# Batch test for measurement of readily biodegradable COD and active organism concentrations in municipal waste waters

**MC Wentzel*, A Mbewe and GA Ekama**
*Department of Civil Engineering, University of Cape Town, Rondebosch 7700, South Africa*

## Abstract

In terms of the current mathematical models for activated sludge systems, it is necessary to categorise the influent COD into five fractions: unbiodegradable soluble and particulate, readily and slowly biodegradable, and heterotroph active biomass. Methods available to quantify these fractions are complex and time-consuming or require activated sludge seed acclimatised to the waste water which may not be available. The results of this study present a batch test procedure to quantify two of the influent COD fractions - readily biodegradable COD (RBCOD) and heterotroph active biomass. The batch test method is relatively simple and requires neither acclimatised activated sludge seed nor independent determination of unbiodegradable COD. For RBCOD concentrations, results from the batch test correlate closely with those from conventional methods.

## Introduction

The objectives of the activated sludge system have expanded to include progressively COD removal, nitrification, denitrification and biological excess P removal (BEPR). Concomitantly, to provide reliable predictions of expected system performances, mathematical models of increasing complexity have been proposed (Dold et al., 1980; Van Haandel et al., 1981; Henze et al., 1987; Dold et al., 1991; Wentzel et al., 1992). In terms of the framework of these models, it is necessary to divide the influent COD into a number of fractions. The currently accepted division of the influent COD is depicted in Fig. 1. The COD of municipal waste waters is divided into three main fractions, viz. unbiodegradable, biodegradable and heterotroph active biomass. The unbiodegradable COD has two subfractions, unbiodegradable particulate and unbiodegradable soluble. The biodegradable COD also has two subfractions, slowly biodegradable (SBCOD) and readily biodegradable (RBCOD); this latter subdivision is based wholly on the dynamic response observed in activated sludge systems (Dold et al., 1980), that is, the division is a biokinetic one **not** a physical separation. Thus, for complete characterisation of a municipal waste water, the five COD fractions need to be quantified.

In this paper a simple experimental procedure is presented to quantify two influent COD fractions - RBCOD and heterotroph active biomass.

## Background

### Measurement of RBCOD

The RBCOD has been identified as being of fundamental importance in design and operation of N (Van Haandel et al.,1982) and N and P (Siebritz et al., 1983; Wentzel et al., 1990; Pitman, 1991) removal systems; the magnitudes of both N and P removal have been linked to the magnitude of the influent RBCOD.

Various methods have been proposed for measurement of RBCOD. These can be categorised as physical or bioassy methods.

*To whom all correspondence should be addressed.
☎ (021) 650-2583; F (021) 650-2603; e-mail markw@cerecam.uct.ac.za
*Received 13 June 1994; accepted in revised form 9 November 1994.*

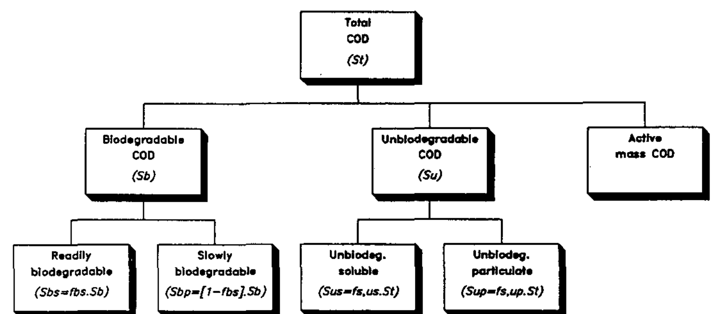


***Figure 1***
*Division of influent COD into its constituent fractions (Dold et al., 1991)*

**Physical methods**: It has been hypothesised that the difference in biokinetic response of activated sludge to RBCOD and SBCOD is due to differences in molecule size - RBCOD consists of relatively small molecules that are readily transported into microbial cells whereas SBCOD comprises larger and more complex molecules that require extracellular breakdown (hydrolysis) to smaller units before uptake and utilisation (Dold et al., 1980; Dold et al., 1986). Accordingly, physical separation of the two biodegradable COD fractions on the basis of molecular size has been proposed as an approximation of the biokinetic division. For physical separation, filtration methods with various filter pore sizes have been used (e.g. Dold et al., 1986; Lesouef et al., 1992; Mamais et al., 1993; Bortone et al.,1993; Torrijos et al., 1993). In evaluating the effect of pore size, Dold et al. (1986) found that for domestic waste water, membranes with cut-off < 10 000 molecular mass gave RBCOD that closely correlated with those determined by the conventional bioassay methods. In contrast, Bortone et al. (1993) found that with an industrial (textile) waste water, membranes with cut-off < 10 000 molecular mass gave RBCOD very much lower (13% of total COD) than that measured in bioassay batch tests (20% of total COD). Recognising that facilities for this type of ultrafiltration were not widely available, Dold et al. (1980) evaluated 0.45 μm filters and found that with domestic waste water a fraction of the SBCOD passed

through the filter causing overestimation of the RBCOD. To overcome this problem, Mamais et al. (1993) successfully investigated flocculation of colloidial material (SBCOD) before filtration through 0.45 μm filters. Torrijos et al. (1993) in an extensive investigation of the characteristics of a domestic waste water, found that 0.1 μm filters gave a true indication of RBCOD without the need for preflocculation.

In all the filtration methods, since both biodegradable and unbiodegradable COD pass through the filter, the unbiodegradable fraction has to be quantified independently and subtracted from the COD of the filtrate to give the RBCOD. This requires effluent from a continuous flow-through activated sludge system (Dold et al., 1986; Mamais et al., 1993; Bortone et al., 1993) or sequencing batch reactor (Torrijos et al., 1993) which may not be available, or measurements of filtered COD over at least 10 d in batch tests (Lesouef et al., 1992), a time-consuming task.

**Bioassay methods**: Since the division between RBCOD and SBCOD is based on biological response rather than physical separation, tests in which the response of activated sludge to waste water is monitored, bioassay tests, have found wider application, either as continuous flow-through systems or batch type experiments. The continuous flow-through systems (Ekama and Marais, 1979; WRC, 1984), while providing good estimates for RBCOD, have been criticised for their cost and difficulty of operation. For procedures using aerobic or anoxic batch experiments, sludge acclimatised to the waste water has to be obtained, either generated in a special laboratory-scale continuous flow-through reactor (Ekama et al., 1986; Sollfrank and Gujer, 1989; Kappelar and Gujer, 1992) or from a full-scale plant (Nicholls et al., 1985). The requirement of a laboratory-scale reactor for sludge generation for the batch methods does not resolve criticisms levelled at the flow-through method, while the option of obtaining sludge from a full-scale plant may not be available if a new plant is to be designed and built. Furthermore, in batch tests the use of sludges from BEPR systems will produce erroneous results for RBCOD due to the phenomenon of RBCOD uptake and storage with P release by polyP organisms under aerobic and anoxic conditions without the utilisation of oxygen or nitrate (Still et al., 1986; Wentzel et al., 1989a; b).

### Influent heterotroph active biomass measurement

The original UCT model (Dold et al., 1980; Van Haandel et al., 1981) did not consider heterotroph active biomass or autrotroph biomass to be present in the influent; for municipal waste waters in South Africa, the sewers generally are short (retention < 6 h) and anaerobic, and were considered unlikely to support active biomass generation. Further, simulations with the UCT model appeared to support this supposition. However, investigations in Europe have indicated that European municipal waste waters can contain a significant heterotroph active biomass fraction (Henze, 1989), up to 20% of the total COD (Kappelar and Gujer, 1992). Seeding of this influent biomass to the activated sludge system can have a significant influence on modelling and design. These findings have highlighted the need for a simple test to quantify this waste-water fraction.

Kappelar and Gujer (1992) describe a batch test to quantify heterotroph active biomass in activated sludge; a small quantity of activated sludge is mixed with centrifuged waste-water supernatant and the oxygen utilisation rate (OUR) response monitored with time. They note that the test can be adapted to quantify the heterotroph active biomass in the waste water by excluding the activated sludge. Details of this modification to the test are limited.

From the brief review above, quantification of influent waste water RBCOD and active biomass is of crucial importance for modelling and design of waste-water treatment systems. Further, the need exists for simple, reliable methods for accurate estimation of these parameters. In this paper the proposals of Kappelar and Gujer (1992), in which the OUR response of waste water is monitored with time, will be refined and developed, to measure simultaneously the influent active biomass and RBCOD concentrations.

## Test procedure

The batch test was undertaken on waste-water samples without activated sludge seed. Waste-water samples were unsettled because the active organisms, being particulate, would largely settle out in the primary settling tank. The procedure for the batch test was as follows: A defined volume (3ℓ) of unsettled municipal waste water, obtained from Mitchell's Plain Treatment Plant, Cape Town, was placed in a continually stirred batch reactor maintained at a constant temperature of 20°C. A sample was drawn to obtain the initial total COD concentration (*Standard Methods*, 1985). In operating the batch test, the surface of the waste water was covered by small plastic balls to limit surface exchange of oxygen. The OUR was monitored continually using an automated technique (Randall et al., 1991) - the DO was raised to 6 mgO/ℓ, the air switched off and the decrease in DO monitored, the rate of decrease giving the OUR; when the DO reached 4 mgO/ℓ, the air was switched on again and the cycle repeated. The pH of the reactor was monitored continually and controlled to pH 7.5 (± 0.2). Because of the low OUR values, the walls of the reactor were thoroughly brushed (regularly during an aeration cycle) to prevent particulate matter adhering to them. At intervals, samples were drawn from the reactor, filtered (0.45 μm) and analysed for nitrate and nitrite. The tests were conducted for approximately 20 h. At the end of the test the contents of the batch reactor were homogenised in a liquidiser, a sample drawn and total COD concentration measured.

## Results

Using the results of one batch test as an example, the OUR (mgO/ℓ·h) versus time (h) response is shown plotted in Fig. 2. The initial and final COD concentrations were 821 and 481 mgCOD/ℓ respectively. No nitrate or nitrite was detected in the test indicating the absence of nitrification, that is, no autotrophic biomass was present in the waste water. Should the presence of nitrifiers in the waste water be a possibility, allyl thiourea can probably be used as a nitrification inhibitor (due to the absence of nitrification, addition of allyl thiourea was not assessed).

Referring to the OUR-time plot (Fig. 2), during the first period of the batch test (< 7.25 h) the OUR exhibits an exponential increase due to heterotroph active biomass growth. After ± 7.25 h, the OUR drops precipitously due to depletion of the RBCOD. For the remainder of the batch test, the OUR exhibits an inverted S pattern typical of saturation kinetics, due to SBCOD utilisation.

## Data interpretation

The data from the batch test can be interpreted in terms of either the UCT (Dold et al., 1980; 1991) or IAWQ (Henze et al., 1987) models. The UCT model was selected, using the data from Fig. 2 as a worked example; interpretation in terms of IAWQ model does not present undue difficulty and is also briefly presented.

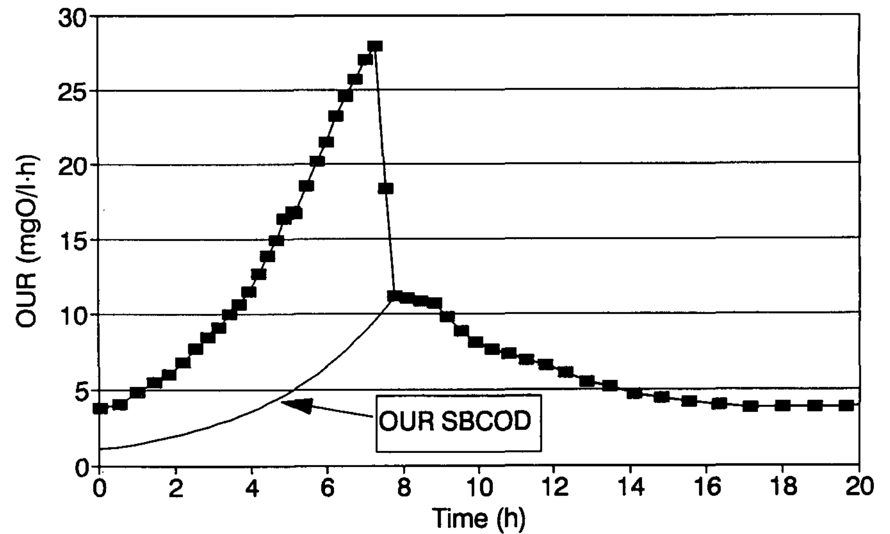


***Figure 2***
*Oxygen utilisation rate (OUR) response with time for aerobic batch on raw municipal waste water from Mitchell's Plain (Cape Town, South Africa). Theoretical OUR for utilisation of the slowly biodegradable COD (SBCOD) plotted from Eq. (11).*

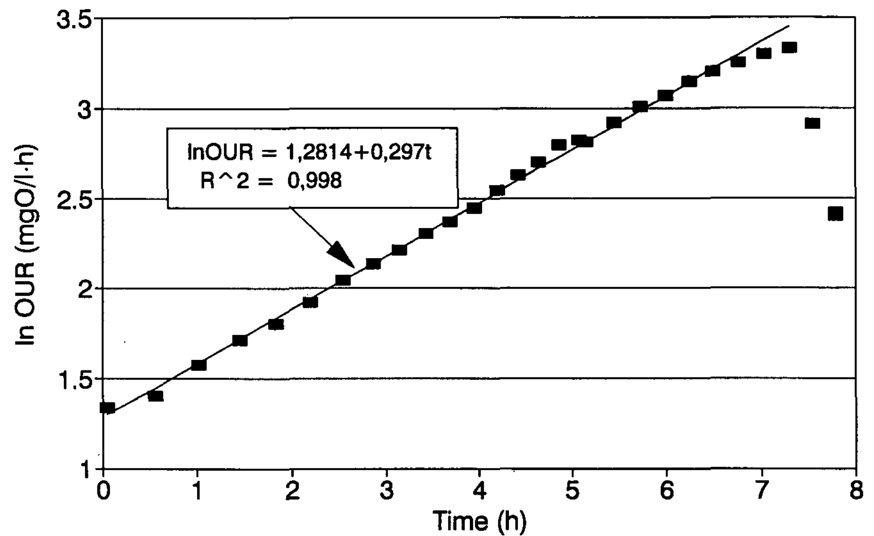


***Figure 3***
*ℓn oxygen utilisation rate (OUR) versus time for the measured OUR data in Fig. 2, up to the precipitous drop in OUR*

For application of the UCT model to the batch test, the model can be simplified by recognising that specific conditions prevail:

- Aerobic conditions - denitrification processes need not be included
- No nitrification - nitrification processes need not be included
- Excess ammonia present - nitrate as an N-source for growth need not be considered
  - transformations from organic to ammonia nitrogen need not be included.

Accepting these conditions, the UCT model can be simplified to that presented in Table 1. In terms of this model the following information can be obtained from the batch test:

- COD recovery (%)
- Waste-water heterotroph active biomass, $Z_{BH(0)}$ (mgCOD/ℓ)
- Waste-water RBCOD, $S_{bsi}$ (mgCOD/ℓ)
- Waste-water heterotroph maximum specific growth rate on RBCOD, $\hat{\mu}_H$ (/d)
- Waste-water heterotroph maximum specific growth rate on SBCOD, $K_{MP}$ (/d)

In the calculations, values have to be assumed for:

- Heterotroph specific death rate, $b_H$ = 0.62/d
- Heterotroph yield, $Y_{ZH}$ = 0.666 mgCOD/mgCOD.

### COD recovery

The acceptability of the data from the batch test can be evaluated by doing a COD mass balance, as follows:

$$\%\text{COD recovery} = \frac{COD_{t=T} + \int_{t=0}^{t=T} OUR \cdot dt}{COD_{t=0}} \cdot 100 \qquad (1)$$

where:

| | | |
|---|---|---|
| t | = | time (h) |
| $COD_{t=T}$ | = | total unfiltered COD concentration at end of test (t=T) (mgCOD/ℓ) |
| OUR | = | oxygen utilisation rate (mgO/ℓ/h) |
| $\int_{t=0}^{t=T} OUR \cdot dt$ | = | integral (area) under the OUR versus time plot between start and end of test (mgO/ℓ) |
| | = | oxygen concentration consumed over the test |

**TABLE 1**
**MATRIX REPRESENTATION OF THE UCT MODEL (DOLD ET AL., 1991) SIMPLIFIED FOR THE CONDITIONS PRESENT IN THE BATCH TEST**

| COMPOUND i / j PROCESS | 1 $Z_{BH}$ | 2 $Z_E$ | 3 $Z_I$ | 4 $S_{ads}$ | 5 $S_{enm}$ | 6 $S_{bs}$ | 7 $S_{us}$ | 8 O | PROCESS RATE, $\rho_j$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 Aerobic growth of $Z_{BH}$ on $S_{bs}$ | 1 | | | | | $-1/Y_{ZH}$ | | $-\frac{1-Y_{ZH}}{Y_{ZH}}$ | $\hat{\mu}_H \left[\frac{S_{bs}}{K_{SH}+S_{bs}}\right] Z_{BH}$ |
| 2 Aerobic growth of $Z_{BH}$ on $S_{ads}$ | 1 | | | $-1/Y_{ZH}$ | | | | $-\frac{1-Y_{ZH}}{Y_{ZH}}$ | $K_{MP} \left[\frac{(S_{ads}/Z_{BH})}{K_{SP}+(S_{ads}/Z_{bh})}\right] Z_{BH}$ |
| 3 Death of $Z_{BH}$ | -1 | $f_E$ | | | $1-f_E$ | | | | $b_H Z_{BH}$ |
| 4 Adsorption of $S_{enm}$ | | | | 1 | -1 | | | | $K_A S_{enm} Z_{BH} (f_{MA} - S_{ads}/Z_{BH})$ |
| **Stoichiometric constants**<br>$Y_{ZH}$ = Heterotroph yield<br>$f_E$ = Endogenous residue<br>$f_{MA}$ = Max. ratio $S_{ads}/Z_{BH}$ | Biological (active) heterotrophic mass<br>M (COD) $L^{-3}$ | Endogenous mass<br>M (COD) $L^{-3}$ | Inert mass<br>M (COD) $L^{-3}$ | Adsorbed slowly biodegradable substrate<br>M (COD) $L^{-3}$ | Enmeshed slowly biodegradable substrate<br>M (COD) $L^{-3}$ | Readily biodegradable (soluble) substrate<br>M (COD) $L^{-3}$ | Unbiodegradable soluble substrate<br>M (COD) $L^{-3}$ | Oxygen<br>M (-COD) $L^{-3}$ | **Kinetic constants**<br>$\hat{\mu}_H$ = Heterotroph max. specific growth rate on $S_{bs}$<br>$K_{SH}$ = Heterotroph 1/2 saturation on $S_{bs}$<br>$K_{MP}$ = Heterotroph max. specific growth rate on $S_{ads}$<br>$K_{SP}$ = Heterotroph 1/2 sat. on $S_{ads}$<br>$b_H$ = Heterotroph specific death rate<br>$K_A$ = $S_{enm}$ specific adsorption rate |

Using the data in Fig. 2 as an example, $COD_{t=0}$ = 821 mgCOD/ℓ; $COD_{t=T}$ = 481 mgCOD/ℓ; $\int_{t=0}^{t=T} OUR \cdot dt$ = 332 mgO/ℓ, then:

$$\%\ COD\ recovery = \frac{481 + 332}{821} \cdot 100 = 99\%$$

Mass balances between 95-105% indicate that the test results are acceptable, and these were generally obtained in most batch tests without undue difficulty (Mbewe et al., 1994).

## Waste-water heterotroph active biomass, $Z_{BH(0)}$

From the simplified UCT model (Table 1), the rate of growth of heterotroph biomass ($dZ_{BH}/dt$) is given by:

$dZ_{BH}/dt$ = growth on RBCOD + growth on SBCOD - death

$$\frac{dZ_{BH}}{dt} = \hat{\mu}_H \frac{S_{bs}}{K_{SH} + S_{bs}} \cdot Z_{BH} + K_{MP} \frac{S_{ads}/Z_{BH}}{K_{SP} + S_{ads}/Z_{BH}} \cdot Z_{BH} - b_H \cdot Z_{BH} \quad (2)$$

where:

$Z_{BH}$ = heterotroph active biomass concentration (mgCOD/ℓ)
$S_{bs}$ = RBCOD concentration (mgCOD/ℓ)
$K_{SH}$ = half saturation constant for RBCOD = 5mgCOD/ℓ
$S_{ads}$ = adsorbed SBCOD concentration (mgCOD/ℓ)
$K_{SP}$ = half saturation constant for SBCOD = 0.027 mgCOD/mgCOD

It can be accepted that during the initial stages of the batch test (before RBCOD is depleted and the OUR drops precipitously) $S_{bs} >> K_{SH}$ and $S_{ads}/Z_{BH} >> K_{SP}$, and therefore:

$$\frac{dZ_{BH}}{dt} = (\hat{\mu}_H + K_{MP} - b_H)Z_{BH} \quad (3)$$

Integrating Eq. (3) and solving yields the active organism concentration at time t [$Z_{BH(t)}$, mgCOD/ℓ] in terms of the initial active organism concentration [$Z_{BH(0)}$, mgCOD/ℓ], time [t, in h] and the net specific growth rate [$(\hat{\mu}_H + K_{MP} - b_H)$, /d] viz:

$$Z_{BH(t)} = Z_{BH(0)} e^{(\hat{\mu}_H + K_{MP} - b_H)t/24} \quad (4)$$

The OUR at time t [$OUR_t$, mgO/ℓ·h] is a function of $Z_{BH(t)}$ and the net specific growth rate:

$$OUR_{(t)} = \frac{1 - Y_{ZH}}{Y_{ZH}} (\hat{\mu}_H + K_{MP}) Z_{BH(t)}/24 \quad (5)$$

Substituting Eq. (4) for $Z_{BH(t)}$ in Eq. (5) and taking natural logs yields:

$$\ln OUR_{(t)} = \ln \left[\frac{1 - Y_{ZH}}{Y_{ZH}} (\hat{\mu}_H + K_{MP}) Z_{BH(0)}/24\right] + (\hat{\mu}_H + K_{MP} - b_H)\, t/24 \quad (6)$$

which is a straight line with:

$$slope = (\hat{\mu}_H + K_{MP} - b_H)/24 \quad (7)$$

$$y\text{-intercept} = \ln(OUR_{(t=0)}) = \ln\left[\frac{1 - Y_{ZH}}{Y_{ZH}} (\hat{\mu}_H + K_{MP}) Z_{BH(0)}/24\right] \quad (8)$$

From a plot of ℓn $OUR_{(t)}$ versus time (h), $Z_{BH(0)}$ can be obtained:

$$Z_{BH(0)} = \frac{e^{(y\text{-intercept})} \cdot 24}{\frac{1 - Y_{ZH}}{Y_{ZH}} \cdot (slope \cdot 24 + b_H)} \quad (mgCOD/ℓ) \quad (9)$$

The OUR values for the data in Fig. 2 up to the precipitous drop in OUR, are shown plotted ℓn OUR versus time (h) in Fig 3. Linear regression yields:

$$\ln OUR = 1.2814 + 0.297\, t \qquad (R^2 = 0.998)$$

Accepting $Y_{ZH}$ = 0.666 mgCOD/mgCOD and $b_H$ = 0.62/d (the value for $b_H$ is probably less for the raw sewage in the batch test than the 0.62/d for normal activated sludge systems because predators probably will not be present in significant concentrations; however, a reduced value for $b_H$ has relatively little influence since $\hat{\mu}_H + K_{MP} >> b_H$), and inserting into Eq. (9) yields:

$$Z_{BH(0)} = \frac{e^{1.2814} \cdot 24}{\frac{1 - 0.666}{0.666} \cdot (0.297 \cdot 24 + 0.62)} = 22\ mgCOD/ℓ$$

This represents 22/821·100 = 2.7% of the waste-water COD, a very minor fraction.

In terms of the IAWQ model, growth and OUR are due to utilisation of RBCOD only, either directly from RBCOD in the influent or from RBCOD generated by SBCOD hydrolysis. However, this does not influence determination of $Z_{BH(0)}$ except that $(\hat{\mu}_H + K_{MP})$ in the equations above is equivalent to the maximum specific growth rate, $\hat{\mu}_H^*$, in the IAWQ model. Accordingly, Eq. (9) can be used directly to determine $Z_{BH(0)}$ in terms of the IAWQ model.

## Heterotroph maximum specific growth rate on SBCOD, $K_{MP}$

The RBCOD concentration is calculated from the concentration of oxygen utilised in its degradation. This requires the OUR before the precipitous drop to be separated into its RBCOD and SBCOD contributions, which is equivalent to separating the overall growth rate $(\hat{\mu}_H + K_{MP})$ into its $\hat{\mu}_H$ and $K_{MP}$ components. These calculated values for $\hat{\mu}_H$ and $K_{MP}$ from the batch test are unlikely to be of value in modelling activated sludge systems. The organism population that develops in the activated sludge system is likely to differ appreciably from that which develops in the batch reactor since the conditions present in the batch test (high COD, low active biomass) differ significantly from those in the acivated sludge system (low COD, high active biomass). Consequently, the two populations probably will have different kinetic constants.

In terms of the UCT model, growth of heterotrophs on RBCOD and SBCOD is independent. The OURs (mgO/ℓ·h) associated with these two growth processes are given by Eq. (5) which can be separated to give:

(1) $$OUR_{RBCOD(t)} \cdot 24 = \frac{1-Y_{ZH}}{Y_{ZH}} \cdot \hat{\mu}_H \cdot Z_{BH(0)} \cdot e^{(\hat{\mu}_H + K_{MP} - b_H)t/24} \quad (10)$$

(2) $$OUR_{SBCOD(t)} \cdot 24 = \frac{1-Y_{ZH}}{Y_{ZH}} \cdot K_{MP} \cdot Z_{BH(0)} e^{(\hat{\mu}_H + K_{MP} - b_H)t/24} \quad (11)$$

Up to the precipitous decrease, the OUR is the sum of both the RBCOD and SBCOD utilisation [Eq. (10) + Eq. (11)]. Once the RBCOD is depleted, which causes the precipitous OUR decrease, the OUR is that for SBCOD only [Eq. (11)]. If the precipitous decrease occurs at t=s hours at which time the OUR is $OUR_{SBCOD(t)}$, then from Eq. (11) $K_{MP}$ is given by:

$$K_{MP} = \frac{OUR_{SBCOD(t=s)} \cdot 24}{\frac{1-Y_{ZH}}{Y_{ZH}} \cdot Z_{BH(0)} \, e^{(\hat{\mu}_H + K_{MP} - b_H) \cdot (t=s)/24}} \quad (12)$$

where:

$OUR_{SBCOD(t=s)}$ = OUR due to SBCOD only, i.e. observed OUR immediately following the precipitous drop in OUR (mgO/ℓ·h)

(t=s) = time immediately following the precipitous drop in OUR (h)

$(\hat{\mu}_H + K_{MP} - b_H)/24$ = slope of ℓn $OUR_{(t)}$ versus time (h) plot.

Using the data in Figs. 2 and 3 as an example, time s = 7.8h; $OUR_{SBCOD(t=7.8h)}$ = 11.2 mgO/ℓ·h; slope ℓn $OUR_{(t)}$ vs time plot = 0.297 (Fig. 3); $Z_{BH(0)}$ = 22 mgCOD/ℓ:

$$K_{MP} = \frac{11.2 \cdot 24}{\frac{1-0.666}{0.666} \cdot 22 \cdot e^{0.297 \cdot 7.8}} = 2.4/d$$

In the IAWQ model, utilisation of RBCOD and SBCOD is not independent; only RBCOD is utilised, either from that present in the waste water or from SBCOD hydrolysis. However, to interpret the data in the batch test to calculate the RBCOD present in the waste water, distinction has to be made between the RBCOD in the waste water and the RBCOD generated from the hydrolysis of SBCOD. To do this, the approach developed here for the UCT model can be followed. Conceptually, in the IAWQ model this amounts to independent utilisation of the two "types" of RBCOD, but does not influence the value calculated for influent waste-water RBCOD. To determine the contribution of SBCOD hydrolysis to the RBCOD, the maximum specific hydrolysis rate, $K_H$, needs to be calculated, as follows:

$$K_H = K_{MP}/Y_{ZH} \quad \text{(mgCOD/mgCOD·d)} \quad (13)$$

For the example presented here,

$$K_H = 2.4/0.666 = 3.6 \text{ mgCOD/mgCOD·d}$$

## Heterotroph maximum specific growth rate on RBCOD, $\hat{\mu}_H$

For the UCT model, the value for $\hat{\mu}_H$ can be calculated from the value for $K_{MP}$ derived above and the slope of the ℓn OUR versus time plot, as follows:

$$\hat{\mu}_H = \text{slope} \cdot 24 - K_{MP} + b_H \quad (14)$$

For the example,

$$\hat{\mu}_H = 0.297 \cdot 24 - 2.4 + 0.62 = 5.4/d$$

For interpretation in terms of the IAWQ model:

$$\hat{\mu}_H^* = (\hat{\mu}_H + K_{MP}) = \text{slope} \cdot 24 + b_H \quad (15)$$

For the example:

$$\hat{\mu}_H^* = 5.4 + 2.4 = 7.8/d$$

## Determination of the influent RBCOD concentration

Knowing $K_{MP}$ and $\hat{\mu}_H$ individually, the $OUR_{SBCOD}$ can now be calculated and subtracted from $OUR_{total}$ to give the $OUR_{RBCOD}$. The RBCOD then is given by $1/(1-Y_{ZH})$ times the area between the observed OUR and the theoretical $OUR_{SBCOD}$ from the start of the batch test (t=0) to the precipitous drop (t=d):

$$RBCOD = \frac{1}{1-Y_{ZH}} \int_{t=0}^{t=d} (OUR_{total} - OUR_{SBCOD}) \cdot dt \quad \text{(mgCOD/ℓ)} \quad (16)$$

$$= \frac{1}{1-Y_{ZH}} \int_{t=0}^{t=d} OUR_{RBCOD} \cdot dt \quad (17)$$

The RBCOD concentration can be found by doing the integration in Eq. (16) graphically or that in Eq. (17) analytically. For the former, the $OUR_{SBCOD}$ from Eq. (11) with $K_{MP}$ = 2.4/d is shown plotted in Fig. 2. The area between the observed OUR and the theoretical $OUR_{SBCOD}$ was determined to be 68.9 mgO/ℓ. Therefore, from Eq. (16)

$$RBCOD = [1/(1-0.666)]\ 68.9 = 206 \text{ mgCOD/ℓ}.$$

For the latter, Eq. (17) is integrated analytically by substituting Eq. (10) for $OUR_{RBCOD}$ and solving the definite integral between t=0 and t=d, viz.:

$$RBCOD = \frac{\hat{\mu}_H \cdot Z_{BH(0)}}{Y_{ZH} \cdot \text{slope} \cdot 24} \cdot \{e^{\text{slope} \cdot t_d} - 1\} \quad \text{(mgCOD/ℓ)} \quad (18)$$

where:

$t_d$ = time of precipitous drop in OUR(h)

slope = slope of ℓn OUR versus time (h) plot

For the example, $\hat{\mu}_H$ = 5.4/d; $Z_{BH(0)}$ = 22 mgCOD/ℓ; $Y_{ZH}$ = 0.666 mgCOD/mgCOD; slope = 0.297; $t_d$ = 7.4 h:

$$RBCOD = \frac{5.4 \cdot 22}{0.666 \cdot 0.297 \cdot 24} \cdot \{e^{0.297 \cdot 7.4} - 1\} = 200 \text{ mgCOD/ℓ}$$

In a comparative test, the results for the conventional flow-through test (Ekama and Marais, 1979) for the same batch of waste water gave RBCOD = 207 mgCOD/ℓ.

In terms of the IAWQ model, to determine the influent RBCOD, an artificial division of the observed OUR has to be made, between $OUR_{RBCOD}$ for influent RBCOD utilisation and $OUR_{SBCOD}$ for utilisation of RBCOD generated from SBCOD hydrolysis.

Equations for these OURs can be derived from the IAWQ model. These are identical to Eqs. (10) and (11) except that:

$$(\hat{\mu}_H + K_{MP}) \text{ in UCT} = \hat{\mu}_H^* \text{ in IAWQ}$$
$$\hat{\mu}_H \text{ in UCT} = (\hat{\mu}_H^* - K_H/Y_{ZH}) \text{ in IAWQ}$$
$$K_{MP} \text{ in UCT} = K_H/Y_{ZH} \text{ in IAWQ.}$$

Equation (18) for the RBCOD concentration also applies except that $\hat{\mu}_H$ is replaced by $(\hat{\mu}_H^* - K_H/Y_{ZH})$ as indicated above.

## Conclusions

A batch test method has been presented to determine two influent waste-water COD fractions, heterotroph active biomass and readily biodegradable COD (RBCOD). The method has advantages over previous methods in that:

- The experimental procedure is relatively simple.
- No mixed liquor acclimatised to the waste water is required.
- Independent determination of unbiodegradable COD is not necessary.
- The only independent constants required for calculation are the heterotroph yield ($Y_{ZH}$) and specific death rate ($b_H$); the procedure is relatively insensitive to the value for $b_H$. All other constants required for calculations are obtained from the experimental data. However, it is unlikely that these constants (UCT model, $\hat{\mu}_H$ and $K_{MP}$; IAWQ model, $\hat{\mu}_H^*$ and $K_H$) will be of much value in modelling and design of activated sludge systems - most probably a population will develop in the activated sludge system that differs appreciably from that in the waste water since the conditions in the waste water (high COD, low active mass) differ significantly from those in the activated sludge system (low COD, high active mass).

Results from a number of batch tests on municipal waste water from Mitchell's Plain and Borchard's Quarry Treatment Plants (South Africa) indicate that the measured RBCOD concentrations correlate closely (within 5%) with those from the conventional flow-through method of Ekama and Marais (1979); Mbewe et al., 1994. For waste waters from both sources, no nitrate could be detected in the batch test, indicating autotroph active biomass was not present in these waste waters. For the Mitchell's Plain waste water, heterotroph active biomass was found to be present in low concentrations, <3% of total COD. However, for Borchard's Quarry waste-water heterotroph active biomass concentration was very variable, ranging from < 5% to > 15% of total COD. From an investigation of operational procedures at the Borchard's Quarry Waste-water Treatment Plant it was found that intermittently waste activated sludge was recycled to the head of the works, and mixed with the incoming influent waste water upstream of the point where waste water was drawn for the batch test. The recycled waste activated sludge was correctly detected in the batch test.

The batch test method presented provides a simple means to quantify two of the five influent waste-water COD fractions. Current research is attempting to extend the batch test to quantify the remaining three COD fractions, unbiodegradable soluble COD, unbiodegradable particulate COD and slowly biodegradable particulate COD.

## Acknowledgements

This research was supported jointly by the Water Research Commission of South Africa and the Foundation for Research Development and is published with their permission. The undergraduate students, LT Dlamini and E Morgenroth, conducted experimental work which contributed to the development of the batch test method and their contribution is gratefully acknowledged.

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