The novel photoelectrochemical oxygen demand (peCOD) monitoring technology proves effective for the pulp and paper industry while expanding its reach to more water-intensive industries and drinking water applications. Maggie Grierson, Justin Dickerman, and Robert Menegotto at Mantech highlight the development of peCOD and its benefits to various applications.

Multiple industries, drinking water facilities adopt peCOD method

An international EUREKA Network project has proven a new method for measuring chemical oxygen demand (COD) in pulp and paper applications that is faster, safer, and greener than the conventional dichromate method (CODcr). The new method is called photoelectrochemical oxygen demand (peCOD), and it eliminates the use of hazardous chemicals such as potassium dichromate, used in the conventional method for measuring COD. Compared to CODcr, peCOD reduces analysis time from 3 hours to less than 15 minutes. EUREKA Network projects are market-driven, international research and development projects funded by organizations in the network's 40-plus member countries.

A study conducted by FPInnovations in Pointe Claire, Quebec, Canada, compares peCOD and CODcr sample results from several effluents at different pulp and paper mills. PeCOD demonstrated a strong correlation to CODcr 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, and effluent monitoring to ensure discharge compliance.

In addition to the pulp and paper industry, peCOD is being employed in other areas that are concerned with wastewater treatment optimization and compliance regulations such as in industrial wastewater treatment and petrochemical facilities as well as in craft breweries. PeCOD has also seen adoption in the drinking water sector because it can provide additional information on natural organic matter (NOM).

The EUREKA project focused on developing technologies for pulp and paper wastewater treatment, with an emphasis on recalcitrant (hard-to-break-down) COD removal. Its other focus was to find a faster, more robust COD method to closely monitor effluent levels, which would promote better process and treatment control. Non-pulp and paper industries producing wastewater face similar challenges regarding treatment and discharge regulations.

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Experimental methods

The peCOD method is based on photo-catalytic degradation of organic material. The technology employs a three-electrode system, including a titanium dioxide (TiO_2) sensor. During analysis, a sample is introduced into the sensor cell that contains the TiO_2. An ultraviolet (UV) LED light is illuminated onto the sensor cell while a potential bias is applied across the sensor and electrode system. The UV light energizes the stable state of the TiO_2 film, which liberates electrons from the working electrode, leaving the immobilized TiO_2 to readily oxidize the organic material in the sample (See Figure 1). The powerful oxidizing potential of TiO_2 ensures that virtually all organic species are oxidized.

The 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 is determined by integrating the photocurrent generated during a reaction, which is used to calculate the final COD result (Figure 2).

PeCOD 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 0.7 milligrams per liter (mg/L) to 15,000 mg/L of COD; however, incorporating dilution can extend this range.

The peCOD technology is available in several configurations, each designed to serve different applications: Benchtop and Portable L100; Automated L100; and Online L100.

The peCOD method cannot analyze samples containing particulates of greater than 50 micrometer (µm) 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 a lot of these particulates, it was critical to first determine the contribution of COD from particulates in effluent samples. Studies conducted by FPInnovations 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) pulp mills were analyzed. Samples were collected with varying ranges of COD, and all peCOD samples were pre-filtered through a 35-µm pore size.

Similar studies were also conducted by Kemira in Espoo, Finland. For these analyses, filtered

Figure 1: peCOD sensor technology

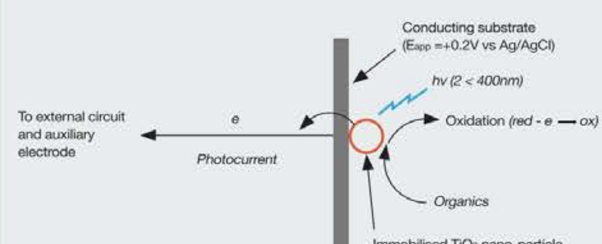


Figure 2: peCOD oxidation profile

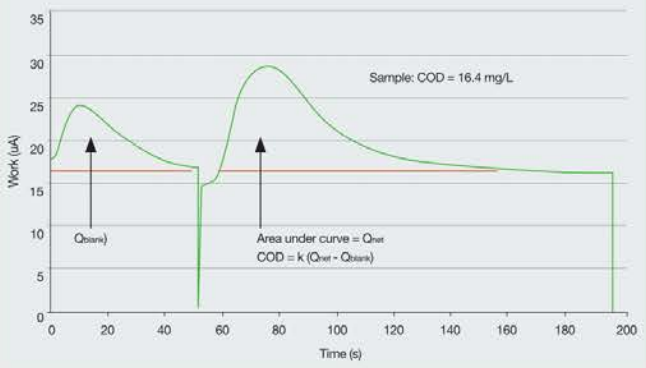


Figure 3. peCOD versus filtered CODcr for primary kraft mill effluents: regular effluent (blue), effluent spiked with weak black liquor (red), and effluent spike with condensate (green).

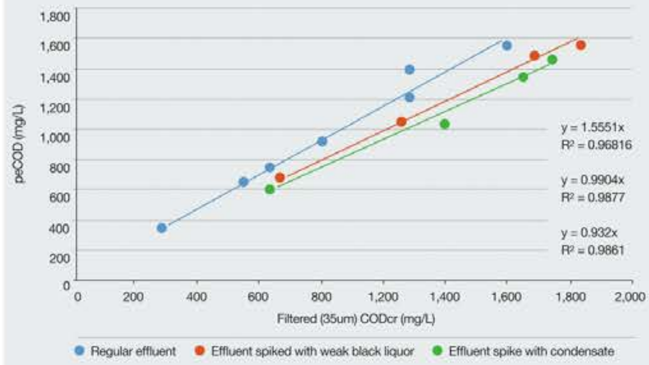
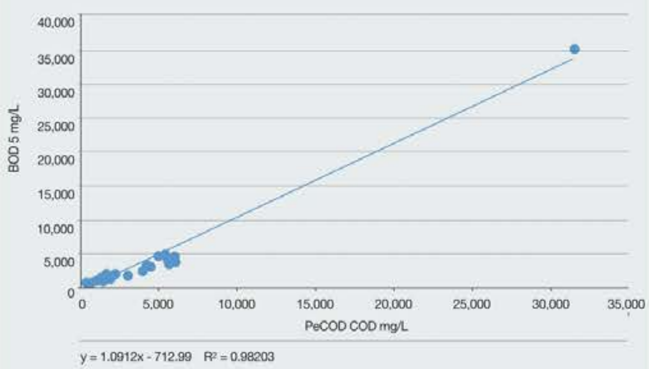


Figure 4: Correlation between peCOD and BOD5 for brewery wastewater.



peCOD is being employed in other areas that are concerned with wastewater treatment optimization and compliance regulations such as in industrial wastewater treatment and petrochemical facilities as well as in craft breweries.

samples were pre-filtered through a 0.45-µm pore size.

Results and discussion

The comparison of peCOD to CODcr, for all effluent sample types, demonstrated very good correlations. A linear regression model was used to calculate the coefficient of determination (r^2) values. All r^2 values were between 0.92-0.99, indicating strong correlation. Figure 3 shows an example of peCOD to CODcr correlations from three of the primary kraft effluents. Kemira also found a strong correlation between peCOD and filtered CODcr and calculated an r^2 value of 0.997.

In addition to determining a strong correlation between peCOD and filtered CODcr, FPInnovations reported that the difference between filtered and unfiltered CODcr samples was never more than 4.9 percent. This result confirmed that particulates did not contribute significantly to the total COD. Therefore, the pre-filtering required by the peCOD method did not have an impact on the overall results.

Industries adopt peCOD method

In a full-scale application, a Chilean pulp and paper mill introduced peCOD to improve its bleaching process efficiency and to reduce excess bleaching chemical consumption. The mill recognized the significance of COD concentration in wash water that was carried to its bleaching process. Wash water with higher COD concentrations resulted in consumption of bleaching chemicals, which meant excess chemical was required to compensate for this loss.

After implementing peCOD, operators were able to receive the wash water COD results in less than 15 minutes. By having closer COD monitoring, operators made real-time decisions and reduced the frequency of high COD events. By avoiding high COD events in both bleaching lines, the mill potentially saved more than 2 metric tons of bleaching chemicals per day, compared to the year prior to implementing peCOD. This approach also led to reduced energy consumption during wastewater treatment and significant cost savings.

In addition to pulp and paper customers, other industries that involve wastewater are using peCOD to improve operations. Clean Harbors in Guelph, Ontario, Canada, is a commercial wastewater treatment company that treats trucked industrial wastewater from a variety of facilities. The company uses a COD concentration cut-off criterion to determine whether to accept or refuse incoming wastewater deliveries. When a truck arrives with a load of wastewater, Clean Harbors takes a sample for peCOD analysis. The fast analysis time has allowed operators to make timely and confident decisions about the incoming wastewater deliveries and to optimize treatment. The final effluent was compared to cBOD results since it is the permit-based parameter limit for discharging to the sewer.

A liquified natural gas (LNG) facility near Calgary, Alberta, Canada, implemented peCOD for effluent compliance, process optimization, and monitoring for hydrocarbon contamination into clean processes. Contamination within the plant is a great concern, as it can lead to a very costly full plant shutdown. Within one week of using peCOD, operators found strong correlation to CODcr and acknowledged that the fast analysis time would be invaluable for future plant upsets and process troubleshooting. The fast peCOD analysis time allows the LNG facility to start-up almost immediately after a complete outage versus waiting 4 hours for the CODcr test result. Getting back to full production quicker and reducing deferred gas volumes saves more than US$100,000 per outage.

Craft breweries are also using peCOD for process monitoring. Some craft brewing companies are required to treat wastewater in-house to meet discharge regulations. Flying Monkeys in Barrie, Ontario, Canada, is a recent peCOD adopter. The brewery wanted to monitor its treatment process and discharge effluent without introducing hazardous chemicals into its facility. The peCOD method provided the alternative that the brewery was looking for while also giving fast COD results. Figure 4 shows a strong correlation between peCOD and BOD5 results from a comparative study of brewery wastewater.

Drinking water application

Outside of the wastewater sector, peCOD is being used in the drinking water industry for improved NOM monitoring. NOM levels are of concern to water treatment plant (WTP) operators because they can react with disinfectants to produce carcinogenic disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). Elevated NOM can also create challenges across the water treatment process.

Traditional methods for measur-

Figure 5: Graphs show peCOD, UV254, and TOC comparisons for four NOM fluctuation events.

Aerial view of industrial wastewater treatment plant in evergreen forest. Credit: Kekyalyaynen, Shutterstock

ing NOM include total organic carbon (TOC), dissolved organic carbon (DOC), and ultraviolet absorbance at 254 nm (UV-254). These parameters provide insight into the overall NOM makeup; however, each has shortcomings and does not indicate the oxidation state of organics. PeCOD does provide a measure of the oxidation state of organics and therefore provides more information about how NOM will respond to treatment.

PeCOD conforms to approved methods from ASTM International (D8084-17) and the Ontario Ministry of Environment, Conservation, and Parks (E3515). A new textbook, *Microbiological Sensors for the Drinking Water Industry*, was released by the International Water Association World Congress and introduces the peCOD parameter to better quantify the oxidation state of NOM in drinking water treatment.

A drinking water utility in Massachusetts, United States, recently adopted peCOD to help predict and control the formation of DBPs. The utility implemented peCOD alongside TOC and UV254 in an online monitoring system. Figure 5 shows the comparison of these three parameters during some events resulting in NOM fluctuation.

Operators at the Massachusetts utility were impressed by the ease of use of the Online L100, in comparison to their other instrumentation, noting that "peCOD was the easiest instrument to operate and maintain, leading to it having the best 'up-time' over the course of the year." Additionally, operators noted that the peCOD parameter was easy to understand, being an empirical measure, as opposed to UV254, which requires a lengthy matrix-specific calibration period to produce useful data.

Conclusion

The EUREKA project confirmed the peCOD method as an accurate and reliable tool for COD monitoring within the pulp and paper industry. Additionally, peCOD has been integrated into other industries including industrial wastewater treatment, petrochemical, craft breweries, source water monitoring, and drinking water treatment. The fast and green peCOD method has been valuable for making timely process decisions, monitoring wastewater during treatment, and having confidence when discharging treated effluent. For drinking and source water monitoring, the peCOD method has also provided information on the reactivity of organics, which isn't measured with other NOM surrogates.

Author's Note

Maggie Grierson and Justin Dickerman are environmental engineers-in-training (EITs) at MANTECH, with expertise in water quality. Robert Menegotto is President and CEO of MANTECH, based in Guelph, Ontario, Canada.