Electronic Supplementary Information for:

Towards the real-time monitoring of industrial wastewater treatment processes via photoelectrochemical oxygen demand measurements

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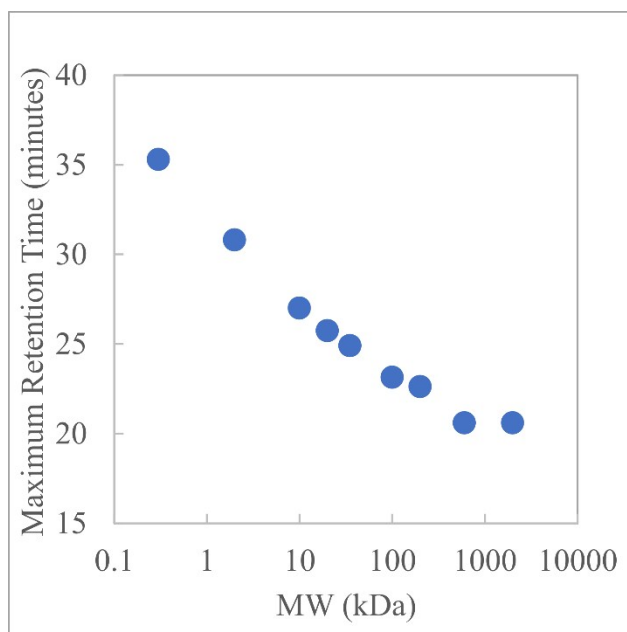
Figure S-1- SEC peak retention times of the PEG/PEO samples used in this study plotted against their molecular weights as reported by the supplier (Sigma Aldrich, Oakville, ON, Canada). For the samples that were reported to have a range of molecular weight values, the average of the high and low values was used for the x-axis value.
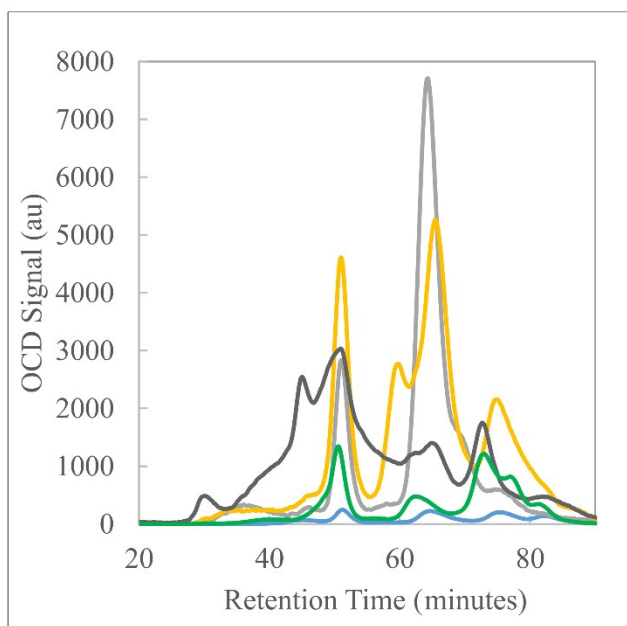

Figure S-2- LC-OCD chromatograms of five industrial wastewater samples provided by an industrial wastewater treatment plant (Aevitas, Brantford, ON, Canada) that receives and treats wastewater from a variety of industrial and commercial facilities.

Table S-1- The PeCOD® L100 analyzer parameters used in this study

Parameter Name	Value	Description
LED Current	Varies	This parameter is set by running either the New Sensor or the Calibration routine. It indicates the level of the LED output required to meet the target I-term (i.e. the current generated at the end of the calibration reference oxidation.).
Applied Potential	400 mV	Sets the reference electrode potential.
Pre-Burn Time	600 s	In peCOD measurement the sample is injected into and oxidized in the thin-layer cell twice. Pre-Burn Time is the first-round oxidation (i.e. Pre-Burn) maximum allowed time before a time out error.
Burn Time	600 s	This is the Maximum allowed time for the second round of oxidation (i.e. Burn) before an "incomplete oxidation" error.
Target I-Term	20.0 c	Sets target I-term for calibration routine.
Minimum Burn Time	240 s	Minimum time for oxidation before termination criteria is satisfied.
Q Negative	-100 µC	Allowable level of the net electric charge (i.e. $Q_{net} = Q_{reference} - Q_{blank}$) that can be measured below the charge generated during the blank oxidation, before a "Less than zero" error will be reported.
Blank Prime Volume	2200 µl	Volume of solution to be primed through PeCOD® analyzer head and through sensor bypass path
Inject Volume	200 µl	Volume of solution to be primed through sensor analysis path.
Advance Volume	20 µl	Volume of solution to be primed through sensor analysis path.
Sample Prime Volume	2200 µl	Volume of solution to be primed through PeCOD® analyzer head and through sensor bypass path.
Precision	PRECISE	Choice of operation type (precise or rapid)
Ref40Intensity	0 ADC	UV Emission level when LED is set to 400mA at 40°C. Measured in detector ADC units.
Current Gain	45.3 µA/V	This is the potentiostat current gain calibration. Should not vary from the default by more than 5%.
Maximum V_{aux}	2.4 V	An error is generated if V_{aux} (i.e. the difference in charge between the auxiliary electrode and the working electrode) exceeds this value during integration.
Maximum V_{ref}	2.4 V	An error is generated if V_{ref} (i.e. the difference in charge between the reference electrode and the working electrode) exceeds this value during integration.
Maximum I-work	150 µA	An error is generated if the current (I-work) generated by oxidation of the sample exceeds this value during integration
Max LED Current	500 mA	The LED current is prevented from exceeding this value. This protects the LED from feedback control loop failure.
Max LED Temp	60°C	An error is generated if the LED temperature proxy exceeds this value during operation.
Max Module Temp	50°C	An error is generated if the processor temperature exceeds this value during operation.
TermGradientC	-0.01 µA/s	When the gradient of I-Work (i.e. d(I-Work)/dt) drops to this value the oxidation is terminated.

Table S-2- SEC system information

Columns	Waters Ultrahydrogel-120, -250 and -500; 7.8 mm × 300 mm (internal diameter × length) connected in series
Detector	Refractive index
Solvent	0.5 M sodium nitrate plus 25 mM (2-cyclohexylamino) ethanesulfonic acid buffer (pH 10)
Sample Injection Volume	20 μL
Sample Concentration	5 to 10 g/L
Calibration	Pre-calibrated with PEG standards up to a molecular weight of 800 kDa

Table S-3- COD$_{Cr}$ results for the macromolecule samples

Macromolecule	MW (kDa)	COD$_{Cr}$ (mg/L)
Ethylene glycol	0.06	623
PEG	0.3	615
	2	561
	10	699
	20	577
PEO	35	611
	100	513
	200	665
	600	574
	2,000	593
Dextran	1	582
	6	525
	40	557
	100	606
	200	575
	550	548
PVP	2,000	568
	10	589
	40	554
	360	562
PAM	1,300	544
	10	599
	41	551
	150	599
	5000-6000	551