J. ENVIRONMENTAL SYSTEMS, Vol. 31(1) 81-103, 2004-2005

DILUTIONS OF GLUCOSE AND GLUTAMIC ACID ANALYZED AS MULTI-ORDER BOD REACTIONS*

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ABSTRACT

The Biochemical Oxygen Demand (BOD) of a mixture of glucose and glutamic acid is a standard test solution which provides a reasonably repeatable value of the 5-day BOD. The objective of this study was to evaluate the reaction order from respirometer data of BOD of glucose and glutamic acid mixtures. The mixtures ranged in increments of 10% from 10% strength (90% dilution) to 100% strength (no dilution). There were 10 replications of each strength of sample, so that the BOD of 100 samples measured at daily intervals for 5 days were available. The data were tested for goodness-of-fit to three BOD reaction models: a first-order model, a half-order model, and an order-n model. The root mean squared error measured the goodness-of-fit. Twenty-six percent of the samples fit the first-order model best, 63% fit the half-order model best, and 11% fit the order-n model best.

INTRODUCTION

Reining [1] analyzed the Biochemical Oxygen Demand (BOD) kinetics of a 1:1 mixture which at full strength contained 175 g/m^3 of glucose and 175 g/m^3 of glutamic acid in a Hach Model 191 Manometric BOD apparatus (Hach Chemical Co., Ames, IA). The samples were prepared according to Standard Methods [2] with the modification that the glutamic acid was neutralized with 1 N potassium

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*Financial support was provided by a Louisiana State University Board of Regents fellowship to the senior author.

hydroxide [3]. This mixture had a theoretical oxygen demand of 357.5 g/m^3. The experimental results consisted of values of oxygen consumed at daily intervals for 5 days. The mixture of glucose and glutamic acid was prepared in 10 different strengths, respectively, 100%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, and 10% of full strength. Ten replications of each strength of sample were prepared. A major objective of this study was to determine how closely the 5-day BOD for each strength of sample compared with the theoretical oxygen demand [1]. A first-order BOD reaction model was applied in which the ultimate BOD was equated to the theoretical oxygen demand while the 10 measured values collected on day 5 yielded the mean of the 5-day BOD as 220.1 g/m^3. These two data points resulted in calculation of a first-order reaction rate coefficient of 0.191 day^{-1}. However, there were large deviations between the daily BOD predictions from the first-order model and the BOD values that were measured on days 1, 2, 3, and 4, but there was, of course, close agreement between the measured and predicted 5-day BOD values [1].

Tangpanichdee [4] analyzed an aggregation of Reining's data [1] in which the mean of the oxygen consumed values for each strength of sample were calculated on days 1, 2, 3, 4, and 5. Then these mean values were analyzed with the result that when the sample strength was 50% or greater, BOD decrease was described better by a half-order BOD equation rather than by a first-order model, while the first-order BOD model described the 10, 20, 30, and 40% strengths better as measured by the root mean squared error. The results of this analysis are shown in Table 1. The first-order BOD model had smaller mean squared errors in four cases out of ten, for the samples having 10%, 20%, 30%, and 40% strength, while the half-order model had lower mean-squared error for the remaining six higher strength samples. The mean of the mean squared error for all of the data was smaller for the half-order model. The half-order model predicted a consistent value for the ultimate BOD with a mean across all of the tests of 221.7 g/m^3, in which there was a narrow range of values from 219.5 to 224.7 g/m^3. By contrast the first-order model predicted a mean ultimate BOD of 245.7 g/m^3, but the predictions showed a trend of increasing ultimate BODs with the increasing strength of the sample so that the values ranged from a low of 211.6 g/m^3 to a high of 276.0 g/m^3. Both the first-order and the half-order rate constants exhibited a trend with the sample strength. The first-order model resulted in a mean rate constant of 0.55 day^{-1} with values ranging from 1.00 day^{-1} to 0.34 day^{-1}. The half-order model resulted in a mean rate constant of 4.70 (g/m^3)$^{1/2}$/day and a range in values from 2.50 (g/m^3)$^{1/2}$/day to 5.90 (g/m^3)$^{1/2}$/day. Thus, the half-order model fit the entire data set better than the first-order model, whether one compared the rate constant, the ultimate BOD, or the mean squared error. An early study [5] applied a graphical method based on linearizing the half-order BOD model to estimate the rate constant and the ultimate BOD from part of the data set, but a least-squares approach is recognized as having a sounder statistical basis than the graphical and linearized equation approach [6].

Table 1. Kinetic Characteristics of First-Order and Half-Order BOD Models When Applied to the Mean Values of Oxygen Uptake for Each Sample Strength[a,b]

Strength of sample	First-order kinetics			Half-order kinetics		
Percent	k_1 day^{-1}	L_0 (g/m^3)	RMSE (g/m^3)^2	$k_{1/2}$ (g/m^3)$^{1/2}$/d	L_0 (g/m^3)	RMSE (g/m^3)^2
10	1.00	211.6	0.53	2.50	224.7	2.23
20	0.61	230.3	0.72	3.10	219.5	2.24
30	0.67	228.7	1.60	4.00	223.1	2.99
40	0.59	237.5	3.80	4.50	223.7	3.82
50	0.53	246.1	7.09	5.00	224.7	5.68
60	0.42	256.7	6.56	4.80	219.8	5.47
70	0.50	245.1	7.93	5.60	219.5	6.67
80	0.45	252.1	7.01	5.80	220.2	4.73
90	0.37	273.0	13.80	5.80	221.9	11.49
100	0.34	276.0	17.08	5.90	219.4	15.35
Mean	0.55	245.7	6.61	4.70	221.6	6.07
Standard deviation	0.19	19.95	5.46	1.19	2.23	4.24

[a] Ultimate BOD, L_0, has been adjusted to the value projected for full strength.
[b] RMSE = Root-mean-squared error between the model and the data.

PURPOSE

The purpose of this investigation was to examine all of the disaggregated data set [1] in which the BOD data would be modeled as:

1. a first-order model, or
2. a half-order model, or
3. an order-n model.

The root-mean-squared error was to be the criterion by which model fit to the data were evaluated.

MODEL FORMULATION

The multi-order BOD model was formulated in differential form as

$$\frac{dL}{dt} = k_n L^n \tag{1}$$

where L is the BOD exerted, g/m^3, t is time, day, n is the dimensionless reaction order, and k_n is the rate constant, $g^{1\text{-}n}m^{3(-1)\ \text{day}-1}$ [7]. Equation (1) integrates to

$$L(t) = [L_0^{1-n} - k_n(1-n)t]^{\frac{1}{1-n}} \tag{2}$$

for n $\neq$ 1. When n = 1, equation (1) integrates to

$$L(t) = L_0 e^{-k_1 t} \tag{3}$$

where L_0 is the BOD remaining at t = 0. In the BOD test the amount of oxygen consumed, y(t), g/m^3, is measured rather than the BOD remaining, L(t), but the terms are related as $y(t) = L_0 - L(t)$. Equation (3) becomes the familiar first-order BOD model

$$y(t) = L_0(1 - e^{-k_1 t}) \tag{4}$$

while equation (2) for n $\neq$ 1 becomes

$$y(t) = L_0 - [L_0^{1-n} - k_n(1-n)t]^{\frac{1}{1-n}} \tag{5}$$

When n = ½ for the half-order reaction, equation (5) becomes

$$y(t) = L_0 - \left[L_0^{1/2} - \frac{k_{1/2}\,t}{2}\right]^2 \tag{6}$$

where $k_{1/2}$ is the rate constant, $g^{1/2}\ m^{-3/2}\ d^{-1}$.

PARAMETER ESTIMATION AND MODEL EVALUATION

The parameters k_n, L_0, and n were evaluated from the experimental data and the first-order, half-order, or order-n BOD model by using the root mean squared error criterion [6-11].

$$RMSE = \sqrt{\frac{\sum_{i=1}^{M}[y(t_i) - \hat{y}(t_i)]^2}{DOF_n}} \tag{7}$$

where $y(t_i)$ is the measured oxygen uptake value on day t_i, $\hat{y}(t_i)$ is the predicted oxygen uptake value on day t_i calculated from equations 4, 5, or 6, depending on the reaction order, M is the number of data points, and DOF_n is the number of degrees of freedom for each reaction order, with $DOF_1 = 3$, $DOF_{1/2} = 3$, and $DOF_n = 2$. Equation (7) was applicable to most of the data, but when n < 1 a special condition may arise in which all of the BOD is consumed prior to t = 5 days so that equation (7) has to be modified.

When n < 1 equation (5) is no longer applicable after a critical time which occurs when all of the BOD has been consumed. The critical time, t_c, occurs in equation (5) when the term $L_0^{1-n} - k_n (1 - n)t_c = 0$, which yields

$$tc = \frac{L_0^{1-n}}{k_n (1-n)} \tag{8}$$

For n = 1, $t_c = \infty$, but when n < 1, t_c has a finite value. t_c is not defined for n > 1. The critical time is important in evaluating BOD parameters and models as equation (5) requires

$$y(t) = L_0 \qquad \text{for } t > t_c \tag{9}$$

The root mean squared error equation for $t > t_c$ is modified to

$$RMSE = \left[\frac{1}{DOF_n} \left\{ \sum_{i=1}^{N} [y(t_i) - \hat{y}(t_i)]^2 + \sum_{N+1}^{M} [y(t_i) - L_0]^2 \right\} \right]^{1/2} \tag{10}$$

here N is the number of data points for which $t_i \leq t_c$. A suggested method for calculating t_c involves estimating the parameters using all of the data in equation (7), then estimating t_c from equation (8), and noting whether t_c was larger than the time corresponding to the last measured data point [5]. If t_c was larger, then it had no role in the analysis and equation (7) did not have to be modified to equation (10). However, if the calculated t_c was less than the time for the last data point, then the data set would be divided and equation (10) would be applied to calculate a new set of k_n, L_0, and n. These values would be applied in equation (8) and equation (10) would be reapplied. A few iterations suffice to calculate parameters k_n, L_0, and n which are consistent with t_c.

APPLICATIONS

The data [1] were analyzed as described previously. The DOF_n was set equal to M – 2 for the first- and half-order BOD models, and to M – 3 for the order-n model. In some cases a preliminary value of t_c was estimated from the data as one would see that $y(t_4) = y(t_5)$, or $y(t_3) = y(t_4) = y(t_5)$. In theses cases t_c was estimated as $t_c = t_4$ or $t_c = t_3$, respectively. After the values of k_n, L_0, and n were available, t_c was calculated from equation (8) to determine whether equation (10) had been applied correctly.

The results of the calculations of the parameters k_1, L_0; $k_{1/2}$, L_0; and k_n, L_0, n, are shown in Table 2 as well as the corresponding RMSE values. The most appropriate model had the smallest RMSE.

Table 2. BOD Parameters Calculated from the Ten Sets of Sample Data

		10% Strength			20% Strength			30% Strength		
Run #	Parameters	1st-order	n-order	Half-order	1st-order	n-order	Half-order	1st-order	n-order	Half-order
1	n	1	1.851	0.5	1	1.114	0.5	1	1.14	0.5
	L_0	22.463	24.589	24.672	41	41	41	64.338	65.202	63.999
	k	1.326	0.131	2.608	0.724	0.493	3.889	1.08	0.649	5.972
	RMSE	1.602	1.355	3.803	1.583 E-7	1.828 E-7	2.018 E-7	1.83	1.967	3.928
2	n	1	1.117	0.5	1	1.848	0.5	1	1.409	0.5
	L_0	17.60	17.86	17.836	37.368	40.504	41.794	45.714	47.751	47.861
	k	1.856	1.413	5.013	1.527	0.105	3.605	2.285	0.615	8.57
	RMSE	9.19 E-7	1.34 E-6	0.035	1.201	0.62	6.101	0.033	0.127	0.105
3	n	1	0.834	0.5	1	0.729	0.5	1	0.76	0.5
	L_0	19.334	19.085	20.979	49.079	46.724	48.287	63.769	61.577	64.589
	k	1.152	1.716	2.539	0.698	1.858	3.582	0.788	1.95	4.247
	RMSE	0.52	0.544	2.244	4.123	4.225	3.868	4.182	4.127	4.621
4	n	1	0.625	0.5	1	0.749	0.5	1	0.677	0.5
	L_0	23.875	22.458	22.61	61.79	57.226	56.597	72.352	66.928	67.774
	k	0.974	2.776	3.707	0.524	1.455	3.361	0.584	2.149	4.076
	RMSE	0.566	0.3	0.146	4.553	5.196	5.085	6.507	6.567	5.232
5	n	1	0.502	0.5	1	0.712	0.5	1	0.469	0.5
	L_0	22.516	19.686	19.679	54.122	47.914	45.174	85.579	65.093	65.675
	k	0.692	2.924	2.951	0.38	0.712	2.641	0.296	3.25	2.883
	RMSE	0.629	0.374	0.32	2.349	2.624	2.374	5.72	6.302	5.462

6	n	1	0.047	0.5	1	0.784	0.5	1	0.321	0.5
	L_0	25.93	22.11	22.274	53.975	50.56	49.618	82.813	66.448	66.54
	k	0.631	9.194	2.936	0.529	1.238	3.148	0.502	8.669	4.511
	RMSE	1.865	0.728	1.545	2.063	2.382	2.89	4.01	3.033	3.393
7	n	1	1.557	0.5	1	1.506	0.5	1	0.42	0.5
	L_0	21.03	22.407	22.987	38.816	40.844	42.943	120.105	82.833	86.241
	k	1.263	0.286	2.585	1.372	0.272	3.612	0.234	4.06	2.87
	RMSE	1.019	1.027	3.253	1.417	0.962	5.778	4.642	4.916	4.32
8	n	1	2.082	0.5	1	0.468	0.5	1	0.221	0.5
	L_0	19.78	21.562	22.437	55.259	43.319	44.101	75.002	65.395	65.494
	k	1.893	0.135	2.629	0.308	2.564	2.269	0.498	11.253	3.989
	RMSE	1.068	0.867	3.932	3.392	4.064	3.508	3.41	1.83	2.556
9	n	1	1.35	0.5	1	0.557	0.5	1	1.434	0.5
	L_0	18.967	20.371	19.2	44.992	33.491	35.256	63.332	65.748	67.037
	k	0.785	0.289	2.156	0.238	1.441	1.068	0.997	0.209	4.116
	RMSE	0.712	0.696	1.798	2.302	2.884	2.495	4.561	4.366	8.885
10	n	1	1.813	0.5	1	0.773	0.5	1	1.434	0.5
	L_0	24.768	28.741	25.487	51.115	47.794	46.944	71.238	65.748	73.583
	k	0.821	0.063	2.35	0.529	1.268	3.075	0.869	0.209	4.289
	RMSE	2.218	2.006	3.504	2.21	2.614	2.679	2.968	4.336	7.823
Mean	n	1	1.326	0.5	1	0.878	0.5	1	0.723	0.5
	L_0	21.059	22.036	22.498	45.854	44.539	44.024	68.848	65.247	66.993
	k	1.059	0.435	2.528	0.625	0.98	3.13	0.666	1.995	4.026
	RMSE	0.581	0.57	2.507	0.883	1.096	2.561	1.758	1.597	3.337

Table 2. (Cont'd.)

Run #	Parameters	40% Strength			50% Strength			60% Strength		
		1st-order	n-order	Half-order	1st-order	n-order	Half-order	1st-order	n-order	Half-order
1	n	1	0.832	0.5	1	0.755	0.5	1	0.743	0.5
	L_0	75.501	74.754	83.017	112.477	108.691	114.678	121.121	117.12	123.905
	k	1.246	2.302	5.165	0.812	2.353	5.678	0.823	2.542	5.943
	RMSE	1.708	1.336	8.899	7.354	7.347	8.892	6.77	6.169	8.096
2	n	1	1.934	0.5	1	1.445	0.5	1	1.442	0.5
	L_0	82.608	88.062	94.285	93.898	96.439	106.757	122.317	127.283	136.295
	k	2.115	0.063	5.363	1.782	0.33	5.945	1.489	0.224	6.435
	RMSE	5.559	4.958	17.357	1.643	1.229	16.323	4.953	4.06	20.261
3	n	1	0.446	0.5	1	0.607	0.5	1	0.583	0.5
	L_0	124.64	85.191	85.448	121.169	107.796	108.122	141.617	120.97	119.875
	k	0.392	6.495	5.27	0.499	3.162	4.909	0.429	3.41	4.975
	RMSE	7.559	7.885	7.041	12.805	13.167	10.922	19.356	20.721	17.439
4	n	1	0.411	0.5	1	0.161	0.5	1	0.529	0.5
	L_0	121.855	104.584	103.814	313.951	121	122.581	219.076	170.486	162.014
	k	0.436	2.4	4.639	0.146	19.615	4.567	0.224	2.989	3.6
	RMSE	14.1898	15.184	12.273	15.004	16.598	17.024	18.904	20.948	18.051
5	n	1	0.505	0.5	1	0.613	0.5	1	0.561	0.5
	L_0	119.56	92.092	91.792	144.529	119.56	115.597	160.03	127.891	123.238
	k	0.299	3.364	3.446	0.338	2.447	4.152	0.28	2.874	3.913
	RMSE	8.531	9.38	8.119	10.847	11.799	9.966	11.212	12.223	10.435

6	n	1	0.551	0.5	1	0.652	0.5	1	0.525	0.5
	L_0	104.726	89.225	89.067	126.321	110.526	107.501	184.945	144.629	142.602
	k	0.415	3.259	3.958	0.423	2.301	4.47	0.85	3.935	4.479
	RMSE	7.322	7.879	6.874	10.071	10.757	8.971	13.699	14.605	12.554
7	n	1	1.32	0.5	1	0.686	0.5	1	0.741	0.5
	L_0	76.01	79.591	77.301	141.22	121.895	120.603	218.503	191.161	169.686
	k	1.122	0.321	6.469	0.574	2.84	6.265	0.85	1.222	4.327
	RMSE	2.875	2.94	5.683	2.703	2.46	2.461	8.243	9.623	8.497
8	n	1	0.648	0.5	1	0.756	0.5	1	0.601	0.5
	L_0	105.212	96.151	96.345	125.801	121.087	126.193	217.707	169.864	158.65
	k	0.531	2.557	4.511	0.755	2.248	5.888	0.85	2.221	3.784
	RMSE	2.149	0.618	1.518	6.629	5.968	6.552	6.813	7.55	6.44
9	n	1	0.668	0.5	1	0.593	0.5	1	0.777	0.5
	L_0	97.307	88.633	88.304	107.296	94.564	94.415	122.627	115.09	112.609
	k	0.523	2.296	4.437	0.471	3.035	4.385	0.531	1.52	4.8
	RMSE	6.678	6.518	4.968	7.017	6.715	5.563	2.849	3.048	4.435
10	n	1	0.595	0.5	1	0.282	0.5	1	0.664	0.5
	L_0	124.254	99.398	94.417	207.508	111.856	112.576	164.585	142.417	136.093
	k	0.307	2.348	3.704	0.221	10.991	4.41	0.391	2.225	4.935
	RMSE	10.218	11.011	9.185	11.189	12.144	12.483	16.895	18.577	15.477
Mean	n	1	0.71	0.5	1	0.754	0.5	1	0.537	0.5
	L_0	95.705	89.246	89.916	122.039	113.951	112.088	157.702	133.517	133.061
	k	0.585	2.081	4.541	0.544	1.729	5.041	0.407	4.088	4.827
	RMSE	4.216	3.973	3.989	8.014	8.243	6.235	7.394	6.73	5.693

Table 2. (Cont'd.)

		70% Strength			80% Strength			90% Strength		
Run #	Parameters	1st-order	n-order	Half-order	1st-order	n-order	Half-order	1st-order	n-order	Half-order
1	n	1	0.661	0.5	1	0.641	0.5	1	0.669	0.5
	L_0	164.353	146.456	143.486	189.72	174.551	177.394	197.482	184.016	188.804
	k	0.46	2.556	5.362	0.579	3.533	6.512	0.627	3.348	6.867
	RMSE	9.155	8.679	6.168	13.626	12.835	10.55	17.512	17.874	15.814
2	n	1	0.881	0.5	1	1.131	0.5	1	0.501	0.5
	L_0	158.027	155.34	163.276	175.696	178.233	190.23	297.097	218.117	216.934
	k	0.872	1.525	6.662	1.15	0.621	7.529	0.266	5.036	5.117
	RMSE	3.25	3.76	13.338	3.94	4.354	21.59	19.436	20.512	17.15
3	n	1	0.83	0.5	1	0.542	0.5	1	0.243	0.5
	L_0	185.627	173.907	158.082	224.572	184.582	183.156	350.99	189.336	189.517
	k	0.433	1.076	5.657	0.381	4.656	5.751	0.188	17.077	4.8
	RMSE	21.609	24.347	19.204	27.98	30.247	25.921	15.95	17.253	16.254
4	n	1	0.54	0.5	1	0.583	0.5	1	0.551	0.5
	L_0	222.631	182.524	180.451	242.041	206.117	202.325	260.409	218.049	215.807
	k	0.363	4.432	5.412	0.387	3.776	5.715	0.396	4.833	6.303
	RMSE	11.31	10.178	8.387	12.017	12.998	10.965	18.417	17.144	13.918
5	n	1	0.664	0.5	1	0.556	0.5	1	0.549	0.5
	L_0	179.796	159.774	157.919	229.279	179.157	174.068	296.516	224.244	217.499
	k	0.458	2.609	5.431	0.311	3.801	5.174	0.253	3.647	4.79
	RMSE	11.221	12.305	11.108	26.765	29.374	25.093	14.386	15.739	13.513

6	n	1	0.892	0.5	1	0.499	0.5	1	0.696	0.5
	L_0	193.32	188.329	182.416	251.605	197.548	196.864	227.053	215.531	224.372
	k	0.595	1.037	6.539	0.333	5.509	5.531	0.709	3.369	7.82
	RMSE	11.685	12.943	10.968	20.945	21.615	18.72	20.091	19.971	17.576
7	n	1	0.729	0.5	1	0.544	0.5	1	0.583	0.5
	L_0	158,555	149.86	152.582	236.996	186.222	182.083	220.998	193.049	193.187
	k	0.637	2.347	6.002	0.317	4.109	5.227	0.458	4.196	6.139
	RMSE	3.616	3.073	6.518	18.571	19.305	16.322	17.92	19.004	16.533
8	n	1	0.718	0.5	1	0.567	0.5	1	0.414	0.5
	L_0	155.792	146.379	148.613	283.698	214.953	199.547	270.091	205.84	215.107
	k	0.637	2.4	5.845	0.188	2.415	3.589	0.286	7.439	4.709
	RMSE	3.616	4.883	7.227	11.734	12.878	10.988	14.596	13.246	12.325
9	n	1	0.669	0.5	1	0.544	0.5	1	0.56	0.5
	L_0	165.685	146.251	131.732	188.229	151.505	149.231	220.948	177.029	173.112
	k	0.276	1.497	3.549	0.34	3.855	4.785	0.31	3.5	4.717
	RMSE	3.644	3.411	2.704	15.836	17.063	14.623	8.474	9.092	7.843
10	n	1	0.903	0.5	1	0.535	0.5	1	0.449	0.5
	L_0	161.802	156.842	140.045	289.282	203.415	193.897	313.422	213.387	219.35
	k	0.453	0.742	5.363	0.193	3.159	3.922	0.225	6.052	4.599
	RMSE	16.031	18.214	13.83	20.162	22.394	19.257	14.892	15.251	13.535
Mean	n	1	0.821	0.5	1	0.578	0.5	1	0.531	0.5
	L_0	171.664	162.208	153.739	202.291	176.951	176.391	244.711	201.129	199.662
	k	0.495	1.238	5.615	0.452	4.04	5.792	0.371	4.911	5.767
	RMSE	8.862	0.518	7.429	7.867	6.444	5.361	15.397	15.062	12.794

Table 2. (Cont'd.)

		100% Strength					100% Strength		
Run #	Parameters	1st-order	n-order	Half-order	Run #	Parameter	1st-order	n-order	Half-order
1	n	1	0.715	0.5	7	n	1	0.533	0.5
	L_0	213.565	203.824	213.256		L_0	293.826	232.359	229.47
	k	0.742	3.118	7.557		k	0.325	4.866	5.82
	RMSE	13.577	13.309	15.171		RMSE	26.21	28.491	24.505
2	n	1	0.609	0.5	8	n	1	0.447	0.5
	L_0	263,176	234.736	235.619		L_0	324.816	237.426	241.994
	k	0.502	4.239	7.195		k	0.272	7.034	5.322
	RMSE	24.306	24.695	20.53		RMSE	13.737	13.41	11.951
3	n	1	0.62	0.5	9	n	1	0.406	0.5
	L_0	224.859	201.876	203.249		L_0	296.352	199.804	208.956
	k	0.52	3.915	6.855		k	0.23	7.431	4.54
	RMSE	25.86	26.904	22.309		RMSE	18.647	19.868	17.645
4	n	1	0.566	0.5	10	n	1	0.509	0.5
	L_0	369.454	271.152	256.492		L_0	292.851	227.831	226.466
	k	0.234	3.554	5.283		k	0.299	5.056	5.318
	RMSE	27.841	30.645	26.09		RMSE	7.249	6.215	5.333
5	n	1	0.509	0.5	Mean	n	1	0.527	0.5
	L_0	364.588	244.558	239.733		L_0	275.475	222.896	220.731
	k	0.194	4.222	4.526		k	0.35	5.084	5.879
	RMSE	27.314	30.492	26.363		RMSE	19.06	19.722	16.908
6	n	1	0.598	0.5					
	L_0	308.724	246.097	234.188					
	k	0.281	3.035	5.248					
	RMSE	14.4	15.795	13.463					

RESULTS

Table 2 lists the results obtained when all of the BOD data collected for each of the 10 strengths of samples were analyzed for L_0, k_n, RMSE, and reaction order-n. Each strength of sample also was analyzed for the above parameters measured from the mean values of BOD recorded each day. Table 3 summarizes the results tabulated in Table 2 by showing the number of times the first-order, half-order, and order-n BOD models had the best fit to the data for each strength of sample. Of the 100 BOD samples which were analyzed, 10 BOD samples for each strength, 22% fit the first-order BOD model best, 56% fit the half-order model best, and 22% fit the order-n BOD model best, with best fit evaluated by the root-mean-squared error criterion. When the models that fit the mean values of BOD data for each strength of sample were tabulated, 10% fit the first-order model best, 60% fit the half-order model best, and 30% fit the order-n model best.

It is apparent that the first-order and the half-order BOD models tend to have their best fit for different parts of the sample strength range. For example, the first-order model is likely to fit the data more frequently for the lower strength samples and less frequently as the sample strength increases. The half-order model

Table 3. Summary to Show How Frequently the Data Fit a BOD Model[a]

Strength of samples, %	Number of times samples had a best fit for the models, including mean		
	First-order	Half-order	n-order
10	3	2	5, M
20	7, M	1	2
30	3	3	4, M
40	1	6	3, M
50	2	4, M	4
60	2	6, M	2
70	2	7, M	1
80	1	9, M	0
90	1	9, M	0
100	0	9, M	1
Sum	22, 1M	56, 6M	22, 3M

[a] M signifies the mean values of BOD data fit this model best as measured by RMSE criterion.

is likely to fit the data frequently for all strengths of samples, but it fits most frequently as the sample strength increases. The order-n BOD model is always a second or third place contender for the best fit to the data across all sample strengths, where it is associated with the 40% and lower strength samples, although it ranked second for the 100% strength samples.

Fewer calculations are involved in fitting a model when the mean values of the BOD data are analyzed rather than all data for each sample, so it is of interest to determine how frequently the model which fit the mean values corresponded to the model that fit the individual data sets. Table 3 shows that for 90% of the sample strengths there was agreement between the most frequently found BOD model and the model found from the mean values. At 30% strength of sample the first-order or the half-order model fit all of the data, but the analysis of the mean values indicated an order-n model had the best fit. Interestingly enough, examination of Table 2 shows that the order-n model selected $n = 0.782$ as the reaction order that had the best fit. This value of n is nearly the mean value of the first-order and half-order reaction orders.

Table 4 shows the critical times that were calculated for each sample. Critical time has a meaning only when the reaction order, n, is less than 1. When the reaction order is 1 or greater the BOD reaction model shows an infinite amount of time is required for all of the BOD to be consumed. The frequency with which various reaction orders occurred are tabulated in Table 5.

Figures 1 and 2 show the behavior of the first-order BOD model parameters, including the rate constant, as a function of sample strength. Similarly, Figures 3 and 4 show the behavior of the half-order BOD model parameters, including the rate constant, as a function of sample strength. The half-order model shows less variation than the first-order model when ultimate BOD is compared with sample strength in Figures 1 and 3. The rate constants k_1 and $k_{1/2}$ show considerable variation with sample strength in Figures 2 and 4.

CONCLUSIONS

This study resulted in the following conclusions:

1. Twenty-two percent of the samples fit the first-order BOD model best, 56% fit the half-order BOD model best, and 22% fit the order-n model best when using the root-mean-squared error criterion as the measure of best fit.
2. Only five BOD measurements were available on a sample, so the number of degrees of freedom had a large effect on the calculated root-mean-squared error. The number of degrees of freedom make it more likely that the first- and half-order BOD models would fit the data better than the order-n BOD model.

Table 4. Critical Time, tc, vs. Sample Strength in which the Row Labeled Mean Shows the Parameters Calculated from Mean Values of the BOD Data

Strength of samples, %	Run no.	Half-order n = 0.5	n-Order	
			n	t_c, day
10	1	3.803	1.851	∞
	2	1.686	1.117	∞
	3	3.442	0.834	5.734
	4	2.557	0.625	3.085
	5	3.007	0.502	3.029
	6	3.204	0.047	2.084
	7	3.662	1.557	∞
	8	3.532	2.082	∞
	9	4.186	1.350	∞
	10	4.563	1.813	∞
	Mean	3.714	1.326	∞
20	1	3.293	1.114	∞
	2	3.531	1.848	∞
	3	3.817	0.729	5.630
	4	4.502	0.749	7.565
	5	5.242	0.712	8.589
	6	4.517	0.748	8.726
	7	3.539	1.506	∞
	8	5.802	0.468	5.446
	9	7.196	0.557	7.422
	10	4.496	0.773	8.357
	Mean	4.265	0.878	13.304
30	1	2.704	1.140	∞
	2	1.613	1.409	∞
	3	3.696	0.760	5.743
	4	4.014	0.677	5.487
	5	5.597	0.469	5.320
	6	3.614	0.321	2.923
	7	6.343	0.420	5.497
	8	4.054	0.221	2.961
	9	3.940	1.434	∞
	10	4.037	1.299	∞
	Mean	4.013	0.723	5.759

Table 4. (Cont'd.)

Strength of samples, %	Run no.	Half-order $n = 0.5$	n-Order	
			n	t_c, day
40	1	3.348	0.832	5.322
	2	3.50	1.934	∞
	3	3.503	0.446	3.262
	4	4.409	0.411	3.923
	5	5.569	0.505	5.633
	6	4.774	0.551	5.138
	7	2.760	1.320	∞
	8	4.347	0.648	5.546
	9	4.243	0.668	5.581
	10	5.383	0.595	6.765
	Mean	4.161	0.710	6.098
50	1	3.675	0.755	5.470
	2	3.304	1.445	∞
	3	4.230	0.607	5.067
	4	4.817	0.161	3.392
	5	5.267	0.613	6.724
	6	4.704	0.652	6.420
	7	3.525	0.686	5.064
	8	3.738	0.756	5.875
	9	4.435	0.593	5.157
	10	4.796	0.282	3.743
	Mean	4.235	0.754	7.536
60	1	3.642	0.743	5.207
	2	3.506	1.442	∞
	3	4.422	0.583	5.198
	4	7.253	0.529	7.993
	5	5.781	0.561	6.661
	6	5.370	0.525	5.685
	7	6.390	0.741	12.311
	8	6.889	0.601	8.766
	9	4.470	0.777	8.502
	10	4.837	0.664	6.988
	Mean	4.788	0.537	5.089
70	1	4.514	0.661	6.237
	2	3.742	0.881	10.042
	3	4.467	0.593	5.311
	4	4.992	0.540	5.387
	5	4.646	0.630	5.790
	6	4.094	0.666	5.274
	7	4.075	0.718	5.879
	8	4.141	0.722	6.104
	9	6.754	0.636	9.432
	10	4.439	0.620	5.575
	Mean	4.415	0.619	5.347

Table 4. (Cont'd.)

Strength of samples, %	Run no.	Half-order $n = 0.5$	n-Order	
			n	t_c, day
80	1	4.058	0.641	5.034
	2	3.546	1.131	∞
	3	4.724	0.542	5.122
	4	5.025	0.583	5.864
	5	5.201	0.556	5.927
	6	5.082	0.599	5.116
	7	5.221	0.544	5.778
	8	8.171	0.567	9.789
	9	5.145	0.544	5.614
	10	7.272	0.535	8.066
	Mean	4.593	0.578	5.204
90	1	3.951	0.669	5.067
	2	5.772	0.501	5.838
	3	5.733	0.243	4.090
	4	4.686	0.551	5.174
	5	6.252	0.549	6.979
	6	3.755	0.696	5.002
	7	4.527	0.583	5.127
	8	6.094	0.414	5.202
	9	5.642	0.560	6.342
	10	6.353	0.449	5.768
	Mean	4.919	0.531	5.219
100	1	3.779	0.715	5.120
	2	4.259	0.609	5.092
	3	4.146	0.620	5.050
	4	6.553	0.566	7.385
	5	6.910	0.509	7.169
	6	5.979	0.598	7.442
	7	5.238	0.533	5.604
	8	5.790	0.447	5.290
	9	6.226	0.406	5.271
	10	5.677	0.509	5.792
	Mean	5.079	0.527	5.360

Table 5. Summary to Show How Frequently the Data Fit a BOD Model of Various Reaction Orders

Strength of samples, %	Number of times samples had a reaction order in this range, including mean, denoted by M		
	$n = 1$	$0.5 < n < 1$	$n < 0.5$
10	6, M	3	1
20	3	6, M	1
30	4	2, M	4
40	2	6, M	2
50	1	7, M	2
60	1	9, M	0
70	0	10, M	0
80	1	9, M	0
90	0	7, M	3
100	0	8, M	2
Sum	18, 1M	67, 9M	15

3. The ultimate BOD predicted from the half-order model showed a smaller variation across the range of dilutions than the prediction from the first-order model.
4. The first-order BOD model fit the data best for 10% and 20% strength samples, while the half-order BOD model fit the data best for all other strength samples.
5. The half-order BOD model showed 65% of the samples had t_c values which indicated all of the BOD was consumed in less than 5 days, while 100% of the samples' BOD was consumed in less than 8.171 days.

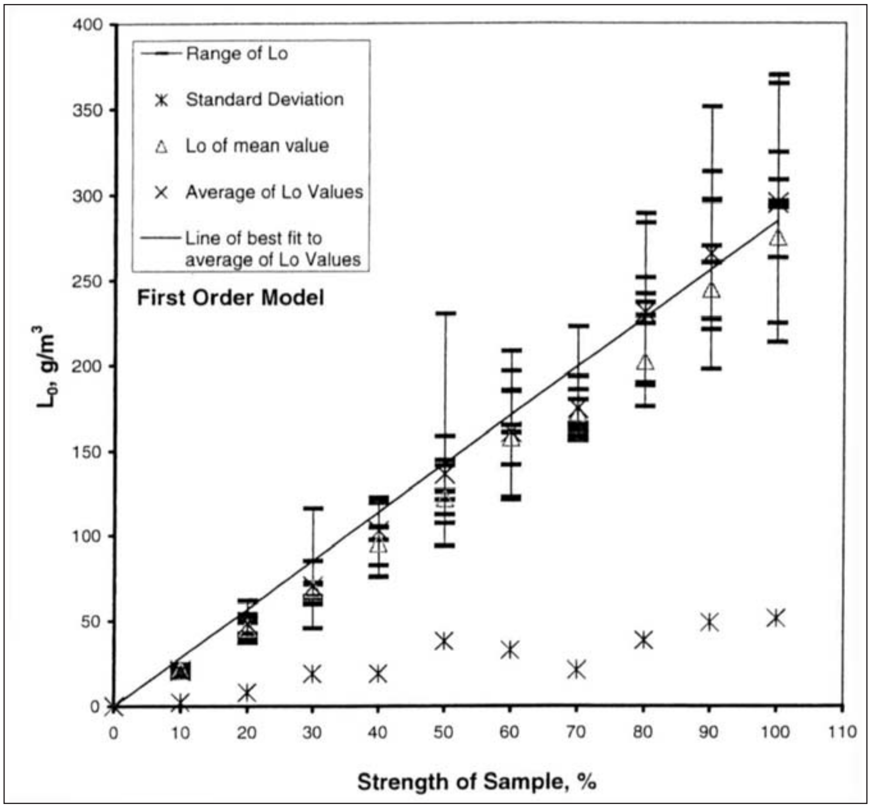

Figure 1. Behavior of first-order ultimate BOD as a function of sample strength.

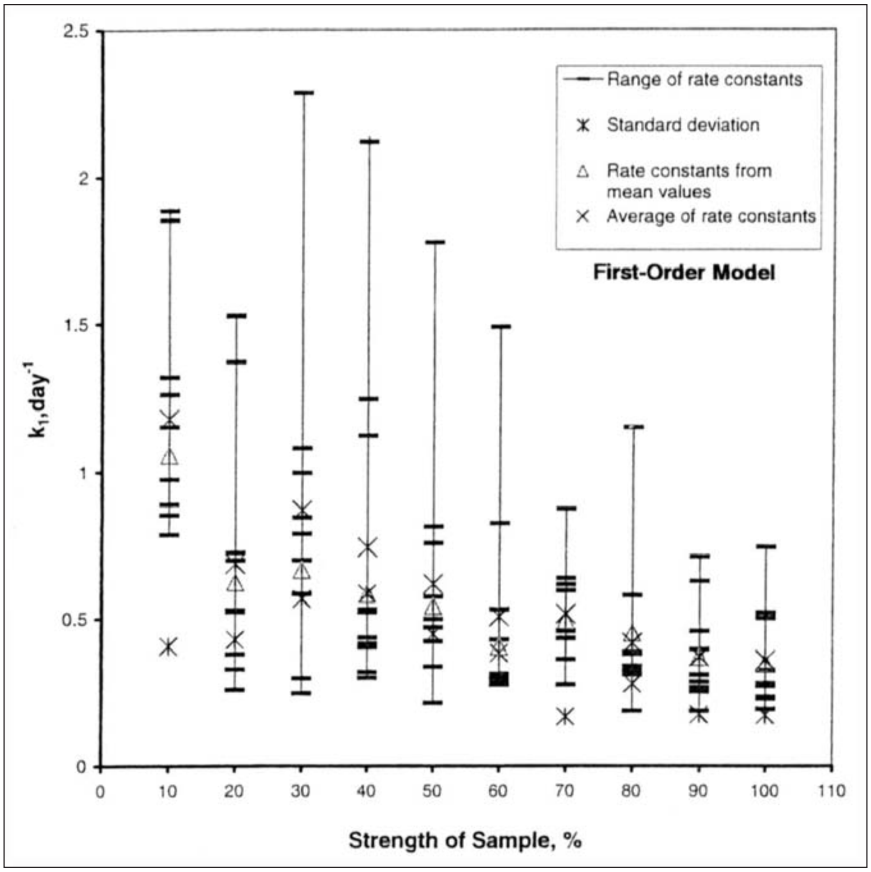

Figure 2. Behavior of first-order BOD model rate constant as a function of sample strength.

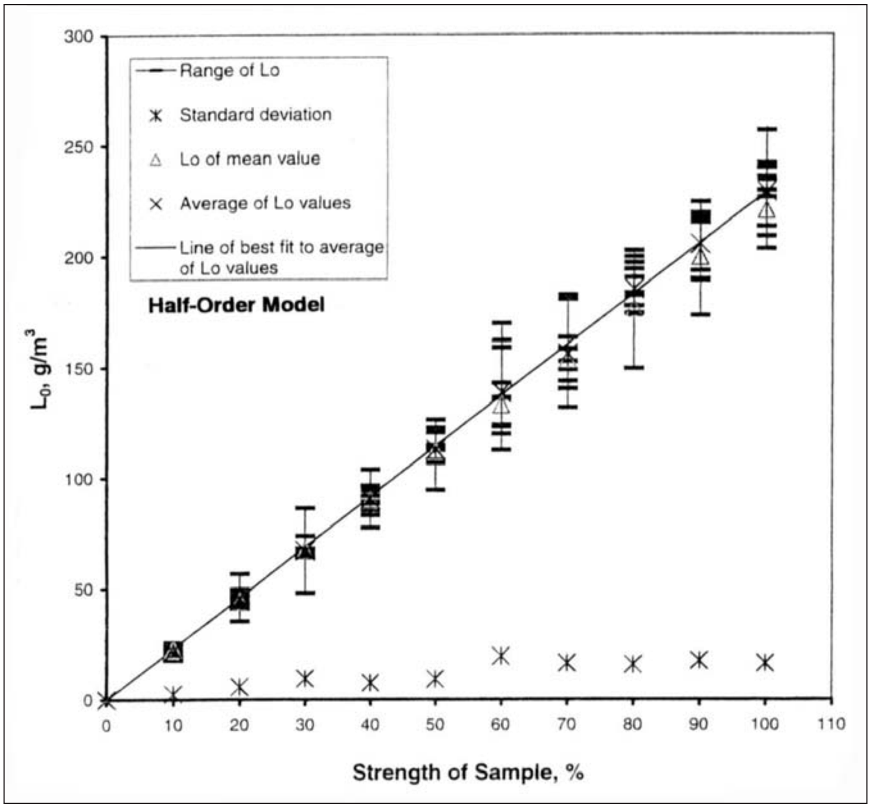

Figure 3. Behavior of half-order ultimate BOD as a function of sample strength.

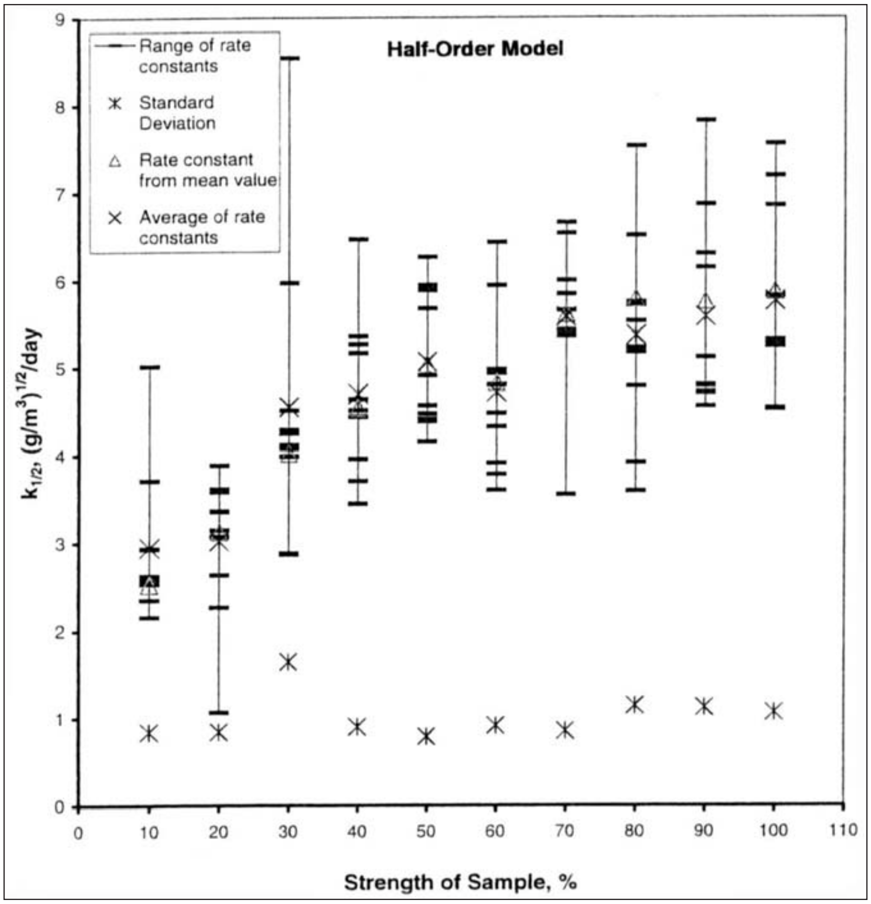

Figure 4. Behavior of half-order BOD model rate constant as a function of sample strength.

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