

References of bibliography for DWES Publication:

Background information:

Biochemical and chemical oxygen demand measurements have been used for over 100 years to qualify and quantify contamination in municipal and industrial wastewater. Biochemical Oxygen Demand, currently a five-day laboratory test labeled BOD₅, is one of the most broadly used parameters for wastewater quality in the world and the standard for municipal sewage treatment. Chemical Oxygen Demand (COD), typically a two-hour test, is more widely used in industrial applications. Often, both of these laboratory methods are measured, recorded and compared over time.

Bibliography:

"Pacific Southwest, Region 9 – Quality Assurance." United States Environmental Protection Agency. Last updated 20 May 2016. 24 Aug 2016 www.epa.gov/region9/qa/

"BIOCHEMICAL OXYGEN DEMAND (BOD) – Standard Method 5210 B (5-day BOD Test)." United States Environmental Protection Agency. Last updated 20 May 2016. 24 Aug 2016 www.epa.gov/region9/qa/pdfs/5210dqi.pdf

ASTM D1252 – 06(2012) Standard Test Methods for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water

Regulatory framework for the use of COD vs TOC:

- The COD usual method (DIN 38409-H41) is using Chromate and Mercury, which are very toxic chemicals. For this reason, there is a tendency to move away from the parameter COD and to promote the use of the parameter TOC.
- Some countries, like Sweden, even banned the use of this methodology.
- The development of TOC as a parameter is being reflected in a number of documents, within the Directive Monitoring of emissions to air and water - Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control) such as:
 - ROM, final draft document: "Total organic carbon (TOC)/Chemical oxygen demand (COD): In some Member States, there is a trend to replace COD by TOC for economic and environmental reasons. The use of chromate and mercury, necessary for the COD determination, can be avoided by determining TOC, which can be measured continuously by on-line analysers."
 - CWW, final draft document: 'Either TOC or COD is monitored. TOC monitoring is the preferred option, because it does not rely on the use of very toxic compounds.'

Bibliography:

http://eippcb.jrc.ec.europa.eu/reference/BREF/ROM_FD_102013_online.pdf : Section 4.3.1, page 82

http://eippcb.jrc.ec.europa.eu/reference/BREF/CWW_Final_Draft_07_2014.pdf : Section 4.2, BAT 4, page 553

Regulatory framework for rejects monitoring:

In the United States, pre-treatment standards are established for all industrial and Publicly Owned Treatment Works (POTWs). Under the authority of the Clean Water Act and subsequent legislation, the National Pollutant Discharge Elimination System (NPDES) was established under the administration of the Environmental Protection Agency (EPA). With minimal exceptions, NPDES is the primary program that manages discharge limits or effluent limitations guidelines (ELG) for the release of process effluent or wastewater to public waterways.

Bibliography:

"NPDES Permit Program Basics." United States Environmental Protection Agency. 24 Aug 2016 https://cfpub.epa.gov/npdes/docs.cfm?document_type_id=8&view=Permit%20Applications%20and%20Forms&program_id=45&sort=name

“State NPDES Program Authority.” United States Environmental Protection Agency. Last updated 19 Feb 2016. 24 Aug 2016 <https://www.epa.gov/npdes/npdes-state-program-information>

In Europe, France has effluent discharge limitations in open waterways requiring BOD < 100 mg/L and COD < 300 mg/L. Germany allows a maximum COD value based on 4 x TOC – “a chemical oxygen demand (COD) level specified in the water discharge permit shall also be deemed to have been met provided the quadruple amount of total organically bonded carbon (TOC), specified in milligrams per litre, does not exceed this level.”

Bibliography:

“Arrêté du 26 mars 2012 relatif aux prescriptions générales applicables aux installations classées relevant du régime de l’enregistrement au titre de la rubrique n° 2710-2 (installations de collecte de déchets non dangereux apportés par leur producteur initial) de la nomenclature des installations classées pour la protection de l’environnement.” Article 35: Valeurs limites de rejet. Current as of 26 March 2012. 21 April 2015 http://legifrance.gouv.fr/eli/arrrete/2012/3/26/DEVP1208907A/jo/ar-ticle_35

“Promulgation of the New Version of the Ordinance on Requirements for the Discharge of Waste Water into Waters.” Article 6, section (3), page 5. Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Germany. Current as of 17 June 2004. 24 Aug 2016 http://www.bmub.bund.de/fileadmin/bmu-import/files/pdfs/allgemein/application/pdf/wastewater_ordinance.pdf

Value of TOC to Oxygen Demand Correlation

TOC analysis is faster and more accurate than either oxygen demand method and is a direct measurement of the organic load. Both forms of oxygen demand are indirect measurements. TOC has an analysis time of 3 to 10 minutes, or 30 minutes for at least three (3) repetitions, compared to two hours for COD or five days for BODs.

The NPDES system allows for “authorized alternatives” to oxygen demand, such as TOC measurement, correlating to oxygen demand, as a means for operators to have faster and more accurate monitoring and process control. In this way, industrial facilities, “non-municipal dischargers”, with wastewater treatment can often trend oxygen demand and anticipate excursions before exceeding their permit limits.

Bibliography:

“Central Tenets of the National Pollutant Discharge Elimination System (NPDES) Permitting Program.” Page 2. United States Environmental Protection Agency. Last updated 7 April 2015. 21 April 2015 <http://water.epa.gov/polwaste/npdes/basics/upload/tenets.pdf>

A pre-treatment facility should work with its state NPDES administrator to execute a long-term, correlation test and replace BOD or COD with TOC as the primary discharge parameter. Regulatory agencies (e.g., USEPA, state DEPs) may have specific requirements on the number of samples and test period. As indicated in a study report by Instrumentation Testing Association of North America, “weekly sample analysis for a minimum of one year to include seasonal variations is recommended for municipal wastewater plant in order to obtain discharge permit”.

Bibliography:

Nutt, Stephen G. and Tran, John of XCG Consultants Ltd. “Addressing BOD5 limitations through Total Organic Carbon Correlations: A Five Facility International Investigation.” Pensacola, Florida: water & Wastewater Instrumentation Testing Association of North America (ITA). January 2013.

Since TOC and oxygen demand methods are inherently different, the historical concern with TOC:COD correlation is the stability of the relationship over time due to any changes in the process stream(s). The variability of organics over time could alter the mathematical relationship to oxygen demand. The

sample matrix, particulate or solids composition, viscosity and turbidity can influence the correlation factor over time.

By measuring TOC every ten minutes and applying the correlation factor:

- COD can be estimated as many as 12 times more frequently than the traditional test
- BOD₅ can be estimated 288 times per day, compared to the traditional test

In Ireland, Influent and effluent samples from 11 WW treatment plants were analyzed.

Result are: Influent agreeable for both BOD and COD to be replaced by TOC. Effluent relationship between COD and TOC but not BOD.

Bibliography:

Replacement of chemical oxygen demand (COD) with total organic carbon (TOC) for monitoring wastewater treatment performance to minimize disposal of toxic analytical waste

Authors: Donata Dubbera; Nicholas F. Graya

Affiliation: Water Technology Research Group, Centre for the Environment, School of Natural Sciences, Trinity College Dublin, Dublin, Ireland

Conclusion that for treatment performance monitoring COD can be reliably replaced with the TOC. Predictive equations could be developed to estimate COD from TOC measurements.

Bibliography:

Replacement of chemical oxygen demand (COD) with total organic carbon (TOC) for monitoring wastewater treatment performance to minimize disposal of toxic analytical waste

Authors: Donata Dubbera; Nicholas F. Graya

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How to Determine the Correlation Factor

There are a number of ways to properly determine the correlation factor between TOC and the oxygen demand parameter of choice, BOD₅ or COD. The method detailed in the Instrumentation Testing Association (ITA) Test Report is specific with corresponding statistical analyses; refer to the Implementation Protocol.

Bibliography:

Nutt, Stephen G. and Tran, John of XCG Consultants Ltd. "Addressing BOD5 limitations through Total Organic Carbon Correlations: A Five Facility International Investigation." Pensacola, Florida: water & Wastewater Instrumentation Testing Association of North America (ITA). January 2013.