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# **Kinetic Constants of Anaerobic Hybrid Reactor Treating Petrochemical Waste**

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In this study, some bio-kinetic models applied to data obtained from experimental studies to determining of most suitable models. A laboratory scale anaerobic hybrid reactor for treating petrochemical wastewater at mesophilic conditions was used. Treatment efficiencies were investigated for different regions at different hydraulic retention times (4, 8, 12, 24 and 48 h) and influent concentrations (1000, 1500, 2000, 3000 and 4000 mg/L), this resulted in organic loading rates ranging 0.5 to 24 kg/m<sup>3</sup> d. The results showed that second-order model and a modified Stover-Kincannon model were the most appropriate models for this reactor. The second-order substrate removal rate constant  $(k_{2(s)})$  was found as 0.2145, 0.01724 and 0.1456 per day for sludge bed region, fixed bed region and overall reactor, respectively. The data obtained from fixed region used for modified Stover-Kincannon model. The maximum removal rate constant  $(U_{max})$  and saturation value constant  $(K_B)$  were found to be 68.97 g/L d and 229.7 g/L d, respectively.

**Key Words: Anaerobic, Hybrid, kinetic, Modelling, Petrochemical, Wastewater.**

# **INTRODUCTION**

Development of petrochemical industry in Iran, construction of new plants and upgradation of existing units lead to generate more wastewater of higher strength. In this paper, the treatment of a petrochemical complex wastewater by an anaerobic hybrid reactor is discussed.

Process kinetics has been used for the mathematical description of both aerobic and anaerobic biological treatment processes. The understanding of process kinetics is essential for the rational design and operation of biological treatment systems, predicting system stability, effluent quality and waste stabilization<sup>1</sup>. The knowledge on kinetics leads to optimization of performance, a more stable operation and a

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better control of the process<sup>2</sup>. Some mathematical models such as Monod, firstorder, second-order, modified Stover-Kincannon, *etc.* are available in literature for describing of biological processes.

The anaerobic hybrid reactor is a combination of an anaerobic sludge blanket (UASB) in the lower part and an anaerobic filter (AF) in the upper part. Since this type of reactor combines a suspended biomass (UASB part) and attached biomass (AF part), it is necessary to consider each region separately in order to calculate the kinetic coefficients of the reactor.

In this study, different mathematical models were applied to data obtained from the reactor operation such as Monod model, second-order kinetic model, modified Stover-Kincannon, Sundstorm model, Grau model and Contois model.

## **EXPERIMENTAL**

**Location:** This study was conducted for 3 years in Arak petrochemical company in central Iran. The products of this complex include: ethylene, propylene, C4, pyrolize benzene, crude oil, polypropylene, high and low density polyethylene (HDPE & LDPE), 1-butane, 1,3-butadiene, poly butadiene, rubber, ethylene oxide, mono, di and triethanol amine, acetic acid, mono, di and triethylene glycol, vinyl acetate, 2-ethyl hexanol, normal butanol and chloro acetyl chloride.

**Model reactor:** A Plexiglas column (15 cm in diameter and 120 cm in height) was used as the anaerobic hybrid reactor in this study. The upper 20 cm of the reactor was operated with fixed bed of corrugated plastic sheet with  $170 \text{ m}^2/\text{m}^3$ specific surface areas. The total volume of the reactor was 18.5 L and the volume of liquid was 15.4 L. Recycle, being designed only for emergency conditions, such as clogging of the distribution system was not used continuously during the experimental study. There are no solids/liquid/gas separation devices in the reactor. The schematic diagram of the model reactor is given in Fig. 1.

The reactor was operated under mesophilic conditions and temperature of the influent flow adjusted to 35 °C by a heat exchanger before entering to the reactor. Two automatically adjustable heating devices were also placed at the bottom and middle of the reactor adjusted the temperature of the liquid inside the reactor whenever required.

**Substrate:** The existing WTP in Arak petrochemical complex consist of physico-chemical treatment followed by an activated sludge treatment of wastewater. The influent to the experimental reactor was provided from output of API oil separator. Basic composition of feed wastewater is presented in Table-1.

**Seeding:** The use of appropriately acclimatized seed is very important at the start up of the reactor. Sufficiently acclimatized seed will give quicker process stability and minimize the start up period. In Iran, hardly any WTP uses anaerobic process for the treatment of petrochemical wastewater. Thus there was no adapted seed for treatment of this type of wastewater. Therefore the reactor was seeded with flocculent sludge from a UASB plant treating dairy wastewater.





ARAK PETROCHEMICAL COMPLEX							
Parameter	Range	Average	Standard deviation	Number of samples			
pH	$4.2 - 12.8$	6.12	3.46	590			
$T (^{\circ}C)$	$33 - 36$	34.5	1.19	145			
$^*$ COD <sub>tot</sub> (mg/L)	600-4900	2075	1075	590			
$\mathrm{COD}_{\mathrm{tot}}$ (mg/L)	600-3900	1726	846	590			
$\mathrm{COD}_{\mathrm{SUS}}/\mathrm{COD}_{\mathrm{tot}}$	0.055-0.097	0.086	0.010	53			
BOD <sub>s</sub> /COD	0.633-0.749	0.684	0.107	19			
$BOD_{20}/COD$	0.688-0.865	0.776	0.123	19			
$TSS$ (mg/L)	20-280	106	59	26			
TDS (mg/L)	300-1070	672	232.5	53			
$TKN$ (mg/L)	$6.1 - 148$	45.2	34.8	53			
$TP \, (mg/L)$	$0.03 - 5.2$	1.5	1.25	53			
Alkalinity (mg/L)	240-440	366	56.4	53			
Sulfur	Negligible						

TABLE-1 BASIC COMPOSITION OF WASTEWATER FROM

Before API oil separator unit.

**Start up:** The reactor was started after 9 months *via* adaptation of seed sludge to petrochemical wastes.

**Operational conditions:** Treatment efficiencies of the reactor were evaluated at different hydraulic retention times (HRT) (4, 8, 12, 24 and 48 h) and organic loading rates  $(0.5{\text -}24 \text{ kg/m}^3 \text{ d})$ . The influent substrate concentrations were 1000, 1500, 2000, 3000 and 4000 mg COD/L. When hydraulically steady state conditions were reached, changing to different HRTs were tried. The influent and effluent COD concentration among the reactor operation time are shown in Fig. 2.



Fig. 2. Influent and effluent COD concentration among the reactor operation time  $SB = Sludge bed$ ,  $HRT = hydraulic retention times$ 

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)<sup>3</sup> and (b) variations in effluent concentration less than  $\pm 10\%$ <sup>4</sup>. Elmitwalli<sup>5</sup> and Mahmoud<sup>6</sup> have also considered these criteria satisfactory. 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 times HRTs<sup>7</sup>.

**Analytical procedures:** 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<sup>8</sup>. pH, COD, alkalinity and biogas volume were measured daily. The COD concentration was determined by the colorimetric method, using a spectrophotometer Hacth DR2010 at wavelength 640 nm. The pH value was measured with 692 pH-meter metrohm. A gas/liquid replacement device measured the volume of biogas.

### **RESULTS AND DISCUSSION**

Model reactor efficiency was evaluated depending on COD removal efficiencies. The results of COD reductions at different operational conditions are given in Table-2.

Operational conditions		Eff. COD		COD Red.			
$C_0$ (mg/L)	HRT(h)	<b>OLR</b> (kg/m <sup>3</sup> d)	<b>SBR</b> (mg/L)	<b>FBR</b> (mg/L)	SBR $(\%)$	FBR $(\%)$	Total $(\%)$
	48	0.50	514	381	48.6	25.9	61.9
	24	1.00	654	448	34.6	31.5	55.2
1000	12	2.00	546	423	45.4	22.5	57.7
	8	3.00	556	396	44.4	28.8	60.4
	4	6.00	650	568	35.0	12.6	43.2
	48	0.75	568	385	62.1	32.2	74.3
	24	1.50	524	353	65.1	32.6	76.5
1500	12	3.00	498	398	66.8	20.1	73.5
	8	4.50	589	408	60.7	30.7	72.8
	4	9.00	957	675	36.2	29.5	55.0
	48	1.00	650	456	67.5	29.9	77.2
	24	2.00	643	418	67.9	35.0	79.1
2000	12	4.00	546	383	72.7	29.9	80.9
	8	6.00	1124	756	43.8	32.7	62.2
	4	12.00	1540	1133	23.0	26.4	43.4
3000	48	1.50	720	493	76.0	31.5	83.6
	24	3.00	672	423	77.6	37.1	85.9
	12	6.00	987	681	67.1	31.0	77.3
	8	9.00	1753	1248	41.6	28.8	58.4
	4	18.00	2143	1614	28.6	24.7	46.2
4000	48	2.00	987	669	75.3	32.2	83.3
	24	4.00	893	608	77.7	31.9	84.8
	12	8.00	1389	965	65.3	30.5	85.0
	8	12.00	2512	1822	37.2	27.5	54.5
	4	24.00	2989	2316	25.3	22.5	42.1

TABLE-2 OPERATIONAL CONDITION AND PERFORMANCE OF THE REACTOR DURING THE EXPERIMENTAL STUDY

 $SBR = Sludge bed region, FBR = Fixed bed region.$ 

The 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 3000 mg/L, HRT = 24 h and OLR =  $3.00 \text{ kg/m}^3$  d. The minimum COD reduction is obtained at influent COD concentration of 4000 mg/L,  $HRT = 4$  h and OLR = 24 kg/m<sup>3</sup> day.

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, second-order model and a modified Stover-Kincannon model were found to be the most appropriate model for the hybrid reactor. Application of these models is given below.

**Second-order model application:** The simplified and linearalized form of second-order kinetic model is given below:



TABLE-3

SBR = Sludge bed region, FBR = Fixed bed region, TR = Total reactor,  $R^2$  values are written in brackets.

$$
\frac{S_0 * HRT}{S_0 - S} = HRT + \frac{S_0}{K_{2(s)}X}
$$
 (1)

where,  $S_0$  and S, influent and effluent substrate concentrations (mg COD/L); HRT, hydraulic retention time (d);  $k_{2(s)}$ , Second-order substrate removal rate constant  $(d<sup>-1</sup>)$  and X, the average biomass concentration in the reactor (mg VSS/L).

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

$$
\frac{\text{HRT}}{\text{E}} = a + b \cdot \text{HRT} \tag{2}
$$

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

**Application of second-order kinetic model for the sludge bed region (SBR):** Data obtained from operation of the reactor that used for the second-order kinetic model for SBR are given in Table-4. From Fig. 3, the values of (a) and (b) can be found as 2.0543 and 1.5316, respectively, with the correlation coefficient of  $R^2$  = 0.85. The second-order substrate removal rate constants  $(k_{2(S)})$  which is calculated from (a) values, are given in Table-4.

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 $\blacklozenge$ 







$S_0$ (mg/L)	HRT(h)	S(mg/L)	$X_{r}$ (mg/L)	Е	$HRT/E(\%)$	$K_{2(s)}(d)$
	1.60	514		0.486	3.29	
	0.80	654		0.346	2.31	
1000	0.40	546	6512	0.454	0.88	0.0748
	0.27	556		0.444	0.60	
	0.13	650		0.350	0.38	
	1.60	568		0.621	2.57	
	0.80	524		0.651	1.23	
1500	0.40	498	6137	0.668	0.60	0.1190
	0.27	589		0.607	0.44	
	0.13	957		0.362	0.37	
	1.60	650		0.675	2.37	
	0.80	643		0.679	1.18	
2000	0.40	546	5249	0.727	0.55	0.1855
	0.27	1124		0.438	0.61	
	0.13	1540		0.230	0.58	
	1.60	720		0.760	2.1	
	0.80	672		0.776	1.03	
3000	0.40	987	5138	0.671	0.60	0.2842
	0.27	1753		0.416	0.64	
	0.13	2143		0.286	0.47	
	1.60	987		0.753	2.12	
	0.80	893		0.777	1.03	
4000	0.40	1389	4762	0.653	0.61	0.4089
	0.27	2512		0.372	0.72	
	0.13	2989		0.253	0.53	
					Average	0.2145

TABLE-4 **E BED BEGION**  $EOD$ 

 $\mathcal{L}^{\mathcal{L}}$ 

The values of (a) and (b) were substituted into last equation in order to develop a formula for predicting of effluent COD concentration by using influent COD concentration and hydraulic retention time:

$$
S = S_0 \left( 1 - \frac{HRT}{2.0543 + 1.5316 \times HRT} \right)
$$

**Application of second-order kinetic model for the fixed bed region:** In this study, biomass concentration in the fixed bed region was measured *via* determination of biomass attached to the media. For this purpose, pieces of media were removed; the biomass washed in the liquid and the VSS concentration was measured. The exercise was repeated for each operation condition (concentration change) and VSS concentrations were obtained for each operation. Data used for a second-order kinetic model are given in Table-5. The values of (a) and (b) were obtained using Fig. 4 for fixed bed region of the reactor.







Fig. 4. Second-order kinetic model application for the fixed bed region

From Fig. 4, the values of (a) and (b) was found as 7.734 and 2.1021, respectively, with the correlation coefficient of  $R^2 = 0.78$ . The values of  $k_{2(S)}$  (second-order substrate removal rate constants) were calculated from (a) values are given in Table-5. The formula for predicting of effluent substrate concentration  $f_{\theta}$  this region of the reactor is given as:  $S = S_0 \left( 1 - \frac{11}{7.734 + 2.10212 \times 100} \right)$  $\left( \begin{array}{c} 1 \\ 1 \end{array} \right)$  =  $\left( \begin{array}{c} 1 \\ 1 \end{array} \right)$ l P  $+ 2.10212 \times$  $= S_0 \left( 1 S = S_0 \left( 1 - \frac{HRF^{11S} \text{ regl}}{7.734 + 2.10212 \times 100} \right)$ 

**Application of Second-order kinetic model for overall reactor:** For predicting the behaviour of overall reactor, a second-order kinetic model was also applied to overall reactor. Data used for this section are given in Table-6 and (a) and (b) values were obtained using Fig. 5.

From Fig. 5, the values of (a) and (b) can be found as 2.0543 and 1.2834, respectively, with very high correlation coefficient of  $R^2 = 0.95$ . The second-order substrate removal rate constants  $(k_{2(S)})$  are given in Table-6.

Formula given below is obtained for predicting effluent COD concentration by using influent COD concentration and hydraulic retention time:

$$
S = S_0 \left( 1 - \frac{HRT}{2.0543 + 1.2834 \times HRT} \right)
$$

**Application of modified Stover-Kincannon model for fixed bed region of the reactor:** Stover and Kincannon have established a kinetic model for biofilm reactor based on total organic loading rate. A special feature of modified Stover-Kincannon model is the utilization of the concept of total organic loading rate as the major parameter to describe the kinetics of an anaerobic filter in terms of organic matter removal and methane production<sup>9</sup>.



Fig. 5. Second-order kinetic model application for overall reactor

$S_0$ (mg/L)	HRT(h)	$S$ (mg/L)	$X_r$ (mg/L)	E	HRT/E $(\%)$	$K_{2(s)}(d)$
	2.00	381		0.619	3.23	
	1.00	448		0.552	1.81	
1000	0.50	423	8978	0.577	0.87	0.0542
	0.33	396		0.604	0.55	
	0.17	568		0.432	0.39	
	2.00	385		0.743	2.69	
	1.00	353		0.765	1.31	
1500	0.50	398	8796	0.735	0.68	0.0830
	0.33	408		0.728	0.46	
	0.17	675		0.550	0.30	
	2.00	456		0.772	2.59	
	1.00	418		0.791	1.26	
2000	0.50	383	7943	0.809	0.62	0.1226
	0.33	756		0.622	0.54	
	0.17	1133		0.434	0.38	
	2.00	493		0.836	2.39	
	1.00	423		0.859	1.16	
3000	0.50	681	7706	0.773	0.65	0.1859
	0.33	1248		0.584	0.57	
	0.17	1614		0.462	0.36	
	2.00	669		0.833	2.40	
	1.00	608		0.848	1.18	
4000	0.50	965	6895	0.859	0.66	0.2824
	0.33	1822		0.545	0.61	
	0.17	2316		0.421	0.40	
		Ť			Average	0.1456

TABLE-6 DATA FOR THE SECOND-ORDER KINETIC MODEL FOR OVERALL REACTOR

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

$$
\frac{dS}{dt} = \frac{Q}{V}(S_0 - S_e)
$$
\n(3)

It can be defined dS/dt in two ways:

$$
\frac{dS}{dt} = \frac{U_{\text{max}}(QS_0 / V)}{K_B + (QS_0 / V)}
$$
(4)

$$
\frac{dS}{dt} = \frac{kXS_e}{K_s + S_e}
$$
 (5)

By combination of eqns. 3 and 4, will result in equation given below:

$$
\left(\frac{dS}{dt}\right)^{-1} = \frac{V}{Q(S_0 - S_e)} = \frac{K_B}{U_{max}} \frac{V}{QS_0} + \frac{1}{U_{max}}
$$
(6)

By solving the eqn. 6 for obtain the Se:

$$
S_e = S_0 - \frac{U_{\text{max}} S_0}{K_B + (QS_0/V)}
$$
\n
$$
\tag{7}
$$

In these equations,  $dS/dt$ , substrate removal rate  $(g/l,d)$ ; V, clean-bed volume of the anaerobic filter (L);  $U_{\text{max}}$ , maximum utilization rate constant (g/L d); KB, saturation value constant (g/L d); k, maximum rate of substrate removal (L/d); X, microorganism concentration (VSS) in the anaerobic filter  $(g/L)$ ; K<sub>s</sub>, half-velocity constant  $(g/L)$ .

By plotting the  $V/[Q(S_0-Se)]$ , the inverse of the loading removal rate *versus* the  $V/OS<sub>0</sub>$ , the inverse of the total loading rate, a straight line graph is obtained and that  $1/U_{\text{max}}$  and KB/U<sub>max</sub> are the intercept and slope of this line, respectively.

The data used for this model are given in Table-7 and the plot of experimental data is shown in Fig. 6 with high correlation ( $R^2 = 0.966$ ). From this figure,  $1/U_{\text{max}}$ and KB/Umax were 0.0145 and 3.3305, respectively. The maximum removal rate constant (U<sub>max</sub>) is 68.97 g/L and the saturation value constant (K<sub>B</sub>) is 229.7 g/L d, of fixed bed region of the reactor. Now, it can be calculate the Se by eqn. 7 as:

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

#### **Conclusion**

Performance of the hybrid model reactor treating petrochemical wastewater was evaluated at different hydraulic retention time and organic loading rates. Biokinetic analyses of the reactor were carried out according to the experimental data. After start-up of the reactor and obtaining hydraulically steady state conditions, the operational conditions were changed. Twenty five different operational conditions were applied by changing influent concentration, hydraulic retention time and organic loading rate.



Fig. 6. Modified Stover-Kincannon model application for the fixed bed region

MODLL FOR THE FIALD DLD REGION							
Q(L/d)	$S_0$ (mg/L)	$S$ (mg/L)	$V/QS_0$ (L d/g COD)	$V/[Q(S_0-S_e)]$ (L d/g COD)			
7.7	514	381	0.783	3.027			
15.4	654	448	0.308	0.977			
30.6	546	423	0.184	0.818			
46.2	556	396	0.121	0.419			
92.4	650	568	0.052	0.409			
7.7	568	385	0.709	2.200			
15.4	524	353	0.384	1.177			
30.6	498	398	0.202	1.006			
46.2	589	408	0.114	0.371			
92.4	957	675	0.035	0.119			
7.7	650	456	0.619	2.075			
15.4	643	418	0.313	0.895			
30.6	546	383	0.184	0.617			
46.2	1124	756	0.060	0.182			
92.4	1540	1133	0.022	0.082			
7.7	720	493	0.559	1.774			
15.4	672	423	0.300	0.808			
30.6	987	681	0.184	0.329			
46.2	1753	1248	0.060	0.133			
92.4	2143	1614	0.022	0.063			
7.7	987	669	0.408	1.266			
15.4	893	608	0.225	0.706			
30.6	1389	965	0.072	0.237			
46.2	2512	1822	0.027	0.097			
92.4	2989	2316	0.011	0.050			

TABLE-7 DATA FOR THE MODIFIED STOVER-KINCANNON MODEL FOR THE FIXED BED REGION

COD removal efficiencies ranging from 42.1 to 85.9 % were achieved. Some kinetic models applied to biological systems for biokinetic modeling of the reactor such as Monod, second-order, Sundstorm, modified Stover-Kincannon, *etc*. The results showed that the second-order model and modified Stover-Kincannon model were 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. Second-order substrate removal rate constants  $(K<sub>2(S)</sub>)$  were 0.2145, 0.0172 and 0.1463 per day for these regions, respectively. This value was found 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 $^{10,11}$ .

If a modified Stover-Kincannon model applied to the fixed bed region, the maximum removal rate constant  $(U_{max})$  and saturation value constant (KB) will be 68.97g/L d and 229.7 g/L d per day, respectively. These values were found as  $U_{\text{max}}$  $= 83.3$  and  $K_B = 85.5$  and 186.3 gl per day in previous studies<sup>9,11</sup>.

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

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