

Trace Level Monitoring of Methanol and Ethanol in Tertiary Treated Effluent by PeCOD™ Chemical Oxygen Demand (COD) Analyser

Keywords: Biological Nutrient Removal (BNR); Ethanol; Methanol; Chemical Oxygen Demand (COD)

Abstract

Organic dosing is an essential process performed to enhance biological nitrogen removal in wastewater treatment plants. The PeCOD™ COD analyser is capable of measuring low levels of methanol and ethanol at the ppb level (LOD 0.2 mg/L COD) in tertiary treated effluent with a low COD background, achieving 100 % recovery of spiked samples at a rate that is far quicker and more sensitive, and is innocuous compared to the standard dichromate test for COD.

Introduction

Lowering nutrient levels in wastewater discharges - in particular nitrates - has become a trend in the wastewater treatment field as a result of increasingly strict regulatory requirements. Many biological wastewater treatment facilities have been restructured in order to meet these stringent discharge permit limitations. However, many existing biological nutrient removal (BNR) processes do not reliably satisfy the stricter permit requirements since wastewater does not always contain a carbon substrate in sufficient amounts for nutrient removal. As a result, several external carbon sources such as ethanol, methanol and acetic acid have been considered to compensate for this deficiency in biological organic carbons¹. This results in an oxygen-deficient environment to encourage the bacteria to consume nitrate and ensures that conversion of nitrate proceeds to the production of nitrogen gas rather than to the more toxic nitrite intermediate.

Methanol is typically added to municipal wastewater as a source of carbon. However, investigations into the use of ethanol as an alternative source of external carbon dosing have intensified, as ethanol can be obtained as a relatively inexpensive and innocuous waste product by comparison. In addition, studies have shown ethanol to be more readily available as a carbon source and that

the rate of denitrification with ethanol is 2-3 times higher than with methanol^{2, 3}.

Typical tertiary treated effluent contains COD of 1-30 mg/L, and in addition to this, methanol concentrations as COD need to be monitored in this background COD to ensure the resultant dosed carbon does not exceed 5 mg/L in the final effluent as specified by the regulatory bodies (as this can upset the COD/BOD balance and any residual nitrate conversion).

The Aqua Diagnostic PeCOD System

Aqua Diagnostic has developed a new rapid, sensitive and green alternative to measuring COD employing recently developed photoactive TiO₂ nanomaterials combined with photocatalytic technologies. The standard method is currently the dichromate COD test. However, this dated method is slow, limited in sensitivity and requires the addition of toxic chemicals (i.e. mercury) to eliminate interferences such as chloride.

Based on the oxidative degradation principle, the innovative aspects of the PeCOD™ method lie in the novel approach to generate and quantify the useful analytical signals⁴ with a sensitivity and speed far greater than any standard method (minutes compared to hours and µg/L compared to > 10 mg/L) as shown in Table 1.

Table 1 – Analytical Figures of Merit and System Requirements

Linear Range (mg COD/L)	0-300
Sample throughput	Up to 20 analyses hr ⁻¹
LOD (mg COD/L)	0.1
Sample Volume	20 µL analyses ⁻¹
Supporting Electrolyte	2M NaNO ₃

Calculated based on particular instrument set-up

System Performance

To meet the water testing requirements, the PeCOD™ system must provide adequate sensitivity and be able to measure small doses of methanol and/or ethanol in relatively low COD background. A standard calibration curve for both ethanol and methanol achieved a limit of detection of 0.1 mg/L COD.

Chlorine and chloride intermediates are typically added in the tertiary stage treatment of wastewater. Chloride, however, has been previously shown to cause interferences in the oxidation of organics and its subsequent COD determination^{5,6}. The standard dichromate method typically uses the addition of the toxic compound mercury sulphate to eliminate this effect. Using the PeCOD™ system, simple techniques are able to be applied to help diminish any chloride interferences without the requirement for addition of toxic substances.

System Validation

Spike recovery of tertiary effluent taken from municipal wastewater treatment plants was performed to validate the detection of both methanol and ethanol in a COD background on the PeCOD™ system. Results obtained provided recoveries close to 100 % for samples spiked with ethanol (Figure 1) and methanol (Figure 2) in the range of 3-7.5 mg/L with a background COD ranging from 20-80 mg/L.

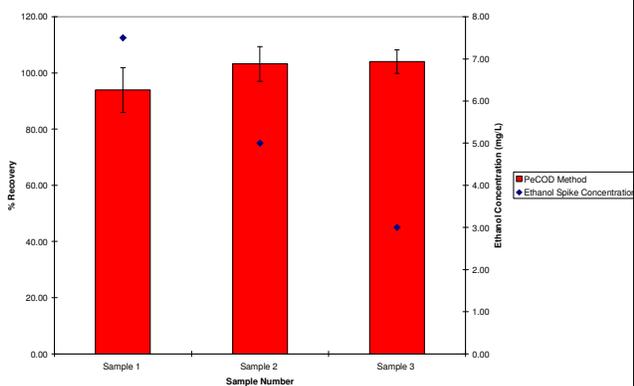


Figure 1 - Percentage recovery of tertiary effluent samples collected from municipal wastewater treatment plants performed on the PeCOD system. All samples were spiked ethanol concentrations ranging from 3-7.5 mg/L, and any dilutions made were made by a factor of 1:20. Error bars of $\pm 1\sigma n-1$ are shown.

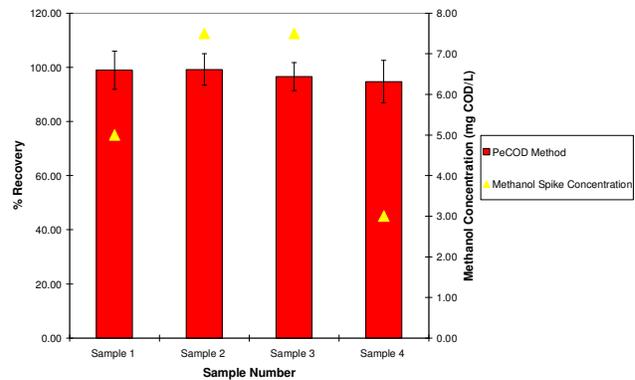


Figure 2 - Percentage recovery of tertiary effluent samples collected from municipal wastewater treatment plants performed on the PeCOD system. All samples were spiked methanol concentrations ranging from 3-7.5 mg/L, and any dilutions made were made by a factor of 1:20. Error bars of $\pm 1\sigma n-1$ are shown.

The limited sensitivity of the dichromate method results in the method being inadequate to measure in such applications, and consequently in the past analysts have had to resort to total organic carbon (TOC) measurements as an alternative⁷. However the informational content of the TOC analysis is less useful than that gained from COD methods with reference to organic contamination⁸. The other nominated alternative for measuring COD is by a UV absorption probe. In reality, however, the UV absorption method can only see carbon double bonds. This means all substances that contains only single bonds such as simple alcohols, sugars, and ketones⁹ escape detection.

Conclusions

Organic dosing is an essential process for the acceleration of bacterial conversion of nitrate to harmless nitrogen gas in the treatment of wastewater. Therefore, the rapid monitoring of methanol and ethanol (two common sources used for organic dosing) in tertiary effluent outfall is essential in order to comply with regulatory standards. The PeCOD™ system provides the ability to accurately monitor in real time typical low methanol and/or ethanol concentrations in an already low COD background without the need for toxic chemical use.

References

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