RAPID COD DETERMINATION BY PHOTOCATALYSIS

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Abstract

BOD_5 is an important standard parameter commonly used to monitor organic load for environmental and process control in a vast range of industries. Using the Aqua Diagnostic PeCOD™ COD analyser to determine COD in a brewery, sugar mill refinery, it has been shown that a scaling factor can be applied to COD measurements to determine an estimated BOD_5 concentration in a range of saline conditions which was well within the 95% confidence level when compared to the standard BOD_5 test.

Introduction

Chemical oxygen demand (COD) and biological oxygen demand (BOD) are two of the most common generic indices used to assess aquatic organic pollution. BOD is often used to evaluate the biodegradable fraction, and COD the total organic pollution load of waters contaminated by reductive pollutants (Kim *et al* 2001, Abuzaid *et al* 1997, Thomas *et al* 1997, Thomas *et al* 1999).

BOD values will generally be lower than COD values. This is due to the substantial differences in the methods of oxidation of the samples. COD measures the oxygen consumed by a very rigorous chemical oxidation under heat whilst BOD5 measures the oxygen demand from microbes living in an incubated environment for 5 days. While COD gives a good estimate of the biogeochemical interactions in waterways, BOD is generally believed to give a better representation of these interactions.

In the industrial world the continuous monitoring of organic load becomes essential to comply with regulatory requirements. Given the practical constraints on real time data introduced by the BOD_5 test, an alternative is its estimation, by correlation, from a rapid COD measurement.

The standard dichromate COD test, although somewhat faster than the BOD_5 test, still takes several hours, and this is too slow for an operation where real time data is essential, such as a Wastewater Treatment Plant (WWTP) where varying COD levels will indicate a varying load on the plant, or an industrial outfall where information pertaining to regulatory compliance must be available quickly.

Figure 1. ?????

In this latter case, the BOD values required for regulatory compliance at WWTP outfalls are usually far too low to admit to BOD measurements (<10 mg/L), and since with the standard dichromate COD test results below 50 mg/l are regarded with caution, it is not capable of acting in this capacity. In addition, dichromate can oxidise chlorides to chlorine so it cannot be used for saline effluents such as desalination brines.

This paper reports on an alternative technology for the measurement of rapid COD that addresses these limitations, and allows COD to be measured with a rapidity that makes real-time estimation of BOD possible.

PeCOD™ Technology

Aquadiagnostic have combined recently developed photoactive TiO_2 nanomaterials with photocatalysis and coulometry to provide an alternative means to standard COD methods.

The ability to monitor in real-time down to the sub ppm level.

Unlike the dichromate method, which determines COD by difference, the PeCOD device directly measures the Chemical Oxygen Demand. It does this by exhaustively oxidising, at a photoanode that is illuminated with UV light and set at a potential bias, all oxidiseable organics in the sample. Thus, the analytical signal is the charge that is harvested during this process.

First reported several years ago (Zhang *et al* 2004) the basis of the technology is a photoactive film of titanium dioxide. Upon irradiation by UV light, a photoelectron and photohole are created with an electrochemical potential of 3.1 V, which has very powerful oxidising properties.

Whereas under irradiation alone the photoelectron/hole pairs have a short lifetime, the application of the potential bias induces an electric field that results in spatial separation that does not otherwise occur. In the presence of an oxidiseable organic, the photohole is consumed, and the photoelectron flows to the external circuit, thus generating a photocurrent.

This contrasts with the use of titanium dioxide that is added to wastewater as a photocatalytic reagent for the bulk degradation of organics, in which dissolved oxygen is required to harvest the photoelectron and allow a net reaction to occur (Hoffman *et al* 1995).

The rapidity of analysis allows the technology to be incorporated into both laboratory and online devices (Figure 1). When employed as an online tool, the instrument is able to provide data to the Plant PLC, that is then able to optimise the various waste treatment or manufacturing processes accordingly.

Typical parameters are shown in Table 1.

System Performance

Studies were undertaken at a brewery and at a sugar mill to measure organic load in the discharge. The studies employed a PeCOD™ online COD

Table 1. Analytical Figures of Merit and System Requirements

Linear Range (mg COD/L)	0-300
	$R^2 = 0.9992$
Sample throughput	20 analyses hr^{-1}
L.o.D (mg COD/L)	0.1*
Sample Volume	10 mL $analyses^{-1}$

analyser (P100) set to measure effluent samples at 15 min cycles. Grab samples were collected for a subset of this trial period where samples were analysed by the PeCOD™ method for COD and externally measured for BOD_5 concentrations. The COD data obtained was greater than the BOD data as is typical for industrial and municipal effluent. The data collected from the P100 online PeCOD COD analyser was compared to the BOD results and an average factor was determined between the two data sets. This value was then adjusted to minimise the sum difference between estimated and laboratory tested BOD data. The resulting factor, for both the brewery and sugar mill results, was 1.83 which is equivalent to a multiplier of 0.55 ±0.02 required to convert COD values to a 5-day BOD estimate. The results for the brewery are shown in Figure 2 and the results for the sugar mill are shown in Figure 3.

COD Comparison to BOD

A paired t-test performed on the BOD and Estimated BOD data set for both the brewery and sugar mill showed no significant difference at the critical · = 0.05 level between the concentrations observed from the Estimated BOD based on the PeCOD COD method and standard reference method for BOD ($t = 2.13$, $P = 0.19$ and $t = 1.75$, $P = 0.85$, respectively) implying a good relationship between estimated BOD and BOD.

In addition a regression test showed a significant correlation at the $P < 0.05$ level (by testing the fully fitted model; Estimated BOD = m [BOD] + [Estimated BOD]; $F = 242$, $P = < 0.001$, $r = 0.97$ and $F = 15.9$, $P = 0.001$, $r = 0.79$, respectively) implying there is a significant correlation between Estimated BOD and standard BOD methods.

Conclusions

The capability to reliably relate COD to BOD_5 using the PeCOD™ analyser and produce an accurate result as a estimate of BOD has been clearly demonstrated at the 95% confidence level. The PeCOD™ system provides the ability to accurately monitor in real-time a wide range of concentrations down to the sub ppm level and enables a good representation of the organic load for both total organics and the organics available for biological consumption.

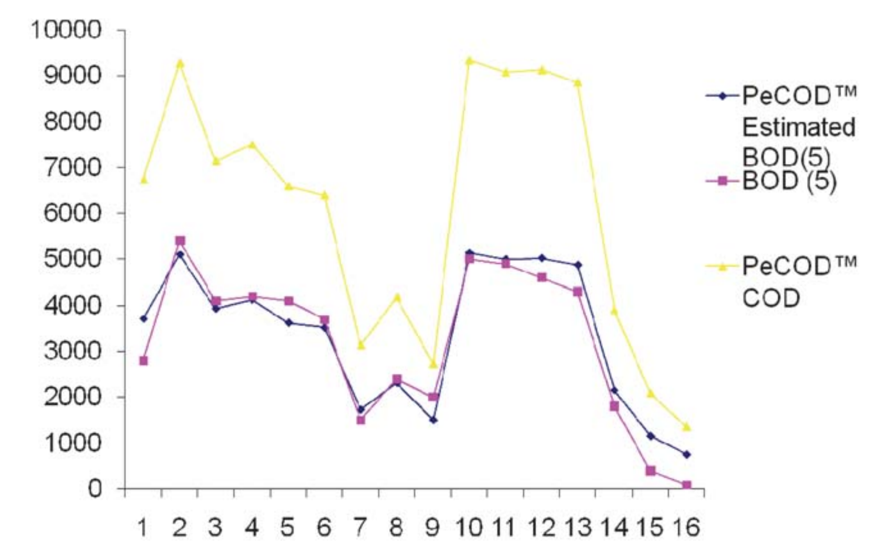

Figure 2. Comparison of COD, BOD_5 and estimated BOD_5 from a brewery.

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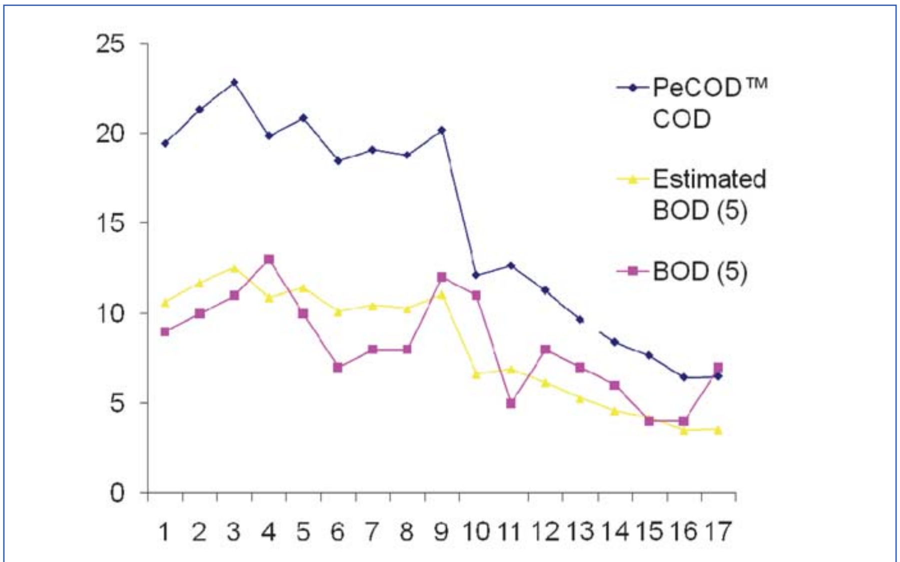

Figure 3. Comparison of COD, BOD_5 and estimated BOD_5 from a sugar mill.