Novel technology for fast COD analysis leads to optimised processing and wastewater treatment for pulp and paper industry

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A recent EUREKA international research project has proven a new method for measuring Chemical Oxygen Demand (COD) that is faster, safer, and greener than the conventional dichromate method (CODcr). The project focused on wastewater effluents within the pulp and paper industry and results showed excellent applicability to the water intensive industry.

The new method for measuring COD is called photoelectro Chemical Oxygen Demand (peCOD), and it eliminates the use of hazardous chemicals, like dichromate, used in the conventional method for measuring COD. The peCOD method does not involve a high-temperature digestion, which reduces the conventional analysis time of three hours to less than 15 minutes.

The main objective of the EUREKA project was to develop new technologies to reduce hard-to-break-down COD, also known as recalcitrant COD, in water intensive industries, namely pulp and paper. peCOD was selected to help evaluate the effectiveness of the different COD treatment technologies at various stages in the pulp and paper process.

To validate the peCOD method, a comparative study was conducted to compare peCOD and CODcr sample results from several effluents at different pulp and paper mills. The peCOD method demonstrated a strong correlation to the CODcr method for all effluent sample types and indicated excellent reproducibility for replicate results.

Since the findings from the project, peCOD has been adopted in pulp and paper mills around the globe. The peCOD method is being used for process savings, improved health and safety for employees and the environment, and greater success meeting discharge compliance regulations.

In addition to the pulp and paper mills, peCOD is being employed by companies servicing the pulp and paper industry, such as chemical suppliers and commercial wastewater treatment facilities.

Introduction

The EUREKA project focused on developing novel technologies to treat recalcitrant COD. Its other important focus was to find a faster, more robust COD method to closely monitor effluent levels, to ensure efficient production, sufficient wastewater treatment, and discharge compliance. It's likely that the EUREKA project was organised in response to stricter environmental regulations imposed on the pulp and paper industry. Pulp and paper mills produce a large volume of wastewater and residual sludge. Some challenges facing pulp and paper operations are: high organic concentrations in production and wastewater effluent, operation costs, performance and impacts to the environment. This article will highlight the development of the peCOD method for COD monitoring and its benefits to the pulp and paper industry by addressing these challenges.

Experimental Methods

The peCOD method for COD analysis is a novel method based on photo-catalytic degradation of organic material. The technology employs a three-electrode system and uses an illuminated titanium dioxide (TiO_2) sensor. During an analysis, sample is introduced into the sensor cell containing the TiO_2. A UV LED light is illuminated onto the sensor cell while a potential bias is applied across the sensor and electrode system. The UV light energises the stable state of the TiO_2 film, which liberates electrons from the working electrode, leaving the immobilised TiO_2 to readily oxidise the organic material in the sample (see *Figure 1*). The powerful oxidising potential of TiO_2 (3.1V) ensures that virtually all organic species are oxidised.

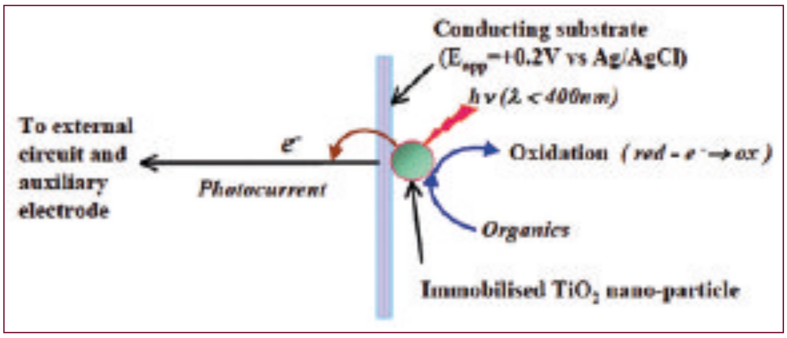

Figure 1: peCOD sensor technology

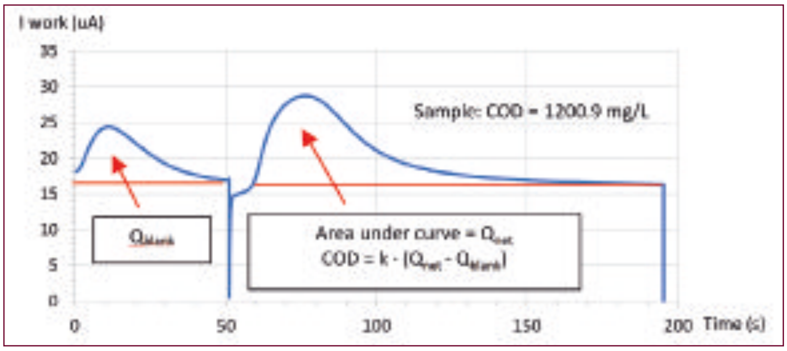

Figure 2: peCOD oxidation profile from the generated photocurrent during oxidation of organic species.

Figure 3: peCOD technology configurations:
a. Benchtop and Portable L100 and b. Automated L100.

Meanwhile, the controlled potential bias across the electrode system forces the liberated electrons to pass onto the auxiliary electrode, where the reduction of oxygen (and other species) takes place. The photocurrent (charge) generated from the flow of liberated electrons is monitored to give a direct measure of the oxidation of organic compounds. The total net charge generated is determined by integrating the photocurrent generated during a reaction, as shown in *Figure 2*.

An exhaustive degradation model is used to calculate the COD from the net charge and blank charge generated during sample analysis. Given that for oxidation by O_2, one oxygen molecule is equivalent to 4 electrons, the Q-value can be used to calculate the equivalent COD, according to *Equation 1*.

$$COD = \frac{Q}{4FV} x\ 32000 \quad (1)$$

The peCOD method eliminates the use of mercury, dichromate, and concentrated acid, which are all found in the traditional CODcr method. Instead, peCOD uses salt and sugar solutions to create baseline COD levels and different calibration concentrations for measuring varying ranges of COD. The testing range is 0.7mg/L to 15000mg/L of COD; however, incorporating dilution can extend this range.

The peCOD technology has two configurations for the pulp and paper industry, each designed to serve different applications (*Figure 3*).

The peCOD method cannot analyse samples containing particulates greater than 50µm, due to the small size of the internal fluidics. Therefore, samples must be pre-filtered if they contain particulate greater than the allowable size.

Since pulp and paper effluents can contain lots of these particulates, it was critical to first determine the contribution of COD from particulates in effluent samples. Studies conducted by FPInnovations in Pointe Claire, QC, Canada, compared filtered peCOD results to filtered and unfiltered CODcr results. Both primary and secondary treated effluents from kraft, thermomechanical (TMP), and bleached chemi-thermomechanical (BCTMP) pulps mills were analysed. Samples were collected with varying ranges of COD, including: regular effluent, effluent spiked with condensates, and effluent spiked with black liquor. All filtered samples were pre-filtered through a 35µm pore size.

Similar comparative studies were also conducted by Kemira in Espoo, Finland. For these analyses, filtered samples were pre-filtered through a 0.45µm pore size.

Results and Discussion

FPInnovations found strong correlations between peCOD and filtered CODcr, with r^2 values of 0.97, 0.99, and 0.99, for regular effluent, effluent spiked with condensates and effluent spiked with black liquor respectively (*Figure 4*). Spiked effluents showed slightly lower peCOD values to CODcr; however, still showed good linear relationship. The linear relationship between the peCOD and filtered CODcr for regular effluent can be defined as:

$$peCOD = 1.15\ x\ CODcr_{filtered};\ r^2 = 0.97 \quad (2)$$

For secondary Kraft effluents the peCOD values were again higher than CODcr values, but exhibited a linear relationship.

Kemira also found a strong correlation between the peCOD method and filtered CODcr. *Figure 5* shows the linear relationship with a r^2 value of 0.997.

In addition to determining a strong correlation between peCOD and filtered CODcr, the difference between filtered and

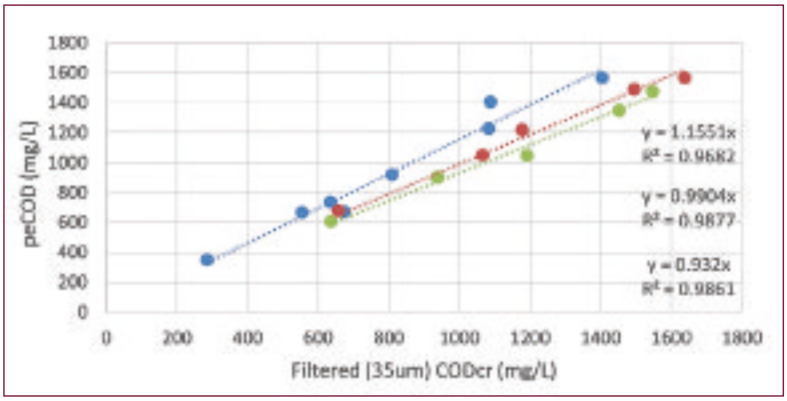

Figure 4: peCOD versus filtered CODcr for primary kraft mill effluents: regular effluent (blue), effluent spiked with weak black liquor (red), and effluent spike with condensate (green).

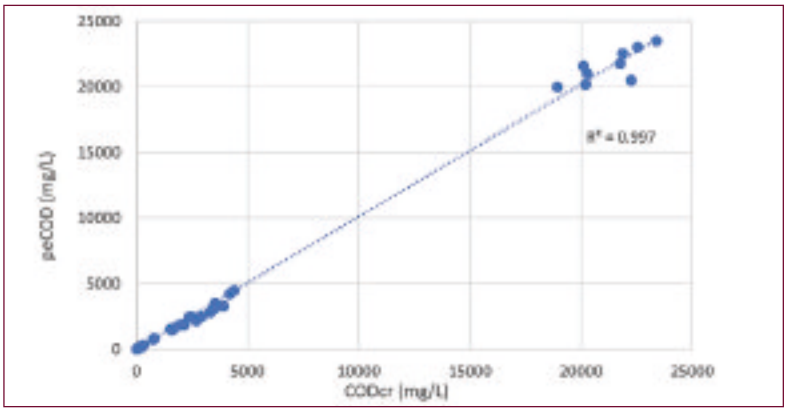

Figure 5: peCOD versus filtered (0.45µm) CODcr for pulp and paper effluent measured at Kemira.

unfiltered CODcr samples was never more than 4.9%. This confirmed that particulates do not contribute significantly to the total COD. Therefore, the pre-filtering required by the peCOD method will not have an impact on the overall results.

Impacts on the Pulp and Paper Industry

Success from the trials performed within this project, as well as from other projects in different applications, helped develop the Benchtop L100 into a commercially available tool for COD monitoring. This project confirmed the strong correlation between peCOD and CODcr and helped solidify the applicability of peCOD in the pulp and paper matrix, for COD monitoring.

With strong peCOD to CODcr correlations proven at primary and secondary treated effluents, as well as other points along mill operations, peCOD can be used to effectively measure COD from multiple points along the pulp and paper process. By adding a battery pack and carrying case, it can also be used as a portable unit to easily measure at different locations within the mill. By allowing closer process monitoring, the peCOD technology has further reaching sustainable impacts through energy and chemical reductions. It is a relatively inexpensive and simple method, considering the difficult nature of the pulp and paper matrix.

The transnational project proved the peCOD method as an accurate COD monitoring tool in the pulp and paper wastewater industry, and users are now proving its value. In addition to the pulp and paper mills, supporting pulp and paper companies are using peCOD for service, troubleshooting, and commercial wastewater treatment.

Customers Using peCOD Method for Process Control, Treatment Optimisation, and Improved Health and Safety

A Chilean pulp and paper mill was searching for a faster COD test to improve their bleaching process efficiency and to reduce excess bleaching chemical consumption. The mill recognised the significance of COD concentration in the wash water carried to their bleaching process, as it determined the dosage of bleaching chemicals. Wash water with higher COD concentrations resulted in consumption of bleaching chemical, which meant excess chemical was added to compensate for this loss.

Prior to having a fast COD test, operators relied on a 7-hour SCAN-test (C 45:00) method. The SCAN method required sample collection, drying, and COD measurement by photometric method to obtain the COD result. This led to inefficient chemical usage, as operators did not have the timely data to monitor the wash water or accurately dose the bleaching chemicals.

After implementing the peCOD method for COD analysis, operators were able to receive the wash water COD results in under 15 minutes. Having the faster analysis time resulted in improved efficiencies within the bleaching process and big savings in chemical costs. The reduction of COD in wash water was achieved by having closer COD monitoring, which allowed operators to make real-time decisions, and reduce the frequency of high COD events (concentrations above 12,000mg/L). This led to optimisation of the pulping process and reduction in bleaching chemical use. By avoiding high COD events in both of the bleaching lines, the mill potentially saved over two tons of bleaching chemicals per day, compared to the year before implementing peCOD, which equates to huge cost savings. By optimising the bleaching process, the mill was able to reduce chemical usage, lower energy usage during the treatment process, and reduce the chemicals in the wash water to treat.

The Benchtop L100 provided critical information to the mill operators, while improving health and safety of the workplace and the environment, by eliminating the need for hazardous chemicals required with the previous method.

Companies that support the pulp and paper industry are also employing peCOD. The chemical company, Kemira, provides wastewater treatment solutions to pulp and paper mills. Kemira Finland uses the Portable L100 (*Figure 3a*) for on-site mill support, to obtain fast COD results that help troubleshoot and optimise treatment processes.

A western Canadian pulp and paper company uses the Benchtop L100 coupled to an autosampler (*Figure 3b*. Automated L100) to measure batches of samples from two of their mills. They are using peCOD to measure COD and develop a correlation to Biological Oxygen Demand (BOD). Although mill operators use COD as the quality parameter to make decisions on treatment, (e.g. chemical dosage), the regulation for discharge in Canada is BOD. Having as peCOD correlation to BOD allows the mill to predict the daily BOD results, which is normally a 5-day test.

Another mill in Georgia, USA, was seeking a COD test method that would not bring hazardous chemicals into the workplace. Without a technical team in the lab to run the traditional dichromate method for COD, the mill attempted to run its wastewater treatment plant using other water quality parameters. However, after facing a discharge compliance fine, and paying expensive lab fees for external COD testing, the mill purchased the Benchtop L100 to measure COD in-mill.

The mill intends to use the fast peCOD results for optimisation of the treatment process, specifically prior to the aeration basin. Having relevant COD data will let operators tune the process to current conditions, apply sufficient treatment, and ensure discharge compliance.

In addition to pulp and paper customers, the commercial wastewater industry is using the peCOD method to improve operations.

Clean Harbors in Guelph, ON, Canada is a commercial wastewater treatment company that accepts industrial wastewater from a variety of facilities, including: pulp and paper, automotive, manufacturing, primary steel, chemical, and dairy. The company has used its automated L100 (*Figure 3b*) since 2015 to test the incoming wastewater from delivery trucks. When a truck arrives with a load of wastewater, Clean Harbors takes a sample for peCOD analysis. The company has a cut-off criterion based on COD concentration to determine whether to accept or refuse the wastewater. The fast peCOD analysis time is critical for operations to prevent delivery trucks from sitting idle at their facility. The peCOD method has allowed operators to make timely and confident decisions about the incoming wastewater deliveries. *Figure 6* shows the comparative data between peCOD and CODcr, collected from the treatment plant. The same stream was also compared to carbonaceous BOD (cBOD) results, which are required by municipal regulations for discharging to the sewer (*Figure 7*).

The strong correlation seen between peCOD, CODcr, and cBOD for industrial wastewater was imperative to the company's decision to invest in the PeCOD®COD Analyser. The peCOD method allows for timely decision making for incoming wastewater as well as monitoring of the wastewater through the treatment process. Before the peCOD method, operators would wait 8 days from the date of discharging wastewater to the sewer before receiving that wastewater's cBOD result from an external laboratory. Having the peCOD correlation to cBOD discharge limits, allows operators to predict the cBOD result in less than 15 minutes, which ensures peace-of-mind with regards to the treated discharge effluent.

Conclusion

Results from the transnational EUREKA project confirmed the peCOD method as an accurate and reliable tool for COD monitoring. With the findings from the project and from our other research partners, the PeCOD® COD Analyser has been implemented into pulp and paper mills for process optimisation, process savings, improved health and safety for employees and the environment, and greater success meeting discharge compliance regulations.

The peCOD method has also been employed in the commercial wastewater industry. The fast peCOD analysis time has been valuable for commercial wastewater treatment operators, to make timely decisions, monitor the wastewater during treatment, and have confidence when discharging treated effluent.

Acknowledgements

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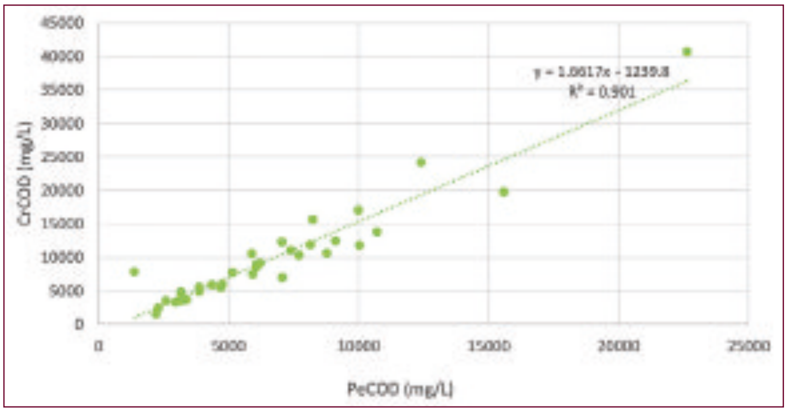

Figure 6: Correlation between peCOD and CODcr results for industrial wastewater

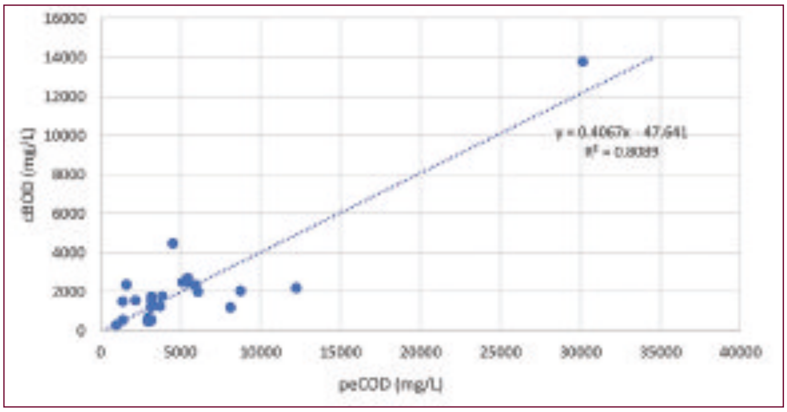

Figure 7: Correlation between peCOD and cBOD results for industrial wastewater

Standards Update

Daven Chamberlain

Chairman PAI/11

This column contains a summary of recent work performed under the auspices of PAI/11, the BSI committee that deals with Methods of Test for Paper, Boards and Pulps.

New or updated standards that have been issued recently:

1. BS EN 1104:2018 Paper and board intended to come into contact with foodstuffs - Determination of the transfer of antimicrobial constituents
2. BS EN ISO 7263-1:2019 Corrugating medium - Determination of the flat crush resistance after laboratory fluting Part 1: A-flute
3. BS EN ISO 7263-2:2019 Corrugating medium - Determination of the flat crush resistance after laboratory fluting Part 2: B-flute (ISO 7263-2:2018)
4. BS ISO 21400:2018 Pulp - Determination of cellulose nanocrystal sulfur and sulfate half-ester content
5. PD ISO/TR 24498:2019 Paper, board and pulps - Estimation of uncertainty for test methods by interlaboratory comparisons

Subject reports and documents submitted for vote / comment have included:

1. Cores: Dimensions; Flat Crush Resistance.
2. Food contact: Enumeration of Yeast and Mould.
3. General: Coating Strength in the Fold; Friction (stylus method); Roughness (stylus method).
4. Printing: Ink Setting Test.
5. Recycling: Decoloration (Bleaching) Potential; Deinking of Printed Paper; Sampling Procedures.
6. Tissue: Disintegration; Surface Friction (for Surface Softness); Tensile Modulus; Vocabulary; Wet Ball Burst Strength.

Current Standards that have been submitted for Periodic Review:

BS 3137 Burst; ISO 187 Standard Atmosphere; ISO 5636-3 Air Permeance (Bendtsen); ISO 5636-4 Air Permeance (Sheffield); ISO 5636-5 Air Permeance (Gurley); ISO 6587 Conductivity of Aqueous Extracts; ISO 9932 MVTR; ISO 11556 Curl; ISO 13821 Edgewise Crush; ISO/TS 20460 Automated Online Testing; ISO 22414 Edge Quality.

Anyone interested in any of the standards or work mentioned above should contact the PAI/11 Chairman (telephone 0300 3020 159 or email daven@pita.co.uk).