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# A Theoretical and Experimental Investigation of Wastewater Treatment for a Polyethylene Terephthalate Production Unit

Leila Vafajoo*[a], Abdolah Mohammadpour[a], Farhad Khorasheh[b]

[a]Chemical Engineering Group, Islamic Azad University, South Tehran Branch, Tehran, Iran
[b]Chemical and Petroleum Engineering Dept., Sharif University of Technology, Azadi Ave., Tehran, Iran
*vafajoo@azad.ac.ir

In this research, mathematical modelling of an anaerobic hybrid bioreactor for effluent treatment of a Poly-Ethylene Terephthalate (PET) unit in a petrochemical complex was performed. The developed model included a combination of a biofilm model for describing the substrate kinetics; a fluidized bed model for determination of species profiles along the reactor length and a bioreactor model for particle distribution inside the reactor.
The reactions performed in the bioreactor included; i) the polymers hydrolysis; ii) fermentation of the resulting monomers; iii) the volatile fatty acids fermentation to Acetate and Hydrogen and iv) the Methane formation as the final product. The reactor was divided into n-segments each being fully mixed and the changes of granule densities at each one caused by granules growth were neglected.
On the other hand, the experimental data obtained from an industrial unit in which, the pH was controlled by adding $NaHCO_3$ and NaOH while; a mixture of Urea, di-ammonium phosphate and molasses were utilized as substrates. The total flow rate inside the 2,200 $m^3$ bioreactor was set 180 $m^3$/h with 0.7 m/h up-flow velocity.
The theoretical data determined from the developed model for the volatile fatty acids' (VFAs) production while the corresponding experimental data obtained from the industrial unit. Moreover, the comparison between the bioreactor effluent's COD determined through both the theoretical and experimental studies were presented. The current model reproduced the experimental data with mean error of 14 % which considering the complexity of the undertaken system was rather satisfying.

## 1. Introduction

The particle structure in a hybrid anaerobic reactor had been studied (Saravanan et al., 2008). On the other hand, the flow inside an aerobic fluidized bed reactor had been studied using axial dispersion model by several researchers (Palatsi et al., 2010).
In this research, an up flow anaerobic contact filter (UACF) was utilized for effluent treatment of an actual Petrochemical Refinery stream containing polyethylene terephthalate (PET). The lower part of the aforementioned biofilter was empty above which suspended growth took place while the upper section of it was filled with random packing upon which occurred the attached growth of particulates.
Moreover, a mathematical model of a hybrid anaerobic reactor was developed. This was validated by data of a petrochemical effluent treatment reactor. In addition, the volatile fatty acid concentration gradient was compared with that of an actual plant data.

## 2. Mathematical modeling

The developed theoretical picture included combination of the following three models; i) a biofilm model for describing the substrate reaction kinetics; ii) a fluidized bed model for determination of particle distribution inside the bioreactor and iii) a bioreactor model for connecting the two aforementioned models illustrating substrate concentration profile inside the bioreactor. (Steyer et al., 1999)

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These three models were coupled and solved utilizing the following assumptions; 1) the granules were spherical with 1 mm diameter and fully fluidized, 2) the mass transfer resistance in the liquid phase was neglected (Yu et al. 2013)., 3) the substrate transfer within biofilm and granule particles was described by Fick's first law, 4) the reactions inside biofilm were expressed by Monod's kinetics and 5) the steady state conditions existed throughout.

**2.1 Biofilm model**

In this model biogranules were considered to have three layers. The mass balance for outer biofilm layer for different components was as follows:

For glucose:

$$4\pi r^2 D_{eg}\left.\frac{dg}{dr}\right|_{r+\Delta r} - 4\pi r^2 D_{eg}\left.\frac{dg}{dr}\right|_{r} = \left(\frac{g x_g}{k_{s,g}}\frac{\mu_{max,g}}{Y_{xg/g}}\right)4\pi r^2 \Delta r \quad (1)$$

By modifying the above equation, the following differential form might be obtained:

$$\frac{d^2 g}{dr^2} + \frac{2}{r}\frac{dg}{dr} = \left(\frac{k_g g}{k_{s,g} + g}\right) \quad (2)$$

Where $k_g$ was defined as:

$$k_g = \frac{\mu_{max,g} x_g}{Y_{xg/g} D_{eg}} \quad (3)$$

Boundary conditions included:

$$\text{at } r = r_1 : \frac{dg}{dr} = 0 \text{ and } \text{ at } r = R, g = g_{bulk}$$

Where $Y_{xg/g}$ was the yield coefficient, g; the substrate concentration (kg COD/$m^3$), $k_{s,g}$ the Monod saturation constant (kg COD/$m^3$), $D_e$; the effective diffusion coefficient ($m^2$/s), $\mu_{max}$ ; the maximum specific growth rate(1/s) and x was the biomass concentration (kg VSS/$m^3$).

For Acetic Acid:

The mass balance equation of acetic acid production from glucose was:

$$\frac{d^2 a}{dr^2} + \frac{2}{r}\frac{da}{dr} = \left(\frac{k_{ga} g}{k_{s,g} + g}\right) \quad (4)$$

In which;

$$k_{ga} = \frac{\mu_{max,g} x_g}{Y_{xg/g} D_{ea}} \quad (5)$$

And boundary conditions included:

$$\text{at } r = r_1 : \left.\frac{da^+}{dr}\right|_{r=r_1} = \left.\frac{da^-}{dr}\right|_{r=r_2} \text{ and } \text{ at } r = R, a = a_{bulk} \quad (6)$$

**2.2 Fluidized bed model**

The reactor parameters utilized were provided in table 1.

In several previous studies, the effect of gas production on bed expansion was taken to be negligible upon the flow pattern in an anaerobic fluidized bed reactor (Shida et al., 2012). Hence, in the present model the effect of gas production in the liquid up-flow velocities was neglected.

*Table 1: bioreactor parameters used in this study*

| Parameters | amount | unit |
|---|---|---|
| Reactor height | 9.5 | m |
| 1. Reactor active height | 8.65 | m |
| 2. Suspended growth height (lower part) | 4.5 | m |
| 3. Random packing height (upper section) | 4.15 | m |

The relationship between the bed void fraction and liquid up-flow velocity was given (Panepinto et al., 2013) as follows;

$$u_s = u_i \varepsilon^n \quad (7)$$

$$u_i = 0.88(u_t) \quad (8)$$

Terminal settling velocity ($u_t$):

$$u_t = \left[\frac{4g(\rho_s - \rho_l)d}{3C_D\rho_l}\right]^{0.5} \quad (9)$$

And $C_D$ was determined from (Saravanan et al., 2008):

$$C_D = (0.955 + \frac{7.28}{Re_t^{0.3}})^2 \quad (10)$$

In addition, the so called parameter n in Eq(6) was given (Saravanan et al., 2008) as follows:

$$n = 3.81Re_t^{-0.034} \quad (11)$$

$Re_t$ was the terminal Reynolds number determined as:

$$Re_t = \frac{\rho_1 u_t d}{\mu_1} \quad (12)$$

In which d was the particle diameter (m), $\rho_l$ the liquid density (kg/m$^3$), us the liquid superficial velocity (m/s) $\varepsilon$ the void fraction and $\mu_1$ was the liquid viscosity (kg/m.s).

To determine the bed's void fraction, $Re_t$ was initially guessed and used in Eq (10) through which, the value of the $C_D$ was calculated. Next, in this iteration loop having all necessary parameters the $u_t$ was determined from Eq(8). Then having this, the calculated value of the $Re_t$ was obtained from Eq (12) and compared with the previously guessed value. This loop was continued until the toleration limit for convergence was satisfied. Hence, $u_i$, n and $u_t$ were determined. Ultimately, having these as well as; the up-flow velocity in the reactor of 1.94x10$^{-4}$ m/s, the bed void fraction was determined.

**2.3 Reactor modeling**

Flow within the reactor was divided into several sections shown in Figure1. Each of these was taken as a completely mixed reactor (CSTR).The variation of density with biogranule size (i.e.; one of the reasons for the bed stratification) was also found to be negligible.

A typical value of 1 mm Sauter-mean diameter (SMD) was utilized to characterize the average biogranule size. Under steady state conditions, the entire column was assumed to be filled with such granules. The number of these biogranules was calculated as follows:

$$N = \frac{\frac{\pi}{4}D^2H \times (1-\varepsilon)}{\frac{\pi}{6}d_{smd}^3} \quad (13)$$

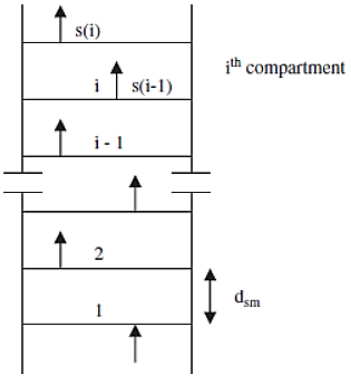


*Figure 1: reactor model scheme*

Thus, the mass balance for the i$^{th}$ component at the steady state was taken to be:

$$s[i] = s[i-1] - \pi d_i^2 D_e \left.\frac{ds}{dr}\right|_R N[i]\left[\frac{1}{\frac{\pi}{4}D^2 \times u_s}\right] \quad (14)$$

The glucose concentration in the bottom-most compartment was determined through; 1) the inlet and recycle flow rates as well as; 2) the influent COD and 3) the initial guess for concentration of glucose in the recycle flow rate. Hence, according to Eq (14) the $i^{th}$ component profile along the reactor height was obtained. This iteration loop was continued upon the concentration of glucose in the recycle flow compared with the previously guessed value until convergence was reached.

**2.4 Model parameter**

Kinetic constants:

The kinetic parameter values and physical parameters used in the present simulation were provided in tables 2 and 3. (Denac et al., 1986)

**2.5 Biomass composition**

The biomass compositions used in the present simulation were taken from a previous open literature work (Steyer et al., 1999). These values were averages of several runs (Martin et al., 2010) in which the glucose degrading acidogen concentration was 65 %, acid degrading methanogens amounted to 11.5 % as well as; the hydrogen utility methanogens consumed was 23.5 %. (Torre et al., 2013)

## 3. Experimental methodology

Spectrometry measurements of the COD in wastewater were carried utilizing a strong oxidizer of potassium dichromate in concentrated sulfuric acid while the silver sulfate was used as a catalyst. Moreover, the well-known invert titration method used to measure the concentration of the fatty acid (i.e.; using 0.1 N NaOH and 0.1 NHCl solutions).

## 4. Results and discussion

Experiments were carried out in a 2,200 $m^3$ reactor with 180 $m^3$/h flow rate and 0.7 $m^3$/h up-flow velocity. (Figure 2)

When the inlet flow rate and volatile fatty acids concentration in the entering stream were known, the acid profile along the reactor height was determined. To provide sampling at different heights, a 5-point reactor was undertaken. Thus, a comparison of the simulated results with that of the actual data obtained experimentally was made possible.

## 5. Conclusions

A mathematical model for a UACF was developed combining several modeling aspects including; a biofilm model describing the substrate kinetics, a bed fluidization model highlighting the granule distribution and a bio-reactor model leading to component profiles along the reactor height. To study the COD removal efficiency, a synthetic medium containing glucose as a carbon source was undertaken. Hence, a biofilm model assuming a Three-layer structure was developed. This model also revealed the profiles of the volatile fatty acids along the reactor. Moreover, a comparison of the model results with actual data obtained experimentally indicated to be rather satisfying. Ultimately, the developed model might be used towards optimization of the understudied production on the industrial scale.

*Table 2: kinetic parameters used in the present model*

| Component | μmax (L/h) | ks (kg COD/$m^3$) | Yx/s (kg biomass/kg COD) |
|---|---|---|---|
| Glucose | 0.05 | 0.140 | 0.036 |
| Acetic acid | 0.01416 | 0.237 | 0.029 |

*Table 3: physical parameters used in the present model*

| De | Amount ($m^2$/s) |
|---|---|
| $De_g$ | $5.278 \times 10^{-11}$ |
| $De_a$ | $7.500 \times 10^{-11}$ |

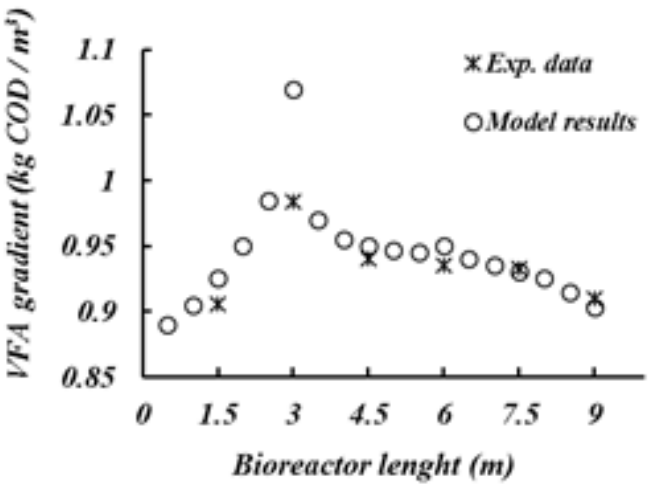


*Figure 2: Variations of the theoretical and experimental effluent COD as a function of the reactor length*

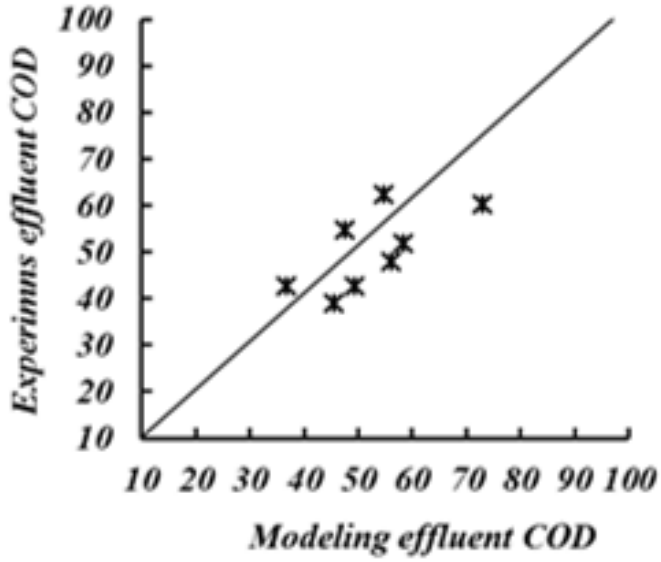


*Figure 3: Parity plot of experimental versus theoretical VFAs concentrations inside the bioreactor ($FLOW_{in}$=85 $m^3$/h, $VFA_{in}$=0.830 kgCOD/$m^3$)*

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