Nanotechnology provides alternative method to dichromate-based COD analysis

A new nanotechnology-based approach, introduced by MANTECH of Ontario, Canada to test chemical oxygen demand without the use of dichromate, is the first alternative method adopted by global regulatory agencies. MANTECH INC. President and CEO **Robert V. Menegotto** explains its significance.

Nanotechnologies hold a lot of promise for improving the world. By offering revolutionary advancements over traditional technologies, including water quality analysis, nanotechnologies bring progress to the efforts for safe, clean water products.

Laboratory staff have known for a long time about the negative health impacts associated with chemical oxygen demand (COD) testing using the traditional dichromate method. However, the determination of COD to measure organic matter in wastewater effluent is required under the European Union (EU) Urban Waste Water Directive 91/271 and no viable safe, user-friendly alternative method existed until 2012.

The traditional COD analysis approach has been used for decades and is based on the use of potassium dichromate, one of the reagents necessary for dichromate COD (CODCr) analysis. Dichromate is listed as a "Substance of Very High Concern" on the Annex XIV list of the EU's REACH regulation. The European Chemical Agency has found potassium dichromate to be carcinogenic, mutagenic, and a reproductive toxin. These properties make the CODCr method potentially unsafe for the analyst, the public, and the environment. As a result, starting September 2017, producers of COD tests will need authorization from the EU to sell these tests, which creates demand uncertainty for end users. In addition, the use of mercury required in the CODCr test to remove chloride interference is scheduled to be prohibited by law in Sweden in January 2016.

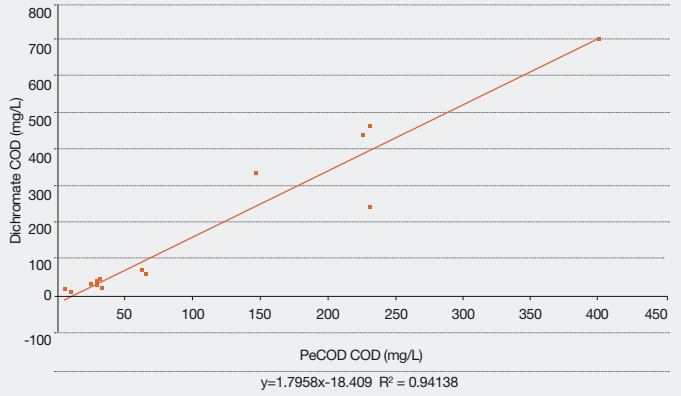
The challenge was to identify an alternative COD analysis method that can overcome the limitations of the traditional CODCr method. The Kappala Association in Sweden recently published a Pre-Commercial Innovation Procurement to "deliver a comparable analysis method to CODCr, which does not involve mercury and preferably not dichromate." A new nano-technology based approach called PeCOD® from MANTECH, based in Ontario, Canada, is the first alternative method adopted by leading global regulatory agencies and selected by the Kappala Association for procurement.

Method E3515 eliminates environmentally hazardous waste and the use of harmful and toxic reagents.

The core of the system is a nanotechnology-based sensor, which consists of an ultraviolet-activated nanoparticle titanium dioxide (TiO_2) photocatalyst. The high electrochemical potential of the TiO_2 gives it a substantial advantage over the modest chemical potential generated by the CODCr method. The PeCOD approach measures photocurrent charge originating from the oxidation of organic species contained in a sample. The result is a very accurate measurement of organic pollution, with no use of dichromate or other hazardous chemicals.

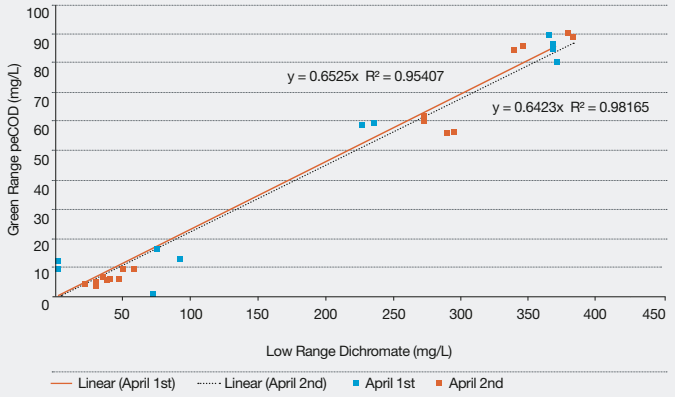
Regulatory approvals are conservative in the water industry because incorrect decisions can have serious impacts for the environment and public health. The nanotechnology-based COD method was first methodically validated by the Ontario Ministry of the Environment and Climate Change (ON MOECC) in Canada. After 20 months of validation testing, in February 2014, the ON MOECC released official method E3515, which replaces the standard CODCr methods previously used within the regulatory agency. A performance comparison between the standard CODCr method and

Figure 1



A scatter plot demonstrates the strong correlation between PeCOD and CODCr for various surface and wastewater samples. Analyzed by the Dutch government laboratory, RWS-CIV, the technology validation is also now underway.

Figure 2



A graph showing the correlation of CODCr to PeCOD methods tested at the Guelph Wastewater Treatment Plant. Samples from influent to effluent and treatment points in between were analyzed. This strong correlation resulted in the city investing in the nanotechnology approach and enabling constant and continuous monitoring of the facility.

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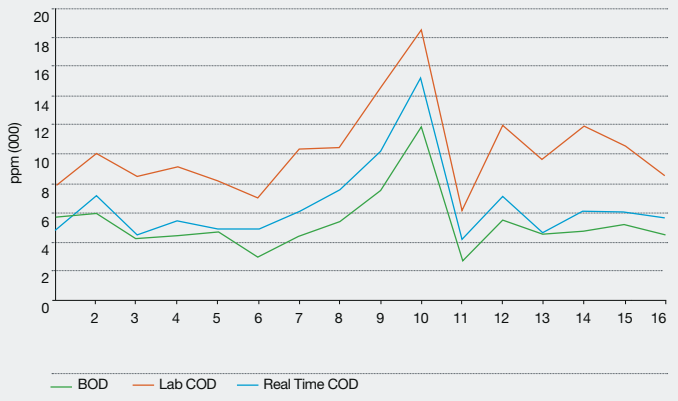
Figure 3



The plot of real-time PeCOD, dichromate COD, and BOD_5 for brewery effluent samples – resulting in R^2 for PeCOD and BOD equivalent to 0.93, as well as R^2 for PeCOD and dichromate COD equivalent to 0.94. R^2 signifies a degree of correlation with 1 being a perfect correlation between 2 data sets. The BOD and dichromate COD were analyzed by an accredited laboratory.

the PeCOD method was provided in a validation report. Method E3515 eliminates environmentally hazardous waste and the use of harmful and toxic reagents.

Vasile Furdui, a research scientist with the MOECC, stated, "Laboratory Services Branch of the Ontario Ministry of the Environment and Climate Change supports the development of new green technology. The new approach for measuring chemical oxygen demand by photo-electrochemical measurement eliminates the use of corrosive (H_2SO_4), carcinogenic ($K_2Cr_2O_7$), toxic ($HgSO_4$), and irritant (Ag_2SO_4) chemicals for the analysis of chemical oxygen demand. Analysis time was significantly reduced and the method detection limit was 1 mg/L O_2."

The MOECC now uses two nanotechnology-based units and relies on them for analysis of samples for enforcement, compliance, and legal purposes. The technology validation is also now underway by the Dutch RWS-CIV Laboratory. Data was obtained during a preliminary validation process and the strong correlation initiated a thorough validation project throughout 2015.

The Ontario-based University of Guelph developed a hypothesis that the nanotechnology approach could correlate to CODCr and rapidly measure organic matter for the Guelph Waste Water Treatment Plant. A strong correlation was discovered, which caused the city to invest in the nanotechnology approach. This also enabled continuous 24-hours per day, every day COD monitoring. Previously, the city only measured COD eight hours per day, five days per week, during laboratory staff working schedules. The PeCOD method provided a significant breakthrough in terms of reducing COD sample analysis time to 15 minutes, versus the approximate three hours for the traditional CODCr test. For wastewater facility operators, this rapid analysis provides the understanding of incoming COD levels, while optimizing plant operations, as well as storm event monitoring and monitoring discharge effluent for regulatory compliance.

One example is from Vertellus Specialty Metals based in the United Kingdom. "We moved from the COD vials to the PeCOD primarily because it allowed us to run our process more efficiently and further adjustments to our process could be made up to ten times a day. With the COD vials, only three or four adjustments could be made," said Mark Westhorpe, the analytical shift leader for Vertellus Specialty Materials. "This increase in efficiency and turnaround time in sample analysis has easily paid for the system, not to mention the added benefit that we're no longer using carcinogenic chemicals to test for COD. We have also seen a reduction in cost of consumables and waste disposal," he said.

Beyond the COD analysis capabilities, the application of the technology is being expanded to biochemical oxygen demand (BOD_5) correlation for rapid, effective compliance monitoring. A PeCOD application for COD testing of potable water sources was also published in the *Journal of American Water Works*

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Events 2015

April

21-23 Dubai, UAE
WETEX 2015, 16th Water, Energy, Technology, and Environment Exhibition, Includes WEF International Pavilion
www.wetex.ae

May

4-5 Huntington Beach, California, USA
19th Annual Water Reuse & Desalination Research Conference, Abstracts due by December 1
Organized by WateReuse Research Foundation
www.watereuse.org

6-8 Shanghai, China
IE Expo Shanghai (IFAT), Asia's Trade Fair for Environmental Technology Solutions
Includes WEF International Pavilion
www.ie-expo.com

10-14 Palermo, Italy
EUROMED 2015: Desalination for Clean Water and Energy, organized by European Desalination Society and Universitá Degli Studi Di Palermo
www.desline.com@gmail.com

12-14 Adelaide, Australia
Ozwater '15, Australia's International Water Conference & Exhibition, organized by Australian Water Association
www.ozwater.org

May

17-19 Portofino, Italy
IDA Conference: New Horizons for Desalination, organized by Rotary Club La Spezia and International Desalination Association
www.idadesal.org

27-28 Montpellier, France
5th HydroGaïa Fair, Water and Economic Developments
www.hydrogaia-expo.com

June

7-10 Anaheim, California, USA
ACE15, Annual Conference & Exposition, organized by American Water Works Association
www.awwa.org

8-10 Washington, DC, USA

Water and Energy 2015: Opportunities for Energy and Resource Recovery in the Changing World, organized by WEF, European Water Association, Japan Sewage Works Association
www.wef.org/WaterEnergy

15-16 Singapore
Workshop on Water Reuse Policies for Direct and Non-Direct Potable and Industrial Users
Organized by National University of Singapore, Institute of Water Policy, National Environmental Research Institute
E: spphctq@nus.edu.sg

July

26-28 San Jose, California, USA
Nutrient Symposium 2015
Organized by Water Environment Federation
www.wef.org

August

4-8 São Paulo, Brazil
FENASAN Brazil 2015: 26th National Congress and Exhibition on Sanitation and Environment Services.
Includes WEF International Pavilion
www.fenasan.com.br

17-19 San Francisco, California, USA
Smart H2O Summit 2015: Sustainable Water Solutions. Held in partnership with The Water Innovation Project
www.smarth2osummit.com

23-28 Stockholm, Sweden
World Water Week in Stockholm
Organized by Stockholm International Water Institute
www.siwi.org

30- September 4 San Diego, California
IDA World Congress 2015: Desalination & Water Reuse, Renewable Water Resources to Meet Global Needs
www.idadesal.org

September

9-11 Santa Marta, Colombia
58th International Congress of Water, Sanitation, Environment, and Renewable Energy, organized by The Colombian Association of Sanitary and Environmental Engineering (ACODAL)
Includes WEF International Pavilion
www.acodal.

13-15 Seattle, Washington, USA
30th Annual WateReuse Symposium
www.watereuse.org

15-18 Johannesburg, South Africa
IFAT Environmental Technology Forum Africa: Water, Sewage, Refuse, and Recycling Solutions for the Mining and Construction Industry
Includes WEF International Pavilion
www.ifatforum-africa.com

26-30 Chicago, Illinois, USA
WEFTEC 2015, 88th Annual Water Environment Federation Technical Exhibition & Conference
www.weftec.org

19-22 Dead Sea, Jordan
4th Water and Development Congress and Exhibition, organized by International Water Association
www.iwa-network.org/WDCE2015

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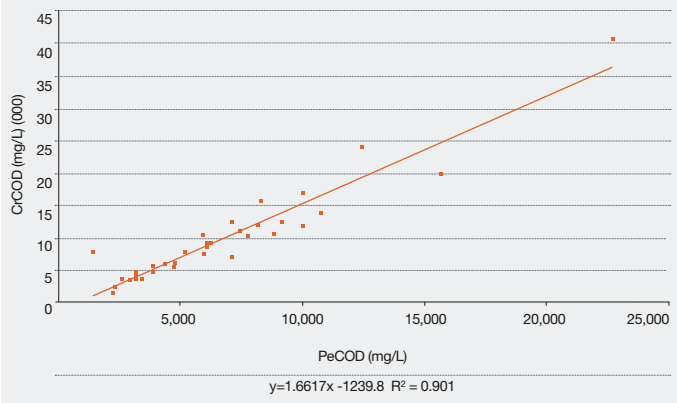
Association's September 2014 issue, titled, "Application of photo-electrochemical chemical oxygen demand to drinking water." According to the article, early technology applications have shown that with nanotechnology based monitoring, removal of natural organic matter is approximately three-and-a-half-times greater than the use of traditional surrogates analysis methods such as Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC) and Ultra-Violet 254 nanometer (UV254). These studies have resulted in real-world adoption of this nano-technology-based approach in these new promising applications that will continue to enhance the protection of the environment and public health, leading to sustainable practices.

Author's Note

Robert Menegotto is the president and chief executive officer of MANTECH INC, based in Guelph, Ontario, Canada. Mr. Menegotto has held product development, sales management, and vice president roles in laboratory and process analytical equipment distribution and manufacturing companies in the United States and Canada. In 2010, Mr. Menegotto started MANTECH INC. to develop and commercialize innovative solutions for water quality testing and monitoring that will protect the environment and the public, leading to sustainable practices.

Figure 4



A scatter plot of PeCOD and BOD for all treated effluent industrial and municipal waste samples from Clean Harbors in Guelph, Ontario, Canada. Wastewater treated is from municipal, automotive, petrochemical, chemical, and food and beverage plants. Beyond the COD analysis capabilities, the application of the technology is being expanded to BOD_5.