IMPROVED MILL PERFORMANCE, WASTEWATER TREATMENT, AND HEALTH AND SAFETY WITH NOVEL COD MONITORING TECHNOLOGY

A recent EUREKA transnational research project proved a new method for measuring Chemical Oxygen Demand (COD) that is faster, safer, and greener than the conventional dichromate method (CODcr) and has excellent applicability to the pulp and paper industry. It is called photoelectro Chemical Oxygen Demand (peCOD). The main objective of the project was to develop new technologies to reduce recalcitrant COD in water intensive industries, with a focus on 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. A comparative study was conducted to compare peCOD and CODcr sample results from several effluents at different pulps mills. The peCOD method demonstrated a strong correlation to the CODcr method for all effluent sample types and indicated excellent reproducibility for replicate results. The outcomes from the project have resulted in global adoption of peCOD in pulp and paper mills for treatment monitoring and process optimisation. Pulp and paper mills benefitting from the peCOD method have experienced process savings, improved health and safety for employees and the environment, and greater success meeting discharge compliance regulations.

Introduction

Pulp and paper mills produce a large volume of wastewater and residual sludge, which is a growing concern as environmental regulations become stricter. Experts are looking for solutions to reduce their fresh-water intake and ultimately achieve close to zero liquid discharge. Other challenges facing pulp and paper operations are: high organic concentrations in production and wastewater effluent, operation costs, performance, and impacts to the environment. The EUREKA project was focused on developing novel technologies to treat recalcitrant COD. It's 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. This article will highlight the development of the peCOD method for COD monitoring and its benefits to the pulp and paper industry.

Experimental Methods

The peCOD method for COD analysis is a novel method based on nanotechnology. It employs a UV-irradiated titanium dioxide (TiO_2) sensor, which is coupled to an external circuit. TiO_2 has more powerful oxidising potential (3.1 V) than the conventionally used dichromate oxidiser (1.6 V). The charge generated during a sample oxidation is used to calculate the total COD within the sample. 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 several configurations, each designed to serve different applications (Figure 1).

This article will focus on the Benchtop and Portable L100 unit and its proven success in the pulp and paper matrix.

The peCOD method cannot handle particulates greater than 50um, 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 35um pore size.

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

Results and Discussion

The correlations between peCOD and filtered CODcr were strong, 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 2). 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:

$$peCOD = 1.15 \times CODcr_{filtered};\ r^2 = 0.97$$

For secondary Kraft effluents, the peCOD values were again higher than CODcr values, but exhibited a linear relationship, as illustrated in Figure 3.

Kemira also found a strong correlation between peCOD method and filtered CODcr. Figure 4 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 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.

Other Findings from the Transnational Project

Hydrogen peroxide (H_2O_2) has been proven as an effective treatment for recalcitrant COD removal. Unfortunately, residual H_2O_2 influences COD results measured with the traditional dichromate method, by falsely increasing the results. However, the effect of residual H_2O_2 is overcome when the COD is analysed with the peCOD technology. There are processes within pulp production where higher residual H_2O_2 concentrations would be expected, for example, following the bleaching process. Therefore, samples collected after the bleaching process would not be suitable for analysis on the dichromate method, without accounting for the contribution from residual H_2O_2. The peCOD method could be used to analyse samples from these processes without being influenced.

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 established that a strong correlation between peCOD and CODcr existed 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, it can also be used as a portable unit to measure at different locations within the mill. The Benchtop L100 is a valuable tool for grab sample analysis, for monitoring any operational (e.g. paper machine) or treatment point of 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. PeCOD is not prone to H_2O_2 interferences, is fast (less than 15-minute analysis time) and does not use hazardous chemicals, making it a green and safe method for COD analysis.

The transnational project provided the scientific data to prove the method as applicable for COD monitoring for the pulp and paper wastewater matrix, and the users are now proving the value.

Customers Using peCOD Method for Process Optimisation, Improved Health and Safety, and Economic Savings

a. b. c. d.

Figure 1: peCOD technology configurations (left to right): a. Benchtop and Portable L100, b. Automated L100, c. Online L100, and d. Online P100.

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 COD concentration of wash water carried to the bleaching process is significant because it determines the required amount of bleaching chemicals. Wash water with higher COD concentrations can result in consumption of bleaching chemical, which means excess chemical must be 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 lead 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. Figure 5 shows the comparison of COD concentration in wash water from 2013 (pre-peCOD) to 2014 (with peCOD). 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". This lead to optimisation of the pulping process and reduction in bleaching chemical use. The mill was able to save $10,000 USD per day by optimising the bleaching process, including: reducing chemical usage and lowering energy usage on the treatment process, by having less chemicals in the wash water to treat.

The Benchtop L100 has provided critical information to the mill operators, while improving health and safety of the workplace and the environment, by eliminated 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 1a.) 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 1b. 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 COD 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.

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.

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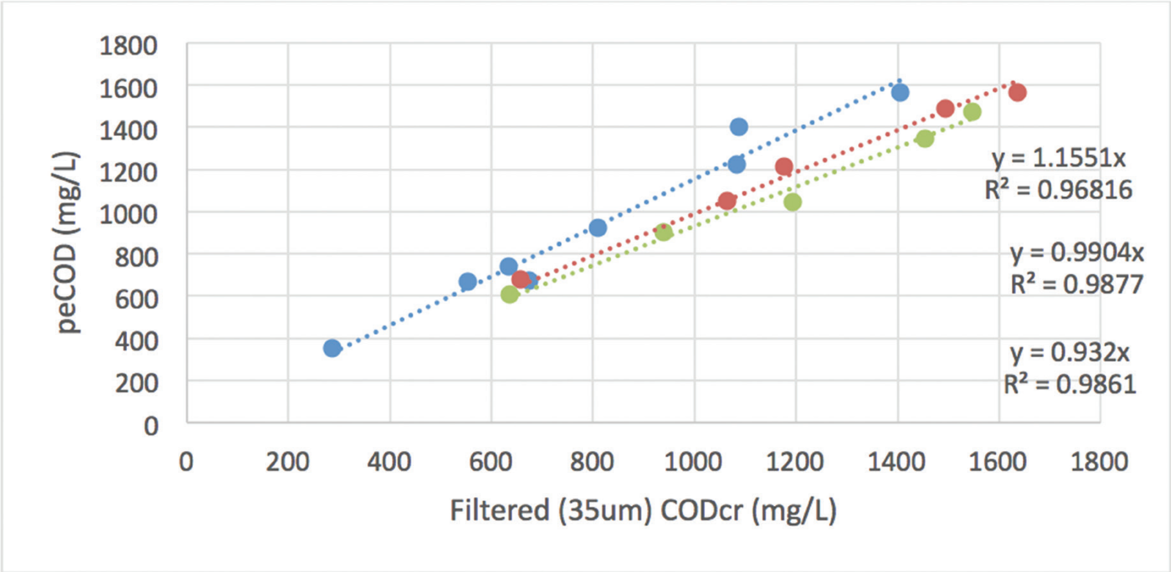

Figure 2: peCOD versus filtered CODcr for primary kraft mill effluents: regular effluent (blue), effluent spiked with weak black liquor (red), and effluent spike with condensate (green).

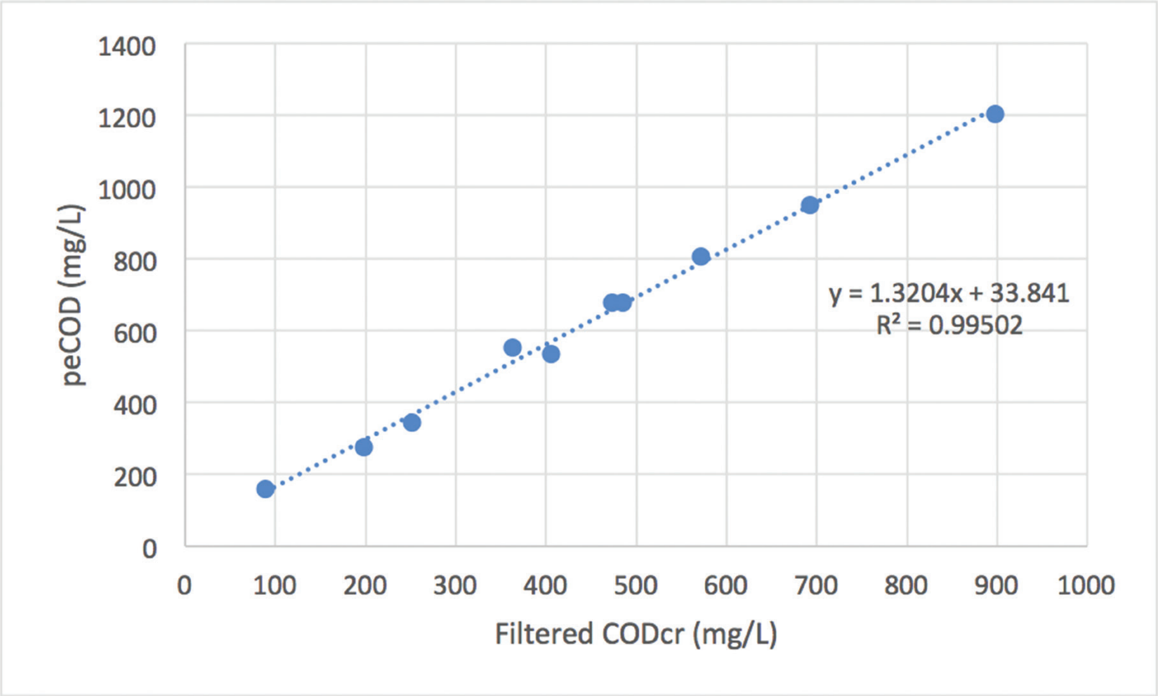

Figure 3: peCOD versus filtered CODcr for secondary kraft mill effluents.

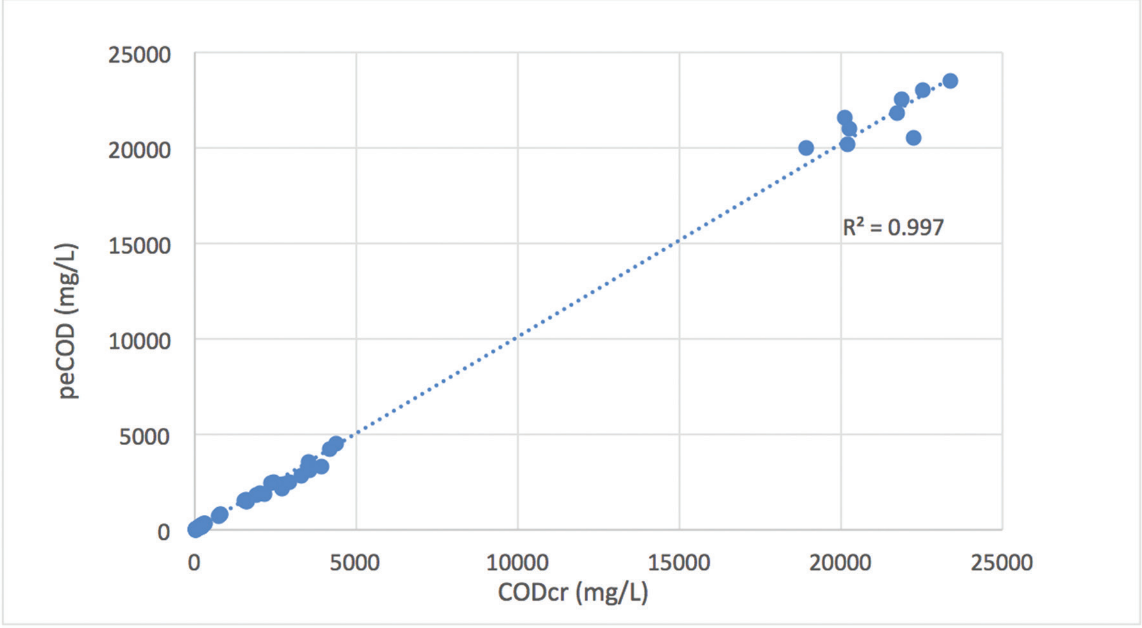

Figure 4: peCOD versus filtered (0.45um) CODcr for pulp and paper effluent measured at Kemira.

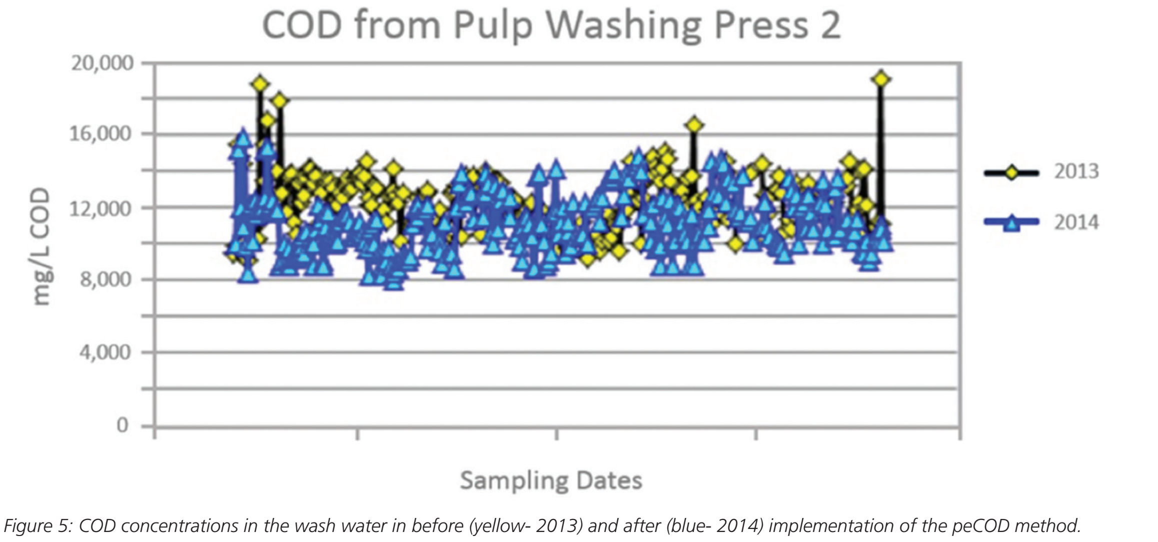

Figure 5: COD concentrations in the wash water in before (yellow- 2013) and after (blue- 2014) implementation of the peCOD method.