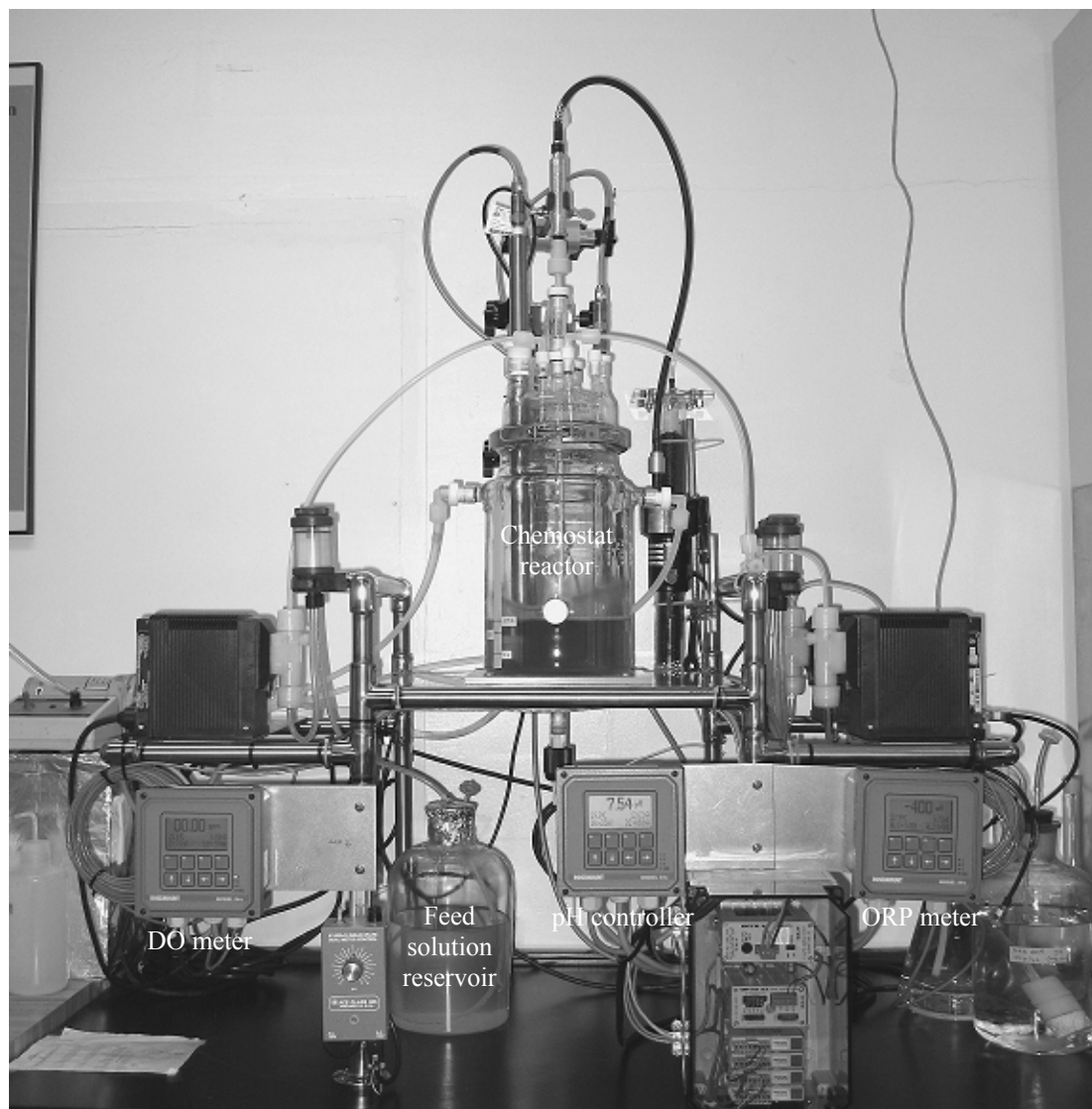


Figure 6-4 Photograph of Experimental Chemostat System for Continuous Flow Biokinetic Studies

6.2.3 Fluidized Bed Bioadsorber Reactor System

Fluidized bed bioadsorber reactor characteristics are summarized in Table 6-2 for the FBBR–GAC and the FBBR–sand columns. FBBR system used for this study was equipped with pH controller linked to the pH pump to maintain a specific pH.

Diaphragm pumps for nutrient, acid or base injection and centrifugal pump with variable speed for recirculation were used. A waterbath was used to maintain constant temperature. The reservoirs for the nutrient, ethanol and acid solutions were all made of glassware. Figure 6-5 illustrates a schematic of the fluidized bed bioadsorber reactor used in this study for biological reduction of sulfate using GAC and sand as reactor media. The influents used for all the reactors were purged with nitrogen gas for the removal of dissolved oxygen, and further the system was maintained perfectly sealed to prevent any penetration of oxygen, so that anaerobic conditions could be maintained in CMBR, chemostat, and FBBR systems.

Table 6-2 Fluidized Bed Bioadsorber Reactor Characteristics

Specifications	FBBR-GAC Process Evaluation (Column1)	FBBR-GAC (Columns 2, 4)	FBBR-sand (Column 3)
Retention time (hr)	2.5 – 2.8	2.7 - 2.8	0.7 - 0.8
Influent flow rate (mL/min)	6	6	6
Feed (mL/min)	4	4	4
Carbon source (mL/min)	2	2	2
Active volume (L)	0.9	0.9	0.28
Active height (inch)	31.1-34.1 (22.2" without expansion)	34.1 (22.2" without expansion)	9.5 (7.0" without expansion)
Expansion rate (%)	40	40	26
Temperature (°C)	30	30	30
Medium specifications	330 ~ 350 g GAC (US mesh 8-10; 2.00 ~ 2.38 mm)	330 ~ 350 g GAC (US mesh 8-10; 2.00 ~ 2.38 mm)	330 ~ 350 g sand (US mesh 20-30; 0.6 ~ 0.84 mm)
Recirculation rate (L/min)	1.55	1.55	1.55
Electron donor and carbon source	Ethanol	Ethanol	Ethanol
Carbon/sulfur ratio	Variable (0.8-1.2)	1	1
pH	Variable (6.5-7.5)	7.5	7.5

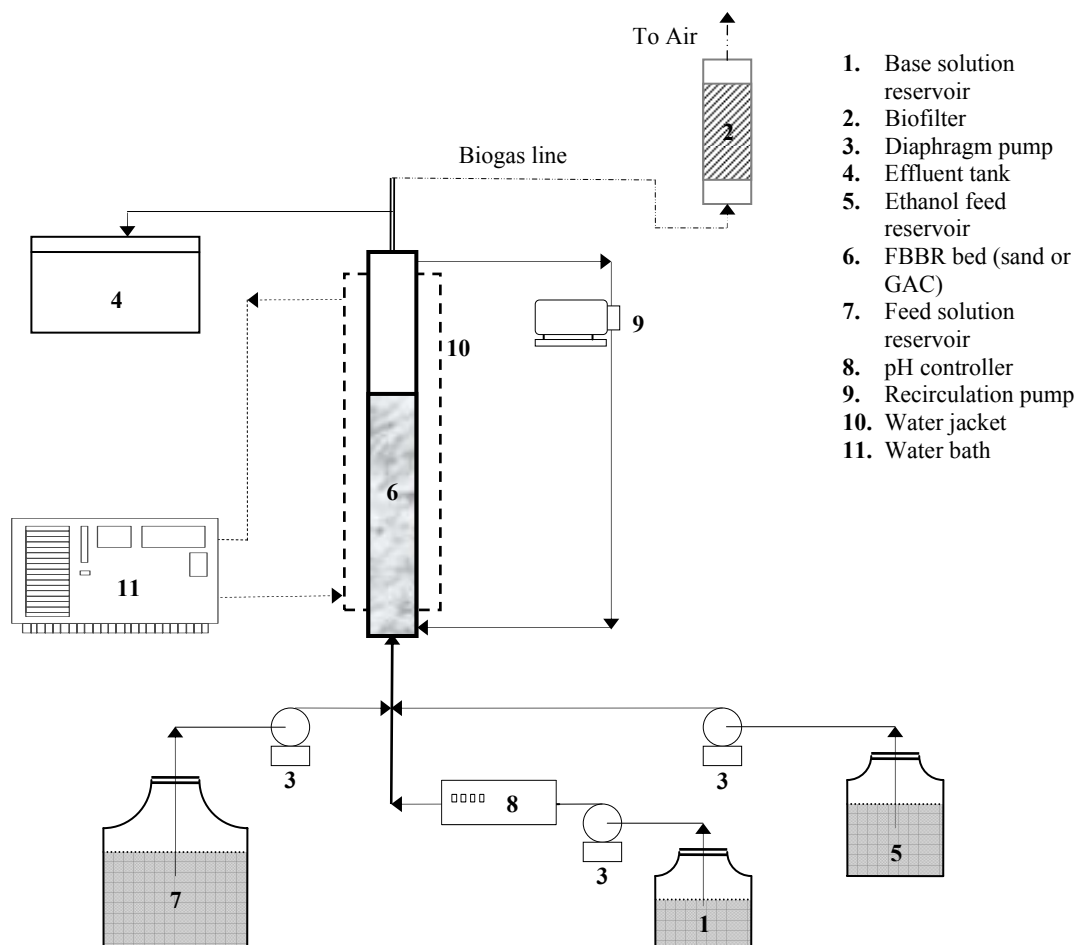


Figure 6-5 Schematic of the Fluidized Bed Bioadsorber Reactor System for Biological Sulfate Reduction Utilizing Ethanol as Carbon Source and GAC or Sand as Support Media

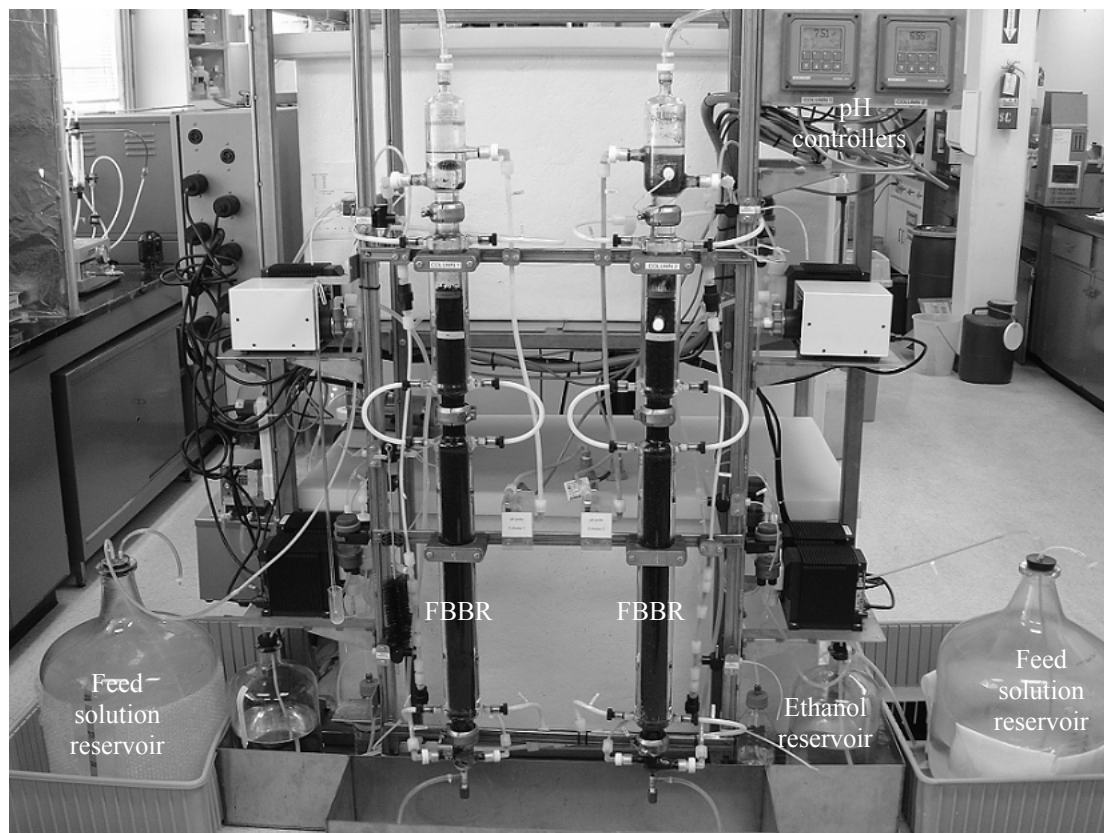


Figure 6-6 Photograph of the Fluidized Bed Bioadsorber Reactor System for Biological Sulfate Reduction Utilizing Ethanol as Carbon Source and GAC or Sand as Support Media

6.2.4 Anaerobic Biofiltration System

A biofilter reactor was designed for removal of produced biogas, mainly hydrogen sulfide from FBBR systems. The reactor consisted of a Plexiglas® cylindrical column containing 1000 g of granular activated carbon. The column had an overall height of 24 in and a diameter of 2.5 in, and was equipped with one outlet located at the top of the column with a diameter of 0.3 in.

Table 6-3 Synthetic Brine Concentrate Composition Used in the Fluidized Bed Bioadsorber Reactors and Chemostat Biokinetic Studies as Nutrient

Constituent	Chemostat (mg/L)	Column 1 FBBR - GAC (mg/L)	Columns 2, 4 FBBR - GAC (mg/L)	Column 3 FBBR - sand (mg/L)
Na ⁺	730	530 - 730	580 - 730	530 - 730
Ca ²⁺	350	350	350	350
Mg ²⁺	140	140	140	140
Cl ⁻	440	440	440	440
Ba ²⁺	0.5	0.5	0.5	0.5
PO ₄ ³⁻	12	12	12	12
NO ₃ ⁻	5	5	5	5
ClO ₄ ⁻	100 µg/L	100 µg/L	100 µg/L	100 µg/L
Se ⁺⁴	100 µg/L	100 µg/L	100 µg/L	100 µg/L
Alkalinity	430	430	430	430
Dissolved Solid	-	4384	4122	3788
Ethanol	704.66	448.42 – 704.66	512.42 – 704.66	448.42 – 704.66
Micro nutrients	2.2	1 – 2.2	2.2	2.2

The reactor was packed with GAC (8-10 U.S. mesh size) and the biogas line was equipped with a peristaltic pump to increase the biogas stream from biogas effluent of FBBR systems to the inlet of biofilter. A perforated tray was placed 2 in above the bottom of the column as a base for the bed medium. The biofilter characteristics are summarized in Table 6-5.

Prior to inoculation, the granular activated carbons were washed and sterilized. The biofilter then was packed with GAC and seeded with 2 L of activated sludge obtained from an urban wastewater treatment plant. The system was maintained perfectly sealed to prevent any escaping of hydrogen sulfide, and to maintain

anaerobic conditions in the biofilter system. The biofilter was fed once a week at the beginning of the FBBR operation for five months, and then fed once a month with a nutrient solution where specifications are provided in Table 6-4. Figure 6-7 illustrates the schematic of the designed anaerobic biofilter system for removal of gaseous hydrogen sulfide generated from the FBBR systems, and Figure 6-8 presents a photograph of the system.

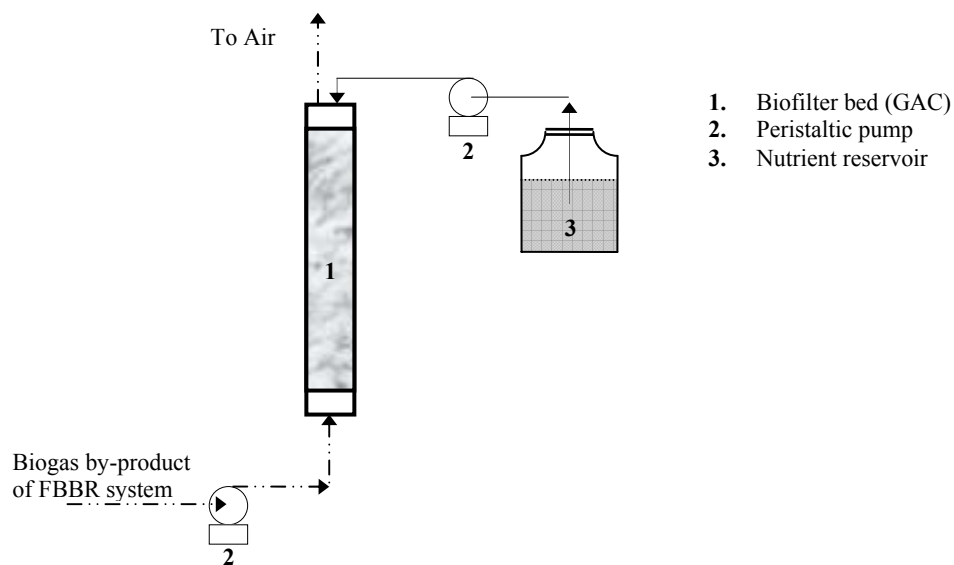


Figure 6-7 Schematic of the Anaerobic Biofilter for Removal of Gaseous Hydrogen Sulfide Generated as By-product of FBBR Systems

Table 6-4 Nutrient Composition for the Anaerobic Biofilter System

Constituent	Concentration (mg/L)	Chemical form
Na ⁺	530	Na ₂ SO ₄ , NaHCO ₃ , NaNO ₃
Ca ²⁺	350	CaCl ₂ 2H ₂ O
Mg ²⁺	140	MgCl ₂ 6H ₂ O
PO ₄ ³⁻	12	NaHCO ₃
NO ₃ ⁻	5	KH ₂ PO ₄
Ba ²⁺	0.5	BaCl ₂
Fe ²⁺	1	Na ₂ SO ₄
Alkalinity	430	FeSO ₄ 7H ₂ O
Amino Acid	14	
Micro nutrients	2.2	

Table 6-5 Anaerobic Biofilter Characteristics

Specifications	Anaerobic Biofilter Column
Active volume (L)	1.5
Active height (inch)	18
Loading rate (L/min)	6
Empty Bed Contact Time (EBCT, sec.)	14.5
Temperature (°C)	27°C ~ 30°C
Medium specifications	1000 g GAC (US mesh 8-10; 2.00 ~ 2.38 mm)

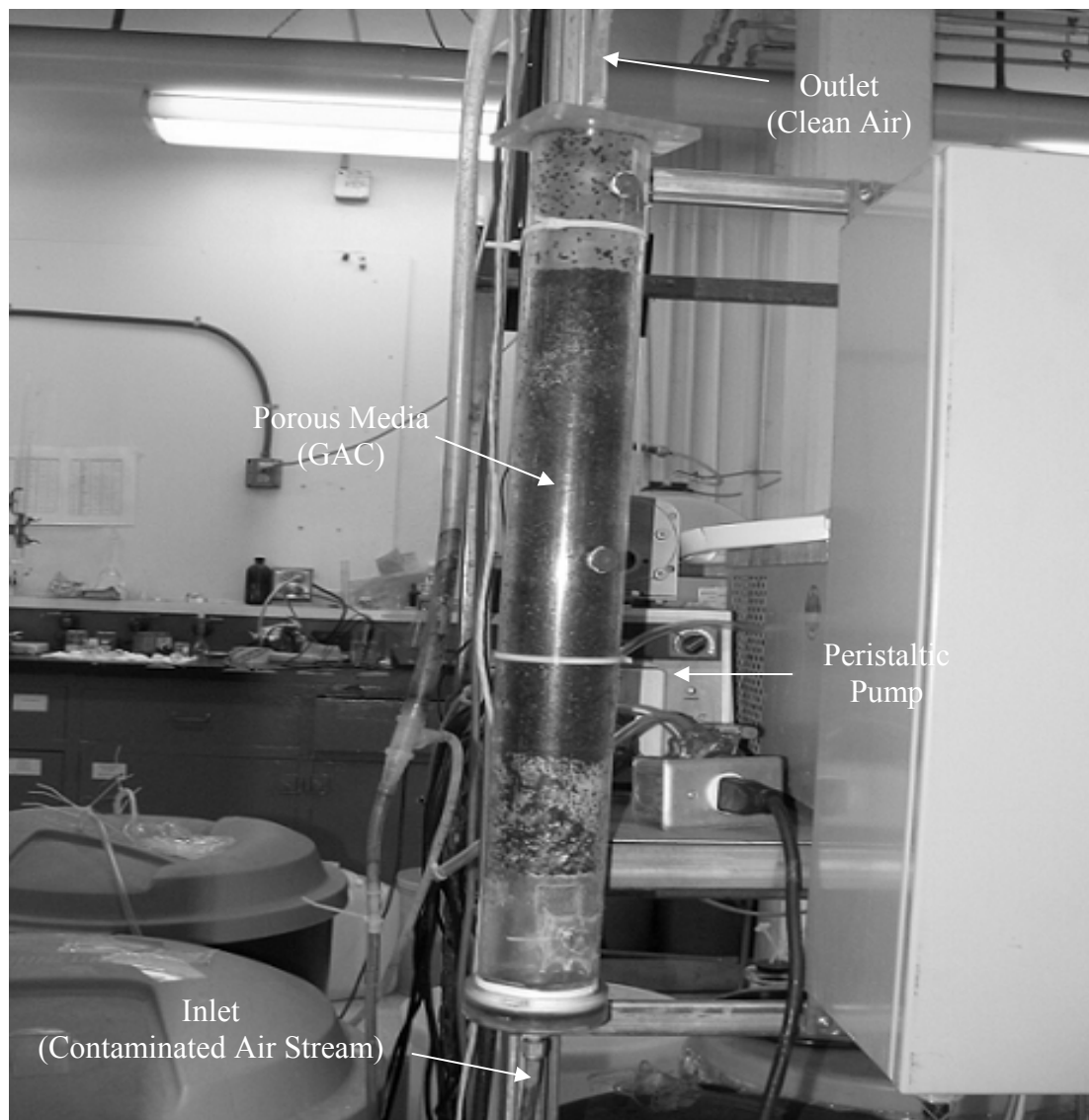


Figure 6-8 Anaerobic Biofilter for Removal of Gaseous Hydrogen Sulfide

6.3 Analytical Methods

6.3.1 Sulfate and Acetate Analysis

The sulfate and acetate concentrations were measured by ion chromatography (DX-100, DIONEX Corporation, Sunnyvale, CA) equipped with a conductivity detector

was used (Standard Methods, 1998; EPA No. 353.2). The eluent used was composed of 0.5 M of sodium carbonate and 0.5 M of sodium bicarbonate for anion analysis. The flow rate of the eluent was maintained at 1.2 mL/min. Nitrogen gas was used as eluent pressurization. When concentration is greater than the calibration range (5 to 30 mg/L), samples were diluted to appropriate ranges. All the experimental samples collected were filtered through 0.2 μ m membrane syringe filters prior to analysis to eliminate any microbial growth and suspended particles. The filtered samples were subsequently stored in refrigerator at 4°C. The accuracy of the instrument was also monitored on a regular basis by calibration and maintenance service.

6.3.2 Ethanol Analysis

Ethanol was analyzed by a gas chromatograph (Perkin Elmer, Avondale, PA) equipped with a flame ionization detector (GC/FID). The chromatographic column used was a glass column (6 ft $\times$ 2 mm ID), packed with GP4 5% Carbowax 20M on 60/80 Carbopack B (Supelco, Bellefonte, Pennsylvania) was employed. Helium was used as a carrier gas at flow rate of 20 mL/min. The injection, detector and oven temperatures were maintained at 150°C, 250°C and 85°C, respectively. Samples were taken and prepared in duplicate, and analyzed.

6.3.3 Hydrogen Sulfide Analysis

Total sulfide analysis was conducted using the iodometric method (Method 4500F, Standard Methods, 1998). The samples were taken carefully with a minimum possibility of aeration, and analyzed immediately. A 5-mL 0.1N of standardized iodine solution (VWR Scientific, West Chester, PA), estimated to be an excess over the amount of sulfide present, was added to a 500-mL flask, followed by a 15-mL distilled water to bring volume to 20 mL. A 200-mL volume of the sample acidified by 2 mL of 6N hydrochloric acid was then added into the flask, followed by a few drops of starch solution. The sample was then titrated with 0.025N of standardized sodium thiosulfate solution (VWR Scientific, West Chester, PA) to pale color. One milliliter 0.0250N iodine solution reacts with 0.4 mg S^{2-} , and the total sulfide is determined by the following equation:

$$mg S^{2-} / L = \frac{[(A \times B) - (C \times D)] \times 16000}{mL Sample}$$

where

A = mL iodine solution,

B = normality of iodine solution,

C = mL $Na_2S_2O_3$ solution, and

D = normality of $Na_2S_2O_3$ solution.

6.3.4 Alkalinity Measurements

Alkalinity was determined by potentiometrical titration method (Method 2320B, Standard Methods, 1998). In this technique, 50 mL of the unfiltered sample was titrated against standard sulfuric acid solution (0.1, 0.025, and 0.01N H_2SO_4) to an end-point of 4.5 or 4.3.

6.3.5 Dissolved Oxygen Measurement

The dissolved oxygen concentrations in the aqueous phase were measured by iodometric method, azide modification (Method 4500C, Standard Methods, 1998). Samples were collected in a 250-mL bottle, and analyzed immediately. 1 mL MnSO_4 solution, followed by 1 mL alkali-iodide-azide reagent was added into the bottle. The bottle then was sealed by a stopper carefully to exclude air bubbles and mixed by inverting it a few times. When precipitate settled sufficiently (to approximately half the bottle volume), 0.1 mL concentrated H_2SO_4 was added, and the bottle sealed and mixed again by inverting several times until dissolution was complete. 201 mL of this sample was then added into a 300-mL volumetric flask. A few drops of starch solution were added, and the sample was titrated with standardized 0.025 M $\text{Na}_2\text{S}_2\text{O}_3$ solution to pale straw color. One milliliter of 0.025 M sodium thiosulfate solution is equal to 1 mg DO/L.

6.3.6 Biomass Assay

The biomass measurement during the operation of the batch and continuous flow chemostat experiments were assayed gravimetrically (Standard Methods, 1998). A measured volume of samples was filtered through a 4.25 cm glass fiber filter (Whatman GF/C, VWR Scientific, West Chester, PA). The filters were then dried at 105°C, and the difference in weight before and after drying was recorded. Subsequently, the filters were placed in 550°C oven for 15-20 min to remove volatile organics. The filters were put in a desiccator to be cooled down and then were weighed again. The difference between the weight after drying and combusting was recorded.

6.3.7 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to examine the extent of biofilm coverage on GAC and sand particles and to observe microstructural and morphological characteristics of the biofilm. The SEM analysis was performed as described by Weber et al. (1978) and Pirbazari et al. (1990). Several GAC and sand particles were randomly selected from the FBBR reactors and fixed for SEM observation. The selected samples were fixed by the method of Karnovsky (1965) as described below. The carbon and sand particles were immersed for 2 hr in 2% paraformaldehyde-2.5% glutaraldehyde solution in 0.1 M sodium phosphate buffer at pH 7.2. The process then followed by a primary fixation for two hours at room temperature, after which the particles were gently and thoroughly washed in 0.1 M

phosphate buffer at pH 7.2, and postfixed in 1% osmium oxide. After dehydration in a graded series of ethanol (50, 70, 80, 90, and 100%), the samples were prepared for critical point drying in a 1:1 100% ethanol-amylacetate solution, and stored overnight in amylacetate. A DCP-1 critical point dryer was used for drying the fixed particles. The particles were then mounted on aluminum stubs and coated with 100 Å gold in a glow-discharge coater to minimize charging and increase the conductivity of the biological material. A Cambridge 360 Scanning Electron Microscope with a resolution of 30 Å and a Link EDS system was used for observing the specimens.

6.3.8 Total Dissolved Solids and Volatile Suspended Solids Measurement

The total dissolved solids (TSS) and volatile suspended solids (VSS) of the influent synthetic brine and effluent of the FBBR system were analyzed using established techniques outlined elsewhere (Standard Methods, 1998; EPA Methods No. 310.1). A measured volume of samples was filtered through a 4.25 cm glass fiber filter (Whatman GF/C, VWR Scientific, West Chester, PA), and dried for 1 hr at 105°C to determine TSS and subsequent ignition at 550°C for 15-20 min, for the determination of VSS.

6.3.9 Sludge Settleability Measurement

The sludge volume index (SVI) was determined to evaluate the settling characteristics of the fluidized bed bioreactor sludge in all the reactors (Standard

Methods, 1998). The SVI is the volume in milliliters occupied by 1 g of a suspension after 30 min settling. The sludge volume index of a biological suspension is an appropriate indicator to monitor the biological processes and settling characteristics of sludge in the activated sludge plant, and is determined by the following relationship.

$$SVI = \frac{\text{settled sludge volume (ml / L)} \times 1000}{\text{suspended solids (mg / L)}}$$

CHAPTER 7

COMPLETELY MIXED BATCH REACTOR (CMBR) BIOKINETIC STUDIES

7.1 Completely Mixed Batch Reactor (CMBR) Biokinetic Studies

The CMBR biokinetic studies were performed to investigate the optimal biological conditions for sulfate reduction utilizing ethanol as carbon source, including temperature, pH, and carbon to sulfur ratio. Four CMBR systems were operated at the same time for each set of experiment with the initial sulfate concentration of 700 mg/L and effect of different C/S ratios, temperatures, and pH were investigated in three sets of experiment, all with the same initial biomass concentration. The results were normalized as illustrated from Figure 7-1 to Figure 7-6. The linear portion of the profiles for both sulfate and ethanol concentrations were considered for estimation of biokinetic coefficients. The estimated zero order rate constants for sulfate reduction and ethanol utilization are presented in Tables 7-1 to 7-3.

7.1.1 Effect of Temperature

The CMBR experiments were conducted at different temperatures of 20, 25, 30, and 35°C and constant pH and C/S ratio of 7.0 and 1.0, respectively, in order to evaluate the effect of reaction temperature on the biokinetics. The sulfate reduction and ethanol utilization profiles are presented in Figures 7-1 and 7-2, respectively. These studies qualitatively showed that the reaction rates improved with temperature up to

35°C. Nonetheless, it is important to note that reaction rate constants for sulfate reduction and ethanol utilization were marginally higher at 35°C than at 30°C, indicating that increase in reaction temperature beyond 30°C did not project a significant advantage in process kinetics, although it would entail higher energy costs from an operational standpoint. The experiment showed a good comparative and reliable result for temperature CMBR study. The highest rate constant obtained at 35°C with values of $k = 13.55$ mg/(L.hr) for sulfate reduction and $k = 20.69$ mg/(L.hr) for ethanol utilization. The lowest rate constant for both sulfate reduction and ethanol consumption achieved at 20°C as expected.

Table 7-1 CMBR Studies - Rate Constants at Different Temperatures

Temperature, °C	Rate Constant, mg/(L . hr)	
	Sulfate Reduction	Ethanol Utilization
20	4.96	8.54
25	8.67	14.41
30	11.71	19.63
35	13.55	20.69

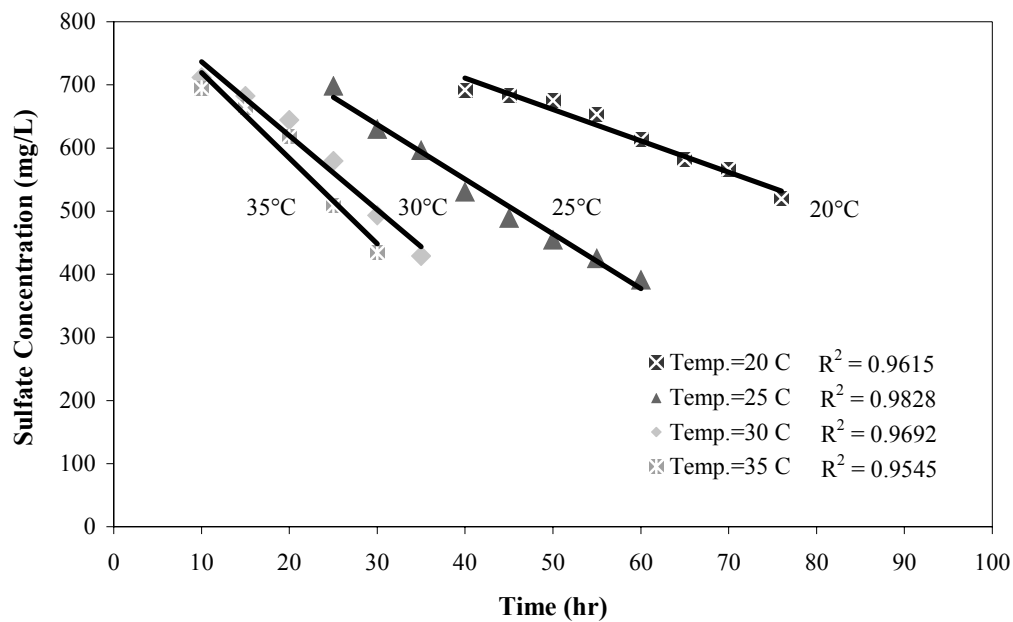


Figure 7-1 Sulfate Reduction in CMBR Studies at Different Temperatures

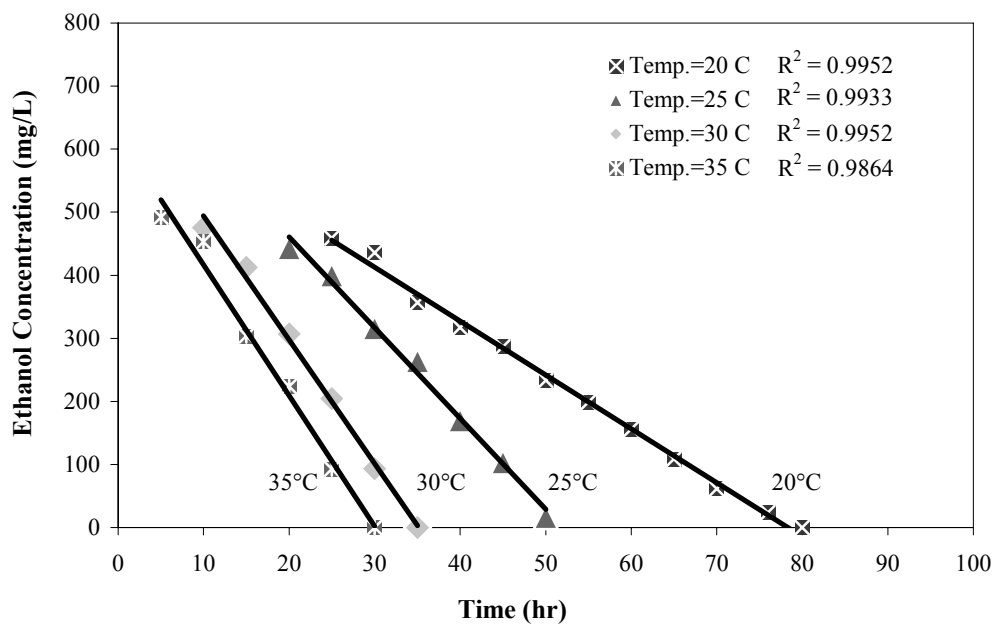


Figure 7-2 Ethanol Utilization in CMBR Studies at Different Temperatures

7.1.2 Effect of pH

The effect of pH on reaction kinetics was studied by performing a series of CMBR experiments at different pHs of 6.0, 7.0, and 8.0 and constant temperature and C/S ratio of 30°C and 1.0, respectively. The results illustrated in Figures 7-3 and 7-4 and Table 7-2 indicated that the reaction rate constant for ethanol utilization was significantly higher at the optimal pH of 7.0 than at a pH of 6.0, as compared to those of sulfate reduction which showed nearly constant reaction rates at different pHs. The maximum rate constant of $k = 12.86 \text{ mg}/(\text{L} \cdot \text{hr})$ was obtained at $\text{pH} = 7.0$ for sulfate reduction and at pH of 8.0 for ethanol utilization with the value of 15.98. The unexpected results obtained in this study with reference to sulfate reduction rate projected the important role of hydrogen ion production in the reaction of sulfate reduction with ethanol (Equation 2-3), which significantly, affected the initial pH of CMBR system in this study. The results demonstrated that as initial pH increased, the rate constant increased significantly with reference to ethanol utilization incorporating better biomass production rate, while it decreased marginally with reference to sulfate reduction. It can be speculated from these results that at higher ethanol utilization rate more biomass with reduced activity and less enzyme were produced that consequently did not incorporate in enhancing sulfate reduction rate.

Table 7-2 CMBR Studies - Rate Constants at Different pHs

pH	Rate Constant, $\text{mg}/(\text{L} \cdot \text{hr})$	
	Sulfate Reduction	Ethanol Utilization
6.0	13.39	11.83
7.0	12.86	14.52
8.0	12.68	15.98

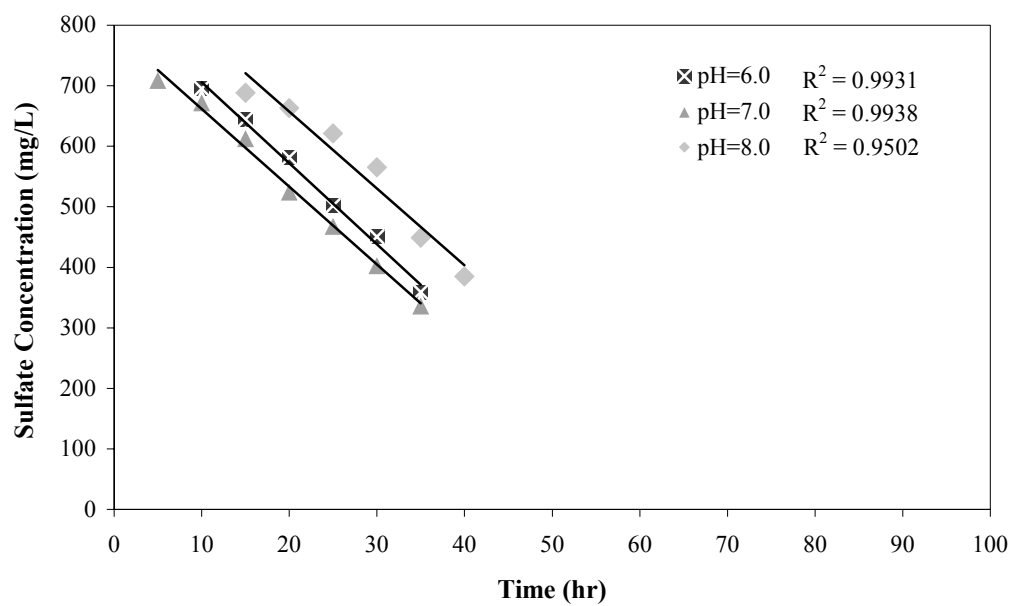


Figure 7-3 Sulfate Reduction in CMBR Studies at Different pHs

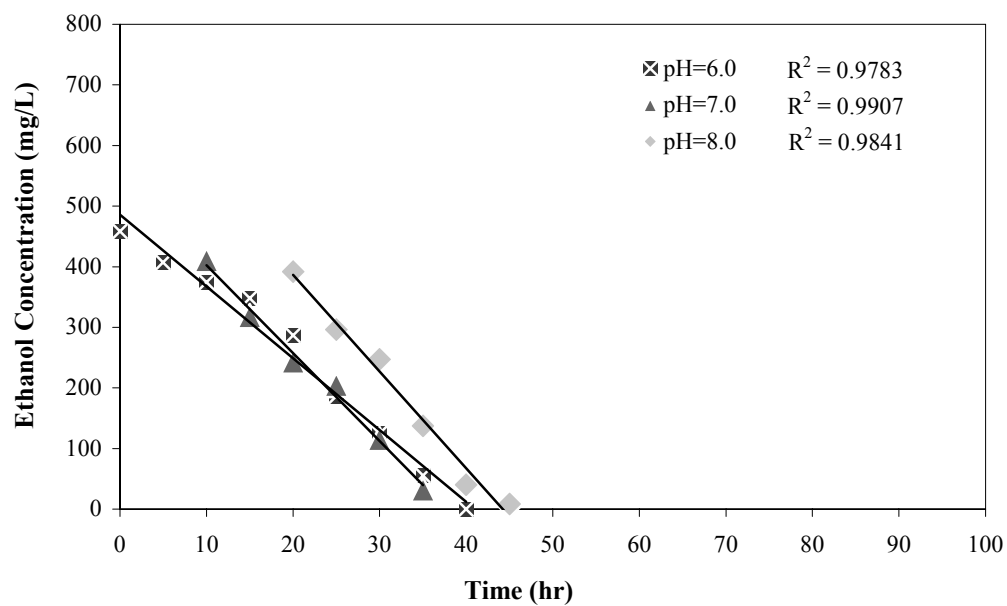


Figure 7-4 Ethanol Utilization in CMBR Studies at Different pHs

7.1.3 Effect of Carbon-to-Sulfur Ratio

The effect of carbon to sulfur ratio on reaction kinetic was evaluated in this study. The CMBR experiments were conducted at different carbon-to-sulfur ratio of 0.8, 1.0, 1.2, and 1.4 and constant temperature and pH of 30°C and 7.0, respectively. The sulfate and ethanol concentration profiles are presented in Figures 7-5 and 7-6. The rate constants for sulfate reduction show a steady increase with the C/S ratio, and at ratio of 1.4, almost the entire sulfate was utilized. However, at lower C/S ratios of 0.8, 1.0, and 1.2, after complete utilization of ethanol, a residual sulfate level maintained in the reactor because the carbon source (ethanol) was the limiting species. The results indicate that higher C/S ratios of 1.2 or 1.4 did not manifest any significant advantage; a C/S ratio of 1.0 represented a near-optimal condition, as reflected by the reaction rate constants presented in Table 7-3. The highest rate constant of $k = 15.66 \text{ mg}/(\text{L} \cdot \text{hr})$ and $k = 17.48 \text{ mg}/(\text{L} \cdot \text{hr})$ was achieved at $\text{C/S} = 1.4$ for sulfate reduction and ethanol utilization, respectively, as compared to the other C/S ratios. The lowest rate constant for both sulfate reduction and ethanol utilization was observed at a C/S ratio of 0.8 as expected.

Table 7-3 CMBR Studies - Rate Constants at Different C/S Ratios

C/S	Rate Constant, $\text{mg}/(\text{L} \cdot \text{hr})$	
	Sulfate Reduction	Ethanol Utilization
0.8	10.63	12.53
1	11.94	15.46
1.2	13.44	17.03
1.4	15.66	17.48

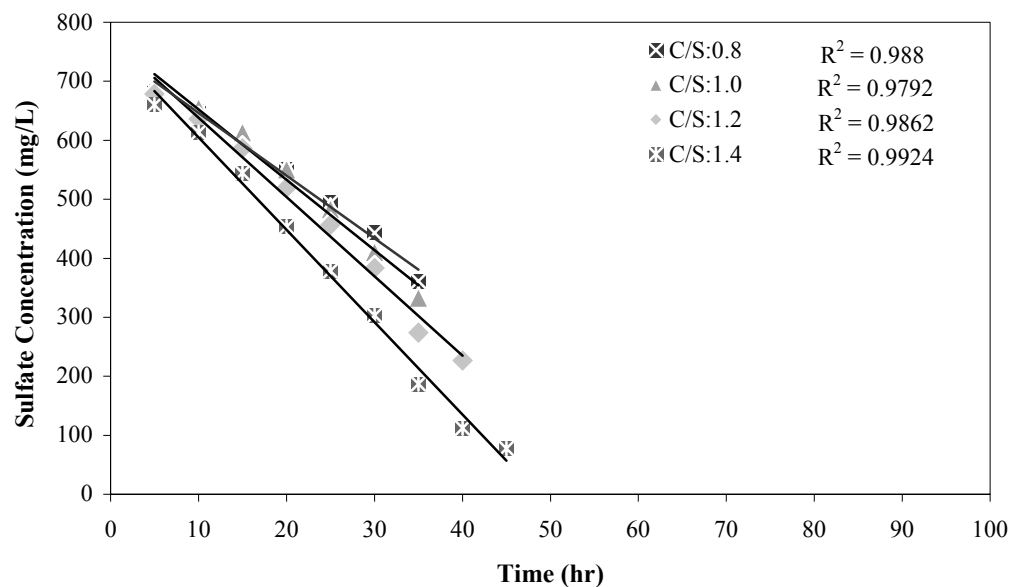


Figure 7-5 Sulfate Reduction in CMBR Studies at Different C/S Ratios

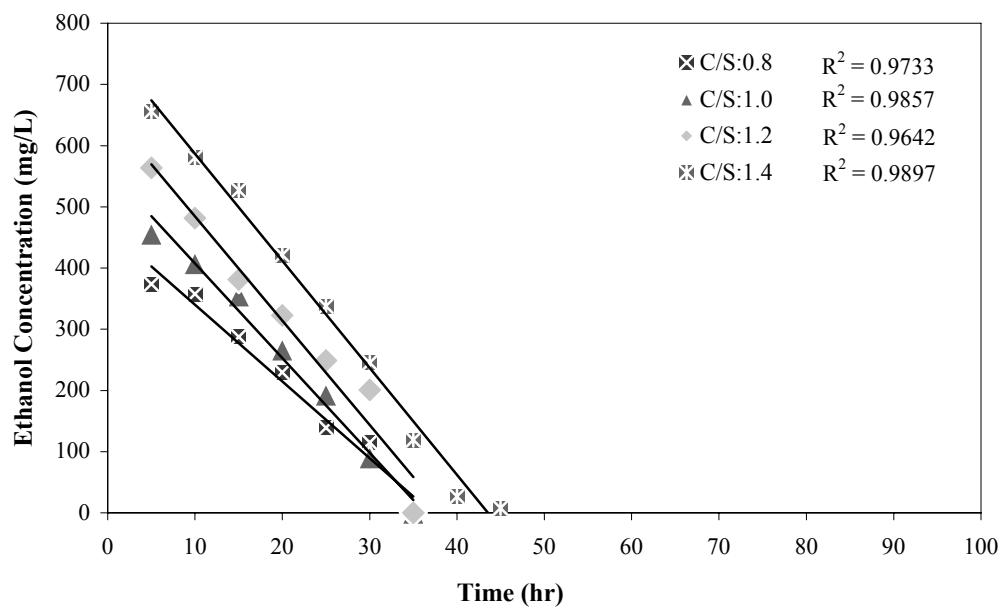


Figure 7-6 Ethanol Utilization in CMBR Studies at Different C/S Ratios

7.2 Summary and Conclusions

The results of CMBR studies demonstrated that the reaction kinetics were improved by increasing the C/S ratio from 1.0 to 1.2 or 1.4. It must be noted that a C/S ratio of 1.0 or 1.2 represented a near-optimal value, because a ratio of 1.4 would employ higher levels of ethanol, leading to the use of more carbon source and formation of higher concentrations of acetate. The effect of temperature on reaction kinetics was evaluated at a pH of 7.0 and a C/S ratio of 1.0. The results depicted in Figures 7-1 and 7-2 and Table 7-1 reflected that it would be advantageous to employ a high temperature of 35°C, although it would be advisable to employ a temperature of 30°C as a compromise between reaction kinetics and energy costs. With regard to CMBR studies at different pH, the initial pH for the series of experiments was adjusted at 6.0, 7.0, and 8.0; however, due to the production of H^+ ions (Equation 2-3), pH gradually dropped throughout the experiment. Nonetheless, pH of 7.0 was chosen to represent optimal value.

The optimal or near-optimal conditions (C/S=1.0, pH=7.0, and temperature=30°C) obtained from the CMBR studies for biological sulfate reduction provided the basis for subsequent chemostat studies to determine biokinetic parameters that would be used in the dynamic modeling and performance prediction of fluidized bed reactor systems.

CHAPTER 8

CHEMOSTAT STUDIES AND MODELING

8.1 Chemostat Studies

Continuous flow chemostat studies were performed to determine the different biokinetic parameters for biological sulfate reduction that would be subsequently employed in modeling of the FBBR process for performance prediction and process simulation. The chemostat experiments were designed on the basis of batch reactor studies discussed earlier. A mixed culture of SRB was introduced to the reactor, and the system was operated in batch mode for one or two days until the system reached steady-state, after which the reactor operation was switched to the continuous flow mode. The influent flowrate was adjusted depending on a desired dilution rate applied to the system. Samples of 5-10 mL volume were taken periodically from the reactor and filtered instantly through 0.2 μm syringe filter for sulfate and ethanol analysis. Samples of 50 mL volume were obtained from the reactor for biomass measurements. At each specific dilution rate, when the system reached steady-state, the biomass and hydrogen sulfide concentrations were measured, and then another dilution rate was employed. Nagpal et al. (2000) examined a series of completely stirred tank reactor (CSTR) studies on sulfate with SRB and ethanol as electron donor and investigated the kinetic parameters (Table 8-1). Their results can not strictly be compared with those of this study, since their CSTR was operated in a different mode. Chemostat studies performed in this study for sulfate reduction by

using a mixed culture of SRBs and employing ethanol as carbon source or electron source was not previously reported by researchers.

Table 8-1 Kinetic Parameters Obtained from the CSTR Studies of Nagpal et al. (2000)

kinetic Parameters	Sulfate Reduction	Ethanol Utilization
Maximum specific growth rate, μ_m	-	0.013 hr ⁻¹
Half-velocity constant, K_s	0.0085 mol/L (816 mg/L)	0.0045 mol/L (207 mg/L)
Maximum yield coefficient, Y	0.75 - 0.93	0.38 - 0.47

8.1.1 Chemostat Studies with Carbon-to-Sulfur Ratio of 1.0

Chemostat biokinetic studies were conducted for a period of about 240 hr to investigate the biokinetic parameters. The experiments were performed at constant temperature and pH of 30°C and 7.5. Carbon to sulfur ratio of 1.0 was employed corresponding to sulfate and ethanol concentration of 1100 mg/L and 706.4 mg/L respectively. The experimental results as well as the model predictions for sulfate, ethanol, and biomass concentrations at different dilution rates are presented in Table 8-2 and Figure 8-1. The chemostat system was operated at five different dilution rates starting with $D = 0.02 \text{ hr}^{-1}$ (retention time of 50 hr). At the first dilution rate of 0.02 hr^{-1} steady state operation was confirmed by reaching the stable sulfate concentration of 637 mg/L; however, complete ethanol utilization was achieved under these conditions. Biomass wash-out started increasing by decreasing the retention time and complete biomass wash-out was occurred at the last employed

dilution rate of 0.1 hr^{-1} (retention time of 10 hr). Biokinetic parameters were estimated as previously explained (Section 4.3) by linear regression of Equations 4-9, and 4-11.

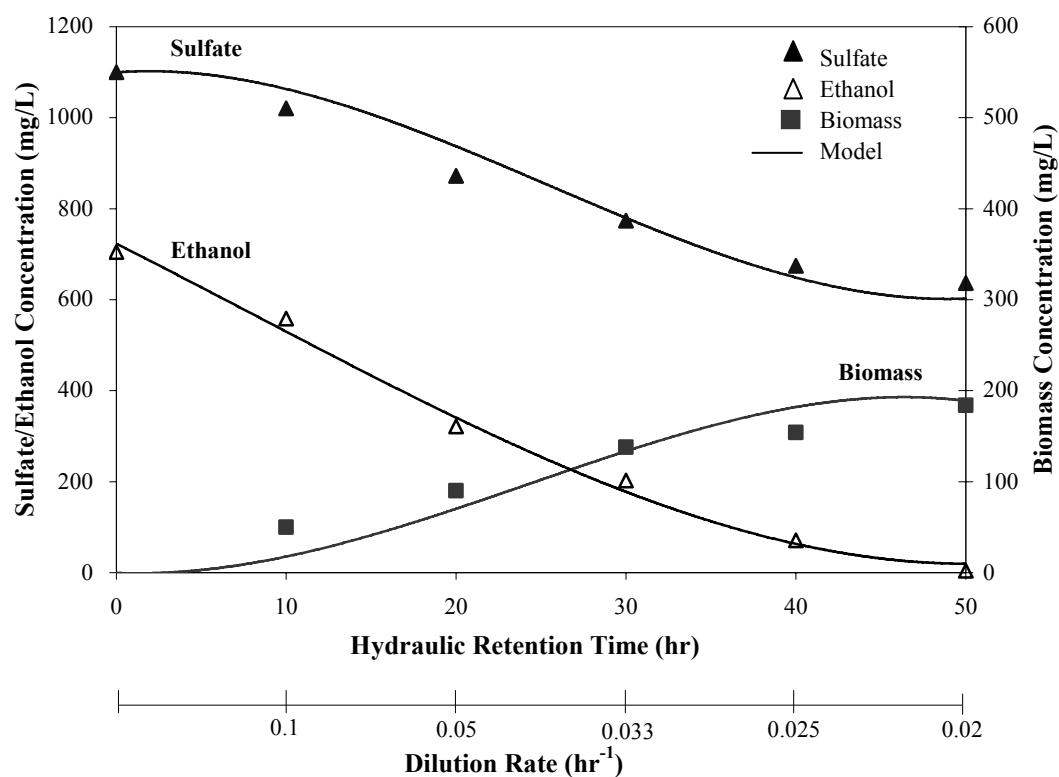


Figure 8-1 Chemostat Experimental and Model Profiles for Steady-State Sulfate, Ethanol, and Biomass Concentration ($C/S = 1.0$)

8.1.2 Chemostat Studies with Carbon-to-Sulfur Ratio of 0.8

Chemostat biokinetic studies with carbon-to-sulfur ratio of 0.8 were conducted for a period of 284 hours to investigate the biokinetic parameters. The experiment was performed at constant temperature and pH of 30°C and 7.5. Carbon to sulfur ratio of 0.8 was employed corresponding to sulfate and ethanol concentration of 1100 mg/L and 564.7 mg/L, respectively. The experimental results as well as the model predictions for sulfate, ethanol and biomass concentrations at different dilution rates are presented in Table 8-3 and Figure 8-2.

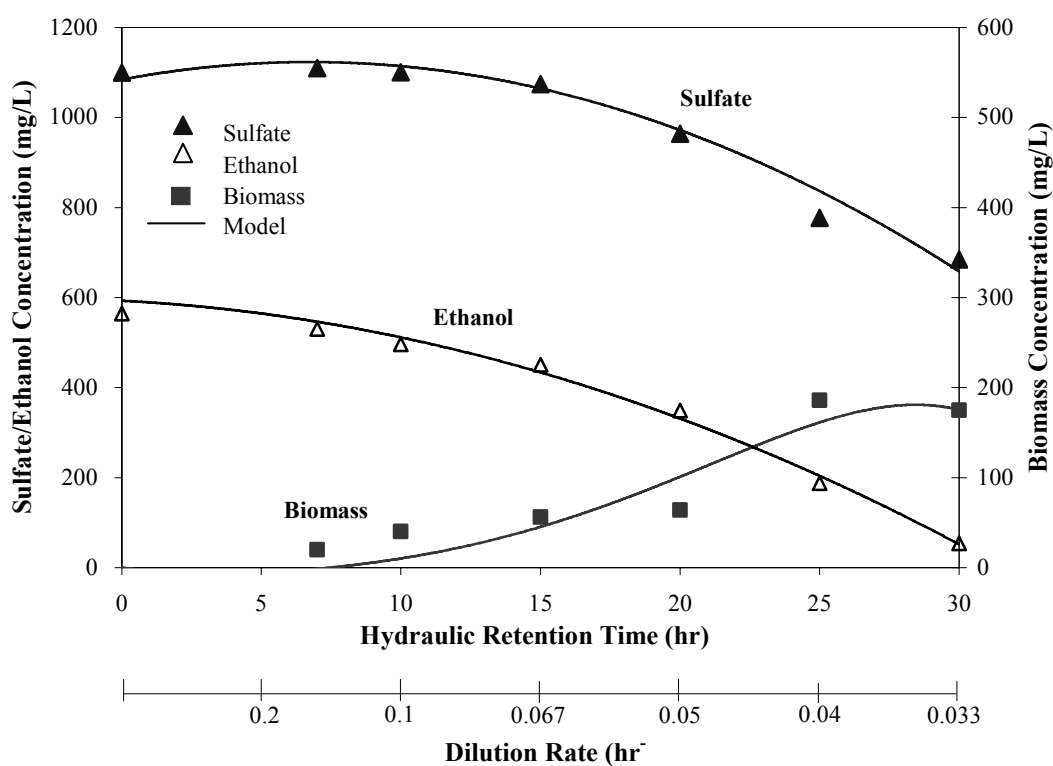


Figure 8-2 Chemostat Experimental and Model Profiles for Steady-State Sulfate, Ethanol, and Biomass Concentration (C/S = 0.8)

These experiments were performed at six different dilution rates commencing with dilution rate of 0.033 hr^{-1} (retention time of 30 hr). At the first dilution rate of 0.033 hr^{-1} steady state operation was confirmed by steady-state concentrations of about 685 mg/L for sulfate, and 44.2 mg/L for ethanol. Biomass wash-out started increasing when the retention time was decreased and complete biomass wash-out occurred at the last employed dilution rate of 0.143 hr^{-1} (retention time of 7 hr).

8.1.3 Chemostat Kinetic Parameters

The biokinetic parameters were estimated from chemostat experiments by a linear regression of Equations 4-9, and 4-11 as previously explained in Section 4.3. The Lineweaver-Burke plots of these studies are presented in Figures 8-3 through 8-8. The microbial yield coefficient, Y and the decay coefficient k_d were determined using the $[1/\theta]$ versus $[(C_0 - C)/M\theta]$ plot based on Equation 4-9 (Section 4.3), which is the plot of the dilution rate as a function of the specific desulfurization rate as presented in Figures 8-3, and 8-4. The slope and intercept of the Lineweaver-Burke plot provided an estimate of the growth yield coefficient, Y , and the decay coefficient, k_d with respect to sulfate reduction and ethanol utilization for carbon-to-sulfur ratio of 1.0. As determined from the plots, Y is equal to 0.7307 mg/mg, and 0.4851 mg/mg for sulfate reduction and ethanol utilization, respectively. The kinetic parameters are presented in Table 8-2.

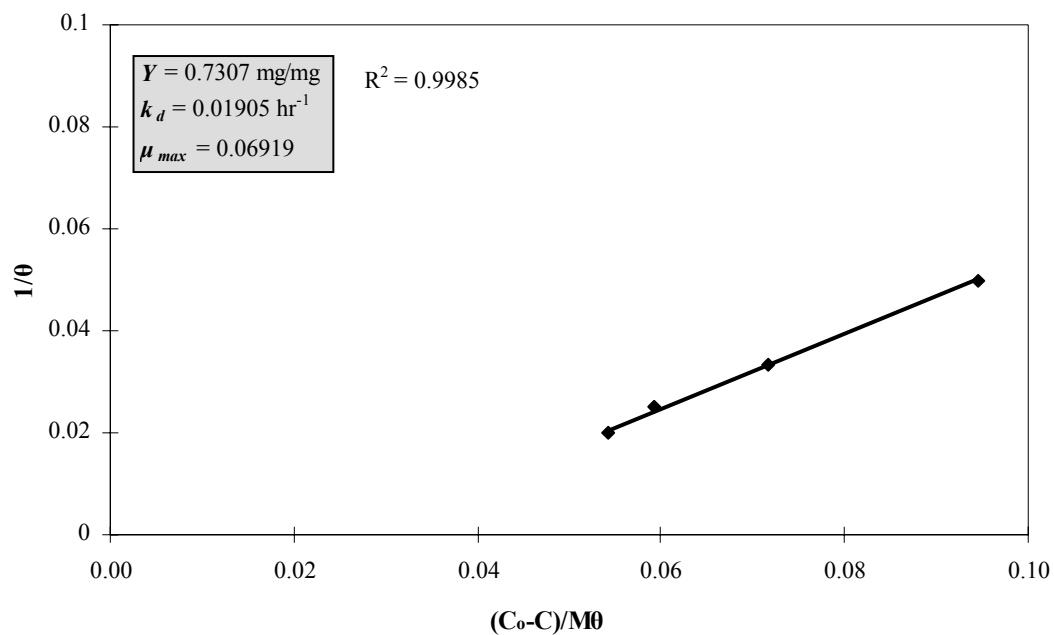


Figure 8-3 Chemostat Experimental Data: Determination of Biokinetic Parameters for Sulfate Reduction ($C/S = 1.0$)

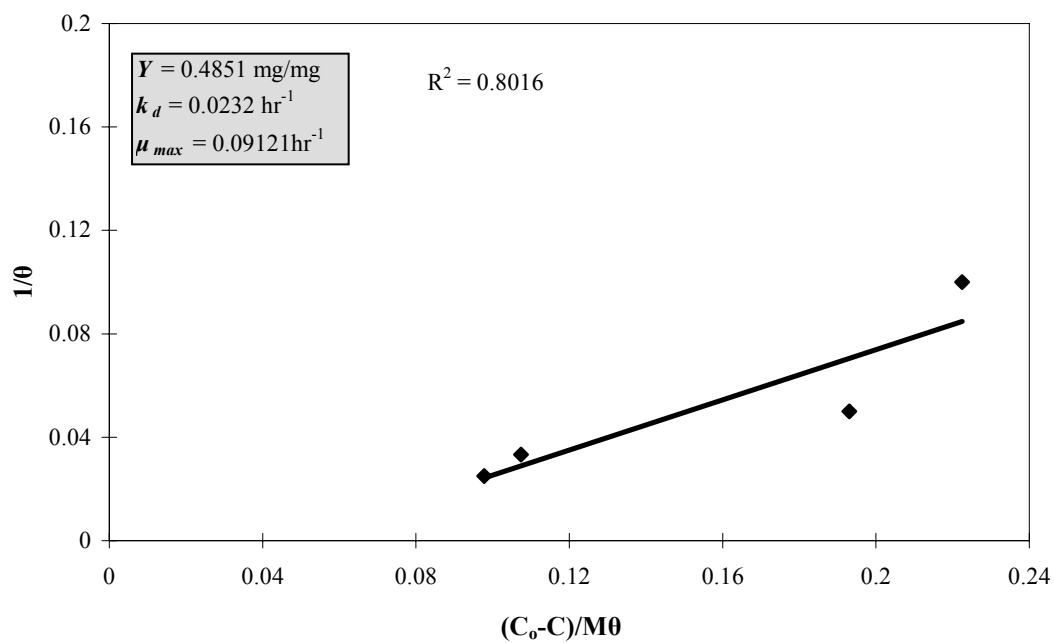


Figure 8-4 Chemostat Experimental Data: Determination of Biokinetic Parameters for Ethanol Utilization ($C/S = 1.0$)

The Monod kinetic parameters, namely, the half-saturation coefficient, K_s , and the maximum substrate utilization rate, k were estimated from the Lineweaver-Burke plot of $[M\theta/(C_0-C)]$ versus $[1/C]$, based on Equation 4-11 (Section 4.3). The reciprocal of intercept of the regression line provided the maximum substrate utilization rate, k , while the half-saturation coefficient, K_s was determined by multiplying the intercept value by the slope of the Lineweaver-Burke plot as presented in Figures 8-5, and 8-7. As determined from the plot, K_s for sulfate reduction and ethanol utilization at carbon-to-sulfur ratio of 1.0 are equal to 370.37 mg/L, and 89.64 mg/L, respectively.

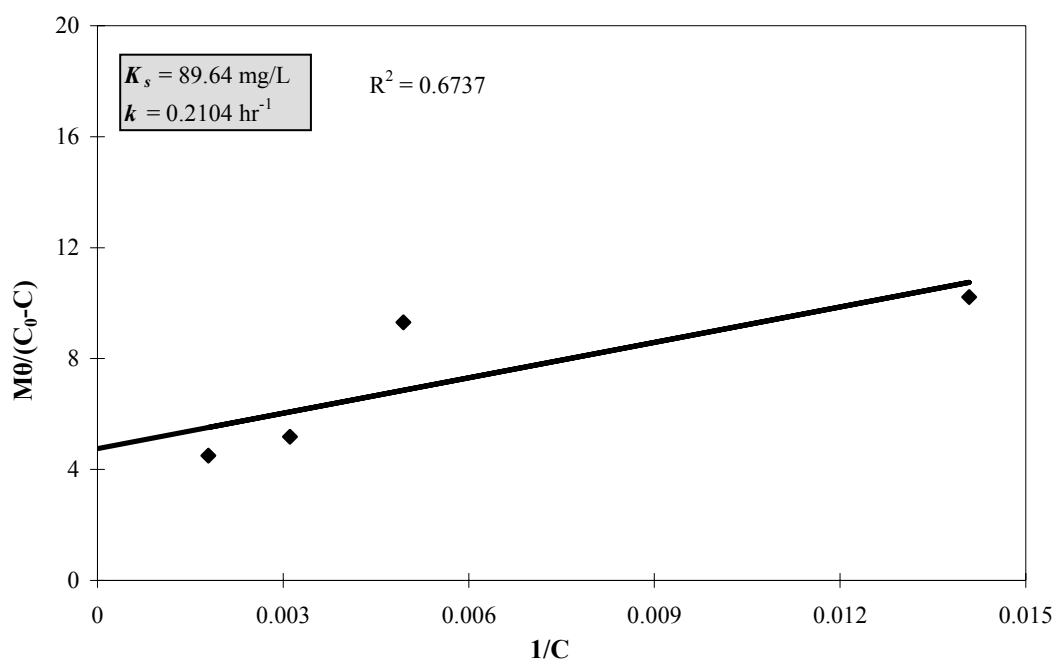


Figure 8-5 Chemostat Experimental Data: Determination of Biokinetic Parameters for Ethanol Utilization (C/S = 1.0)

Table 8-2 Kinetic Constants Obtained from Ethanol-limiting Chemostat at
C/S = 1.0

kinetic Parameters	Sulfate Reduction	Ethanol Utilization
Maximum specific growth rate, μ_m	0.0692 hr ⁻¹	0.102 → 0.0921 hr ⁻¹
Half-velocity constant, K_s	370.37 mg/L	89.64 mg/L
Maximum yield coefficient, Y	0.7307 mg/mg	0.4851 mg/mg
Endogenous decay coefficient, k_d	0.01905 hr ⁻¹	0.0232 hr ⁻¹

The biokinetic parameters for carbon-to-sulfur ratio of 0.8 were determined from the liner regression of Equations 4-9, and 4-11 as explained earlier in this section. From Equation 4-9, the estimate of the microbial yield coefficients, Y with respect to sulfate reduction was 0.5621 mg/mg, and with respect to ethanol utilization 0.5062 mg/mg, as presented in Figures 8-6, and 8-8. Subsequently, the intercept of the plot provided the decay coefficient, k_d of 0.0047 hr⁻¹, and 0.0125 hr⁻¹ for sulfate reduction, and ethanol utilization, respectively. A Lineweaver-Burke plot shown in Figure 8-7 using Equation 4-11 yielded the half-saturation coefficient, K_s , and the maximum substrate utilization rate, k , while the maximum specific growth rate was found by multiplying the value of k by Y . The biokinetic parameters estimated from these equations for C/S ratio of 0.8, are presented in Table 8-3.

Table 8-3 Kinetic Constants Obtained from Ethanol-limiting Chemostat at $C/S = 0.8$

kinetic Parameters	Sulfate Reduction	Ethanol Utilization
Maximum specific growth rate, μ_m	0.0525 hr ⁻¹	0.0712 hr ⁻¹
Half-velocity constant, K_s	293.80 mg/L	51.74 mg/L
Maximum yield coefficient, Y	0.5621 mg/mg	0.5062 mg/mg
Endogenous decay coefficient, k_d	0.0047 hr ⁻¹	0.0125 hr ⁻¹

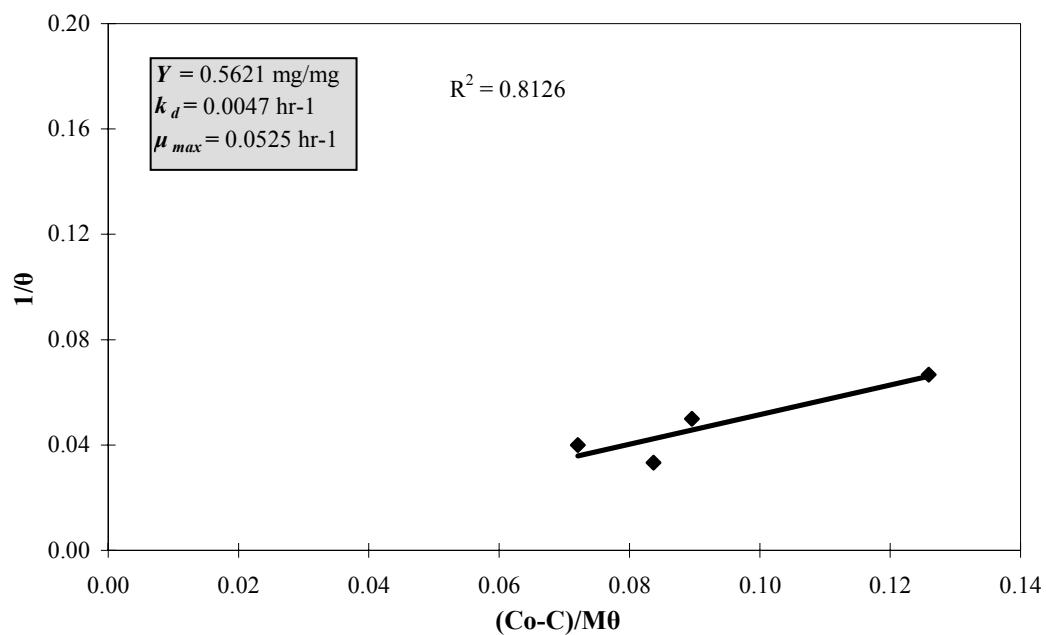


Figure 8-6 Chemostat Experimental Data: Determination of Biokinetic Parameters for Sulfate Reduction ($C/S = 0.8$)

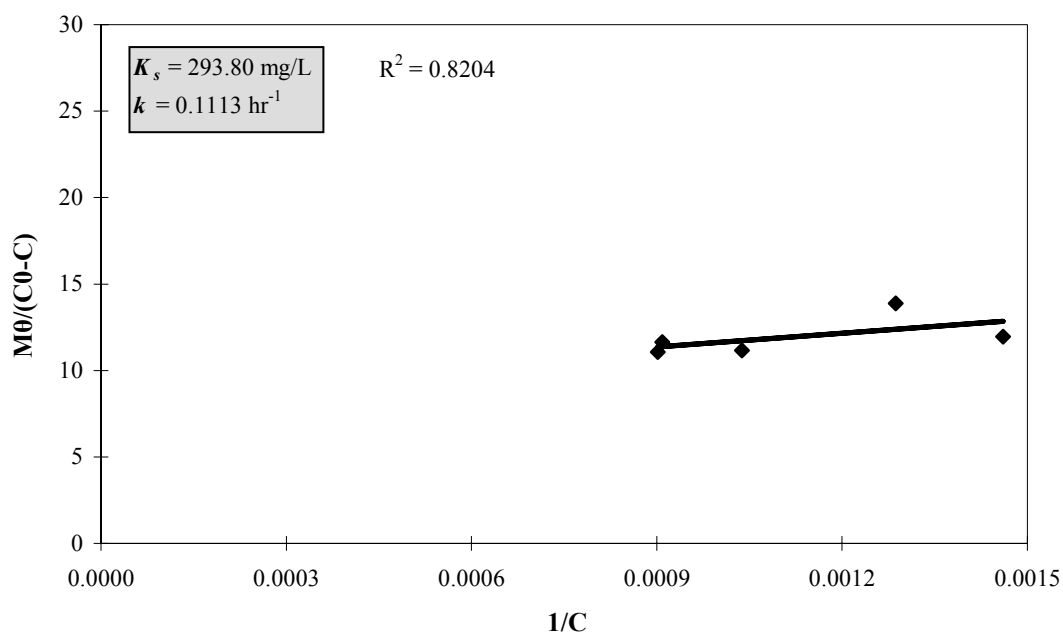


Figure 8-7 Chemostat Experimental Data: Determination of Biokinetic Parameters for Sulfate Reduction ($C/S = 0.8$)

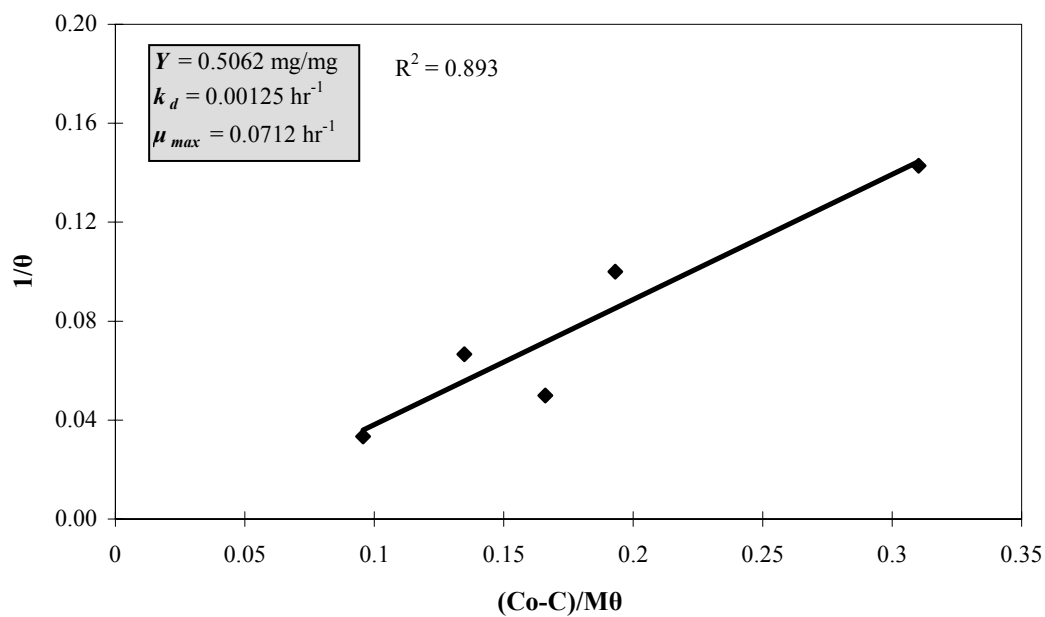


Figure 8-8 Chemostat Experimental Data: Determination of Biokinetic Parameters for Ethanol Utilization ($C/S = 0.8$)

8.1.4 Comparison of Chemostats with Carbon-to-Sulfur Ratios of 1.0 and 0.8

Chemostat studies facilitated a comparison of the reaction kinetics for biological sulfate reduction, relevant for the design of the FBBR system. The batch reactor studies showed that the overall reaction kinetics economically and biologically achievable can occur at the pH of 7.5, C/S ratio of 1.0, and temperature of 30°C. However, two sets of chemostat experiments at different C/S ratios of 1.0 and 0.8 were further conducted to not only determine the biokinetic parameters, but also to investigate the biological activity in the sulfate reduction process with respect to kinetic and economic viewpoint in a continuous flow system. A comparison of the yield coefficients in Tables 8-2, and 8-3 showed that C/S ratio of 1.0 was capable of greater biomass production ($Y = 0.7307$ mg/mg) than C/S ratio of 0.8 ($Y = 0.5621$ mg/mg). The Monod half-saturation constant, K_s was estimated to be 21% more at C/S ratio of 1.0 than was for 0.8, indicating faster biokinetic activity in the former C/S ratio. Nevertheless, the Monod maximum substrate utilization rate, k for sulfate reduction for C/S ratio of 0.8 was 0.097 hr^{-1} , about 12% lower than that for 0.8 of 0.111 hr^{-1} . This phenomenon may be explained as the following. At high sulfate concentrations, the sulfate reduction reaction rate will be controlled predominantly by the maximum substrate utilization rate, and therefore, the reaction rates shall be slower for C/S ratio of 0.8 than for that of 1.0. As evident from the results, The C/S ratio of 1.0 is more favorable with respect to faster kinetics, and subsequently, better sulfate reduction efficiency. However, C/S ratio of 0.8 has an inherent advantage over C/S ratio of 1.0 with reference to lower costs.

8.1.5 Chemostat Dynamics and Model Verification

Experimental data pertaining to the steady-state concentrations of sulfate, ethanol, and biomass (obtained at each dilution rate) were compared with the theoretical predictions as previously shown in Figures 8-1 and 8-2. The results demonstrated a good agreement between the experimental data and model predictions for both carbon to sulfur ratios of 1.0 and 0.8. The model appeared to predict that the hydrogen sulfide concentration in chemostat would be very low at lower dilution rates, as the experimental values of sulfate concentration in the reactor were larger than the theoretically predicted values. Subsequently, it can be concluded that the accumulation of the hydrogen sulfide in the reactor at low dilution rate might have inhibited the biomass growth. A carbon-to-sulfur ratio of 1.0 was chosen to investigate the performance of fluidized bed bioadsorber reactor with GAC and sand due to better sulfate degradation and faster kinetics obtained at this C/S ratio. Prior to FBBR studies, sensitivity analysis was investigated on the chosen C/S ratio of 1.0 to evaluate the influence of individual biokinetic parameters on the overall chemostat dynamics.

8.1.6 Chemostat Model Simulation and Sensitivity Studies

Chemostat model simulation and sensitivity analyses were conducted for steady-state sulfate reduction, and ethanol utilization profiles and the model predictions were compared with the experimental results (as presented in Figures 8-9 through 8-24). As discussed earlier (Section 4.5), the advantages of sensitivity studies in the

chemostat modeling were to obtain information on process conditions that can be altered for enhancing process efficiency and to identify the key parameters that have marked influence on process dynamics; also to estimate the accuracy of the result in order to verify the model parameters for developing the FBBR model. The parameters studied included the maximum specific growth rate, μ_m , half-velocity constant, K_s , maximum yield coefficient, Y , and endogenous decay coefficient, k_d . The profiles of normalized effluent concentration (influent-effluent concentration ratio) with 15%, and 30% increase or decrease in each of these parameters over their typical values were used to demonstrate the changes in the model profiles. The chemostat dynamics for sulfate reduction exhibited high sensitivity to the maximum specific growth rate, μ_m as illustrated in Figures 8-9, and 8-10, projecting lower normalized steady-state effluent concentrations as the specific growth rate increases.

Subsequently, similar sensitivity pattern on chemostat dynamics was observed for ethanol utilization profile as shown in Figures 8-11, and 8-12. These results showed the profound influence of maximum specific growth rate on the process, and consequently, on the FBBR process dynamics. The results clearly demonstrated that a higher maximum specific growth rate increases the level of sulfate reduction and ethanol utilization at different dilution rates.

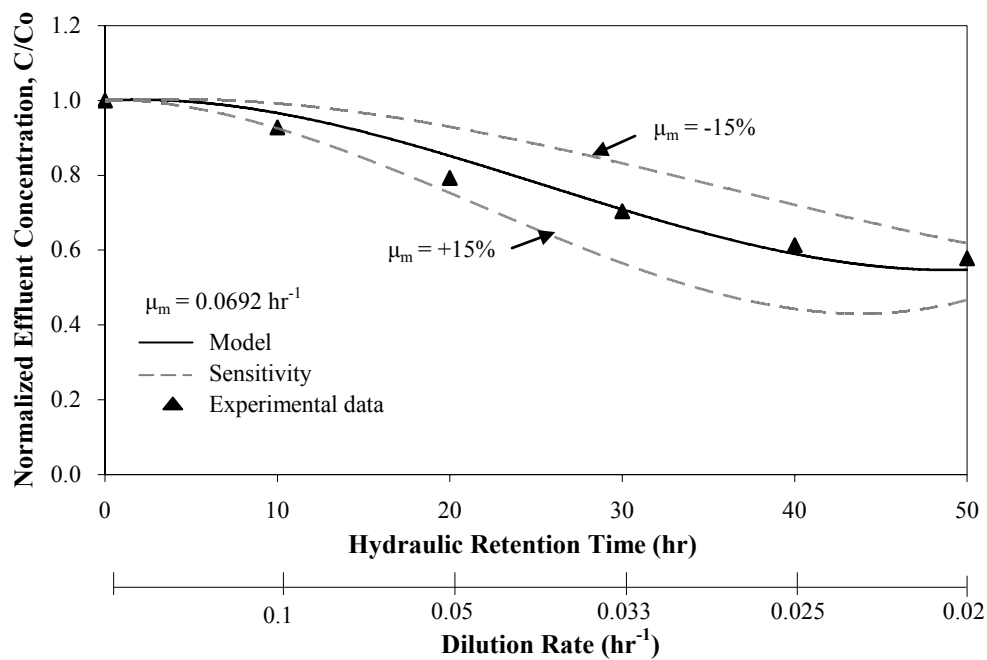


Figure 8-9 Effect of Maximum Specific Growth Rate, μ_m on Chemostat Dynamics for Sulfate Reduction ($C/S = 1.0$)

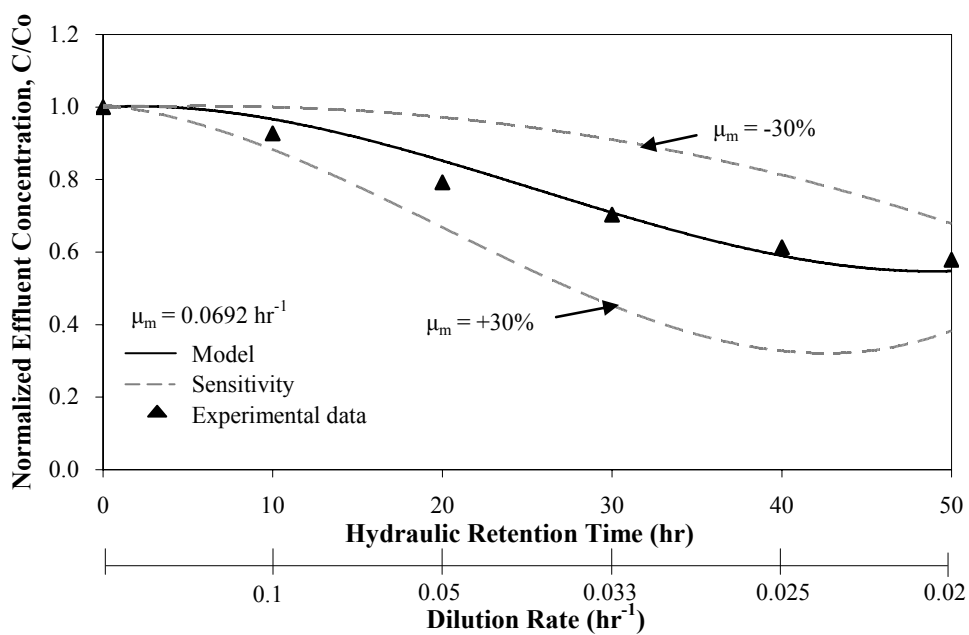


Figure 8-10 Effect of Maximum Specific Growth Rate, μ_m on Chemostat Dynamics for Sulfate Reduction ($C/S = 1.0$)

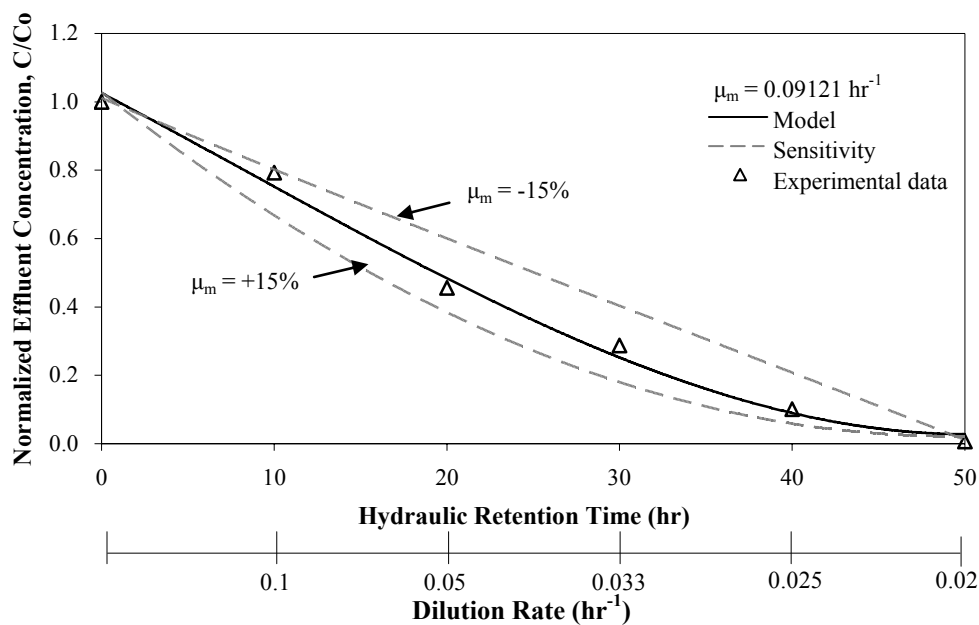


Figure 8-11 Effect of Maximum Specific Growth Rate, μ_m on Chemostat Dynamics for Ethanol Utilization ($C/S = 1.0$)

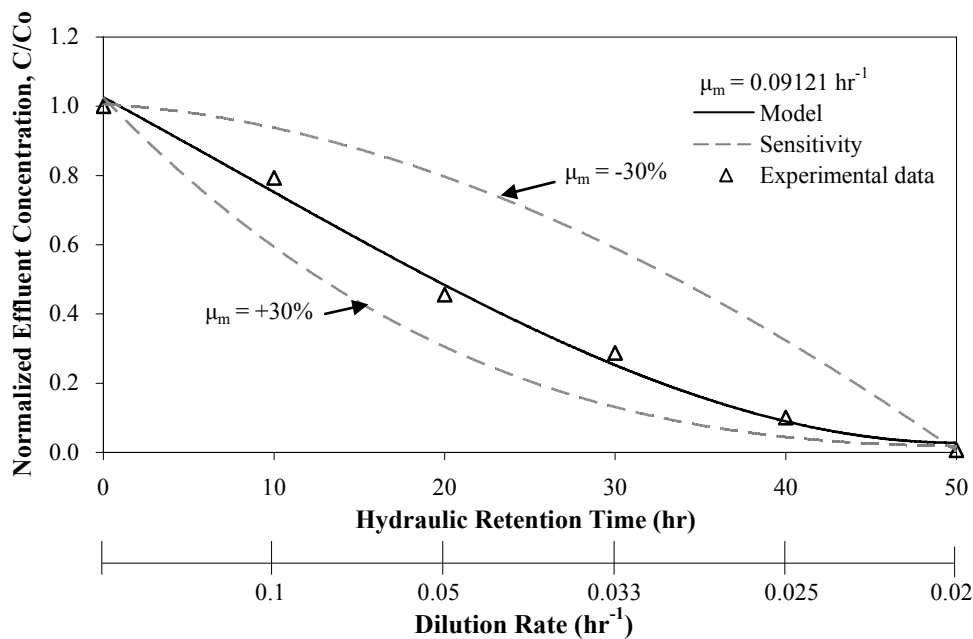


Figure 8-12 Effect of Maximum Specific Growth Rate, μ_m on Chemostat Dynamics for Ethanol Utilization ($C/S = 1.0$)

The sensitivity of chemostat dynamics for sulfate reduction with respect to half-velocity constant, K_s was investigated. As depicted in Figures 8-13, and 8-14, the simulations were conducted 15% or 30% increase and decrease over the best-fit values. The results indicated that the steady-state normalized effluent concentrations increase when half-velocity constant increases which demonstrated lower sulfate reduction. The sensitivity analyses for steady-state ethanol utilization at different dilution rates followed the same pattern as those of sulfate reduction. The results are presented in Figures 8-15, and 8-16.

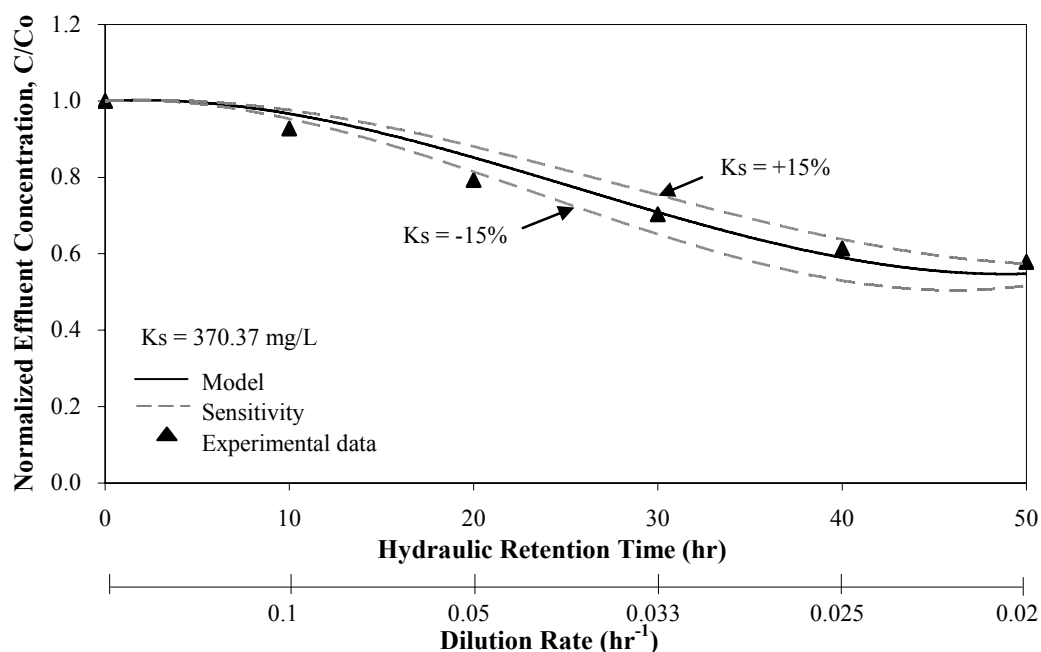


Figure 8-13 Effect of Half-velocity Constant, K_s on Chemostat Dynamics for Sulfate Reduction ($C/S = 1.0$)

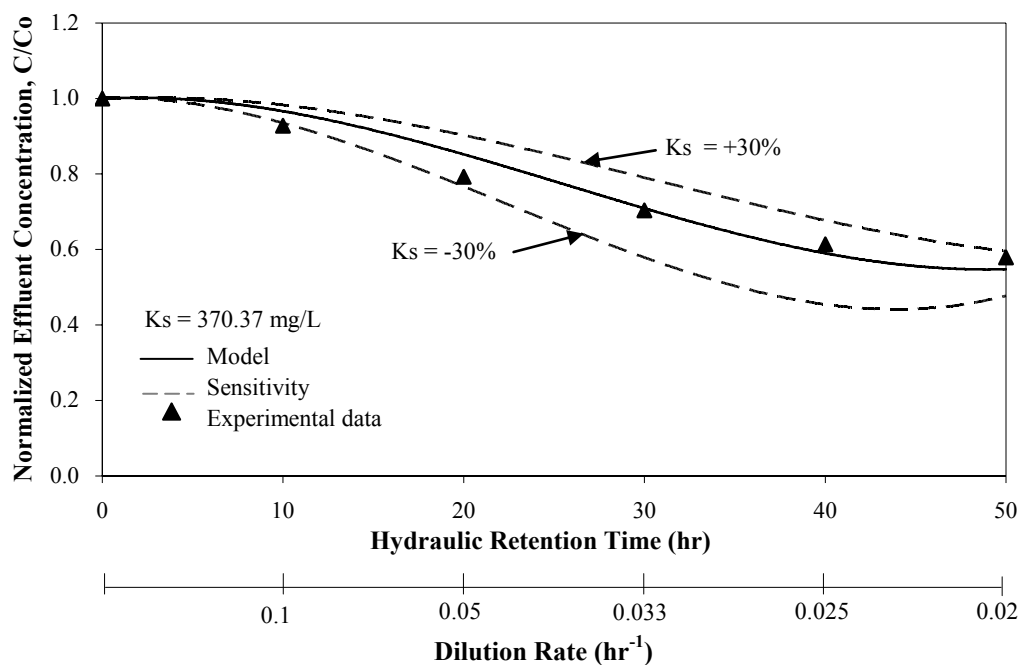


Figure 8-14 Effect of Half-velocity Constant, K_s , on Chemostat Dynamics for Sulfate Reduction ($C/S = 1.0$)

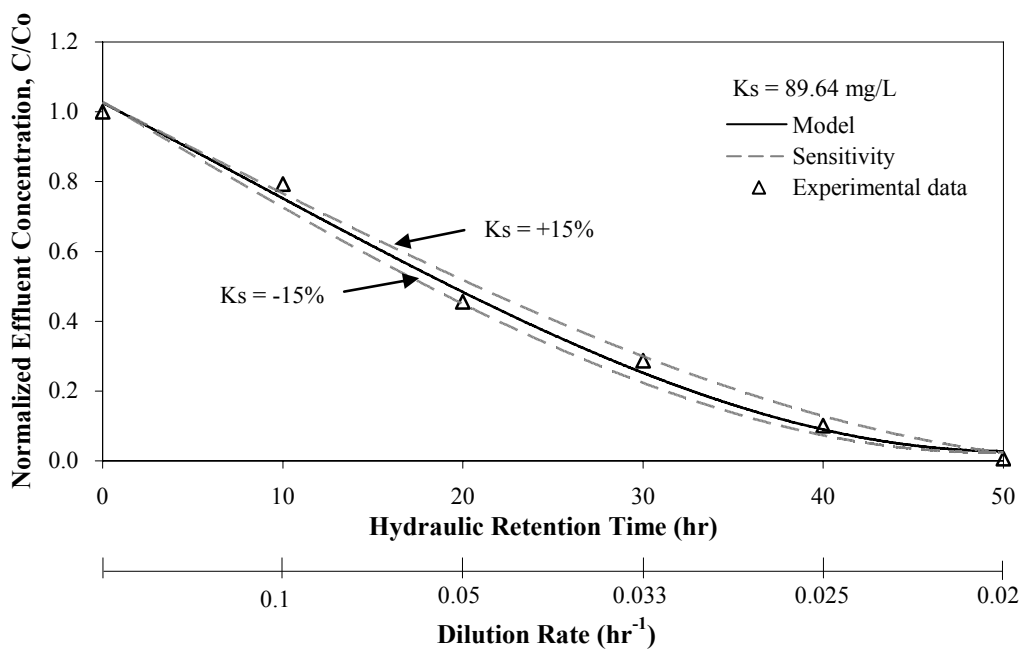


Figure 8-15 Effect of Half-velocity Constant, K_s , on Chemostat Dynamics for Ethanol Utilization ($C/S = 1.0$)

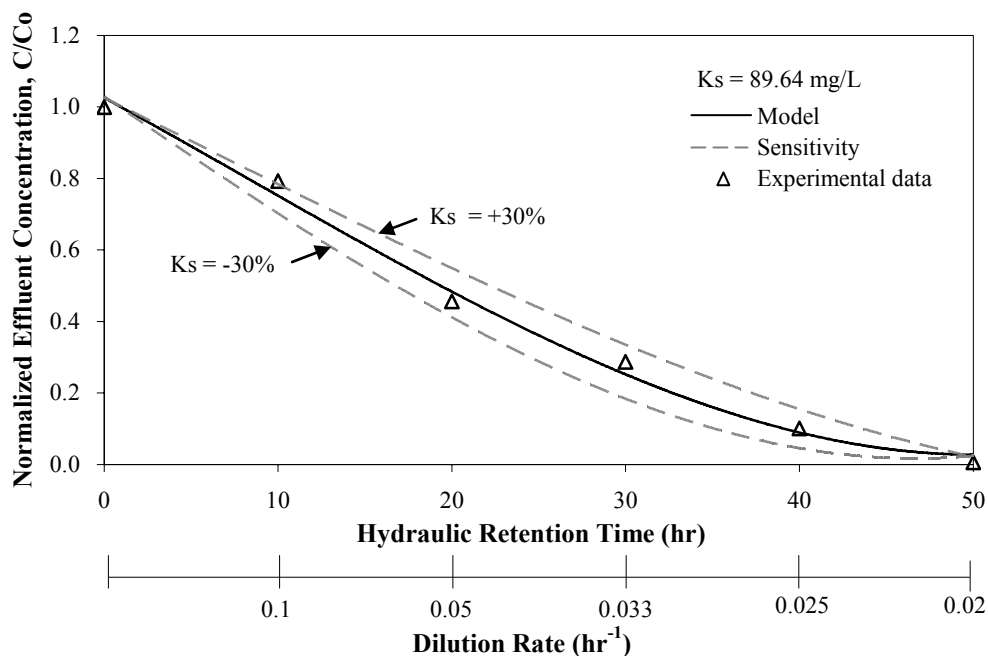


Figure 8-16 Effect of Half-velocity Constant, K_s on Chemostat Dynamics for Ethanol Utilization ($C/S = 1.0$)

The sensitivity analyses performed with respect to endogenous decay coefficient, k_d projected similar outcome as did half-velocity constant. The results are illustrated in Figures 8-17, 8-18, 8-19, and 8-20. The simulations were conducted with a 15%, and 30% increase or decrease over the best-fit values of endogenous decay coefficient for sulfate reduction ($k_d = 0.0190 \text{ hr}^{-1}$), and ethanol utilization ($k_d = 0.0232 \text{ hr}^{-1}$). The results indicated that the level of sulfate reduction decreases as decay coefficient increases.

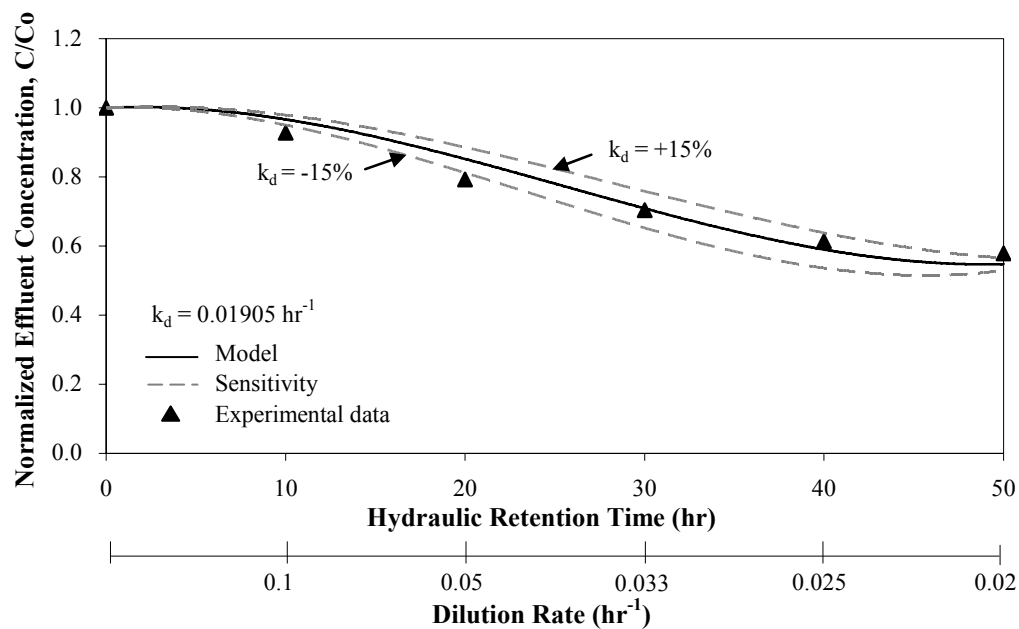


Figure 8-17 Effect of Endogenous Decay Coefficient, k_d on Chemostat Dynamics for Sulfate Reduction ($C/S = 1.0$)

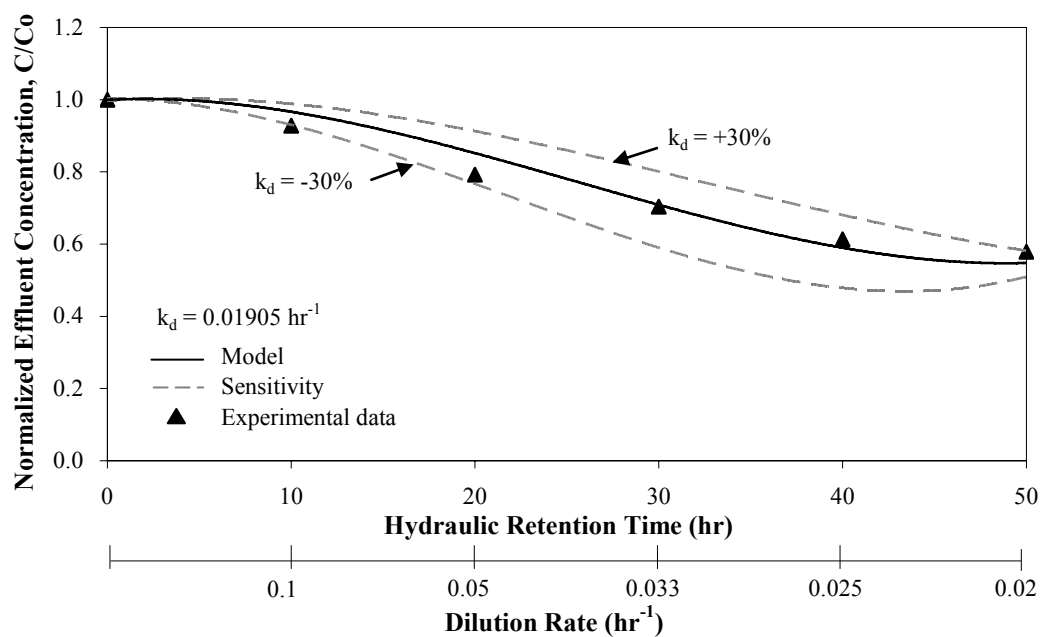


Figure 8-18 Effect of Endogenous Decay Coefficient, k_d on Chemostat Dynamics for Sulfate Reduction ($C/S = 1.0$)

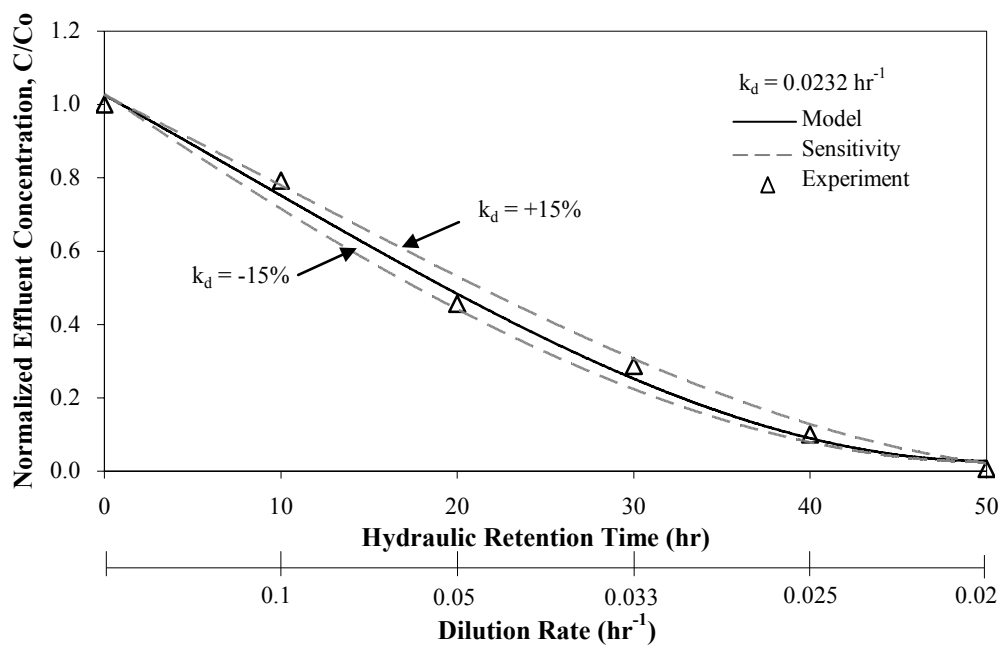


Figure 8-19 Effect of Endogenous Decay Coefficient, k_d on Chemostat Dynamics for Ethanol Utilization ($C/S = 1.0$)

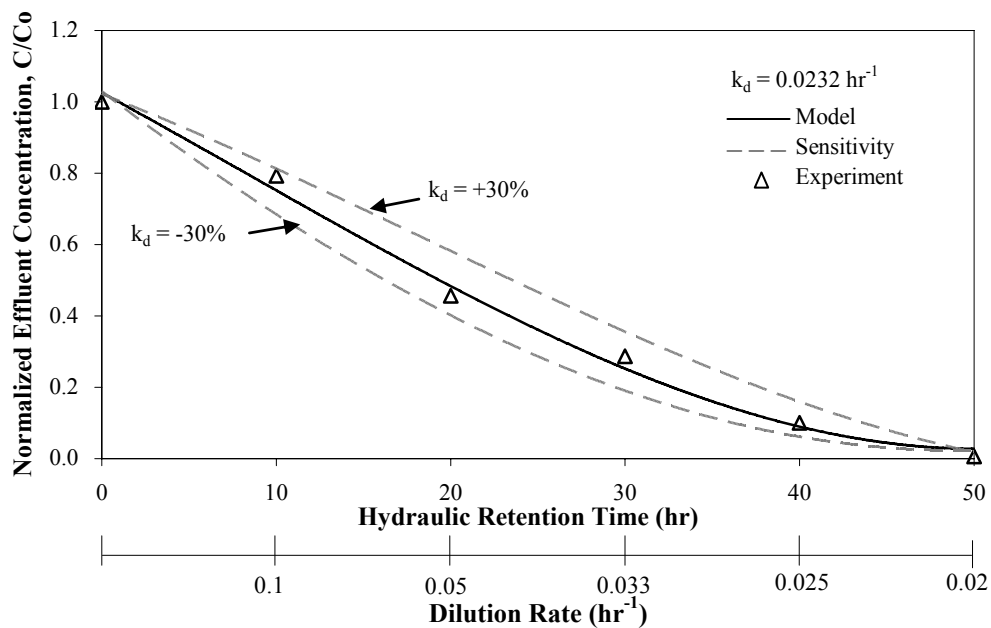


Figure 8-20 Effect of Endogenous Decay Coefficient, k_d on Chemostat Dynamics for Ethanol Utilization ($C/S = 1.0$)

Simulation studies were further conducted with respect to the microbial yield coefficient, Y for sulfate reduction and ethanol utilization. The results with $\pm 15\%$, and $\pm 30\%$ variations, are presented in Figures 8-21, 8-22, 8-23, and 8-24. It was observed that the yield coefficient has insignificant influence on the chemostat dynamics for both sulfate reduction and ethanol utilization.

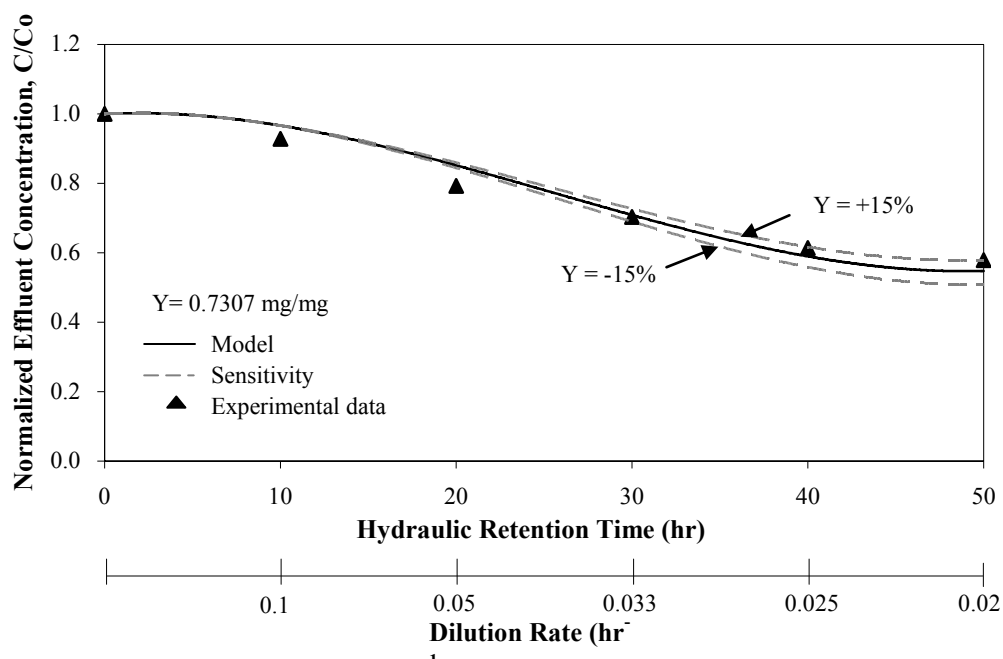


Figure 8-21 Effect of Maximum Yield Coefficient, Y on Chemostat Dynamics for Sulfate Reduction ($C/S = 1.0$)

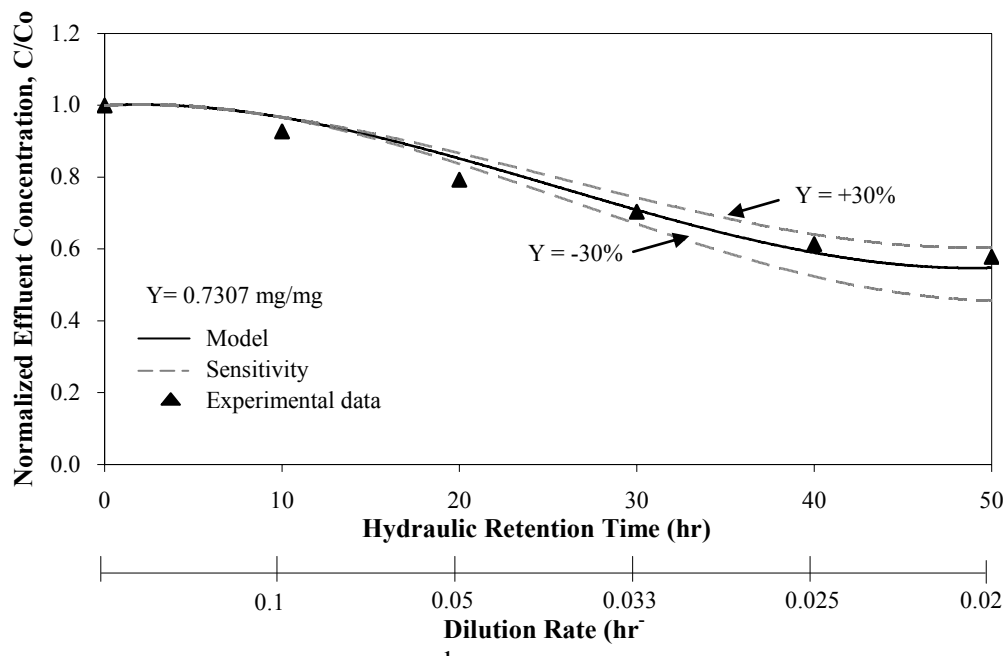


Figure 8-22 Effect of Maximum Yield Coefficient, Y on Chemostat Dynamics for Sulfate Reduction ($C/S = 1.0$)

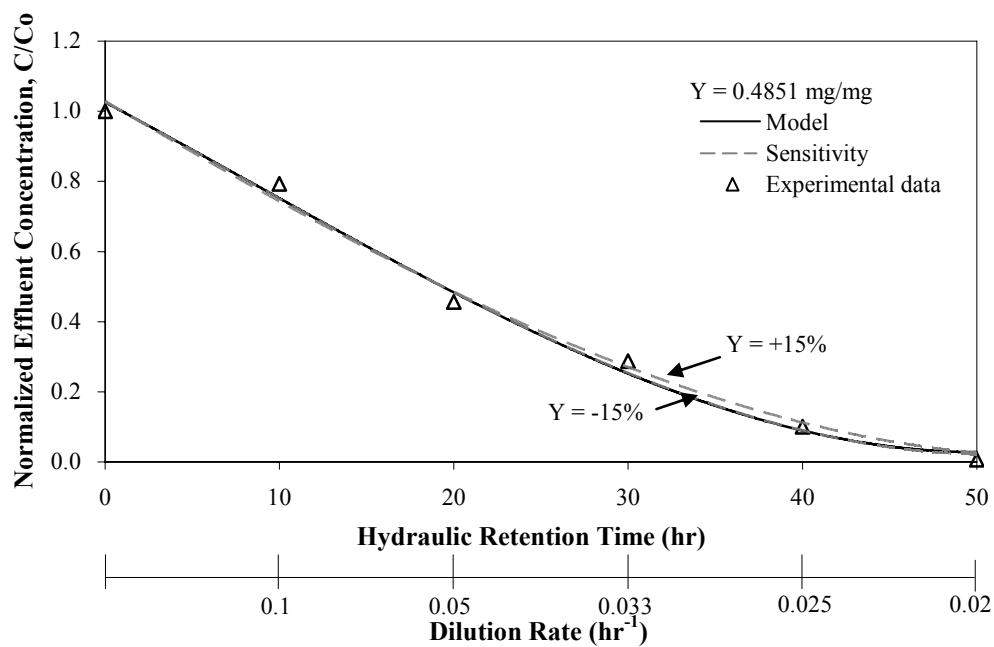


Figure 8-23 Effect of Maximum Yield Coefficient, Y on Chemostat Dynamics for Ethanol Utilization ($C/S = 1.0$)

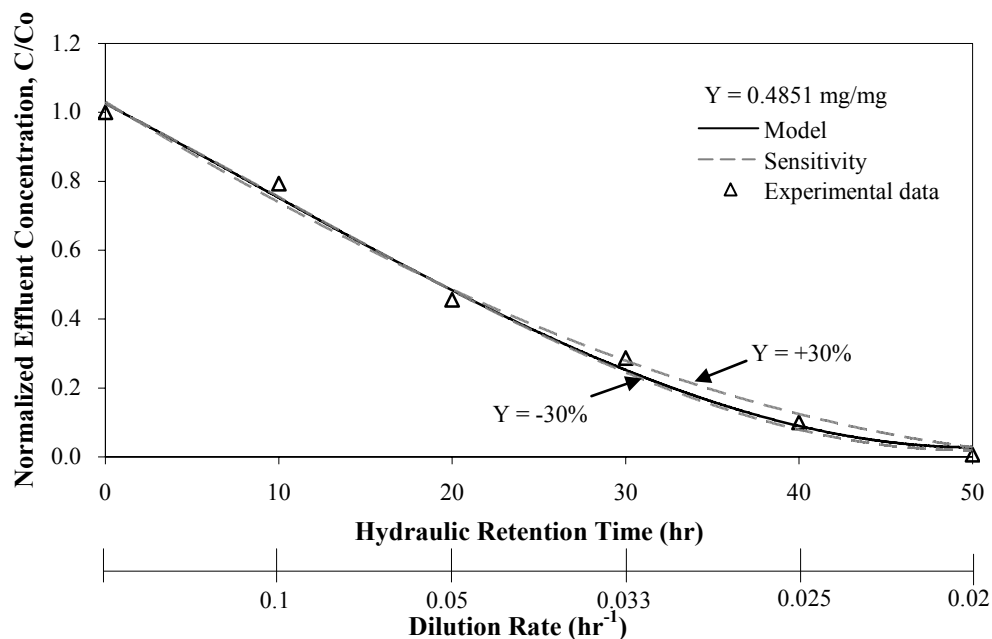


Figure 8-24 Effect of Maximum Yield Coefficient, Y on Chemostat Dynamics for Ethanol Utilization ($C/S = 1.0$)

8.1.7 Effect of Hydrogen Sulfide Toxicity on Biokinetic Parameters

Chemostat studies were conducted using ethanol as carbon source at a temperature of 30°C , a pH of 7.5, and a C/S ratio of 0.8 and 1.0. These experiments employed an influent sulfate concentration of 1100 mg/L and ethanol concentrations of 706.4 mg/L and 563.7 mg/L corresponding to C/S ratios of 0.8 and 1.0, respectively. At each specific dilution rate, when the chemostat system reached steady state, the hydrogen sulfide concentrations were measured, and another dilution rate was employed. The maximum hydrogen sulfide concentration of 58 mg S^{2-}/L obtained at dilution rate of 0.02 for C/S ratio of 1.0. Owing to the low concentration of H_2S , the presence of aqueous hydrogen sulfide in the chemostat system had no toxicity effect

on the biological activity of sulfate reducing bacteria. Consequently, biokinetic parameters obtained from these studies did not reflect the biological toxicity attributable to H_2S production during sulfate reduction. The results of hydrogen sulfide concentrations for the chemostat systems at different dilution rates are summarized in Appendix B, Tables B-3 and B-6 for carbon-to-sulfur ratios of 1.0 and 0.8, respectively.

8.2 Summary and Conclusions

The chemostat studies provided a comparison of the reaction kinetics for sulfate reduction and ethanol utilization under different carbon-to-sulfur ratios of 1.0 and 0.8. More importantly, these experiments provided estimates of biokinetic parameters including the Monod kinetic coefficients, the microbial decay coefficient, and the microbial yield coefficient. Chemostat results validated the chemostat model as good agreement was observed between the experimental data and model predictions. Chemostat model sensitivity studies showed that maximum specific growth rate, μ_m had maximum effect on chemostat dynamics with reference to sulfate reduction and ethanol utilization, while the maximum yield coefficient, Y had the least effect on chemostat dynamics.

CHAPTER 9

FLUIDIZED BED BIOADSORBER REACTOR STUDIES: EXPERIMENTAL RESULTS AND MODEL VERIFICATION

9.1 Tracer Studies for Determination of Dispersion Coefficient and Evaluation of the FBBR Fluid Dynamics

The fluid dynamic characteristics of the FBBR system for this study were investigated by tracer experiments before the operation of the process. Potassium chloride (KCl) was chosen as a non-adsorptive and conservative tracer for this study. One milliliter of the KCl solution at a concentration of 150 g/L was injected into the feed stream at the bottom of the FBBR under non-bioactive conditions, and periodically samples were collected at the reactor outlet. The outlet tracer concentrations were determined by conductivity measurements as described in Standard Methods (2000).

For a typical one-second pulse injection, the expected maximum tracer concentration in the fluid phase was in the order of 15 g/L or lower. The operational features of the reactor used in the tracer studies were similar to those of real FBBR conditions, as depicted in Table 9-1. The system was operated at two recirculation flow rates of 1600 mL/min and 2200 mL/min, corresponding to bed expansions of 20% and 40%, respectively. The tracer analysis provided information on residence time distributions within the FBBR, axial dispersion and tracer diffusion.

Table 9-1 Characteristics of the Fluidized Bed Bioadsorber Reactor

Specifications	
Activated carbon (g)	450
Adsorbent size (mm)	8-10 US mesh (2.00 - 2.38 mm)
Active reactor volume (m ³)	0.001055
Active reactor height (m)	0.52
Cross section area of reactor (m ²)	0.00203
Influent flow rate (mL/min)	13
Retention time (hr)	1.35
Recirculation rate (mL/min)	3120
Upflow velocity (m/sec)	0.0256
Fluidization rate (%)	40
Recirculation ratio	240:1

The results of the tracer tests are presented in Figures 9-1 and 9-2 for bed expansions of 20% and 40%, corresponding to recycle flow rates of 1600 mL/min and 2200 mL/min, respectively. Figure 9-1 presents the actual effluent concentration profiles of the tracer as a function of time, while Figure 9-2 depicts the normalized effluent concentration profiles as a function of normalized time. The normalized effluent tracer concentration is the ratio of the actual concentration C_i to a hypothetical concentration C_{io} that represents the mass of the tracer pulse per unit volume of the reactor. Mass balance evaluations based on outlet tracer concentrations integrated over the entire sampling time confirmed the conservative nature of the tracer.

The non-dimensional tracer analysis scenario depicted in Figure 9-2 presents a better and clearer picture of reactor residence time distributions.

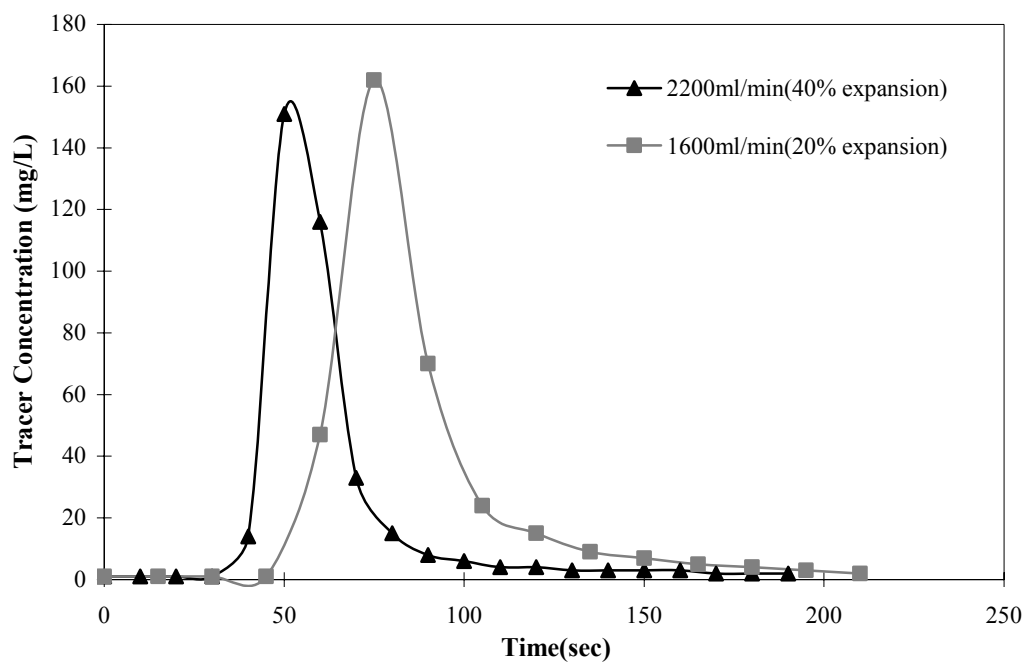


Figure 9-1 Tracer Analysis for FBBR Studies: Effluent Concentration Profiles as Functions of Time

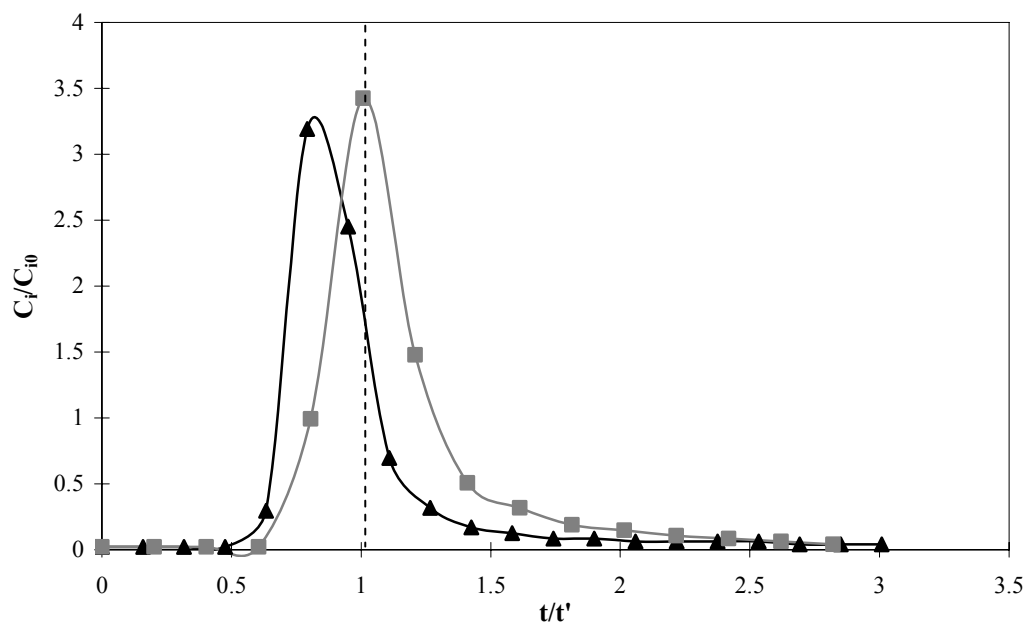


Figure 9-2 Tracer Analysis for FBBR studies: Normalized Effluent Concentration Profiles as Functions of Normalized Time

At 20% bed expansion, the maximum effluent concentration was attained at the average reactor residence time corresponding to a normalized time “ t/t' ” of unity. However, at 40% bed expansion, the maximum effluent concentration was observed at t/t' of 0.8, illustrating the fact that most of the fluid elements experienced a lower reactor residence time than the expected average residence time. Additionally, at a bed expansion of 20%, the results showed that the FBBR dynamics more closely resembled a plug-flow reactor with a significantly higher residence time. Furthermore, the study demonstrated for specific reactor design and flow parameters that reactor operation at 20% bed expansion with recycling would be advantageous under the process conditions.

For small amounts of dispersion, the dimensionless tracer concentration at position H , corresponding to the end of the reactor, is expressed as a function of dimensionless time (Weber, 1972):

$$\frac{C_i}{C_{i_o}} = \frac{1}{(4\pi N_d)^{0.5}} \exp\left[-\frac{(1-\theta^o)^2}{4N_d}\right] \quad (9-1)$$

$$D_z = N_d v_z H \quad (9-2)$$

where

C_{i_o} = Ratio of M_T , the mass of tracer injected as a pulse, to V_R , the volume of the reactor, (mg/L)

C_i = Actual effluent tracer concentration, (mg/L)

θ^o = Ratio of specific time to average time, t/t' , (dimensionless)

D_z = Dispersion Coefficient, (m^2/s)

N_d = Dispersion Number, (dimensionless)

At $t/t' = 1$ for 20% expansion, $C_i/C_{io} = 3.424$ and the reactor dispersion number and dispersion coefficient can be determined from Equations 9-1 and 9-2, and similarly for 40% expansion, at $t/t' = 0.79$ corresponding to the maximum $C_i/C_{io} = 3.191$ as summarized in Table 9-2.

Table 9-2 Dispersion Number and Dispersion Coefficient for the Fluidized Bed Bioadsorber Reactor at Different Recirculation Flowrates

	20% expansion (1600 mL/min)	40% expansion (2200 mL/min)
Dispersion Number (N_d)	0.0068	0.0078
Dispersion Coefficient (D_z)	0.877×10^{-4}	1.61×10^{-4}

As the dispersion number decreases and approaches zero, the flow characteristics and the normalized effluent concentration profiles approach those of a plug flow reactor (PFR) whose dispersion number is zero under theoretically ideal conditions.

9.2 FBBR Process Evaluation and Effect of Different Carbon-to-Sulfur Ratios, pHs, and Initial Sulfate Concentrations

A series of fluidized bed bioadsorber reactors with ethanol as a carbon source were operated to study the sulfate reduction by SRB. The purpose of each column study is presented in Table 9-3.

Table 9-3 Description and Application of the Fluidized Bed Bioadsorber Reactor (FBBR) Systems

Column	Description and Application
Column 1	• Used GAC as supporting media and ethanol as carbon source. • Used for process evaluation employing various operational parameters: different pHs, carbon-to-sulfur ratios, and initial sulfate concentrations.
Column 2	• Used GAC as supporting media and ethanol as carbon source. • Used for model verification employing different initial sulfate concentrations.
Column 3	• Used sand as supporting media and ethanol as carbon source. • Used for process evaluation and model verification employing different initial sulfate concentrations. • Used to study the in-situ hydrogen sulfide stripping of the FBBR process.
Column 4	• Used sand as supporting media and ethanol as carbon source. • Used for model verification employing low initial sulfate concentration of 600 mg/L.

The first FBBR column (Column 1) with GAC as a supporting media was operated for 396 days and the effect of various operational parameters and different initial concentration of the compound in the synthetic brine was studied throughout the column operation. Different pHs, carbon to sulfur ratios, and initial sulfate concentrations were employed in the system throughout the course of FBBR operation. During the first 40 days the effect of combination of both sulfate and

nitrate in the medium was evaluated. For a nitrate level of 300 mg/L, complete removal of nitrate and 12-15% sulfate removal was obtained. The nitrate concentration was gradually reduced to 5 mg/L over a period of 28 days. The reactor started with the initial sulfate concentration of 500 mg/L, and at this stage the sulfate removal efficiency reached 56%. Sulfate was increased to 600, 700, 800, 900, 1000, and 1100 mg/L on days 49, 81, 159, 171, 177, and 215, respectively. The results including the effluent acetate concentration as by-product of the process are illustrated in Figures 9-3 to 9-12.

9.2.1 Effect of Carbon-to-Sulfur Ratio

A carbon to sulfur ratio of 0.8 was applied to the column and a maximum sulfate removal of 56.7% was obtained. Subsequently, C/S ratios of 1.2 and 1.0 were applied to the system and the maximum sulfate removals of 88.2 and 80.46% were achieved, respectively. The C/S ratio was then lowered from 1.2 to 1.0 on day 303 with the corresponding ethanol concentration of 706 mg/L. Consequently, a significant decrease in the sulfate reduction efficiency was observed. The reactor then reached the steady state sulfate reduction of about 80% at pH of 7.5. These results demonstrated the importance of carbon source (ethanol) and C/S ratio as a controlling factor regarding the process efficiency.

9.2.2 Effect of pH

In the FBBR feasibility study the effect of pH on the reactor performance was evaluated. The pH was increased from 6.2 to 7.0 on day 141 by addition of 0.5N NaOH, using a pH controller. The sulfate reduction improved 78% as a result of pH increase. The pH was further increased to 7.5 on day 155 and after which the sulfate reduction reached 83%. These studies demonstrated that the optimal pH was 7.5 corresponding to a C/S ratio of 1.2. For these studies, the reactor maintained on C/S ratio of 1.2 with initial sulfate of 1100 mg/L, and the corresponding ethanol concentration of 846 mg/L.

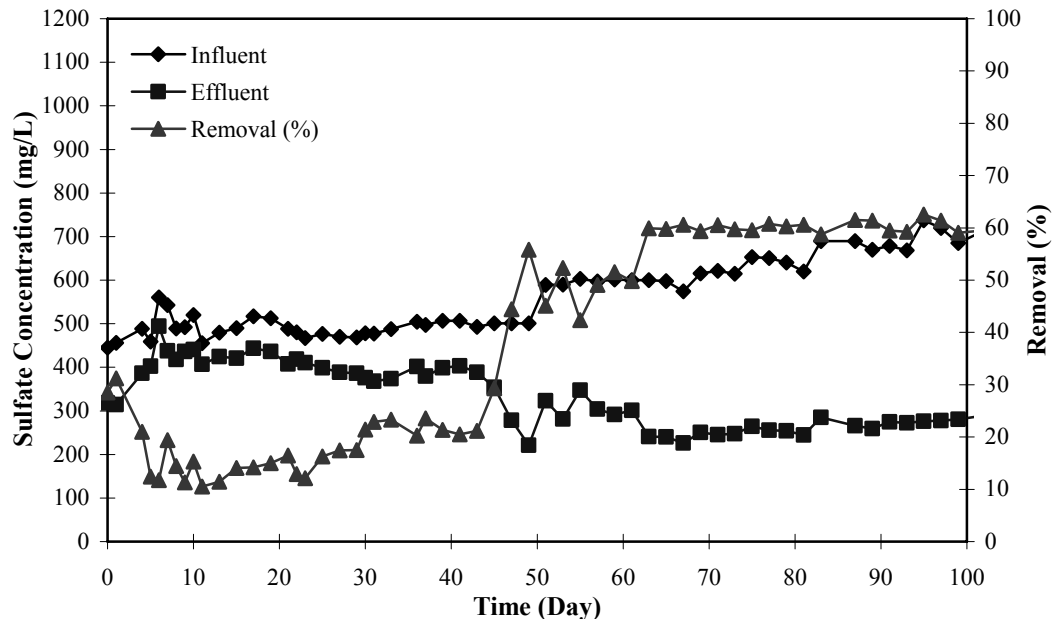


Figure 9-3 Influent and Effluent Sulfate Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 1, Days 0 - 100)

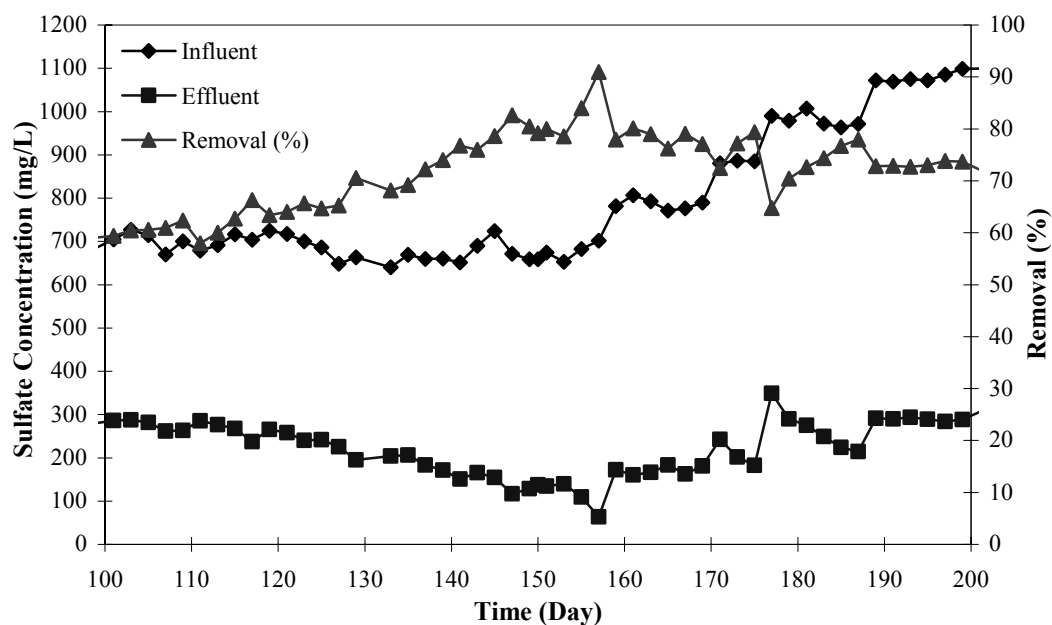


Figure 9-4 Influent and Effluent Sulfate Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 1, Days 100 - 200)

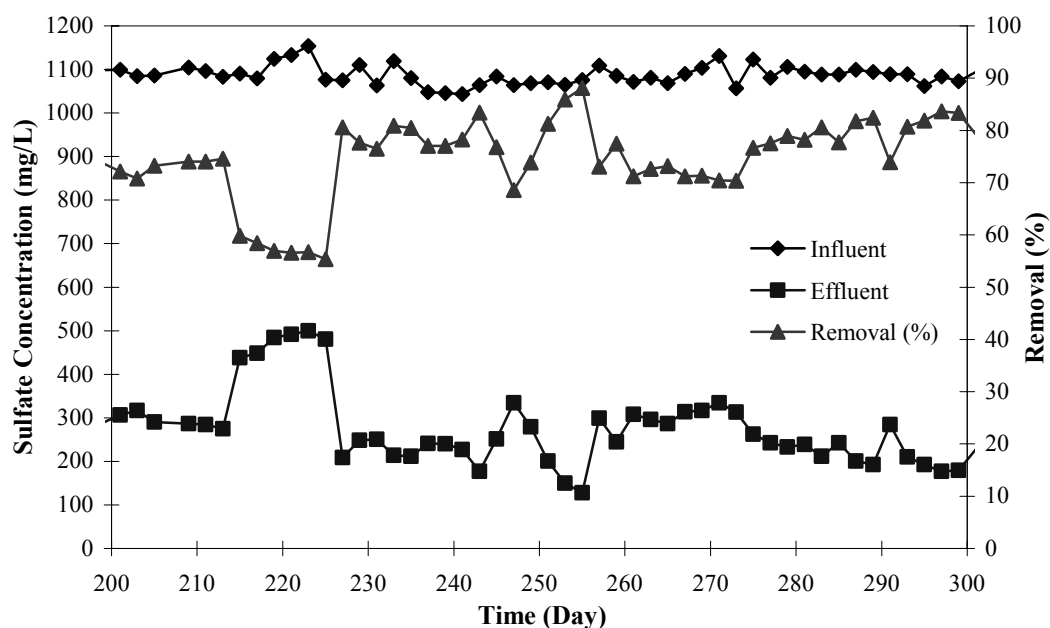


Figure 9-5 Influent and Effluent Sulfate Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 1, Days 200 - 300)

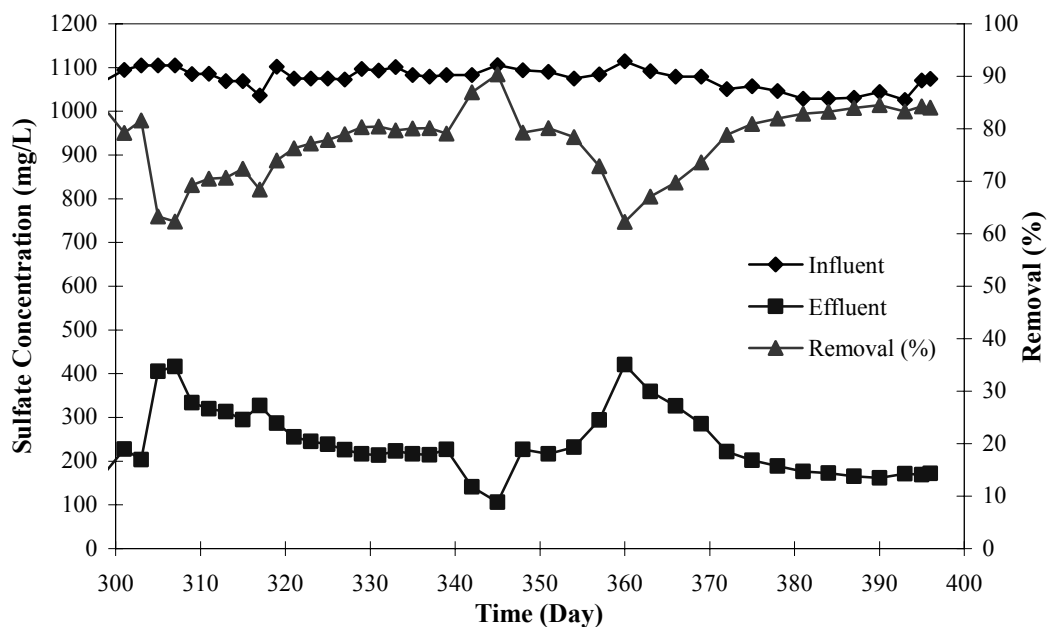


Figure 9-6 Influent and Effluent Sulfate Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 1, Days 300 - 400)

The ethanol utilization in the process was between 85% and 100% as shown in Figures 9-7 through 9-9. The pH increase to 7.0 on day 141 and subsequently to 7.5 on day 155 also reflected increase in ethanol utilization that correlated directly with the improvement in sulfate reduction. When the C/S ratio was lowered from 1.2 to 1.0, the ethanol utilization increased to 100%. However, owing to biomass loss due to reactor cleaning on days 203, 205, 207, 216 and 221, ethanol utilization dropped to about 91%. It must be noted that on day 224, the top 2.5 inches of GAC was also removed to clean up the dead biofilm grown on the GAC, and it was replaced by new activated carbon of the same particle size. The ethanol utilization drop appeared to be due to FBBR maintenance and cleaning as well as medium replacement. The

ethanol removal again reached 100% on day 240. The reactor was eventually shut down after 261 days of operation. The Operational changes throughout the experiment are summarized in Appendix C.

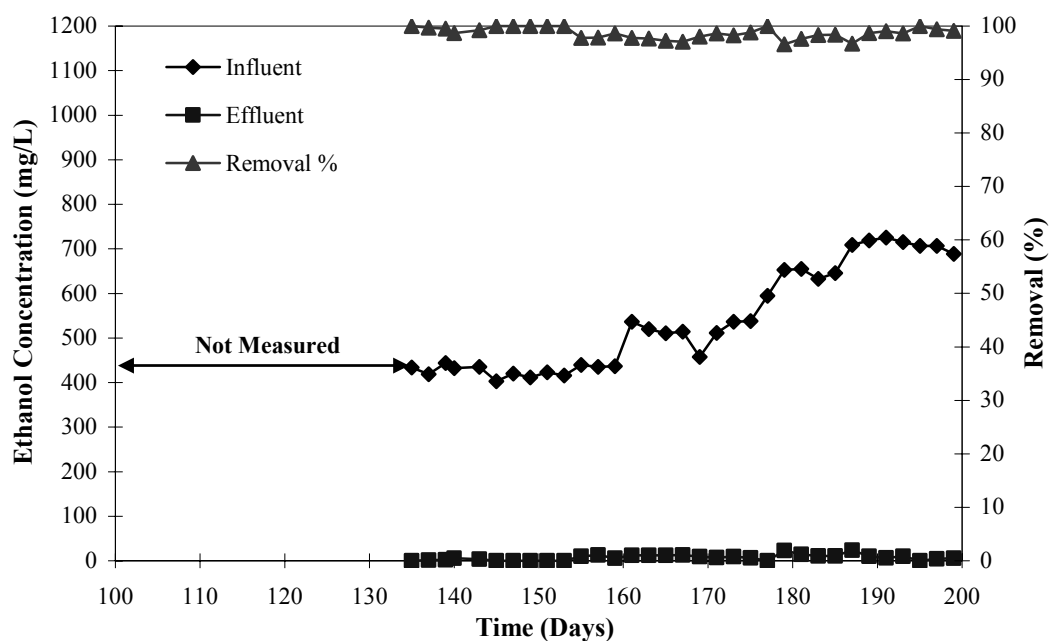


Figure 9-7 Influent and Effluent Ethanol Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 1, Days 100 - 200)

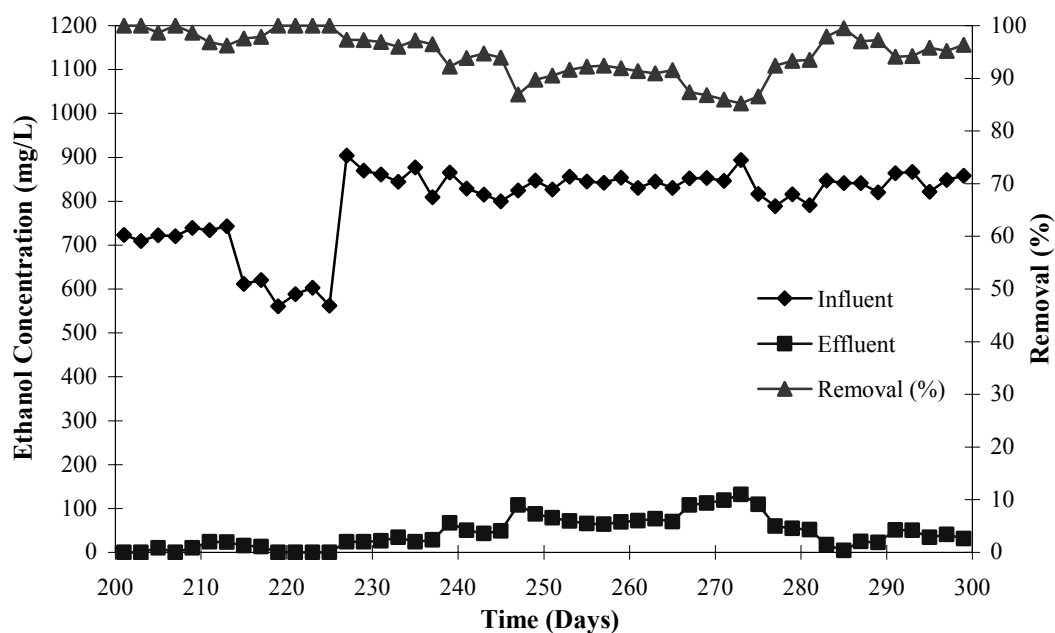


Figure 9-8 Influent and Effluent Ethanol Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 1, Days 200 - 300)

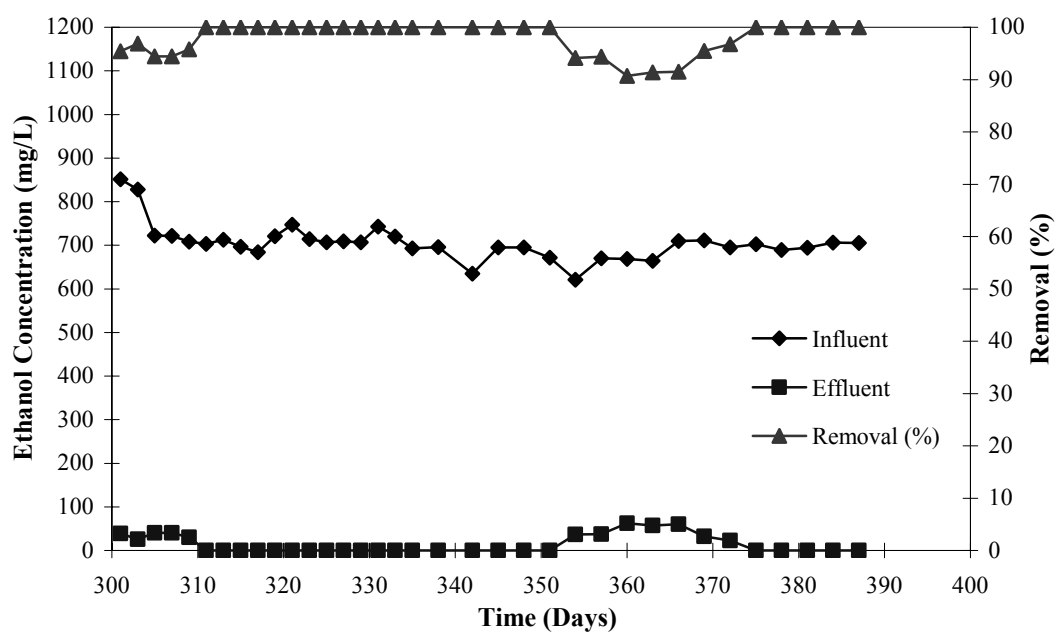


Figure 9-9 Influent and Effluent Ethanol Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 1, Days 300 - 400)

The acetate concentrations in Column 1 were monitored from day 160 when the influent sulfate concentration was increased from 700 mg/L to 800 mg/L. The results are presented in Figure 9-10 and 9-11. The acetate concentrations in the reactor effluent were measured because acetate was the product of simultaneous ethanol utilization and sulfate reduction. Column 1 was operated with a C/S ratio of 1.0 until day 215, during which time the ratio was varied from 0.8 to 1.2 on day 225. The ethanol concentration was always maintained in stoichiometric proportion to the influent sulfate concentration, so as to maintain the desired C/S ratio. In this column, the ethanol removal was between 87% and 100%, as shown in Figures 9-7 through 9-9. The ethanol removal nearly reached 100% before the influent sulfate concentration was increased from 800 to 900 mg/L. At a sulfate concentration of 1100 mg/L, the ethanol removal corresponding to a C/S ratio of 1.0 ranged between 96% and 100%. It must be noted that the SRB utilized ethanol as the carbon substrate and converted the ethanol to acetate. A comparison of ethanol concentration and acetate concentration profiles presented in Figures 9-7 through 9-9, and Figures 9-10 and 9-11, respectively, indicate that the acetate production closely followed the stoichiometry of sulfate removal; and, as the sulfate removal increased, the acetate production also increased, leading to high concentrations of acetate in the reactor effluent.

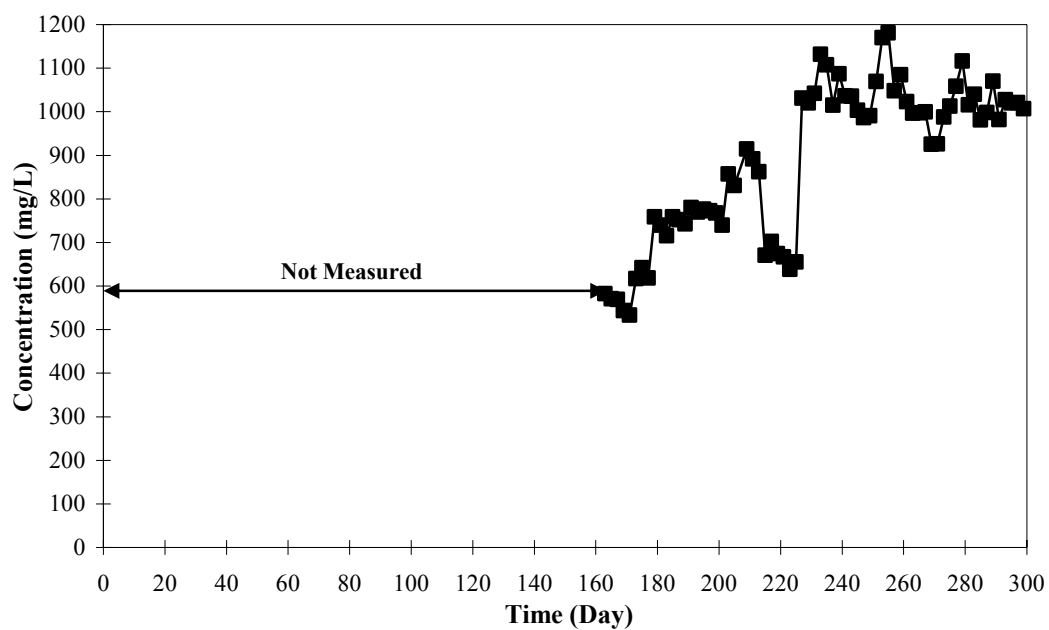


Figure 9-10 Effluent Acetate Concentration Profile in FBBR – GAC
(Column 1, Days 0 - 300)

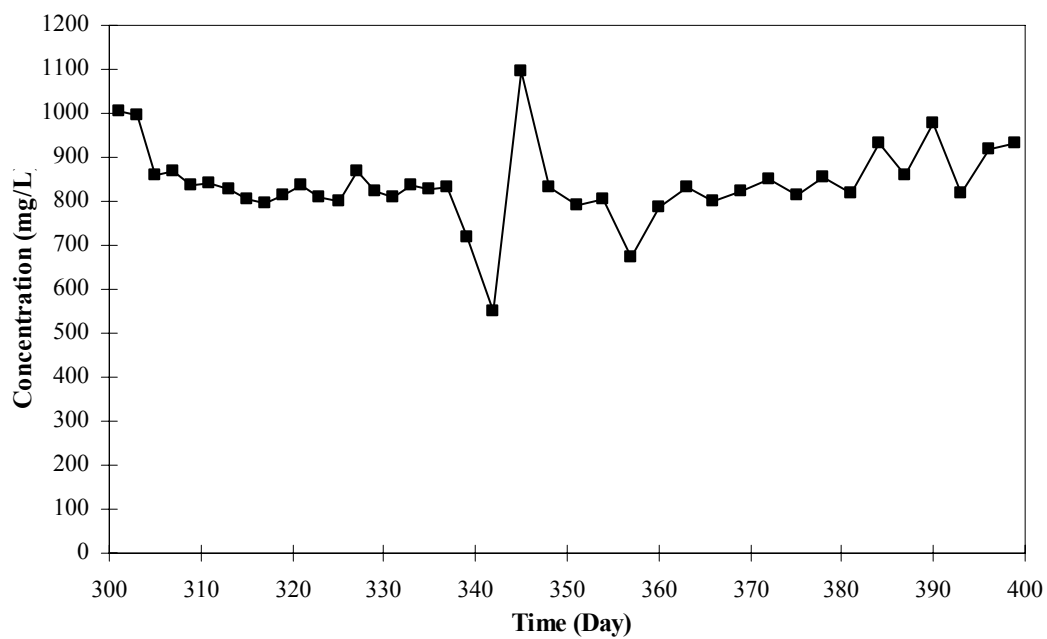


Figure 9-11 Effluent Acetate Concentration Profile in FBBR – GAC
(Column 1, Days 300 - 400)

The hydrogen sulfide concentration profile for Column 1 is presented in Figure 9-12. Mass balance calculations showed that the total sulfide concentrations closely followed the effluent sulfate concentrations. When reactor pH was increased from 6.2 to 7.0 (day 274), as shown in Figure 9-12, the H_2S concentration data were well supported by the sulfate reduction efficiencies in the column. At first, when the pH was increased from 6.2 to 7.0 (day 274), the sulfate removal efficiency increased from 71% to 77%, and further improved to 82% on day 288, as illustrated in Figure 9-5. Subsequently, the pH was increased from 7 to 7.5 (day 290), and the H_2S concentration remained steady at 290 mg/L on day 295. However, during this period, the sulfate removal efficiency immediately dropped to 74%, a factor that could be explained by the shock caused by the sudden introduction of basic solution. The reactor efficiency recovered, exhibited a substantial improvement, and reached 83% on day 300, as shown in Figure 9-6. These results indicated only minor stoichiometric deviations between the extent of sulfate reduction and level of H_2S production. Subsequently, the C/S ratio was decreased from 1.2 to 1.0 on day 303, resulting in a reduction in reactor performance, as reflected by lower H_2S production. However, the reactor performance experienced a gradual recovery from day 306 to day 347. It was observed that this reduction in C/S ratio caused a significant decrease in the sulfate removal efficiency from 82% to 63%, as reflected in Figure 9-6. However, continued operation of the reactor for a few days witnessed a gradual recovery in performance efficiency from 63% to 80% (day 330). At this point, reactor cleaning was necessary to prevent hydraulic problems, and this activity

resulted in loss of some active biomass on days 339 and 340. The H_2S concentration decreased marginally to about 285 mg/L and subsequently increased to about 320 mg/L (day 182) when sufficient biomass had grown and reactor efficiency improved with increase in microbial population.

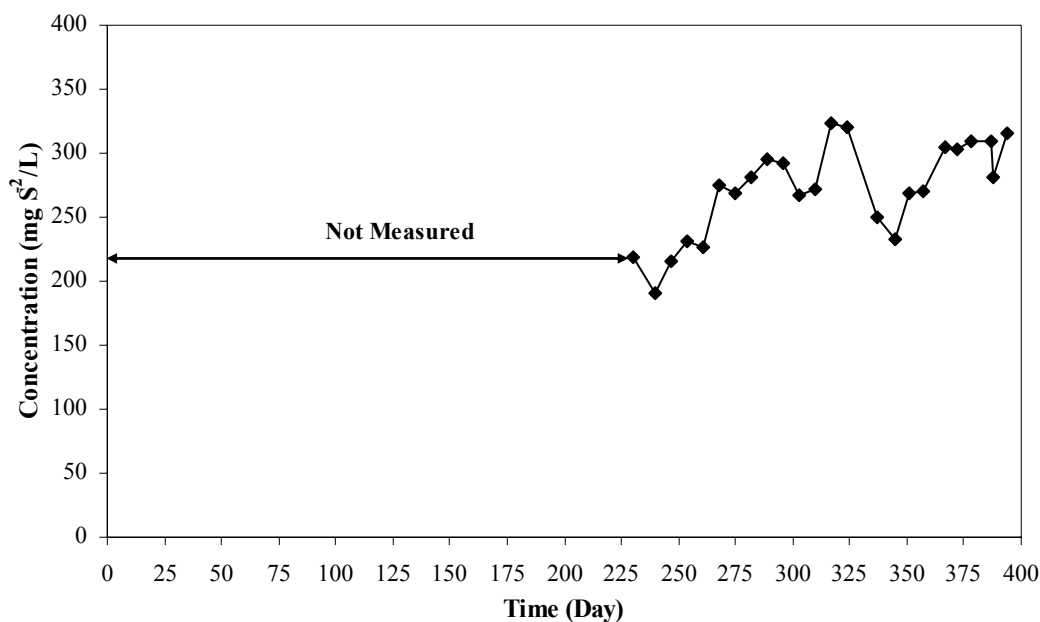


Figure 9-12 Hydrogen Sulfide Concentration Profile for the FBBR – GAC (Column 1)

It was observed that the H_2S production dropped even after reactor cleaning, as its concentration decreased from 320 mg/L to 230 mg/L between days 336 and 351. However, the column performance manifested a gradual but steady improvement, as reflected by a steady increase in H_2S concentration from 230 mg/L to 315 mg/L on day 260. During this period after media replacement and reactor cleaning, the reactor performance decreased temporarily, but recovered after several days. During the

recovery phase, the efficiency increased significantly from 62% on day 360 to 80% on day 371, and eventually to 84% after 17 days, and reached a steady-state value of 84% on day 397, as reflected in Figure 9-6. At this point, the column experienced steady-state operation for over 8 days, and therefore its operation was terminated.

9.3 Laboratory-Scale FBBR-GAC and FBBR-sand Column Studies

9.3.1 FBBR – GAC Column Study

A FBBR system (Column 2) with the characteristics presented in Table 6-2 was operated to study the sulfate reduction for the purpose of model calibration and verification by using ethanol as carbon source and granular activated carbon as media. The profiles of sulfate, ethanol, effluent acetate (process by-product), and hydrogen sulfide concentration are illustrated in Figures 9-13 to 9-16. The reactor operation was commenced in batch mode with initial sulfate concentration of 800 and maintained until complete ethanol utilization obtained at day three; then it was switched to the continuous mode with influent flowrate of 6 mL/min and C/S of 1.0. The column was operated in four stages each, with different initial sulfate concentrations of 800, 900, 1000, and 1100 mg/L. The sulfate removal reached the steady-state operation of %68.9, %66.7, %70.2, and 89.0% for sulfate of 800, 900, 1000, and 1100 mg/L respectively. The pH was maintained at 7.5 by pH controller and injection of 0.5N HCl throughout the column experiment. At the end of first stage, initial sulfate concentration of 800 mg/L, the excess biomass growth on top of the column was removed and influent tubing line was cleaned; subsequently, the

sulfate removal dropped on day 13 and recovered after 7 days. The operational changes for this FBBR – GAC column study are summarized in Appendix C.

The ethanol utilization observed in the reactor demonstrated that nearly complete removal of ethanol (96 - 99%) obtained at each different initial sulfate stages. In the last stage of column operation (initial sulfate concentration of 1100 mg/L), sulfate was reduced by 87% and complete ethanol removal was achieved. The effluent acetate concentrations indicated that more than 95% of ethanol converted to acetate.

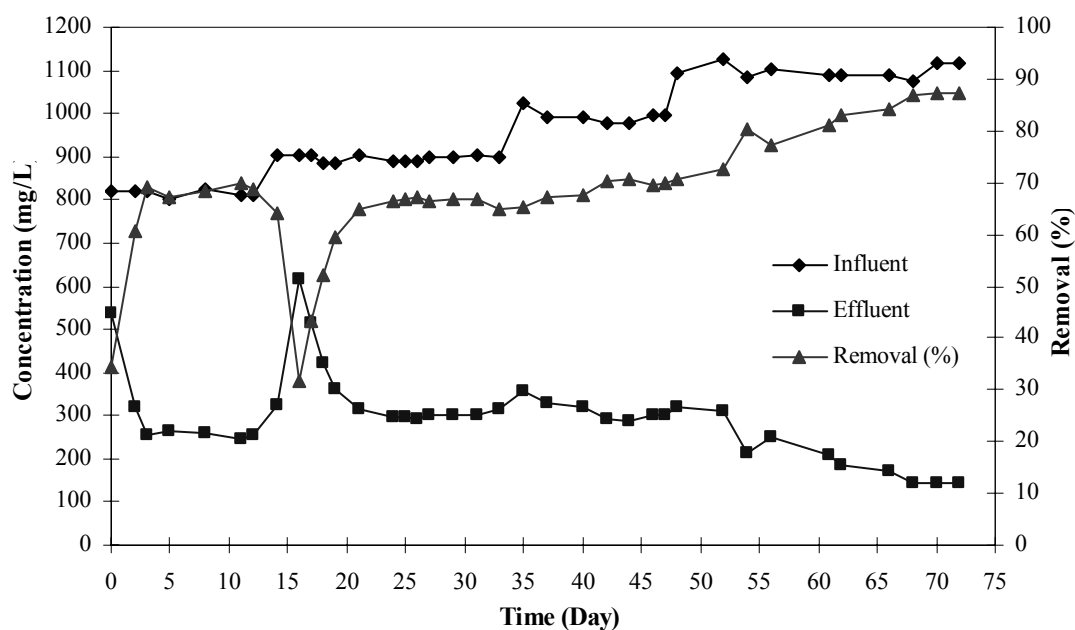


Figure 9-13 Influent and Effluent Sulfate Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 2)

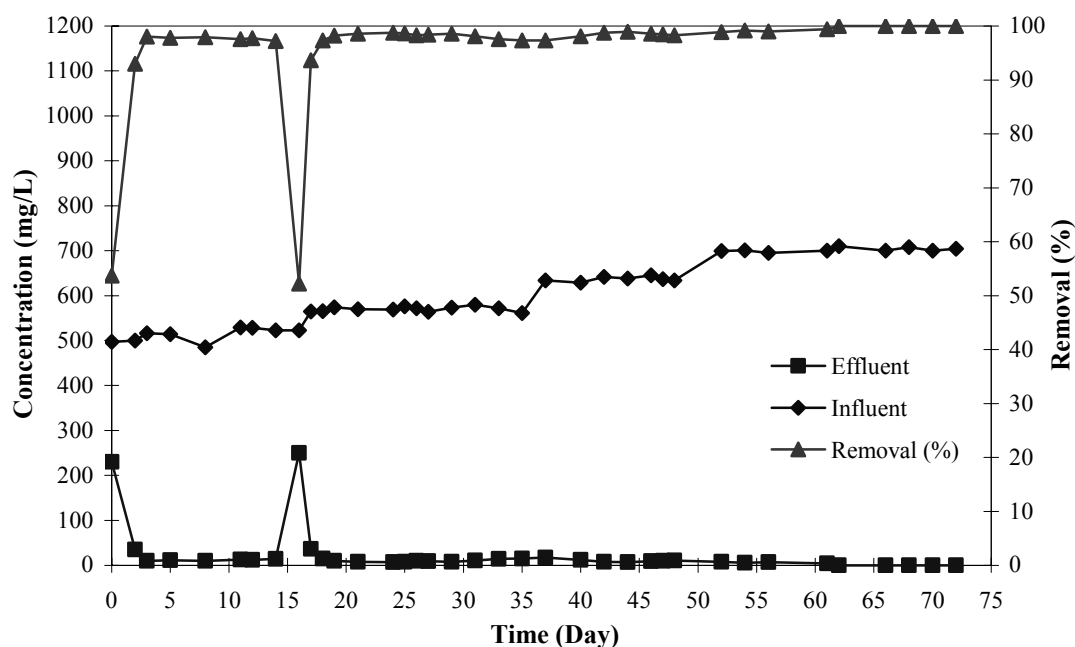


Figure 9-14 Influent and Effluent Ethanol Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 2)

The acetate concentrations in Column 2 were monitored throughout the duration of reactor operation (73 days). The acetate concentrations progressively increased from 340 mg/L to about 905 mg/L, as shown in Figure 9-15. It can be easily observed that the acetate concentrations followed the sulfate reduction and ethanol consumption patterns, in accordance to the reaction stoichiometry. For example, the drop in sulfate reduction (Figure 9-13) and ethanol consumption (Figure 9-14) on day 16 is well reflected by the low acetate concentration of 340 mg/L (Figure 9-15). Similarly on day 52, the sulfate reduction of 72% is reflected by ethanol consumption of 98% and acetate concentration of nearly 900 mg/L. These results indicated that acetate is not

progressively utilized or metabolized as a carbon source, once the utilization of ethanol is completed.

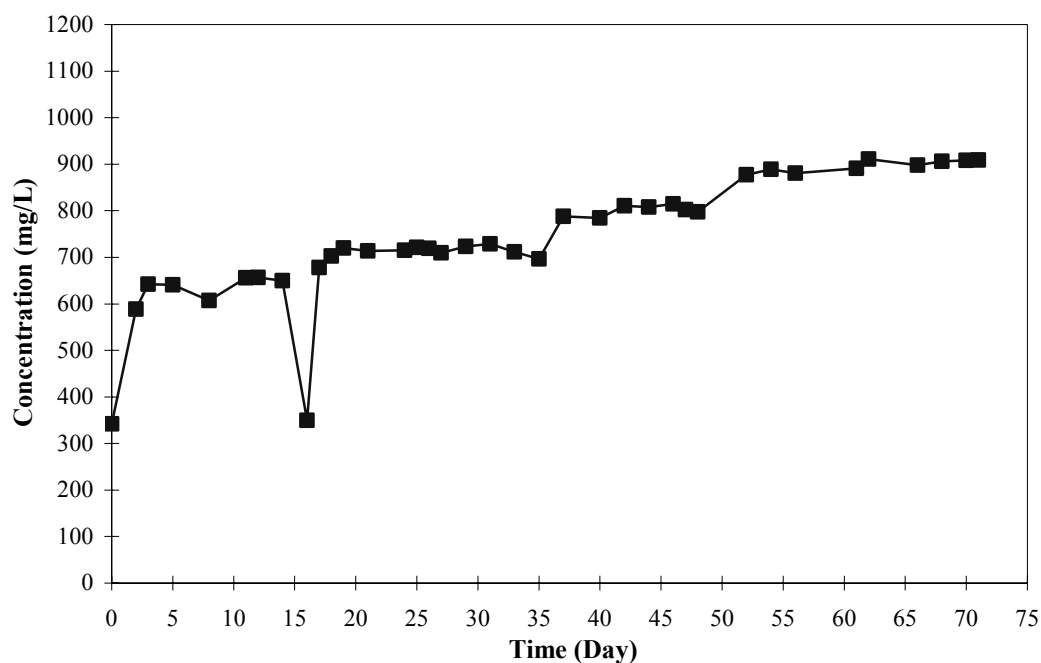


Figure 9-15 Effluent Acetate Concentration Profile in FBBR – GAC (Column 2)

The hydrogen sulfide concentration in this column steadily decreased from 230 mg/L at the commencement of reactor operation to about 215 mg/L on day 10. However, after day 12 the hydrogen sulfide levels dropped substantially from about 215 mg/L to about 85 mg/L, reflecting the low sulfate reduction of 31%. Later, when the reactor efficiency increased to about 73% on day 67, the hydrogen sulfide concentration correspondingly increased to about 360 mg/L. These results clearly demonstrated that the hydrogen sulfide production approximately followed the

reaction stoichiometry of sulfate reduction and ethanol utilization. Aqueous H_2S concentration of the effluent was analyzed weekly and the results are presented in Figure 9-16. As described in the previous section, the complete H_2S production followed the stoichiometric patterns of sulfate reduction process, projecting the same profile pattern as the sulfate removal efficiency profile.

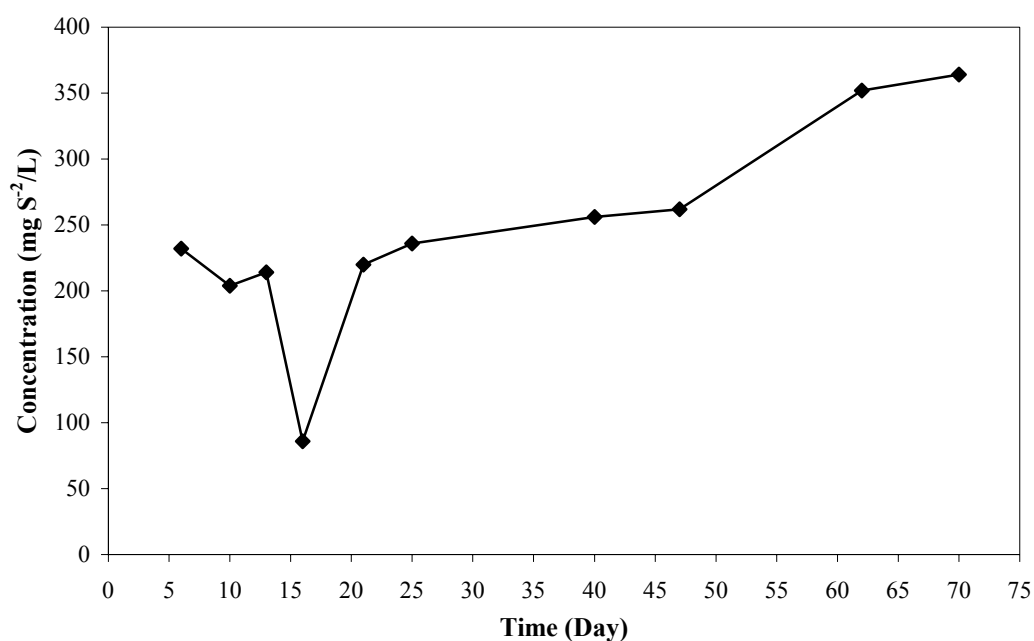


Figure 9-16 Hydrogen Sulfide Concentration Profile for the FBBR – GAC (Column 2)

9.3.2 FBBR – sand Column Study

A typical FBBR system (Column 3) was operated to study the sulfate reduction employing sand as supporting medium and ethanol as carbon source. The sand particles were coated with the biomass obtained from the previous column study

(Column 2) and the reactor operation was commenced in the batch mode with recirculation for five days to achieve a fine biofilm coating of the GAC using a mixed culture of sulfate-reducing bacteria. The effluent sulfate reduction profiles are shown in Figure 9-17. The sulfate removal reached 92% on day 5 with the initial sulfate concentration of 700 mg/L; then the system was switched to continuous mode operation at an influent flowrate of 6 mL/min. The C/S ratio in the influent stream was kept at 1.0 and influent sulfate concentration of 700 mg/L was maintained for 14 days. In this phase of study, the sulfate removal efficiency reached a steady-state value of 71%. In the next phase, the sulfate concentration was raised to 800 mg/L and maintained for 7 days and sulfate removal of 74% was experienced. Subsequently, the column was fed with 900 mg/L of sulfate and maintained under the same operating condition for 29 days, at which stage removal efficiency reached 72.5%. On day 50, the influent sulfate concentration was increased to 1100 mg/L, and a sulfate removal of 75% was obtained. The removal then started to increase and reached 79% possibly due to prolific biomass growth. It is important to note that the column operation had to be frequently interrupted for removal of excess biomass. The operational changes for Column 3 are summarized in Appendix C.

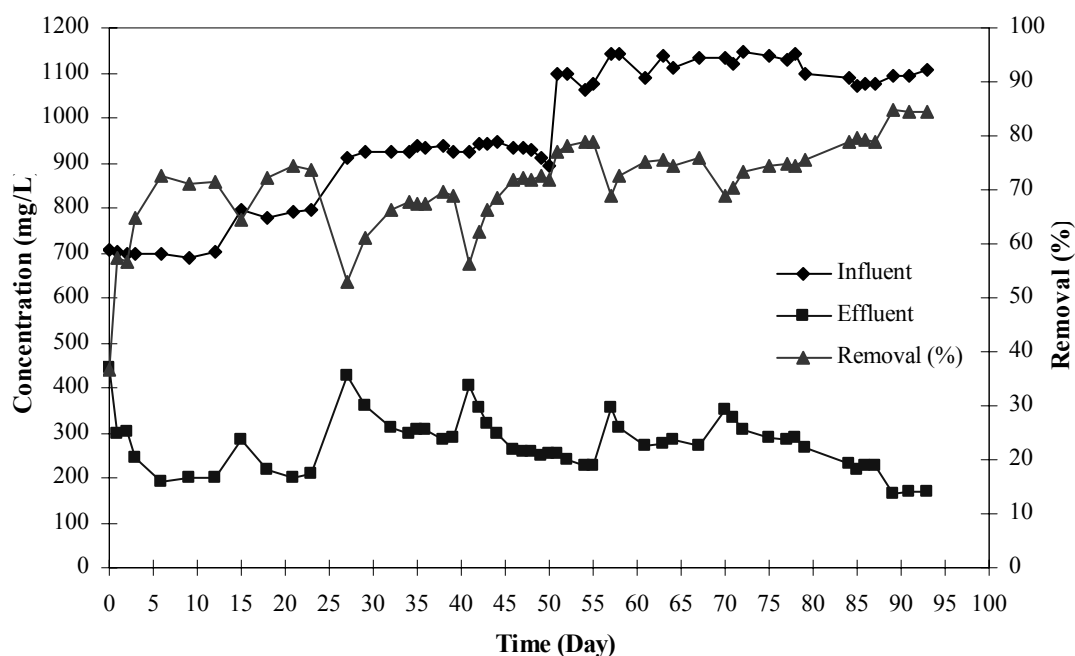


Figure 9-17 Influent and Effluent Sulfate Concentration Profiles and Removal Efficiencies in FBBR – sand (Column 3)

The effluent ethanol concentrations and ethanol utilization levels are depicted in Figure 9-18. The reactor pH was adjusted to a constant value of 7.5 and the C/S ratio was maintained constant at 1.0. The results indicated that after the influent sulfate concentration was increased to the maximum value of 1100 mg/L, the ethanol consumption increased from 69% to about 92% (day 32), and eventually to nearly 100% on day 90. As the column operation progressed, the ethanol consumption manifested a gradual increase at higher influent sulfate concentrations.

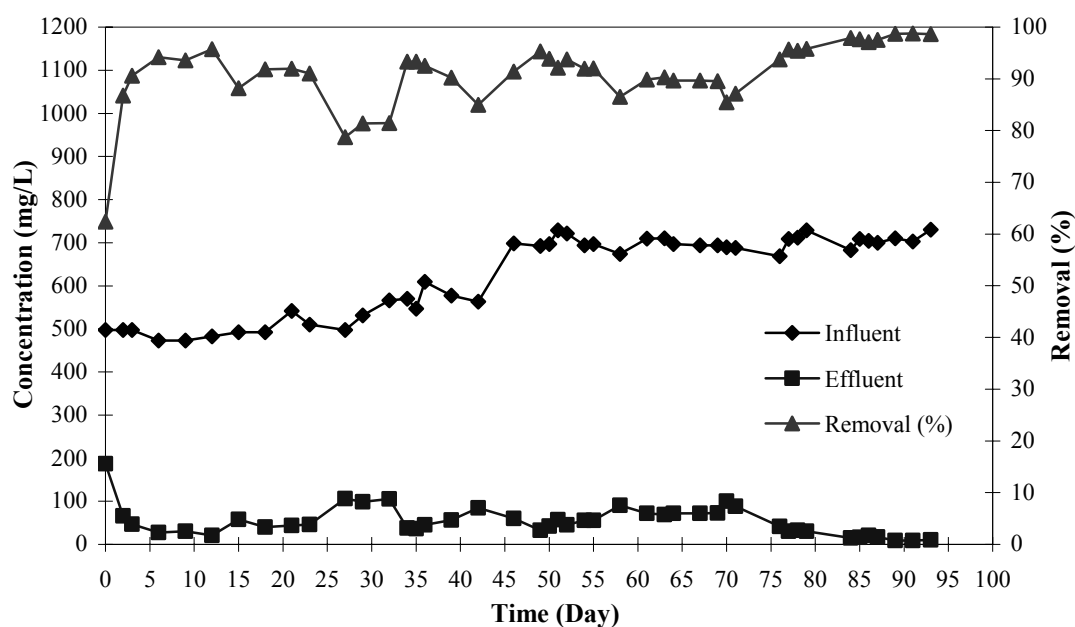


Figure 9-18 Influent and Effluent Ethanol Concentration Profiles and Removal Efficiencies in FBBR – sand (Column 3)

The ethanol consumption further increased after the hydrogen sulfide stripping operation on day 85. The results emphasized that reactor cleaning and hydrogen sulfide stripping improved ethanol consumption and overall reactor efficiency.

The acetate concentration in Column 3 was monitored throughout the duration of reactor operation (93 days). It must be noted that the acetate production often closely followed the stoichiometric patterns of ethanol consumption and sulfate removal. This is so because acetate is the metabolic organic product of ethanol utilization in the biological sulfate reduction process. As presented in Figure 9-19, the acetate concentrations progressively increased from 180 mg/L to about 810 mg/L,

maintaining a stoichiometric relation with the ethanol concentration profile shown in Figure 9-18. A comparison of ethanol consumption (Figure 9-18) and acetate production (Figure 9-19) adequately validates the stoichiometric pattern. These results further indicate that acetate is not further utilized in the process, once ethanol is completely depleted as the carbon source.

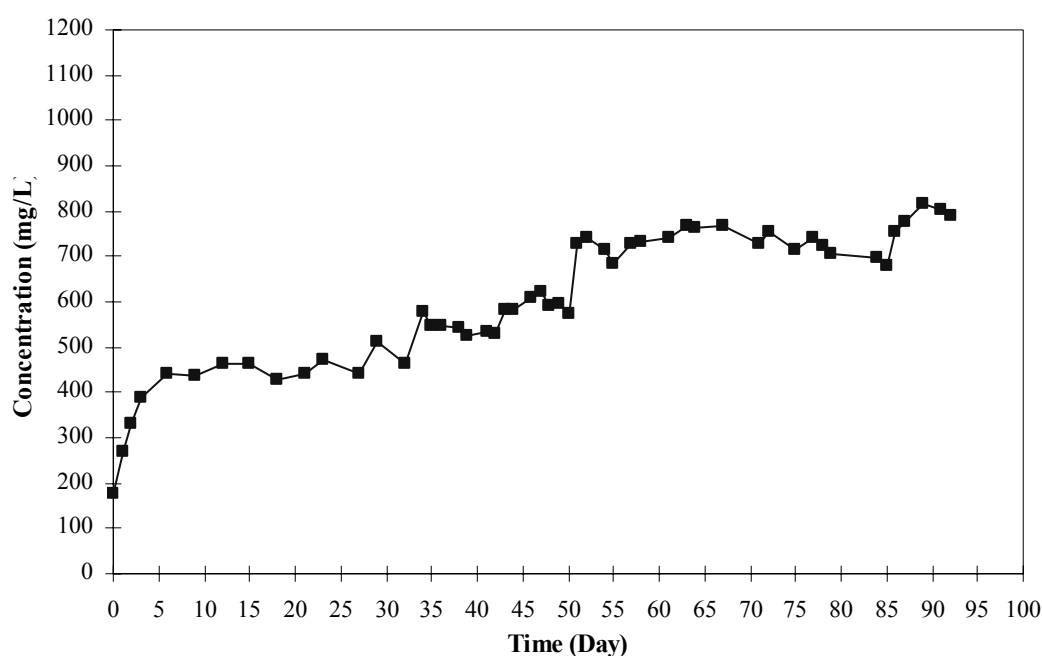


Figure 9-19 Effluent Acetate Concentration Profile in FBBR – sand (Column 3)

9.4 Effect of H₂S Stripping in FBBR – sand Process

In order to investigate the effect of hydrogen sulfide on the removal efficiency, the column was purged in-situ with nitrogen gas. The investigation was commenced on day 85 for duration of 5 days, employing nitrogen gas as stripper at flowrate of 30 mL/min through a fine-bubble stainless diffuser (Figure 9-20). The diffuser was

placed near the top of the sand bed with 33in of diffused water height above it. The pH of the system was maintained at 7.5 by automatic injection of appropriate amount of basic or acid solutions. The column was stripped for five days, during which time the H_2S concentration dropped from 282 mg/L to 216 mg/L. This resulted in an increase in sulfate removal efficiency from 79% to 85.5%, owing to lower H_2S toxicity. This study clearly indicated the significance of nitrogen stripping of hydrogen sulfide in the FBBR system with respect to sulfate removal efficiency. The aqueous phase H_2S concentration profile for the FBBR-sand process is presented in Figure 9-21; demonstrating that the hydrogen sulfide concentrations closely followed the patterns of effluent sulfate concentrations and removals. As may be observed from figures, the hydrogen sulfide concentration steadily increased from 150 mg/L at the commencement of reactor operation to about 305 mg/L on day 60. At this point, the hydrogen sulfide production dropped from about 300 mg/L to 255 mg/L, owing to reactor cleaning and biomass washout. The reactor performance then manifested a gradual but steady improvement, as reflected by a steady increase in H_2S concentration from 255 mg/L to 284 mg/L on day 72. The H_2S remained at the steady-state concentration of about 285 mg/L for 12 days. The hydrogen sulfide stripping was performed on the FBBR system on day 85 as described earlier in this section.

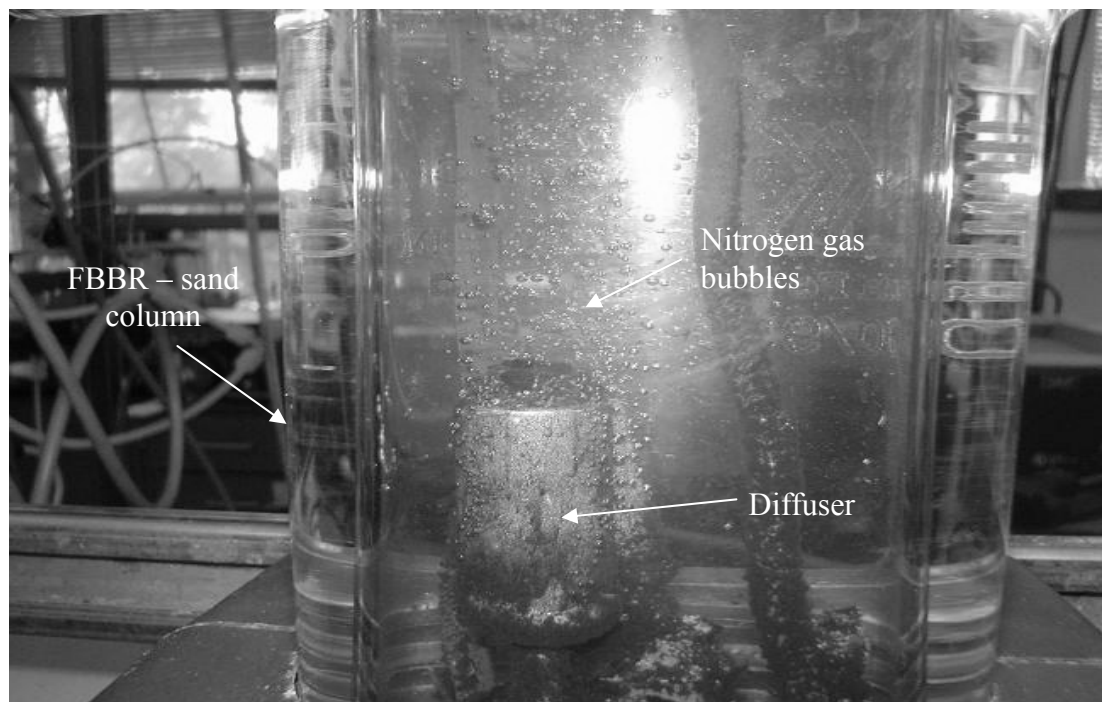


Figure 9-20 Hydrogen Sulfide Stripping in FBBR – sand Column by Nitrogen Gas

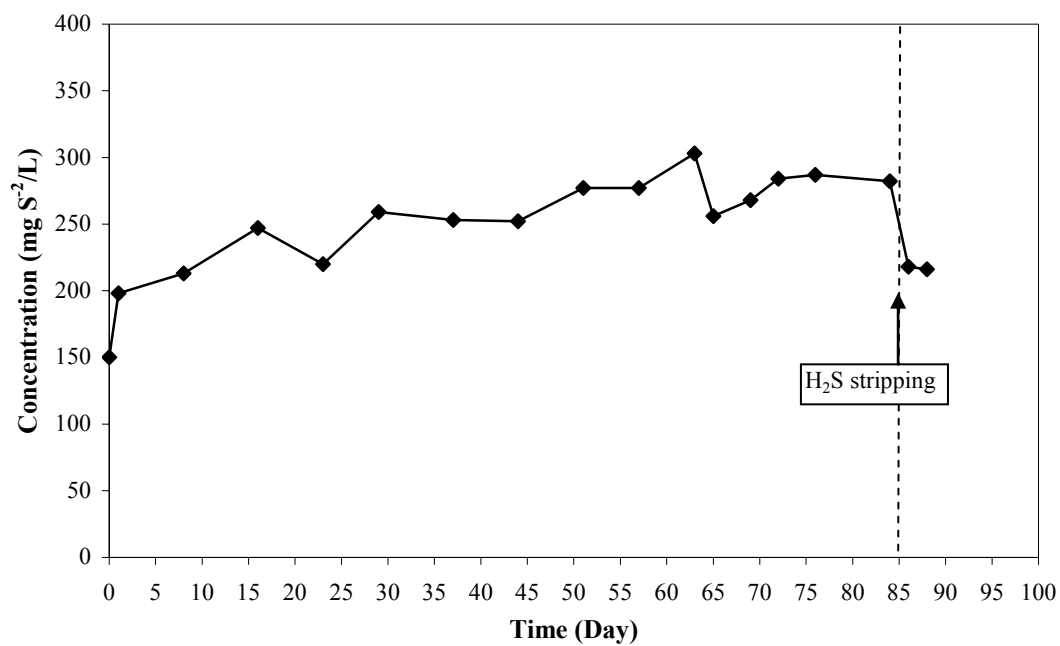


Figure 9-21 Hydrogen Sulfide Concentration Profile for the FBBR – sand (Column 3)

At the final stages of operation, the GAC and sand particles were randomly withdrawn from the FBBR reactors, and prepared for scanning electron microscopy analysis as described in Section 6.3.7, to determine the extent of the biofilm growth on the surfaces. Figures 9-22 and 9-23 present typical micrographs of bacterial growth on GAC and sand particles, respectively. As evident from the figures, the GAC particles appears to support a denser biofilm growth. These observations were consistent in their findings of Pirbazari et al. (1990), who investigated the nature of microbial growth and coverage on different types of solid surfaces employed in biofilm processes for water or wastewater treatment applications.

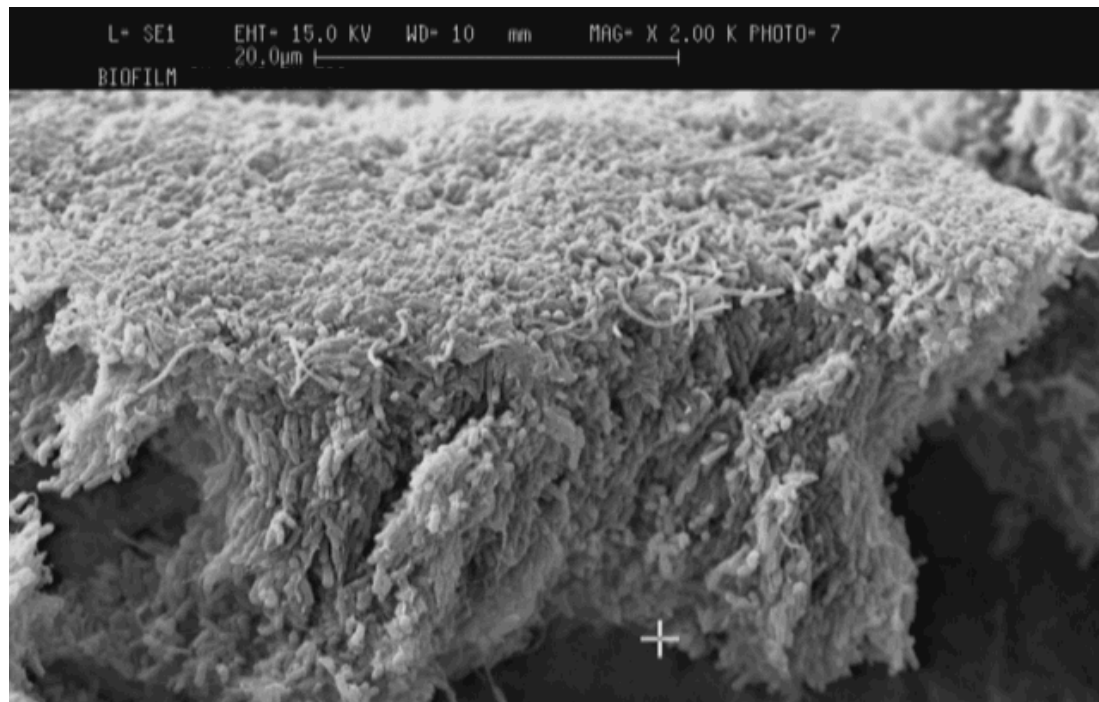


Figure 9-22 Scanning Electron Micrograph for sand particles covered with biofilm of Sulfate Reducing Bacteria (FBBR – GAC)

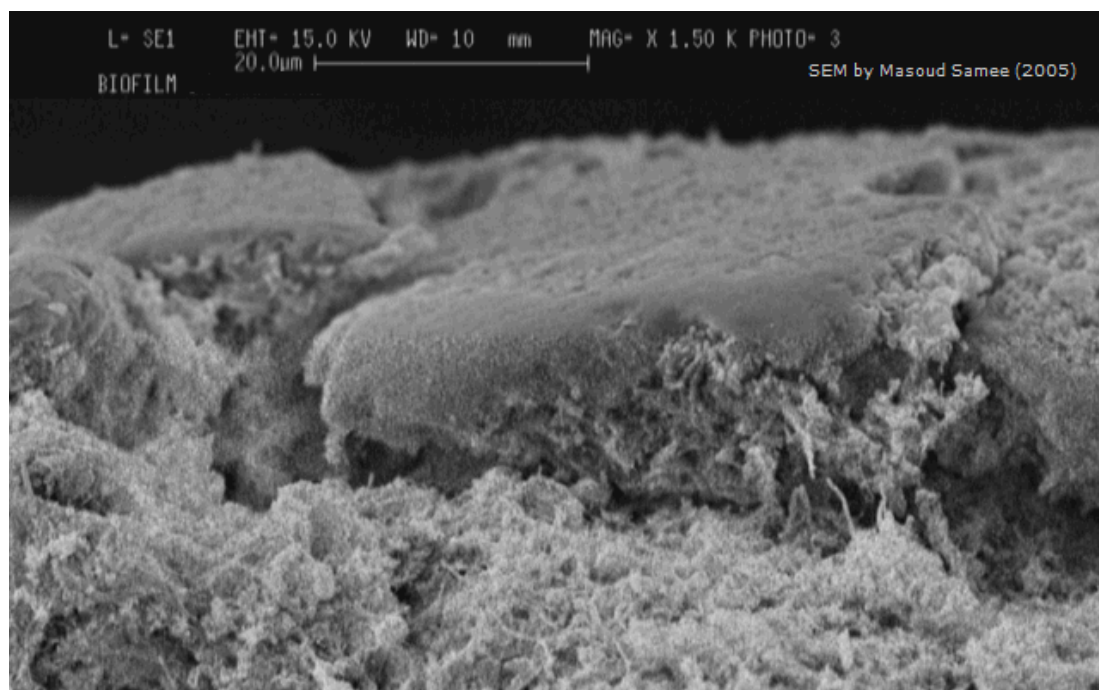


Figure 9-23 Scanning Electron Micrograph for GAC particles covered with biofilm of Sulfate Reducing Bacteria (FBBR – sand)

9.5 FBBR – GAC Column Study with Low Sulfate Concentration

A FBBR system (Column 4) with the characteristics depicted in Table 6-2 was operated to study the sulfate reduction at low sulfate concentration of 600 mg/L, and to calibrate the model and verify its predictive capacity. Similar to the earlier FBBR studies, ethanol was used as carbon source, and granular activated carbon was employed as supporting medium. The pH and temperature were kept constant at 7.5 and 35°C, respectively. The reactor commenced in batch mode with initial sulfate concentration of 600 and maintained until complete ethanol utilization obtained on day two; then it was switched to the continuous mode with influent flowrate of 6 mL/min and C/S of 1.0.

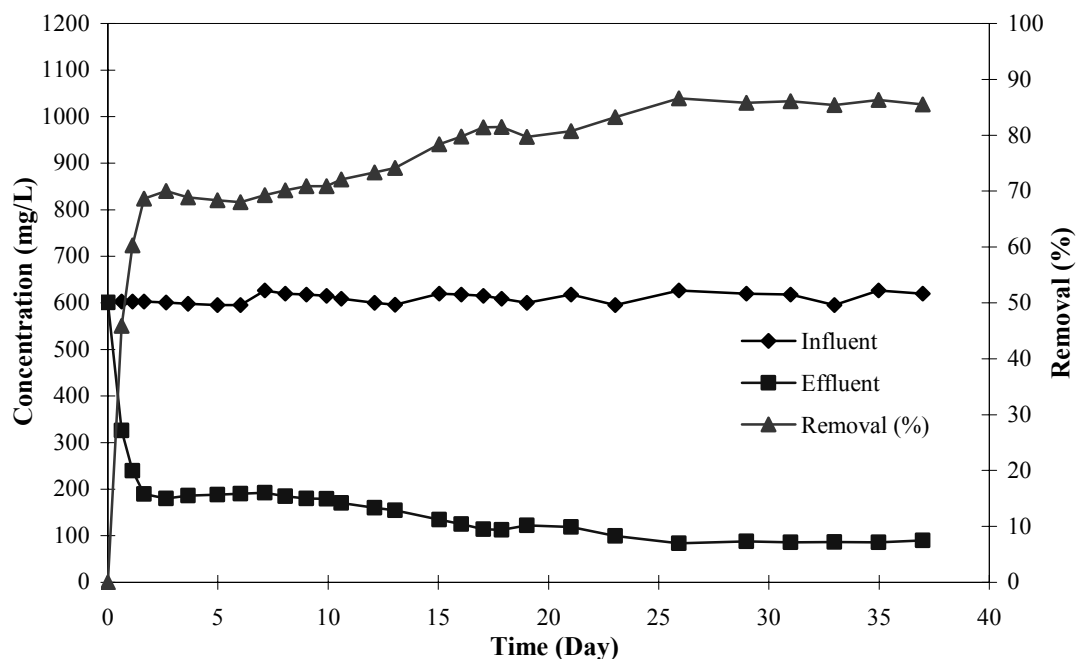


Figure 9-24 Influent and Effluent Sulfate Concentration Profiles and Removal Efficiencies in FBBR – GAC (Column 4)

The column operated in two stages each with different hydraulic retention times of 2.5 hr and 4.5 hr. The sulfate removals under steady-state condition reached 68.5% and 85.5% for HRTs of 2.5 hr, and 4.5 hr respectively. The results of these studies are presented in Figure 9-24. The operational changes for this FBBR – GAC column are summarized in Appendix C.

9.6 Gaseous H₂S Removal by Anaerobic Biofilter

Hydrogen sulfide present in biogas product of anaerobic degradation of sulfate in the FBBR systems was removed using a laboratory-scale anaerobic biofilter with GAC as supporting medium. The schematic of the anaerobic biofilter used for this study is illustrated in section 6.2.4 (Figures 6-7 and 6-8). The biofilter reactor was operated consistently during the period of FBBRs operation and the effluent H₂S concentrations in the biofilter gas stream were found to be below the detection limit. Green-colored biomass and significant scales were observed over the period of biofilter operation (more than 2 years) indicating the presence of green sulfur bacteria (GSB) and conversion of H₂S to elemental S⁰. The specific type of anaerobic bacteria populations capable of removing hydrogen sulfide was speculated to be a species of green sulfur bacteria *Cholorobium limicola* which are ideal bacteria in anaerobic biological removal process of gaseous hydrogen sulfide (Syed et al., 2006). These specific bacteria can gradually grow and dominate among the population of anaerobic microorganisms in presence of light, carbon dioxide, and inorganic constituents.

9.7 Model Parameter Estimation

The model parameters were determined through a series of experiments as described in Section 5.6. The results are presented in Tables 9-4, 9-5, and 9-6. The corresponding calculations are summarized in Appendix E. Adsorption isotherm studies were performed for sulfate on activated carbon and the results indicated that sulfate had no adsorption affinity for the adsorbent. It can be speculated that sulfate ions are hydrophilic, and they form hydrogen bonding with the water molecules instead of binding with the functional groups on the GAC surface and therefore, adsorption phenomenon for sulfate was disregarded in this research.

The Monod biokinetic parameters were obtained through chemostat studies as previously discussed (Section 4.3). The external film transfer coefficient, k_{fc} and liquid diffusivity were evaluated using the correlation proposed by Wakao and Funazkri (1979). The maximum biofilm thickness, $T_{b,max}$ and the biofilm density were estimated through a series of laboratory experiments on the biofilm-coated sand and GAC particles (as described in Section 5.6.3). Biofilm diffusion coefficient, D_b was determined from the free liquid diffusivity, D_l by using the ratio $D_b/D_l = 0.8$, as suggested by Williamson and McCarty (1976). Axial substrate dispersion coefficient, D_z was determined from the tracer experiments as previously described in Section 9.1. This parameter was also determined using the correlation of Chung and Wen (1968), and the obtained value was significantly small owing to high mixing rate in

the FBBR systems. Subsequently, the axial substrate dispersion coefficient, D_z was neglected in the predictive model.

Table 9-4 Model Parameters for FBBR – GAC & sand Columns

Column No.	Media	C_o (g/m ³)	Q (m ³ /hr)	k_{fc} (m/hr)	D_z (m ² /hr)	D_b (m ² /hr)
1	GAC	1100	3.6×10^{-4}	0.200	9.1×10^{-8}	5.30×10^{-6}
2	GAC	600 – 1100	3.6×10^{-4}	0.200	9.1×10^{-8}	5.30×10^{-6}
3	sand	600 – 1100	3.6×10^{-4}	0.358	7×10^{-8}	5.30×10^{-6}
4	GAC	600	3.6×10^{-4}	0.200	9.1×10^{-8}	5.30×10^{-6}

Table 9-5 Model Parameters for FBBR – GAC & sand Columns

Column No.	Media	D_l (m ² /hr)	d_p (m)	M_b (g/m ³)	$T_{b,max}$ (μm)
1	GAC	6.63×10^{-6}	0.00219	105000	71
2	GAC	6.63×10^{-6}	0.00219	105000	71
3	sand	6.63×10^{-6}	0.00072	62000	22
4	GAC	6.63×10^{-6}	0.00219	105000	71

Table 9-6 Monod Biokinetic Parameters (C/S ratio of 1.0)

kinetic Parameters	Sulfate Reduction
Maximum specific growth rate, μ_m	0.0692 hr ⁻¹
Half-velocity constant, K_s	370.37 g/m ³
Maximum yield coefficient, Y	0.7307 g/g
Endogenous decay coefficient, k_d	0.01905 hr ⁻¹

9.8 Predictive Modeling, Simulations of FBBR Systems and Verification of the Model with Experimental Results

FBBR studies were conducted to determine the sulfate removal efficiencies and to verify the predictive capability of the proposed model. The experimental data were obtained for a series of FBBR experiments employing varying operational conditions including different influent sulfate concentrations, different hydraulic retention times, and effect of hydrogen sulfide stripping, and the results were compared with the FBBR model prediction profiles. The model parameters employed are presented in Tables 9-4, 9-5, and 9-6 which include biokinetic parameters, initial biofilm thickness, influent sulfate concentration, biofilm density, mass transfer coefficient, influent flowrate, and diffusion coefficient. The experimental data and model predictions for the FBBR-GAC and sand columns are compared in Figures 9-25 through 9-28. As evident from these figures, good agreement is observed between experimental data and the predicted profiles validating the predictive capability of the FBBR model. The slight deviations observed between the experimental data and model predictions can be attributed to the small uncertainties in the estimated biokinetic parameters obtained from the chemostat studies, and the toxic effect of H_2S on the performance of SRB in the FBBR systems.

9.8.1 FBBR – GAC Column Prediction/Simulation Analyses

Model prediction studies were conducted for the FBBR-GAC column with initial sulfate concentration of 600 mg/L (Column 4). A comparison of the experimental

data and the model prediction profile is presented in Figure 9-25. As evident, the developed fluidized bed bioreactor model is able to accurately predict the experimental results. Subsequently, a good agreement was observed between the experimental data and model profiles. This aspect is attributed to the fact that the effect of hydrogen sulfide toxicity on the microbial activity was insignificant, owing to the low initial sulfate concentration and the corresponding H_2S production.

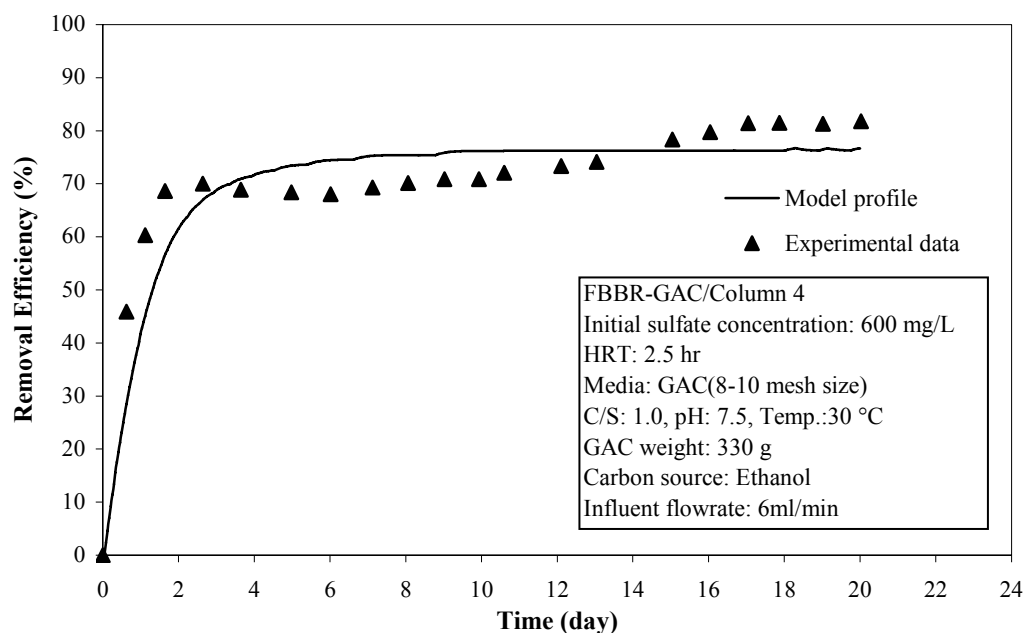


Figure 9-25 Experimental Data and Model Profile for the FBBR – GAC (Column 4) with Initial Sulfate Concentration of 600 mg/L

The study indicated that the predicted sulfate reduction efficiency in Column 4 reached the steady state of about 75%, as compared to 72% reduction obtained from the experimental results. The sulfate reduction efficiency further increased to about

81% after 17 days of operation owing to high biomass accumulation at the bottom of the reactor that contributed to the more biological activity. Moreover, as time progressed, the microbial growth rate and activity increased substantially due to higher substrate loading. Consequently, part of the biomass on the GAC particles was sheared away from the biofilm and transferred to the liquid phase of the reactor. This feature was visually observed after day 15 of the operation, and it was presumably responsible for the increased biological activity and sulfate removal efficiency. These processes resulted in higher liquid phase biomass concentrations, consequently leading to greater biodegradation and more rapid approach to steady state conditions. This aspect was qualitatively observed in Columns 2 and 3 as well.

The FBBR model prediction was further investigated for Column 2, and the result is presented in Figure 9-26. The predicted steady-state sulfate reduction efficiencies of 82%, 84%, 86%, and 87% were obtained with the influent sulfate concentrations of 800, 900, 1000, and 1100 mg/L, respectively. The corresponding experimental data showed a nearly 15% less sulfate reduction efficiency than the predicted data owing to the toxicity effect of H_2S as previously discussed.

Prediction/simulation studies were also performed for Column 1, and the results are depicted in Figure 9-27. Model prediction focused on the time period between 300 to 400 days of the reactor operation where the optimal condition of C/S of 1.0, pH of 7.5, and influent sulfate concentration of 1100 mg/L were maintained.

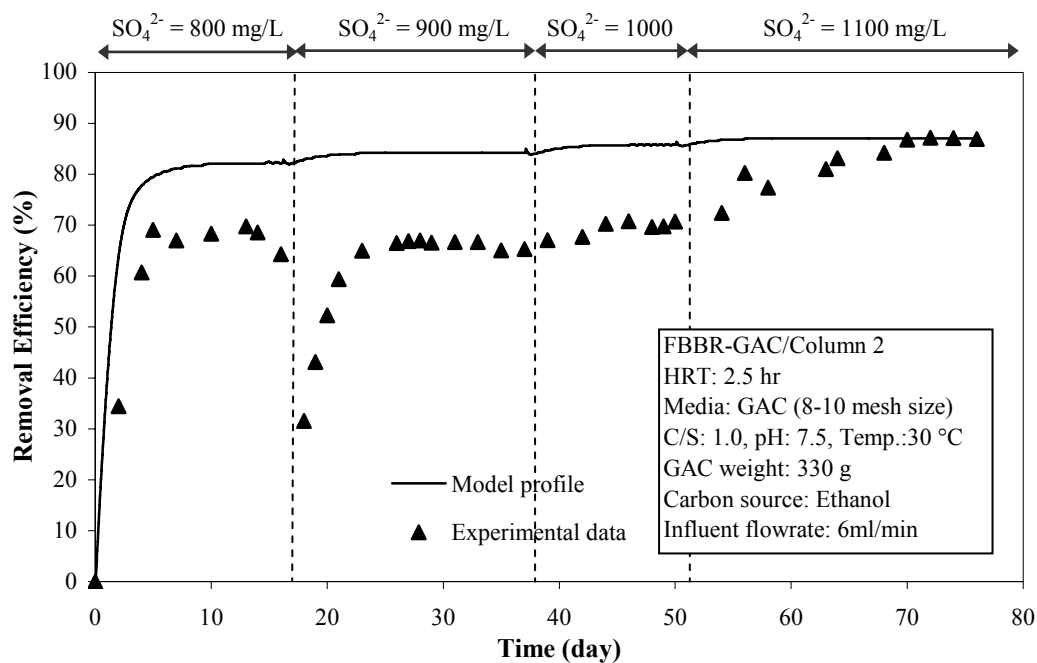


Figure 9-26 Experimental Data and Model Profile for the FBBR – GAC (Column 2)

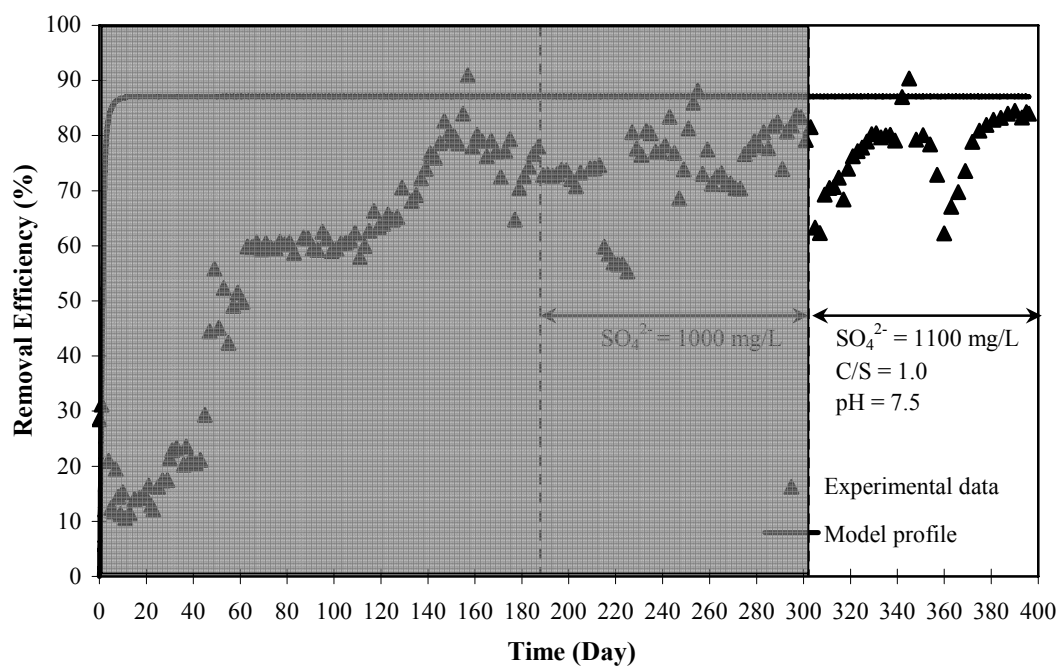


Figure 9-27 Experimental Data and Model Profile for the FBBR – GAC (Column 1, Days 300 – 400)

9.8.2 FBBR – sand Column Prediction/Simulation Analyses

The FBBR model prediction was further performed for the fluidized bed bioreactor with sand as the supporting media, and the corresponding results are presented in Figure 9-28. These studies also revealed the important aspect of hydrogen sulfide toxicity on the performance of SRBs in the reactor as previously discussed. However, this phenomenon was suppressed by nitrogen stripping of hydrogen sulfide on day 87. Subsequently, the results indicated a good agreement between the experimental data and model profile (days 89-93). It is important to note that the suspended biomass in the reactor also contributed to enhancing the sulfate reduction, as discussed earlier.

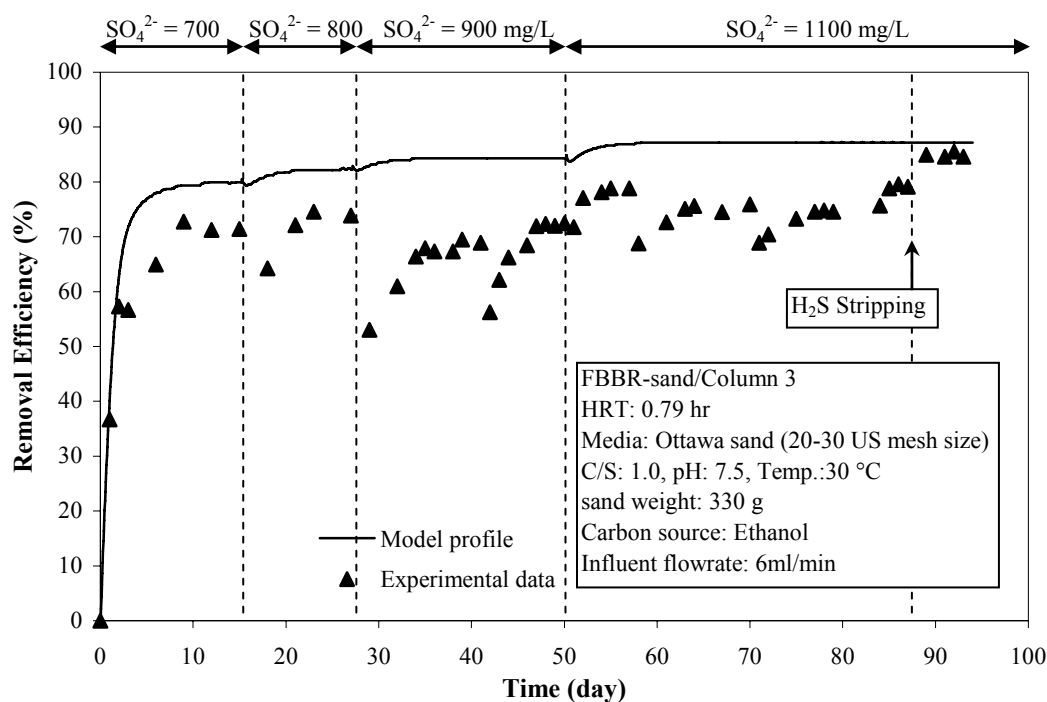


Figure 9-28 Experimental Data and Model Profile for the FBBR – sand (Column 3)

9.9 Effect of Hydrogen Sulfide Toxicity on the FBBR Simulation Results

In the chemostat studies for biological sulfate reduction, the maximum hydrogen sulfide concentration was 58 mg S^{2-} /L, observed at dilution rate of 0.02 and a C/S ratio of 1.0. The observed H_2S concentrations in these studies were significantly lower than the threshold toxic concentration of 250 mg/L as reported by Van Houten et al. (1997). The presence of aqueous hydrogen sulfide in the chemostat system had no toxicity effect on the sulfate reducing bacteria and consequently, on the biokinetic parameters obtained from these studies. However, due to high H_2S concentration experienced in the FBBR systems (as high as 360 mg S^{2-} /L), the toxicity effect should be considered as a potential inhibiting factor on the activity and performance of SRBs. The toxicity effect may well describe the discrepancy between the experimental data for sulfate reduction in Columns 1, 2, 3, and 4 and the predicted profiles in Figures 9-25 to 9-28. This important feature was observed in the FBBR-sand column as shown in Figure 9-28. The hydrogen sulfide concentration in the reactor reached the maximum of 300 mg/L at the steady-state condition with influent sulfate concentration of 1100 mg/L, experiencing lower sulfate removal efficiency as expected in the predicted model profile. However, the H_2S stripping process performed on the reactor on day 83, decreased the hydrogen sulfide concentration to 220 mg/L, and therefore, significantly increased the sulfate removal efficiency, demonstrating a better agreement of the experimental results with the predicted model profile. This phenomenon was further observed in Column 4 with the constant influent sulfate concentration of 600 mg/L, and maximum hydrogen sulfide

concentration of 170 mg/L. Subsequently, the effect of H₂S toxicity on the microbial activity was insignificant, owing to the experienced low concentration of hydrogen sulfide, and therefore, a good agreement was observed between the experimental profile and the model predictions as presented in Figure 9-25. It is interesting to note that the predicted model would not project the hydrogen sulfide toxicity effect on simulation of FBBR system due to the negligible effect of H₂S on the chemostat systems used for estimation of biokinetic parameters. The values of biokinetic parameters estimated from chemostat studies did not reflect the toxic inhibition effect attributable to H₂S. Subsequently, the employed biokinetic parameters as inputs to the predictive model, will overestimate the performance of the FBBR process.

9.10 FBBR Model Sensitivity Analyses

Simulation and sensitivity analyses of the FBBR model with respect to the sulfate reduction efficiency were performed, and the model prediction and experimental data were compared, as illustrated in Figures 9-29 through 9-40. In order to demonstrate the changes in the FBBR removal efficiency profiles due to parameter variation, a 30 percent increase or decrease was employed on the kinetic parameters. The sensitivity evaluation of the model for biokinetic parameters was important from several viewpoints, as discussed in Section 5.9. These studies provided an evaluation of the process variables affecting the FBBR process such as influent contaminant concentration, biological parameters, and biomass concentration. Moreover, they

determined the parameters which have significant influence on the process dynamics which further can provide relevant information on parameters that can be adjusted and tuned to alter process conditions and improve the process efficiency.

Sensitivity studies were conducted for a typical fluidized bed bioreactor (Column 3). These studies were investigated with respect to the maximum specific growth rate, μ_m as depicted in Figure 9-29. As evident from the figure, maximum specific growth rate significantly influenced the FBBR removal efficiency in that 30 percent decrease in this parameter reduced the removal efficiency by nearly 16 percent. On the other hand, a 30 percent increase in this parameter improved the steady state removal efficiency by 5 to 7 percent.

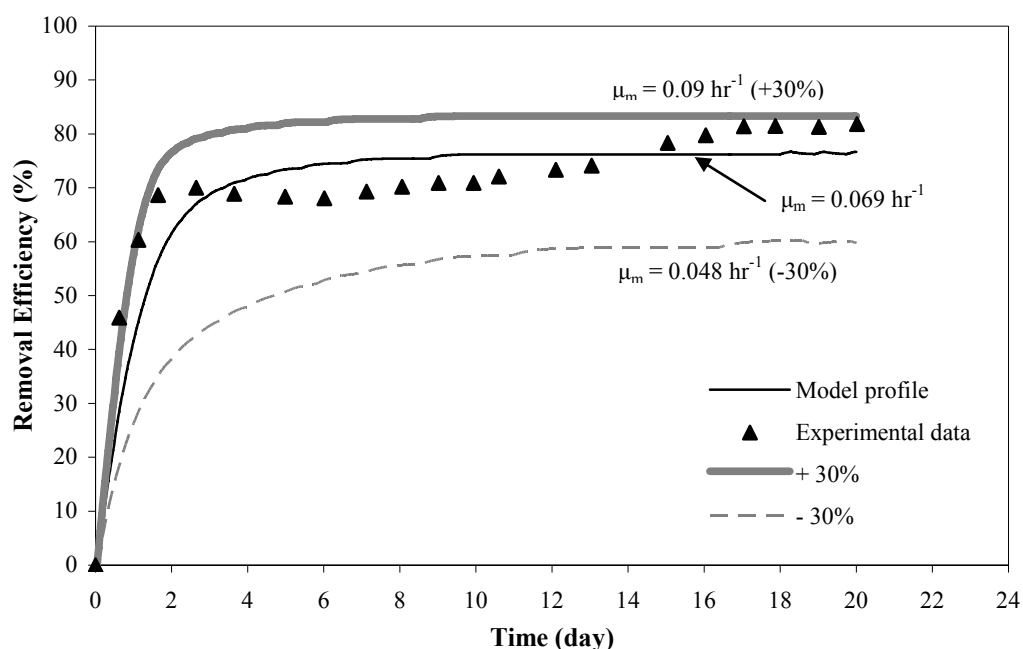


Figure 9-29 Effect of Maximum Specific Growth Rate, μ_m on FBBR Dynamics for Sulfate Reduction in FBBR-GAC (Column 4)

These studies were further performed with respect to the half-velocity constant, K_s as presented in Figure 9-30. The simulations were conducted with a 30% increase and decrease over the typical value of 370 mg/L. The results indicated that the level of sulfate reduction increases as the half-velocity constant decreases. Figure 9-30 shows that a 30% decrease in the Monod half-saturation coefficient (K_s of 259 mg/L) resulted in a 7% more reduction in the steady-state effluent concentration, similarly a 30% increase in half-saturation coefficient (K_s of 481 mg/L) caused a 7% decrease in the removal efficiency.

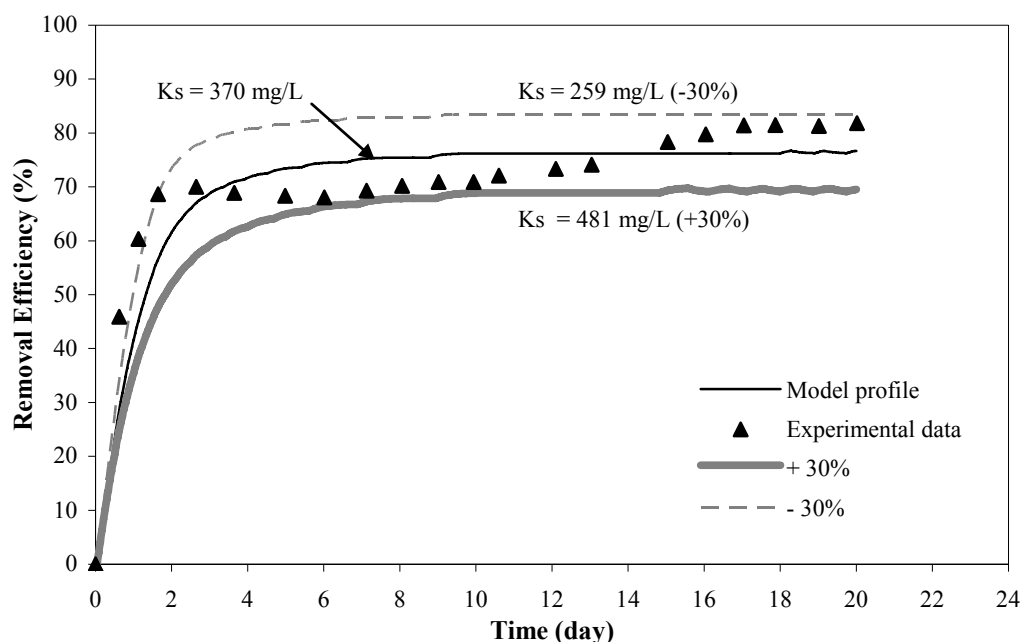


Figure 9-30 Effect of Half-velocity Constant, K_s on FBBR Dynamics for Sulfate Reduction in FBBR-GAC (Column 4)

A similar effect was observed for changes of $\pm 30\%$ in the endogenous decay coefficient, k_d as illustrated in Figure 9-31. The simulations were conducted for

endogenous decay coefficients of 0.025 hr^{-1} , and 0.013 hr^{-1} corresponding to a 30% increase and decrease over the typical value of 0.019 hr^{-1} . The results clearly demonstrated that a higher endogenous decay coefficient rate decreases the level of sulfate reduction. It was observed that a 30% increase in the decay coefficient resulted in an 11% lower sulfate reduction in the steady-state effluent concentration, while a 30% decrease resulted in 9% higher removal efficiency.

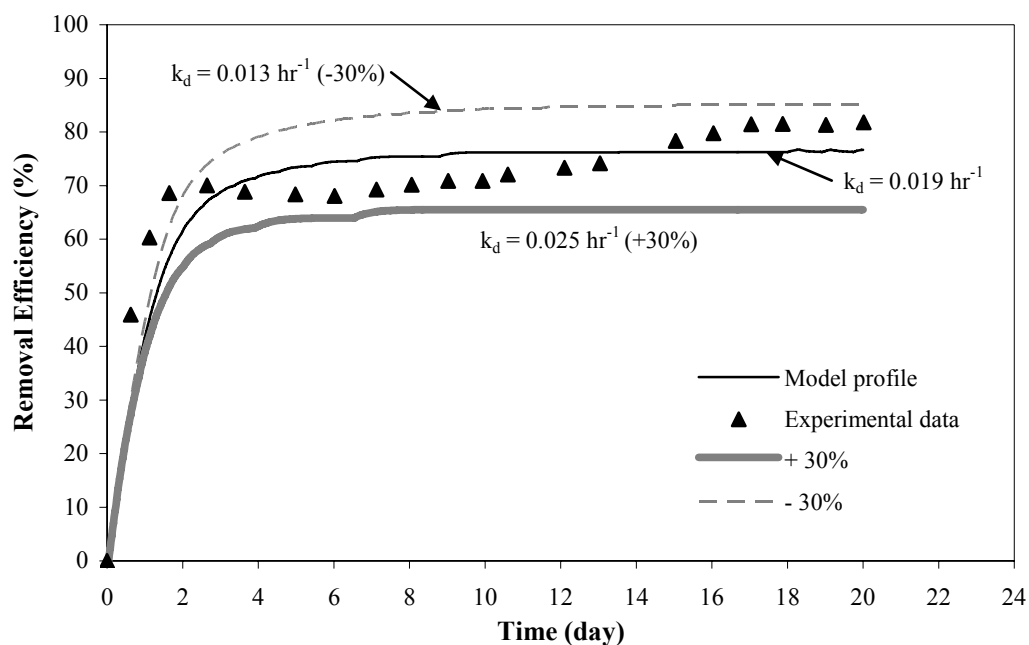


Figure 9-31 Effect of Endogenous Decay Coefficient, k_d on FBBR Dynamics for Sulfate Reduction in FBBR-GAC (Column 4)

More sensitivity studies were conducted to investigate the significance of yield coefficient, Y on the process dynamics. The corresponding results are depicted in Figure 9-32. The 30% increase or decrease in the parameter to 0.73 mg/mg did not

reflect a significant influence on the predicted model. As evident from the results, the predicted model reached the steady-state sulfate reduction efficiency of 76% at different yield coefficients of 0.51, 0.73, and 0.95 mg/mg. This aspect was previously observed in the chemostat sensitivity analyses, demonstrating that the FBBR sensitivity studies qualitatively followed the same pattern as those of chemostat studies.

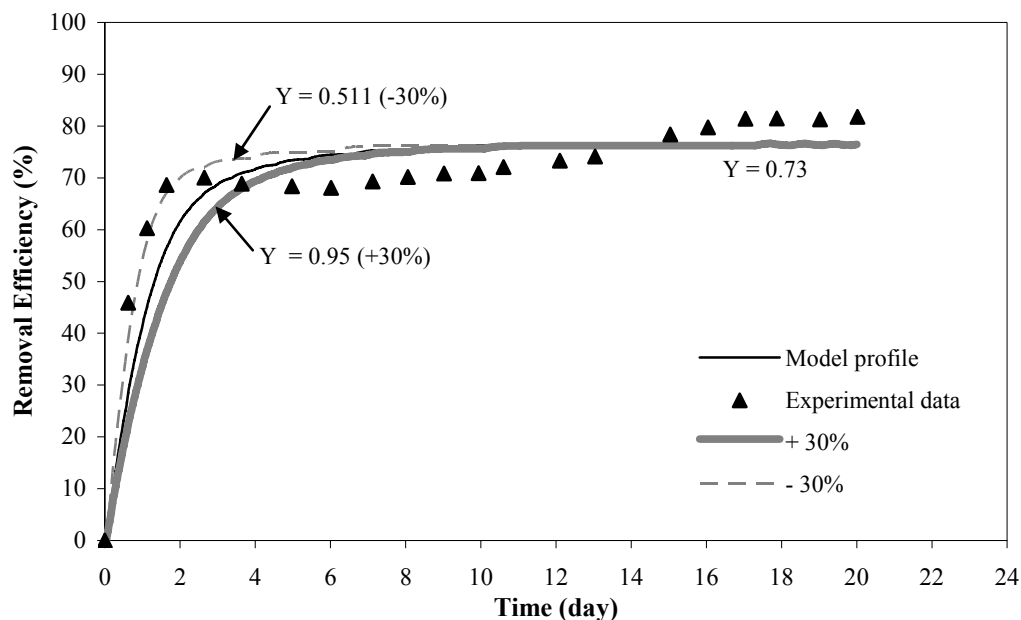


Figure 9-32 Effect of Maximum Yield Coefficient, Y on FBBR Dynamics for Sulfate Reduction in FBBR-GAC (Column 4)

The model sensitivity studies were further performed for Columns 2, and 3 with respect to the to maximum specific growth rate, μ_m endogenous decay coefficient, k_d yield coefficient, Y , and half-velocity constant, K_s . The results of these studies

presented in Figures 9-33 through 9-40, qualitatively followed similar patterns as those of Column 4, as discussed earlier in this section.

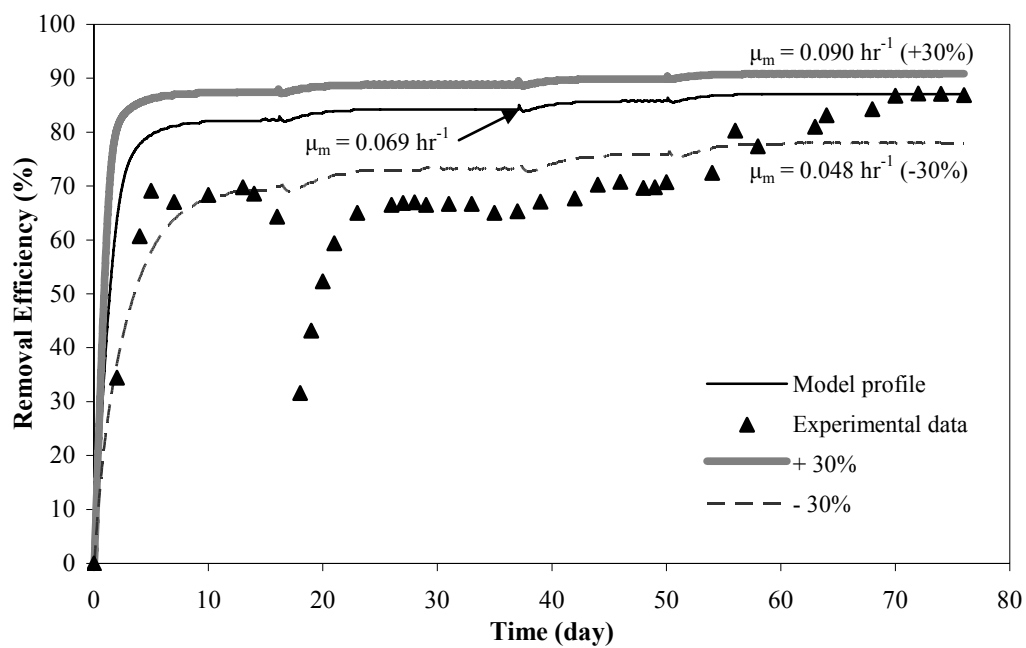


Figure 9-33 Effect of Maximum Specific Growth Rate, μ_m on FBBR Dynamics for Sulfate Reduction in FBBR-GAC (Column 2)

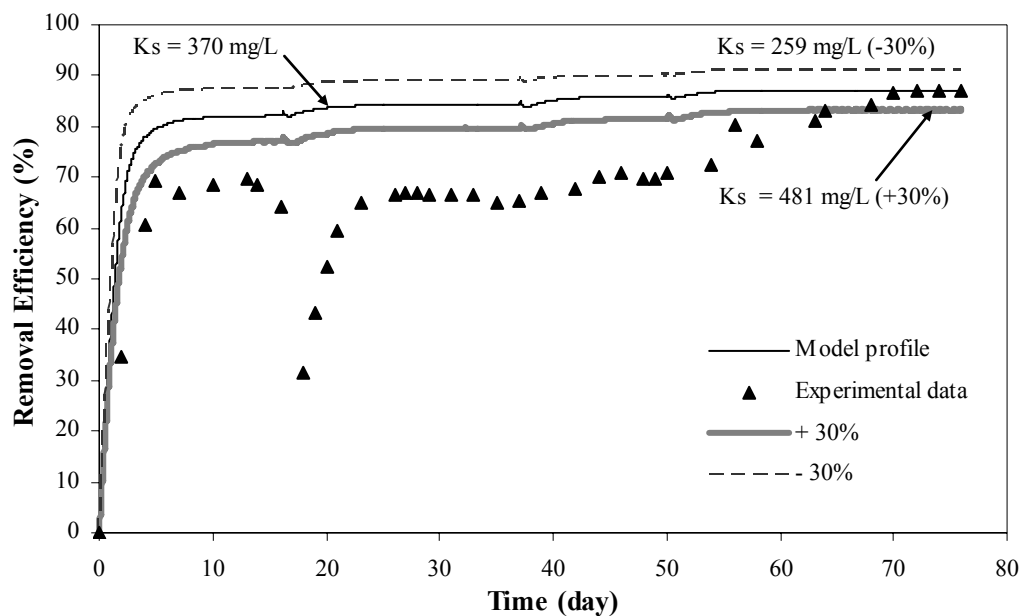


Figure 9-34 Effect of Half-velocity Constant, K_s on FBBR Dynamics for Sulfate Reduction in FBBR-GAC (Column 2)

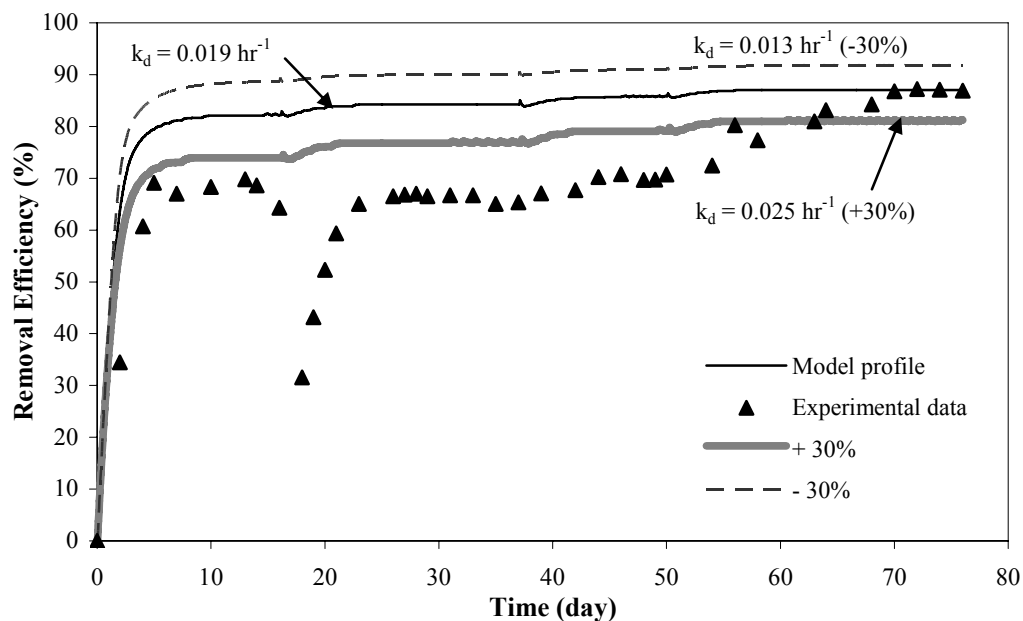


Figure 9-35 Effect of Endogenous Decay Coefficient, k_d on FBBR Dynamics for Sulfate Reduction in FBBR-GAC (Column 2)

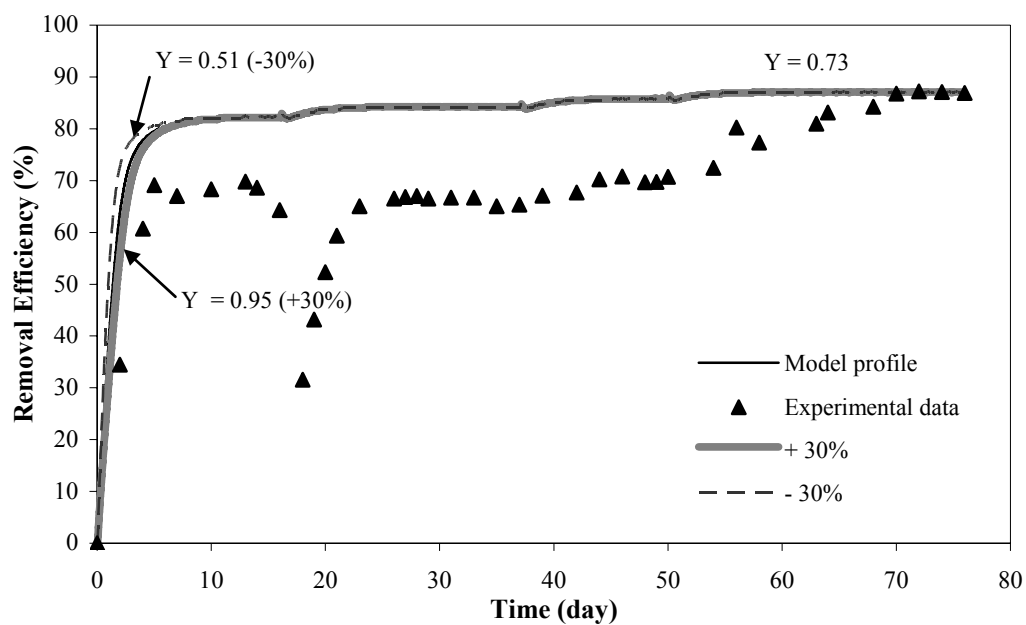


Figure 9-36 Effect of Maximum Yield Coefficient, Y on FBBR Dynamics for Sulfate Reduction in FBBR-GAC (Column 2)

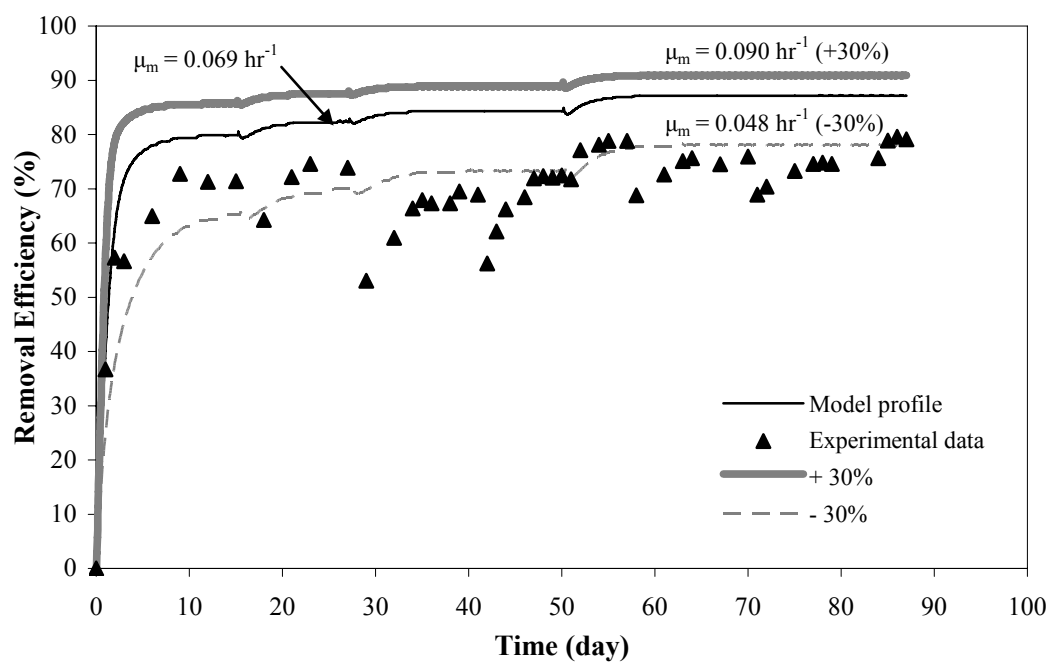


Figure 9-37 Effect of Maximum Specific Growth Rate, μ_m on FBBR Dynamics for Sulfate Reduction in FBBR-sand (Column 3)

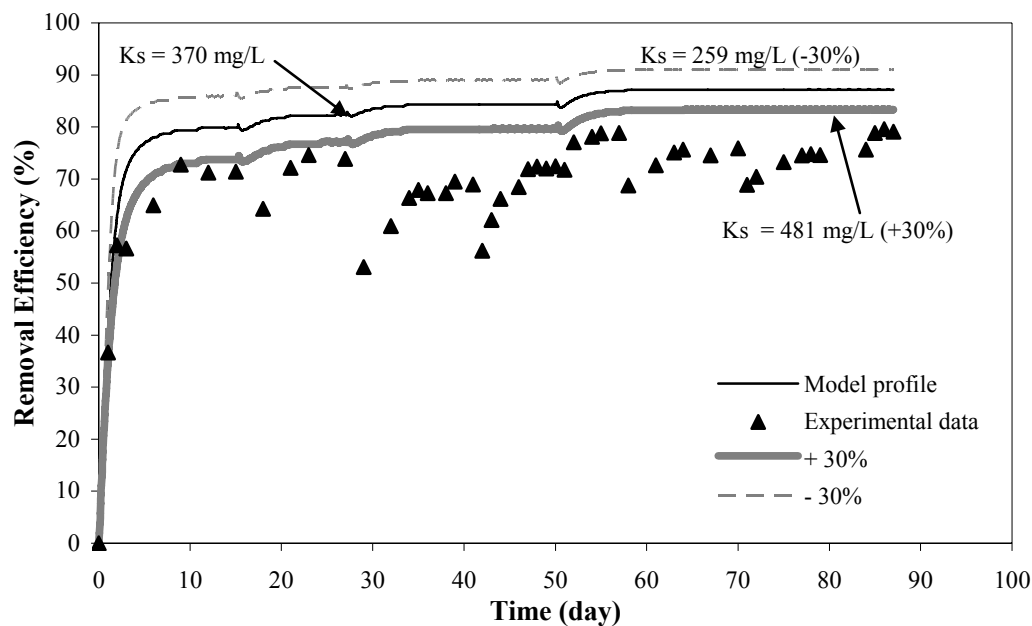


Figure 9-38 Effect of Half-velocity Constant, K_s on FBBR Dynamics for Sulfate Reduction in FBBR-sand (Column 3)

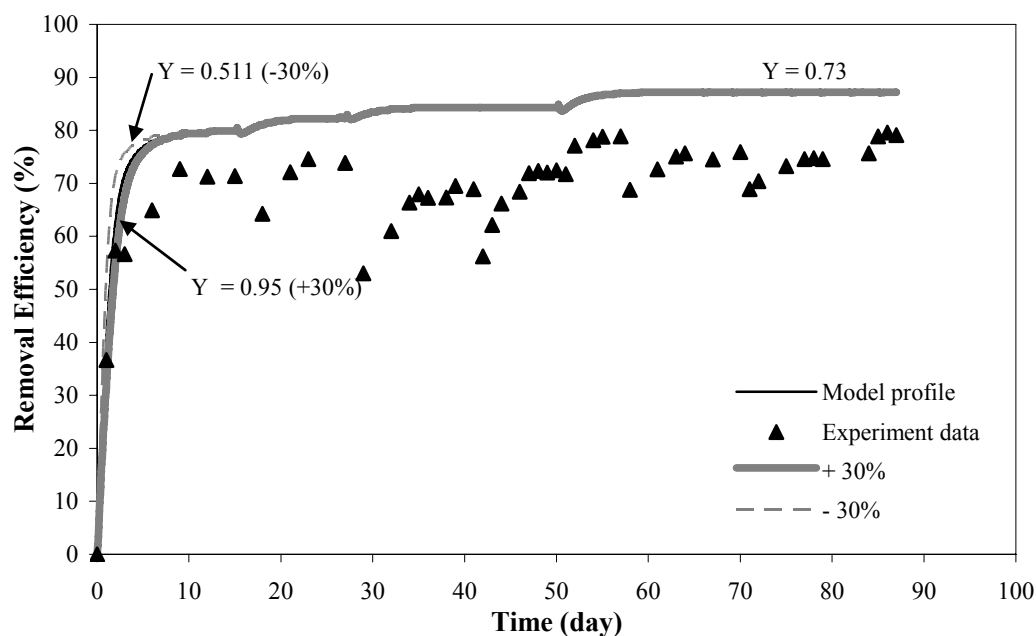


Figure 9-39 Effect of Maximum Yield Coefficient, Y on FBBR Dynamics for Sulfate Reduction in FBBR-sand (Column 3)

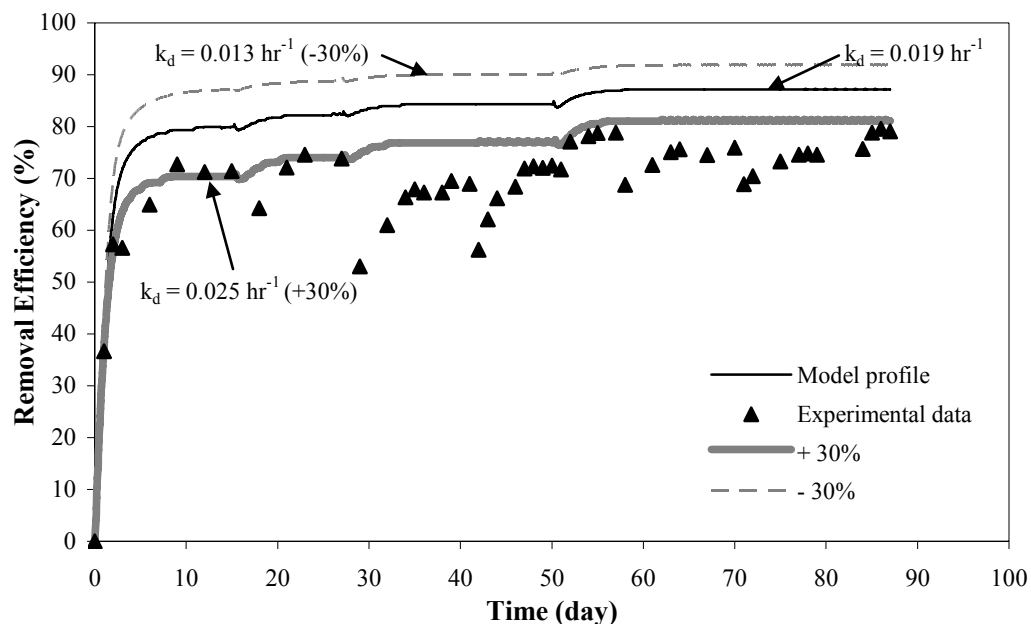


Figure 9-40 Effect of Endogenous Decay Coefficient, k_d on FBBR Dynamics for Sulfate Reduction in FBBR-sand (Column 3)

9.11 Upscaling Studies and Results

Upscaling to design a pilot FBBR was accomplished by using the techniques of dimensional analysis and similitude techniques as outlined by Den and Pirbazari (2000), and Badriyha et al. (2003). It is important to note that (as previously described in Section 5.7), the Monod biokinetic coefficients (k and K_s) are intrinsic properties of microbial culture and are therefore independent of geometric and dynamic properties. Hence, in the present study, the following properties have identical values regardless of scale: (i) influent concentration; (ii) particle density and packing porosity; and (iii) Monod kinetic constants. A scale-up relationship was

developed by equating the biochemical reactivity modulus, E_r wherein the biodegradation was the predominant mechanism.

$$\frac{HRT_L}{HRT_S} = \left(\frac{R_{p,L}}{R_{p,S}} \right)^2 \left(\frac{Da_{ov,S}}{Da_{ov,L}} \right) \quad (9-1)$$

In this relationship the Damköhler number was held constant for upscaling, consequently the hydraulic retention time was proportional to the square of the activated carbon particle size, and the subsequent equation is presented as follows:

$$\frac{HRT_L}{HRT_S} = \left(\frac{R_{p,L}}{R_{p,S}} \right)^2 \quad (9-2)$$

In the present up-scale study, Equation 9-2 was employed, and a particle diameter of 2.83 mm (US mesh size of 6-8) was considered for a up-scale FBBR system vis-à-vis 2.19 mm (US mesh size of 8-10) for a laboratory-scale. Consequently, Equation 9-2 is presented as below:

$$\frac{HRT_L}{HRT_S} = 1.7 \quad (9-4)$$

In the above relationship, the scale-up factor for hydraulic retention time is 1.7, and therefore an HRT_L of 4.25 hr was considered for the FBBR up-scale design. These studies were performed with the influent flowrate of 0.5 million gallons per day (MGD). The design parameters are presented in Table 9-7.

Table 9-7 Design Parameters for the Pilot FBBR System

Parameters	
GAC particle diameter (m)	0.00283
Bed volume (m^3)	67.03
Recirculation rate (m^3/hr)	498
Dynamic fluid viscosity (kg/m.hr)	2.873
Fluid density (kg/m^3)	995.71
Reynolds Number, Re	82.7
External film transfer coefficient, k_{fc} (m/hr)	0.18
Axial substrate dispersion coefficient, D_z (m^2/hr)	8.96×10^{-8}
Free liquid diffusivity, D_l (m^2/hr)	6.73×10^{-6}
Biofilm diffusion coefficient, D_b (m^2/hr)	5.39×10^{-6}

The results indicated that the selected adsorber particle size of 2.83 mm did not have much influence on the up-scaled parameters. However, an insignificant effect was observed for the external film transfer coefficient, k_{fc} with the value of 0.18 m/hr for the pilot-scale system vis-à-vis 0.2 m/hr for the laboratory-scale system. This slight variability would not have significant influence on the values of the overall Damköhler numbers, Da_{ov} for both systems. These scale-up parameters were based on the influent flowrate and hydraulic retention time of 0.5 MGD and 4.25 hr,

respectively. The influent flowrate was split to five streams of 260 L/min each, and subsequently, five identical FBBR reactors in parallel were designed. The design dimensions are presented in Table 9-8.

Table 9-8 Characteristics of the Pilot-Scale FBBR System

Specifications	
Number of FBBR systems	5
FBBR diameter (m)	2.7
FBBR active volume (m ³)	67
FBBR active height (m)	11.4
Influent flowrate of each reactor (L/min)	260

These studies were further extended to scale up the biofilter system. As previously discussed, no significant deviations were observed in the scale-up parameters based on the designed influent flowrate and hydraulic retention time of 0.5 MGD and 4.25 hr, respectively. Therefore, it can be concluded that it would not impound significant effect on the performance of the FBBR system, and consequently similar profile pattern with regard to sulfate reduction and the subsequent hydrogen sulfide production could be expected for the upscaled FBBR system. Subsequently, the pilot-scale biofilter system was designed based on the retention time of 14.5 sec (same as the laboratory-scale retention time), and a loading rate of 115 L/min. The characteristics of the laboratory-scale and pilot-scale systems are presented in Table 9-9. The biogas from the laboratory-scale FBBR system was pumped into the biofilter by using a peristaltic pump with the flowrate of 6 L/min. Two centrifugal

pumps, each with maximum flowrate of 58 L/min can be selected to pump the biogas into the scaled biofilter.

An isometric representation of the pilot-scale treatment system created by SolidWorks software (2005) is presented in Figure 9-41. The design computations are summarized in Appendix F.

Table 9-9 Characteristics of the Pilot-Scale Biofilter System

Specifications	Laboratory-scale	Up-scale
Active volume (m ³)	1.6×10^{-3}	28
Biofilter diameter (m)	6.35×10^{-2}	2
Active height (m)	0.45	6
Loading rate (L/min)	6	115
Empty Bed Contact Time (EBCT, sec.)	14.5	14.5
Medium specifications	(US mesh 8-10; 2.00 ~ 2.38 mm)	(US mesh 8-10; 2.00 ~ 2.38 mm)

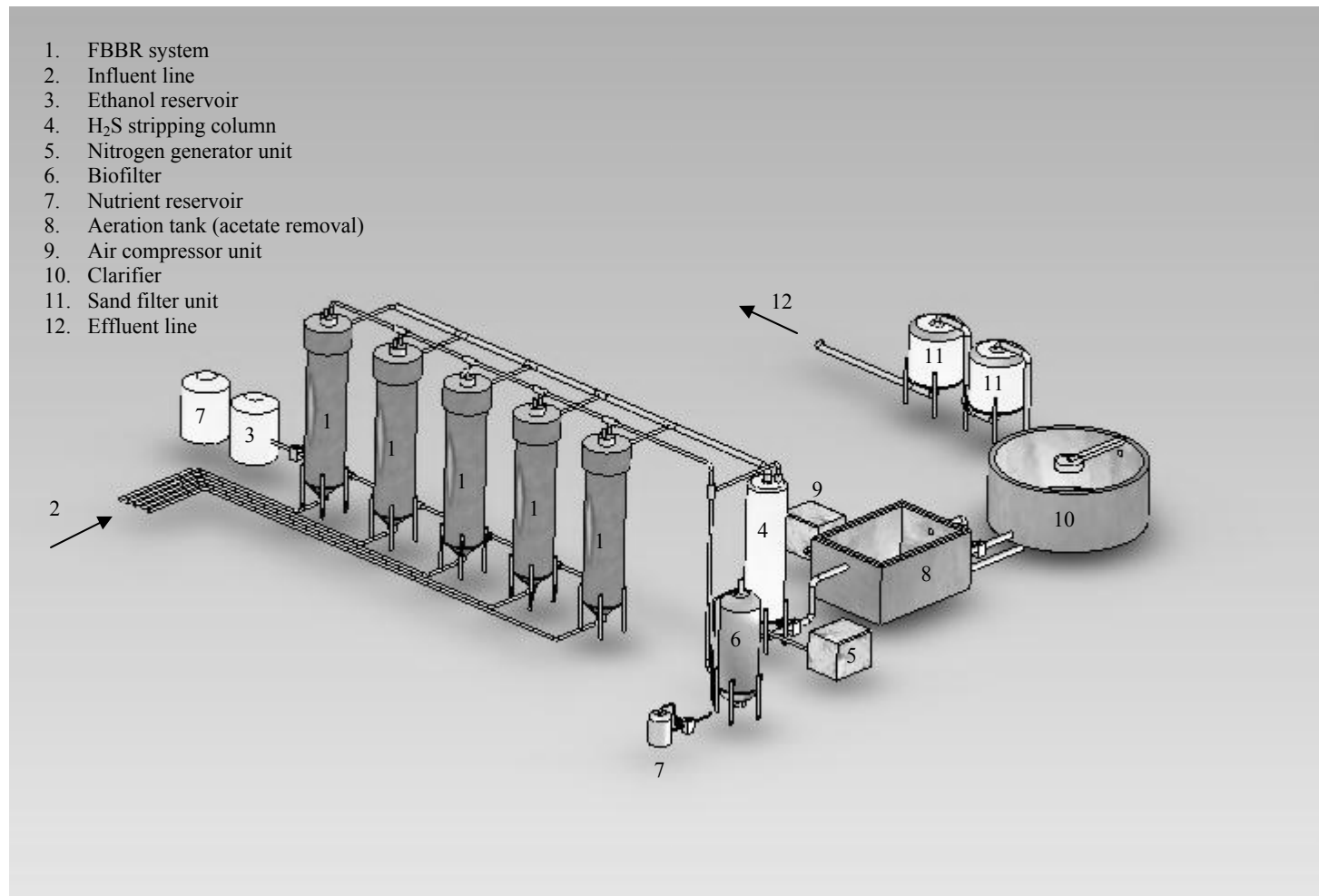


Figure 9-41 Isometric Schematics of Upscale Biological Sulfate Reduction Process

9.12 Summary and Conclusions

- The results of the FBBR studies demonstrated that the process was significantly affected by hydrogen sulfide concentration, influent sulfate concentration and the hydraulic retention time. These studies clearly demonstrated that the hydrogen sulfide and acetate production (by-products of the process) closely followed the reaction stoichiometry of sulfate reduction and ethanol utilization. It was observed that the FBBR column with GAC as supporting media experienced more sulfate reduction efficiency than did the sand column. Nevertheless, the FBBR-sand column can be operated under lower hydraulic retention time, and therefore, may be more favorable from an economic viewpoint.
- The FBBR model facilitated an analysis of process dynamics with different media, influent sulfate concentration and hydraulic retention time. The model prediction and experimental data were in good agreement under variety of different process and operating conditions. However, owing to hydrogen sulfide toxicity as well as uncertainties with regard to the estimated biokinetic parameters from the chemostat studies, slight deviation between the experimental data and model profiles were experienced.

- Model sensitivity studies established the dependence of FBBR process dynamics on various model parameters. Sensitivity analyses for the FBBR model indicated that the maximum specific growth rate, μ_m the Monod half saturation constant, K_s and decay coefficient, k_d had significant influence on the process dynamics, where as μ_m had the most profound effect. However, growth yield coefficient, Y had no significant effect on the process dynamics and performance efficiency. It was also observed that these analyses are qualitatively similar to those of chemostat studies.
- Scanning electron microscopy (SEM) study demonstrated the extent of bacterial growth as well as the homogeneity of the biofilm layers grown on GAC and sand bioparticles. It was observed that the activated carbon supported significantly more biomass than did sand particles.

CHAPTER 10

GRAND SUMMARY, CONCLUSION AND RECOMMENDATIONS

10.1 Final Summary and Conclusions

This research evaluated the biological sulfate reduction process for the treatment of brine concentrate from reverse osmosis brine obtained from desalination of high-sulfate waters. The purpose using this technology was to produce the potential for membrane scaling due to precipitation of sulfate salts of calcium, and barium in brine concentrate. The process involved the use of FBBR process for sulfate reduction so that the MWDSC could operate reverse osmosis process at high recoveries of over 90-95%. The overall summary and conclusions of this study are presented in the ensuing section.

10.1.1 Completely Mixed Batch Reactor Biokinetic Studies

The CMBR biokinetic studies were investigated to evaluate the optimal biological conditions for sulfate reduction utilizing ethanol as carbon source, including temperature, pH, and carbon to sulfur ratio. The first CMBR studies were conducted at different carbon-to-sulfur ratio of 0.8, 1.0, 1.2, and 1.4 and constant temperature and pH of 30°C and 7.0, respectively. The experimental results of CMBR biokinetic studies projected that the reaction kinetics were improved by increasing the C/S ratio. However, the results reflected by the reaction rate constants demonstrated that higher

C/S ratios of 1.2 or 1.4 did not manifest any significant advantage over a C/S ratio of 1.0 (represented a near-optimal condition). The highest rate constants of $k = 15.66$ mg/(L.hr) and $k = 17.48$ mg/(L.hr) were achieved at C/S = 1.4 for sulfate reduction and ethanol utilization, respectively, as compared to the other C/S ratios. The lowest rate constants for both sulfate reduction and ethanol utilization were observed at a C/S ratio of 0.8 as expected. The CMBR studies were further performed at different temperatures of 20, 25, 30, and 35°C to investigate the effect of temperature on reaction kinetics under a constant pH and C/S ratio of 7.0 and 1.0, respectively. These studies qualitatively demonstrated that the reaction rates for sulfate reduction and ethanol utilization improved with temperature up to 35°C; nonetheless, it is important to note that reaction rate constants were marginally higher at 35°C than at 30°C, indicating that increase in temperature beyond 30°C did not project a significant advantage, although it would entail higher energy costs from an operational standpoint. The last CMBR studies were conducted to evaluate the effect of pH on reaction kinetics at different pHs of 6.0, 7.0, and 8.0 and constant temperature and C/S ratio of 30°C and 1.0, respectively. The maximum rate constant of $k = 12.86$ mg/(L.hr) was obtained at pH = 7.0 for sulfate reduction and at pH of 8.0 for ethanol utilization with the value of $k = 15.98$ mg/(L.hr). It was observed that the reaction rates for sulfate reduction were marginally different at various pHs. These unexpected results were presumably due to the production of hydrogen ions in the reaction of sulfate reduction with ethanol, which consequently resulted in a gradual decrease in pH of the system during the period of the CMBR operation, and

since the control of pH was not possible, the results for the pH-CMBR studies were not quite reliable with regard to sulfate reduction at constant pH. These investigations further demonstrated that the near-optimal pH, C/S ratio and temperature values were 7.0, 1.0, and 30°C, respectively. The optimal or near-optimal conditions estimated from the CMBR studies for biological sulfate reduction provided the basis for subsequent chemostat studies under different carbon-to-sulfur ratios to determine biokinetic parameters used in the modeling and the process dynamics, and predicting the performance of fluidized bed reactor systems.

10.1.2 Chemostat Studies

The chemostat studies provided a comparison of the reaction kinetics for sulfate reduction and carbon source utilization (ethanol utilization) at carbon-to-sulfur ratios of 1.0 and 0.8. Additionally, these chemostat experiments provided estimates of biokinetic parameters including the Monod kinetic coefficients, microbial yield coefficient, and the microbial decay coefficient. Furthermore, these chemostat studies provided insights into the basic design of a continuous flow system such as fluidized bed reactor (FBBR) with reference to process variables such as organic substrates, sulfate loading, sulfate concentrations, biomass concentrations, hydraulic retention times (HRTs), and carbon-to-sulfur ratios. These studies also facilitated a comparison of the reaction kinetics for biological sulfate reduction, with regard to the design of a continuous flow reactor system exemplified by the FBBR.

The batch reactor studies showed that the overall reaction kinetics favored the use of a C/S ratio of 1.0 vis-à-vis 0.8. A comparison of the yield coefficients in Tables 8-2 and 8-3 demonstrated that C/S ratio of 1.0 was capable of greater biomass production than a ratio of 0.8. The Monod maximum substrate utilization rate for sulfate reduction at C/S of 1.0 is 0.102 hr^{-1} , was about 30% lower than that for C/S of 0.8. At high sulfate concentrations, the sulfate reduction appeared to be controlled predominantly by the maximum substrate utilization rate, and therefore, the reaction rates would be slower for C/S of 0.8 than that of 1.0. Consequently, a carbon-to-sulfur ratio of 1.0 was chosen to investigate the performance of the FBBR with GAC and sand as better sulfate degradation and faster kinetics were obtained.

10.1.3 Simulation of Chemostat Dynamics

In chemostat dynamic simulations, the experimental data were compared with the theoretical predictions to evaluate the influence of various biokinetic parameters with reference to sulfate reduction, and further, to verify and validate the chemostat model for estimating biokinetic parameters used in the FBBR model. The results demonstrated a good agreement between the experimental data and model predictions for both carbon to sulfur ratios of 1.0 and 0.8. The chemostat model appeared to predict that the hydrogen sulfide concentration in chemostat would be very low at lower dilution rates, as the experimental values of sulfate concentration in the reactor were larger than the theoretically predicted values. Subsequently, it can

be concluded that the accumulation of the hydrogen sulfide in the reactor at low dilution rate might have inhibited the biomass growth. Sensitivity analyses were performed at the optimal C/S ratio of 1.0 to evaluate the influence of individual biokinetic parameters on the overall chemostat dynamics. These studies demonstrated that the maximum specific growth rate, μ_m had maximum effect on chemostat dynamics with reference to sulfate reduction and ethanol utilization, while the maximum yield coefficient, Y had the least effect on chemostat dynamics.

10.1.4 FBBR – GAC and sand Column Studies

The FBBR investigations compared the performances of several reactor systems (designated as Column 1 through Column 4) with reference to sulfate reduction efficiency. These reactors were operated with ethanol as electron donor and carbon source, and two types of support media, namely, granular activated carbon (GAC) and sand under different process conditions. The various process variables investigated included sulfate loading, hydraulic retention time (HRT), pH, carbon-to-sulfate ratio, and minor operation factors. The FBBR systems were operated to evaluate and maximize biological sulfate reduction efficiencies of the treated brine concentrate at various influent sulfate concentrations of 600, 700, 800, 900, 1000, and 1100 mg/L. The FBBR studies were commenced with the operation of Column 1 with GAC as supporting media. Different pHs, carbon to sulfur ratios, and initial sulfate concentrations were employed in the system throughout the course of its operation. The results demonstrated that ethanol was an efficient carbon source that

manifested sulfate reduction efficiencies in the range of 80-85% under general conditions, and in the vicinity of 90-95% under optimal condition ($C/S=1.0$, $pH=7.5$, and temperature= $30^{\circ}C$). A FBBR-GAC system (Column 2) was operated at different initial sulfate concentrations to study the sulfate reduction profile for the purpose of model calibration and verification by using ethanol as carbon source, and constant pH and temperature of 7.5 and $30^{\circ}C$, respectively. These results indicated that the sulfate removal efficiencies reached the steady-state operation of %68.9, %66.7, %70.2, and 89.0% for sulfate concentrations of 800, 900, 1000, and 1100 mg/L respectively. A FBBR system (Column 3) was further operated to study the sulfate reduction employing sand as supporting medium and ethanol as carbon source. This column exhibited a steady-state sulfate reduction efficiency of 75% at hydraulic retention time of 0.8 hr under optimal condition. In order to investigate the effect of hydrogen sulfide on the removal efficiency, the FBBR-sand column was purged in-situ with nitrogen gas for five days. Consequently, the hydrogen sulfide concentration decreased about 23% during this period, resulting in 6.5% improvement in sulfate removal efficiency, owing to lower H_2S toxicity. The results demonstrated the effect of hydrogen sulfide toxicity on the performance of sulfate reducing bacteria, and clearly indicated the significance of nitrogen stripping in the FBBR system with regard to sulfate removal efficiency. The last FBBR system (Column 4) was operated to study the sulfate reduction at low sulfate concentration of 600 mg/L, and to calibrate the model and verify its predictive capacity. This

column reached the steady-state sulfate reduction efficiency of 68.5% after 3 days of its operation at the hydraulic retention time of 2.5 hr.

The FBBR system with different media (GAC and sand) was investigated, as previously described, and the results were compared. The results indicated that the sulfate reduction efficiency in the FBBR-GAC column was 11% more than that of the sand column. However, the sand column was operated under lower hydraulic retention time (HRT of 0.8 hr) compared to the GAC column (HRT of 2.5 hr), and therefore, incorporates smaller reactor requirement, and consequently lower energy cost.

The results of these investigations revealed that in Columns 1, 2, 3, and 4, the carbon source utilization and hydrogen sulfide production patterns closely followed the sulfate reduction reaction stoichiometric with minor deviations, as anticipated. Furthermore, the acetate production from the utilization of ethanol (carbon source) closely followed the stoichiometry of ethanol consumption.

10.1.5 Anaerobic Biofiltration of Hydrogen Sulfide

The study showed that anaerobic biofiltration would be a potential treatment method for H_2S gas stream. Green-colored biomass was observed in the biofilter column indicating the presence of green sulfur bacteria (GSB). Furthermore, the presence of a dark precipitate indicated the conversion of H_2S to elemental S^0 . The specific type

of anaerobic bacteria populations capable of removing hydrogen sulfide was speculated to be a species of phototrophic green sulfur bacteria (GSB) *Cholorobium limicola*. These anaerobic bacteria were desirable due to their ability to subsist on natural light and inorganic substrates. Anaerobic biofilters using GAC as packing medium demonstrated the potential for cost-effective sulfide elimination. Additionally, the anaerobic biofiltration of H_2S and its subsequent conversion to elemental sulfur is important from the economic perspective of sulfate recovery.

10.1.6 FBBR Modeling

The FBBR experimental results were used to verify the mathematical model developed for the sulfate reduction process. The model incorporated all the important features of biodegradation and assumed that biodegradation occurred not only in the biofilm immobilized onto GAC particles, but also in the liquid phase suspension. Sensitivity analyses of the model provided a good qualitative appreciation of the parameters influencing the sulfate reduction process dynamics under a variety of operating and process conditions such as feed sulfate concentrations, and biokinetic parameters including the specific growth rate, μ_m Monod half saturation coefficient, K_s yield coefficient, Y , and decay coefficient, k_d . The sensitivity analyses results indicated that the FBBR model was highly sensitive to Monod half saturation constant and maximum specific growth rate, whereas variations in the growth yield coefficient as well as the influent sulfate concentrations did not have significant

impact. It was demonstrated that the predictive model developed in this study was a useful tool for predicting the performance of FBBR system and proved useful in the design of pilot-scale. Furthermore, the scale-up techniques presented in this study may prove useful in effecting a smooth transition from laboratory-scale to full-scale with minimal pilot-scale studies.

10.1.7 FBBR Process Upscaling

Subsequent to model verification, upscaling strategies were developed to design a pilot-scale FBBR process employing the techniques of dimensional analyses and similitude. In this regard, several aspects were considered including the kinetics of film transfer, and biodegradation (adsorption phenomenon was disregarded in this study owing to the weak affinity of sulfate for the support media tested). It must be noted that, the Monod biokinetic coefficients (k and K_s) were intrinsic properties of microbial culture and were hence independent of the geometric and dynamic properties of the FBBR. Therefore, the following properties were maintained identical in the upscaling formulation, namely, influent concentration; particle density, packing porosity, and Monod kinetic coefficients. It must be noted, from the standpoint of practical design, that these studies provided an efficient and cost-effective method for design of full-scale FBBR systems, so that pilot-scale testing could be treated as a confirmatory rather than an exploratory procedure. Under this scenario, only limited pilot-scale testing would be required before the design of a full-scale FBBR process.

10.2 Future Work

The following recommendations are to be employed for future research:

- Post treatment processes should be investigated pertaining to aerobic removal of acetate generated as the by-product of the FBBR system during biological sulfate reduction.
- More biofiltration studies should be conducted with reference to anaerobic removal of hydrogen sulfide generated in the biological reduction of sulfate.
- More in-situ nitrogen stripping of hydrogen sulfide in FBBR processes should be investigated. Furthermore, more studies should be conducted with regard to hydrogen sulfide removal from FBBR effluent stream.

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APPENDICES

Appendix A. Experimental Data for the CMBR Biokinetic Studies

Table A - 1 Experimental sulfate results from completely mixed batch reactor (CMBR) studies at different carbon-to-sulfur ratios, and constant pH = 7.0, temperature = 30°C, initial sulfate concentration = 700 mg/L, and biomass concentration (VSS) = 90-100mg/L

Time (hr)	Carbon-to-Sulfur Ratio			
	0.8	1.0	1.2	1.4
	Sulfate concentration (mg/L)	Sulfate concentration (mg/L)	Sulfate concentration (mg/L)	Sulfate concentration (mg/L)
0	687.7	685.0	689.8	676.9
5	683.4	684.2	678.7	660.1
10	649.2	655.4	636.1	613.2
15	602.1	614.1	586.2	544.8
20	549.7	551.2	519.8	453.4
25	494.3	484.0	456.7	378.8
30	442.9	410.9	383.6	303.4
35	361.0	333.4	274.1	187.0
40	354.7	330.8	226.6	112.3
45	357.0	331.1	222.1	77.5
50	353.7	333.1	216.6	67.9
55			213.8	60.0
65			210.8	54.4

Table A - 2 Experimental ethanol results from completely mixed batch reactor (CMBR) studies at different carbon-to-sulfur ratios, and constant pH = 7.0, temperature = 30°C, initial ethanol concentration = 448 mg/L, and biomass concentration (VSS) = 90-100mg/L

Time (hr)	Carbon-to-Sulfur Ratio			
	0.8	1.0	1.2	1.4
	Ethanol concentration (mg/L)	Ethanol concentration (mg/L)	Ethanol concentration (mg/L)	Ethanol concentration (mg/L)
0	374.8	458.0	582.2	662.4
5	373.7	455.9	563.7	655.6
10	357.6	407.8	481.6	580.3
15	287.4	354.8	381.3	527.1
20	229.5	266.8	322.8	421.3
25	139.1	192.8	248.9	337.7
30	115.2	90.6	201.0	245.4
35	0.0	0.0	0.0	119.3
40	0.0	0.0	0.0	26.6
45	0.0	0.0	0.0	7.8
50	0.0	0.0	0.0	0.0
55			0.0	0.0
65			0.0	0.0

Table A - 3 Experimental sulfate results from completely mixed batch reactor (CMBR) studies at different temperatures, and with pH = 7.0, C/S = 1.0, initial sulfate concentration = 700 mg/L and biomass concentration (VSS) = 90-100 mg/L

Time (hr)	Temperature (°C)			
	20	25	30	35
	Sulfate concentration (mg/L)	Sulfate concentration (mg/L)	Sulfate concentration (mg/L)	Sulfate concentration (mg/L)
0	735.0	715.9	720.0	708.1
5	728.0	706.2	708.0	695.6
10	725.6	716.1	712.0	694.9
15	736.1	709.9	682.5	664.3
20	730.8	706.6	644.5	618.0
25	734.1	700.2	579.5	508.4
30	708.0	631.8	493.2	434.0
35	700.4	598.4	428.8	432.7
40	692.0	532.3	433.3	435.2
45	683.7	490.8	444.3	446.2
50	675.3	456.4	441.3	447.7
55	653.6	427.1		
60	613.4	392.9		
65	581.4	397.0		
70	566.7	403.8		
76	519.5			
80	513.1			
85	517.0			
90	517.8			

Table A - 4 Experimental ethanol results from completely mixed batch reactor (CMBR) studies at different temperatures, and with pH = 7.0, C/S = 1.0, initial ethanol concentration = 448 mg/L and biomass concentration (VSS) = 90-100 mg/L

Time (hr)	Temperature (°C)			
	20	25	30	35
	Ethanol concentration (mg/L)	Ethanol concentration (mg/L)	Ethanol concentration (mg/L)	Ethanol concentration (mg/L)
0	501.9	494.6	511.9	491.7
5	505.6	496.6	500.5	492.0
10	492.4	491.4	475.2	452.9
15	487.1	465.7	412.2	303.8
20	478.2	442.9	306.8	224.0
25	459.0	400.0	204.3	92.6
30	436.0	315.8	93.1	0.0
35	356.5	264.0	0.0	0.0
40	317.2	170.2	0.0	0.0
45	286.9	103.7	0.0	0.0
50	233.5	16.7	0.0	0.0
55	198.8	0.0		
60	156.0	0.0		
65	108.4	0.0		
70	61.2	0.0		
76	24.0			
80	0.0			
85	0.0			
90	0.0			

Table A - 5 Experimental sulfate results from completely mixed batch reactor (CMBR) studies at different pH, and with temperature = 30°C, C/S = 1.0, initial sulfate concentration = 700 mg/L and biomass concentration (VSS) = 90-100 mg/L

Time (hr)	pH		
	6.0	7.0	8.0
	Sulfate concentration (mg/L)	Sulfate concentration (mg/L)	Sulfate concentration (mg/L)
0	713.7	699.7	704.2
5	710.7	709.9	714.2
10	695.3	673.0	711.2
15	644.6	613.7	688.7
20	581.4	525.6	663.3
25	501.6	469.2	621.2
30	450.5	404.0	565.0
35	359.1	337.2	448.9
40	332.2	317.3	384.9
45	315.6	301.9	368.1
50	298.6	305.1	359.0
55	294.3	292.4	369.8
60	291.7	287.0	354.5

Table A - 6 Experimental ethanol results from completely mixed batch reactor (CMBR) studies at different pH, and with temperature = 30°C, C/S = 1.0, initial ethanol concentration = 448 mg/L and biomass concentration (VSS) = 90-100 mg/L

Time (hr)	pH		
	6.0	7.0	8.0
	Ethanol concentration (mg/L)	Ethanol concentration (mg/L)	Ethanol concentration (mg/L)
0	458.2	441.7	423.1
5	407.0	406.7	405.4
10	374.3	410.9	398.1
15	348.1	318.2	404.0
20	286.6	243.3	391.8
25	186.5	204.7	296.4
30	124.7	115.7	247.0
35	55.3	32.1	137.3
40	0.0	0.0	40.3
45	0.0	0.0	8.3
50	0.0	0.0	0.0
55	0.0	0.0	0.0
60	0.0	0.0	0.0

Appendix B. Experimental Data for the Chemostat Studies

Table B - 1 Experimental results from chemostat studies at 30°C, C/S = 1.0, pH = 7.5, influent sulfate concentration = 1100 mg/L, and influent ethanol concentration = 705 mg/L

Time (hr)	Flowrate (mL/min)	Dilution rate (hr ⁻¹)	Sulfate Conc. (mg/L)
0.0	0.6	0.020	635.5
4.5	0.6	0.020	610.5
17.3	0.6	0.020	629.8
23.7	0.6	0.020	635.1
29.0	0.6	0.020	639.1
41.5	0.6	0.020	635.5
46.0	0.6	0.020	637.3
53.0	0.7	0.025	645.8
65.0	0.7	0.025	664.5
71.0	0.7	0.025	669.0
77.0	0.7	0.025	675.2
89.5	0.7	0.025	674.6
99.5	1.0	0.033	694.2
114.5	1.0	0.033	724.5
123.0	1.0	0.033	750.9
137.3	1.0	0.033	771.9
142.0	1.0	0.033	776.1
149.0	1.5	0.050	798.9
161.0	1.5	0.050	872.0
165.0	1.5	0.050	871.8
169.7	1.5	0.050	872.1
172.0	2.9	0.10	898.1
185.0	2.9	0.10	1020.5
187.5	2.9	0.10	1030.5
189.5	2.9	0.10	1048.1
195.0	2.9	0.10	1055.1

Table B – 1: Continued Experimental results from chemostat studies at 30°C,
C/S = 1.0, pH = 7.5, influent sulfate concentration
= 1100 mg/L, and influent ethanol concentration
= 705 mg/L

Time (hr)	Ethanol Conc. (mg/L)	H ₂ S Conc. (mg S ²⁻ /L)	Biomass Conc. (mg/L) VSS
0.0	4.5	-	184
4.5	4.5	-	184
17.3	4.5	-	184
23.7	4.5	-	184
29.0	4.5	-	184
41.5	4.5	-	184
46.0	4.5	58	184
53.0	41.0	-	154
65.0	51.6	-	154
71.0	63.2	-	154
77.0	71.2	-	154
89.5	70.8	46	154
99.5	125.2	-	138
114.5	158.0	-	138
123.0	188.4	-	138
137.3	201.1	-	138
142.0	202.4	38	138
149.0	240.6	-	90
161.0	310.6	-	90
165.0	319.7	-	90
169.7	323.1	24	90
172.0	364.8	-	50
185.0	530.5	-	50
187.5	542.9	-	50
189.5	557.6	-	50
195.0	558.7	24	50

Table B - 2 Chemostat experimental and model results at steady-state and different dilution rates for C/S = 1.0

Dilution rate hr⁻¹	Sulfate (Exp.) mg/L	Sulfate (Model) mg/L	Ethanol (Exp.) mg/L	Ethanol (Model) mg/L	Biomass (Exp.) mg/L	Biomass (Model) mg/L
0.020	636.4	557.8	4.5	4.5	184	217.2
0.025	674.9	600.0	71.0	91.3	154	200.7
0.033	774.0	771.7	202.4	117.5	138	137.5
0.05	871.9	921.3	321.4	229.4	90	77.2
0.1	1020.6	1062.1	558.7	525.6	50	16.8

Table B - 3 Hydrogen sulfide analysis result for chemostat studies at C/S = 1.0

Dilution rate (hr⁻¹)	Total Sulfide (mg S⁻²/L)
0.014	75.0
0.017	65.0
0.02	70.0
0.025	90.0
0.033	80.0
0.05	60.0
0.1	16.0
0.2	2.0

Table B - 4 Experimental results from chemostat studies at 30°C, C/S = 0.8, pH = 7.5, influent sulfate concentration = 1100 mg/L, and influent ethanol concentration = 565 mg/L

Time (hr)	Flowrate (mL/min)	Dilution rate (hr ⁻¹)	Sulfate Conc. (mg/L)
0.0	-	-	1042.1
4.0	-	-	991.6
8.0	-	-	887.6
18.5	-	-	576.9
20.8	-	-	573.6
67.3	1.0	0.033	693.8
77.5	1.0	0.033	688.3
91.0	1.2	0.040	669.0
95.0	1.2	0.040	669.0
99.0	1.2	0.040	688.3
115.5	1.2	0.040	688.0
120.5	1.2	0.040	685.4
139.7	1.2	0.040	779.4
149.5	1.2	0.040	775.2
163.5	1.2	0.040	785.8
172.5	1.5	0.050	811.5
188.5	1.5	0.050	947.5
198.5	1.5	0.050	963.5
210.8	1.5	0.050	963.7
222.0	2.0	0.067	1023.4
235.0	2.0	0.067	1082.1
240.0	2.0	0.067	1086.1
243.0	2.9	0.10	1102.0
248.0	2.9	0.10	1098.3
258.8	2.9	0.10	1107.0
267.0	4.2	0.143	1128.8
271.0	4.2	0.143	1109.0
283.5	4.2	0.143	1109.7

Table B - 4: Continued

Experimental results from chemostat studies at 30°C,
C/S = 0.8, pH = 7.5, influent sulfate concentration =
1100 mg/L, and influent ethanol concentration =
565 mg/L

Time (hr)	Ethanol Conc. (mg/L)	H ₂ S Conc. (mg S ²⁻ /L)	Biomass Conc. (mg/L) VSS
0.0	513.2	-	-
4.0	434.3	-	-
8.0	342.1	-	-
20.8	4.3	-	-
67.3	30.0	-	175
77.5	54.0	42	175
91.0	42.3	-	186
95.0	40.9	-	186
99.0	53.5	-	186
115.5	100.9	-	186
120.5	114.8	-	186
139.7	185.1	-	186
149.5	179.0	-	186
163.5	199.2	32	186
172.5	240.1	-	64
188.5	332.5	-	64
198.5	349.6	-	64
210.8	348.0	-	64
222.0	371.5	-	56
235.0	381.4	-	56
240.0	383.3	24	56
243.0	391.6	-	40
248.0	410.4	-	40
258.8	422.4	20	40
267.0	482.9	-	20
271.0	465.6	-	20
283.5	465.7	20	20

Table B - 5 Chemostat experimental and model results at steady-state and different dilution rates for C/S = 0.8

Dilution rate hr⁻¹	Sulfate (Exp.) mg/L	Sulfate (Model) mg/L	Ethanol (Exp.) mg/L	Ethanol (Model) mg/L	Biomass (Exp.) mg/L	Biomass (Model) mg/L
0.03	684.6	645.0	54.0	106.2	175	175.0
0.04	777.3	849.7	187.8	148.2	186	162.4
0.05	963.6	976.8	348.8	252.2	64	98.1
0.07	1074.1	1084.8	450.4	492.3	56	49.4
0.10	1100.2	1098.0	496.4	551.4	40	6.1

Table B - 6 Hydrogen sulfide analysis result for chemostat studies for C/S = 0.8

Dilution rate (hr⁻¹)	Total Sulfide (mg S⁻²/L)
0.020	50.0
0.025	44.0
0.033	29.0
0.05	23.0
0.1	22.0

Appendix C. Experimental Data for the FBBR Studies

Table C - 1 Summary of operational changes in FBBR – GAC (Column 1)

Time (day)	Operational Changes
1	Biofilter connection, Alkalinity: 109 mg/L as CaCO ₃
4	Recirculation stopped
21	Nitrate decreased from 300 to 150 mg/L
25	Nitrate decreased from 150 to 100 mg/L
37	Nitrate decreased from 100 to 75 mg/L
43	Nitrate decreased from 75 to 30 mg/L
49	Nitrate decreased from 30 to 5 mg/L
50	SO ₄ ²⁻ increased from 500 to 600 mg/L
54	Reactor Cleaning
67	SO ₄ ²⁻ increased to 650 mg/L, Alkalinity: 160 mg/L as CaCO ₃
81	SO ₄ ²⁻ increased to 700 mg/L
85	Alkalinity: 200 mg/L as CaCO ₃
104	Alkalinity: 225 mg/L as CaCO ₄
106	Alkalinity: 330 mg/L as CaCO ₅
122	Alkalinity: 335 mg/L as CaCO ₆
98	Reactor cleaning
133	PO ₄ (doubled), 12 mg/L
139	Amino acid added
141	Reactor Cleaning - Add GAC 35g
153	Expansion increased 20% more
160	SO ₄ ²⁻ increased to 800 mg/L, Ethanol: 512 mg/L
170	SO ₄ ²⁻ increased to 900 mg/L, Ethanol: 577 mg/L
176	SO ₄ ²⁻ increased to 1000 mg/L, Ethanol: 641 mg/L
188	SO ₄ ²⁻ increased to 1100 mg/L, Ethanol: 705 mg/L, Alkalinity: 400 mg/L
200	Alkalinity: 430 mg/L as CaCO ₃
215	C/S changed to 0.8

Table C - 1: Continued Summary of operational changes in FBBR – GAC
(Column 1)

Time (day)	Operational Changes
225	C/S changed to 1.2
227, 239	Reactor cleaning
242	Selenium added (1 mg/L)
244	Perchlorate added (100 ug/L)
248	Selenium addition stopped
254	Selenium added (100ug/L)
269	Reactor cleaning
274	pH changed from 6.2 to 7.0
290	pH changed from 7 to 7.5
303	C/S changed to 1.0
339, 340	Reactor stop & cleaning
342, 351, 356	Reactor stop & Cleaning
357	GAC 40 g replaced

Table C - 2 Experimental results from fluidized bed bioreactor studies (Column 1) at 30°C with GAC as supporting media, and ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
0	318.1	-	-
1	314.0	-	-
4	386.1	-	-
6	494.5	-	-
7	437.4	-	-
8	418.2	-	-
9	436.1	-	-
10	440.3	-	-
11	407.2	-	-
13	424.5	-	-
15	421.0	-	-
17	443.5	-	-
19	435.9	-	-
21	407.8	-	-
22	418.2	-	-
23	410.2	-	-
25	399.0	-	-
27	388.2	-	-
29	386.3	-	-
30	375.8	-	-
31	368.1	-	-
33	374.0	-	-
36	402.0	-	-
37	380.0	-	-
39	398.4	-	-
41	402.9	-	-
43	388.7	-	-
45	354.3	-	-
47	278.0	-	-

Table C – 2: Continued Experimental results from fluidized bed bioreactor studies (Column 1) at 30°C with GAC, and ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
49	221.3	-	-
51	323.3	-	-
53	281.3	-	-
55	347.4	-	-
57	304.0	-	-
61	301.0	-	-
63	240.6	-	-
65	240.3	-	-
67	226.2	-	-
69	250.2	-	-
71	245.4	-	-
73	247.7	-	-
75	264.3	-	-
77	255.2	-	-
79	254.4	-	-
81	244.4	-	-
83	284.6	-	-
87	265.5	-	-
89	258.9	-	-
91	274.8	-	-
93	272.4	-	-
95	276.1	-	-
97	277.8	-	-
99	280.6	-	-
101	286.2	-	-
103	287.5	-	-
105	281.5	-	-
107	261.6	-	-

Table C – 2: Continued Experimental results from fluidized bed bioreactor studies (Column 1) at 30°C with GAC, and ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
109	263.5	-	-
111	285.1	-	-
115	267.3	-	-
117	237.2	-	-
119	265.2	-	-
121	258.2	-	-
123	240.5	-	-
125	242.0	-	-
127	225.6	-	-
129	195.4	-	-
133	204.0	-	-
135	205.9	0.0	-
137	183.2	1.2	-
139	171.6	2.0	-
141	151.1	5.6	-
143	165.9	3.5	-
145	154.8	0.0	-
147	116.7	0.0	-
149	128.9	0.0	-
150	137.5	0.0	-
151	134.9	0.0	-
153	139.9	0.0	-
155	109.3	9.8	-
157	63.4	13.3	-
159	172.4	6.1	-
161	160.3	11.9	-
163	166.3	12.0	582.4
165	183.2	12.3	570.5

Table C – 2: Continued Experimental results from fluidized bed bioreactor studies (Column 1) at 30°C with GAC, and ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
167	162.4	12.9	569.3
169	181.0	9.1	543.2
171	242.4	6.9	533.3
173	202.0	9.3	616.6
175	182.9	6.4	641.9
177	348.8	0.0	618.2
179	289.6	23.1	758.3
181	275.1	14.2	739.6
183	249.3	10.6	715.3
185	224.2	10.6	758.7
187	214.5	23.4	752.3
189	291.1	9.7	742.3
191	289.6	6.8	780.2
193	293.5	9.9	769.3
195	289.4	0.0	776.3
197	284.3	4.2	772.7
199	288.7	6.0	767.3
201	306.2	0.0	739.4
203	316.9	0.0	857.3
205	290.4	9.9	830.3
209	286.9	10.5	914.3
211	284.3	24.3	891.3
213	275.1	23.0	862.2
215	438.2	15.0	670.4
217	448.5	13.4	702.2
219	484.3	0.0	674.3
223	499.8	0.0	638.2
225	480.5	0.0	654.9

Table C – 2: Continued Experimental results from fluidized bed bioreactor studies (Column 1) at 30°C with GAC, and ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
227	208.4	24.3	1031.3
229	248.4	23.7	1020.1
231	250.3	26.5	1042.0
233	213.8	1131.6	34.0
237	240.7	1015.2	28.6
239	240.2	1087.2	67.1
241	227.1	1036.0	50.6
243	176.8	1035.2	43.1
245	251.3	1003.0	48.6
247	334.4	985.9	107.8
249	279.1	990.9	87.1
251	200.5	1069.1	78.4
253	149.9	1169.7	71.7
255	127.6	1180.9	65.6
257	298.9	1048.0	64.1
259	244.3	1084.7	69.0
261	308.1	1023.2	71.9
263	296.2	996.8	76.2
265	286.7	996.9	69.9
267	314.0	999.6	107.7
269	316.6	925.6	112.4
271	334.3	926.1	119.0
273	313.2	988.0	131.9
275	262.3	1012.5	109.5
277	242.9	1058.4	59.9
279	232.7	1116.6	54.3
281	238.6	1015.5	51.6
283	211.3	1040.1	17.4

Table C – 2: Continued Experimental results from fluidized bed bioreactor studies (Column 1) at 30°C with GAC, and ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
285	242.5	980.8	4.2
287	200.9	997.8	24.8
289	192.5	1070.1	22.5
291	284.3	982.0	50.8
293	210.0	1027.7	50.0
295	192.8	1020.2	34.3
297	177.2	1020.8	40.5
299	178.9	1006.8	31.5
301	227.5	1002.9	39.1
303	203.8	995.8	25.9
305	405.4	857.3	40.2
307	416.5	868.6	40.2
309	333.5	835.2	29.8
311	320.1	840.0	0.0
315	295.2	802.9	0.0
317	327.1	793.9	0.0
319	287.0	812.5	0.0
321	255.0	837.6	0.0
323	245.2	811.2	0.0
325	238.2	801.5	0.0
327	225.9	866.6	0.0
329	216.3	822.1	0.0
331	213.7	807.0	0.0
333	223.5	834.8	0.0
335	216.3	825.9	0.0
337	214.5	833.8	0.0
339	226.6	717.3	0.0
342	141.2	549.8	0.0

Table C – 2: Continued Experimental results from fluidized bed bioreactor studies (Column 1) at 30°C with GAC, and ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
345	106.4	1094.9	0.0
348	226.9	833.5	0.0
351	216.8	790.5	0.0
354	232.2	804.1	36.4
357	294.4	674.6	37.7
360	420.4	784.6	62.3
363	359.2	830.1	57.3
366	326.3	800.8	60.2
369	285.1	823.4	32.1
372	222.0	849.8	22.5
375	201.9	815.3	0.0
378	188.9	853.7	0.0
381	176.5	816.3	0.0
384	172.8	933.1	0.0
387	165.2	858.7	0.0
390	161.9	975.2	0.0
393	171.5	817.6	0.0
395	168.8	916.7	0.0
396	171.9	933.9	0.0

Table C - 3 Summary of operational changes in FBBR - GAC (Column 2)

Time (day)	Operational Changes
13	SO ₄ ²⁻ increased from 800 to 900 mg/L, ethanol: 512 to 577 mg/L
34	SO ₄ ²⁻ increased to 1000 mg/L, ethanol: 641 mg/L
40	Excess biomass generation observed at top of the GAC bed
45	Excess biomass at top of the GAC bed was removed
47	SO ₄ ²⁻ increased to 1100 mg/L, ethanol: 705 mg/L
51	Excess biomass on top of the GAC bed was removed

Table C - 4 Experimental results from fluidized bed bioreactor studies (Column 2) at 30°C, pH = 7.5 with GAC as supporting media, and ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
0	536.2	230.0	289.2
2	321.5	35.0	608.3
3	252.7	10.0	653.8
5	263.8	11.2	652.0
8	261.3	10.2	668.6
11	244.5	12.9	667.7
12	254.1	12.0	663.4
14	323.4	14.6	616.8
16	617.5	249.8	950.8
17	513.8	36.0	939.1
18	422.8	15.0	585.9
19	359.4	10.3	779.4
21	316.0	8.0	811.9
24	297.7	7.0	971.5
25	294.7	8.0	1044.5
26	293.5	10.0	1043.9
27	301.2	9.0	1058.6

Table C - 4: Continued Experimental results from fluidized bed bioreactor studies (Column 2) at 30°C, pH = 7.5, GAC as supporting media, and ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
29	300.2	8.0	1083.7
31	301.2	11.0	1049.8
33	313.9	14.0	1058.5
35	354.6	15.0	986.4
37	326.7	17.0	1162.1
40	320.5	12.0	1145.9
42	291.5	8.0	1103.9
44	285.2	7.0	1138.8
46	301.8	9.0	1075.1
47	300.9	10.0	1074.6
48	320.3	11.0	1179.4
52	310.7	8.0	1116.1
54	213.8	6.0	954.1
56	249.6	7.0	920.5
61	207.4	4.0	892.2
62	183.8	0.0	899.1
66	171.5	0.0	934.0
68	142.4	0.0	934.9

Table C - 5 Summary of operational changes in FBBR - sand (Column 3)

Time (day)	Operational Changes
1	Reactor cleaning, pH adjustment to 7.5
9	Floating biomass on top of the sand bed was removed
14	SO ₄ ²⁻ increased from 700 to 800 mg/L, Ethanol: 448 to 512 mg/L
21	SO ₄ ²⁻ increased to 900 mg/L, Ethanol: 576 mg/L
40	Reactor cleaning, 30 g sand was added, pH adjustment to 7.5
27	pH = 6.5 over night, pump went off
27	Reactor cleaning, high base injection to the column (probe problem)
50	SO ₄ ²⁻ increased to 1100 mg/L, Ethanol: 705 mg/L
55	Reactor cleaning, Floating biomass was removed
69	Reactor cleaning, Floating biomass was removed
79	Biomass generation on top of the sand bed & column inner wall
88	H ₂ S Stripping with N ₂ gas, Q _{N2} :30 mL/min

Table C - 6 Hydrogen sulfide analysis results for the FBBR – sand (Column 3)

Time (day)	mg S ⁻² /L	Time (Day)	mg S ⁻² /L
1	150	63	277
8	198	65	303
16	213	69	256
23	247	72	268
29	220	76	284
37	259	84	287
44	253	86	282
51	252	88 (H ₂ S Stripping)	218
57	277	90 (H ₂ S Stripping)	216

Table C - 7 Experimental results from fluidized bed bioreactor studies (Column 3)
 at 30°C, pH = 7.5, sand as supporting media, and ethanol as carbon
 source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
0		186.9	175.4
1	299.4	-	267.8
2	303.2	65.8	330.4
3	245.0	46.7	390.3
6	190.6	27.4	439.6
9	197.8	30.3	435.9
12	200.3	20.6	461.2
15	284.0	58.2	461.8
18	216.9	40.3	429.8
21	200.7	43.7	442.4
23	208.5	45.7	469.9
27	427.7	105.8	439.5
29	360.3	99.0	510.2
32	310.3	105.0	464.8
34	295.9	38.0	577.1
35	306.2	36.5	546.8
36	305.6	45.5	548.5
38	286.1	-	542.3
39	287.2	56.4	524.3
41	404.5	-	531.8
42	356.3	84.8	530.5
43	317.9	-	580.5
44	299.6	-	580.5
46	262.6	59.8	609.2
47	258.5	-	623.2
48	259.4	-	593.4

Table C - 7: Continued Experimental results from fluidized bed bioreactor studies (Column 3) at 30°C, pH = 7.5, sand as supporting media, as ethanol as carbon source

Time (day)	Sulfate Conc. (mg/L)	Ethanol Conc. (mg/L)	Acetate Conc. (mg/L)
49	251.0	32.5	593.8
50	252.7	42.5	572.3
51	252.0	57.3	729.4
52	240.3	45.0	742.9
54	225.1	55.9	716.8
55	227.1	55.5	684.6
57	357.0	-	729.1
58	313.1	90.7	733.1
61	271.4	72.1	743.3
63	277.0	68.8	765.9
64	282.8	72.2	765.0
67	272.8	71.7	768.0
71	352.0	72.5	726.0
72	331.1	100.2	756.2
75	306.9	88.5	712.6
77	289.9	41.9	739.8
78	284.3	30.7	721.6
79	290.2	32.6	707.9
84	266.9	30.6	697.9
85	230.7	14.5	678.3
86	219.0	16.5	753.1
87	224.7	20.4	774.5
89	224.9	17.2	815.2
91	164.6	9.1	803.7
92	168.2	8.6	791.3
93	170.3	10.1	778.7

Table C - 8 Experimental results from fluidized bed bioreactor studies (Column 4)
 at 30°C, initial sulfate concentration = 600 mg/L, C/S = 1.0, pH = 7.5,
 GAC as supporting media, and ethanol as carbon source

Time (day)	Sulfate Concentration (mg/L)
0	600.8
1	326.1
1	239.3
2	189.1
3	180.1
4	186.1
5	188.2
6	190.2
7	192.5
8	185.0
9	180.0
10	179.0
11	170.0

Table C - 8: Continued

Experimental results from fluidized bed bioreactor studies (Column 4) at 30°C, initial sulfate concentration= 600 mg/L, C/S = 1.0, pH = 7.5, GAC as supporting media, and ethanol as carbon source

Time (day)	Sulfate Concentration (mg/L)
12	160.0
13	154.2
15	134.2
16	125.2
17	114.2
18	112.8
19	122.0
21	119.0
23	99.6
26	83.9
29	87.8
31	85.8
33	86.8
35	85.8
37	89.8

Appendix D. Sulfur Mass Balance

The sulfur mass balance for the entire biological sulfate reduction process was investigated in this study including the following individual reactors: (i) FBBR system, (ii) hydrogen sulfide stripping unit, and (iii) anaerobic biofilter column. These aspects are discussed in Appendices D₁, D₂, and D₃, respectively. The overall scheme for the mass balance study is presented in Figure D-1, where it must be noted that this analysis was performed for both laboratory-scale and pilot-scale systems for a typical influent sulfate concentration of 1070 mg/L. Furthermore, as previously discussed (Section 9.6), the H₂S concentration in the gaseous effluent of the anaerobic biofilter was below the detection limit of the instruments used (less than 42 mg/m³ or 30 ppb, the California Ambient Air Quality standard for hydrogen sulfide based on a 1 hour averaging time). Additionally, the sulfate concentration in the effluent stream of the FBBR system proved to be less than 250 mg/L (the Secondary Maximum Contaminant Level specified by the US EPA based on taste). The sulfur mass balance analysis demonstrated that the aqueous H₂S concentration in the effluent stream of the H₂S stripping process was about 3 mg/L, higher than the federal standard of 2 µg/L for freshwaters or saltwaters (Water Quality Criteria, US EPA2006d). Therefore, further treatment was necessary to eliminate the remaining hydrogen sulfide from the effluent stream, using one of the following alternatives: (i) H₂S oxidization by hydrogen peroxide or aeration (conversion of hydrogen sulfide to sulfate), or (ii) H₂S adsorption by GAC column.

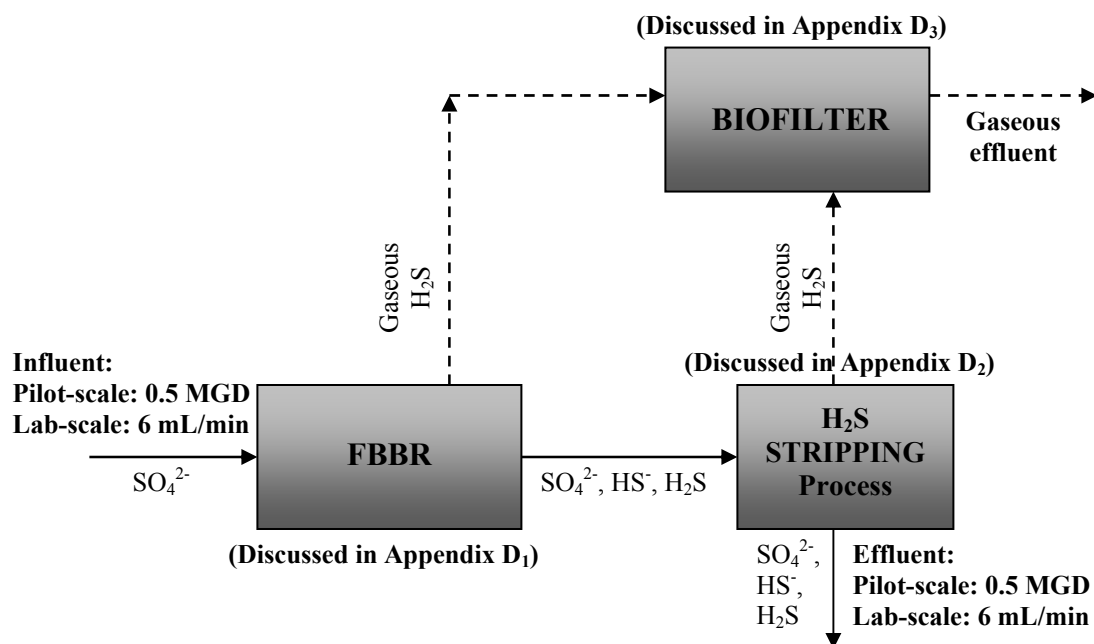


Figure D - 1 Sulfur Mass Balance Diagram for the Biological Sulfate Reduction Process

Appendix D₁. Fluidized Bed Bioadsorber Reactor (FBFR)

An important aspect was the sulfur mass balance for the FBFR system, wherein hydrogen sulfide production was an important factor. Details are provided in this section on the sulfur mass balance and reaction stoichiometry as well as on the sulfide speciation (due to the hydrogen sulfide equilibria between the gaseous and aqueous phases). The sulfate reduction in biologically active fluidized bed adsorbers was accompanied by the production of hydrogen sulfide, and its subsequent conversion to other sulfide forms including the sulfide and bisulfide ions based on the pH conditions. Therefore, it was anticipated that the measurements of total sulfides in the effluents would provide indications on the biological activity and the

extent of conversion of sulfate within the reactors. The HS^- and H_2S concentrations in the reactor were determined theoretically, and these values were compared with the experimental results. Additionally, the effects of temperature and pH on the concentration of H_2S in liquid phase and HS^- were evaluated. The results of these studies are presented in Tables D₁-6, and D₁-7, and Figures D₁-3, and D₁-4.

In the present investigation, the purpose of acquiring thermodynamic data was to evaluate the feasibility of the biochemical reactions associated with biological sulfate reduction, based on free energy considerations. The biochemical processes involved in the anaerobic degradation of sulfur compounds can be represented by an oxidation-reduction or electron donor-acceptor scheme. The theoretical values of the Gibbs free energies (ΔG°) calculated from thermodynamic data indicate the feasibility of these reactions. The thermodynamics data for some species of biological interest are also listed in Table D₁-1 (Mosey, 1985).

Table D₁ - 1 Standard Gibbs free energies of formation for various species

Substance	State	G°_f (kJ/mole)	Substance	State	G°_f (kJ/mole)
CH_4	g [*]	-50.7	SO_4^{2-}	aq	-743.9
CO_2	g	-358.9	H_2S	aq	-27.3
HCO_3^-	aq ^{**}	-586.5	HS^-	aq	12.6
CO_3^{2-}	aq	-527.6	S^{2-}	aq	83.6
CH_3COOH	aq	-399.1	H_2O	l ^{***}	-237.0
CH_3COO^-	aq	-372.0	H^+	aq	0
O_2, H_2	g	0	OH^-	aq	-157.2

*: gas; **: aqueous; ***: liquid

The standard redox potential (E°) is calculated from ΔG° of the half reaction using the relation $E^\circ = (\Delta G^\circ)/(n.F)$, where n is the number of electrons in the half-reaction and F is the Faraday constant expressed as mV equivalents (96.42 J/mV). Table D₁-2 shows the main half-reactions involved in the biological oxidation and reduction of C and S compounds and the values of their standard Gibbs free energy and standard redox potentials. The ΔG° for the two carbon sources, namely, ethanol and acetate, are presented below:

Ethanol:

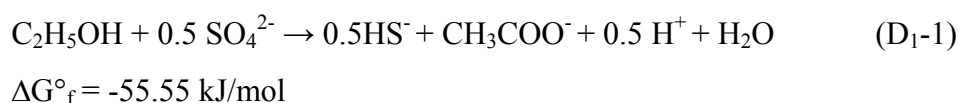


Table D₁ - 2 Half-reactions and energies involved in the biological oxidation and reduction of C and S compounds

	Half Reaction	G°_f (kJ)	E°
	Hydrogen		
R1	$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	0	0
	Organic matter		
R2	$\text{CH}_3\text{COO}^- + 9\text{H}^+ + 8\text{e}^- \leftrightarrow 2\text{CH}_4 + 2\text{H}_2\text{O}$	-203	264
R3	$2\text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^- \leftrightarrow \text{CH}_3\text{COO}^- + 4\text{H}_2\text{O}$	-147	190
R4	$\text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^- \leftrightarrow 2\text{CH}_4 + 3\text{H}_2\text{O}$	-175	248
	Sulfur		
R5	$\text{SO}_4^{2-} + 8\text{H}^+ + 6\text{e}^- \leftrightarrow \text{S}^\circ + 4\text{H}_2\text{O}$	-204	353
R6	$\text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- \leftrightarrow \text{HS}^- + 4\text{H}_2\text{O}$	-191	248
R7	$\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- \leftrightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$	-231	300
R8	$\text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^- \leftrightarrow \text{S}^{2-} + 4\text{H}_2\text{O}$	-120	156
R9	$\text{S}^\circ + \text{H}^+ + 2\text{e}^- \leftrightarrow \text{HS}^-$	-13	131

Table D₁ - 3 Competition between SRB and MPB for acetate and hydrogen

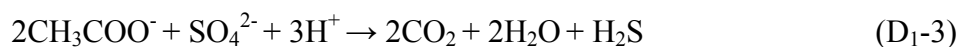
From Table D ₁ - 2	Reaction	G°(kJ)
Acetate		
0.5×R ₂ - 0.5×R ₃ = R ₂ - R ₄ = R ₄ -R ₃	CH ₃ COO ⁻ + H ₂ O ↔ CH ₄ + HCO ₃ ⁻	-28.3
R ₆ - R ₃	SO ₄ ²⁻ + CH ₃ COO ⁻ ↔ HS ⁻ + 2HCO ₃ ⁻	-44.5
R ₇ - R ₃	SO ₄ ²⁻ + CH ₃ COO ⁻ + H ⁺ ↔ H ₂ S + 2HCO ₃ ⁻	-84.4
Hydrogen		
R ₄ -4×R ₁	HCO ₃ ⁻ + 4H ₂ + H ⁺ ↔ CH ₄ + 3H ₂ O	-175.1
R ₆ -4×R ₁	SO ₄ ²⁻ + 4H ₂ + 1H ⁺ ↔ HS ⁻ + 4H ₂ O	-191.4
R ₇ -4×R ₁	SO ₄ ²⁻ + 4H ₂ + 2H ⁺ ↔ H ₂ S + 4H ₂ O	-231.3

Ethanol:



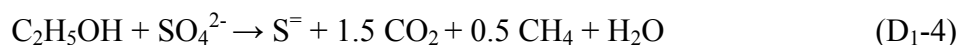
$$\Delta G^\circ_f = -15.91 \text{ kcal/mol ethanol}$$

Acetate:



$$\Delta G^\circ_f = 47.06 \text{ kJ/mol}$$

The overall stoichiometry for growth on ethanol is:



In the anaerobic digestion process, sulfate is reduced to sulfide, which is distributed between H₂S in the gas phase; and H₂S, HS⁻, and S²⁻ in the aqueous phase, and insoluble metallic sulfides. The equilibrium between H₂S in the gas phase and free H₂S in solution is governed by Henry's law.

$$[\text{H}_2\text{S}]_{\text{aq}} = H[\text{H}_2\text{S}]_{\text{g}} \quad (\text{D}_1-5)$$

Where H is the Henry's constant which can be calculated at 30°C from Van Hoff's equation;

$$\text{Log } H = \frac{-\Delta H}{RT} + k \quad (\text{D}_1\text{-6})$$

Where ΔH for H_2S is $1.85 \text{ kcal/kmol} \times 10^3$ and k is 5.88

$$\text{Log } H = \frac{-1.85 \times 10^3 \text{ kcal/kmol}}{(1.987 \text{ kcal/kmol})(273.15 + 30)^\circ \text{K}} + 5.88 = 2.809$$

$$\rightarrow H = 644 \text{ atm}$$

Equilibria:



At low pH values the aqueous hydrogen sulfide is more dominant than HS^- ; at pH 7.5 the first reaction is predominant and 22.5% of the total sulfide is in the form of aqueous H_2S .

Table D₁ - 4 Percentages of aqueous H_2S and HS^- at different pHs

pH	Percentage of H_2S	Percentage of HS^-
4	99.9	0.1
5	98.9	1.1
6	90.1	9.9
7	47.7	52.3
7.5	22.5	77.5
8	8.3	91.7
8.5	2.8	97.2
9	0.89	99.1

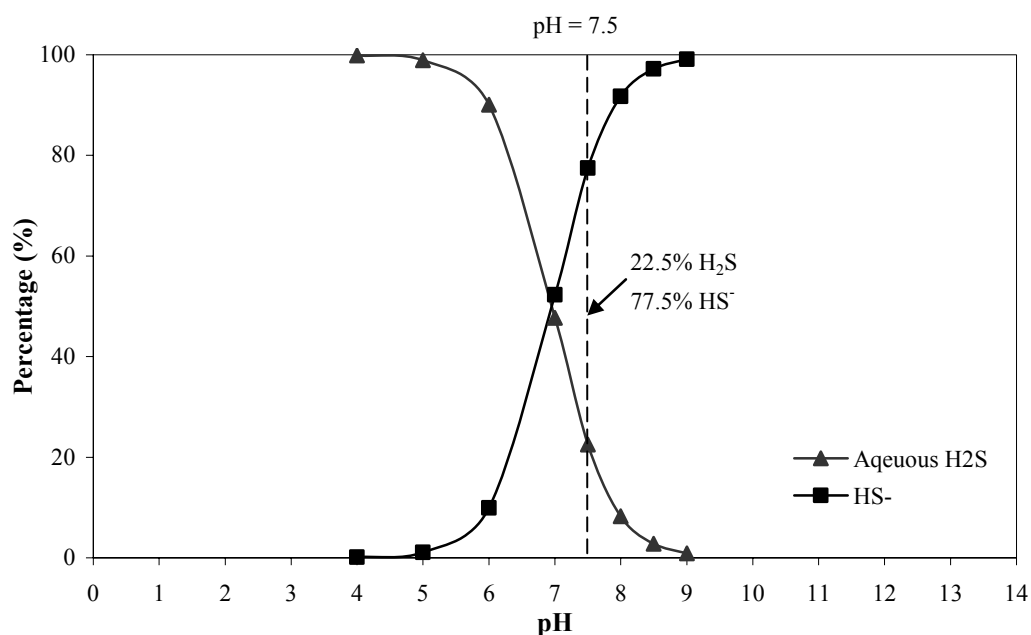


Figure D₁ - 1 Percentages of H₂S and HS⁻ in Aqueous Form at Different pHs

At first the total sulfide was measured by Iodometric Standard method. Two samples were taken and analyzed from Column 1, and the results are presented in Table D₁-5.

Table D₁ - 5 Sulfide concentrations of two samples from FBBR effluent

Diluted Sample (mL)	Iodine (mL)	Na ₂ S ₂ O ₃ (mL)	mg S ²⁻ /L
200	10	32.25	310
200	5	12.25	310

Based on the analyzed total sulfide concentration of 310 mg S²⁻ /L, the concentrations of HS⁻ and H₂S at different temperatures and pHs were calculated theoretically as shown below:

Operating condition: (pH = 7.5, temperature = 30°C)

The conditional ionization constant:

$$K'_1 = \frac{[H^+][HS^-]}{[H_2S]} \quad (D_1-9)$$

Dissociation constant for zero ionic strength pK_1 at $T = 30^\circ\text{C}$ (303.15 °K):

$$pK_1 = 32.55 + 1519.44/T - 15.672 \log T + 0.02722T \quad (D_1-10)$$

$$pK_1 = 32.55 + 1519.44/303.15 - 15.672 \log 303.15 + 0.02722 \times 303.15$$

$$pK_1 = 6.9214$$

Ionic Strength:

$$I = TDS \times 2.5 \times 10^{-5} \quad (D_1-11)$$

TDS for Column 1: 28000

$$I = 28000 \times 2.5 \times 10^{-5} = 0.7$$

Debye-Huckel A parameter:

$$A = 0.7083 - 2.277 \times 10^{-3}T + 5.399 \times 10^{-6}T^2 \quad (D_1-12)$$

$$A = 0.7083 - 2.277 \times 10^{-3} \times 303.15 + 5.399 \times 10^{-6} \times 303.15^2$$

$$A = 0.5142$$

Ion Activity Coefficient:

$$pf_m = A \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (D_1-13)$$

$$pf_m = 0.5142 \left(\frac{\sqrt{0.7}}{1 + \sqrt{0.7}} - 0.3 \times 0.7 \right) = 0.1263$$

Conditional ionization constant:

$$K'_I = 10^{-pK_1 + 2pf_m} \quad (D_1-14)$$

$$[H^+] = 10^{-pH + pf_m} \quad (D_1-15)$$

Then,

$$K'_I = 10^{-6.9214 + 2 \times 0.1263} = 2.144 \times 10^{-7}$$

$$[H^+] = 10^{-7.5 + 0.1263} = 4.23 \times 10^{-8}$$

and,

$$[H_2S] = \frac{S_T}{1 + \frac{K'_1}{[H^+]}} \quad (D_1-16)$$

Total sulfide concentration:

$$310 \text{ mg/L} = 310 \times 10^{-3} / (2 + 32.066) = 0.0091 \text{ M}$$

$$[H_2S] = \frac{0.0091}{1 + \frac{2.144 \times 10^{-7}}{4.23 \times 10^{-8}}} = 0.0015 \text{ M} = 51.083 \text{ mg/L as S}$$

and,

$$[HS^-] = 310 - 51.083 = 258.92 \text{ mg/L as S}$$

Influent and effluent sulfate concentrations of the sample obtained for sulfide analysis are as below:

Influent SO_4^{2-} concentration: 1070 mg/L

Effluent SO_4^{2-} concentration: 129 mg/L

$$\text{SO}_4^{2-} \text{ removal: } 1070-129 = 941 \text{ mg/L} = \frac{941 \times 32.066}{96.066} = 314.1 \text{ mg S}^{2-}/\text{L} \text{ which is}$$

nearly equal to the total sulfide concentration of 310 mg/L as determined by iodometric method. The deviation observed can be attributed to the experimental error from sulfate analysis by ion chromatography. The sulfur mass balance performed for the biological sulfate reduction processes at different temperatures and pHs are presented in Tables D₁-6 and D₁-7, while, the FBBR effluent concentrations of [HS⁻] and [H₂S] in percentages at different temperatures and pHs are shown in Figures D₁-2 and D₁-3. The complete picture of the sulfur mass balance for the biological sulfate reduction process including the FBBR system, hydrogen sulfide stripping process, and anaerobic biofilter with a typical influent sulfate concentration of 1070 mg/L is illustrated in Figures D₃-3 and D₃-4 for the laboratory-scale and pilot-scale systems, respectively.

Table D₁ - 6 Sulfur mass balance at temperature of 30°C for different pH and influent SO₄²⁻ concentration of 1070 mg/L, effluent SO₄²⁻ of 129 mg/L, and K_a (K'₁) of 2.1 × 10⁻⁷

pH	Total Effluent Sulfide, mg S ²⁻ /L	[H ⁺] mg/L	[H ₂ S] mg/L as S	%[H ₂ S]	[HS ⁻] mg/L as S	%[HS ⁻]
5	310	1.3 × 10 ⁻⁵	305	98.4	4.9	1.6
5.5	310	4.2 × 10 ⁻⁶	295.1	95.2	14.9	4.8
6	310	1.3 × 10 ⁻⁶	267	86.2	43	13.8
6.5	310	4.2 × 10 ⁻⁷	206	66	104	33.6
7	310	1.3 × 10 ⁻⁷	119	38	191	61.6
7.5	310	4.2 × 10 ⁻⁸	51	16	259	83.5
8	310	1.3 × 10 ⁻⁸	18	6	292	94.1

Table D₁ - 7 Sulfur mass balance at pH of 7.5 for different temperatures and influent SO_4^{2-} concentration of 1070 mg/L, effluent SO_4^{2-} of 129 mg/L, and total effluent sulfide of 310 mg S^{2-} /L

Temp °C	$K_a(K'_1)$	$[\text{H}^+]$ mg/L	$[\text{H}_2\text{S}]$ mg/L as S	% $[\text{H}_2\text{S}]$	$[\text{HS}^-]$ mg/L as S	% $[\text{HS}^-]$
15	1.338×10^{-7}	4.196×10^{-8}	74.02	23.9	235.98	76.1
20	1.583×10^{-7}	4.208×10^{-8}	65.09	21	244.91	79
25	1.852×10^{-7}	4.218×10^{-8}	57.51	18.6	252.49	81.4
30	2.144×10^{-7}	4.229×10^{-8}	51.08	16.5	258.92	83.5
35	2.456×10^{-7}	4.241×10^{-8}	45.65	14.7	264.35	85.3

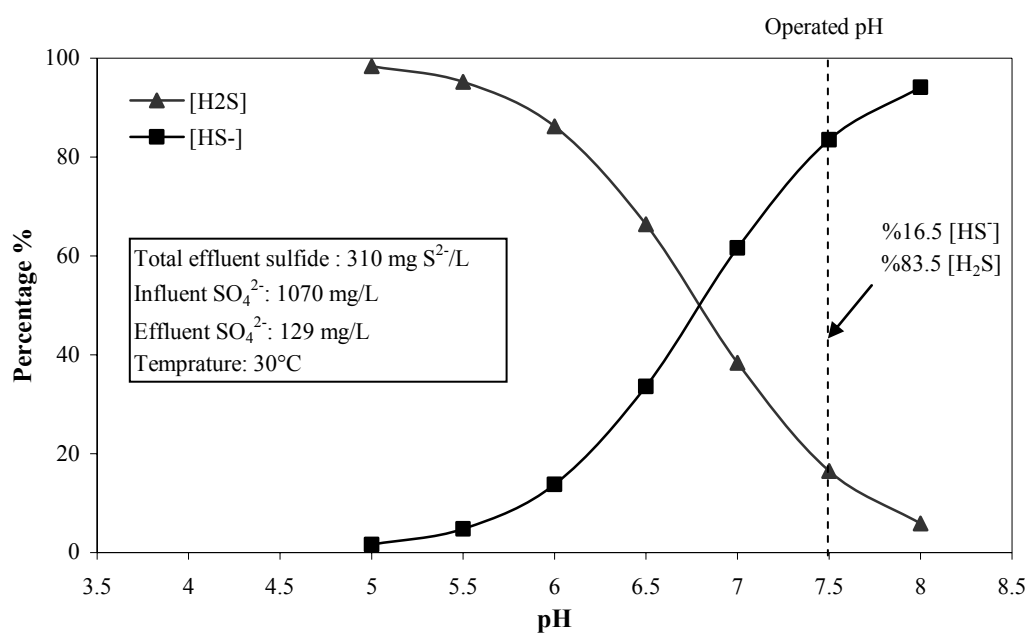


Figure D₁ - 2 Effluent Concentrations of HS^- and H_2S in the FBBR System at Different pHs

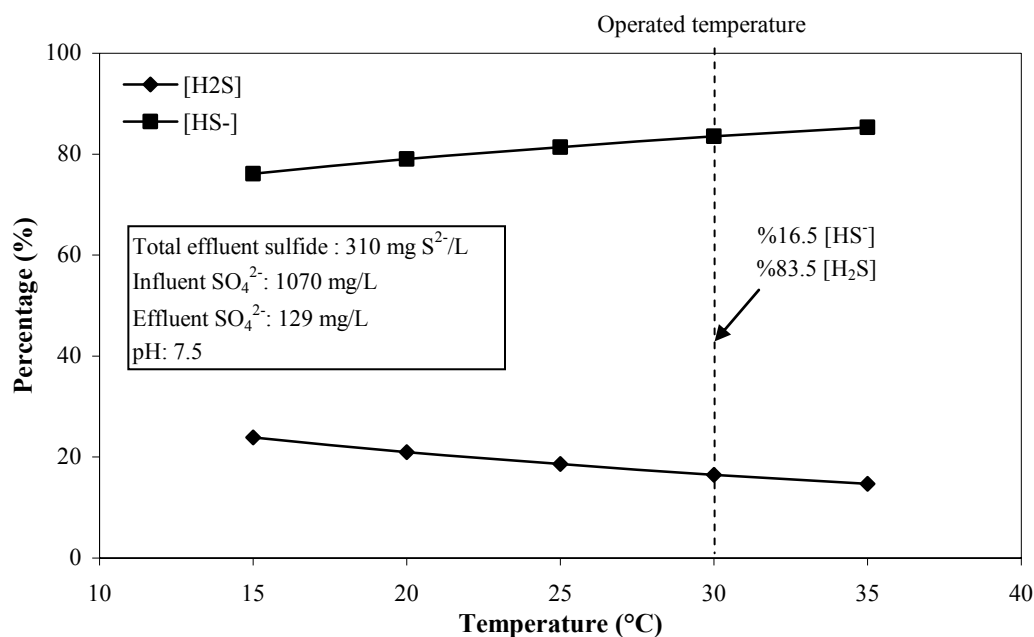


Figure D₁ - 3 Effluent Concentration of HS⁻ and H₂S in the FBBR System at Different Temperatures

Appendix D₂. Hydrogen Sulfide Stripping Process

The sulfur mass balance was investigated for the H₂S stripping process alone. As previously discussed (Appendix D₁), in the FBBR process with a typical influent sulfate concentration of 1070 mg/L (total sulfur (S_T) of 357 mg/L) and 88% sulfate removal efficiency at optimal condition (pH=7.5, C/S=1.0, and temperature=30°C), 335 mg/L sulfur was produced in liquid-phase (S_{SO4}: 43 mg/L, S_{H2S}: 48 mg/L, and S_{HS-}: 251 mg/L), while 4.5% of the total sulfur was generated in the form of gaseous H₂S. Prior to hydrogen sulfide stripping, the effluent pH could be decreased to 5.0, nearly increasing the aqueous hydrogen sulfide concentration to 305 mg/L,

representing 98.4% of the total sulfide (Table D1-6, $S_{H_2S, aq}$: 287 mg/L). Subsequently, H_2S stripping was performed with 99% efficiency, generating 80% of the total sulfur in the gaseous effluent ($S_{H_2S, gas}$: 284 mg/L). The final effluent from the stripping process accounted for 14% of the total sulfur, the hydrogen sulfide, bisulfide, and sulfate concentrations being 3 mg/L, 5 mg/L, and 129 mg/L, respectively. The sulfur mass balance for the H_2S stripping process is depicted in Figures D2-1 and D2-2 for the laboratory-scale and pilot-scale processes, respectively. The theoretical sulfur mass balance was found to be in agreement with experimental results, within the limits of experimental and analytical errors.

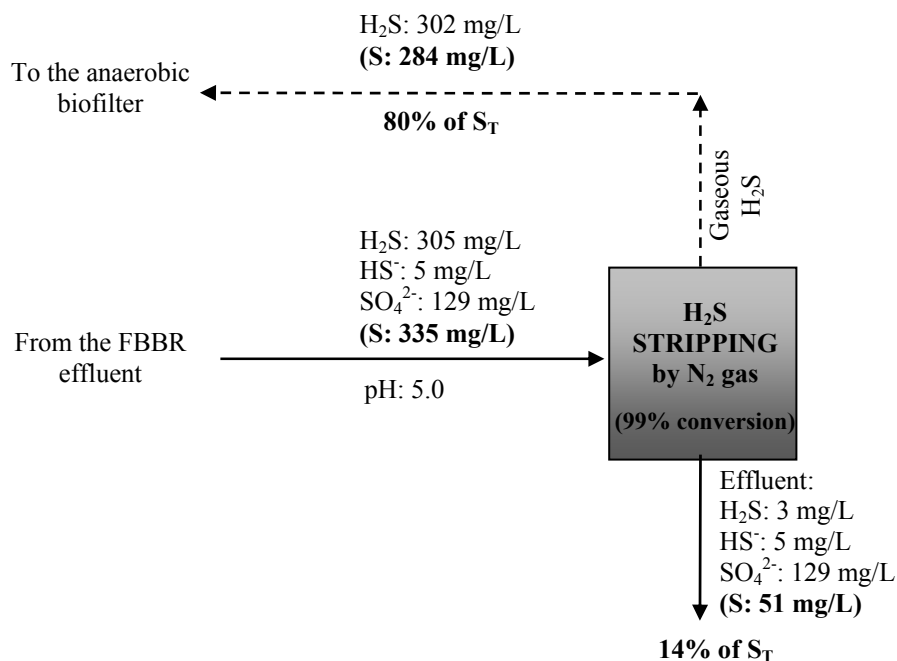


Figure D2 - 1 Sulfur Mass Balance for Laboratory-Scale H_2S Stripping Process

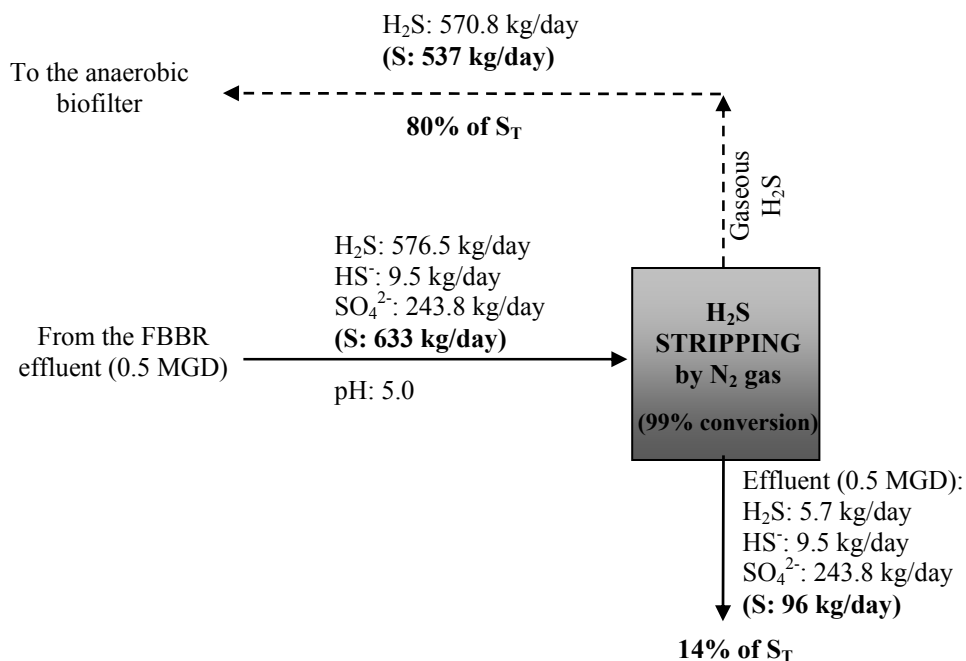


Figure D₂ - 2 Sulfur Mass Balance for Pilot-Scale H₂S Stripping Process

Appendix D₃. Anaerobic Biofilter

The sulfur mass balance was performed for the anaerobic biofiltration of hydrogen sulfide in the biological sulfate reduction process. It was observed from the FBBR studies (Section 9.2) that a steady state sulfate removal efficiency of 88% was experienced for an influent sulfate concentration of 1100 mg/L, under optimal conditions (C/S=1.0, pH=7.5, and temperature=30°C). An average total sulfide concentration of 310 mg S²⁻/L was generated at this steady state of 88%. The sulfur mass balance studies for FBBR system (Appendix D₁) revealed that 16.5% of the total sulfide was produced in the form of aqueous H₂S at pH 7.5, accounting for 98% of the total sulfide at pH 5.0, and consequently, resulting in about 302 mg/L of

gaseous H_2S after stripping with nitrogen. Thus, the laboratory-scale FBBR system with influent flowrate of 6 mL/min generated about 2.8 g/day of gaseous hydrogen sulfide, vis-à-vis about 601×10^3 g H_2S /day for the upscaled system. The total influent concentration of the gaseous hydrogen sulfide was 318 mg/L for a typical operational case, representing 84% of the total sulfur. As previously discussed (Section 9.6), the biofilter unit was capable of maintaining over 99.9% H_2S removal efficiency, and the subsequent H_2S levels in the effluent gas stream were below the analytical detection limits. Therefore, it can be stated that 84% of the total sulfur (S : 299 mg/L) remained in the biofilter in the form of elemental sulfur (visible in the biofilter bed as deposits), an important factor from the standpoints of sulfur recovery and process economics. The sulfur mass balance for the anaerobic biofiltration of H_2S is depicted in Figures D3-1 and D3-2 for the laboratory-scale and pilot- scale processes, respectively.

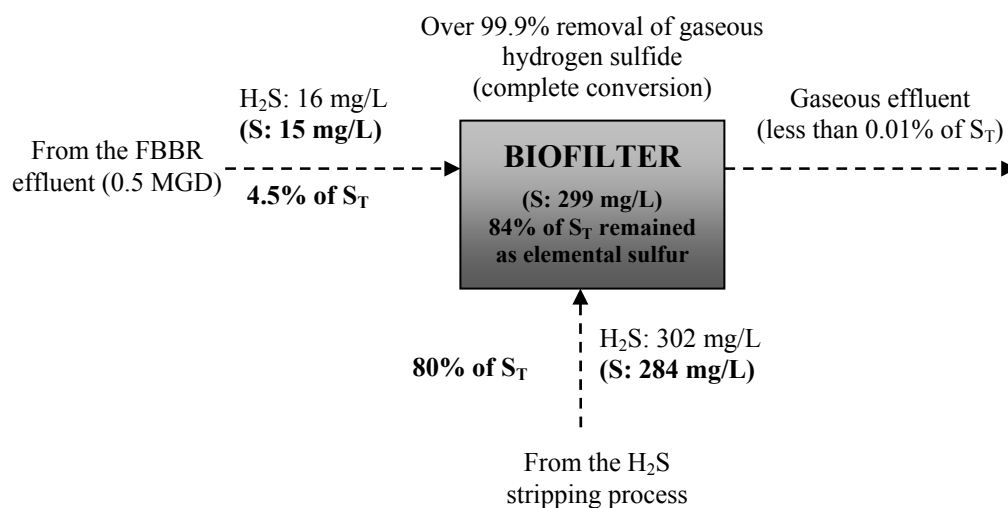


Figure D3 - 1 Sulfur Mass Balance for Laboratory-Scale Anaerobic Biofiltration

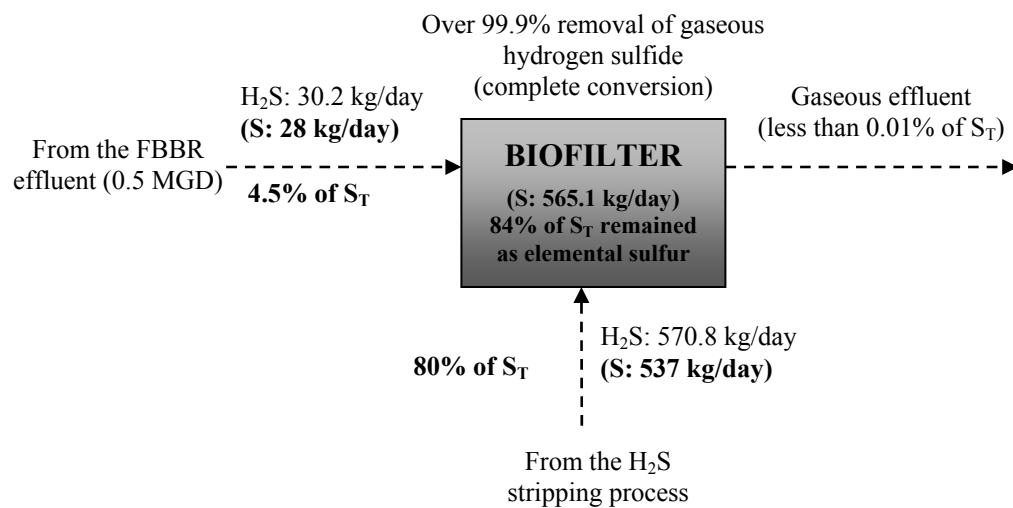


Figure D₃ - 2 Sulfur Mass Balance for Pilot-Scale Anaerobic Biofiltration

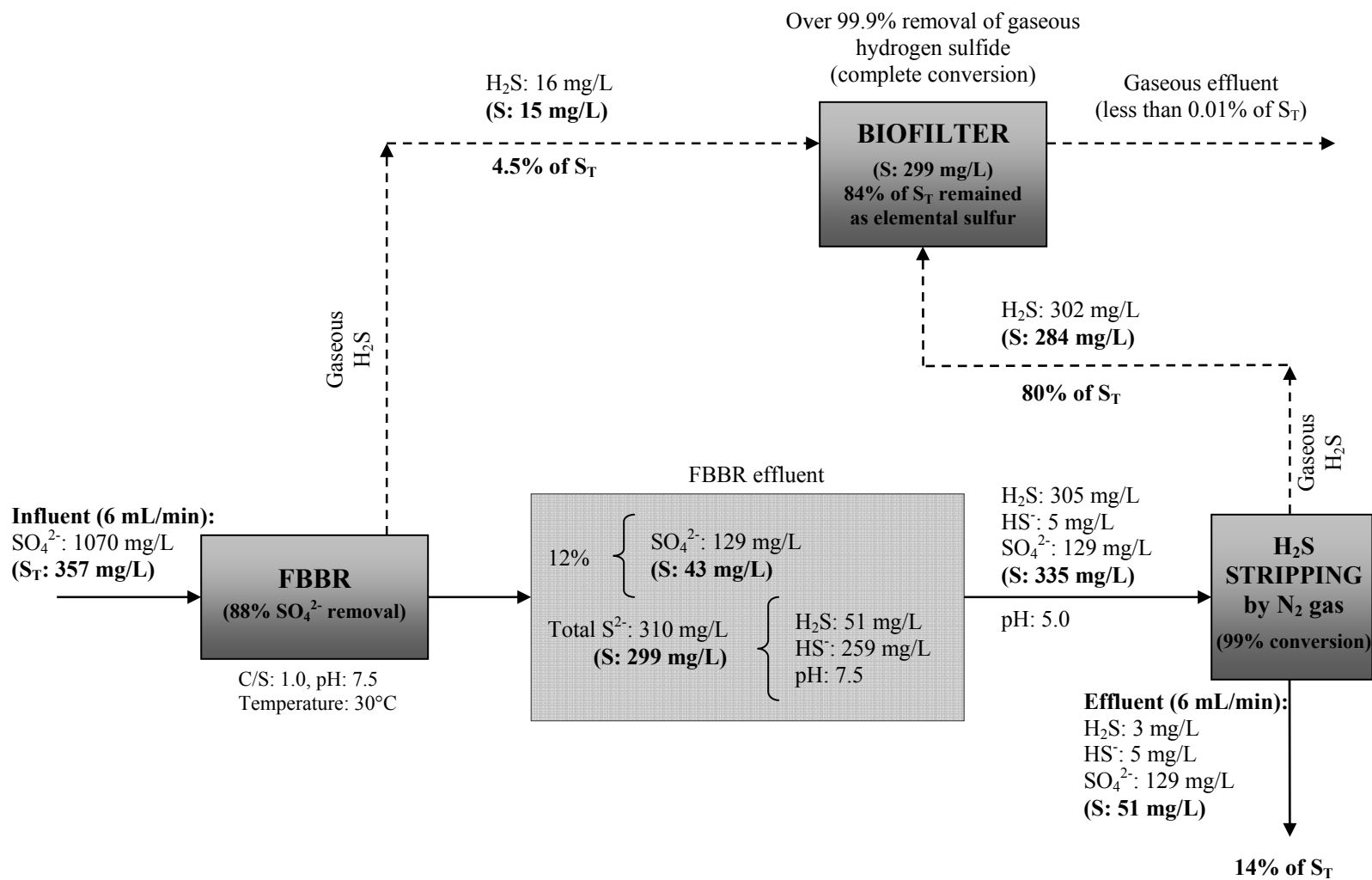


Figure D₃ - 3 Sulfur Mass Balance Diagram for Laboratory-Scale Treatment Process

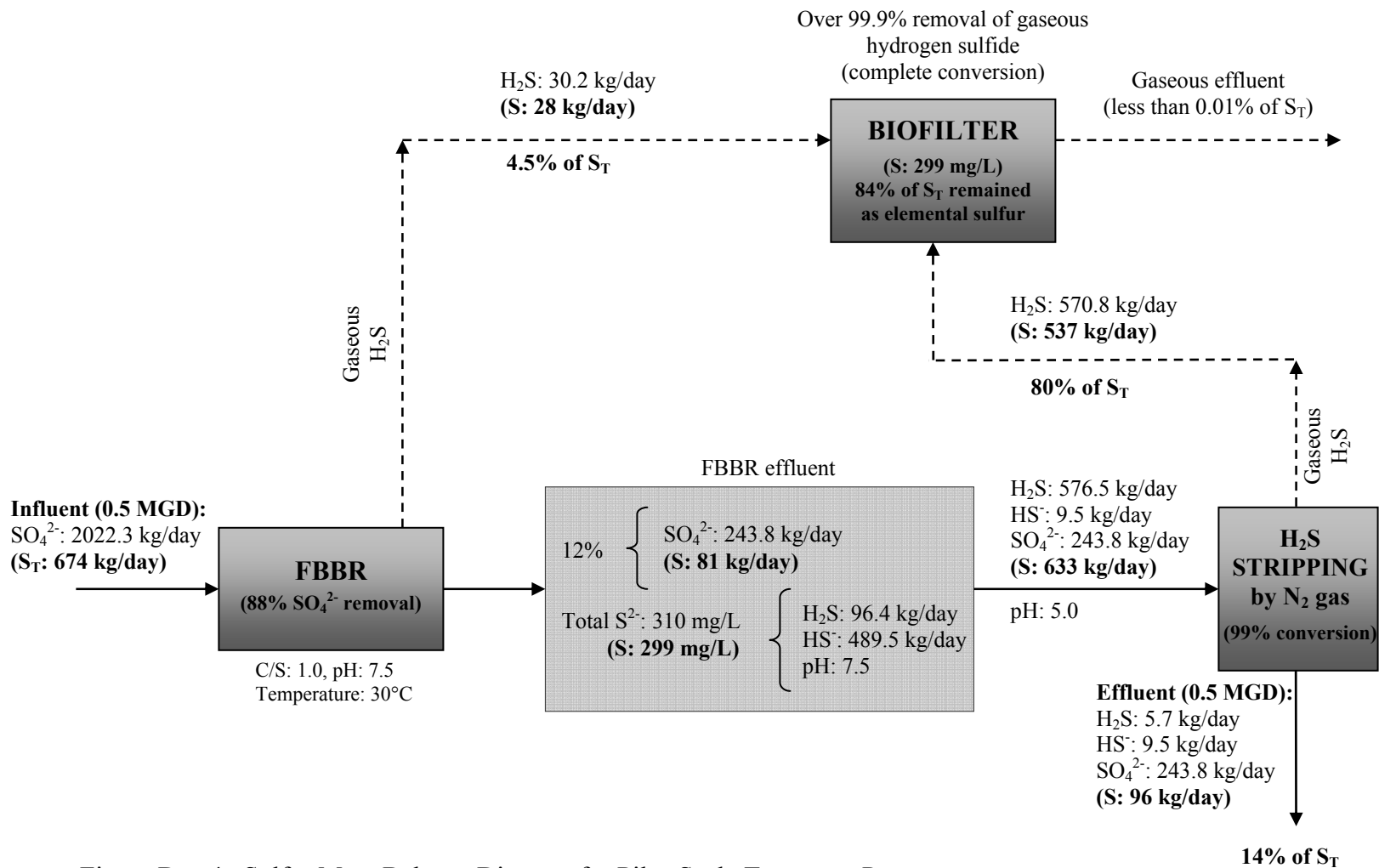


Figure D₃ - 4 Sulfur Mass Balance Diagram for Pilot-Scale Treatment Process

Appendix E. Model Parameter Calculations

E.1 Axial substrate dispersion coefficient

Chung and Wen (1968):

GAC:

GAC radius, US mesh 8-10, R_p : 0.0011 m

Gravitational acceleration, g : 9.81 m/s²

Fluid density at 30°C, d_l : 995.71 kg/m³

GAC density, d_p : 480 kg/m³

Fluid viscosity, μ : 0.000798 kg/m.s = 2.873 kg/m.hr

Recirculation flowrate, Q : 1.55 L/min = 0.093 m³/hr

Cross section area of FBBR column, A : 0.0011 m²

Superficial velocity in the axial direction, v_s : 0.0227 m/s = 81.614 m/hr

$$Ga = \frac{8R_p^3 d_l g (d_p - d_l)}{\mu^2} \quad (E_1-1)$$

$$Ga = \frac{8(0.0011)^3 \times 995.71 \times 9.81 \times |(480 - 995.71)|}{(0.000798)^2} = 83087.17$$

$$Re = \left(\frac{2R_p d_l}{\mu} \right) v_s \quad (E_1-2)$$

$$Re = \left(\frac{2 \times 0.0011 \times 995.71}{0.000798} \right) \times 0.0227 = 61.94$$

$$Re_{mod} = (33.7^2 + 0.0408 Ga)^{1/2} - 33.7 \quad (E_1-3)$$

$$Re_{mod} = (33.7^2 + 0.0408 \times 83087.17)^{1/2} - 33.7 = 33.57$$

$$P_a = \frac{\text{Re}_{\text{mod}}}{\text{Re}} \quad (\text{E}_1\text{-4})$$

$$P_a = \frac{33.57}{61.94} = 0.54$$

$$\frac{D_z d_l P_a}{\mu} = \frac{\text{Re}}{0.20 + 0.011 \text{Re}^{0.48}} \quad (\text{E}_1\text{-5})$$

$$D_z = \frac{\mu \text{Re}}{d_l P_a (0.20 + 0.011 \text{Re}^{0.48})} \quad (\text{E}_1\text{-6})$$

$$D_z = \frac{0.000798 \times 61.94}{995.71 \times 0.36 (0.20 + 0.011 \times 61.94^{0.48})} = 0.000328 \text{ m}^2/\text{s}$$

$$D_z = 9.1 \times 10^{-7} \text{ m}^2/\text{hr}$$

Sand:

Sand radius, R_p : 0.00036 m

Sand density, d_p (silica sand): 2660 kg/m³

$$Ga = \frac{8(0.00036)^3 \times 995.71 \times 9.81 \times |(2660 - 995.71)|}{(0.000798)^2} = 9528.46$$

$$\text{Re} = \left(\frac{2 \times 0.00036 \times 995.71}{0.000798} \right) \times 0.0227 = 20.37$$

$$\text{Re}_{\text{mod}} = (33.7^2 + 0.0408 \times 9528.46)^{1/2} - 33.7 = 5.34$$

$$P_a = \frac{5.34}{20.37} = 0.262$$

$$D_z = \frac{0.000798 \times 20.37}{995.71 \times 0.262 (0.20 + 0.011 \times 20.37^{0.48})} = 0.000252 \text{ m}^2/\text{s}$$

$$D_z = 7 \times 10^{-8} \text{ m}^2/\text{hr}$$

E.2 Free liquid diffusivity

GAC and sand:

Perry and Green (1984):

$$F = \text{Faraday's constant, } 96489 \text{ coul. (g.equiv.)}^{-1}$$

$$R = \text{gas constant, } 8.3145 \text{ J/mol.K}$$

$$T = 273 + 30 = 303 \text{ K}$$

$$Z_l = 2$$

$$v_1, v_2 = 2 (\text{Na}^+), 1 (\text{SO}_4^{2-})$$

$$\lambda_1, \lambda_2 = 85, \text{ and } 53 \text{ at } 30^\circ\text{C, S cm}^2.\text{equiv}^{-1}$$

$$D_l = \frac{RT}{F^2 Z_l} \left(\frac{v_1 + v_2}{v_1} \right) \left(\frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} \right) \quad (\text{E}_2\text{-1})$$

$$D_l = \frac{8.3145 \times 303}{96489^2 \times 2} \left(\frac{2+1}{2} \right) \left(\frac{85 \times 53}{85 + 53} \right) = 6.63 \times 10^{-6} \text{ m}^2/\text{hr}$$

E.3 Biofilm diffusion coefficient

Williamson and McCarty (1976):

$$\frac{D_b}{D_l} = 0.8 \quad (\text{E}_3\text{-1})$$

$$D_b = 6.63 \times 10^{-6} \times 0.8 = 5.3 \times 10^{-6} \text{ m}^2/\text{hr}$$

E.4 External film transfer coefficient

Wakao and Funazkri (1978):

$$Sh = 2 + 1.1 Re^{1/2} Sc^{1/3} \quad (E_4-1)$$

$$Sh = \frac{2R_p}{D_l} k_{fc} \quad (E_4-2)$$

$$Sc = \frac{\mu}{d_l D_l} \quad (E_4-3)$$

Substituting Equations E₁-2, E₄-2, and E₄-3 into E₄-1:

$$k_{fc} = \frac{D_l}{R_p} + 0.778 \left(\frac{v_s}{R_p} \right)^{1/2} \left(\frac{d_l}{\mu} \right)^{1/6} D_l^{2/3} \quad (E_4-4)$$

GAC:

$$k_{fc} = \frac{6.63 \times 10^{-6}}{0.0011} + 0.778 \times \left(\frac{81.614}{0.0011} \right)^{1/2} \left(\frac{995.71}{2.873} \right)^{1/6} (6.63 \times 10^{-6})^{2/3} = 0.2 \text{ m/hr}$$

Sand:

$$k_{fc} = \frac{6.63 \times 10^{-6}}{0.00036} + 0.778 \times \left(\frac{81.614}{0.00036} \right)^{1/2} \left(\frac{995.71}{2.873} \right)^{1/6} (6.63 \times 10^{-6})^{2/3} = 0.36 \text{ m/hr}$$

E.4 Biofilm Parameters

GAC:

$$T_{b,\max} = \frac{\Delta V}{4\pi R_p^2 N_p}$$

$$T_{b,\max} = \frac{5.79 \times 10^{-5}}{4\pi(0.0011)^2 \times 54230} = 7.1 \times 10^{-5} \text{ m} \rightarrow 71 \text{ } \mu\text{m}$$

sand:

$$T_{b,\max} = \frac{\Delta V}{4\pi R_p^2 N_p}$$

$$T_{b,\max} = \frac{1.45 \times 10^{-5}}{4\pi(0.00036)^2 \times 404000} = 2.2 \times 10^{-5} \text{ m} \rightarrow 22 \text{ } \mu\text{m}$$

GAC:

$$M_b = \frac{W_b}{A_{tp} T_{b,\max}}$$

$$M_b = \frac{6.119}{0.82 \times 7.1 \times 10^{-5}} \cong 105000 \text{ g/m}^3$$

sand:

$$M_b = \frac{W_b}{A_{tp} T_{b,\max}}$$

$$M_b = \frac{0.8978}{0.658 \times 2.2 \times 10^{-5}} \cong 62000 \text{ g/m}^3$$

Appendix F. Approximate Design of the Post-treatment Process for Biological Sulfate Reduction

F.1 FBBR system

Type: Cylindrical

Total influent flowrate: 0.5 MGD = 1314.2 L/min

Number of FBBR systems: 5

HRT: 4.25 hr

Reactor diameter: 9 ft = 2.74 m

Area: 5.91 m^2

Active bed volume, $V = Q \times t = 262 \times 4.25 \times 60 / 1000 = 66.8 \text{ m}^3$

Active bed height: $H = V / A = 66.8 / 5.91 = 11.3 \text{ m}$

Reactor height: 11.3 + 1.2 = 12.5 m

Table F - 1 Characteristics of the FBBR System

Specifications	
Number of reactors	5
Diameter (m)	2.7
Height (m)	12.5
Influent flowrate of each reactor (L/min)	260

F.2 H₂S stripping column

Inlet flowrate: 0.5 MGD = 1314.2 L/min

Column diameter: 8 ft = 2.44 m

Column height: 5:1 ratio = $2.44 \times 5 = 12.2$ m

F.3 Aeration tank

Type: Rectangular

Process: Activated-sludge process for acetate removal with high-rate aeration

$S_0 = 900$ mg /L (steady-state effluent acetate concentration in the FBBR-GAC at influent concentrations of 1100 mg/L and 705 mg/L for sulfate and ethanol, respectively)

Influent volatile suspended solids to reactor are negligible (less than 20 mg/L)

Typical kinetic coefficients for activated-sludge process (Metcalf & Eddy textbook, 1991, page 394):

$$k = 5 \text{ day}^{-1}$$

$$K_S = 65 \text{ mg BOD}_5 / \text{L}$$

$$Y = 0.65 \text{ mg VSS/mg BOD}_5$$

$$k_d = 0.07 \text{ day}^{-1}$$

Metcalf & Eddy textbook, page 550:

$$MLSS = 8000 \text{ mg/L}$$

$$\frac{MLVSS}{MLSS} = 0.8$$

$$MLVSS = 8000 \times 0.8 = 6400 \text{ mg/L}$$

Metcalf & Eddy textbook, page 699:

$$\frac{1}{\theta_c^M} \approx Yk - k_d \quad (\text{F}_3\text{-1})$$

$$\frac{1}{\theta_c^M} \approx 0.65 \times 5 - 0.07 = 3.18 \text{ day}^{-1} \rightarrow \theta_c^M \approx 0.31 \text{ day}$$

$$\theta_c = SF(\theta_c^M) = 16 \times 0.31 = 5 \text{ day}$$

$$Q = 0.5 \text{ MGD}$$

Metcalf & Eddy textbook, page 394:

$$Y = 0.65 \text{ mg VSS/mg BOD}_5$$

$$S_0 = 900 \text{ mg/L}$$

$$98\% \text{ acetate removal efficiency} \rightarrow S = 18 \text{ mg/L}$$

$$X = 6400 \text{ mg/L}$$

Metcalf & Eddy textbook, page 388:

$$S = \frac{K_s(1 + \theta_c k_d)}{\theta_c(Yk - k_d) - 1} \quad (\text{F}_3\text{-2})$$

$$S = \frac{65(1 + 5 \times 0.07)}{5(0.65 \times 5 - 0.07) - 1} = 5.89 \text{ mg/L}$$

Reactor volume:

Metcalf & Eddy textbook, page 593:

$$V_r = \frac{\theta_c Q Y (S_0 - S)}{X(1 + k_d \theta_c)} \quad (\text{F}_3\text{-3})$$

$$V_r = \frac{5 \times 0.5 \times 0.65(900 - 18)}{6400(1 + 0.07 \times 5)} = 0.17 \text{ MG}$$

Hydraulic retention time, θ at peak:

$$HRT = V/Q_{pk} = 0.17 \text{ MG} / 1 \text{ MGD} = 0.17 \text{ day} \times 24 = 4.0 \text{ hr}$$

$$\begin{aligned}
 HRT \text{ (with recirculation)} &= V/Q_{pk} = 0.17 \text{ MG} / (1 + 1 \times 0.5) \text{ MGD} \\
 &= 0.25 \text{ day} \times 24 = 6.0 \text{ hr}
 \end{aligned}$$

Aeration tank dimensions:

$$V_r = 0.17 \text{ MG} = 643 \text{ m}^3$$

Length: 20 m

Width: 15 m

$$\text{Height: } 642 / (20 \times 15) = 2.14 \text{ (SWD)} + 0.6 \text{ (FB)} = 2.74 \text{ m} \rightarrow \text{Height: 3 m}$$

F.4 Clarifier

Type: Circular

Metcalf & Eddy textbook, pages 475, and 477:

$$\text{Flowrate: } 0.5 \text{ MGD} = 1890 \text{ m}^3/\text{day}$$

$$HRT_{ave.}: 2 \text{ hr}$$

$$\text{Reactor volume: } 1890 \times 2 / 24 = 157 \text{ m}^3$$

$$\text{Dimensions: Depth: } 3 \text{ (SWD)} + 0.6 \text{ (FB)} = 3.6 \text{ m}$$

$$\text{Reactor area: } V/\text{depth} = 157 / 3.6 = 44 \text{ m}^2$$

$$\text{Diameter: } \sqrt{\frac{4 \times 44}{\pi}} = 7.5 \text{ m}$$

FBBR effluent settleability:

$$SVI = \frac{\text{settled sludge volume (ml / L)} \times 1000}{\text{suspended solids (mg / L)}} \quad (\text{F}_4\text{-1})$$

$$SVI = \frac{68 \times 1000}{5080} = 13.4 \text{ ml/mg} < 50 \text{ ok (highly settleable)}$$

F.5 Sand filter

Type: Cylindrical

Number of filters:

$$N = 1.2Q^{0.5} \quad (\text{F}_5\text{-1})$$

$$N = 1.2 \times 0.5^{0.5} = 0.85 \rightarrow N = 2$$

Total required bed area:

$$\begin{aligned} A &= 0.5 \text{ MGD} = 347 \text{ GPM} \div 6 \text{ GPM/ft}^2 \\ &= 57 \text{ ft}^2 = 5.3 \text{ m}^2 \end{aligned}$$

$$\text{area of each filter: } 5.3 / 2 = 2.64 \text{ m}^2$$

Each filter consists of 2 cells and a central gullet to ensure favorable hydraulic characteristics during backwash:

$$\text{Area of each cell: } 2.64 / 2 = 1.32 \text{ m}^2$$

$$\text{Diameter: } \sqrt{\frac{4 \times 1.32}{\pi}} = 1.29 \text{ m} \rightarrow \text{diameter: } 1.5 \text{ m}$$

$$\text{Height: } 6 \text{ ft} = 1.82 \text{ m} \rightarrow \text{height: } 2 \text{ m}$$

$$\text{Cell area} = 1.32 \text{ m}^2 < 93 \text{ m}^2 \quad \text{ok}$$

$$347 \text{ GPM} / 14.25 \times 2 \times 2 = 5.9 \approx 6 \quad \text{ok}$$