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A double exponential model for biochemical oxygen demand

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Abstract

Biochemical oxygen demand (BOD) exertion patterns in anaerobically treated farm dairy wastewater were investigated on a laboratory scale. Oxygen uptake was typically characterised by a period of rapid oxygen exertion, a transitional "shoulder" phase and a period of slower activity. A multi-species model, involving rapidly degradable and slowly degradable material, was developed, leading to a double exponential model of BOD exertion as follows:

$$BOD_t = BOD'_{u1}(1 - e^{-k_1 t}) + BOD'_{u2}(1 - e^{-k_2 t})$$

where t is time, BOD'_{u1} and BOD'_{u2} are apparent ultimate BOD (BOD_u) values, and k_1 and k_2 are rate constants. The model provided an improved description of BOD exertion patterns in anaerobically treated farm dairy wastewater in comparison to a conventional single exponential model, with rapidly degradable rate constant values (k_1) ranging from 2.74 to 17.36 d^{-1}, whilst slowly degradable rate constant values (k_2) averaged 0.25 d^{-1} (range 0.20–0.29). Rapidly and slowly degradable apparent BOD_u estimates ranged from 20 to 140 g/m^3 and 225 to 500 g/m^3, respectively, giving total BOD_u levels of 265–620 g/m^3. The mean square error in the curve fitting procedure ranged between 20 and 60 g^2/m^6, with values on average 70% lower (range 31–91%) than those obtained for the single exponential model. When applied to existing data for a range of other wastewaters, the double exponential model demonstrated a superior fit to the conventional single exponential model and provided a marginally better fit than a mixed order model. It is proposed that the presence of rapidly degradable material may be indicated from the value of the first rate constant (k_1) and the time to 95% saturation of the first exponential function. Further model development is required to describe observed transitional and lag phases.

Keywords: Farm dairy; Biochemical oxygen demand; Modelling; Rapidly degradable carbon; Slowly degradable carbon; Wastewater

1. Introduction

Biochemical oxygen demand (BOD) exertion during the microbiological breakdown of organic matter present in wastewaters has conventionally been described using a single exponential function (Metcalf and Eddy, 1991). The common form of the model is as follows:

$$BOD_t = BOD_u(1 - e^{-kt}), \tag{1}$$

where BOD_t is the biochemical oxygen demand exerted at time t (g/m^3), BOD_u is the ultimate biochemical oxygen demand (g/m^3), k is the first-order rate constant (d^{-1}), and t is the time (d).

This approach was based on a first-order kinetic model assumption first reported by Phelps (1909) and has been widely adopted since that time. However, many authors have cautioned against the supposition that this model adequately describes the BOD exertion behaviour of all wastewaters (Orford and Ingram, 1953; Fujimoto, 1961; Hewitt et al., 1979; Adrian and Sanders, 1992,

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1998; Borsuk and Stow, 2000). Accordingly, a number of alternative models have been proposed based on half-order (Adrian and Sanders, 1992), second-order (Young and Clark, 1965; Tebbutt and Berkun, 1976) and mixed-order (Hewitt et al., 1979; Borsuk and Stow, 2000) kinetics. The half-order and second-order models have met with limited success, however the mixed-order model as applied by Borsuk and Stow (2000) has provided an excellent fit to long-term wastewater BOD data.

As pointed out by both Swamee and Ohja (1991) and Borsuk and Stow (2000), the BOD reaction involves a complex interaction between non-uniform organic substrates and a mixed microbial population and the multi- order model was proposed to address this reality. Alternatively, in this paper we propose that the BOD reaction may be conceived as a system of concurrent, possibly interacting, individual first-order reactions, each of which, depending on the nature of the substrate groups present, would be expected to show maximum exertion at a range of times during the process of the overall reaction. The total BOD exerted at any time would be obtained from the arithmetic sum of the individual reactions viz

$$\mathrm{BOD}_t = \mathrm{BOD}_{u1}(1-\mathrm{e}^{-k_1 t}) + \mathrm{BOD}_{u2}(1-\mathrm{e}^{-k_2 t}) + \cdots + \mathrm{BOD}_{u(n)}(1-\mathrm{e}^{-k_n t}), \quad (2)$$

where $\mathrm{BOD}_{u1}, \mathrm{BOD}_{u2}, \ldots, \mathrm{BOD}_{u(n)}$ are BOD_u values corresponding to substrate groups $1, 2, \ldots, n$ and k_1, $k_2, \ldots, k_n$ are first-order rate constants corresponding to substrate groups $1, 2, \ldots, n$.

Support for a concurrent multi-exponential approach may be derived from substantial evidence in the microbiological literature that heterotrophic microorganisms, growing under both carbon limited and carbon sufficient suspended growth conditions, simultaneously utilise the range of carbon compounds available to them (Kovarova-Kovar and Egli, 1998). Furthermore, the existence of dual-nutrient-limited growth regimes (e.g., carbon and nitrogen or carbon and phosphorus) in microbial cultures has been established (Kovarova-Kovar and Egli, 1998). In relation to the appropriate number of exponential terms in the model, some initial guidance may be obtained from wastewater characterisation studies, in which biodegradable organic carbon fractions present in domestic wastewaters have been classified as readily degradable and slowly degradable (Ekama and Marais, 1979; Dold et al., 1980). Henze (1992) further classified domestic wastewater components into readily biodegradable, readily hydrolysable, slowly hydrolysable, soluble inert and insoluble inert materials. Readily biodegradable material present in raw domestic wastewater typically includes specific compounds such as low molecular weight volatile fatty acids (VFAs), which may account for 50–70% of the readily biodegradable fraction (Henze, 1992) and initial oxygen uptake rates for most readily biodegradable substrates, as measured in the BOD test, have been reported as 10–20 times those occurring during the subsequent endogenous phase (Eckenfelder, 1989). A multi-exponential model would allow an estimation of the type and relative amount of readily degradable material present on the basis of the magnitude of the first stage rate constant (k_1) and the associated BOD_u.

Application of a double exponential approach to the analysis of oxygen uptake data obtained from respirometric studies on raw sewage sludge and pine sawdust was outlined by Haug (1993), who stated that improved accuracy of fit to that obtained with the conventional single exponential model could sometimes be obtained by division of substrates into fractions with different first-order rate constants. Raw domestic sludge biodegradable volatile solids were divided into a 19% "fast" fraction (rate constant $0.15\,\mathrm{d}^{-1}$) and an 81% "slow" fraction (rate constant $0.05\,\mathrm{d}^{-1}$) in one case and a 40% "fast" fraction (rate constant $0.015\,\mathrm{d}^{-1}$) and a 60% "slow" fraction (rate constant $0.004\,\mathrm{d}^{-1}$) in a second example. For pine sawdust a "fast" fraction of 71% and a "slow" fraction of 29% were chosen, with corresponding rate constants of 0.15 and $0.02\,\mathrm{d}^{-1}$ respectively. No further details of the methodology used or analysis of the accuracy of fit were presented however.

Estimation of both k and BOD_u have been carried out using various techniques (Moore et al., 1950; Tsivoglou, 1958; Sheehy, 1960; Fujimoto, 1961) including least squares methods (Thomas, 1950; Hewitt and Hunter, 1975; Hewitt et al., 1979). Bayesian approaches (Constable and McBean, 1977; Borsuk and Stow, 2000) have also been reported.

BOD data have historically been important in both wastewater treatment process and natural water quality applications, and continue to be utilised. However, given the limited time frames over which data sets are typically available, and the fact that tests are rarely run to completion, mathematical techniques for the prediction of maximum cumulative oxygen uptake (i.e., BOD_u) are required, and good estimates of k values necessary for model implementation.

In this research we propose that the pattern of BOD exertion in anaerobically pre-treated farm dairy wastewater may be described as combination of two concurrent first-order kinetic reactions. The model assumes the presence of rapidly degradable substrate (material 1), plus slowly degradable substrate (material 2), which degrades to rapidly degradable products (material 1). If first-order dynamics are assumed for both decay processes, then the rate equations are as follows:

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = k_3 c_2 - k_1 c_1 \quad (3)$$

and

$$\frac{\mathrm{d}c_2}{\mathrm{d}t} = -k_2 c_2, \quad (4)$$

where c_1 is the rapidly degradable BOD remaining (g/m^3), c_2 is the slowly degradable BOD remaining (g/m^3), $k_{1,2}$ are the first-order decay constants (d^{-1}) and k_3 is the first-order formation constant for rapidly degradable material arising from slowly degradable material d^{-1}).

Integrating these equations gives:

$$c_1(t) = \frac{k_3 c_2(0)}{(k_2 - k_1)} e^{-k_2 t} + \left(c_1(0) - \frac{k_3 c_2(0)}{(k_2 - k_1)}\right) e^{-k_1 t}, \tag{5}$$

where $c(t)$ is the BOD present at any time t (g/m^3) and $c(0)$ is the BOD present at zero time (g/m^3).

Since

$$c(t) = \mathrm{BOD}_u - \mathrm{BOD}_t \tag{6}$$

and

$$c(0) = \mathrm{BOD}_u \tag{7}$$

then

$$\mathrm{BOD}_{t1} = \mathrm{BOD}_{u1} - \left(\mathrm{BOD}_{u1} - \frac{k_3 \mathrm{BOD}_{u2}}{(k_2 - k_1)}\right) e^{-k_1 t} - \left(\frac{k_3 \mathrm{BOD}_{u2}}{(k_2 - k_1)}\right) e^{-k_2 t}, \tag{8}$$

and since

$$c_2(t) = c_2(0) e^{-k_2 t} \tag{9}$$

then

$$\mathrm{BOD}_{t2} = \mathrm{BOD}_{u2}(1 - e^{-k_2 t}). \tag{10}$$

Therefore and noting that $k_1 > k_2$:

$$\mathrm{BOD}_t = \mathrm{BOD}_{u1} - \left(\mathrm{BOD}_{u1} + \frac{k_3 \mathrm{BOD}_{u2}}{(k_1 - k_2)}\right) e^{-k_1 t} + \left(\frac{k_3 \mathrm{BOD}_{u2}}{(k_1 - k_2)}\right) e^{-k_2 t} + \mathrm{BOD}_{u2} - \mathrm{BOD}_{u2} e^{-k_2 t}. \tag{11}$$

Re-arranging, and inserting the term containing k_3 into each of the large brackets below, gives

$$\mathrm{BOD}_t = \left(\mathrm{BOD}_{u1} + \frac{k_3 \mathrm{BOD}_{u2}}{(k_1 - k_2)}\right)(1 - e^{-k_1 t}) + \left(\mathrm{BOD}_{u2} - \frac{k_3 \mathrm{BOD}_{u2}}{(k_1 - k_2)}\right)(1 - e^{-k_2 t}). \tag{12}$$

Eq. (12) may now be simplified to

$$\mathrm{BOD}_t = \mathrm{BOD}'_{u1}(1 - e^{-k_1 t}) + \mathrm{BOD}'_{u2}(1 - e^{-k_2 t}), \tag{13}$$

where BOD'_{ui} is the apparent BOD_{ui}.

For Eqs. (12) and (13), as time tends to infinity, then

$$\mathrm{BOD}_t = \mathrm{BOD}'_{u1} + \mathrm{BOD}'_{u2} = \mathrm{BOD}_{u1} + \mathrm{BOD}_{u2}. \tag{14}$$

We also show that

$$\frac{\mathrm{BOD}'_{u1}}{\mathrm{BOD}'_{u2}} = \frac{\left(\mathrm{BOD}_{u1} + \frac{k_3}{(k_1 - k_2)} \mathrm{BOD}_{u2}\right)}{\left(\mathrm{BOD}_{u2} - \frac{k_3}{(k_1 - k_2)} \mathrm{BOD}_{u2}\right)}. \tag{15}$$

Thus the relationship between actual and apparent BOD_u values is

$$\frac{\mathrm{BOD}_{u1}}{\mathrm{BOD}_{u2}} = \frac{\mathrm{BOD}'_{u1}}{\mathrm{BOD}'_{u1}}\left(1 - \frac{k_3}{(k_1 - k_2)}\right) - \left(\frac{k_3}{(k_1 - k_2)}\right). \tag{16}$$

Farm dairy wastewater arises from milk harvesting activities carried out on dairy farms. In New Zealand, dairy farming is an intensive pasture based production system, with animals generally kept outdoors throughout the year. Milk harvesting typically occurs twice daily over 1–3 h/day, during which time animals are held on a concrete surfaced yard prior to entry to the farm dairy. Washdown of the milking and yard areas also takes place twice daily, with typical water usage estimated at 0.05 m^3/animal d, with a range of 0.03–0.07 m^3/animal d (Heatley, 1996). The mixed raw wastewater contains manure, spilt milk, feed and cleaning chemicals. Pretreatment may comprise a coarse screen and/or stone trap, followed by a waste stabilisation pond system and/or land treatment. A two-stage anaerobic plus facultative waste stabilisation pond system has been widely used to provide farm dairy wastewater treatment prior to discharge to natural waters (Dakers, 1979; Dakers and Painter, 1983; Hickey and Quinn, 1992). The standard design loading rate range for anaerobic ponds in New Zealand has been 0.020–0.028 kg-BOD$_5$/m^3 d (Vanderholm, 1984; Heatley, 1996), with reported effluent quality ranging from 159 to 240 g-BOD$_5$/m^3 (Warburton, 1979; Mason, 1997).

2. Methods

2.1. Location

Anaerobically pretreated wastewater was obtained from a waste stabilisation pond system treating wastewater from a farm dairy located at Massey University, Palmerston North, New Zealand (latitude 40°S). A herd of up to 500 pasture fed Friesan cows, of average weight 500 kg, was milked twice daily in the farm dairy. Resulting wastewater from yard washing was pre-treated by coarse screening and then discharged to the pond system, whilst wastewater from the milking area was discharged directly to the sewer downstream of the screen. The anaerobic pond had water surface dimensions of 31.5 m by 27.7 m, with side batters of approximately 2:1 (h:v) and was 4.6 m deep at the centre, giving a nominal volume of 1900 m^3. The design organic loading rate for the pond was 0.024 kg-BOD$_5$/m^3 d. The anaerobic pond also received stormwater runoff from an adjacent feed pad area, along with small quantities of manure and spilt feed. However, the majority of feed pad waste was removed mechanically. Seasonal milking activity ceased on 19.06.01 and recommenced on 01.08.01.

2.2. Sampling and preservation

Samples were collected at 15–18 day intervals from 29.05.01 (day 1) until 22.08.01 (day 86). A 5 l sample of treated wastewater from the anaerobic pond effluent was collected from the pond outlet pipe using manual grab sampling. Samples were returned to the laboratory within 30 min of collection and analyses for BOD commenced immediately.

2.3. Analyses

Carbonaceous BOD (CBOD) was determined according to a proposed respirometric procedure (Clesceri et al., 1998), using a Hach BODTrak apparatus (Hach Chemical Company, Loveland, Colorado, USA). Nitrification was inhibited with Hach nitrification inhibitor and distilled water blanks run along with all analyses. BOD readings were automatically recorded at 0.02–0.03 d (29–43 min) intervals for 10.5 days. Calibration of the BODTrak unit was carried out using a mixture of 150 g/m^3 each of glucose and glutamic acid, seeded with 10% (v/v) anaerobic pond effluent. Corrected standard BOD_5 values on five replicate glucose/glutamic acid samples averaged 207 g/m^3 (range 204–214 g/m^3) which was within the acceptable range of 198 ± 30.5 g/m^3 (Hach Chemical Company, Loveland, Colorado, USA). All remaining BOD analyses were conducted in duplicate. The apparatus and power supply were checked for electronic "noise" and found to be within normal limits.

2.4. Modelling

BOD data were fitted to single and double exponential expressions of the forms shown in Eqs. (1) and (13) above, by a least squares technique, using "Matlab" (The Mathworks Inc., Natick, Mass., USA). Accuracy of fit was determined from the mean square error (MSE) of the differences between the modelled and experimental data points, and the times to 95% exertion of BOD (t_n (95%)) for each function in the double exponential model also calculated.

3. Results

3.1. Anaerobic pond effluent

Oxygen demand curves for anaerobic pond effluent showed a distinctive, three-phase profile, comprising an initial period of rapid oxygen uptake, a shoulder-like transition phase and then an extended period of slower oxygen uptake activity (Fig. 1). This pattern was observed throughout the study period. The existence of similar patterns for carbonaceous BOD, comprising two oxygen uptake phases separated by a plateau, was reported by Swamee and Ohja (1991). Individual data points demonstrated a degree of scatter or "noise" which was not attributable to the instrument or to the power supply.

The double exponential model was found in all cases to provide a markedly superior fit to the data when compared to the single exponential function (Fig. 1 and Table 1). The fit was particularly improved at early time (Fig. 1a and c) and slight differences were also apparent toward the end of the slower oxygen uptake period. Mean square error values for the double exponential model ranged between approximately 20 and 60 g^2/m^6 (Table 1) and were on average 70% lower (range 31–91%) than those obtained for the single exponential model.

Rate constants for the first function in the double exponential expression varied widely, ranging from 2.74 to 17.36 d^{-1} (Table 1), with a mean value of 7.27 d^{-1}. Replication was relatively close on days 17, 52 and 70 however, with both values within ±2.3–4.9% of the mean, but a much wider variation, with values varying by as much as ±21.7–34.7% of the replicate means, occurred on days 1, 35 and 86. Values for the slowly degradable rate constant (k_2) showed less variability, with a range of 0.20–0.29 d^{-1} (Table 1) and a mean of 0.25 d^{-1}. Replicate values in this case were typically close throughout the study period, with a range of ±0.30–6.9% around the replicate means, except on day 86, when the variation was ±15.1%. In the case of apparent rapidly degradable ultimate BOD (BOD'_{u1}) estimates, these showed a wide degree of variation, from 20 to 140 g/m^3 over the study period. Values on day 86 were atypically high however and with the exception of one of the replicates on day 1, relatively consistent values, within the range 34–58 g/m^3, were obtained during days 1 and 70 (Table 1). It should be noted, in relation to the results for day 86, that milking activity recommenced between days 70 and 86, with a consequent increase in pond loading. Apparent slowly biodegradable ultimate BOD (BOD'_{u2}) estimates varied from 225 to 500 g/m^3 over the entire study period and from 225 to 320 g/m^3, between days 1 and 70. Predicted total apparent BOD_u levels were thus 265–620 g/m^3 (Table 1).

Calculated times to reach 95% saturation of each of the functions in the double exponential model averaged 0.54 d (range 0.17–1.09) and 12.31 d (range 10.17–15.23) respectively (Table 1). Maximum modelled reaction rates for the rapid oxygen uptake phase averaged 339 g/m^3 d (range 54–621) whilst the corresponding rates for the second exponential function averaged 76 g/m^3 d (range 54–147) (Table 2).

Differences in both predicted BOD_u and BOD_u:BOD_5 ratios between the two models were marked, with higher values predicted by the double exponential model in each case (Tables 1 and 3). The BOD_u:BOD_5 ratios aris-

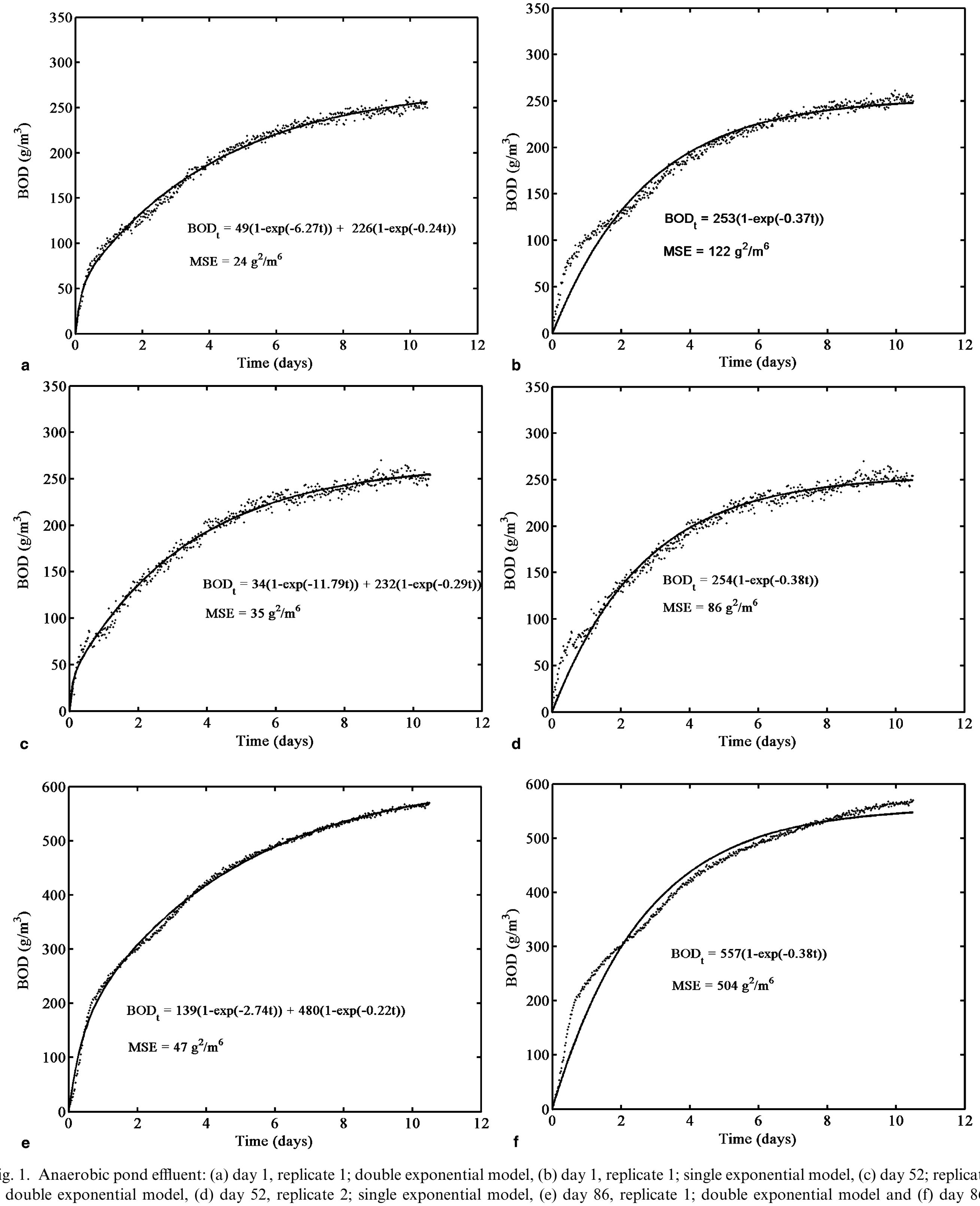

Fig. 1. Anaerobic pond effluent: (a) day 1, replicate 1; double exponential model, (b) day 1, replicate 1; single exponential model, (c) day 52; replicate 2; double exponential model, (d) day 52, replicate 2; single exponential model, (e) day 86, replicate 1; double exponential model and (f) day 86, replicate 1; single exponential model.

ing from the double exponential model averaged 1.34:1, approximately 9% lower than the standard ratio of 1.47:1 quoted for domestic wastewater (Metcalf and Eddy, 1991).

Table 1
Double and single exponential model parameters: anaerobic pond effluent

Day	Replicate	Double exponential model								Single exponential model		
		k_1 (d^{-1})	k_2 (d^{-1})	BOD'_{u1} (g/m^3)	BOD'_{u2} (g/m^3)	BOD_u (g/m^3)	MSE (g^2/m^6)	t_1 (95%) (d)	t_2 (95%) (d)	k (d^{-1})	BOD_u (g/m^3)	MSE (g^2/m^6)
1	1	6.27	0.24	49	226	275	24	0.48	12.59	0.37	254	122
	2	3.04	0.24	18	260	278	21	0.98	12.67	0.28	268	30
17	1	5.84	0.20	58	309	367	37	0.51	15.23	0.31	330	191
	2	5.30	0.22	46	302	348	36	0.56	13.58	0.31	323	126
35	1	8.54	0.26	34	247	281	36	0.35	11.40	0.35	267	87
	2	17.36	0.28	36	242	278	41	0.17	10.73	0.37	265	106
52	1	11.26	0.25	46	245	291	23	0.27	11.86	0.37	272	122
	2	11.79	0.29	34	232	266	35	0.25	11.33	0.38	254	86
70	1	5.50	0.26	40	319	359	45	0.54	11.58	0.33	342	108
	2	5.91	0.23	48	321	369	44	0.51	12.80	0.32	345	140
86	1	2.74	0.22	139	480	619	47	1.09	13.80	0.38	557	504
	2	3.64	0.29	114	500	613	61	0.82	10.17	0.43	581	382

Note: $BOD_u = BOD'_u$ (Eq. (14)).

Table 2
Modelled BOD reaction rates and BOD exertion at t_1 (95%): anaerobic pond effluent

Day	Replicate	Maximum BOD reaction rates		
		$k_1 \times BOD'_{u1}$ (g/m^3 d)	$k_2 \times BOD'_{u2}$ (g/m^3 d)	Ratio
1	1	308	54	5.7
	2	54	62	0.9
17	1	339	61	5.6
	2	245	67	3.7
35	1	293	65	4.5
	2	621	68	9.2
52	1	517	62	8.3
	2	397	67	5.9
70	1	221	82	2.7
	2	282	75	3.7
86	1	382	104	3.7
	2	414	147	2.8

Table 3
Double and single exponential model BOD_u:BOD_5 ratios: anaerobic pond effluent

Day	Replicate	Double exponential model		Single exponential model	
		BOD_5 (g/m^3)	BOD_u:BOD_5	BOD_5 (g/m^3)	BOD_u:BOD_5
1	1	205	1.33	215	1.19
	2	200	1.40	200	1.34
17	1	250	1.46	260	1.27
	2	250	1.40	255	1.27
35	1	215	1.31	220	1.22
	2	220	1.27	220	1.19
52	1	220	1.31	230	1.19
	2	210	1.26	215	1.18
70	1	270	1.32	280	1.23
	2	270	1.37	280	1.25
86	1	460	1.35	475	1.17
	2	500	1.23	510	1.14

3.2. Other wastewaters

Raw farm dairy wastewater carbonaceous BOD data (Ellwood, 1997) was modelled using both the single and double exponential approaches. A markedly improved visual fit and substantially lower mean square error values, with an average reduction of 86%, were obtained when using the double exponential model (Fig. 2 and Table 4).

Similar results were obtained when the domestic wastewater data of Orford and Ingram (1953) were modelled (Fig. 3). The double exponential provided a significantly improved fit (MSE 0.57), when compared to the conventional single exponential model (MSE 17.32), a reduction of 97%. The double exponential model also predicted slightly higher BOD_u values (5–6%) than either the single exponential model or the prediction made by Fujimoto (1961), using the same data. It was noted that the first-order rate constant of 0.28 d^{-1} obtained in the present simulation was somewhat higher than the value of 0.23 d^{-1} (0.1 d^{-1} with base 10) predicted by Fujimoto (1961). However, the poor fit of early time data in this case was in fact noted by Fujimoto, who commented that "it is suggested that in the early stage of biochemical oxidation the reaction proceeds faster than the first-order reaction with $k = 0.1$".

Four sets of long term (140 d) wastewater total BOD data presented by Borsuk and Stow (2000) were successfully modelled using the double exponential approach (Fig. 4). Mean square error values were marginally improved in three out of four cases and slightly higher in one case, when compared to the values reported for a multi-order model (Table 5). Since total BOD (rather than CBOD) was measured and the BOD values were low, it is likely that nitrogenous BOD was included the oxygen uptake patterns shown.

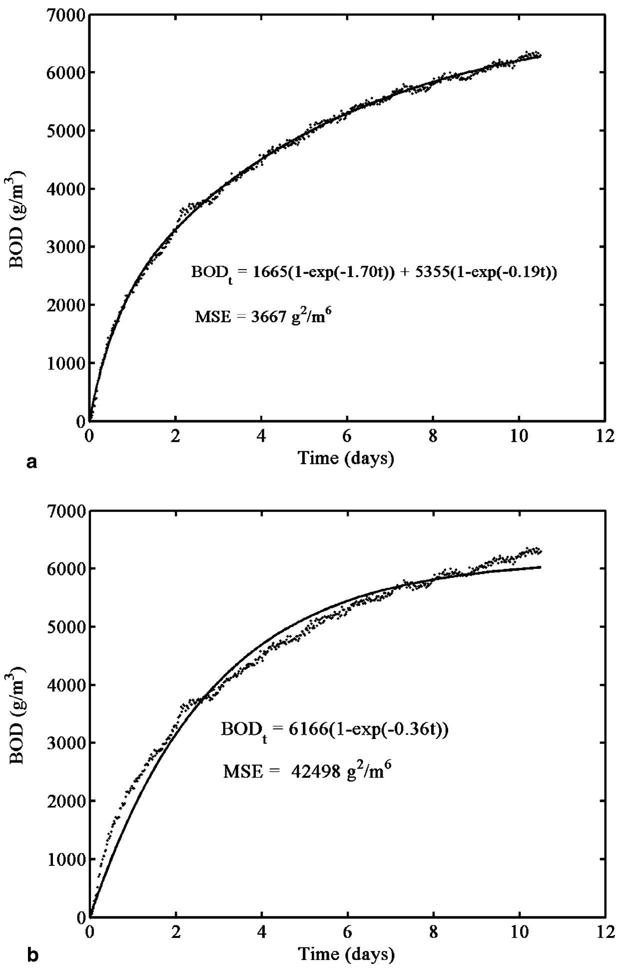

Fig. 2. Raw farm dairy wastewater; data of Ellwood (1997), 27.11.96, replicate 1: (a) double exponential model and (b) single exponential model.

Table 4
Mean square error values for the double exponential model vs the single exponential model; raw farm dairy wastewater: data of Ellwood (1997) (g^2/m^6)

Sample date	Replicate	Double exponential model	Single exponential model
27.11.96	1	3670	42,500
	2	4540	43,605
11.12.96	1	38,270	117,890
	2	12,985	127,430
	3	7890	73,620

4. Discussion

4.1. Modelling

The double exponential model provided a substantially improved fit to oxygen uptake data, for a range of wastewater types and degrees of treatment, in comparison to the conventional single exponential

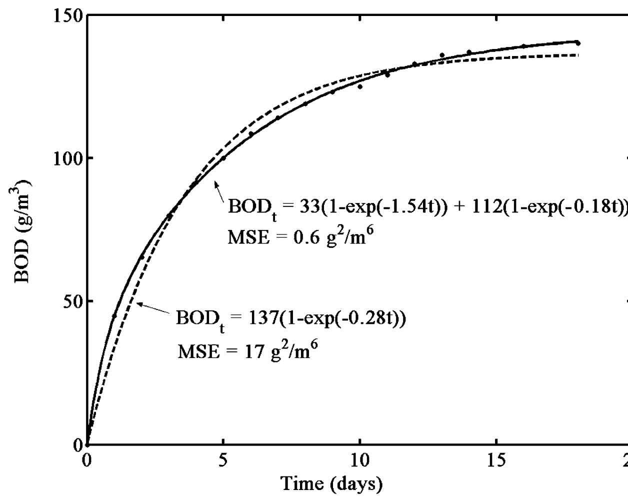

Fig. 3. Domestic wastewater; data of Orford and Ingram (1953); double and single exponential models.

approach. This suggested that the previously discussed mechanistic basis for the model, involving the simultaneous utilisation of mixed substrates (Kovarova-Kovar and Egli, 1998) and the concept of rapidly and slowly degradable fractions in wastewater (Ekama and Marais, 1979; Dold et al., 1980) was appropriate. However, the model was not conclusively validated from a conceptual viewpoint, since several other approaches would also predict double exponential functions. For example, micro-organisms have a number of complex multi-stage pathways available for the initial metabolism of complex substrates and the observed BOD at any time may therefore be derived as the sum of many exponentials. Nonetheless, if two of these functions were more significant than the others, the double exponential would still provide a good fit. We believe, therefore, that this flexibility provides further support for the double exponential approach and that it is better to first posit a multi-species model with simple linear interactions, than a lumped material model with more complicated, nonlinear decay functions, as in the mixed-order approach.

The consistent improvement obtained over the single exponential model further suggested that the double exponential model could be preferentially applied in the analysis of BOD data. In cases where the data were adequately modelled by a single exponential function, the double exponential model would indicate this through the estimation of identical rate constants.

However, certain specific portions of the oxygen uptake curves for anaerobic pond effluent were not closely modelled by the double exponential function. In particular, the transitional "shoulder", observed in all cases, the latter portion of the rapid uptake phase and the initial lag phase, observed on day 86 (Fig. 1e), were inadequately described. The ability of micro-organisms to sense and respond to chemical concentration gradients

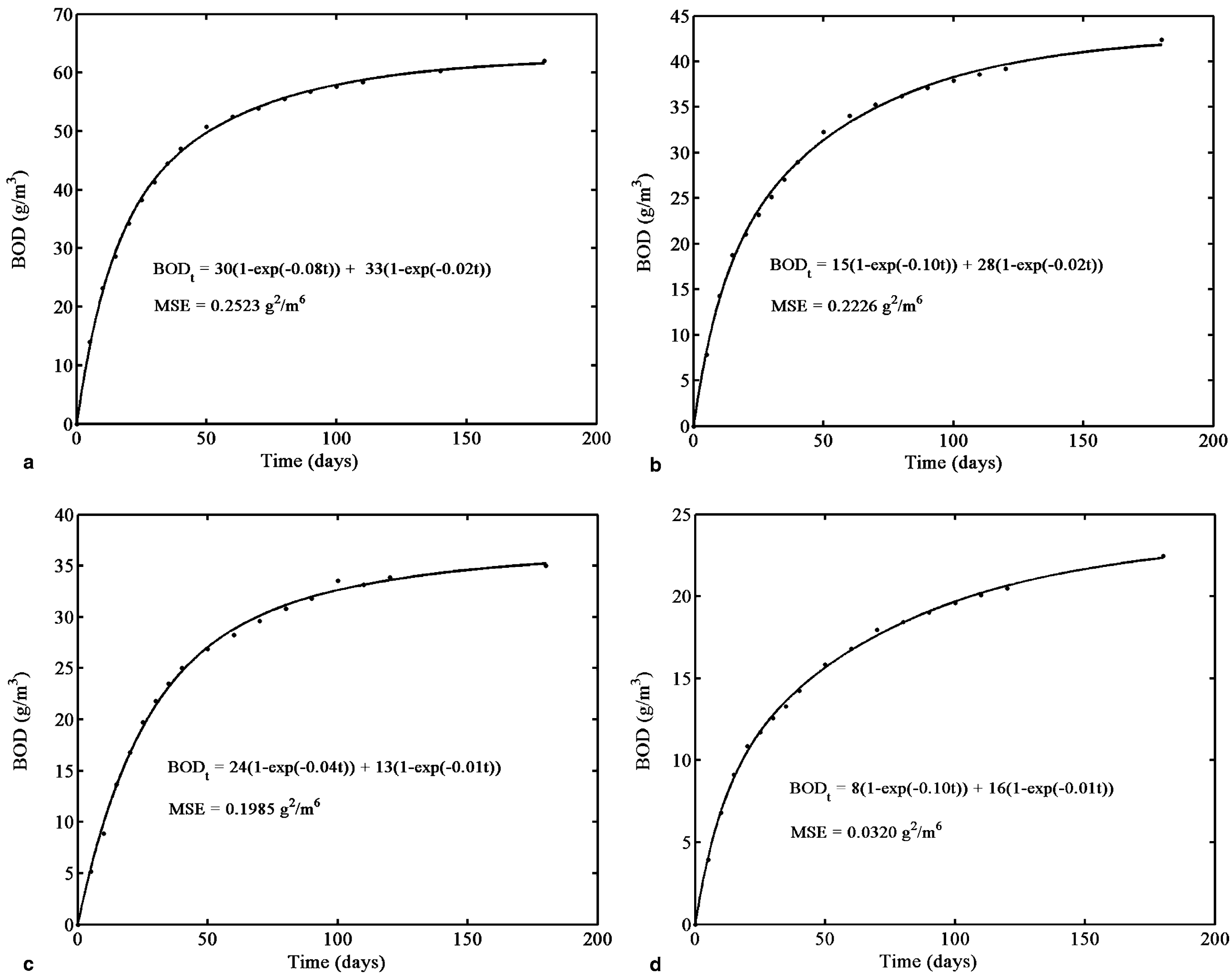

Fig. 4. Data of Borsuk and Stow (2000), double exponential model: (a) Package plant effluent. (b) Industrial effluent. (c) WWTP-city effluent. (d) WWTP-rural effluent.

Table 5
Mean square error values for the double exponential model vs the multi-order model of Borsuk and Stow (2000) (g^2/m^6)

Sample	Double exponential model	Borsuk and Stow (2000)
Package plant	0.2523	0.2270
Industrial effluent	0.2226	0.2444
WWTP-city	0.1985	0.2231
WWTP-rural	0.0320	0.0449

and switch their behaviour accordingly (e.g. chemotaxis) is well established in the literature (Manson et al., 1998). In this context, the transitional "shoulder" phase may reflect the response of micro-organisms to decreasing concentrations of rapidly degradable substrate and consequent preparation for entry into anticipated stationary phase. This phenomenon has been observed in *Mycobacterium smegmatis*, where cells entered stationary phase prior to complete depletion of the glycerol carbon source provided (Smeulders et al., 1999). The remaining substrate was subsequently utilised during stationary phase. Thus the transitional phase observed here may represent the effect of metabolic switching from predominantly rapidly degradable to principally slowly degradable substrate groups. A mathematical description of this phenomenon and the initial lag phase observed requires further model development.

When applied to a more unconventional situation, in which the pattern of BOD exertion was unusually slow and furthermore, did not show a clear separation into fast and slow time scales (data of Borsuk and Stow, 2000), the double exponential model provided a very good fit, as discussed above. However, since the multi-order model provided nearly as good a fit with only three parameters, as the double exponential did with four parameters, we cannot say conclusively which is the best model for this situation from a mathematical viewpoint.

4.2. Estimation of readily degradable material

We propose that the presence of readily degradable carbon may be indicated by the magnitude of the rate constant in the first exponential function. Analysis of the data of Orford and Ingram (1953) indicated a k_1 value of $1.53\ d^{-1}$, whilst the minimum k_1 values for anaerobic pond effluent and raw farm dairy wastewater in the present work were 2.74 and $1.04\ d^{-1}$, respectively. These rate constants were all significantly different from the corresponding k_2 values and the data was reasonably well fitted by the double exponential model. Associated times to 95% saturation of the first function ranged from 0.17 to 1.95 d, providing an indication of the time taken to exhaust the bulk of the rapidly degradable material. Whilst an absolute threshold between rate constants for the metabolism of readily and slowly degradable material was not established in this research, it seems reasonable to propose that substantial quantities of readily degradable material will be indicated by k_1 values above $1.00\ d^{-1}$ and times to 95% saturation of the first function (t_1 (95%)) less than 2 d.

Fitting a double exponential model to observed BOD data allowed estimation of the two rate constants k_1 and k_2, and the saturation constants BOD'_{u1} and BOD'_{u2}, but not the three independent parameters k_3, BOD_{u1} and BOD_{u2}. That is, we cannot directly determine the initial amounts of rapidly, and slowly, degradable materials. However, since k_2 and k_3 will likely have similar values, then an indication of the ratio of the independent saturation constants may be determined if, for exploratory purposes, these two rate constants are assumed to be equal. Proceeding on this assumption, the ratio $k_3/(k_1 - k_2)$ for anaerobic pond effluent averaged 0.05 with a range of 0.02–0.09 and the corresponding ratios of BOD_{u1}:BOD_{u2} averaged 0.11 (range −0.02 to 0.18) (Table 6). If the single negative value is ignored then the values become 0.13 with a range of 0.07–0.18. Since BOD_u is known, the actual amounts of BOD_{u1} and BOD_{u2} may then be calculated, and the initial quantities of rapidly degradable and slowly degradable material assessed.

Table 6
Estimated ratios of BOD_{u1} and BOD_{u2} (for $k_3 = k_2$)

Day	Replicate	$k_3/(k_1 - k_2)$	BOD'_{u1}/BOD'_{u2}	BOD_{u1}/BOD_{u2}
1	1	0.04	0.22	0.17
	2	0.08	0.07	−0.02
17	1	0.03	0.19	0.15
	2	0.04	0.15	0.10
35	1	0.03	0.14	0.10
	2	0.02	0.15	0.13
52	1	0.02	0.19	0.16
	2	0.02	0.14	0.12
70	1	0.05	0.13	0.07
	2	0.04	0.15	0.10
86	1	0.09	0.29	0.18
	2	0.09	0.23	0.12

A further indication of the presence of rapidly degradable material may be obtained from consideration of oxygen uptake rates. For anaerobic pond effluent, maximum modelled oxygen uptake rates for each function, representing apparent rapidly degradable and slowly degradable material, averaged 339 and 76 g/m^3 d respectively, giving a mean ratio of 4.7:1 (range 0.9–9.2) (Table 2). These ratios are somewhat less than the 10–20 range reported by Eckenfelder (1989), most likely due to the failure of the double exponential model to precisely model oxygen uptake at early time.

5. Conclusions

Oxygen demand curves generated for anaerobically treated farm dairy effluent showed a distinctive, three-phase profile, comprising an initial period of rapid oxygen uptake, a shoulder-like transition phase and then an extended period of slower oxygen uptake activity.

A double exponential model, in which rapidly degradable and slowly degradable material were represented by separate functions, provided a markedly improved statistical and visual fit to BOD exertion data for anaerobically treated farm dairy wastewater, in comparison to the fit provided by a single exponential model. The mean square error in the double exponential curve fitting procedure ranged between 20 and 60 g^2/m^6, with values on average 70% lower (range 31–91%) than those obtained for the single exponential model. Rapidly degradable rate constant values for anaerobically treated farm dairy wastewater ranged from 2.74 to $17.36\ d^{-1}$, whilst slowly degradable rate constant values (k_2) averaged $0.25\ d^{-1}$ (range 0.20–0.29). Corresponding rapidly and slowly degradable apparent BOD_u estimates ranged from 20 to 140 g/m^3 and 225 to 500 g/m^3, respectively, giving total BOD_u levels of 265–620 g/m^3.

The double exponential model provided an improved fit to raw farm dairy wastewater and to domestic wastewater oxygen uptake data in comparison to that obtained using a conventional single exponential model, with reductions in MSE of 86% and 97% respectively. A marginally improved fit to a range of wastewater data was found in comparison to that reported for the multi-order model of Borsuk and Stow (2000). It was suggested that the presence of rapidly degradable material may be indicated when the value of the first rate constant (k_1) is greater than $1.0\ d^{-1}$ and the time to 95% saturation of the first exponential function (t_1 (95%)) is less than 2.0 d.

Further model development is required in order to model the observed transitional and initial lag phases.

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