NEW BIO-ELECTRODE SENSORS ALLOW FOR REAL-TIME BOD MEASUREMENT

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Bio-electrode sensors (BES) are an emerging technology for the monitoring of water quality. They allow the user to put their finger on the pulse of the metabolic activity of a microbial community. The concept of BES technology is not new, with the research into microbial fuel cells dating back over a century.

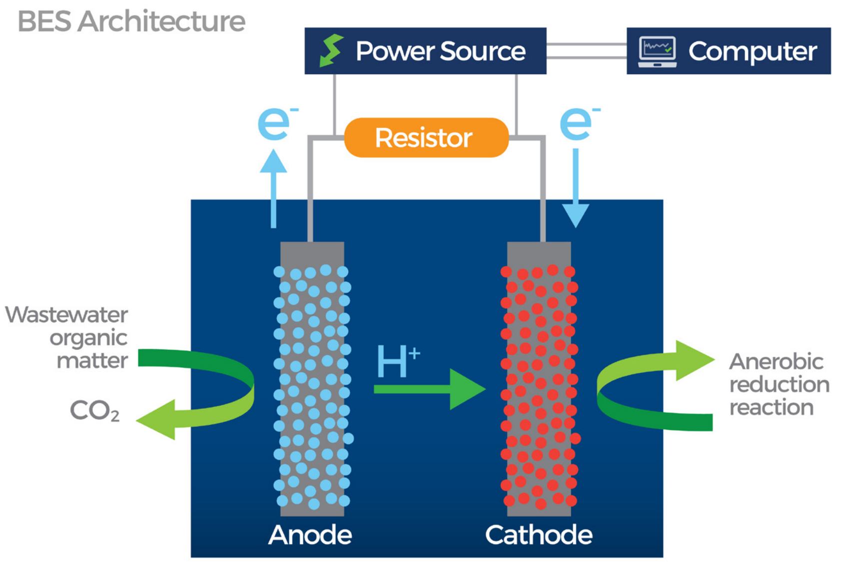
Thanks largely to technical advancement and cost-effective components, the technology is only now becoming attractive for wastewater applications. The most recognizable BES technology is the microbial fuel cell that harnesses the energy produced by exo-electrogenic bacteria when they consume organic compounds to produce electrical energy.

The basic architecture of a BES system is an anode/cathode pair, with a resistor positioned between them. Exo-electrogenic microbes on the anode oxidize organic material in the wastewater and the electrons are transferred to the cathode through the circuit. Protons (H+) created at the anode migrate to the cathode to recombine with the electrons which have travelled through the circuit, creating a complete electrical circuit. Electrons travelling through the resistor are measured and logged.

Protobacteria, such as those from the Geobacter genus, typically colonize the anode and oxidize organic carbon material. Through metabolic pathways that evolutionarily predate the presence of atmospheric oxygen, these bacteria can use the metallic anode as an electron receptor.

Monitoring of the microbial derived electrical current provides novel real-time insight into biological treatment rates and efficiencies. The data generated can also provide rapid insights into water quality characteristics.

BES sensors are attractive because they have low power and maintenance requirements, and provide novel data on microbial activity that can be leveraged in wastewater process optimization. They can be installed in a similar fashion to a standard wastewater probe (either submerged in a tank or installed in a pipe). All that is required for maintenance of a pre-inoculated probe is a regular supply of soluble organic material for the resident microbial populations. Therefore, the probes must be maintained in a proprietary synthetic wastewater when not being used for measurement.



Schematic of a bio-electrode system.

Output from the sensor is a voltage measurement, which is typical of other sensors such as pH, conductivity or ORP. The standard signal output being a voltage signal allows for BES sensors to be easily integrated into an existing data acquisition system or a developed SCADA system. In addition, the low power requirement means that BES sensors are attractive for remote locations or in situ water quality monitoring.

Island Water Technologies recently launched the first commercial BES platform, SENTRY-AD™. It monitors microbial activity in anaerobic digesters to aid in process optimization and stability. For this research project a standard SENTRY-AD probe was used in a bench-scale setting to determine if there was a relationship between the signal generated by the probe and carbonaceous biochemical oxygen demand ($CBOD_5$) of a wastewater sample.

The project's hypothesis was that the metabolic activity recorded from the exo-electrogenic bacteria, as measured by the BES, would be directly correlated to the presence of biologically oxidizable organic carbon in a water sample. Traditionally, the biologically oxidizable organic carbon is quantified by the consumption of oxygen in Wheaton bottles over five days (the $CBOD_5$ test). It was hypothesized that a BES sensor's output would be an analogous means of measurement of $CBOD_5$.

In this study, the relationship between BES output and $CBOD_5$ concentration was confirmed, and a strong linear relationship (R2 = 0.98) between the total

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charge transferred and the $CBOD_5$ concentration (standard Wheaton bottle method) was identified.

Replacement of the current standard method is of interest because it requires five days and skilled lab personnel to obtain precise and accurate results. Also, setup of the test is relatively time-consuming (two hours) which makes the test less practical when regularly running a small quantity of samples, and impractical in remote locations. A BES sensor that is effective for quantification of $CBOD_5$ would liberate the measurement from a lab setting, and the real-time quantification would create the potential for optimization of wastewater treatment trains, based on real-time influent and effluent water quality.

In this experiment, the sensors were run as batch reactors with regular flushing of the probe with buffered solution between each test. The response of the sensor was recorded until it fell to background levels (deemed to be caused by endogenous respiration). After this period, a feed synthetic wastewater was put in the cup to sustain the microbial community until another sample was prepared.

Bench-scale testing was performed on a synthetic wastewater with sodium acetate as a source of $CBOD_5$, and on domestic wastewater samples collected directly from the septic settling tank at Dalhousie University's Bio-Environmental Engineering Centre. Wastewater at the collection site has already undergone settling and is low in solids (<25 mg/L). A range of $CBOD_5$ concentration was created from the domestic wastewater samples by diluting samples in phosphorus buffer with the addition of minerals and nutrients.

Two metrics were used to create a relationship with $CBOD_5$: total charge transferred (integrated current); and max current. A strong linear relationship between charge transferred and $CBOD_5$ concentration was found, with the domestic wastewater relationship having an R2 of 0.98. A relationship between the maximum current $CBOD_5$ was also apparent. However, it was non-linear and only a maximum measurable concentration of 25 mg/L $CBOD_5$ when sodium acetate was the carbon source and 80 mg/L $CBOD_5$ with domestic wastewater. The limitation on the quantification of $CBOD_5$ is a satiating response (biological limitation). However, when using total charger transferred to quantify $CBOD_5$ there were no identifiable limits for total charge response.

Standard BES probe and data acquisition system used for this study.

Analytical processing times for max current output were near-instantaneous after inserting a sample. The relationship of max current output with $CBOD_5$ concentration suggests that further BES development has the potential to provide continuous real-time measurements of $CBOD_5$ from an in situ installation. Using this sodium acetate based, synthetic wastewater, the satiating response in maximum current was identified at approximately 25 mg/L $CBOD_5$, representing the maximum biological uptake rate for this exo-electrogenic biofilm.

A Monod-type relationship was examined as a fit for the max current data but it was a poor fit, suggesting that the response limitations are not a simple substrate limitation. More in-depth analysis of the relationship will provide avenues of investigation to improve BES sensor architecture.

Analysis time for total charge transfer for the domestic wastewater was linearly dependent on $CBOD_5$ concentration with an R2 = 0.95. This was an anticipated result as the measurement of charge transfer is complete when the organic substrates are consumed.

The results of this work are very encouraging for the potential of BES to act as real-time tools for monitoring $CBOD_5$ concentrations in wastewater streams. The data shows a strong correlation between both the instantaneous current and charge transfer with $CBOD_5$. Improvements of the architecture and operation of the BES technology will focus on reducing the time required for $CBOD_5$ quantification and improving the quantifiable range of the max current relationship.

The team at Dalhousie University and Island Water Technologies are interested in installing a demonstration bioelectrode sensor technology for real-time BOD quantification at municipal wastewater treatment facilities across Canada and the U.S. The technology could be used for monitoring end-of-pipe wastewater being discharged from the facility or wastewater streams internal to the treatment process. ■

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