# Batch test for characterisation of the carbonaceous materials in municipal wastewaters

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## Abstract

As input to the current mathematical models for activated sludge systems, it is necessary to quantitatively characterise the influent COD. Existing methods are complex and time-consuming, or require activated sludge seed acclimatised to the wastewater, which may not be available. A batch test procedure is presented to quantify five influent COD fractions - unbiodegradable soluble (USCOD) and particulate (UPCOD), readily (RBCOD) and slowly (SBCOD) biodegradable, and heterotrophic active biomass (HAB). The method is relatively simple and does not require acclimatised activated sludge. For RBCOD and USCOD, results from the batch test correlate closely with those from conventional methods. However, for UPCOD and SBCOD, the correlation with conventional tests is poor, and the batch test estimates are not sufficiently accurate for design and simulation; this aspect requires further investigation. For HAB, the batch test estimates could not be evaluated as no conventional tests for this parameter are available.

## Nomenclature

### Abbreviations

| | |
|---|---|
| AS | Activated sludge |
| BEPR | Biological excess phosphorus removal |
| BT | Batch test |
| F-RBCOD | Fermentable readily biodegradable COD |
| FFRW | Flocculated filtered raw wastewater |
| HAB | Heterotrophic active biomass |
| OUR | Oxygen utilisation rate |
| $OUR_e$ | OUR for endogenous respiration |
| $OUR_{syn}$ | OUR for biodegradable COD utilisation (heterotroph synthesis) |
| RBCOD | Readily biodegradable COD |
| SBCOD | Slowly biodegradable COD |
| SCFA | Short-chain fatty acids |
| UPCOD | Unbiodegradable particulate COD |
| USCOD | Unbiodegradable soluble COD |

### Symbols

| | |
|---|---|
| f | Heterotroph endogenous residue fraction (mgCOD/mgCOD) |
| $f_{S,up}$ | Fraction of total COD that is unbiodegradable particulate (mgCOD/mgCOD) |
| $f_{S,us}$ | Fraction of total COD that is unbiodegradable soluble (mgCOD/mgCOD) |
| $MO_C$ | Mass of oxygen consumed by heterotrophs over the batch test (mgO/$\ell$) |
| $S_{bi}$,$S_{be}$ | Biodegradable COD concentration; influent/initial, end of test (mgCOD/$\ell$) |
| $S_{bpi}$, $S_{bpe}$ | Biodegradable particulate COD concentration; influent/initial, end of test (mgCOD/$\ell$) |
| $S_{bsai}$ | Short-chain fatty acid concentration; influent/initial (mgCOD/$\ell$) |
| $S_{bsfi}$ | Fermentable readily biodegradable COD concentration; influent/initial (mgCOD/$\ell$) |
| $S_{bsi}$ | Readily biodegradable COD concentration; influent/initial (mgCOD/$\ell$) |
| $S_{ti}$, $S_{te}$ | Total COD concentration; influent/initial, end of test (mgCOD/$\ell$) |
| $S_{upi}$, $S_{upe}$ | Unbiodegradable particulate COD concentration; influent/initial, end of test (mgCOD/$\ell$) |
| $S_{usi}$, $S_{use}$ | Unbiodegradable soluble COD concentration; influent/initial, end of test (mgCOD/$\ell$) |
| $Y_{ZH}$ | Heterotroph specific yield (mgCOD/mgCOD) |
| $Z_{BHi}$, $Z_{BHe}$ | Heterotrophic active biomass; influent/initial, end of test (mgCOD/$\ell$) |
| $Z_{Ee}$ | Endogenous residue concentration; end of test (mgCOD/$\ell$) |

## Introduction

To aid the design and operation of the single sludge activated sludge system, a number of steady state design models (e.g. WRC, 1984; Wentzel et al., 1990) and kinetic simulation (e.g. Dold et al., 1980, 1991; Van Haandel et al., 1981; Henze et al., 1987, 1995; Wentzel et al., 1992) have been developed, to progressively include aerobic COD removal and nitrification, anoxic denitrification and anaerobic/anoxic/aerobic biological excess phosphorus removal (BEPR). In terms of the framework of these design procedures and kinetic models, the influent carbonaceous material (measured in terms of the COD parameter) is subdivided into a number of fractions (Fig. 1): The COD of municipal wastewaters is divided into three main fractions, unbiodegradable, biodegradable and heterotrophic active biomass (HAB). The unbiodegradable COD has two subfractions, unbiodegradable particulate (UP)COD and unbiodegradable soluble (US)COD. The biodegradable COD also has two subfractions, slowly biodegradable (SB)COD and readily biodegradable (RB)COD. The RBCOD is further subdivided into two subfractions, short-chain fatty acids (SCFA) and fermentable (F-)RBCOD. Thus, for complete characterisation of a municipal

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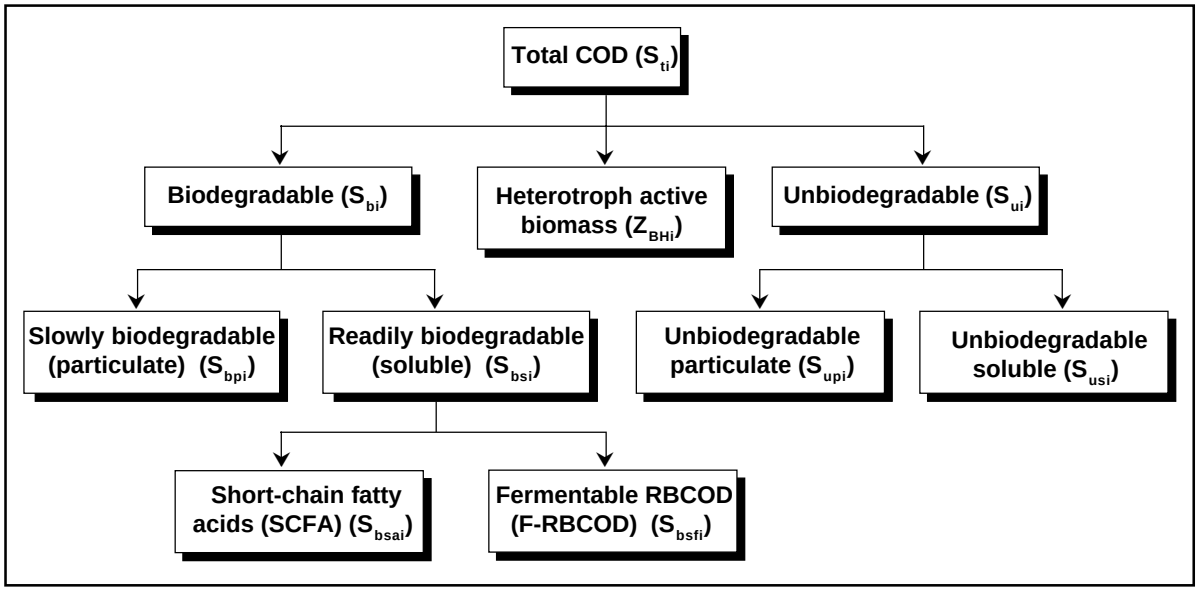


***Figure 1***
*Division of influent COD into its constituent fractions (Dold et al., 1991)*

wastewater, six COD fractions need to be quantified.

The degree of wastewater characterisation required depends on the type of activated sludge system to be designed/simulated: For organic material (COD) removal only, the global COD ($S_{ti}$) parameter and an elementary characterisation is adequate, i.e. biodegradable ($S_{bi}$) and USCOD and UPCOD ($S_{usi}$ and $S_{upi}$ respectively). If nitrification is included, no additional information on the COD is necessary (but, additional information on the N material is). With biological N removal (denitrification), additional information on the biodegradable COD fractions, RBCOD ($S_{bsi}$) and SBCOD ($S_{bpi}$), is required, since these two COD fractions produce different rates of denitrification (Van Haandel et al., 1981). With BEPR, additionally information on the RBCOD subfractions is necessary, SCFA ($S_{bsai}$) and F-RBCOD ($S_{bsfi}$), since these two RBCOD subfractions induce different responses in the anaerobic reactor of the BEPR system (Wentzel et al., 1990) (also, information on the P materials is required). If seeding with the influent is significant, information on HAB ($Z_{BHi}$) is required. Whichever design or simulation is undertaken, it will be only as reliable as the wastewater characteristics that serve as input.

Existing procedures for quantifying the COD fractions are either physically or biologically (bioassay tests) based, or a combination of both. For the physical methods, these have been developed principally to quantify RBCOD: It has been hypothesised that the observed differences 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, 1986). Accordingly, physical separation of the two biodegradable COD fractions on the basis of molecular size has been proposed as an approximation of the observed 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.,1994; Torrijos et al., 1994). Success with the filtration methods has been closely linked to the filter pore size used - the larger the pore size, the more "particulate" material passes through the filter and the less accurate the separation between RBCOD and SBCOD. To overcome this problem, Mamais et al. (1993) and Mbewe et al. (1995) successfully investigated flocculation of colloidal material (SBCOD) before filtration through 0.45 μm filters. However, in all the filtration methods, since both biodegradable and unbiodegradable COD pass through the filter, the unbiodegradable fraction has to be quantified independently (by means of bioassay type tests) 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., 1994; Mbewe et al., 1995) or sequencing batch reactor (Torrijos et al., 1994) which may not be available, or measurements of filtered COD over 10 d in batch tests (Lesouef et al., 1992), a time-consuming task. Physical methods can be used to reliably determine SCFA, by e.g. gas chromatography, titration and therefore the two RBCOD subfractions are not considered further in this paper.

Since in the models the division of the influent COD is based principally on biological responses, tests in which the response of activated sludge to wastewater is monitored (bioassay tests) have found wider application than the physically based tests. A wide variety of bioassay test techniques have been developed which can be categorised as either continuous flow-through systems or batch type systems. The continuous flow-through systems (WRC, 1984; Ekama et al., 1986), while providing good estimates for all COD fractions, have been criticised for their cost and difficulty of operation. For procedures using batch experiments, sludge acclimatised to the wastewater has to be obtained, either generated in special lab-scale continuous flow-through reactors (Ekama et al., 1986; Sollfrank and Gujer, 1991; Kappelar and Gujer, 1992) or from a full-scale plant (Nicholls et al., 1985). The requirement of a lab-scale reactor for sludge generation for the batch methods does not resolve criticisms of the flow-through methods, while the option of obtaining sludge from a full-scale plant may not be available if a new plant is to be built. Furthermore, in batch type experiments the use of sludge from BEPR systems will produce erroneous results for RBCOD due to RBCOD uptake and storage

under aerobic and anoxic conditions without utilisation of oxygen and nitrate (Wentzel et al., 1989). In any event, the batch type experiments do not provide accurate estimates for all the COD fractions; in particular it is difficult to obtain an acceptable estimate for SBCOD and UPCOD, and USCOD requires batch test operation for at least 10 d (Lesouef et al., 1992).

To overcome the problems with the existing bioassay type methods, Wentzel et al. (1995) developed a simple batch test method to quantify two of the influent COD fractions - RBCOD and HAB. Unlike the existing methods, this batch test procedure does not require an activated sludge seed - the raw (unsettled) influent wastewater is aerated for about 12 h and the oxygen utilisation rate (OUR) monitored continually (Fig. 2). From the OUR-time curve, the COD recovery, HAB, RBCOD, and HAB maximum specific growth rates on RBCOD and SBCOD can be calculated. Initial indications were that the batch test provided good estimations for RBCOD compared to conventional methods. In this paper, the batch test method estimate for RBCOD will be more extensively evaluated, by comparing RBCOD results from the batch test to those from conventional methods. Also, attempts to extend the batch test method to quantify three of the remaining COD fractions are described, USCOD, UPCOD and SBCOD.

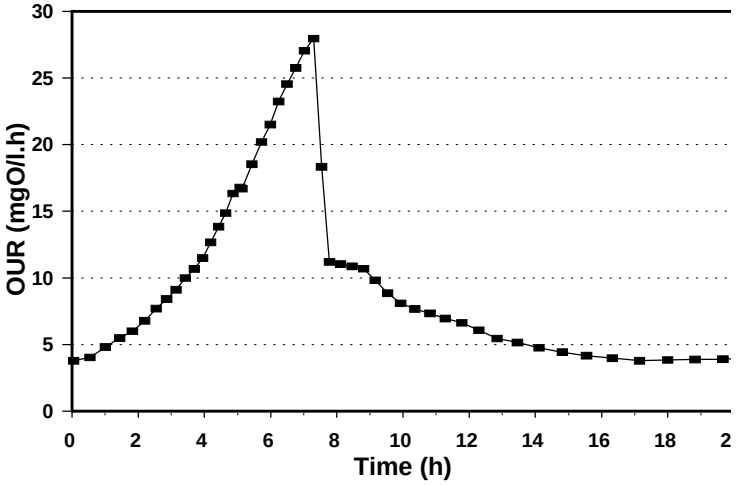


***Figure 2***
*Oxygen utilisation rate (OUR) response with time for aerobic batch test on raw municipal wastewater (from Wentzel et al., 1995)*

## Methods

### Wastewater collection

Wastewater from two sources was used for the experimental investigation, Borcherds Quarry and Mitchells Plain Treatment Plants (Cape Town, South Africa). Batches of raw (unsettled) wastewater were collected from the inlet works to the treatment plants (after screens, but before degritting), transported to the laboratory and stored in stainless steel tanks at 4°C for a period of approximately two weeks. Storage for more than about three weeks leads to significant changes in the sewage; storage for two weeks minimised this possibility. Regularly, the contents of the tanks were thoroughly mixed and wastewater samples drawn off into a plastic container. The wastewater was diluted to approximately 500 mgCOD/ℓ with tap water so that the OURs measured in the batch test would not be excessively high.

### Readily biodegradable (RB)COD and heterotrophic active biomass (HAB)

The batch test procedure detailed by Wentzel et al. (1995) and Mbewe et al. (1995) was followed: After warming the diluted wastewater to 20°C, a defined volume (3 ℓ) was placed in a continually stirred batch reactor, maintained at a constant temperature of 20°C. A sample was drawn for the initial total COD concentration (*Standard Methods*, 1985). The OUR was monitored continuously using an automated technique (Randall et al., 1991; Wentzel et al., 1995), taking due care to limit surface exchange of oxygen (Mbewe et al., 1995). The pH was also monitored continuously and controlled to pH 7.5 (±0.2). Due to the low OUR values, the walls of the reactor were thoroughly brushed (regularly during an aeration cycle) to prevent adherence of particulate matter. At regular intervals, samples were drawn from the reactor, filtered (0.45 μm) and analysed for nitrate and nitrite (Technicon Auto Analyser). In none of the batch tests conducted were nitrate or nitrite detected, even when the batch tests were run for >3 d, i.e. nitrification was negligible indicating the absence of autotrophic biomass in the wastewater. Accordingly, the method did not require modification to take nitrification into account. At the end of the batch test, a sample was drawn, homogenised in a liquidiser and analysed for total COD.

From the batch tests the following information was derived using the procedures in Wentzel et al. (1995) and Mbewe et al. (1995): COD recovery (%); wastewater HAB; wastewater RBCOD. For the RBCOD measurements, the accuracy was evaluated by comparing the results from the batch test with results from the conventional flow-through square wave bioassay test (WRC, 1984; Ekama et al., 1986). This unit was operated as specified by Ekama et al. (1986) and received the same wastewater used in the batch tests, at the same COD concentration. For wastewater HAB, no conventional tests are available for comparison.

### Unbiodegradable soluble (US) COD

After the precipitous drop in OUR (ca. 4 to 8 h depending on RBCOD and HAB concentrations, Fig. 2), the only soluble COD remaining should be USCOD. Accordingly, at the end of the batch test (one or more days), 1 ℓ of the batch reactor contents was drawn from the reactor, flocculated and then filtered: The sample was dosed with 10 mℓ of stock aluminium sulphate [$Al(SO_4)_3 \cdot 15H_2O$, Merck] solution (stock at 50 g/ℓ). The mixture was stirred rapidly (ca. 200 r/min) for 2 min (rapid mix phase) and then poured slowly into a perspex cylinder (settling column) equipped with a magnetic stirrer. The contents of the column were stirred slowly (ca. 1 r/min) for 30 min (flocculation phase) (observations indicated that the time for flocculation probably could be reduced considerably, to about 5 to 10 min, but this was not investigated). During the flocculation phase, the flocs coalesced and settled out to leave a "clear" liquid zone. A 50 mℓ sample was drawn from the clear liquid zone and filtered through a glass fibre filter (Whatman's GF/C) and the COD of the filtrate determined. The filtrate from the glass fibre filter was then filtered through 0.45 μm filter paper (Millipore HVLP) and the COD of this filtrate also determined. The filtrate COD should give USCOD. Both glass fibre and 0.45 μm filters were used to determine if the 0.45 μm filter could be replaced with glass fibre filters to reduce costs. To assess the results

from the batch test for USCOD, these were compared to values obtained with the conventional method of Ekama et al. (1986): Effluent from a lab-scale aerobic activated sludge system at 12 d sludge age treating the same wastewater used for the batch tests at the same COD concentration (for system details see Mbewe et al., 1995) was also subjected to flocculation-filtration and the filtrate COD measured; this will give the USCOD (Ekama et al., 1986).

### Unbiodegradable particulate (UP)COD and slowly biodegradable (SB)COD

Having developed the batch test method to quantify three of the influent COD fractions, namely RBCOD ($S_{bsi}$), HAB ($Z_{BHi}$) and USCOD ($S_{usi}$), it remained to find a method that can distinguish between SBCOD ($S_{bpi}$) and UPCOD ($S_{upi}$). At the start of the batch test procedure, the total COD ($S_{ti}$) is made up of the five influent COD fractions:

$$S_{ti} = S_{usi} + S_{upi} + S_{bsi} + S_{bpi} + Z_{BHi} \quad (1)$$

where:

i denotes influent/initial, i.e. at the start of the batch test.

For the influent, even with $S_{ti}$ measured directly and $S_{usi}$, $S_{bsi}$ and $Z_{BHi}$ determined using the batch test procedures set out above, it is not possible to differentiate between $S_{bpi}$ and $S_{upi}$. Furthermore, physical separation techniques, such as flocculation filtration, also cannot separate these two fractions, since both are particulate.

During the course of the batch test the two unbiodegradable COD fractions ($S_{usi}$ and $S_{upi}$) remain unaffected by biological action. The two biodegradable COD fractions ($S_{bsi}$ and $S_{bpi}$) are biologically utilised, which results in oxygen consumption and generation of HAB ($Z_{BH}$). The HAB undergoes death/lysis/endogenous respiration producing endogenous residue ($Z_E$) and SBCOD ($S_{bp}$) which is utilised in the same fashion as the influent SBCOD. Thus, at the end of the batch test (after the precipitous drop in OUR, Fig. 2), all the RBCOD has been consumed and the total COD ($S_{te}$) is made up of:

$$S_{te} = S_{use} + S_{upe} + S_{bpe} + Z_{BHe} + Z_{Ee} \quad (2)$$

where:

e denotes the end of the batch test.

Since the unbiodegradable COD fractions remain unaffected in the test, and unbiodegradable COD generation can be considered to be negligible (Mbewe et al., 1995):

$$S_{te} = S_{usi} + S_{upi} + S_{bpe} + Z_{BHe} + Z_{Ee} \quad (3)$$

In Eqs. (1) and (3) the parameters $S_{ti}$, $S_{te}$ and $S_{usi}$ are known from direct measurement and $S_{bsi}$ and $Z_{BHi}$ from calculation on the batch test data; also, OUR with time is available from measurement. The parameters $S_{bpi}$, $S_{bpe}$, $Z_{BHe}$ and $Z_{Ee}$ are unknown. It is evident that to quantify the unknowns, additional information has to be obtained from the batch test. Six methods were developed to attempt to obtain the necessary additional information (Mbewe et al., 1995). In all these methods, it was assumed that sufficient time had elapsed by the end of the batch test for all the SBCOD to have been consumed, i.e. $S_{bpe} = 0$; this reduces the number of unknowns to three.

#### *Division of OUR*

In this method, it was proposed to divide the OUR into its biodegradable COD utilisation ($OUR_{syn}$) and endogenous respiration ($OUR_e$) components. The batch tests were run for approximately 60 h, at which time the OUR had decreased to an approximately constant low value, due to endogenous processes. From this low OUR value, a line was back-projected to the start of the test, the OUR below this line being $OUR_e$ and above the line $OUR_{syn}$. From the area under $OUR_{syn}$, the influent biodegradable COD ($S_{bi}$) could be quantified, and, subtracting the known $S_{bsi}$, $S_{bpi}$ and thus $S_{upi}$ determined. However, the method did not provide reasonable, consistent estimates; for example, $S_{upi}$ as a fraction of $S_{ti}$ ($f_{S,up}$) varied from -0.14 to +0.45. Clearly the method used to divide the measured OUR was flawed. One possible reason is that $Z_{BH}$ varies considerably over the course of the batch test and therefore so will $OUR_e$.

#### *Selective pasteurisation*

In the method above, the problem was estimation of $OUR_e$. If $OUR_e$ could be reduced to such low values that it contributes negligibly to the measured OUR, then this problem may be overcome. From the work of Bhatla and Gaudy (1965) on the BOD-time curve (similar to the batch test here), a major contribution to $OUR_e$ is predation. If predation can be eliminated, then $OUR_e$ may be small compared to $OUR_{syn}$ and could be neglected. To eliminate predation in the batch tests, the influent wastewater was selectively pasteurised, by heating to 50°C for 5 min, then cooling to 20°C for the batch test - this selectively kills predators, but not bacteria (Bhatla and Gaudy, 1965). However, selective pasteurisation resulted in behaviour that deviated considerably from that in batch tests without prior pasteurisation - the precipitous drop in OUR was reduced, whereafter the OUR exhibited a second OUR peak, a feature not seen in any non-pasteurised batch tests. Possibly this feature was due to the heating process altering the nature of the wastewater, causing part of the SBCOD to become more easily degraded. Therefore this method was abandoned.

#### *Extended aeration*

In this method the batch test was run for an extended period (at least 3 d), and it was assumed that $Z_{BH}$ would be negligible at the end of the test, i.e. $Z_{BHe} = 0$ in Eq. (3). With this assumption, $OUR_e$ can be calculated (Mbewe et al., 1995) and so also $S_{bi}$, $S_{bpi}$ and $S_{upi}$. However, the values for $S_{upi}$ as a fraction of $S_{ti}$ ($f_{S,up}$) were unreasonably high (0.36 to 0.49), indicating that appreciable $Z_{BH}$ was still present at the end of the test. Also, running the batch test for >3 d would detract from its practical application.

The failure of the methods above to provide reliable, consistent estimates for $S_{bpi}$ and $S_{upi}$ led to a change in approach - it was decided to attempt to quantify $Z_{BHe}$, the HAB at the end of the batch test. If this parameter is known, then, provided that $S_{bi}$ has been depleted in the batch test, sufficient information is available to quantify the remaining unknown parameters because oxygen demand, $S_{bp}$, $Z_{BH}$ and $Z_E$ are stoichiometrically and kinetically related via the yield coefficient and endogenous respiration (Mbewe et al., 1995). The following three methods attempt to quantify $Z_{BHe}$.

#### *OUR at the end of the batch test*

In this method $Z_{BHe}$ was calculated from the absolute value for the OUR at the end of the batch test. However, values for $f_{S,up}$ from this method showed considerable variability, -0.11 to + 0.32. In examining the calculation procedure, it was evident that the procedure is sensitive to the absolute value for the OUR at the end of the test ($OUR_{ee}$). $OUR_{ee}$ has a very low value, 0.7 to 1.8 mgO/ℓ·h; relatively

small errors in the measurement of $OUR_{ee}$ (±0.5 mgO/ℓ·h) are significant compared to the absolute value, and cause significant errors in the calculated $f_{S,up}$.

### *Acetate addition*

In the batch test, HAB at the start can be quantified from the exponential increase in OUR caused by the growth of heterotrophs on RBCOD. It was proposed to duplicate this technique at the end of the batch test by adding the artificial RBCOD sodium acetate, thereby to determine $Z_{BHe}$ and hence $S_{bpi}$ and $S_{upi}$. With the addition of an artificial substrate, in this case sodium acetate, the possibility exists that the biomass behaviour will deviate from that with wastewater substrate. Thus, it was decided to assess this method before the full batch test procedure was implemented: About 2 h after the precipitous drop in OUR, 20 mℓ of a stock sodium acetate (Merck, analar) solution was added to give a concentration of 102 mgCOD/ℓ batch reactor (about the RBCOD concentration of the diluted raw wastewater). From the area under the OUR for acetate consumption, a value for the heterotrophic yield ($Y_{ZH}$) could be calculated. From 11 such tests, $Y_{ZH}$ = 0.646 mgCOD/mgCOD, with standard error of the mean of 0.007. This value corresponds closely to the value measured with wastewater (0.666; Dold and Marais, 1986). Thus it appeared that the behaviour with acetate conformed to that with wastewater RBCOD; the measured $Y_{ZH}$ value also lent support to the "standard" value for $Y_{ZH}$ = 0.666 used in all other calculations. Accordingly, the batch test was run for 2 d and then a known concentration of sodium acetate added (102 mgCOD/ℓ batch reactor). From the results for 10 such tests, it was found that $f_{S,up}$ was variable, and considerably higher than expected (0.05 to 0.49). It would appear that the method underestimates $Z_{BHe}$, which leads to $f_{S,up}$ being overestimated. It was speculated that the underestimation of $Z_{BHe}$ was due to the inability of all heterotrophs in the batch test to metabolise acetate - some kind of acclimatisation would be required, which would not be possible in the batch test.

### *Raw sewage filtrate addition*

Instead of adding sodium acetate, in this method raw sewage filtrate was added after 48h. Initial indications were that, of the six methods, this appeared to hold the most promise for development and therefore it was investigated more intensively.

The batch test detailed above was run for 2 d (investigations indicated that running the test for 3 or 4 d did not influence the results significantly). Raw (unsettled) municipal wastewater from the same source (Mitchells Plain) and batch used to start the batch test was filtered through glass fibre filters (Whatman's GF/C) and the filtrate refiltered through 0.45 µm filters (Millipore HVLP); the prefiltration through glass fibre filters was to reduce blinding of the 0.45 µm filters. After 2 d of batch test, 1 ℓ of the batch test mixed liquor was drawn off and analysed for total COD and flocculation filtration COD (see above). The 1 ℓ drawn off was replaced with 1 ℓ of raw wastewater 0.45 µm filtrate. The batch test was run for a further 12 h, or until the OUR dropped precipitously. In operation of the test, difficulties were experienced in filtering the raw wastewater through 0.45 µm filters; even with prefiltration through glass fibre filters, the 0.45 µm filters were rapidly blinded so that at least 10 filters had to be used, making the procedure arduous and expensive. To resolve this problem, the flocculation procedure described above for USCOD was applied to the raw wastewater prior to filtration; this reduced blinding of 0.45µm filters considerably and experimental evidence indicated that the preflocculation step did not influence the behaviour significantly. Also, to reduce costs it was found that the 0.45 µm filters could be replaced with glass fibre filters without influencing the results.

After adding the flocculated filtered raw wastewater (FFRW) to the batch test, the OUR exhibited an exponential increase similar to that at the start of the test. From this exponential increase in OUR, the HAB concentration in the batch test at the time of filtrate addition could be determined by following the procedures set out by Wentzel et al. (1995) and Mbewe et al. (1995). Independent tests indicated that the FFRW exhibited no biological activity, i.e. it contained no HAB. Accordingly, taking due account of dilution, the HAB immediately prior to adding the FFRW could be calculated; this is $Z_{BHe}$ in Eq. (3). With this value known, the wastewater biodegradable COD ($S_{bi}$) can be calculated from (Mbewe et al., 1995):

$$S_{bi} = [MO_C - (1-f)(Z_{BHi} - Z_{BHe})]/[(1-Y_{ZH}) + (1-f)Y_{ZH}] \quad (4)$$

where:

$MO_C$ = Mass of oxygen consumed by heterotrophs over the batch test (mgO/ℓ)
= Area under the OUR-time profile from start of test to adding FFRW

f = Heterotroph endogenous residue fraction
= 0.2 (Dold et al., 1980)

With $S_{bi}$ calculated and $S_{bsi}$ available from above, $S_{bpi}$ can be quantified from:

$$S_{bpi} = S_{bi} - S_{bsi} \quad (5)$$

and $S_{upi}$ can be found from Eq. (1).

To evaluate the results from the batch test for SBCOD and UPCOD, these were compared to values obtained using the conventional method of Ekama et al. (1986): A lab-scale aerobic activated sludge system at 12 d sludge age was operated in parallel receiving the same wastewater as influent that was used for the batch tests, at the same COD concentration. Following the procedures of Ekama et al. (1986), steady state data for the lab-scale system was used to calculate UPCOD, USCOD and hence biodegradable COD. From measurements on HAB and RBCOD (see above), the SBCOD also could be calculated.

## Results

Four to twelve batch tests were conducted on each of the 23 batches of wastewater collected (Table 1); HAB and RBCOD were determined for all wastewater batches, USCOD from wastewater batch 5, and UPCOD and SBCOD from wastewater batch 17. A full OUR-time profile for one such test is shown in Fig. 3 - the first ca. 10 h of the OUR profile are relevant for RBCOD and HAB; the profile after this time is for USCOD (ca. 24 h) and UPCOD and SBCOD.

### % COD recoveries

Following the procedures set out by Wentzel et al. (1995), the % COD recoveries were calculated for all the batch tests. From a statistical analysis (Laubscher, undated) on % COD recoveries, 3 out of 67 batch tests for Borcherds Quarry and 7 out of 138 for Mitchells Plain were identified as outliers and so were rejected for further analysis. The % COD recovery is a function of the batch test method and should not be specific to each batch of wastewater tested. Accordingly, probability plots of the retained % COD recoveries for the batch tests on wastewaters from Borcherds

**TABLE 1**
**WASTEWATER (WW) SOURCE, BATCH NUMBER AND RESULTS FOR COD FRACTIONS FROM BATCH TEST (BT) AND CONVENTIONAL TESTS (AS = ACTIVATED SLUDGE). EACH VALUE IS THE MEAN OF A NUMBER OF TESTS, WITH STANDARD ERROR OF THE MEANS IN ( ) AND NUMBER OF TESTS IN [ ].**

| WW source | WW batch No | Wastewater COD components as a fraction of total COD (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | HAB | RBCOD | | USCOD | | UPCOD | | SBCOD | |
| | | BT | BT | Square wave | BT | AS effluent | BT | AS reactor | BT | AS reactor |
| Borcherds Quarry | 1 | 7 (1.5)[5] | 20 (2.0)[5] | 21 (1.2)[11] | - | - | - | - | - | - |
| | 2 | 10 (1.0)[5] | 11 (0.7)[5] | - | - | - | - | - | - | - |
| | 3 | 9 (0.7)[8] | 15 (0.9)[8] | 15 (1.6)[5] | - | - | - | - | - | - |
| | 4 | 7 (1.0)[8] | 20 (0.9)[8] | 17 (1.6)[7] | - | - | - | - | - | - |
| | 5 | 9 (0.7)[5] | 21 (0.9)[6] | 20 (0.9)[6] | 10 (0.8)[6] | 9 (0.7)[6] | - | - | - | - |
| | 6 | 11 (1.4)[5] | 23 (0.4)[6] | 21 (1.1)[7] | 10 (1.0)[6] | 9 (0.8)[6] | - | - | - | - |
| | 7 | 16 (1.7)[9] | 18 (1.0)[9] | 18 (1.4)[7] | 8 (0.5)[6] | 8 (0.5)[6] | - | - | - | - |
| | 8 | 14 (1.8)[10] | 18 (1.4)[10] | 17 (0.8)[14] | 11 (0.3)[4] | 10 (0.8)[4] | - | - | - | - |
| | 9 | 10 (1.7)[7] | 17 (0.9)[7] | 18 (1.1)[7] | 10 (0.4)[8] | 8 (0.6)[8] | - | - | - | - |
| Mitchells Plain | 10 | 4 (0.6)[9] | 17 (1.2) [9] | 18 (1.1)[10] | 8 (0.9)[9] | 8 (0.6)[9] | - | - | - | - |
| | 11 | 3 (0.2)[8] | 17 (0.7)[7] | 18 (1.4)[12] | 9 (0.9)[5] | 8 (0.9)[5] | - | - | - | - |
| | 12 | 11 (1.2)[5] | 19 (1.1)[5] | 19 (1.6)[9] | 9 (0.7)[11] | 8 (0.7)[11] | - | - | - | - |
| | 13 | 10 (1.4)[12] | 25 (0.8)[10] | 20 (1.1)[12] | 9 (0.7)[12] | 7 (0.5)[12] | - | - | - | - |
| | 14 | 6 (0.8)[8] | 19 (0.9)[9] | 17 (1.8)[10] | 8 (0.4)[12] | 7 (0.6)[12] | - | - | - | - |
| | 15 | 9 (1.5)[7] | 19 (1.0)[8] | - | 7 (0.5)[12] | 7 (0.6)[12] | - | - | - | - |
| | 16 | 5 (0.9)[6] | 22 (1.9)[7] | 21 (0.6)[17] | 9 (0.8)[7] | 5 (0.5)[7] | - | - | - | - |
| | 17 | 8 (1.1)[12] | 27 (0.6)[10] | 23 (0.7)[17] | 8 (0.7)[14] | 8 (0.4)[14] | 20[10] | 9[20] | 37 | 51 |
| | 18 | 6 (0.8)[10] | 26 (1.5)[11] | 20 (1.2)[8] | 8 (0.7)[10] | 7 (0.8)[10] | 18[10] | 9[20] | 42 | 50 |
| | 19 | 9 (1.4)[9] | 24 (1.5)[9] | 24 (1.1)[10] | 8 (0.6)[6] | 7 (0.7)[6] | 8[6] | 12[21] | 51 | 48 |
| | 20 | 7 (1.0)[9] | 22 (1.1)[10] | 21 (1.9)[6] | 8 (0.6)[10] | 7 (0.4)[10] | 22[9] | 5[10] | 41 | 60 |
| | 21 | 12 (1.4)[9] | 20 (0.8)[8] | 21 (1.1)[10] | 8 (0.6)[9] | 6 (0.5)[9] | - | - | - | - |
| | 22 | 3 (0.5) [4] | 20 (0.5)[4] | - | - | - | - | - | - | - |
| | 23 | 7 (1.0)[9] | 18 (1.3)[8] | 19 (1.9)[9] | 8 (0.9)[9] | 7 (0.8)[9] | 18[7] | 18[15] | 48 | 45 |

Quarry and Mitchells Plain were constructed (Fig. 4), and the means and standard deviations determined. The mean % COD recoveries for Borcherds Quarry and Mitchells Plain wastewaters were 96% and 99%, with standard errors of the mean of 0.76% and 0.82% respectively. It is evident that the COD recoveries were good, lending credibility to the reliability of the measurements and to the batch test itself.

### Heterotrophic active biomass (HAB)

HAB was determined from a plot of ln(OUR) vs. time, from the start of the test up to the OUR precipitous drop (Fig. 3) (Wentzel et al., 1995). From a statistical analysis (Laubscher, undated), 2 and 7 batch test values for HAB for Borcherds Quarry and Mitchells Plain wastewaters respectively were rejected as outliers. For each batch of wastewater, the mean HAB and standard error of the mean were determined (Table 1). For Mitchells Plain wastewater, usually HAB was present in low concentration, ranging from 3 to 10% of total COD. However, on occasion (2 out of 14 wastewater batches, Table 1) concentrations were >10% of total COD. These high values could be traced to operational procedures at the treatment plant - sludge handling facilities were shut down for maintenance and repairs and waste sludge recycled to the head of the works, upstream of the point where the wastewater was collected for the batch tests. For Borcherds Quarry wastewater, HAB concentrations were variable, ranging from 7 to 16% of total COD. From an investigation of the operational procedures at the Treatment Plant, it was found that intermittently waste activated sludge was recycled to the head of the works and mixed with the incoming wastewater upstream of the point where the wastewater was drawn for the batch tests. Results obtained from the batch test for HAB could not be evaluated against results from any conventional test, since no conventional tests are available. However, as is evident from the above, the batch test consistently reflected changes in HAB concentration that could be traced to plant operation.

### Readily biodegradable (RB)COD

RBCOD was calculated from the batch test OUR-time profiles as detailed by Wentzel et al. (1995). From a statistical analysis (Laubscher, undated), 0 and 6 batch test values for RBCOD for Borcherds Quarry and Mitchells Plain wastewaters respectively were rejected as outliers. For each batch of wastewater, the mean RBCOD and standard error of the mean were determined (Table 1).

To evaluate the values for RBCOD obtained from the batch tests, daily the RBCOD for the batch of wastewater was determined also using the flow-through square wave method (WRC, 1984; Ekama et al., 1986). For each batch of wastewater, the mean RBCOD and standard error of the mean from this method also were determined (Table 1). In Fig. 5 the mean values for the different wastewater batches for RBCOD as a % of total COD from the batch tests are plotted against the corresponding values obtained from the conventional flow-through square wave method. From the plot it is evident that the two methods give results that correspond closely.

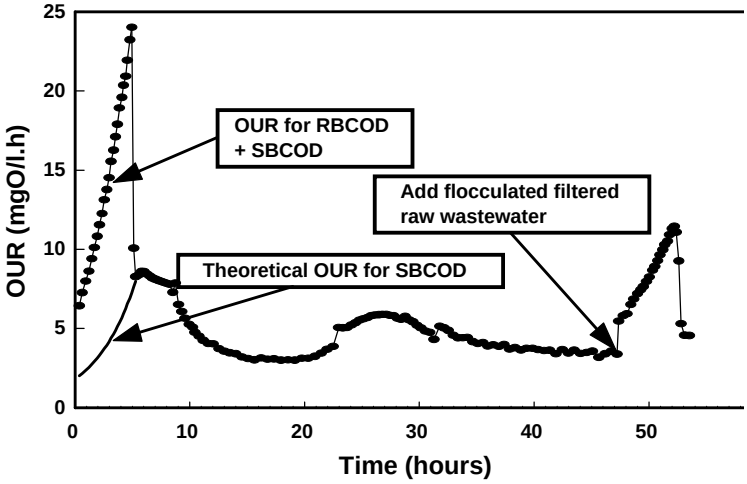


***Figure 3***

*Oxygen utilisation rate (OUR) response with time for aerobic batch test on raw municipal wastewater from Mitchells Plain (Cape Town, South Africa). Flocculated (Alum) filtered (0.45 μm) raw municipal wastewater added after 48 h.*

### Unbiodegradable soluble (US)COD

USCOD was determined in the batch test as the flocculated-filtered COD after one or more days. Also, USCOD was determined as the flocculated-filtered COD of the effluent from the lab-scale activated sludge system. From a statistical analysis (Laubscher, undated), no data were rejected as outliers. From the data it was evident that increasing the length of time of the batch test from one to two or more days did not significantly influence the values obtained for USCOD. Further, both glass fibre and 0.45 μm filters were used - from the data for USCOD, close correlation was obtained between the two types of filters. Evidently, to reduce costs the 0.45 μm filters can be replaced with glass fibre filters. For each batch of wastewater, the mean USCOD and standard deviation of the mean were determined from the batch test and from the activated sludge system effluent data (Table 1). To evaluate the values for USCOD obtained from the batch tests, in Fig. 5 the mean values for the different wastewater batches for USCOD as a % of total COD from the batch tests are plotted against the corresponding values obtained from the activated sludge system effluent. From the plot it is evident that the batch test method gives values that tend to be slightly higher than those from the activated sludge system effluent; this may be due to the inability of the organisms within the batch test to degrade some of the soluble biodegradable material in the wastewater, or due to the generation of USCOD in the batch test. However, the differences in USCOD between the two methods are relatively small (<10%) - the estimates provided by the batch test are acceptable for design and modelling purposes. Furthermore, values for USCOD as a fraction of total COD ($f_{S,us}$) from the batch test ($f_{S,us}$ = 0.07 to 0.10) fall within the range of values to be expected for a South African raw municipal wastewater ($f_{S,us}$ = 0.04 to 0.10; WRC, 1984). The batch test method does have the advantage over the conventional activated sludge effluent method in that it is not necessary to obtain effluent from a long sludge age activated sludge system.

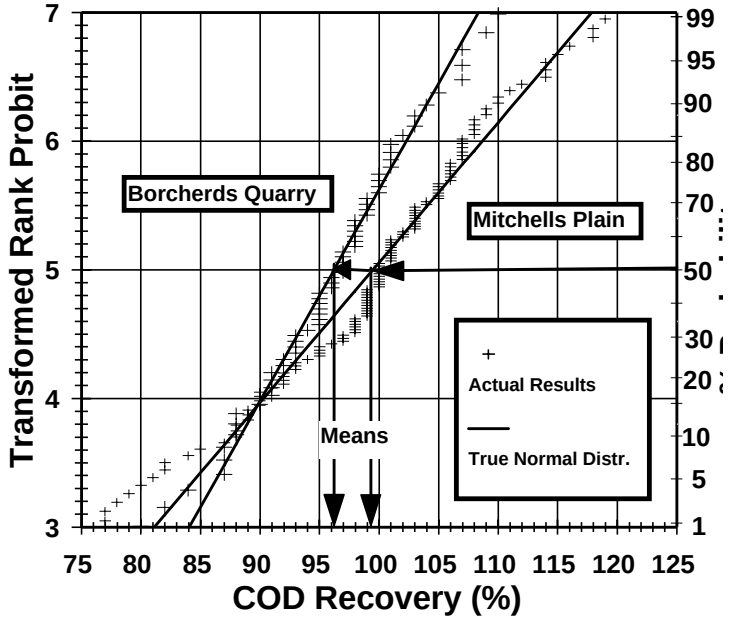


***Figure 4***

*Probability plot of %COD recovery for the batch tests on raw municipal wastewater from Borcherds Quarry and Mitchells Plain (Cape Town, South Africa)*

### Unbiodegradable particulate (UP)COD and slowly biodegradable (SB)COD

For the batch test method, all the information required to calculate SBCOD from Eqs. (4) and (5) and UPCOD from Eq. (1) is available from the batch test data. For each batch test, UPCOD and SBCOD as fractions of the total COD ($f_{S,up}$ and $f_{S,bp}$ respectively) were calculated, and the mean values determined for each wastewater batch, see Table 1. For the activated sludge system, estimates for HAB and RBCOD are required to determine SBCOD, but cannot be obtained from measurements on the system - for the purpose of calculation, HAB from the batch test was used and RBCOD from the parallel flow-through square wave system (see above). For each wastewater batch, the measured data were averaged, and the averages used to calculate UPCOD and SBCOD as fractions of total COD ($f_{S,up}$ and $f_{S,bp}$ respectively), see Table 1.

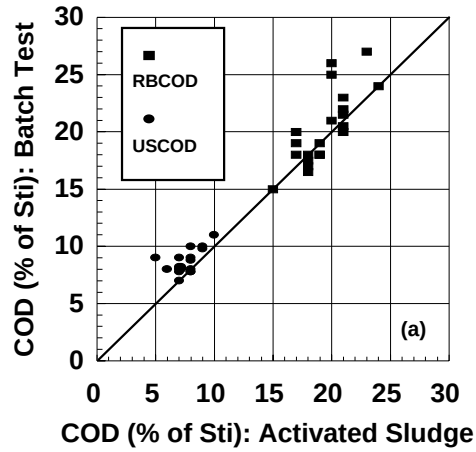


***Figure 5***

*Comparison between readily biodegradable (RB) COD and unbiodegradable soluble (US) COD measured in conventional activated sludge system type tests (Ekama et al., 1986) and batch tests. Each point plotted is the mean of a number of tests (Table 1).*

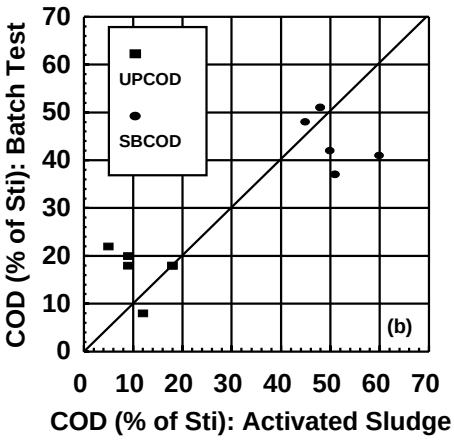


***Figure 6***

*Comparison between unbiodegradable particulate (UP)COD and slowly biodegradable (SB)COD measured in conventional activated sludge system type tests (Ekama et al., 1986) and batch tests. Each point plotted is the mean of a number of tests (Table 1).*

To evaluate the values for UPCOD and SBCOD obtained from the batch tests, for the different wastewater batches the mean values for $f_{S,up}$ and $f_{S,bp}$ respectively from the batch tests are plotted against the corresponding values obtained from the activated sludge system in Fig. 6. Comparing the $f_{S,up}$ values derived from the two methods, the values for $f_{S,up}$ from the batch test ($f_{S,up}$ = 0.08 to 0.22) and the activated sludge system ($f_{S,up}$ = 0.05 to 0.19) fall within the same range. Furthermore, the ranges of $f_{S,up}$ values from both tests compare reasonably with those quoted in the literature for South African raw municipal wastewaters ($f_{S,up}$ = 0.07-0.20; WRC, 1984). However, it is evident that, with the exception of wastewater batch 23, the direct correlation between the $f_{S,up}$ values for the individual batches of wastewater is poor. For all the batches of wastewater tested, the $f_{S,up}$ values for the two methods were averaged; the batch test gave values that tended to be higher ($f_{S,up}$ = 0.17) than those from the conventional activated sludge method ($f_{S,up}$ = 0.11).

Since UPCOD ($f_{S,up}$) tends to be overestimated in the batch test compared to the activated sludge system (accepted as the datum), the SBCOD should be underestimated. From Fig. 6, as expected the direct correlation between the values for $f_{S,bp}$ from the two test methods is poor. However, because the absolute values for $f_{S,bp}$ are very much larger than those for $f_{S,up}$, the relative differences between $f_{S,bp}$ estimates from the two tests are smaller than the relative differences between $f_{S,up}$ estimates.

## Conclusions

The batch test method developed in this investigation for characterisation of municipal wastewaters has advantages over previous methods in that:

- The experimental method is relatively simple.
- No activated sludge or other seed is required.
- The only independent constants required for calculation are the heterotrophic yield ($Y_{ZH}$), endogenous residue fraction for the heterotrophs (f), and specific death rate ($b_H$): Dosing the batch test with known concentrations of acetate showed that the value for $Y_{ZH}$ in the literature ($Y_{ZH}$ = 0.666 mgCOD/mgCOD, Dold and Marais, 1986; Dold et al., 1991) can be accepted; the batch test procedure is relatively insensitive to the value for $b_H$. All other constants required for the calculations are obtained from the experimental data.
- A single method provides estimates for complete characterisation of the wastewater; in conventional methods a number of parallel tests need to be run for complete characterisation.

The batch test was evaluated by comparing its results with those from conventional methods accepted as standard in the literature. Results from 205 batch tests on municipal wastewater from Borcherds Quarry (67) and Mitchells Plain (138) (Cape Town, South Africa) indicate that:

- Autotrophic active biomass was not present in either wastewater (no nitrification in batch tests).
- Batch test values for RBCOD concentrations correlate closely with those from the conventional flow-through square wave method (WRC, 1984; Ekama et al., 1986).
- Although the values for HAB could not be compared quantitatively to conventional methods (none are available), qualitatively the batch test was able to detect correctly variations in HAB caused by changes in plant operation.
- Batch test values for USCOD compare reasonably well to those derived from the effluent of a long sludge age activated sludge system (Ekama et al., 1986).
- Batch test values for UPCOD fall in the same range as estimates from the conventional activated sludge system method (Ekama et al., 1986). However, the direct correlation between values from the two tests is poor. For the present, the batch test does not provide estimates for UPCOD that are sufficiently accurate for use in design and simulation.
- The errors in UPCOD are reflected in the estimate for SBCOD. However, because the absolute value for SBCOD is very much higher than for UPCOD, the relative error in SBCOD is much less.

It is evident that the deficiency of the batch test procedure to obtain a reliable estimate for UPCOD remains and is an aspect that requires further investigation.

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