MICROBIAL ATTACHMENT PROPERTIES IN
EXPANDED-BED, ACTIVATED CARBON ANAEROBIC FILTERS

by

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ABSTRACT

A completely mixed, expanded-bed, anaerobic granular activated carbon filter was operated on synthetic wastewaters in which acetate was the only organic carbon source. Steady-state performance was achieved for two influent acetate concentrations: namely, 800 and 1,600 mg/L. Steady-state removal efficiencies in chemical oxygen demand, dissolved organic carbon, and acetate exceeding 96, 97, and 98 percent were obtained, respectively. A steady-state biofilm kinetic model was employed for analyzing the two sets of "steady-state" data. The modeling effort was successful in describing trends and effects; however, insufficient data were available to properly calibrate the model and obtain reliable values for the parametric constants.

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KEYWORDS: acetate / anaerobic filter / activated carbon / expanded bed / methanogenesis / kinetics /
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LIST OF SYMBOLS

A  Surface Area of Carbon Particles, $L^2$

b  Specific Decay Coefficient, $T^{-1}$

$b_s$  Shear Loss Coefficient, $T^{-1}$

$b'$  Combination of Specific Decay and Shear Loss Coefficient, $T^{-1}$

D  Molecular Diffusivity of the Substrate in Water, $L^2T^{-1}$

$D_f$  Molecular Diffusivity of the Substrate in Biofilm, $L^2T^{-1}$

J  Substrate Flux, $ML^{-2}T^{-1}$

k  Monod Maximum Utilization Rate of the Substrate, $T^{-1}$

$K_S$  Monod Half-Velocity Coefficient, $ML^{-3}$

L  Liquid Layer Thickness, L

$L_f$  Biofilm Thickness, L

Q  Feed Flow Rate, $L^3T^{-1}$

$R_1$  Rate of Substrate Removal by Suspended Microorganisms, $MT^{-1}$

$R_2$  Rate of Substrate Removal by Attached Microorganisms, $MT^{-1}$

S  Substrate Concentration in the Effluent, $ML^{-3}$

$S_f$  Substrate Concentration in the Biofilm, $ML^{-3}$

$S_0$  Substrate Concentration in the Influent, $ML^{-3}$

$S_S$  Substrate Concentration on the Biofilm Surface, $ML^{-3}$

$X_f$  Biofilm Density, $ML^{-3}$

Y  Bacterial Yield Coefficient

z  Biofilm Direction Coordinate

$S_f^*$  $S_f/K_S$

$L_f^*$  $L_f/\tau$

$z^*$  $z/\tau$

$\tau$  $\sqrt{2K_SD_f/kX_f}$
1. INTRODUCTION

The increase in energy cost in recent years makes energy-intensive wastewater treatment processes undesirable. Conventional aerobic biological treatment is energy intensive because of the need for oxygen transfer and the management of large volumes of biological solids. Anaerobic processes, on the other hand, are energy efficient since they require no oxygen, produce very little biological solids, and produce a useful by-product in the form of methane gas.

Anaerobic processes are usually limited by the very low growth rate of methanogenic organisms. Due to this limitation, suspended growth anaerobic treatment systems require very lengthy detention times (10-30 days). The anaerobic filter process, which is an attached growth treatment system, allows for the accumulation of methanogens within the reactor and thereby permits treatment in much shorter detention times (e.g., 1 day or less).

Despite the advantages of the conventional anaerobic filter, this process has generally been unable to provide effluent quality suitable for direct discharge. Recent results indicate that using granular activated carbon as the attachment medium gives steady-state effluent quality equal to that attainable from activated sludge. The main advantage of the activated carbon seems to be that it provides for better attachment and accumulation of methanogenic organisms. The validity of this observation needs to be tested, and the mechanisms of biomass accumulation and improved substrate removal need to be elucidated.
The objectives of this research were to:

a. Test the hypothesis that the completely mixed, expanded-bed, activated carbon, anaerobic filter is capable of producing very low steady-state residual organic concentration when subjected to a wide range of loading rates.

b. Evaluate the relative influences of residual organic concentration and turbulence due to liquid and gas mixing on the accumulation of methanogens in the process.

c. Develop and evaluate mathematical models to predict the performance of the process under varying operating conditions, and to utilize these models to optimize the design of anaerobic filters.

A pilot-scale, completely mixed, anaerobic filter, packed with granular activated carbon was operated using acetic acid as a feed substrate. Effluent recycle was employed to maintain the bed in the expanded mode in order to allow for digester gas release and complete mixing of the reactor contents. This anaerobic filter was operated with two influent acetic acid concentrations. The purpose for varying the influent substrate concentrations was to assess the effects of increased gas production and biomass accumulation.
2. LITERATURE REVIEW

2.1 Anaerobic Filter

The anaerobic filter is basically a column filled with solid media and sealed from the atmosphere to maintain an oxygen-free environment. The waste to be treated is distributed across the bottom of the filter and flows upward so that the filter is completely submerged. Anaerobic microorganisms become attached to the filter media and trapped in the void spaces. As the waste passes through the filter it contacts with a large biological mass and is stabilized by the metabolic activity of these microorganisms.

The anaerobic filter was first studied by Young and McCarty (1969) in the treatment of dilute synthetic wastes at ambient temperature. Their success, and the increasing cost of energy, encouraged many investigators to study the potential of the anaerobic filter process for the treatment of various wastes. Some of these results are summarized in Table 1.

Results show that the anaerobic filter is suited for the treatment of dilute wastes with short hydraulic retention times at low temperatures and at organic loading rates comparable to those associated with the activated sludge process. Due to the attachment of the biological solids on the media, the anaerobic filter does not require effluent or solids recycle. The anaerobic filter is resistant to shock loading (Jennett and Dennis, 1975; Young, 1968) and can be operated with an intermittent feed cycle (Young, 1968). Clark and Speece (1970) found that the anaerobic filter can be operated adequately in the pH range of
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<td>Volatile acid and protein carbohydrate</td>
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<td>26.5-212</td>
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<td>70</td>
<td>1-1.5&quot; stone</td>
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<td>7.9-74-4</td>
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<td>Lovan &amp; Foree (1972)</td>
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<td>50-400</td>
<td>15-330</td>
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<td>Haug et al. (1977)</td>
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<td>32</td>
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<td>35</td>
<td>-</td>
<td>1&quot; Berl saddles</td>
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<td>Heat treatment &amp; liquor</td>
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<td>-</td>
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<td>35</td>
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<td>80-93</td>
<td>41-244</td>
<td>9.3</td>
<td>35</td>
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<td>Friedman et al. (1980)</td>
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<td>40-50</td>
<td>165.3</td>
<td>24</td>
<td>35</td>
<td>-</td>
<td>bio-ring</td>
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<td>21.7-25.6</td>
<td>-</td>
<td>granular activated carbon</td>
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<td>Pailthrop et al. (1971)</td>
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<td>3,000</td>
<td>41-79</td>
<td>33-145</td>
<td>13-59</td>
<td>19-22</td>
<td>-</td>
<td>1 1/2&quot; stone</td>
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<td>Wilson &amp; Timpany (1973)</td>
<td>Sulfite liquor dilute waste</td>
<td>1,300-5,300</td>
<td>27-58</td>
<td>125-375</td>
<td>89-95</td>
<td>35</td>
<td>-</td>
<td>1&quot; polypropylene Intalox saddles</td>
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<td>Donovan et al. (1980)</td>
<td>Heat treatment liquor</td>
<td>6,500-11,500</td>
<td>50-70</td>
<td>156.3-563</td>
<td>16.8-96</td>
<td>35</td>
<td>62-67</td>
<td>9-cm plastic pall rings</td>
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<td>Genung et al. (1978)</td>
<td>Raw municipal waste water</td>
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<td>-</td>
<td>20.5-33.5</td>
<td>-</td>
<td>-</td>
<td>brick, stone</td>
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<td>Taylor (1972)</td>
<td>Starch-gluten plant waste</td>
<td>8800</td>
<td>64</td>
<td>237</td>
<td>22</td>
<td>32</td>
<td>-</td>
<td>1-3&quot; crushed rock</td>
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<td>Guar plant waste</td>
<td>4340-12130</td>
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<td>160-690</td>
<td><strong>N24</strong></td>
<td>36.7</td>
<td>58.80.4</td>
<td>-</td>
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<td>Hovious et al. (1972)</td>
<td>Petro chemical wastes</td>
<td>1500</td>
<td>10-13</td>
<td>40-145</td>
<td>72</td>
<td>34</td>
<td>-</td>
<td>1&quot; river gravel</td>
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* based on empty bed volume  
** based on initial void volume
6-8, which is a wider range than that recommended for the Anaerobic digestion process. Toxicity tests conducted by Hovious et al. (1973) and Parkin and coworkers (1980, 1983) indicated that the anaerobic filter affords an advantage over a CSTR when some types and concentrations of toxicants are present.

Generally, the anaerobic filter is best suited for the treatment of completely soluble wastes. Filter failure may occur due to clogging by accumulated solids produced from cell synthesis or from suspended solids in the influent.

Long start-up periods are generally required for efficient waste treatment. The slow start-up limitation may be solved by seeding the filter with a viable culture of anaerobic organisms (Young, 1968).

Media properties rather than bed porosity were found to be the primary factors which affect treatment efficiency (Frostell, 1979; Van Den Berg and Lentz, 1980). Frostell (1979) compared the COD removal efficiencies among three anaerobic filters filled with different media having approximately the same surface area. The plastic saddle-filled filter (porosity 0.9) and the ceramic Raschig ring-filled filter (porosity 0.68) did not give better results when compared with the low porosity (0.42) stone-filled filter under identical operating conditions.

Van Den Berg and Lentz (1980) found, from studies conducted in tubes, that the COD removal efficiency in anaerobic filters increased with decreasing reactor diameter. This is due to the greater surface area per unit volume which the smaller reactors have and which allow a greater degree of biological growth per unit reactor volume.
El-Shafie and Bloodgood (1973) achieved a very high organic loading (2,560 lb/day/1,000 cu ft or 41 kg/day/m$^3$) by placing upflow anaerobic filters in series. Khan et al. (1981) and Suidan et al. (1981) used four granular activated carbon anaerobic filters in series to treat synthetic phenol and catechol solutions. The carbon particles proved highly satisfactory in retaining the biological mass within the reactor. An advantage of activated carbon compared to inert packing materials in anaerobic filters is that a high COD reduction can be obtained from the start, although the biological activity is initially low or absent.

Chian and DeWalle (1977) and DeWalle and Chian (1979) evaluated a completely mixed anaerobic filter with effluent recycle in treating a high strength acidic landfill leachate. They concluded that the complete mixing of the filter permitted the effective treatment of the high strength acidic waste without the need for adding costly buffers.

DeWalle et al. (1980) conducted a statistical evaluation of performance data of anaerobic filter treatment of domestic sewage. Their results showed that the influent BOD was the primary factor determining the removal efficiency and that the actual effluent concentration was independent of the influent concentration.

The submerged filter has also been applied successfully as a denitrification process. Seidel and Crites (1970) and Tamblyn and Sword (1970) used this process for the biological denitrification of highly nitrified subsurface drainage waters and activated sludge effluent.

2.2 Anaerobic Fluidized Beds

Liquid fluidized beds of particles with attached microbial growth are gaining in popularity as an alternative process for wastewater treatment.
Friedman et al. (1971) first demonstrated the possibilities of such processes using an activated carbon fluidized bed reactor. Jeris et al. (1974) used a granular-carbon fluidized-bed reactor to achieve high-rate biological denitrification. The fluidized bed process has also been investigated for treating phenolic wastes (Holladay et al., 1977; Lee and Scoll, 1977) and soluble organic wastes (Butts, 1978) under aerobic conditions. The performance of fluidized bed reactors treating various wastes under anaerobic conditions is summarized in Table 2. It is noteworthy that this process is capable of achieving high organic removal percentages at low temperatures ($10^\circ$C) when treating low strength wastes (COD $< 600$ mg/l) at short hydraulic retention times (several hours) and at high organic loading rates ($> 300$ lb COD/day/1,000 cu ft or 48 Kg COD/day/m$^3$) (Switzenbaum and Jewell, 1978).

The fluidized bed process overcomes the problems of the packed bed anaerobic filter and includes the advantages of (a) greater surface area availability for biological growth per unit of reactor volume, (b) constant head loss, (c) no danger of clogging, and (d) easier media removal procedure (Jeris et al., 1974).

The fluidized bed process is not without problems. Particle "washout" may occur as the thickness of the attached biological film increases. This problem may be solved by separating a portion of the bed from the reactor when the bed reaches a maximum level. After removing excess biomass from the medium, the cleaned particles are returned to the reactor for reseeding (Barbara et al., 1980; Sutton et al., 1980).
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<th>COD Removal (%)</th>
<th>Org. Loading* (lb/1000 ft$^3$/day)</th>
<th>Hydraulic Detention** (hr)</th>
<th>Temperature ($^\circ$C)</th>
<th>CH$_4$ (%)</th>
<th>Filter Media</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jewell, et al. (1979)</td>
<td>Primary settled domestic sewage</td>
<td>88-305</td>
<td>92</td>
<td>41-2188</td>
<td>0.08-3</td>
<td>20</td>
<td>-</td>
<td>expanded ion-exchange resin polyvinyl-chloride particles</td>
</tr>
<tr>
<td>Switzenbaum &amp; Jewell (1978)</td>
<td>Synthetic waste glucose (soluble COD)</td>
<td>200-600 (soluble COD)</td>
<td>25-86</td>
<td>50-2700</td>
<td>0.33-6</td>
<td>10-30</td>
<td>-</td>
<td>500 micron aluminum oxide</td>
</tr>
<tr>
<td>Bell et al. (1980)</td>
<td>Decant liquor from thermal conditioning waste sludge (soluble)</td>
<td>4408-9386 (soluble)</td>
<td>49-75</td>
<td>262-1664</td>
<td>-</td>
<td>31-38</td>
<td>70-47</td>
<td>sand</td>
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<td>Suidan et al. (1983)</td>
<td>Synthetic coal gasification wastewater</td>
<td>1300-2700</td>
<td>90</td>
<td>80-160</td>
<td>24</td>
<td>35</td>
<td>70-80</td>
<td>granular activated carbon</td>
</tr>
</tbody>
</table>

* Based on empty bed volume.
** Based on initial void volume.
The bed expansion characteristics of fluidized particles with attached microbial growth have been studied by Andrews and Tien (1979), Ngian and Martin (1980), and Tsezes and Benedek (1980). They obtained expressions that related the bed expansion to the fluid velocity or biological film volume in the reactor.

2.3 Mathematical Models of Fixed-Film Processes

A predictive mathematical model of a treatment process is very important to engineering design and decision making. In recent years, some progress has been made on developing fixed-film process models. The first model of fixed, bacterial films were derived by assuming that the substrate-removal mechanism is organic adsorption followed by a first-order surface reaction (Ames et al., 1962). Later, a second-order, ordinary differential equation that describes simultaneous molecular diffusion and biological kinetics with a bacterial film of finite depth was employed (Atkinson and Dauod, 1968; Harremöes, 1976; Harris and Hansford, 1976). Mueller and Mancini (1976) developed mathematical models by neglecting liquid-layer mass transport and biofilm diffusion. Both Monod kinetics and first-order kinetics were found to be adequate for simulating steady-state data of anaerobic filters. Mehta et al. (1972) developed their model by assuming that mass transport to the biofilm surface controls the substrate-removal rate. Williamson and McCarty (1976), assuming a homogeneous bacterial layer, employed the concepts of substrate utilization, mass transport, and molecular diffusion to establish their model. More recently, Rittmann and McCarty (1978) developed a variable-order model, which maintains all essential biofilm concepts while providing an explicit analytical solution for substrate flux.
While the previous models were developed for inert support media, the use of activated carbon in fixed-film processes greatly complicates the modeling procedure due to the strong adsorptive property of the carbon. In developing a model for organic removal in a granular activated carbon column, Benedek (1980) stated that four sequential steps for organic removal must be considered: (a) substrates transfer from solution to the bacterial film, (b) simultaneous diffusion and reaction in the film, (c) adsorption of nondegradable and degradable organics, and (d) desorption of organics from the carbon whenever departure from equilibrium is brought about by a decrease in feed concentration or by bacterial acclimation to previously poorly degraded organics.

Jennings (1975) developed a steady-state model for biological utilization of soluble organics in expanded-bed activated carbon columns. However, this model did not include adequate description of adsorption dynamics, although his model applied reasonably well for the relatively non-adsorbing compounds—glucose and sodium lactate—which he studied. Andrews and Tien (1975) presented a model for biological activity in upflow carbon columns by assuming complete mixing of the liquid phase and the carbon particles. Their model is not predictive because it requires a column data for parameter evaluation. Peel and Benedek (1976) developed a model which assumes plug flow conditions for the liquid phase and a stationary solid phase. Additional assumptions contain a mass transfer limitation between the bulk fluid and the outer surface of the bacterial film. Their model was found adequate for predicting long-term performance, although it predicted much higher organic removal at the initial state of column operations than actually occurred. More recently,
Ying and Weber (1979) developed a model for an expanded-bed activated carbon system by assuming a plug flow liquid phase and mass transport control of substrate uptake rate. Both completely mixed solid phase and stationary solid phase assumptions have been used in modeling their system.
3. SCOPE OF THE INVESTIGATION

The overall goals of this research were to (a) elucidate the mechanisms of methanogen attachment, growth, and loss in an expanded-bed, completely mixed, anaerobic filter packed with granular activated carbon and (b) determine if low residual organics concentration can be achieved from such a reactor. The experimental results were employed in the development and verification of a mathematical model to be used in optimizing the design of this process.

A pilot-scale completely mixed, expanded-bed, granular activated carbon anaerobic filter was used as the apparatus for this study. Acetic acid was selected as the sole organic carbon substrate in the feed. The reason for using acetate was that it promotes only the growth of methanogens, which represent the most sensitive and slowest growing population in anaerobic processes. Granular activated carbon was selected as the microbial attachment surface because previous studies have suggested that this medium allows for attainment of higher attached microbial accumulation and, consequently, higher organic loading rates and lower residual substrate concentrations. Steady-state performance parameters were evaluated for two loading conditions of acetate. The experimental data were employed for the development and evaluation of a mathematical biofilm model that includes the interactions among biofilm growth, attachment, and loss, as well as substrate utilization.

The steady-state data collected on the acetate-fed anaerobic filters were employed to evaluate a biofilm kinetic model for the completely mixed, expanded-bed anaerobic filter. The proposed model includes
transport across a liquid diffusion layer followed by transport and utilization within a biofilm. For substrate utilization, a Monod-type expression was used, while the growth rate was described by a growth yield coefficient minus a biomass attribution rate found from the effluent volatile solids concentration and biomass decay. The proposed model was an advancement to the model developed by Rittmann and McCarty (1980) because it includes biofilm growth and loss through decay and shear stress loss; however, the application of the proposed model was simplified because of the completely mixed nature of the reactors. Therefore, model evaluation focused on biofilm processes of substrate utilization, mass transfer, and biofilm growth and loss without becoming entangled in complex solute-transport algorithms.
4. CONCEPTS OF THE STEADY-STATE BIOFILM MODEL

In a completely mixed expanded-bed activated-carbon bioreactor, the total reactor volume is composed of three separate phases: The bulk liquid volume, the biofilm volume, and the carbon particle volume. A homogeneous biofilm is assumed to surround the carbon granules with a thickness \( L_f \). A liquid layer of depth \( L \) is located between the bulk fluid and the outer surface of the biofilm. Substrate is transported from the bulk liquid to the biofilm surface through the liquid layer. Substrate utilization by microorganisms and molecular diffusion occur within the biofilm. Finally, the nondegraded substrate that diffuses across the biofilm can be adsorbed onto the carbon surface.

Figure 1 shows the conceptual basis for the biofilm model. Substrate concentration within the biofilm is assumed to change only in the \( z \)-direction, which is normal to the surface of the biofilm. The idealized bacterial film has a uniform cell density, \( X_f \), which is assumed constant with depth, and a uniform thickness of \( L_f \). \( L_f \) is constant for a steady-state biofilm (Rittmann and McCarty, 1980).

Material balances can be written for the liquid phase and the biofilm:

(a) Liquid Phase Substrate Material Balance

A steady-state substrate material balance over the reactor volume of a completely mixed reactor is as follows:

\[
Q S_o - Q S = R_1 + R_2 \quad (1)
\]

where \( Q \) = Flow Rate \((\text{L}^3\text{T}^{-1})\)

\( S_o \) = Influent Substrate Concentration \((\text{M}_S\text{L}^{-3})\)

\( S \) = Effluent Substrate Concentration \((\text{M}_S\text{L}^{-3})\)
Figure 1. Conceptual Basis for Biofilm Model, after Rittmann and McCarty (1981).
\[ R_1 = \text{Liquid phase substrate removal by dispersed microorganism} \quad (M_s T^{-1}) \]

\[ R_2 = \text{Substrate removal by bacterial uptake within the biofilm} \quad (M_s T^{-1}). \quad R_2 \text{ is equal to the mass transported from the bulk liquid phase, i.e.,} \]

\[ R_2 = \frac{D}{L} A (S - S_S) \quad (2) \]

in which \( D = \text{Molecular diffusivity of the substrate in the liquid} \quad (L^2 T^{-1}) \)

\( A = \text{Surface area of carbon particles covered with biofilm} \quad (L^2) \)

\( L = \text{Liquid layer depth} \quad (L) \)

\( S_S = \text{Substrate concentration on the biofilm surface} \quad (M_s L^{-3}) \)

Since the liquid phase substrate removal by dispersed microorganism \( R_1 \) is usually insignificant, it can be neglected.

Substituting equation (2) into equation (1) and deleting the aqueous phase substrate utilization rate results in

\[ Q (S_0 - S) = \frac{D}{L} A (S - S_S) \quad (3) \]

(b) Substrate Material Balance Within the Biofilm

Because the active biofilm thickness is generally less than 150 \( \mu \text{m} \) (Atkinson and Fowler, 1974), while the radius of a carbon particle used in this study is 500 \( \mu \text{m} \), curvature effects are small, and the carbon surface can be assumed to be flat.

In reference to Figure 2, a steady-state substrate material balance can be written over a differential distance \( \Delta z \) within the biofilm:
Flux in - Flux out = Rate of substrate removal

\[ D_f \frac{\partial S_f}{\partial z} \bigg|_z - D_f \frac{\partial S_f}{\partial z} \bigg|_{z+\Delta z} = \frac{kS_fX_f}{S_f+K_S} \Delta z \quad (4) \]

in which

\( S_f \) = substrate concentration within the biofilm \((M_s L^{-3})\)

\( X_f \) = biofilm microbial density \((M_x L^{-3})\)

\( D_f \) = substrate diffusion coefficient in biofilm \((L^2 T^{-1})\)

\( z \) = distance normal to biofilm surface \((L)\)

\( k \) = maximum specific utilization rate of substrate \((M_s M_x^{-1} T^{-1})\)

\( K_S \) = half-velocity coefficient \((M_s L^{-3})\)

Dividing equation (4) by \( \Delta z \) and letting \( \Delta z \) tend towards zero gives:

\[ \frac{d^2 S_f}{dz^2} = \frac{kS_fX_f}{D_f(K_S+S_f)} \quad (5) \]

The appropriate boundary conditions are:

\[ S_f = S_s \text{ at } z = 0 \quad (6) \]

\[ \frac{dS_f}{dz} = 0 \text{ at } z = L_f \quad (7) \]

Equations (5), (6), and (7) cannot be solved analytically. By defining

\[ \tau = \left( \frac{2K_SD_f}{kX_f} \right)^{1/2} \quad (8) \]

\[ S_f^* = \frac{S_f}{K_S} \quad (9) \]

\[ L_f^* = \frac{L_f}{\tau} \quad (10) \]

and

\[ z^* = \frac{z}{\tau} \quad (11) \]
equations (5), (6), and (7) can be transformed to dimensionless forms:

\[ \frac{d^2 S_f^*}{dz^2} = \frac{2S_f}{1 + S_f^*} \]  

(12)

with boundary conditions:

\[ S_f^* = S_s^* \text{ at } z^* = 0 \]  

(13)

\[ \frac{dS_f^*}{dz^*} = 0 \text{ at } z^* = L_f^* \]  

(14)

(c) Material Balance on Biomass

For deriving a biomass material balance for a steady-state biofilm, the assumption of uniform biofilm density of active microorganisms dictates that

\[ 0 = \int_{0}^{L_f} \frac{Y_k X_f S_f}{K_s + S_f} \, dz - b X_f L_f - b_s X_f L_f \]  

(15)

in which

\[ Y = \text{the true yield of bacteria mass per unit of substrate mass utilized (M}_x M_s^{-1}) \]

\[ b = \text{the specific decay or maintenance-respiration coefficient (T}^{-1}) \]

\[ b_s = \text{shear loss or wash-off coefficient (T}^{-1}) \]

Since steady-state removal is assumed, then a substrate material balance for a completely mixed reactor dictates that
\[
\frac{Q}{A} (S_o - S) = \int_0^{L_f} \frac{kX_fS_f}{K_S + S_f} \, dz
\]

where \( A \) is the total biomass attachment area. Equation 16 assumes that no soluble substrate is released as a result of microbial decay. Substituting equation 16 into equation 15 yields

\[
0 = \frac{YQ}{A} (S_o - S) - b X_f L_f - b' X_f L_f
\]

If the steady-state substrate flux, \( \frac{Q}{A} (S_o - S) \), is denoted as \( J \) and the decay coefficient, \( b \), and the attrition coefficient, \( b_s \), are combined to give \( b + b_s = b' \), then equation (17) can be rearranged to give a steady-state biofilm thickness, \( L_f \), as

\[
L_f = \frac{JY}{b' X_f}
\]
5. RESEARCH PROCEDURE

5.1 Experimental Apparatus

The experimental apparatus used for this study was a completely mixed, expanded-bed activated carbon anaerobic bioreactor. Figure 2 represents a schematic diagram of this unit. This reactor system consists of:

a) A 20-l, foil-covered glass reservoir containing an acetate solution nine times more concentrated than the desired feed concentration. The solution was pumped into the suction side of the recycle loop of the filter using a positive displacement FMI pump model RP-G6-ISAN (Fluid Metering, Inc., Oyster Bay, NY).

b) A 50-l polyethylene reservoir containing a solution of trace nutrients, ammonia, and phosphate present at levels 9/8 times as concentrated as the desired feed concentration. The salt dilution water was pumped into the suction side of the recycle loop of the filter at a flow rate that was eight times the flow rate of the organic concentrate using a positive displacement FMI pump model RP-G50-ISAN (Fluid Metering, Inc., Oyster Bay, NY). The sum of the two flows equalled the total flow to the treatment system.

c) The main body of the treatment system consisted of a jacketed column, an influent header, an effluent structure, a recycle loop, and a constant temperature recirculating bath. The jacketed column was constructed of Plexiglas (Figure 3). Effluent recycle for expansion of the activated carbon media was withdrawn from a port 111 cm above the main column base. The upper 25 cm of the column served as a gas
Figure 2. Schematic Diagram of Expanded-Bed Anaerobic Filter, after Suidan et al. (1983).
Figure 3. Design Details of Anaerobic Filter Column, after Suidan et al. (1983).
liquid separation compartment. The recycle loop was constructed of 1.27 cm PVC tube and a model 1P799-1/2 H.P. centrifugal steel pump (Dayton Electric Manufacturing Company, Chicago, IL). The gas collection system consisted of one 6.5-L buret, two 4-L balancing reservoirs, and 6.5 L of displacement liquid (a wet gas meter was employed as necessary). The constant temperature circulator was used to maintain a system temperature of 35°C.

5.2 Synthetic Substrates

The synthetic substrates used in this study contained acetic acid as an organic carbon source, as well as various salts and vitamins. Table 3 lists the salts and vitamins added per gram of feed COD. The organic substrate was prepared in the 20-L foil-covered glass reservoir at a strength that was 9 times the required feed concentration. The salt solution, on the other hand, was prepared in a 50-L polyethylene reservoir at 9/8 times the required feed strength. Sodium hydroxide was added to the organic substrate concentration at levels that permitted the maintenance of close-to-neutral pH within the reactor.

5.3 Research Procedure

The column was charged with 2.4 Kg of 16 x 20 Mesh granular activated carbon (Calgon Corp., Pittsburgh, PA), and the feed flow rate was adjusted to result in an empty bed contact time of approximately 1 day. The selection of this value of residence time was based on previous experience with this type of treatment.

The anaerobic filter was previously used in another research contract (Suidan et al., 1983) where it was fed a mixture of volatile fatty acids. For this study, the feed substrate to this reactor was switched to
<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl$_3$</td>
<td>7.48</td>
</tr>
<tr>
<td>MnCl$_2$·2H$_2$O</td>
<td>1.82</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
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</tr>
<tr>
<td>CaCl$_2$·2H$_2$O</td>
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<tr>
<td>CoCl$_2$·6H$_2$O</td>
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</tr>
<tr>
<td>Na$_2$B$_4$O$_7$·10H$_2$O</td>
<td>0.44</td>
</tr>
<tr>
<td>Na$_3$Citrate</td>
<td>67.91</td>
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<tr>
<td>(NH$_4$)$_6$Mo$_7$O$_27$·4H$_2$O</td>
<td>0.80</td>
</tr>
<tr>
<td>KH$_2$PO$_4$</td>
<td>157.26</td>
</tr>
<tr>
<td>Na$_2$PO$_4$·H$_2$O</td>
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<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
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<tr>
<td>NH$_4$Cl</td>
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<tr>
<td>CaCl$_2$·2H$_2$O</td>
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<tr>
<td>MgCl$_2$·6H$_2$O</td>
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</tr>
<tr>
<td>Biotin</td>
<td>0.011</td>
</tr>
<tr>
<td>Folic Acid</td>
<td>0.011</td>
</tr>
<tr>
<td>Pyridoxine Hydrochloride</td>
<td>0.052</td>
</tr>
<tr>
<td>Riboflavin</td>
<td>0.026</td>
</tr>
<tr>
<td>Thiamin</td>
<td>0.026</td>
</tr>
<tr>
<td>Nicotinic Acid</td>
<td>0.026</td>
</tr>
<tr>
<td>Pantothenic Acid</td>
<td>0.026</td>
</tr>
<tr>
<td>B12</td>
<td>0.00005</td>
</tr>
<tr>
<td>p-aminobenzoic Acid</td>
<td>0.026</td>
</tr>
<tr>
<td>Thiocytic Acid</td>
<td>0.026</td>
</tr>
</tbody>
</table>
800 mg/l of acetic acid. This gave a fairly low loading rate and was selected to accentuate the importance of the filter media when biomass growth potential was relatively low. The anaerobic filter was operated on a continuous basis until steady-state conditions were observed. Steady-state conditions were defined by a constant rate of methane production and by only small and random variations in effluent soluble COD, organic carbon, and acetic acid levels.

The performance of the anaerobic filter was monitored throughout the experiment by the following analyses:

1. influent and effluent pH and alkalinity,
2. effluent soluble COD,
3. influent and effluent total COD,
4. influent and effluent dissolved organic carbon (DOC),
5. influent and effluent acetic acid concentration,
6. effluent volatile solids, ammonia and organic nitrogen, and
7. gas production rate and composition.

Once the anaerobic filter reached steady-state operating conditions, samples of granular activated carbon were withdrawn from the reactor under anaerobic conditions. The samples were analyzed for organic nitrogen, a measure of biomass.

Once the first steady state was achieved and analyzed, the same procedure was repeated employing twice the acetic acid feed concentration used previously.

5.4 Analytical Methods

Samples obtained from the influent reservoirs and the anaerobic filter effluent and media were analyzed according to the procedures in
Standard Methods for the Examination of Water and Wastewater, 15th edition (1982), with the exception of the following analyses:

1. Gas analysis was performed on a Fisher Model 25V Gas Partitioner using certified calibration standards.

2. Samples for acetate analysis were acidified to pH 2 prior to gas chromatographic separation using a Hewlett-Packard 5840 gas chromatograph and a 92-cm long, 2-mm I.D. glass column packed with 0.3% Carbowax with 0.1% phosphoric acid on 60/80 Carbopack.

3. Dissolved organic carbon (DOC) was analyzed using a Dohrmann Model DC-80 carbon analyzer (EnvironTech/Dohrmann, Santa Clara, CA).
6. RESULTS AND DISCUSSION

6.1 Experimental Results

Prior to use in this study, the same experimental apparatus was employed in another project for the treatment of a synthetic wastewater containing a mixture of volatile fatty acids (Suidan et al., 1983). This wastewater contained acetic, propionic, butanoic, and pentanoic acids at concentrations of 500, 100, 50, and 50 mg/l, respectively. The anaerobic activated carbon filter was operated on this wastewater for a period of 260 days. During this period, the granular activated carbon empty-bed hydraulic detention time was maintained at one day, thus resulting in a COD volumetric loading rate of 0.862 Kg/m³-day. The anaerobic activated carbon filter gave efficient conversion of the volatile fatty acids to methane. Acetic acid was the only volatile acid detected in the effluent from the filter. During the latter 50 days of operation of this filter, steady-state performance was observed. During this period, respective reductions in acetic acid, COD, and DOC of 94.0, 95.8, and 96.3 percent were observed.

The mixture of volatile fatty acids present in the feed to the anaerobic filter during the previous study resulted in influent COD and DOC concentrations of 862 and 340 mg/l, respectively. When the present study was initiated, the feed to the anaerobic filter was switched to 800 mg/l of acetic acid, having COD and DOC levels of 853 and 230 mg/l, respectively. With the granular activated carbon empty-bed hydraulic detention time maintained at the previous level of one day, the new mode of operation kept the loading rate on the filter virtually unchanged. This permitted the continued operation of the filter without the need for an extended acclimation period, which accelerated the attainment of steady-state.
During the conduct of the present study, the completely mixed, expanded-bed, granular activated carbon anaerobic filter was operated under two levels of feed acetate concentrations; these were 800 and 1600 mg/l, respectively. The 800 mg/l acetic acid feed level was maintained for 252 days, whereas the 1600 mg/l concentration was fed to the system for 140 days. Figures 4-6 and 7-9 present the time-dependent response of the anaerobic reactor when fed 800 and 1600 mg/l of acetate, respectively. Table 4 presents the average "steady-state" performance for both loading periods.

The data presented in Figures 4-6 reveal that relatively stable performance was attainable within a relatively short period of time. The cumulative methane production data, presented in Figure 4, is a linear function of time and averages 1.75 l of methane per day. The maximum potential for methane production if all the influent organic matter were utilized would be 1.93 l of methane per day. The total steady-state COD concentration present in the effluent from the anaerobic filter averaged 26 mg/l or 3.05 percent of the influent level. Consequently, the steady-state effluent total COD added to the chemical oxygen demand equivalent of the methane gas produced accounted for 93.72 percent of the COD entering the anaerobic system. The remaining 6.28 percent of the COD entering the system was not accounted for and may be attributable to a number of factors, some of which are: (a) loss of methane by diffusion through Tygon brand tubing; (b) COD oxidation through sulfate reduction, with some of the sulfide produced being retained within the filter, this represents a maximum contribution of 2.90 percent; (c) experimental error; and (d) biomass accumulation. The effluent concentration data presented in Figures 5 and 6 exhibited an appreciable degree of variation at first
Figure 4. Cumulative Methane Production for the Feed of 800 mg/L of Acetic Acid
Figure 5. Influent and Effluent COD and DOC for the Feed of 800 mg/l of Acetic Acid.
Figure 6. Influent and Effluent Acetic Acid for the Feed of 800 mg/l of Acetic Acid.
Figure 7. Cumulative Methane Production for the Feed of 1600 mg/l of Acetic Acid.
Figure 8. Influent and Effluent COD and DOC for the Feed of 1600mg/l of Acetic Acid.
Figure 9. Influent and Effluent Acetic Acid for the Feed of 1600 mg/l Acetic Acid.
Table 4. Average Steady-State Performance

<table>
<thead>
<tr>
<th></th>
<th>800 mg/l</th>
<th>1600 mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Influent</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total COD, mg/l</td>
<td>848 ± 32*</td>
<td>1689 ± 122</td>
</tr>
<tr>
<td>Soluble DOC, mg/l</td>
<td>321 ± 5</td>
<td>616.2 ± 20.4</td>
</tr>
<tr>
<td>Acetate, mg/l</td>
<td>803 ± 117</td>
<td>1579 ± 69</td>
</tr>
<tr>
<td>pH</td>
<td>6.3 ± 0.1</td>
<td>6.20 ± 0.01</td>
</tr>
<tr>
<td>Alkalinity, mg/l</td>
<td>173 ± 4</td>
<td>977.5 ± 21.2</td>
</tr>
<tr>
<td><strong>Effluent</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total COD, mg/l</td>
<td>26 ± 10</td>
<td>67 ± 10</td>
</tr>
<tr>
<td>Soluble COD, mg/l</td>
<td>25 ± 7</td>
<td>67 ± 18</td>
</tr>
<tr>
<td>Soluble DOC, mg/l</td>
<td>7 ± 2</td>
<td>19.0 ± 4.1</td>
</tr>
<tr>
<td>Acetate, mg/l</td>
<td>5 ± 2</td>
<td>22.8 ± 5</td>
</tr>
<tr>
<td>Total Suspended Solids, mg/l</td>
<td>3.5 ± 0.5</td>
<td>10.0 ± 2.0</td>
</tr>
<tr>
<td>Volatile Suspended Solids, mg/l</td>
<td>2.9 ± 0.7</td>
<td>9.0 ± 4.0</td>
</tr>
<tr>
<td>pH</td>
<td>7.50 ± 0.10</td>
<td>7.40 ± 0.03</td>
</tr>
<tr>
<td>Alkalinity, mg/l as CaCO₃</td>
<td>599 ± 16</td>
<td>1465 ± 3.5</td>
</tr>
<tr>
<td><strong>Gas</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane Production Rate, l/day</td>
<td>1.75 ± 0.42</td>
<td>3.75 ± 0.47</td>
</tr>
<tr>
<td>% CH₄</td>
<td>91 ± 0.7</td>
<td>91.86 ± 1.08</td>
</tr>
<tr>
<td>l CH₄ produced/g COD removal</td>
<td>0.33</td>
<td>0.36</td>
</tr>
<tr>
<td><strong>Organic N</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Influent Total, mg/l</td>
<td>0.73 ± 0.18</td>
<td>1.11 ± 0.01</td>
</tr>
<tr>
<td>Influent Soluble, mg/l</td>
<td>0.30 ± 0.19</td>
<td></td>
</tr>
<tr>
<td>Effluent Total, mg/l</td>
<td>0.95 ± 0.12</td>
<td>1.30 ± 0</td>
</tr>
<tr>
<td>Effluent Soluble, mg/l</td>
<td>0.61 ± 0.09</td>
<td>0.5 ± 0.09</td>
</tr>
<tr>
<td>Virgin Carbon, mg/g of carbon</td>
<td>4.42 ± 0.15</td>
<td>4.07 ± 0.07</td>
</tr>
<tr>
<td>Carbon Samples, mg/g of carbon</td>
<td>5.10 ± 0.27</td>
<td>5.27 ± 0.15</td>
</tr>
</tbody>
</table>

* Value are mean ± standard deviation
glance; however, the logarithmic concentration scale makes instability apparent, not actual.

The acetic acid concentration in the feed was doubled to 1600 mg/ℓ on day 253 of operation, and this feed level was continued for another 140 days. It is of interest to note that methane production more than doubled to a daily rate of 3.90 ℓ immediately after the increase in the acetate feed level. This immediate increase in the methane production rate was accompanied by an increase in the effluent acetate concentration to about 20-30 mg/ℓ, which corresponds to more than twice the previous steady-state effluent concentration of 5 mg/ℓ. It is possible to explain these observations with a simple kinetic expression that gives an increase in the methane production rate when the bulk concentration of acetate increases, even though there was no major change in active biomass. The facts that the effluent acetic acid concentration remained above 20 mg/ℓ throughout this phase of the study and that the organic nitrogen per gram of activated carbon in the reactor did not exhibit an appreciable increase over the level that prevailed during the first phase suggest that little net growth of methanogens occurred throughout the second phase of the study, or that a much lower than reported $K_s$ value should be used for the conversion of acetate methane. Work currently in progress will help in further understanding this phenomenon.

Steady-state operating conditions appeared to prevail between days 70 and 140 of this experiment. During this period, methane production averaged 3.18 ℓ/day. The sum of chemical oxygen demand equivalents of the methane gas produced and the total COD in the effluent from the reactor during this period accounts for 100.85 percent of the influent COD. This material balance supports the hypothesis that a little growth took place during the second phase of the study.
The immediate doubling of the methane production rate as a result of the doubling of the influent acetate concentration from 800 to 1600 mg/l is contrary to what was reported previously by Khan et al. (1981) and Suidan et al. (1981), who observed that an increase in the feed substrate level to an anaerobic activated carbon filter resulted in a gradual increase in gas production accompanied by an appreciable degree of substrate adsorption, which was followed by biological regeneration of the carbon and finally steady-state. The previous investigators, however, used the strongly adsorbing catechol and phenol as their respective substrates, whereas in this study a very poorly adsorbing substrate, acetate, was used. The results obtained from this study shed light on the performance of this system when adsorption is not a major removal mechanism. For poorly adsorbing substrates, biodegradation controls the substrate's fate.

6.2 Analysis of Steady-State Biofilm Kinetics

A biofilm kinetic model and its associated assumptions were described in Section 4. This model will be evaluated using the steady-state COD data generated in this study.

6.2.1 Parameter Evaluation

Several input parameters are required for the biofilm model; these are:

(a) Liquid Layer Thickness L

L can be calculated from the equation (Jennings, 1975)

\[ L = \frac{D(R_{em})^{0.75}S_{c}^{2/3}}{5.7v} \]
where

$$D = \text{molecular diffusivity of the substrate in the liquid} \quad (L^2T^{-1}) \quad (19)$$

$$R_{em} = 2\rho d_{p} v e / (1 - e) \quad (20)$$

$$S_{c} = \mu / \rho D$$

$$v = \text{superficial, or empty bed, flow velocity through reactor} \quad (LT^{-1}) \quad (21)$$

$$\mu = \text{absolute viscosity of liquid} \quad (ML^{-1}T^{-1})$$

$$\rho = \text{density of liquid} \quad (ML^{-3})$$

$$e = \text{porosity of bed}$$

$$d_{p} = \text{diameter of spherical particles} \quad (L)$$

(b) Molecular diffusivity of the substrate in the liquid, \( D \)

Molecular diffusivity of acetate is taken from reported literature values (Perry and Chilton, 1973) and corrected to 35°C by the empirical correlation of Wilke and Chang (1955).

$$D = \frac{(7.4 \times 10^{-8}) (\phi M_{B})^{0.5} T}{\mu^{0.6} v_{A}} \quad (22)$$

where

$$M_{B} = \text{molecular weight of solvent}$$

$$T = \text{temperature, °K}$$

$$\mu = \text{solution viscosity, centipoises}$$

$$v_{A} = \text{solute molal volume at the normal boiling point, cm}^3/\text{g mole}$$

$$\phi = \text{association factor for solvent}$$

\( = 2.6 \) for water as solvent

(c) Molecular diffusivity of the substrate in the biofilm, \( D_{f} \)

The molecular diffusivity within the biofilm, \( D_{f} \), is less than \( D \), because a significant part of the biofilm is made of
bacteria and their extracellular polymers. The ratio $D_f/D = 0.8$
found by Williamson and McCarty (1976) is used in this study.

(d) Monod half-velocity coefficient, $K_s$, maximum utilization rate, $k$
biofilm density $X_f$, true yield, $Y$, and specific decay
coefficient, $b$.

These biological parameters can initially be taken from
published data (Atkinson and Fowler, 1974; Lawrence and McCarty,
1961; Williamson and McCarty, 1976) and allowed to vary reasonably
to fit the experimental data.

(e) Biofilm thickness, $L_f$

The steady-state biofilm thickness can be calculated by
equation (18).

Table 5 summarized column parameters used as mathematical
model inputs.

6.2.2 Model Verification

The steady-state biofilm kinetic model described by Equations 12-14
and 17-18 was solved numerically using the model constants given in Tables 5 and 6.
The data in Table 6 represent the model solution and the actual values of
the kinetic constants used in obtaining these solutions. The substrate flux, $J_p$, predicted for the 800 mg/ascus feed acetate concentration agrees very well
with the flux value compiled from the experimental data. However, for the
phase in which 1600 mg/ascus of acetate was fed to the system, the mathematical
model predicts a more than doubling of the biofilm thickness and substrate
flux. Apparently, this is not in agreement with the experimental data,
since these data suggest no or limited net growth during the second phase
of the experiment.
Table 5
Summary of Column Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry carbon particle density $\rho_p$, g/cm$^3$</td>
<td>0.668</td>
</tr>
<tr>
<td>Bed porosity, $\varepsilon$</td>
<td>0.52</td>
</tr>
<tr>
<td>Carbon particle diameter $d_p$, cm</td>
<td>0.1</td>
</tr>
<tr>
<td>Modified Reynolds number, $R_{em}$</td>
<td>27.8</td>
</tr>
<tr>
<td>Schmidt number $S_c$</td>
<td>455.2</td>
</tr>
<tr>
<td>Liquid layer thickness $L$, cm</td>
<td>0.0022</td>
</tr>
<tr>
<td>Molecular diffusivity in water $D$, cm$^2$/day</td>
<td>1.37</td>
</tr>
<tr>
<td>Molecular diffusivity in biofilm $D_f$, cm$^2$/day</td>
<td>1.099</td>
</tr>
<tr>
<td>Weight of activated carbon $W$, gm</td>
<td>2,400</td>
</tr>
<tr>
<td>Total external surface area of carbon particles $A$, cm$^2$</td>
<td>107,790</td>
</tr>
</tbody>
</table>
Table 6. Summary of Biological Parameters and COD Fluxes

<table>
<thead>
<tr>
<th>COD (mg/ℓ)</th>
<th>Flux (mg COD/day cm²)</th>
<th>Influent</th>
<th>Effluent</th>
<th>Actual J_a</th>
<th>Predicted J_p</th>
<th>L_f (cm)</th>
<th>K_S (mg/cm³)</th>
<th>k (mg/mg-day)</th>
<th>X_f (mg VSS/cm³)</th>
<th>ϒ (mg/mg)</th>
<th>b' (day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>848</td>
<td>25</td>
<td>0.0495</td>
<td>0.0491</td>
<td></td>
<td></td>
<td>0.0041</td>
<td>0.15</td>
<td>10.0</td>
<td>25</td>
<td>0.04</td>
<td>0.019</td>
</tr>
<tr>
<td>1689</td>
<td>67</td>
<td>0.0975</td>
<td>0.1210</td>
<td></td>
<td></td>
<td>0.0102</td>
<td>0.15</td>
<td>10.0</td>
<td>25</td>
<td>0.04</td>
<td>0.019</td>
</tr>
</tbody>
</table>
An insufficient number of steady-state data sets were collected during the short duration of this study to allow for accurate calibration of the mathematical model. Consequently, the modeling attempted here should be regarded as an introduction to the modeling tool rather than resulting in refined parameters suitable for performance predictions.
7. CONCLUSIONS

Based on the findings of this study, the following conclusions can be drawn:

1. The complete mix, expanded-bed, activated carbon anaerobic filter is capable of achieving a very high COD removal efficiency (96%) when subjected to relatively low feed acetate concentrations.

2. Activated carbon particles provide a good medium for attached bacterial growth.

3. A biofilm kinetic model which includes a liquid diffusion layer and a homogeneous biofilm surrounding an idealized carbon particle of spherical shape appears to be adequate in describing the steady-state COD removal in the anaerobic filter. Further refinements in the selected kinetic constants are needed, however.
REFERENCES


