CHANGE OF GUARD – CAN $CBOD_5$ AND TSS TAKE A BACK SEAT?

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ABSTRACT

When analysing wastewater treatment plant performance and compliance of treated effluent discharge, two main parameters are tested: $CBOD_5$ (carbonaceous biochemical oxygen demand), and total suspended solids (TSS).

$CBOD_5$ testing is a time-consuming process that takes 5-6 days before the laboratory results are received, making it difficult to detect and react to any non-compliance issues in time. Further, the accuracy of this test has also been questioned since all the organic matter may not have degraded at the end of the 5-day test period. Moreover, it only measures biodegradable organic matter content.

Apart from the $CBOD_5$, nutrients and pathogen parameters, discharge consents in Aotearoa typically specify a TSS limit. Generally, treated effluent from medium to large sized biological wastewater plants in Aotearoa have a TSS of around 10 mg/L or less. TSS testing is generally completed in line with the consent conditions, meaning that limited data is available through discrete data points, making it difficult to monitor and improve the performance of a plant.

So, what are the alternatives?

This paper will explore the feasibility of replacing $CBOD_5$ tests with on-line Total Organic Carbon (TOC) measurements. There is a definite correlation between $CBOD_5$ and TOC in typical municipal wastewaters. Internationally, various plants have successfully managed to revise their permits to allow them to use TOC as a surrogate for $CBOD_5$ by establishing a ratio between the two parameters.

For TSS, we will explore the potential of replacing the tests with on-line measurements of turbidity to establish turbidity as a surrogate for TSS. It is noted that it may be feasible to establish a correlation between TSS and turbidity through an intense testing and analysis regime.

The key benefits of these alternative test regimes are as follows.

- Savings in time and resources,
- Availability of real-time data for performance monitoring, optimisation and troubleshooting,
- Availability of voluminous set of data during plant performance and upgrade studies.

KEYWORDS

Wastewater, science, $CBOD_5$, TOC, TSS

PRESENTER PROFILE

Kia ora koutou katoa!

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1 INTRODUCTION

Discharge consents in Aotearoa have compliance limits on CBOD (carbonaceous biochemical oxygen demand) and TSS (total suspended solids). These parameters require laboratory analysis to obtain results. The analysis can be time consuming and resource hungry. This results in lack of sufficient data and its availability at the right time.

Through this paper, the authors would like to introduce, to Aotearoa, the concept of substituting the measurement of CBOD with TOC (total organic carbon) and laboratory TSS measurements with on-line TSS meters and turbidity analysers.

Internationally, several authorities in the US and Europe have either moved away from or are in the process of moving away from testing for CBOD.

This paper discusses the benefits, overseas experience, and applicability in Aotearoa.

2 CBOD and COD TESTS

Currently, the two most popular tests to quantify organic pollution are measurements of carbonaceous Biochemical oxygen demand (CBOD) and Chemical oxygen demand (COD).

Sections below discuss these tests and their pros and cons. This discussion will function as a precursor to the alternate tests proposed in the later sections.

2.1 Carbonaceous Biochemical Oxygen Demand (CBOD)

CBOD is a common parameter used to indicate the organic pollutant strength of wastewater.

2.1.1 Description

BOD tests measure the oxygen consumed by microorganisms in a water sample. In carbonaceous biochemical oxygen demand (CBOD) tests, the nitrogenous oxygen demand is inhibited by addition of an inhibitor such as 2-chloro-6-(trichloromethyl) pyridine (TCMP) (Bridgewater et al., 2012). Hence CBOD tests measure oxygen consumed for degradation of biodegradable organic matter only.

In the test sample, oxygen is used to degrade organic material, oxidize organic material, and oxidize reduced forms of nitrogen. The dissolved oxygen (DO) is measured at the start of the test period and again at the end of the incubation period (Bridgewater et al., 2012).

The standard incubation period for CBOD is 5 days at 20°C, indicated as $CBOD_5$. Conventionally, complete biochemical oxidation of organic matter is viewed as complete in water samples after 20 days. However, a 20-day test period is too long to address exceedances in compliance concentrations (Delzer & McKenzie, 2003). The 5-day test assumes most oxidation has been completed and is used as a standard test for CBOD around the world.

2.1.2 Pros and Cons

Advantages of CBOD tests are (Bridgewater et al., 2012):

+ Well established and recognised throughout the world for a long time,
+ Easily undertaken by all accredited laboratories,
+ Relatively inexpensive.

Disadvantages of CBOD tests include (Bridgewater et al., 2012):

- Laboratory testing for CBOD takes 5 days,
- Large error tolerance,
- Errors during sample collection and maintaining homogeneity during transfer,
- Not undertaken frequently due to limited resources, resulting in inadequate data for process analysis,
- Low repeatability.

Many factors affect the accuracy and precision of CBOD measurements, such as:

- Method of sample collection,
- Soluble versus particulate organics,
- Settleable and floatable solids,
- Oxidation of reduced iron and sulphur compounds,
- Lack of mixing of samples,
- Variable laboratory environments such as incubator temperatures,
- Lack of micro-organism population in samples – a seed may be needed to conduct the test.

2.2 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a quantification of the organic pollutant content of wastewater. It measures the amount of oxygen used when an oxidant reacts with the test sample, rather than micro-organisms in the CBOD tests.

2.2.1 Description

COD testing uses oxidants like potassium dichromate, potassium iodate or potassium permanganate. The test measures all organic contaminants which can be oxidised in the sample, including those that are not biodegradable. The testing procedure takes 2-3 hours in a laboratory, excluding the cooling times. COD testing is useful when the sample contains toxic compounds, heavy metals, and cyanides, which are toxic for the micro-organisms in the CBOD test.

The test includes addition of a silver sulphate catalyst to effectively oxidise straight-chain aliphatic compounds. Mercuric sulphate is also added to remove interference of chlorides (Bridgewater et al., 2012).

2.2.2 Pros and Cons

Advantages of a COD test are as follows.

+ Well established and recognised throughout the world for a long time,
+ Easily undertaken by all accredited laboratories,
+ Shorter duration (2-3 hours) compared to a CBOD test,
+ Does not rely on microbial growth for oxidation,
+ Inexpensive

Disadvantages of a COD test are listed below (Bridgewater et al., 2012).

- Generation of hazardous wastes due to the reagents (mercury, hexavalent chromium, sulfuric acid, and silver) used,
- Results can be sensitive to changes in room temperatures,
- Vials could and have exploded during digestion and cooling,
- Test reagents are known carcinogens.

3 TOTAL ORGANIC CARBON (TOC)

Total organic carbon (TOC) is a measure of the amount of organic compounds contained in a water sample. Testing can be done by online analysers or by analysers in a laboratory.

The following paragraphs discuss the test procedure and its pros and cons.

3.1 Description

Technological advances like TOC analysers offer a direct method of measuring organic material in water. Unlike CBOD and COD, which use oxygen demand to measure organic material, TOC analysers measure and quantify the carbon present in the sample directly.

In a TOC analyser, the organic matter is oxidised to carbon dioxide, which is then measured. The oxidation is undertaken by combustion, UV persulphate or heated persulphate.

3.2 Pros and Cons

The advantages of TOC analysis over the CBOD and COD tests are as follows.

+ Complete oxidation of all organic compounds,
+ Distinct identification of organic and inorganic carbon,
+ Accuracy unaffected even if low concentrations of organics are to be measured,
+ Greater sensitivity and versatility,
+ Fast measurements with results available in under 5 minutes,
+ On-line and laboratory models of TOC analysers available, thus highly effective in effluent monitoring as well as process control.

Standard Methods 5310 states, *"Total Organic Carbon is a more convenient and direct expression of total organic content...measurement of TOC is of vital importance to operation of water treatment and waste treatment plants."*

Metcalf and Eddy refer to the use of TOC tests as a substitute for the CBOD test (Metcalf & Eddy Inc. et al., 2013).

There are as such no technical disadvantages of the TOC analysis over the cBOD and COD tests. However, there are a few challenges as noted below.

- Level of acceptance of the test by the authorities for process control and regulatory compliance,
- Set-up costs can be high,
- Laboratory set-up required,
- No plant operational guidelines for TOC

4 PROPOSAL

In Aotearoa, CBOD and COD tests are more popular, with CBOD being the accepted compliance parameter.

Given the various disadvantages and challenges of the CBOD and COD tests, the authors suggest either replacement or supplementation of these tests with TOC measurement. As described below, testing of TOC for compliance is becoming more common overseas because of the advantages it offers. Moreover, it is not a new test and is well established.

4.1 Correlations

Plants that have moved to TOC measurement have demonstrated a definite relationship between CBOD, COD and TOC. Based on extensive data for a specific wastewater, these organisations have been successful in establishing a meaningful relationship, to convince the regulatory authorities. This enabled them to switch to TOC measurements for compliance instead of CBOD.

4.2 Benefits

In conducting our research and talking to the practitioners overseas, the following benefits were highlighted.

- Easier and faster analysis of organic content in the effluent,
- Errors inherent with analysis of CBOD are eliminated
- Less labour, hence more frequent analysis is feasible,
- Extensive data sets can be acquired, necessary for process changes and upgrades
- Process control optimisation, troubleshooting and adjustments can be undertaken much quicker

5 OVERSEAS EXPERIENCE

Research has revealed that many water authorities overseas are moving away from CBOD testing. Sections below present some examples.

5.1.1 European Union

The Urban Wastewater Treatment Directive stipulates that CBOD can be replaced by TOC if a relationship can be established (The European Commission, 2016).

The Industrial Emissions Directive mentions the need for TOC or COD monitoring daily for compliance of industrial plants. This is a shift away from CBOD. In Germany, COD testing is preferred; however, the authors understand that there is progress to move this to TOC shortly (AZO Sensors, 2021).

5.1.2 India

The Bureau of Indian Standards (BIS) highlights a preference for COD testing over CBOD. India's Central Pollution Control Board (CPCB) states that on-line TOC can be used to estimate CBOD or COD "if a repeatable empirical relationship is established." (Central Pollution Control Board, 2018) As such, it appears that nondispersive infrared (NDIR) detector methods are preferred (Serajuddin, Chowdhury, & Ferdous, 2018).

5.1.3 United States

In the US, systems and regulations in some states allow substitution of CBOD. Specifically, to COD or TOC when a long-term correlation has been demonstrated (U.S. Code of Federal Regulations, 1984).

Areas in US that have successfully proven correlations between CBOD and TOC and have varied their permits accordingly, include:

- City of Santa Cruz Wastewater Treatment Facility, California
- Inland Empire Utilities Agency, California
- City of Boulder Public Works Wastewater Treatment Facility, Colorado
- Metropolitan Water Reclamation District of Greater Chicago
- Clark County Water Reclamation District, Nevada

5.2 Reference Sites/Plants

The authors met with personnel from two public water works in the US where they have successfully moved away from CBOD for regular compliance reporting to TOC. The following sections present a summary of the discussions.

5.2.1 Santa Cruz, California

The City of Santa Cruz was the first plant in the US to develop a long-term correlation of CBOD to TOC. They developed a correlation out of necessity. The plant was constrained by the CBOD test limitations, their laboratory conditions and reporting. The inconsistencies with CBOD results, and lack of repeatability, led them to look at alternative options.

CBOD and TOC were measured for 16 months to develop a long-term correlation. The correlation coefficient (R^2) value was 0.953 (Babatola & Xu, 2009).

Based on their extensive work, they were able to modify the permit to replace CBOD with TOC. The plant has been using TOC in their permit since 2007. Every two to three years, they are required to validate the equation, with a California Water Board regulator accepting the validation.

5.2.2 Chicago, Illinois

The Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) operates seven wastewater reclamation plants.

Following a successful application to the Illinois EPA, a study was implemented to establish the corelations between CBOD and TOC.

Based on an in-depth statistical analysis (regression equations and correlation coefficients) of the sampling results, a correlation was established, which was accepted by the Illinois EPA. The permits specify CBOD concentrations with a note saying that CBOD value is based on the TOC correlation equation (Brose, 2021).

MWRDGC anticipate that during their next permit renewal period in four years' time, they will be required to validate the correlations by carrying out CBOD and TOC testing.

6 TOTAL SUSPENDED SOLIDS (TSS)

Apart from $CBOD_5$, nutrient and pathogen parameters, discharge consents in Aotearoa specify a TSS concentration limit. Generally, treated effluent from medium to large sized biological wastewater plants in Aotearoa have a TSS of approximately 10 mg/L or less. TSS testing is generally completed per consent conditions, so it can be measured as infrequently as once a month.

6.1 Limitations of Laboratory Testing

TSS are measured by filtering the sample followed by drying and weighing residues under specified conditions. However, this method although practiced widely does introduce sources of error as described below (Bridgewater et al., 2012):

- Method of sample collection and maintaining homogeneity during transfer,
- Allowable exclusion of large floating particles or submerged agglomerates of nonhomogeneous materials from sample,
- Evaporation hindered by crust formation – adding weight to the final sample,
- Drying temperatures and heating duration,
- Addition of moisture during post-drying desiccation,
- Sample degradation before weighing,
- Excess water on filter shall cause it to stick to weighing dish or pan for drying and removal may cause loss of some filter material, and
- Samples with residual high oil or grease are hard to cool to a constant weight.

The Sections below discuss a suggested approach to minimise these sources of error.

6.2 Proposal

Due to the limitations discussed in the previous section, and the need for a labour resource for sample collection transport and analysis, the authors suggest reporting through on-line TSS or turbidity analysers as a substitute for laboratory measured TSS.

On-line turbidity measurement is normal at Water Treatment Plants, due to the drinking water standards. On-line TSS analysers have been used in activated sludge plants and biosolids processes.

However, this practice of employing on-line turbidity or TSS analysers can be employed on treated effluent lines at wastewater treatment plants. This is especially relevant on plants based on membrane bioreactors or membrane filtration, where the TSS concentrations are very low (<5ppm, often <2ppm). Through a rigorous process of testing and analysis, a suitable correlation between TSS and turbidity can be easily obtained.

The benefits of such a switch to on-line measurements are listed below.

- Reduced labour for sample collection, testing and analysis,
- Continuous real time data available necessary for controls and monitoring,
- Eliminates errors seen in laboratory testing of TSS.

7 APPLICATION IN AOTEAROA

There are two aspects to explore for application of the concept in Aotearoa.

7.1 Treatment Plant Level

TOC data will assist in improving the process control and operations of the plant. There are a number of activated sludge plants in Aotearoa that can install TOC analysers to monitor, control, optimise and troubleshoot their operations. With an established correlation between TOC and CBOD, the plants will have extensive and quick data on CBOD, thus facilitating process control decisions.

In addition, there are several membrane bio-reactor plants (MBRs) and membrane filtration plants, which are well controlled and monitored and have stringent requirements for TSS in the effluent. Such plants will benefit from continuous TSS measurement either through an on-line TSS analyser or correlated with an on-line turbidity analyser.

7.2 Regulatory Level

The discharge consents stipulate concentrations, and mass loads, for CBOD and TSS in the final effluent. Regional Councils can explore the feasibility of accepting TOC correlated CBOD readings. Because of the ease of collecting TOC data, more data will be available for the Regional Council, which will assist them in their overall monitoring of the receiving environment.

It is acknowledged that the acceptance of TOC correlated CBOD readings by regulatory authorities may be a lengthier process and will require further research. However, steps can be taken in the present at various levels by the wastewater industry to study and implement the feasibility of the approach presented by the authors.

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