Application of an anaerobic hybrid reactor for petrochemical effluent treatment
Mohammad Taghi Jafarzadeh, Naser Mehrdadi and Seyed Jamaladdin Hashemian

ABSTRACT
An anaerobic hybrid reactor (UASB/Filter) was used for petrochemical wastewater treatment in mesophilic conditions. The seeded flocculent sludge from a UASB plant treating dairy wastewater, acclimatized to the petrochemical wastes in a two-stage operation. After start up, under steady-state conditions, experiments were conducted at OLRs of between 0.5 and 24 kg TCOD m⁻³ d⁻¹, hydraulic retention times (HRT) of 4–48 h and up-flow velocities 0.021–0.25 mh⁻¹. Removal efficiencies in the range of 42–86% were achieved at feed TCOD concentrations of 1,000–4,000 mg L⁻¹. The results of reactor performance at different operational conditions and its relations are presented and discussed in this paper. Then, the obtained data are used for determination of kinetic models. The results showed that a second-order model and a modified Stover–Kincannon model were the most appropriate models for this reactor. Finally, the biogas production data were used for the determination of biogas production kinetics.

Key words | anaerobic, biogas, hybrid, kinetics, modeling, petrochemicals

INTRODUCTION
Traditional anaerobic processes are good limited by low rates of organic matter removal, long hydraulic retention times (HRT), accumulation of excessive residual organic matter and intermediate products. Recent developments in anaerobic treatment processes, especially high retention of biomass in the reactor, has made it possible to decouple solids retention time (SRT) and hydraulic residence time in high-rate anaerobic reactors. Several anaerobic reactors have been successfully applied to the treatment of various industrial wastes (Macarie 2000). According to a report published in 1990 from some companies that made anaerobic reactors, there were more than 1,330 anaerobic reactors in the world (Macarie 2000). But it is important to note that the majority of the reactors (76%) was used in food industries and the number of reactors applied for petrochemical waste treatment was very low (Jafarzadeh et al. 2005).

Several authors reported that up to a certain limit, the treatment efficiency of complex wastewaters, in high rate anaerobic reactors increases with increasing organic loading rate (OLR). A further increase of OLR will lead to some operational problems resulting in treatment efficiency deterioration (Kalyuzhnyi et al. 1998). As we know, the applied OLR is related to HRT and COD concentration. For this reason, OLR is an inadequate design parameter to assure good performance of anaerobic reactors. Young (1991) reported that HRT was the most important parameter affecting COD removal performance. The up-flow velocity is another important factor affecting the efficiency of up-flow reactors (Wiegant 2001). The effect of HRT could manifest itself as a result of its direct relation to the liquid up-flow velocity (Vup) and also to the solids contact time in the reactor and so the possibility of solids to coalesce or to be entrapped in the sludge bed. Moreover, the HRT is a major parameter, which determine the SRT (Zeeman & Lettinga 1999). The SRT can indirectly influence the solids removal through changing the physical–chemical and biological characteristics of the sludge bed in addition to biogas production.

Petrochemical wastewater contains some nondegradable, toxic or inhibitor components that influence reactor performance and its applicable OLRs. A wide range of organic and hydraulic loading rates has been reported in the literature for anaerobic reactors, depending on the substrate used and the quality and quantity of the microbial community. Some authors reported 52–90% COD removal efficiency for reactors treating petrochemical effluents (Macarie 1992; Kleerebezem et al. 1997; Page et al. 1999; Younge et al. 2000).
Process kinetics has been used for the mathematical description of biological treatment processes. The understanding of process kinetics is essential for the rational design and operation of biological treatment systems and for predicting system stability, effluent quality, and waste stabilization. Sound knowledge on kinetics leads to optimization of performance, a more stable operation, and a better control of the process (Pavlostatis & Giraldo-Gomez 1991). Some mathematical models are available in the literature for description of biological processes.

In this study, the effect of OLR, HRT and up-flow velocities of hybrid reactor treating petrochemical effluent was investigated at different influent COD concentrations. Finally, different mathematical models were applied to data obtained from the reactor operation and the best models were evaluated.

**MATERIALS AND METHODS**

**Location**

This study was conducted at the Arak petrochemical company in the center of Iran. Some products of this complex are: ethylene; propylene; pyrolize benzene; crude oil; polypropylene; high and low density polyethylenes; poly butadiene rubber; ethylene oxide; ethanol amines; acetic acid; ethylene glycols; vinyl acetate; and chloro acetyl chloride.

**Experimental setup**

In this study, a Plexiglas column (15 cm in diameter and 120 cm in height) was used as the anaerobic hybrid reactor (Figure 1). The upper 20 cm of the reactor was operated with a fixed bed of corrugated plastic sheet with 170 m² m⁻³ specific surface areas. The total volume of the reactor was 18.5 L and the volume of liquid was 15.4 L. There aren’t any solids/liquid/gas separation devices in the reactor. The reactor was operated under mesophilic conditions and the temperature of the influent flow was adjusted to 35 °C by a heat exchanger before entering in to the reactor. Also two automatically adjustable heating devices placed at the bottom and middle of the reactor adjusted the temperature of the liquid inside the reactor.

**Feed**

The output of the existing API oil separator entered the reactor. The basic composition of the wastewater is presented in Table 1. Biological treatment processes require macronutrients such as nitrogen as nitrate or ammonium salts and phosphorus as phosphorus salts for bacterial metabolism, growth, activity and stability of process. Also, all methanogens use ammonia as nitrogen source. The total chemical oxygen demand (TCOD) : N : P ratio of the wastewater is 1,726 : 45.2 : 1.5 or 700 : 18.33 : 0.61. But a suitable TCOD : N : P ratio for anaerobic treatment is about 700 :

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Average</th>
<th>Standard deviation</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.2–12.8</td>
<td>6.12</td>
<td>3.46</td>
<td>590</td>
</tr>
<tr>
<td>T, °C</td>
<td>33–36</td>
<td>34.5</td>
<td>1.19</td>
<td>145</td>
</tr>
<tr>
<td>*COD₉₉₉, mg L⁻¹</td>
<td>600–4,900</td>
<td>2,075</td>
<td>1,075</td>
<td>590</td>
</tr>
<tr>
<td>COD₉₉₉, mg L⁻¹</td>
<td>690–3,900</td>
<td>1,726</td>
<td>846</td>
<td>590</td>
</tr>
<tr>
<td>COD₂₀⁵/COD₉₉₉</td>
<td>0.55–0.972</td>
<td>0.856</td>
<td>0.102</td>
<td>53</td>
</tr>
<tr>
<td>BOD₂⁵/COD</td>
<td>0.633–0.749</td>
<td>0.684</td>
<td>0.107</td>
<td>19</td>
</tr>
<tr>
<td>BOD₂₀⁵/COD</td>
<td>0.913–1.234</td>
<td>0.776</td>
<td>0.123</td>
<td>19</td>
</tr>
<tr>
<td>TDS, mg L⁻¹</td>
<td>300–1,070</td>
<td>672</td>
<td>232.5</td>
<td>53</td>
</tr>
<tr>
<td>TKN, mg L⁻¹</td>
<td>6.1–148</td>
<td>45.2</td>
<td>34.8</td>
<td>53</td>
</tr>
<tr>
<td>TP, mg L⁻¹</td>
<td>0.03–5.2</td>
<td>1.5</td>
<td>1.25</td>
<td>53</td>
</tr>
<tr>
<td>Alkalinity, mg L⁻¹</td>
<td>240–440</td>
<td>366</td>
<td>56.4</td>
<td>53</td>
</tr>
</tbody>
</table>

*Before API oil separator unit.
5:1 (Bitton 1999). Thus, phosphoric acid is added to the wastewater to compensate for phosphorus.

**Seeding**

The use of appropriate seed is very important at the start up of the reactor. Because sufficient seed quality will result in process stability and minimize the start up period (Lettinga & van Lier 2005). In Iran the anaerobic process is nowhere used to treat petrochemical waste. Therefore the reactor was seeded with flocculent sludge from a UASB Plant treating dairy wastewater.

**Start up**

The results of biological oxygen demand (BOD) tests at different dilutions and comparing the curves with typical BOD curves showed that there is a lag period and increase in the toxicity to bacteria to degrade petrochemical wastes, thus it is necessary to adapt the microbial cells to these wastes. At the beginning of this study (before measurement of BOD values), the reactor was run for 5 months without adaptation but it was unsuccessful. So it was decided to adapt the sludge in two stages. In the first stage, the synthetic wastewater made from dry milk was fed to the reactor. Then in second stage, the concentration of chemical oxygen demand (COD) was increased in the feed at 10% increment per cycle till it reached 100%.

**Operational conditions**

After successful start up was completed on week 40, the influent COD concentration changed stepwise from 1,000 to 4,000 mg L⁻¹. At each COD changing steps, the HRT of the reactor changed from 48 to 24, 12, 8 and 4 h, respectively, which resulted in different OLRs. By changing the HRT and influent COD concentrations, 25 different operational conditions were applied and COD removal efficiencies measured after reaching to hydraulically steady state conditions. When hydraulically steady state conditions were reached, changing to other HRTs was tried (Figure 2). The criteria for hydraulic steady state were the following: (a) an operation period of more than 10 times the HRT (and more than 2 weeks) (Noyola et al. 1988); and (b) variations in effluent concentration lower than ±10% (Polprasert et al. 1992). A real steady state would only be achieved in the sludge bed, and consequently in the reactor, if the operation period is at least three SRTs (van Haandel & Lettinga 1994).

**Analytical methods**

Samples of the influent and effluent of the model reactor were taken and analyzed according to Standard Methods for the Examination of Water and Wastewater (APHA et al. 1995). The pH, COD, alkalinity and biogas volume were measured daily.

**Experimental design**

The experimental protocol was designed to examine the effect of different OLRs, HRTs and up-flow velocities on the operational and performance of the reactor. All experiments were performed under hydraulically steady state conditions.

**RESULTS AND DISCUSSION**

**Start up**

The start up of the reactor was relatively long because the system had not been adapted to the petrochemical wastes previously. After 10 months, the adaptation period had been completed and a COD removal of 70.3% was obtained at OLR = 2.0 kg m⁻³ d⁻¹ and HRT = 18 h.

**Steady state performance**

The influent and effluent COD of the reactor during the operation period, and the results for different OLRs and HRTs along with performance indicators are presented in Table 2.

**Removal efficiency**

The performance of the experimental hybrid reactor based on total COD removals at various HRTs, OLRs and up-flow
velocities is shown in Figures 3 to 5, respectively. A COD reduction of the system ranging from 42.1 to 85.9% was achieved. The maximum COD reduction is obtained at influent COD concentration of 3,000 mg L\(^{-1}\), HRT = 24 h and OLR = 3.0 kg m\(^{-3}\) d\(^{-1}\). The minimum COD reduction is obtained at influent COD concentration of 4,000 mg L\(^{-1}\), HRT = 4 h and OLR = 24 kg m\(^{-3}\) d\(^{-1}\). The COD reduction at about average COD concentration of this petrochemical complex (1,726 mg L\(^{-1}\)) ranged between 43.4 and 80.9% depending on operational conditions (Table 2).

### Table 2 | Summary of the conditions during the operation period of the experimental setup

<table>
<thead>
<tr>
<th>Phase of study</th>
<th>Time, d</th>
<th>(C_0, \text{mg L}^{-1})</th>
<th>HRT, h</th>
<th>OLR, kg m(^{-3}) d(^{-1})</th>
<th>(V_{up}, \text{m h}^{-1})</th>
<th>Effluent COD, mg L(^{-1})</th>
<th>COD Red, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1–105</td>
<td>11,000</td>
<td>48</td>
<td>0.50</td>
<td>0.021</td>
<td>381</td>
<td>61.9</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>1.00</td>
<td>0.042</td>
<td>448</td>
<td>55.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>2.00</td>
<td>0.083</td>
<td>423</td>
<td>57.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>3.00</td>
<td>0.125</td>
<td>396</td>
<td>60.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.00</td>
<td>0.250</td>
<td>568</td>
<td>43.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>106–200</td>
<td>1,500</td>
<td>48</td>
<td>0.75</td>
<td>0.021</td>
<td>385</td>
<td>74.3</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>1.50</td>
<td>0.042</td>
<td>353</td>
<td>76.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>3.00</td>
<td>0.083</td>
<td>398</td>
<td>73.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>4.50</td>
<td>0.125</td>
<td>408</td>
<td>72.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>9.00</td>
<td>0.250</td>
<td>675</td>
<td>55.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>201–301</td>
<td>2,000</td>
<td>48</td>
<td>1.00</td>
<td>0.021</td>
<td>456</td>
<td>77.2</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>2.00</td>
<td>0.042</td>
<td>418</td>
<td>79.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>4.00</td>
<td>0.083</td>
<td>383</td>
<td>80.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>6.00</td>
<td>0.125</td>
<td>756</td>
<td>62.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>12.00</td>
<td>0.250</td>
<td>1,133</td>
<td>43.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>302–422</td>
<td>3,000</td>
<td>48</td>
<td>1.50</td>
<td>0.021</td>
<td>493</td>
<td>83.6</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>3.00</td>
<td>0.042</td>
<td>423</td>
<td>85.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>6.00</td>
<td>0.083</td>
<td>681</td>
<td>77.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>9.00</td>
<td>0.125</td>
<td>1,248</td>
<td>58.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>18.00</td>
<td>0.250</td>
<td>1,614</td>
<td>46.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>423–560</td>
<td>4,000</td>
<td>48</td>
<td>2.00</td>
<td>0.021</td>
<td>669</td>
<td>83.3</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>4.00</td>
<td>0.042</td>
<td>608</td>
<td>84.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>8.00</td>
<td>0.083</td>
<td>965</td>
<td>85.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>12.00</td>
<td>0.125</td>
<td>1,822</td>
<td>54.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>24.00</td>
<td>0.250</td>
<td>2,316</td>
<td>42.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Hydraulic retention time

The obtained results (Figure 3) showed that the reduction of COD reached a maximum at HRT = 24 h and then decreased gradually with increase of HRT. This could be the result of decrease in biogas production and up-flow velocities, which resulted in lower mixing and contact between substrate and biomass. At certain HRT, the TCOD reduction will increase by increasing the influent...
COD concentration, because of more biogas production resulting in more agitation and contact between substrate and biosolids (Figure 3). The increase in reactor performance will be only 10% if the HRT increase from 12 to 24 h resulted in a reactor volume increase of twice. Also the results showed that reactor performance decreased gradually to less than 60% at HRTs lower than 12 h.

**Organic loading rate**

The results of the reactor performance versus OLR are shown in Figure 4. It can be see from this figure that up to a certain limit, the treatment efficiency increases with increasing OLR depending on influent COD concentration. The results showed that reduction of COD reached a maximum at OLRs ranging from 2.5 to 3.7 kg m$^{-2}$ d$^{-1}$. A further increase of OLR by increasing the HRT and influent COD concentration resulted in less COD reduction because of biosolids washout. As shown in Figure 4, at certain OLRs, as for the HRT effect, the TCOD reduction will increase by increasing the influent COD concentration because of more biogas production resulting in more agitation and contact between substrate and biosolids. The applied OLR is related to the HRT and influent substrate concentration. Using applied loading rate alone as a process parameter, doubling the OLR while holding the influent concentration constant, would be expected to decrease efficiency by 5 to 45%. Young (1991) found this value by about 18–15%.

**Up-flow velocity**

As shown in Figure 5, at constant up-flow velocity, the reduction performance increases with COD concentration increasing, because of more agitation and contact between biosolids and substrate resulted from more biogas production. The maximum COD reduction of about 85% was achieved at up-flow velocity ranging from 0.02 to 0.04 m$^{-1}$ and COD concentration of 3,000 mg L$^{-1}$. Increasing of up-flow velocity resulted in biomass washout in the effluent because the biosolids are flocculent type not granular. Also, at constant COD concentration, the reduction performance decreased with increasing upflow velocity because increasing the upflow velocity could increase the hydraulic shearing force, which counteracts the removal mechanism through exceeding the settling velocity of more particles and detachment of the captured solids, and consequently deteriorates the removal efficiency.

**Kinetic models**

The results of some applied models are summarized in Table 3. As shown in Table 3, the correlation of these models is relatively low. As a result of the calculations, a second-order model and a modified Stover–Kincannon model were found to be the most appropriate models for the hybrid reactor. Application of these models is given below.

The simplified and linearized form of the second-order kinetic model is given below:

$$\frac{S_0 \theta}{S_0 - S} = \theta + \frac{S_0}{K_{2(s)}X}$$

where, $S_0$ and $S$, influent and effluent substrate concentrations (mg COD/L); $\theta$, HRT (d); $K_{2(s)}$, Second-order substrate removal rate constant (d$^{-1}$); and $X$, the average biomass concentration in the reactor (mg VSS/lit).

As $(S_0-S/S_0)$ expresses the substrate removal efficiency symbolized as $E$ and if the second term of the right side of this equation is accepted as a constant, the equation below will be given:

$$\frac{\theta}{E} = a + b\theta$$

where $a = S_0/(K_{2(s)}X)$, and $b$ is a constant greater than unity.

The second-order kinetic model applied for the sludge bed, fixed bed and overall reactor are shown in Figures 6 to 8. From Figure 6, The values of (a) and (b) can be found as 2.0543 and 1.5316, respectively, for the sludge bed region, with a correlation coefficient of $R^2 = 0.85$. These values found as 7.734 and 2.1021 with $R^2 = 0.78$ for the fixed bed region and 2.0543 and 1.2834 with $R^2 = 0.95$ for the overall reactor (Figures 7 and 8). Thus, by substituting these values in the above equation, the formulas for predicting of effluent substrate concentration for different regions of the reactor are given as:
for sludge bed region:

\[
S = S_0 \left( 1 - \frac{\theta}{2.0543 + 1.5316\theta} \right)
\]

for fixed bed region:

\[
S = S_0 \left( 1 - \frac{\theta}{7.734 + 2.1021\theta} \right)
\]

for overall reactor:

\[
S = S_0 \left( 1 - \frac{\theta}{2.0543 + 1.2834\theta} \right)
\]

Stover and Kincannon have established a kinetic model for biofilm reactors based on total OLR. A special feature of the modified Stover–Kincannon model is the utilization of the concept of total OLR as the major parameter to describe the kinetics of an anaerobic filter in terms of organic matter removal and methane production (Yu et al. 1998).

Equations of the modified Stover–Kincannon model are shown below:

\[
\frac{dS}{dt} = \frac{Q}{V} (S_0 - S_c)
\]  

(3)

We can define \(dS/dt\) in two ways:

\[
\frac{dS}{dt} = \frac{U_{\text{max}}(QS_0/V)}{K_B + (QS_0/V)}
\]  

(4)

### Table 3: Summary result of application of some kinetic models

<table>
<thead>
<tr>
<th>Name of model</th>
<th>Formulation(s)</th>
<th>Parameter</th>
<th>Obtained values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monod</td>
<td>(\frac{1}{\theta} = Y L_d - b)</td>
<td>(Y, b, \text{d}^{-1})</td>
<td>0.1661 (0.45)</td>
</tr>
<tr>
<td></td>
<td>(L_d = \frac{1}{K_S} + \frac{1}{S_{\text{max}}})</td>
<td>(K_S, \text{mg COD/L})</td>
<td>0.0155 (0.45)</td>
</tr>
<tr>
<td></td>
<td>(V = \frac{K_B}{U_{\text{max}}} \frac{Q S_0}{V} + \frac{1}{U_{\text{max}}})</td>
<td>(K_B, \text{g/L.d})</td>
<td>932 (0.15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(U_{\text{max}}, \text{g/L.d})</td>
<td>0.478 (0.15)</td>
</tr>
<tr>
<td>Modified Stover–Kincannon</td>
<td>(\frac{Q(S_i - S_c)}{S_i + K_S} = \frac{U_{\text{max}}}{Q S_i} + \frac{1}{U_{\text{max}}})</td>
<td>(K_B, \text{g/L.d})</td>
<td>229.7 (0.97)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(U_{\text{max}}, \text{g/L.d})</td>
<td>68.97 (0.97)</td>
</tr>
<tr>
<td>Sundstorm</td>
<td>(L = \frac{L_{\text{max}}}{S + K_S})</td>
<td>(L_{\text{max}}, \text{kg COD/m}^3 \cdot \text{d})</td>
<td>6.2 (0.22)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(K_S, \text{mg COD/L})</td>
<td>1,144 (0.22)</td>
</tr>
<tr>
<td>Grau et al.</td>
<td>(S = \frac{S_0(1 + b \theta)}{\mu_m \theta_c})</td>
<td>(b, \text{d}^{-1})</td>
<td>0.79 (0.57)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\mu_m, \text{d}^{-1})</td>
<td>0.453 (0.57)</td>
</tr>
<tr>
<td>Second order</td>
<td>(\frac{S_0 \theta}{S_0 - S} = a + b \theta)</td>
<td>(a)</td>
<td>2.0543 (0.85)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b)</td>
<td>1.5316 (0.85)</td>
</tr>
</tbody>
</table>

Note: SBR: sludge bed region, FBR: fixed bed region, TR: total reactor, \(R^2\) values are written in brackets.

Figure 6 | Second-order kinetic model application for the sludge bed region.

Figure 7 | Second-order kinetic model application for the fixed bed region.

Figure 8 | Second-order kinetic model application for total reactor.
\[
\frac{dS}{dt} = kXS_e \quad \text{(5)}
\]

Combination of Equations (3) and (4), will result in the equation given below:

\[
\left(\frac{dS}{dt}\right)^{-1} = \frac{V}{Q(S_0 - S_e)} = \frac{K_B V}{U_{\text{max}} Q S_0} + \frac{1}{U_{\text{max}}}
\]

By solving Equation (6) to obtain \( S_e \):

\[
S_e = S_0 - \frac{U_{\text{max}} S_0}{K_B + (QS_0/V)} \quad \text{(7)}
\]

In these equations, \( dS/dt \), substrate removal rate (gL\(^{-1}\)d\(^{-1}\)); \( V \), clean-bed volume of the anaerobic filter (L); \( U_{\text{max}} \), maximum utilization rate constant (gL\(^{-1}\)d\(^{-1}\)); \( K_B \), saturation value constant (gL\(^{-1}\)); \( k \), maximum rate of substrate removal (Ld\(^{-1}\)); \( X \), microorganism concentration (VSS) in the anaerobic filter (gL\(^{-1}\)L); \( Q_s \), half-velocity constant (gL\(^{-1}\)).

By plotting the \( V/(Q(S_0 - S)) \), the inverse of the loading removal rate versus the \( V/QS_0 \), the inverse of the total loading rate, a straight line graph is obtained and \( 1/U_{\text{max}} \) and \( K_B/U_{\text{max}} \) are the intercept and slope of this line, respectively. The plot of experimental data is shown in Figure 9 with high correlation \( (R^2 = 0.966) \). From this figure, \( 1/U_{\text{max}} \) and \( K_B/U_{\text{max}} \) were 0.0145 and 3.3305, respectively. The maximum removal rate constant \( U_{\text{max}} \) is 68.97 gL\(^{-1}\) and the saturation value constant \( K_B \) is 229.7 gL\(^{-1}\)d\(^{-1}\), for the fixed bed region of the reactor. Now, we can calculate the \( S_e \) from Equation (7) as:

\[
S_e = S_0 - \frac{68.97 S_0}{229.7 + (QS_0/V)}
\]

**Biogas production**

Biogas production is an important parameter for anaerobic treatment systems. The specific biogas production rate versus the OLR is plotted in Figure 10, which confirms that the biogas production rate was a function of the OLR and that it could be described similarly to organic substrate removal kinetics (Yu et al. 1998). The biogas production rate can be expressed as follows:

\[
G = \frac{G_{\text{max}}(QS_i/V_i)}{G_B + (QS_i/V_i)}
\]

where, \( G \), is specific biogas production rate (L L\(^{-1}\)d\(^{-1}\)), \( G_{\text{max}} \) is maximum specific biogas production rate (L L\(^{-1}\)d\(^{-1}\)), \( QS_i/V_i \), is OLR (gL\(^{-1}\)d\(^{-1}\)) and \( G_B \) is constant value.

The inverse of the biogas production rate is plotted against the inverse of the OLR; a straight line portion of intercept and slope of line gives \( 1/G_{\text{max}} \) and \( G_B/G_{\text{max}} \), respectively. This graph is given in Figure 11. From this figure, \( G_{\text{max}} \) and \( G_B/G_{\text{max}} \) can be estimated as 11.173 LL\(^{-1}\)d\(^{-1}\) and 85.83 gL\(^{-1}\)d\(^{-1}\) respectively with high correlation coefficient \( (R^2 = 0.90) \), respectively. Buyukkamaci & Filibeli (2002) found these values as 33.3 LL\(^{-1}\)d\(^{-1}\) and 88.45 gL\(^{-1}\)d\(^{-1}\) for synthetic substrate made from molasses, respectively. Therefore, the above equation comes to this form:

\[
G = \frac{11.17(QS_i/V_i)}{85.83 + (QS_i/V_i)}
\]

**CONCLUSION**

The results of the study showed that petrochemical wastewater can be satisfactorily treated by means of high-rate anaerobic
processes, specifically with the use of a hybrid reactor. High TCOD removals of between 42 and 86% at OLRs of 0.5–24.0 kg COD m⁻³d⁻¹ and HRTs between 4 and 48 h were achieved in this study. The maximum specific biogas production rate of 11.17 LL⁻¹d⁻¹ was in the same order of magnitude as the rates achieved in earlier studies.

Performance of the hybrid model reactor treating petrochemical wastewater was evaluated at different HRTs and OLRs. COD removal efficiencies ranging from 42.1 to 85.9% were achieved. Some kinetic models were applied to biological systems for biokinetic modelling of the reactor. The results show that the second-order model and modified Stover–Kincannon model are the most suitable models. Therefore, these models could be used in the design and operation of this type of reactor.

The second-order model was applied to the suspended growth region, the fixed bed region and the overall reactor. The second-order substrate removal rate constant (K₂) was 0.2145, 0.0172, and 0.1463 per day for these regions, respectively. This value was found to be 0.217 per day for municipal wastewater, 10.81 per day for synthetic wastewater, 38.5 per day for landfill leachate, and 1.655 and 13.6 per day for glucose wastes (Buyukkamaci & Filibeli 2002).

If a modified Stover–Kincannon model is applied to the fixed bed region, the maximum removal rate constant (Uₘₐₓ) and saturation value constant (Kₛ) will be 68.97 and 229.7 g L⁻¹d⁻¹, respectively. These values were found to be Uₘₐₓ = 85.3 and Kₛ = 85.5 and 186.3 g L⁻¹d⁻¹ in previous studies (Buyukkamaci & Filibeli 2002).

Finally, it can be concluded that the second-order model and modified Stover–Kincannon model have high correlation to data obtained from the hybrid model reactor and these models could be used for design and operation of this type of reactor.

**REFERENCES**


First received 6 October 2009; accepted in revised form 23 September 2010