PECOD INLINE COD MONITORING FOR REAL TIME RESULTS

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INTRODUCTION

Water is an essential element for life resulting in the direct relationship between water availability, population density, and quality of life. Water has specific characteristics that helps to determine the quality prior to use. Water quality is dependent on its constituents that can be divided into organic and inorganic substances. It is very challenging to make distinction between physical, chemical, or biological species so gross parameters are the most easily measured and commonly used descriptions of water quality. An example of a gross parameter is biochemical oxygen demand (BOD) used to determine the aerobic destructibility of organic substances. BOD is the measure of oxygen used in the metabolism of biodegradable organics, specifically carbonaceous oxidation of organic compounds and can be equally referred to as cBOD to denote the carbonaceous biochemical oxygen demand.

Carbonaceous BOD (cBOD) is measured within 5 days, which is the internationally referenced period. The specific 5-day interval is when 70% of the biologically convertible substances are broken down with the remaining substances extrapolated based on the kinetic first-order reaction (Tchobanoglous and Schroeder, 1987). With a less than ideal measuring period to obtain results, other analytical methods of measuring organic content are used to help approximate the cBOD. A common parameter used in association with cBOD is the chemical oxygen demand (COD). The COD test is used to measure the organic content, as well as the inorganic content by determining the oxygen equivalent. With the COD test measuring all organic and inorganic components, values are traditionally higher than that of cBOD.

The COD can be further fractionized into particulate and soluble COD. The benefit of breaking down the COD into components is to assist with wastewater treatability (Metcalf and Eddy, 2014). There is currently no standardization on the definition of soluble and particulate COD but commonly used methodology include filtration and precipitation of suspended solids.

The concentration of organic compounds in wastewater can also be defined by the biodegradable COD (bCOD) that comprises of soluble, colloidal, and particulate biodegradable components (Metcalf and Eddy, 2014). The biodegradable soluble COD (bsCOD) is used to quantify the depletion of biodegradable organic compounds since it is part of the kinetic expression in determining stoichiometry of organic matter oxidized. This is a significant parameter for many processes in wastewater treatment, particularly for the aeration system. The aeration system must be designed to satisfy several requirements including the oxygen demand for the biological oxidation of bCOD (Metcalf and Eddy, 2014).

$$\mathrm{C_aH_bO_c}N_d + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{NH_3} \qquad (1)$$

A new patented nanotechnology currently available to measure soluble COD (sCOD) is the photoelectrochemical Oxygen Demand (peCOD) method. The peCOD method for COD analysis completes an analysis in 15 minutes, while overcoming the limitations of current COD analysis methods for a variety of water applications. The peCOD directly measures photocurrent charge originating from the oxidation of the organic contamination in a sample. The core technology that hosts the oxidation process is the peCOD sensor, which consists of a UV-activated nanoparticle titanium dioxide (TiO_2) photo catalyst coupled to an external circuit. The oxidizing potential of UV-illuminated TiO_2 ensures that virtually all species will be fully oxidized giving a true measure of sCOD.

The peCOD has proven to be an excellent cBOD screening tool, providing accurate cBOD estimates in just minutes versus the standard 5-day cBOD test in a variety of industries. Exceptional correlation can be observed between the two methods, even stronger than the dichromate COD approach due to the peCOD not requiring pre-digestion of sample.

To further investigate the correlation of peCOD with cBOD, specifically with municipal wastewater, MANTECH began working with Ontario Clean Water Agency (OCWA) in 2015. MANTECH installed an At-Line L100 PeCOD® at the final effluent of Clarkson Wastewater Treatment Plant (WWTP) in Mississauga. The peCOD system sits several meters away from the cBOD composite sampler, sharing the same sample line. The peCOD analyzes on an hourly basis providing a sCOD value on the hour, where the cBOD composite sampler collects a representative 24-hour sample. The system has been running continuously since June 2016.

With an extensive data set, water quality parameters can be compared to determine the extent of correlation between peCOD and cBOD at Clarkson WWTP. With a strong correlation between the two methods the peCOD can provide a reliable, green and fast cBOD screening tool to check compliance and improve operations.

METHODOLOGY

The inline peCOD system currently installed at the Clarkson WWTP is an inline sCOD monitoring device providing real time results on the plant effluent. The other wastewater quality parameters, cBOD and COD, are composite samples that were manually collected and sent to an external lab for analysis. The methods of analysis for each wastewater quality parameter are very different but both are relative to reporting the organic matter content.

The conventional COD test currently performed in most labs measures the oxygen equivalent of the organic and some inorganic matter using a strong oxidizing agent (potassium dichromate) in an acidic medium (Tchobanoglous and

Schroeder, 1987). The addition of a catalyst and high temperatures help the oxidation of certain organic compounds. The oxidizing agent is the excess dichromate and the remaining dichromate at the end of the reaction is recorded in terms of equivalent oxygen (mg/L). The following equation represents the measurement of the organic matter.

$$\mathrm{C_aH_bO_c}N_d + \mathrm{Cr_2O_7^{-2}} + \mathrm{H^+} \xrightarrow{\text{Catalyst + Heat}} \mathrm{Cr^{+3}} + \mathrm{CO_2} + \mathrm{H_2O} + NH_4^+ \qquad (2)$$

This effective method for determining COD takes about 3 hours but certain inorganic constituents can cause interference with the test, such as chloride and peroxide. Chloride tolerance with this method can be achieved with the addition of mercury but there are obvious health and environmental concerns with the presence of mercury. There is currently no inline or online model for the dichromate COD method.

The peCOD requires no harmful chemicals like that of the conventional COD method basing all operations on salt and sugar solutions. When a sample analysis is initiated, the sample is introduced into a microcell containing the TiO_2 sensor. The TiO_2 is irradiated by UV light, and a potential bias is applied. The UV light creates a photo hole in the TiO_2 sensor allowing for photocurrent to be measured. The TiO_2 is a very powerful oxidizing agent (+3.1 V) that will readily lead to the transfer of electrons from organic species in the cell. It is because of this increased oxidizing power that peCOD is able to measure certain organics such as nicotinic acid, benzene, diethylamine, and many others that are difficult to oxidize.

$$\mathrm{C_aH_bO_c}N_d + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{NH_3} \qquad (3)$$

By applying an appropriate potential bias to the system, liberated electrons are forced to pass into the external circuit where the reduction of oxygen (or other species) takes place. The charge is monitored and gives a direct measure of the oxidation of organic compounds. The measured charge, *Q*, is simply the total amount of electron transfer that results from the degradation of all compounds in the sample. Given that one oxygen molecule is equivalent to 4 electrons the measured *Q* value can be easily converted into an equivalent O_2 concentration (or oxygen demand) in mg/L. Figure 1 below illustrates how the technology works and the significance of oxidizing soluble organics on TiO_2.

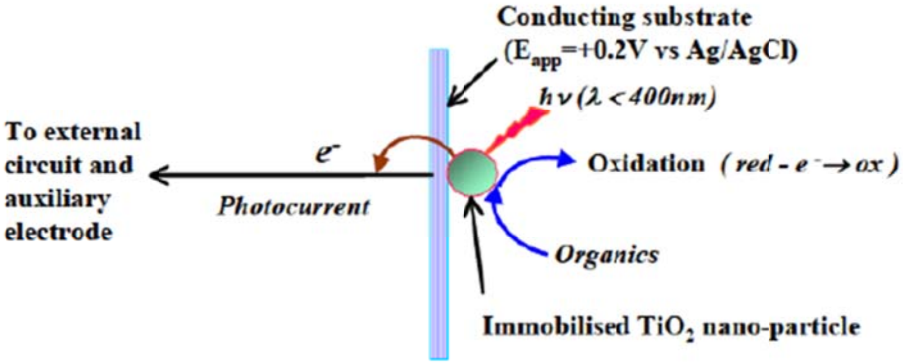

FIGURE 1: PECOD SENSOR TECHNOLOGY

The peCOD system at Clarkson WWTP utilizes settling within a sample cup to separate the suspended solids before being analyzed for sCOD. The peCOD can handle solids up to 50 µm, any larger and there is great potential to clog the small valves inside the unit. The final effluent it is analyzing does have suspended solids but has not been an issue for the system since installed at the end of 2015. It will analyze the soluble portion of the sample from the continuously flowing sample cup every hour. The system has the capability to sample up to every 15 minutes but for this project kept the frequency conservative.

The general peCOD operating range is 0.07 mg/L – 15,000 mg/L of COD with 4 refined sub ranges for accuracy. Clarkson WWTP's final effluent is currently utilizing a peCOD range suitable for 10 mg/L – 150 mg/L COD. The analysis requires sample to be a neutral pH (4-10). If the pH is not neutral the At-Line L100 PeCOD® has the capability to auto adjust with NaOH or H_2SO_4. The pH at Clarkson WWTP final effluent is close to neutral so no adjustment is ever required.

The results are obtained from the system manually or through the use of a remote software with a wireless connection. The system can run unattended up to two weeks before reference solutions need to be refilled and four weeks for a sensor change. The only requirement needed for the peCOD system is sample flow of at least 10 ml/min to the sampling cup. The setup of the At-Line L100 PeCOD® is displayed in Figure 2.

The peCOD system pumps up 20 mL of final effluent from the sample cup that is continuously flowing to the 35 mL mixing vessel on top of the system. Within the 35 mL mixing vessel, electrolyte is pumped in and mixed in the appropriate ratio. Once the sample is mixed and stirred it is pumped from the mixing vessel to the peCOD unit to be analyzed. The system also performs a quality control check every 8 samples with a 120 mg/L COD sorbitol based standard. If the quality control check is not within 10% then a calibration is run and another quality check is analyzed before resuming regular sampling operation.

FIGURE 2: AT-LINE L100 PECOD® LOCATED AT CLARKSON WWTP FINAL EFFLUENT IN MISSISSAUGA, ONTARIO. THE CBOD SAMPLER LOCATED BESIDE THE UNIT (FEATURED TO THE LEFT).

The cBOD and COD results are provided by OCWA through their client's external lab. The cBOD results are from daily 24-hour composites collected at roughly 8:00 am each day from the final effluent cBOD sampler. The cBOD test utilized is the 5-day test and it may be an extra day or more before results are received by OCWA. To approximate the cBOD of Clarkson WWTP's treated discharge into Lake Ontario conventional dichromate COD is run several times a week on a composite. These results were applied with the peCOD data to verify relevance and correlation.

RESULTS

The peCOD sampled every hour, but to make fair comparisons to the 24-hour daily composite cBOD and COD results the peCOD data was averaged starting at 8:00 am for a 24-hour period. All presented figures represent daily averaging to encompass when the sample was collected.

The peCOD and cBOD data of Clarkson WWTP final effluent are overlaid in Figure 3 from June 2016 to January 2017. The green area graph illustrates the peCOD data with the axis on the left, which maximizes out at 150 mg/L. The cBOD data is illustrated as the dark blue line graph with the axis on the right up to 15 mg/L. On average the peCOD and cBOD data for the sampling period were 43 mg/L and 5.3 mg/L, respectively.

The data from Figure 3 was statistically analyzed in Figure 4 to compare peCOD and cBOD results from the final effluent of Clarkson WWTP. It was determined that the correlation index between the two was a 0.81 linear relationship.

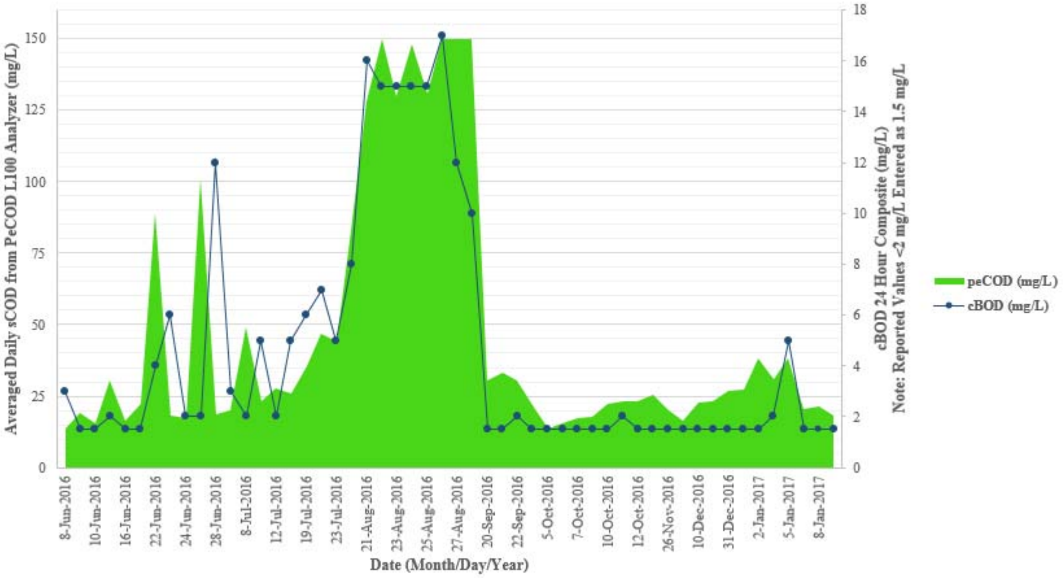

FIGURE 3: AVERAGED DAILY SCOD FROM AT-LINE PECOD (GREEN) AND 24-HOUR COMPOSITE CBOD (BLUE) AT CLARKSON WWTP FINAL EFFLUENT (MG/L) IN MISSISSAUGA ONTARIO

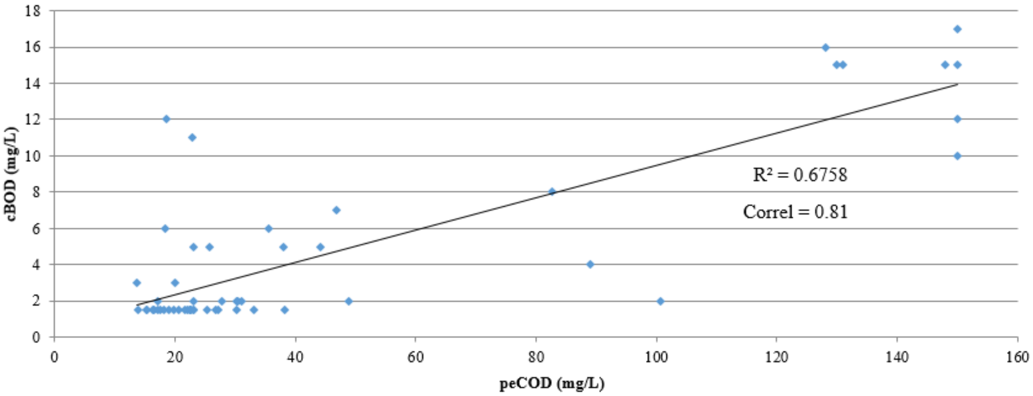

FIGURE 4: DATA ANALYSIS OF SCOD FROM AT-LINE PECOD AND 24-HOUR COMPOSITE CBOD AT CLARKSON WWTP FINAL EFFLUENT (MG/L) IN MISSISSAUGA ONTARIO

The same peCOD data set used in Figure 3 and 4 was further applied to compare the composite dichromate COD data from Clarkson WWTP final effluent. The comparison is seen in Figure 5 with both COD methods plotted on the same y-axis and the dichromate COD represented as an orange line graph. Similar to above the averaged peCOD and dichromate COD values were 43 mg/L and 28 mg/L, respectively.

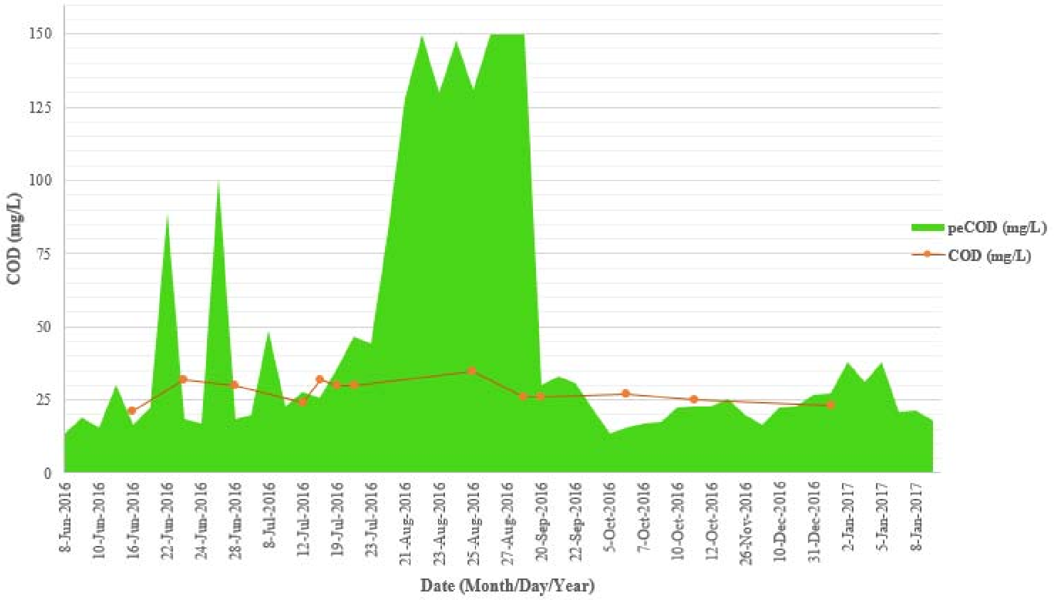

FIGURE 5: AVERAGED DAILY SCOD FROM AT-LINE PECOD (GREEN) AND 24-HOUR COMPOSITE DICHROMATE COD (ORANGE) AT CLARKSON WWTP FINAL EFFLUENT (MG/L) IN MISSISSAUGA ONTARIO

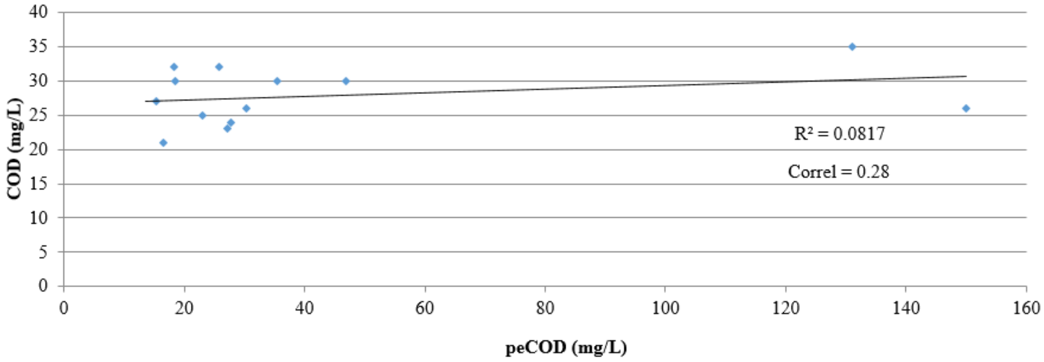

FIGURE 6: DATA ANALYSIS OF SCOD FROM AT-LINE PECOD AND 24-HOUR COMPOSITE COD AT CLARKSON WWTP FINAL EFFLUENT (MG/L) IN MISSISSAUGA ONTARIO

The data from Figure 5 was statistically processed in Figure 6 to compare the peCOD and COD results from the final effluent of Clarkson WWTP. It was determined that the correlation index between the two COD methods was 0.28.

The data currently used at Clarkson WWTP final effluent for compliance and precursory screening was plotted together to determine if there were significant trends. The overall trend is illustrated in Figure 7 with the accompanying statistical analysis displayed in Figure 8. The right y-axis in Figure 7 represents the cBOD (mg/L) and the left y-axis displays the COD (mg/L). The correlation from Figure 8 between the collected daily cBOD and dichromate COD composite samples was 0.72.

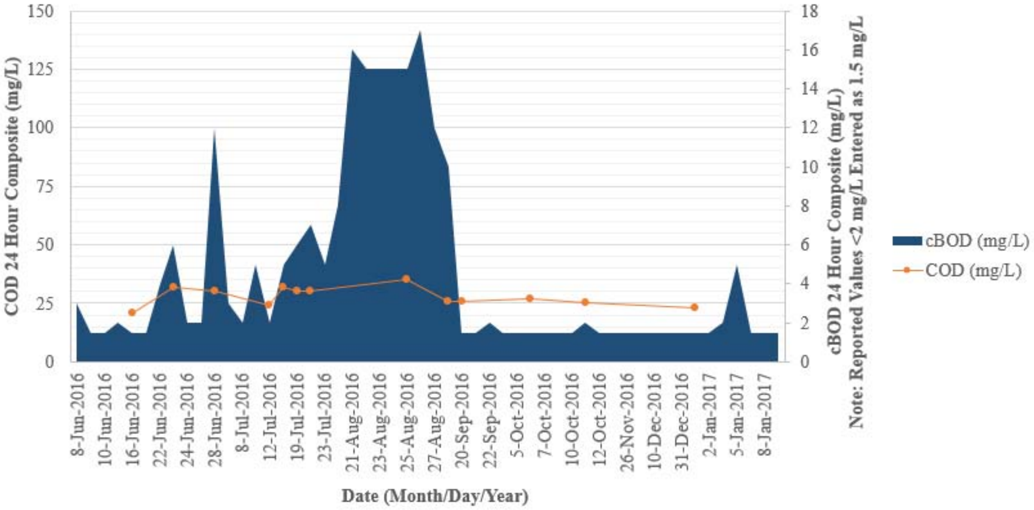

FIGURE 7: 24-HOUR COMPOSITE BOD (BLUE) AND 24-HOUR COMPOSITE DICHROMATE COD (ORANGE) AT CLARKSON WWTP FINAL EFFLUENT (MG/L) IN MISSISSAUGA ONTARIO

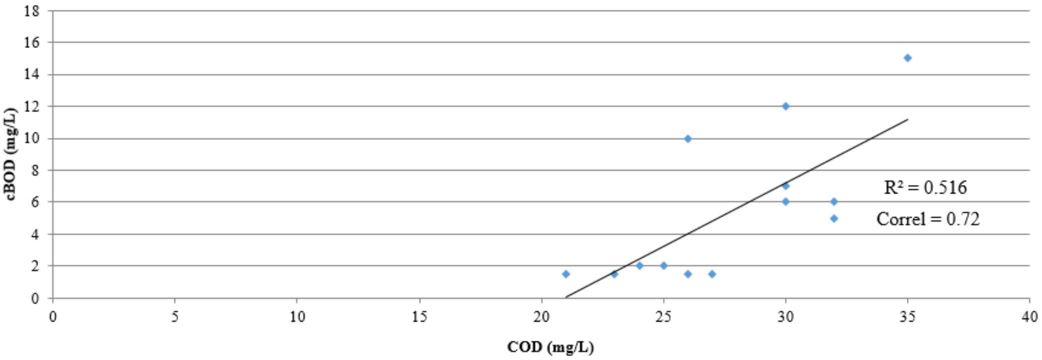

FIGURE 8: DATA ANALYSIS OF 24-HOUR COMPOSITE BOD AND 24-HOUR COMPOSITE DICHROMATE COD AT CLARKSON WWTP FINAL EFFLUENT (MG/L) IN MISSISSAUGA ONTARIO

The data utilized in Figures 8 to 8 was removed of abnormalities to provide a robust data set. The overall data still encases the true values of the above figures, but there was an increasing sensitivity with the peCOD. The sensitivity of the peCOD resulted in high COD events that were not always measured by cBOD or dichromate COD. This is illustrated is Figures 9 and 10.

Figure 9 illustrates the raw data displaying all high COD events from the daily average of hourly peCOD results in green to the 24-hour daily composite cBOD in blue. This is similarly seen in Figure 10 with peCOD compared to 24-hour daily composite COD in orange.

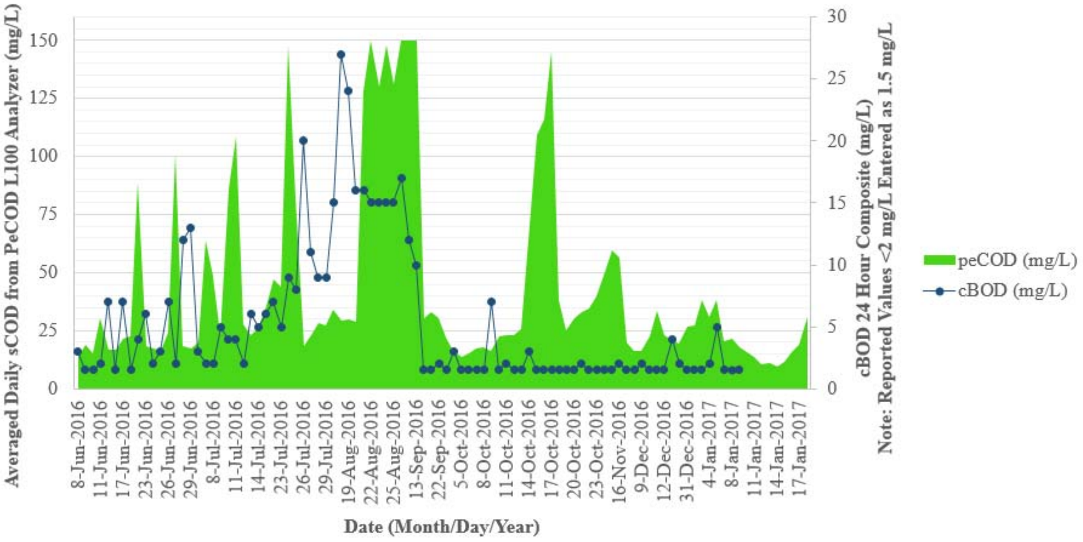

FIGURE 9: RAW AVERAGED DAILY SCOD FROM AT-LINE PECOD (GREEN) AND 24-HOUR COMPOSITE CBOD (BLUE) AT CLARKSON WWTP FINAL EFFLUENT (MG/L) IN MISSISSAUGA ONTARIO

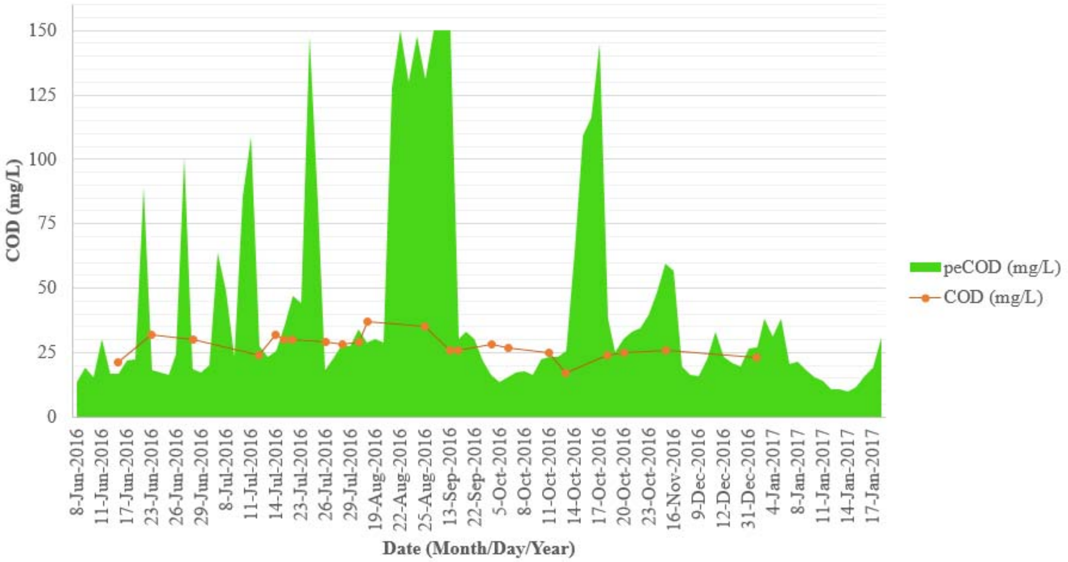

FIGURE 10: RAW AVERAGED DAILY SCOD FROM AT-LINE PECOD (GREEN) AND 24-HOUR COMPOSITE COD (ORANGE) AT CLARKSON WWTP FINAL EFFLUENT (MG/L) IN MISSISSAUGA ONTARIO

DISCUSSION

The analytical methods utilized at Clarkson WWTP to monitor final effluent water quality returning to Lake Ontario, 5-day cBOD and dichromate COD, both have limitations. The duration of the cBOD test is a significant constraint where the dichromate COD provides 3-hour results, but imposes a significant environmental hazardous and is a manual analysis. The peCOD study completed on final effluent wastewater samples at the Clarkson WWTP between June 2016 to January 2017 displayed great potential in providing environmentally safe and real time sCOD results to precursor that of compliance cBOD.

The trend illustrated in Figure 3 depicts the peCOD's sensitivity to high organic loads being released into Lake Ontario in real time that was later confirmed with the external lab's cBOD results. The large spike occurrence that occurred at the end of July 2016 into August 2016 was a known event of an aeration tank being taken off line for maintenance.

The peCOD was able to pick up on higher than normal levels sCOD within the final effluent. The routine dichromate COD tests were completed with slightly elevated results, a 15% increase but nothing that would have caused alarm. The cBOD and peCOD values during this time period increased by 73% and 70% respectively. This correlation is further reinforced in Figure 4 with a regression analysis, R-squared value of 0.67 and a correlation coefficient of 0.81. This reinforces great degree of a linear relationship between peCOD and cBOD.

The degree of a linear relationship was not similarly represented between peCOD and dichromate COD, as displayed in Figures 5 and 6. This was due to two separate analysis methods being utilized to capture a different portion of the organic matter being oxidized. The high electrochemical potential of the TiO_2 gives the peCOD a substantial advantage over the modest chemical potential generated by the dichromate method. Both COD methods are capable of capturing the oxygen equivalent of the organic matter but dichromate is a chemical based analysis and the peCOD is a photoelectrochemical measurement which adds difficulty in making a direct comparison.

Traditionally, cBOD values have always been lower than COD values since cBOD measures the amount of oxygen required for bacteria to degrade the organic matter, while COD is the measure of all organic and inorganic matter regardless of whether or not the constituents will be consumed. The dichromate COD and peCOD method also can not differentiation between the biologically oxidizable or inert organic matter where cBOD can. The cBOD results and dichromate COD results do have a strong correlation in Figure 8 since they are always going to be proportionally measuring the same subset of organics indirectly, similar to that of peCOD and BOD.

Both COD analysis methods provide a strong correlation to cBOD, but the peCOD is more advantageous with its green nanotechnology, ease of use for inline integration, and better sensitivity to high organic loads. The sensitivity of the peCOD was illustrated in Figure 9 with the cBOD plotted as well. There were a dozen events that occurred between June 2016 and January 2017 that created spiked peCOD results and minimal fluctuation with cBOD and even dichromate COD (Figure 10). The peCOD is capable of oxidizing large chain molecules and other organics to their full potential that bacteria may not be able to consume or cannot be chemically broken down. The increased oxidizing power of the peCOD is better able to measure certain organics such as nicotinic acid, benzene, diethylamine, and many others. Further investigation of the final effluent sample complex would help determine other organics that may be oxidized by the peCOD but not fully captured with other water quality parameters.

The current At-Line L100 PeCOD® is best to be operated inside a temperature and humidity control building out of harsh operating conditions. The system also utilizes settling to achieve separation of suspended solids, which is less than ideal for locations further downstream of the WWTP. There is currently a peCOD model, the Online P100 PeCOD® that is specifically designed to handle high particulate loads and harsher operating conditions with a built in 50 µm metal mesh filter that is self-back flushing. With the promising correlation between the peCOD and cBOD results obtained at the final effluent it is of great interest to further the study at other treatment points to further build on the relationship.

CONCLUSIONS

The peCOD study with OCWA at the Clarkson WWTP was successful in obtaining a strong correlation between peCOD and cBOD, further demonstrating the potential for photoelctrochemical determination of COD in the wastewater industry. When compared to dichromate COD, the peCOD had an expanded scale of resolution capturing full oxidation of organic matter. Provided the need for rapid response time in WWTPs it is conceivable that the peCOD could easily be integrated for inline COD monitoring to improve WWTP operations.

ACKNOWLEDGEMENT

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