ADVANCING THE TREATMENT OF INDUSTRIAL WASTEWATER VIA INTEGRATION OF PECOD$^{®}$ AND LC-OCD ANALYTICAL TOOLS

ADVANCING THE TREATMENT OF INDUSTRIAL WASTEWATER VIA INTEGRATION OF PECOD® AND LC-OCD ANALYTICAL TOOLS

By

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LAY ABSTRACT

Many industrial facilities do not treat their wastewater on-site and instead ship it to specialized treatment facilities. Ensuring that the treated effluent meets the stringent discharge regulations is a challenging task for such facilities as the composition of the incoming feed to the treatment process changes with each shipment. In this work, application of two new analytical tools, PeCOD® and Liquid Chromatography-Organic Carbon Detection (LC-OCD), for measurement and characterization of industrial wastewater organic pollution respectively, has been investigated.

The conventional method of measuring organic pollution, Chemical Oxygen Demand (COD), requires 2-3 hours to complete. Herein the suitability of an alternative parameter, Photoelectrochemical Oxygen Demand (peCOD), that can be measured in approximately 15 minutes for replacing COD analysis in industrial wastewater plants was investigated.

Implementation of effective treatment processes that are operated at their optimum conditions is required to meet the stringent discharge regulations. Advanced Oxidation (AO) is an effective method of industrial wastewater treatment. Herein, optimum AO treatment conditions were studied via application of the LC-OCD analysis for organic pollution characterization.

ABSTRACT

In 2012, mandatory effluent quality standards were established in Canada as part of the Wastewater Systems Effluent Regulations (WSER) with compliance deadlines starting in 2020. Maintaining the treatment process efficacy to meet these new stringent discharge regulations is extremely challenging at treatment facilities that treat wastewater from multiple industries due to the high variation in the composition of the incoming feed to the process. In this work, application of two new analytical tools, PeCOD® and Liquid Chromatography-Organic Carbon Detection (LC-OCD), for measurement and characterization of industrial wastewater organic pollution respectively, has been investigated.

Organic pollution is commonly measured as Chemical Oxygen Demand via the dichromate method (COD_{Cr}) which requires 2-3 hours to complete. Thus this method is not suitable for applications that require rapid and frequent pollution monitoring. The Photoelectrochemical Oxygen Demand (peCOD) is an alternative parameter of organic pollution that can be measured in approximately 15 minutes via a method that utilizes the high oxidation potential of UV-irradiated TiO_2 nano-particulates. Herein peCOD suitability to replace COD_{Cr} for analysis of industrial wastewater was investigated. The results indicated that for both untreated (i.e. incoming) and treated (i.e. effluent) industrial wastewater samples, peCOD results are lower than COD_{Cr} results. However, for the effluent samples, the two methods’ results are strongly correlated. Containing hard to oxidize materials (i.e. macromolecules) and high concentrations of chloride and nitrogenous compounds were identified as potential causes of difference between the results of the two methods.

When there is variation in the composition of the incoming wastewater to a treatment process, information about the wastewater composition is required for process optimization. Thus optimization cannot be based solely on bulk measurements of organic pollution (e.g. COD). In this study, a novel combination of LC-OCD analysis with Design-Of-Experiments (DOE) methods was used to optimize the Fenton Advanced Oxidation (AO) treatment conditions in terms of chemical reagent concentrations, to develop statistical models of the process, and to identify potential mechanisms of COD removal.

In Memory of

Dr. Hossein Hooshiar Rad

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List of Abbreviations

AO	advanced oxidation
BOD	biochemical oxygen demand
CCD	central composite design
COD	chemical oxygen demand
COD_{Cr}	chemical oxygen demand measured via the dichromate method
CI	confidence interval
CHES	2-(Cyclohexylamino) ethanesulfonic acid
DOC	dissolved organic carbon
DOE	design of experiments
DR	dilution ratio
EF	electrochemical Fenton
Eff.	effluent
EG	ethylene glycol
EPA	Environmental Protection Agency
F	Faraday constant
GC	gas chromatography
HPLC	high performance liquid chromatography
i	photocurrent
ICP-OES	inductively coupled plasma optical emission spectrometry
ID	internal diameter

LC-MS	liquid chromatography–mass spectrometry
LC-OCD	liquid chromatography-organic carbon detection
LED	light emitting diode
min	minute
MOECC	Ministry of Environment and Climate Change
M_n	number average molecular weight
mPES	modified polyethersulfone
M_r	relative molecular mass
M_v	viscosity-average molecular weight
M_w	weight-average molecular weight
MW	molecular weight
NOM	natural organic matter
NTU	nephelometric turbidity units
OCD	organic carbon detector
OND	organic nitrogen detector
peCOD	photoelectrochemical oxygen demand
PAM	polyacrylamide
PEG	polyethylene glycol
PEO	polyethylene oxide
PVP	polyvinylpyrrolidone
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RI	refractive index

RT	retention time
R	ratio of hydrogen peroxide molar concentration over ferrous ion molar concentration
Q	net charge
S	ratio of hydrogen peroxide molar concentration (mM) over the COD (mg/L) of the wastewater sample
SA	surface area
SEC	size exclusion chromatography
SNR	specific nitrification rate
TOC	total organic carbon
ThOD	theoretical oxygen demand
UV	ultraviolet
UVD	ultraviolet detector
WSER	Wastewater Systems Effluent Regulations
wt %	percentage by weight

Chapter 1: Introduction and Background

According to Environment and Climate Change Canada, every year over 150 billion liters of untreated and undertreated wastewater is discharged into Canadian waterways [1]. Wastewater Systems Effluent Regulations (WSER) were established in 2012 and came into effect in 2015 that include mandatory minimum effluent quality standards [1]. These regulations that have established compliance deadlines starting in 2020 require wastewater treatment facilities to design systems with maximum flexibility and the capacity to handle any potential process upsets. As shown in Figure 1, there are three different types of facilities within the industrial wastewater treatment sector that will be affected by these regulations:

1. Manufacturing facilities that generate the industrial wastewater itself but then also treat it 'on-site' before it is directly released into the local sewer system or the environment. There are multiple industrial wastewater types including process cooling water, pulp and paper mill effluents, textile industry waste, and metalworking fluids.
2. Wastewater treatment plants run by local municipalities that receive and treat both municipal and industrial wastewater. An operational challenge is to frequently monitor the quality of the incoming industrial wastewater delivered to their plant via the local sewer system. In order to meet the federal WSER criteria that came into force in 2015, municipalities across Canada are updating their by-laws associated with the discharge of industrial wastewater into the local sewer system.

For example, in Ontario, the City of Brantford was the first to establish new by-laws in April 2014 that specifically target the discharge of industrial wastewater. According to the report from the City of Brantford's Public Works Commission, these actions were taken primarily "to protect the health, safety and well-being of persons, the natural environment…and to prevent public nuisances". In February 2016, Toronto City Council voted to amend their sewer-use by-laws to address a number of concerns including the discharge of industrial wastewater from the food and automotive sectors. Other municipalities in Ontario (including Barrie, Guelph, Hamilton, Kitchener, and Ottawa) are in the process of updating their sewer use by-laws and it is widely anticipated will develop similar by-laws to target the discharge and treatment of industrial wastewater.

3. Specialized treatment facilities that receive shipments of industrial wastewater from manufacturing facilities (like the ones listed above but choose instead not to do any on-site treatment and ship it away) for a fee. The operation of these specialized facilities is quite challenging given the large diversity of the shipments from the different manufacturing facilities. There are numerous such companies (including Clean Harbors, GFL Environmental, and Aevitas) that take on the responsibility of first treating and then discharging the treated wastewater into the local sewer system. The challenges faced by this type of treatment facility is the focus of this project.

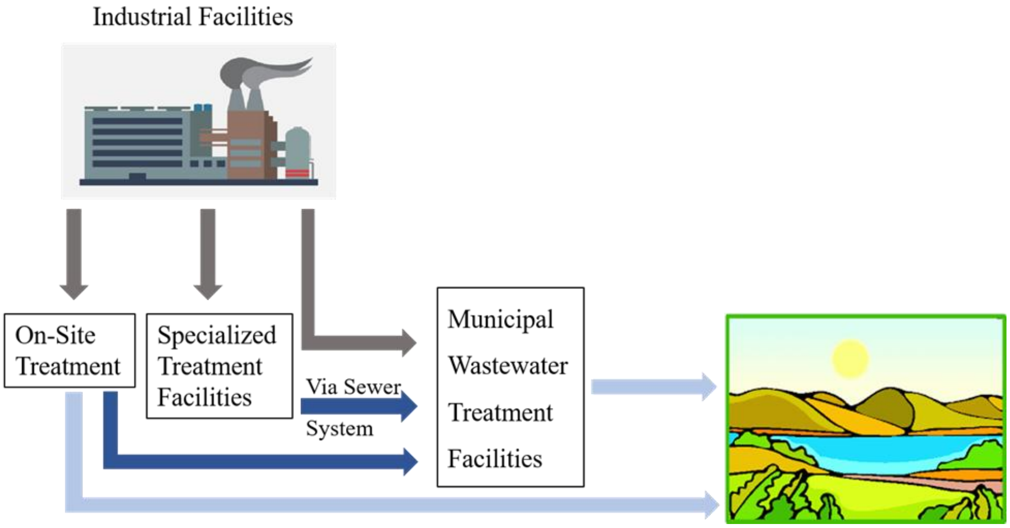


Figure 1- Schematic illustration of the different types of industrial wastewater treatment facilities. The specialized treatment facilities that treat wastewater from different industries are the focus of this study.

1.1 Project Background: City of Brantford New Sewer System By-Law

Under the previous by-law of the City of Brantford, if industrial, commercial and institutional facilities were not able to meet by-law limits, it would not be considered a violation of the by-law as long as they had an over-strength agreement with the City which included a payment to the City for accepting the wastewater. There were no upper discharge limits for wastewater parameters in the previous by-law, which was problematic for the City's wastewater treatment plant as it was not designed for treating industrial wastewater. A number of potential problems caused by over-strength discharging are listed below:

- Inhibitory substances present in industrial wastewater, lead to prevention of nitrification at the City's treatment plant due to the sensitivity of the microorganisms involved.
- The frequent and sudden changes in the quality of the incoming wastewater to the City's treatment plant caused by over-strength discharges is an issue since municipal wastewater has a more consistent quality and quantity compared to industrial wastewater.
- Total peak loadings from industrial, commercial and institutional facilities could lead to the overloading to the City's treatment plant to exceed 100 % of its treatment capacity without any warning[2].

To reduce the problems caused by over-strength discharges, a new by-law was developed in April 2104 which in addition to more stringent discharge limits, obligates the over-strength dischargers to commit to a timeline for achieving compliance with the new by-law. Under the new by-law, very stringent limits have been set for Chemical Oxygen Demand (COD) and nitrification inhibition which is determined by the Specific Nitrification Rate (SNR) test as described by Bye et al.[3]. A comparison of the previous and new limits for these two parameters is provided in Table 1[2]. Enhancement of treatment processes at already existing plants is required for meeting these stringent regulations.

Table 1- Comparison of previous and new limits for discharge into the City of Brantford sanitary sewers

Parameter	Previous Limit (mg/L)	New Limit (mg/L)
Chemical Oxygen Demand (COD)	1000	600
Nitrification Inhibitory	NA	6.3 %

This work was done in collaboration with Aevitas, an industrial wastewater treatment facility in Brantford which treats tanker truck shipments of wastewater from approximately one hundred industrial, manufacturing, and commercial facilities. To give an account of the extent of variation in the quality of the incoming wastewater loads this treatment plant receives in terms of both organic and inorganic pollution, a histogram of the incoming wastewater loads' COD (Figure 2) and the frequency of occurrence and the concentration range of the top inorganic ions (i.e. metals) that are present in their incoming wastewater loads (Table 2) are provided respectively. Figure 2 and Table 2 are based on the facility's 2014 historical data. Additionally, a picture of a subset of the incoming wastewater samples obtained from this plant is provide in Figure 3 to show that the immense variation in the quality of the samples is even visually evident.

A variety of treatments are used to treat the incoming wastewater loads before they are discharged to the sewer system including insoluble oil removal, heavy metal removal, polymer flocculation and pH adjustment. The Aevitas team are aiming to enhance their treatment process to achieve compliance with the new by-law. To help with their endeavors, the application of two relatively new analytical techniques (i.e. PeCOD®

and LC-OCD) as potential solutions for the following challenges were investigated in this work:

1. Inline monitoring of wastewater organic pollution
2. Optimization of treatment process for dynamically varying wastewater

Any treatment plant that has variation in the quality of its incoming wastewater is likely to face these challenges. A description of the above-mentioned challenges is provided next.

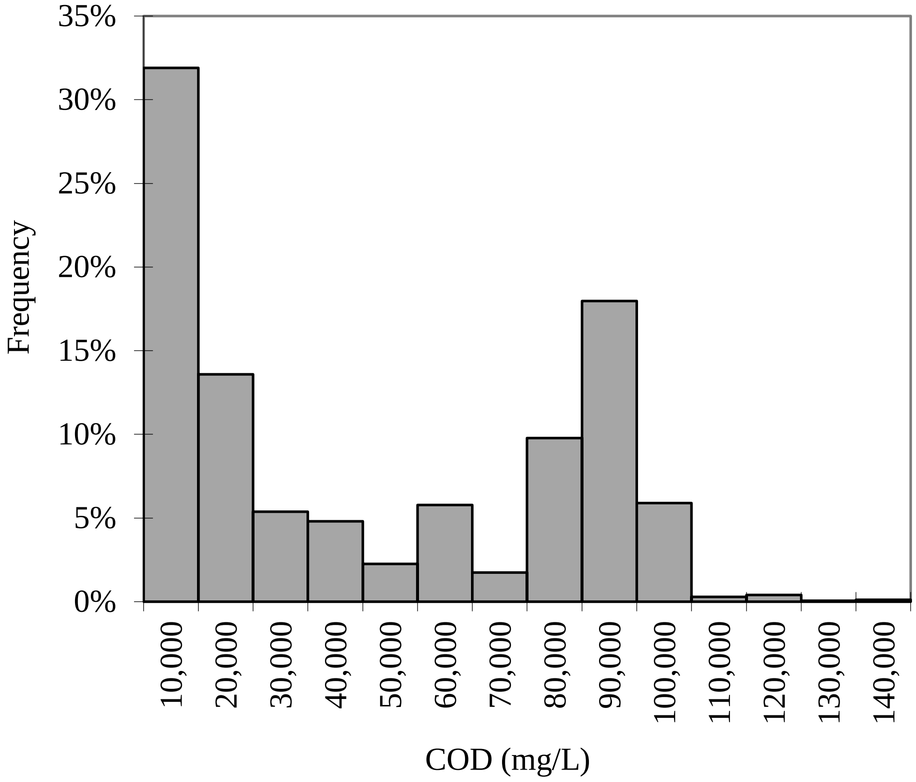


Figure 2- Histogram of the COD values for the incoming wastewater loads of the specialized treatment facility that this study has been in collaboration with. The data used for plotting the histogram was obtained from the facility’s 2014 historical data.

Figure 3- Picture of a subset of untreated (incoming) wastewater samples used in this study.

Table 2- A summary of frequency and concentration ranges for the ten elements that are most often detected in the incoming wastewater loads of the treatment facility in this study.

Element	Frequency of Occurrence in Incoming Wastewater Loads	Range of Concentration (mg/L) in Incoming Wastewater
Boron	91%	0 to 4500
Barium	47%	0 to 450
Nickel	10%	0 to 1250
Copper	26%	0 to 180
Iron	66%	0 to 150000
Lead	10%	0 to 500
Manganese	47%	0 to 700
Phosphorus	70%	0 to 100000
Titanium	18%	0 to 20
Zinc	51%	0 to 2800

1.2 Inline Monitoring of Organic Pollution

Lack of fast responding technologies that can function under the hustle conditions of wastewater treatment has set back the automation of wastewater treatment processes in comparison to other industries [4]. Currently at most treatment facilities only infrequent wastewater quality monitoring is performed via analysis of grab samples and composite samples by laboratory-based techniques [4]. Inline real-time monitoring has the following advantages compared to laboratory-based techniques [4]:

- Enables real-time process control
- Captures variation in wastewater quality with high resolution
- Ensures compliance with discharge regulations on a permanent basis
- Eliminates the need for sample collection and retrospective analysis

One of the main aspects of wastewater quality is its organic pollution level. Inline monitoring of organic pollution can immensely revolutionize wastewater treatment processes due to the aforementioned advantages. The need for a rapid and frequent method of organic pollution monitoring is more evident in wastewater treatment plants that treat wastewater from a variety of industries as they face a number of challenges. The first challenge is the extremely large variations in the quality of the wastewater from different manufacturing facilities and the resulting effect on treatment efficacy. The second challenge is the frequency at which the incoming shipments of wastewater arrive at the treatment plant; it is not unreasonable for a new shipment to arrive approximately every 30 minutes. Both of these challenges have rendered many of the conventional methods and techniques for wastewater treatment including the conventional methods of organic pollution measurement obsolete.

In the next chapter of this study, the feasibility of application of a new technology called PeCOD® for inline monitoring of industrial wastewater organic pollution has been investigated.

1.2.1 Conventional Methods of Organic Pollution Measurement

One of the most important aspects of organic pollution is oxygen demand as it poses an indirect threat to aquatic life by reducing water bodies dissolved oxygen level. The two indexes that are used for oxygen demand measurement are Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). Oxygen demand can also be indirectly calculated from Total Organic Carbon (TOC). Measurement of the three indexes of oxygen demand is based on oxidation of the sample. A summary of the oxidants used and the time required for each method is provided in Table 3 [5].

BOD measurement is not suitable for analysis of industrial wastewater as the toxic species commonly present in industrial wastewater such as heavy metal ions and cyanides are toxic to the microorganisms used in the test [4]. Additionally, the test is highly variable due to the diversity in the microbial population of different seed sources and also the method's reliance on the experience and skills of the analyst [4].

TOC is the only index among the three that can be measured in only several minutes and therefore can be used for inline monitoring of organic pollution. However, in addition to requiring expensive equipment, its main drawback is that it does not differentiate between the different oxidation states of organics (i.e. organics at different oxidation states but with the same number of carbons all have the same TOC) [5].

Compared to BOD, COD measurement requires less time and is not affected by the presence of toxic species. Often for systems with no sudden changes in wastewater composition, a correlation between COD and BOD can be obtained [4]. Additionally, COD requires less expensive equipment compared to TOC. Hence, COD is the preferred index compared to BOD and TOC for many applications [6]. However, it has several drawbacks that are further discussed in what follows.

Table 3- Different indexes for oxygen demand determination (oxidants used and the required analysis time)

Index	Oxidant Used	Required Analysis Time
BOD	Oxidation by microorganisms	5 days
COD	$K_2Cr_2O_7$ $Mn_2 (SO_4)_3$	1.5 - 3 hours
TOC	O_2 $Mn_2 (SO_4)_3$ • $K_2 S_2O_8$ • Heat • Combination of the above with various catalysts	Several minutes to hours depending on the method used

The Standard Methods for the Examination of Water and Wastewater [7], defines COD as “the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence".

The standard method of measuring COD has three different variations: Open reflux method, closed reflux-titrimetric method, and closed reflux-colorimetric method. In all three variations of the test, the oxidant is the dichromate ion ($Cr_2O_7^{2-}$). The last variation of the test (i.e. closed reflux-colorimetric method) is the most commonly used as it consumes less reagent compared to the open reflux method and its procedure is considered to be safer compared to the titrimetric method. The procedure consists of heating the sample for up to 2 hours with sulfuric acid and a strong oxidizing agent (potassium dichromate) at 150 ^{o}C. Under these conditions the oxidizable organic compounds reduce the dichromate ion ($Cr_2O_7^{2-}$) to the green chromic ion (Cr^{3+}). After the COD vial has cooled down to room temperature, a colorimetric method is used to measure the concentration of the produced Cr^{3+} based on the intensity of the green color. The COD reagent also contains silver nitrate for catalysis and mercuric sulfate for masking the potential interference caused by chloride ions [5]. This effect is studied further in Chapter 4.

This method is not suitable for inline monitoring applications due to the long analysis time required. It should be noted that shorter digestion times can be used if the samples are composed of easy to oxidize materials or if the samples have a fairly uniform composition [5]. However, this is not the case for industrial wastewater. Additionally, it has two main drawbacks: application of expensive and hazardous reagents and production of hazardous wastes of mercury, hexavalent chromium, sulfuric acid, silver, and acids [7].

Potassium dichromate which is the main substance required for the conventional COD measurement (hereafter referred to as the dichromate method) is currently listed as a “substances of very high concern” under REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) due to being carcinogenic, mutagenic, and toxic for reproduction. A ban is set to be imposed on its application in Europe starting from September 2017 thereafter application of the dichromate method will require special authorization [8][9]. Mercuric sulfate is another toxic reagent used in the dichromate method. Sweden has already banned application of mercury and other countries are planning to ban or reduce its application [10][9].

To minimize the disposal cost and reduces exposure of the analyst to hazardous compounds, the Mn III COD Reagent was developed which does not contain mercury, chromium, and silver and uses $Mn_2(SO_4)_3$ as the oxidant. However, for samples containing chloride, this method cannot be used without prior removal of chloride. Additionally, for most organic compounds it only achieves approximately 80% oxidation [5].

Given the variable nature of industrial wastewater, the need for an inline method of wastewater characterization at various steps of the treatment process is evident. However, as described above the currently used method for COD measurement is not suitable for inline applications. Additionally, with the bans being imposed on the hazardous materials used in the dichromate method the need for an alternative environmentally safe method has never been more evident than it is now.

1.2.2 Alternative Methods of COD Measurement

Several alternative methods have been proposed for organic pollution measurement based on electrocatalytic, photocatalytic and photoelectrocatalytic principles [11]. The electrocatalytic methods do not have the oxidation power required for real applications and toxic metal leaching is also a concern associated with their application. The photocatalytic method is more promising, however, the fast recombination of photogenerated electrons and holes in this method have reduced its efficiency [11]. The photoelectrocatalytic method has overcome this pitfall of the photocatalytic method and is further discussed in the next section. Ultraviolet (UV) spectroscopy [12] and measurement of the enthalpy increase by the reaction of sodium hypochlorite with the organic content of water samples [13] are some of the other developed approaches for rapid COD measurement. A summary of these alternative methods and some of their key specifications are provided in Table 4.

COD measurement based on photoelectrocatalytic principles is the method investigated in this work for analysis of industrial wastewater samples. A brief description of the method’s principles and the commercial instrument that utilizes this method is provided in the next section.

Table 4- Alternative methods of COD measurement and their specifications (measurement range and analysis time)

Method	COD Range	Time Requirement
Combustion at high temperature (1200°C) and direct measurement of the consumed oxygen [14]	1-10,000 mg/L	3 minutes
Thermal sensor (Enthalpy change measurement) [13]	5–1000 mg/L	5- 7 minutes
Ultraviolet Spectroscopy [12]	0-360 mg/L	2 minutes
Electrocatalytic determination with Pt/PbO_2 [15]	20-25,000 mg/L	1 minutes
Flow injection ozonation chemiluminescence [16]	0.6-24 mg/L	12 min
TiO_2 photocatalytic oxidation [17]	0.2-8 mg/L	10 min

1.2.3 Introduction to the PeCOD® Method

COD measurement based on photoelectrochemical oxidation principles yields a parameter known as the Photoelectrochemical Oxygen Demand (peCOD). The peCOD measurement is based on the efficient utilization of the high oxidizing power of electron holes generated by UV irradiation of TiO_2 nano-particulates which takes place in several steps a short description of which is provided below:

1. UV illumination of TiO_2: This steps results in generation of electron/hole pairs. The high oxidation power (+ 3.2 V) of the photoholes generated in this step is the basis of this method as photoholes are reported to be capable of oxidizing all

types of organic compounds present in water/wastewater. Oxidation of organics takes place via two pathways:

   i. Photohole oxidation pathway: Direct capture of electrons from the species by the photoholes at the TiO_2 surface
   ii. Hydroxyl radical oxidation pathway: Efficient water oxidation by the photoholes in samples with high water concentration leads to the formation of hydroxyl radicals which are strong oxidizing agents that can oxidize the other species.

   The efficiency of photocatalytic degradation depends on the degree of electron-hole recombination which is a rapid reaction that should be supressed.

2. Suppression of electron-hole recombination: For suppressing the electron-hole recombination, TiO_2 nanoparticles are fixed on an inert conductive substrate and a potential bias is applied to it which forces the photoelectrons to pass through an external circuit which delivers them to an auxiliary electrode where the dissolved oxygen content of the samples plays the role of an electron acceptor and a reduction reaction happens.
3. Converting the photocurrent signal into COD: The photocurrent generated by the electro-photocatalytic oxidation of the organics can be used as a signal for measuring COD. The net charge produced in the process can be calculated by Equation 1 where *i* is the photocurrent and Q is the net charge. Q represents the total number of electron transfers. Since oxidation with one oxygen molecule is

equal to four electron transfers COD can be calculated from the net charge by applying the Faraday's law and obtaining Equation (2) [18].

$$Q = \int idt \qquad (1)$$

$$\text{COD (mg } O_2\text{/L)} = \frac{Q}{4FV} * 32000 \qquad (2)$$

(F: Faraday constant, V= Sample volume)

The PeCOD® Analyzer is a commercial COD analyzer that has been developed based on the photo-electrochemical method of COD determination. It is a safe and environmentally friendly method that eliminates the use of mercury, dichromate and concentrated acid generating results in approximately 10 to 20 minutes based on the COD range of the samples. The PeCOD® Analyzer is available as both inline and benchtop configurations. Pictures of the benchtop and inline configurations of the PeCOD® Analyzer are provided in Figure 4. The parameter measured by the PeCOD® Analyzer is referred to as photoelectrochemical oxygen demand and the abbreviation "peCOD" with lower case p is used for denoting it. Measuring peCOD via the PeCOD® Analyzer is referred to as the PeCOD® method in this work.

In 2014, the Ministry of Environment and Climate Change (MOECC) released Method E3515 based on the PeCOD® Analyzer. However, it is not yet approved under the MOECC's effluent regulations, and therefore the industrial wastewater sector has not adopted the technology due to the uncertainty of approval. In addition, even with the MOECC adoption, other provinces do not automatically follow suit and wish to have their own testing completed.

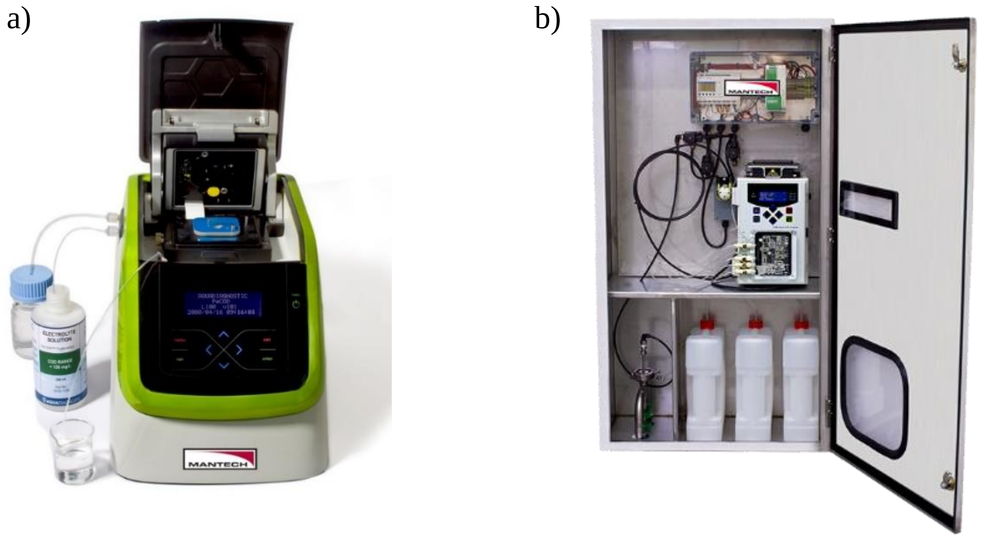


Figure 4- Pictures of the PeCOD® Analyzer (2-a: Benchtop format, 2-b: In-line format)

In the next chapter, an assessment of the feasibility of the application of the PeCOD® Analyzer in an industrial wastewater treatment plant for analysis of untreated (incoming) and treated (effluent) wastewater is provided. In addition, in chapters 3 and 4 limitations of both the PeCOD® and dichromate methods have been investigated. The different scientific and technical advances that were realized in this project are required to advance the use of the PeCOD® technology into the industrial wastewater sector.

1.2.4 Objectives

The objective of this study has been to assess the feasibility of application of the PeCOD® method as a substitute for the conventional dichromate method of COD measurement in an industrial wastewater treatment plant that treats tanker truck shipments of wastewater from multiple industrial, manufacturing, and commercial facilities.

The study was conducted in two phases. In the first phase (chapter 2), a library of untreated (incoming) and treated (effluent) wastewater samples was analyzed with the PeCOD® method and the results were compared to results obtained with the dichromate method. Several correlations between the results of the two methods were obtained for different sample types and conditions. The suitability of application of correlations in the absence of an absolute agreement between the results of the two methods is also discussed in what follows.

In the second phase of this study (chapters 3 and 4), a series of control experiments were conducted to investigate the potential causes of difference between the results of the two methods. Some of the main characteristics of industrial wastewater such as containing hard to oxidize materials (i.e. macromolecules), high concertation of chloride, nitrogenous compounds and other inorganic species and also high turbidity levels were investigated.

1.3 Optimization of Treatment Process for Dynamically Varying Wastewater

At specialized treatment facilities that accept and treat tanker truck shipments of wastewater from multiple industrial, manufacturing, and commercial facilities maintaining the treatment process efficacy to meet discharge regulations is very challenging as typically the composition of the incoming feed to the process changes with each shipment from a different facility. Additionally, the new stringent discharge regulations have created a need for additional treatment steps at already existing plants.

1.3.1 Advanced Oxidation Processes

Advanced oxidation (AO) is a broad term used for water/wastewater treatment methods that are based on the generation of highly reactive species such as the hydroxyl radicals [19]. Some of the different types of AO processes are shown in Table 5 [20]. AO is widely used as a pretreatment and/or ‘polishing’ step for the treatment of various wastewater sources from industrial processes and the destruction of particular contaminants in water sources. It has a high treatment efficacy for many different compounds and thus is ideally suited as a treatment technology for specialized facilities that receive shipments of wastewater from large networks of industrial, manufacturing, and commercial facilities.

Although a great amount of research has been done on the diverse AO technologies and their applications, there is still an immense need for the optimization of AO technologies as they have high operational costs due to the application of costly materials[19].

Table 5- Different AO processes

Category	AO Process	Process Principles
Chemical	Fenton's Reagent	H_2O_2/Fe^{2+}
	Peroxonation	O_3/ H_2O_2
Photochemical	Photolysis of H_2O_2	H_2O_2/UV
	Photolysis of O_3	Photolysis of O_3
	Photo-Fenton	H_2O_2/Fe^{2+}/UV)
	Heterogeneous Photocatalysis	(TiO_2/UV)
Sonochemical	Sono-Fenton	OH° radicals are formed by sonolysis of water molecules
Electrochemical	Anodic Oxidation	OH° radicals are directly formed at the anode surface by oxidation of water
EF Process	Electrochemical-Fenton	Cathodic electrogeneration of hydrogen peroxide and catalytic regeneration of Fe^{2+}

1.3.2 Conventional Analytical Tools for AO Process Optimization

Previous optimization studies of AO-based processes can be grouped into two general categories. The first category includes those that focus on the destruction of all organic components in the wastewater from a single specific source such as pharmaceutical manufacturing[21][22], pulp and paper processing[23], food manufacturing[24], or textile manufacturing[25]. These studies typically use bulk analytical measurements of the organic contaminants (including COD [21-24], BOD [22], and TOC [22-25]) and because the wastewater composition is fairly consistent from the single source, it is rather straightforward to optimize the AO process conditions in terms of treatment efficiency. The second category is comprised of studies that focus on the destruction of a particular component (e.g. pesticide/herbicide[26][27], synthetic dye[28], chlorophenol [29]) that is present in a particular wastewater source. These studies monitor the destruction of the known component as a function of the AO process conditions using advanced analytical techniques such as gas chromatography(GC) [29], gas chromatography-mass spectrometry (GC-MS)[29], high-performance liquid chromatography (HPLC) [27] [28], or liquid chromatography–mass spectrometry (LC-MS)[27][28].

At industrial wastewater facilities that the composition of wastewater is continuously changing the primary challenge is how to optimize the process – bulk measurements of organic content (e.g. COD, BOD, TOC) give no information about the specific composition and specialized advanced analytical techniques (e.g. GC, HPLC, LC-MS) are unsuitable due to the complex composition. Therefore, application of a relatively new analytical technique, LC-OCD, was investigated in this work for optimization of AO for industrial wastewater with variable compositions. Next, an introduction to the LC-OCD method is provided.

1.3.3 Introduction to the LC-OCD Analytical Tool

As shown in Figure 5, water/wastewater analytical techniques have either a high mass balancing capability or a high compound identification capability. Liquid Chromatography-Organic Carbon Detection (LC-OCD) is an analytical tool that was developed approximately 25 years ago to fill this ‘analytical gap’ especially in characterizing the amount of natural organic matter (NOM) in water/wastewater sources. In this method, mass balancing is done by Dissolved Organic Carbon (DOC) measurement and qualitative information about the DOC is also obtained [30]. The method uses a size exclusion column combined with an organic carbon detector (OCD), organic nitrogen detector (OND), and a UV absorption detector (UVD) to fractionate samples according to their size and hydrophobicity [31]. A schematic illustration of the system outline is provided in Figure 6. Organic carbon detection is done with the *Gräntzel* thin-film reactor, which is a UV thin-film reactor where organic carbon is converted into carbon dioxide by UV irradiation. The carbon dioxide produced is measured by high-sensitivity infrared spectrometry [32]. The UV light exposure and residence time in the reactor are sufficient for quantitative organic carbon detection [31].

In the LC-OCD analysis of water samples from natural sources, Huber et al.[31] observed a standard pattern and they associated the various peaks with different organic matter fractions developing a terminology for each fraction. In this technique, the NOM pool is divided into five fractions: Biopolymers, humic substances, building blocks, lower molecular weight acids and lower molecular weight neutrals [31].

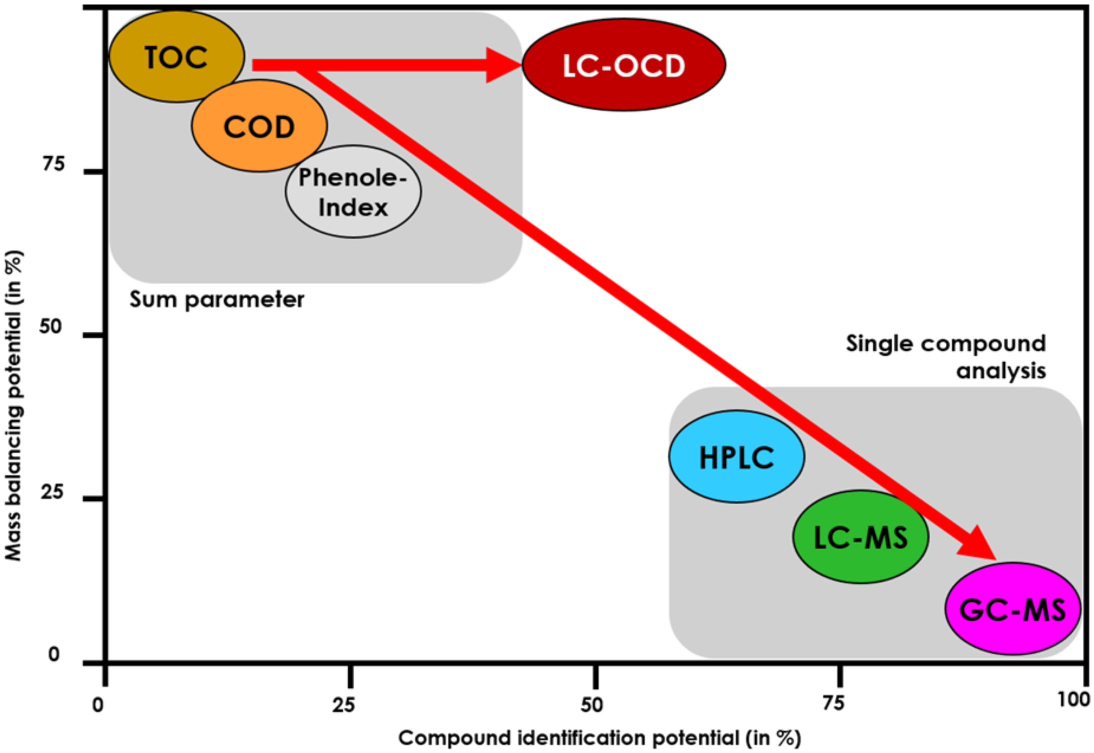


Figure 5- Comparison of different analytical techniques' mass balancing potential and compound identification potential (Credit: DOC-Labor [30])

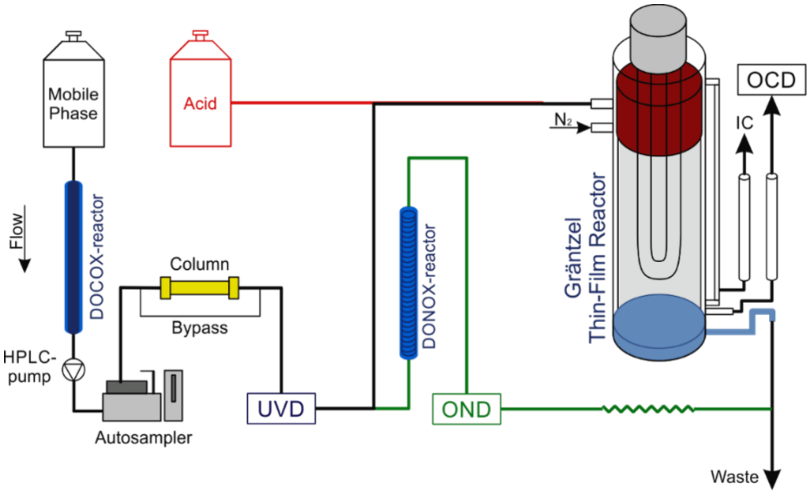


Figure 6- Schematic illustration of LC-OCD system outline (Credit: DOC-Labor [30])

LC-OCD has been applied to study NOM fractions in surface water [33], municipal wastewater [34], and sea water that contribute to membrane fouling [35], and the efficacy of different NOM removal treatments [34-35]. Additionally, it has been utilized in studying the treatment of recalcitrant organic matter in paper mill effluent [36], and also the effect of photo-oxidation on alteration of NOM in cooling water [37]. LC-OCD analysis provided valuable insight regarding the composition of the samples and its effect on the treatment efficiency that was otherwise not available through conventional bulk measurements such as COD and TOC.

1.3.4 Objectives

In the fifth chapter of this study, a novel combination of Design-Of-Experiments (DOE) methods and the LC-OCD analysis was used with actual wastewater samples in order to investigate dependence of organic matter (i.e. COD) removal obtained via the Fenton process on sample composition. Also, the study aimed to optimize the Fenton process treatment conditions in terms of chemical reagent concentrations, develop statistical models of the process, and identify potential mechanisms of COD removal.

Additionally, the LC-OCD analysis has also been used in the third chapter of this study to obtain an account of molecular weight distribution for treated (effluent) industrial wastewater samples to help with the interpretation of results of obtained with the PeCOD® Analyzer in chapter 2.

Chapter 2: Assessment of Application of PeCOD® for Analysis of Industrial Wastewater

2.1 Introduction

Wastewater treatment plants that receive wastewater from different industries and commercial facilities via truckload can immensely benefit from the application of a rapid method of organic pollution measurement for analyzing both their incoming and effluent loads.

At these treatment plants, an initial screening of the waste load is required before the offloading of the incoming waste trucks. This screen checks for hazardous materials and allows the rejection of the waste truck if the hazardous materials cannot be received by the treatment plant. The results of the screening tests are also required for pricing the treatment. A list of the tests done for the screening of the waste loads and the techniques used is provided as supplemental material in Table A-1. While rapid measurement methods exist for most of the water quality parameters that should be determined for an incoming load to decide on its course of treatment, the 2-3 hour process of COD measurement for determination of organic pollution hinders the treatment process at such facilities.

Furthermore, in case of failure to meet the discharge regulations, wastewater treatment plants are obligated to pay a surcharge, the amount of which is determined based on a number of water quality parameters one of which is organic pollution of the final effluent that is reported as either BOD or COD. Considering the limited capacity of the holding tanks, by the time the COD of the final effluent is determined it might be too late to do any subsequent treatments in case the measured COD is over the regulatory discharge limit and the treatment plant is left with no option other than paying the surcharge. With the discharge regulations becoming more stringent in the coming years, application of an inline method of organic pollution measurement would be beneficial not only for rapid monitoring of the final effluent but for monitoring treatment efficiency at different points in the plant that would result in an overall enhanced treatment.

In this section, the feasibility of application of the PeCOD® Analyzer for analysis of the incoming wastewater loads of an industrial wastewater treatment facility and also treated wastewater (effluent) samples collected from the same treatment facility has been investigated.

2.2 Materials and Methods

2.2.1 Operation of the PeCOD® Analyzer

All peCOD measurements were done using a benchtop PeCOD® Analyzer (L100) connected to an AutoMax™ 73 auto-sampler and PC-Titrate™ software provided by MANTECH. TiO_2 sensors with chloride tolerance (Aqua Diagnostic) were utilized. The PeCOD® unit can be operated in four different COD ranges (Blue Range: 0-25 mg/L, Green Range: 0-150 mg/L, Yellow Range: 0-1500 mg/L, Red Range: 0-15000 mg/L). However, for application of each COD range, the electrolyte and calibrant that is specific to that COD range should be used.

2.2.1.1 Calibration of the PeCOD® Analyzer

The PeCOD® Analyzer was calibrated before analysis of each sample set. The calibration solutions were prepared per the following recipes:

Red Range calibration solutions:

- Reference solution: Red Range calibrant (MANTECH) with COD of 12000 mg/L diluted with lithium nitrate electrolyte (MANTECH) with dilution ratio of 1/50.
- Blank solution: Ultrapure water (obtained from a Millipore Milli-Q system) mixed with lithium nitrate electrolyte (1 unit of water mixed with 49 units of electrolyte).

Yellow Range calibration solutions:

- Reference solution: Yellow Range calibrant (MANTECH) with COD of 1200 mg/L diluted with lithium nitrate electrolyte (MANTECH) with dilution ratio of 1/10.
- Blank solution: Ultrapure water (obtained from a Millipore Milli-Q system) mixed with lithium nitrate electrolyte (1 unit of water mixed with 9 unit of electrolyte).

Calibrations were done in the automated mode of the system. In this mode, by selection of the calibration schedule of the PC-Titrate™ software, all the required steps of calibration which include priming of the ports, analysis of the Blank solution and analysis of the Reference solution will be performed automatically. At the end of the calibration schedule, values of the following parameters are reported by the software:

- M: The ratio of expected COD (i.e. 12000 mg/L for Red Range and 1200 mg/L Yellow Range) over the charge generated during the oxidation of the reference solution (measured in COD (mg/L) /µA).

- C: The charge generated during the blank oxidation.
- I-term: The current generated at the end of the reference oxidation.

The accepted ranges for the calibration parameters are reported in Table 6.

Table 6- PeCOD® calibration parameters

Analysis Range	M ((mg/L)/µA)	C (µC)	I-Term (µA)
Red	0.02-0.06	500-800	≥ 14
Yellow	0.02-0.04	450-750	≥ 14

M is the most important calibration parameter and an indicator of the sensor's age. As the sensor gets older the charge generated declines and the M value increases. Once the M value is over 0.06 ((mg/L)/µA) in the Red Range and over 0.04 ((mg/L)/µA) in the Yellow Range, the sensor lifetime is over. It was recommended by the supplier that the sensors should be used for a maximum of one month and after that a replacement is required.

The C value is an indicator of the blank quality and subsequently the electrolyte quality. A high C value indicates that the blank solution or the electrolyte used for making it has been contaminated. The I-term value indicates whether the LED (i.e. the source of UV light in the PeCOD® Analyzer) has been set correctly. The LED is only set during the first 90 seconds of a calibration. The only way to increase the I-term to fit into the appropriate range is by repeating the calibration.

Performance of two back to back calibrations was recommended by the supplier for insuring the sensor has been sufficiently conditioned for sample analysis. For the first time a sensor is installed a greater number of calibrations (i.e. 3 to 4) is needed.

In the case that after repeated calibrations the calibration parameters do not meet the required values, troubleshooting must be performed to identify the source of the issue. Troubleshooting guidelines are provided in Appendix C.

2.2.1.2 Sample Analysis with the PeCOD® Analyzer

Following the calibration step, a quality control with the calibrant solution was done to ensure that the system was calibrated. If the quality control results were within 5 % of the target COD value (i.e. 12000 mg/L in Red Range and 1200 mg/L in Yellow Range), the sample analysis would have been started. Sample analysis was done in the automated mode of the PeCOD® Analyzer. In this mode using the PC-Titrate™ software, the analyzer is scheduled to automatically analyze a set of samples and report the results.

The Red Range (i.e. COD <15000 mg/L) was used for the analysis of the untreated (incoming) wastewater samples. 0.2 ml of sample is required when operating the system in the Red Range. All samples, were diluted 50 times with lithium nitrate electrolyte (MANTECH) before introduction to the analysis cell. The dilution was done automatically by the auto-sampler right before the sample was analyzed. Before the analysis starts, the system is primed six times with the diluted sample. The system is also primed six times with ultra-pure water in between sample analysis. The priming steps are also included in the PC-Titrate™ software schedule and take place automatically,
After the completion of the analysis of each sample set (each sample set included at maximum of 5 samples), another quality control with the calibrant solution was performed to ensure the unit remained calibrated throughout the analysis.

The Yellow Range (i.e. COD <1500 mg/L) was used for the analysis of the treated (effluent) wastewater samples. 2 ml of sample is required when operating the system in the Yellow Range. All samples, were 10 times diluted by the auto-sampler with lithium nitrate electrolyte (MANTECH) before introduction to the analysis cell. After the completion of the analysis of each sample set (each sample set included at maximum of 5 samples), another quality control with the calibrant solution was performed to ensure the unit remained calibrated throughout the analysis. The integrity of the calibrant was checked periodically using a sorbitol (Sigma Aldrich) solution standard. In case of failure to pass this check (only happened once in the course of this work), a new batch of calibrant was obtained and the tests done with the faulty calibrant were repeated.

2.2.2 Dichromate COD (COD_{Cr}) Analysis

For COD_{Cr} measurement of the untreated (incoming) wastewater samples the HACH High Range Plus COD digestion vials were used as per the manufacturer’s instructions. The HACH High Range Plus COD digestion vials are suitable for COD measurement in the 200-15000 mg/L range. The method is consisted of a 2-hour digestion of the vials at 150 °C in a reactor block (DRB 200, HACH) followed by absorbance measurement (wavelength 620 nm) with a spectrophotometer (DR 3900, HACH) after the vials have cooled down to room temperature.

For COD_{Cr} measurement of the treated (effluent) wastewater samples the HACH High Range COD digestion vials (EPA approved method) were used as per the manufacturer’s instructions. The HACH High Range COD digestion vials are suitable for COD measurement in the 20-1500 mg/L range. The digestion time, digestion temperature and absorbance measurement wavelength are the same as what was described for the untreated (incoming) wastewater samples.

2.2.3 Wastewater Sample Source and Sample Preparation

2.2.3.1 Untreated (Incoming) Wastewater Samples

A library of 37 untreated (incoming) wastewater samples was collected over a course of four months from an industrial wastewater treatment plant (Aevitas, Brantford, Ontario, Canada). The Aevitas facility receives and treats loads of wastewater that are generated by a wide variety of industrial and commercial facilities. The samples were stored at 4 ^{o}C and the experiments were conducted in less than one week from the date of sample collection. Three measurements were done on each sample:

i. Total COD_{Cr}: Conventional dichromate COD measurement without any pre-treatment of the sample except dilution

ii. Filtered COD_{Cr}: Conventional dichromate COD measurement with centrifugation (1500 RPM, 10 minutes) followed by filtration (45 µm dissolution filter (Thermo Scientific™ SUN-SRi™ SunFlo™ Dissolution Filters)) as sample pre-treatment

iii. peCOD: PeCOD® analysis with the same pre-treatment steps as Filtered COD_{Cr}

A schematic summary of the experimental procedure is shown in Figure 7.

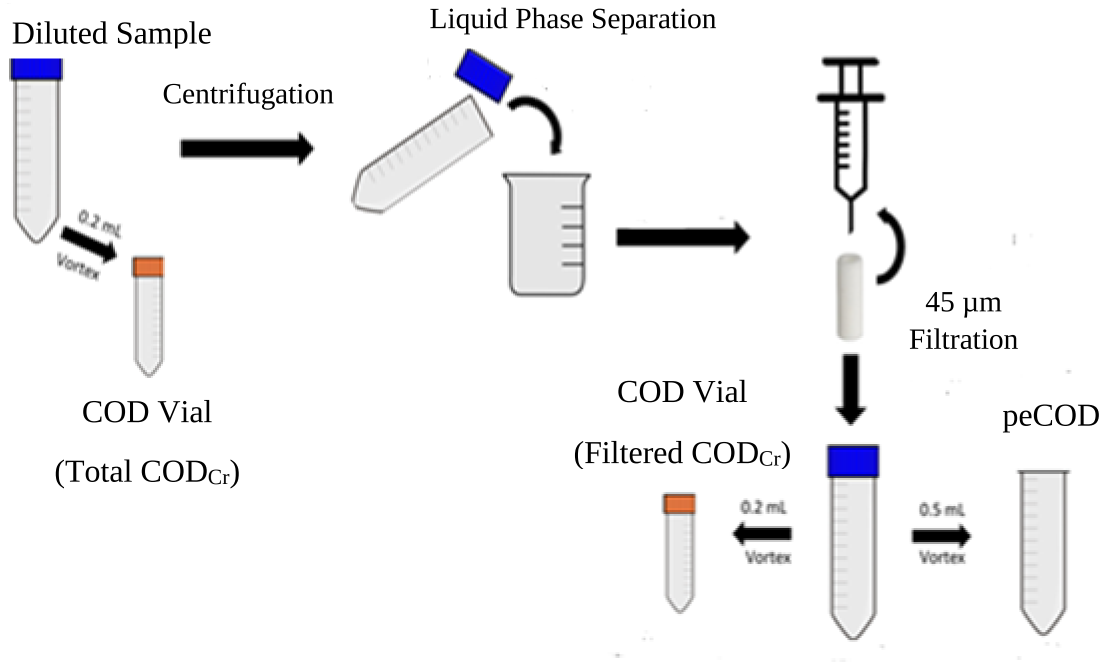


Figure 7- Schematic of the experimental workflow for the untreated (incoming) wastewater samples

2.2.3.2 Treated (Effluent) Wastewater Samples

A library of 30 effluent samples was collected over a course of eight months from the same industrial wastewater treatment plant where the untreated (incoming) wastewater samples were obtained from (Aevitas).

Samples were diluted with ultrapure water (obtained from a Millipore Milli-Q system) to allow the measurements to be done within the specified range for both methods (COD<1500 mg/L). The pH of the samples was measured using a sympHony™ SB20 meter (VWR) to ensure pH is within the recommended range for the PeCOD® Analyzer (4<pH<10).

The chloride concentrations (chloride QUANT kit, VWR) were monitored at the Aevitas plant. This information was used to ensure the chloride concentration of the samples is below the interference threshold concentration for both methods. (HACH HR COD method: 2000 mg/L, PeCOD® Yellow Range: 2000 mg/L)

The concentration of metals was also monitored at Aevitas plant via inductively coupled plasma optical emission spectrometry (ICP-OES) which was negligible for all the effluent samples tested in this study

For peCOD measurement, all samples were filtered with a 45 µm dissolution filter (Thermo Scientific™ SUN-SRi™ SunFlo™ Dissolution Filters) to prevent the clogging of the internal tubes of the PeCOD® Analyzer. As the effect of 45 µm filtration was determined to be negligible for the effluent samples the dichromate results reported for the effluent samples is without filtration (Total COD_{Cr}).

2.2.4 Total Solid (TS) Content Measurement

Total Solid (TS) measurements were done for 19 untreated (incoming) wastewater samples. The measurements were done on diluted samples. This was because the samples had to be diluted for COD_{Cr} measurement and for obtaining the most accurate comparison between the COD_{Cr} results and the TS results, the same solution prepared for the COD_{Cr} measurements were used for the TS measurements. For each sample the TS measurement was done both prior and post filtration. The filtration performed was the same as the filtration step that is required in the PeCOD® method (i.e. 45 µm filtration) described in part 2.2.3. The percentage of difference in the TS content of the diluted sample prior and post filtration was subsequently calculated.

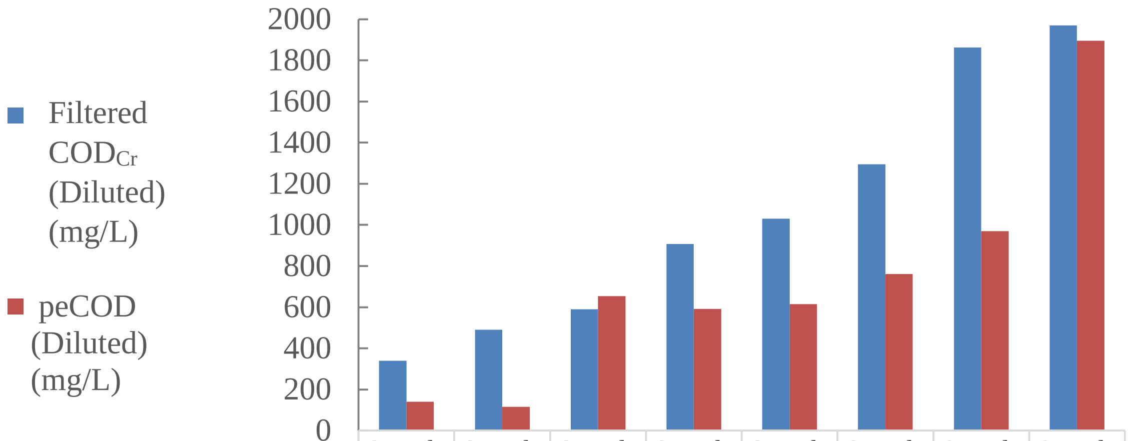
For TS measurement, first the sample was mixed by shaking the sample container. Then 20 ml of the well-mixed sample was placed into a weighed container via a 10 ml pipet (MANTECH). Plastic caps of 50 ml Falcon tubes (VWR) were used in this study as containers for TS measurements. The sample was then stored in an incubator (Fisher Scientific Isotemp) at 70 °C for 24 hours. After that the container with the dried sample in it was weighed with a digital balance (Mettler- Toledo). The increase in weight in comparison to the weight of the empty container was considered as the TS content of the sample. The weighing was done three times for each sample and the average value was used for TS content calculation. It should be noted that if the standard method for TS measurement was to be employed, the samples had to be stored at 103 to 105 °C [7].

2.3 Results and Discussion

2.3.1 Untreated (Incoming) Industrial Wastewater Samples

The peCOD and the Filtered COD_{Cr} results obtained for a subset of the incoming samples tested (samples with Filtered COD_{Cr} < 2000 mg/L after dilution) is shown in the accompanying table of Figure 8. The bar plots shown in Figure 8 are providing a comparison of the peCOD and Filtered COD_{Cr} results obtained for each sample. The same information is provided for samples with after dilution Filtered COD_{Cr} results in the 2000-5000 mg/L range and also 5000-8000 mg/L range as Figure A-1 and Figure A-2 of Appendix B respectively. In presentation of this data the dilution ratios have intentionally not been accounted for, to provide the actual readings obtained by each method when analyzing the same sample. As shown in Figure 8 and Figures A-1 and A-2 of Appendix B, it is evident that there is significant discrepancy between peCOD and Filtered COD_{Cr} results and the degree of this discrepancy varies from sample to sample even for samples that are in the same COD range. For instance, in the sample set shown in Figure 8, the peCOD and COD_{Cr} results have a good agreement for Sample 8 (i.e. 4 % difference), however, for Sample 7 the difference in the results of the two methods is about 50 % with the lower result belonging to the PeCOD® method. Considering this, the PeCOD® method cannot be used as a direct replacement of the dichromate method for analysis of the incoming industrial wastewater samples studied in this work. In what follows, it is investigated whether the PeCOD® method can be utilized for analysis of untreated (incoming) wastewater samples via application of correlations that convert peCOD results into COD_{Cr} results.

If a strong correlation was found to exist between the results of the PeCOD® method and the dichromate method, it would allow for the conversion of peCOD to COD_{Cr} and replacing the dichromate method with the PeCOD® method would be streamlined. Thus, the first phase of this study focused on the investigating whether such correlations exist under different conditions.



	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
% Difference	59	77	-11	35	40	41	48	4
Filtered CODCr (Diluted) (mg/L)	340	490	590	908	1030	1294	1863	1970
peCOD (Diluted) (mg/L)	141	115	653.7	592	614.6	761	970	1895.9

Figure 8- Comparison of Filtered COD_{Cr} and peCOD results for a subset of the incoming samples with diluted $COD_{Cr} < 2000$ mg/L. Dilution factors are not accounted for in the presentation of the data.

Figure 9, is a plot of peCOD vs. Total COD_{Cr} for all the untreated (incoming) wastewater samples tested in this study. It can be seen that the majority of the samples diverged significantly from the perfect agreement condition (i.e. peCOD= Total COD_{Cr}) and that the results of the two methods are not correlated (R^2=0.34).

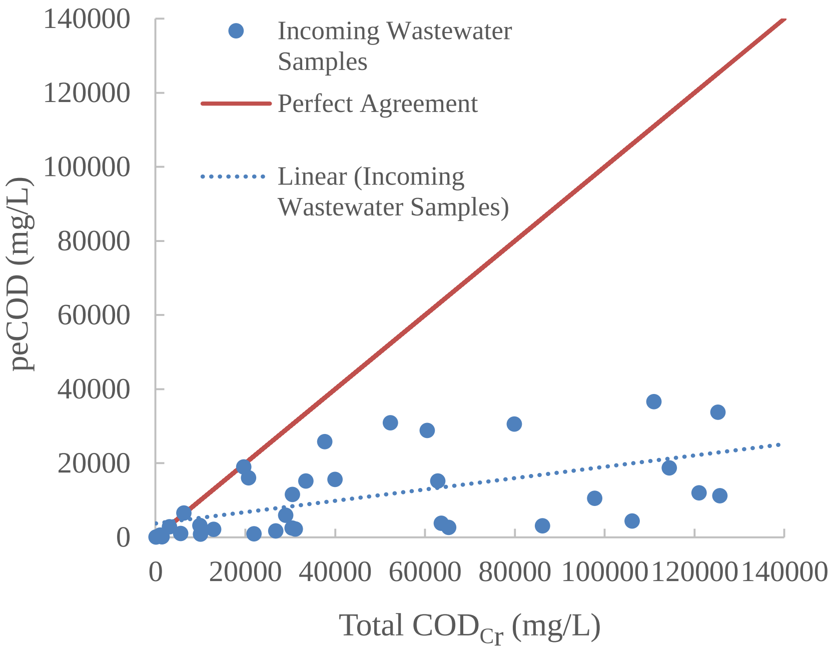


Figure 9- Comparison of peCOD and COD$_{Cr}$ results for the untreated (incoming) wastewater samples. The solid line is representing the condition of perfect agreement between the results of the two methods (i.e. peCOD= Total COD$_{Cr}$).

Most untreated (incoming) industrial wastewater samples in this study contained high concentration of particulate COD. In the peCOD method, however, large (> 45 µm) particulates have to be removed from the samples prior to analysis to prevent clogging of the internal ports of the PeCOD® Analyzer. To understand the effect of this mandatory filtration step on the COD measurements of our samples, the difference in the Filtered COD$_{Cr}$ results and Total COD$_{Cr}$ results was compared against the difference in the TS content of the filtered and unfiltered samples. As shown in Figure 10 for the majority of the samples a higher difference in the TS content of the filtered and unfiltered samples corresponds to a higher difference in the Total COD$_{Cr}$ and Filtered COD$_{Cr}$ results. It can be concluded that for samples with high TS content, the filtration step has a significant effect on the COD reading of the sample. To account for this filtration effect, peCOD should be compared against filtered COD_{Cr} and not the Total COD_{Cr}. Some applications do not require knowledge of the COD contribution of large particulate matter present in the wastewater and remove large particulates by centrifugation or settling before the COD analysis. Nonetheless, as shown in Figure 11, for the samples analyzed in this study, Filtered COD_{Cr} results and Total COD_{Cr} results are correlated (R^2=0.84). Hence, correlations can be used for estimation of Total COD_{Cr} from the filtered results for applications that required the knowledge of Total COD content.

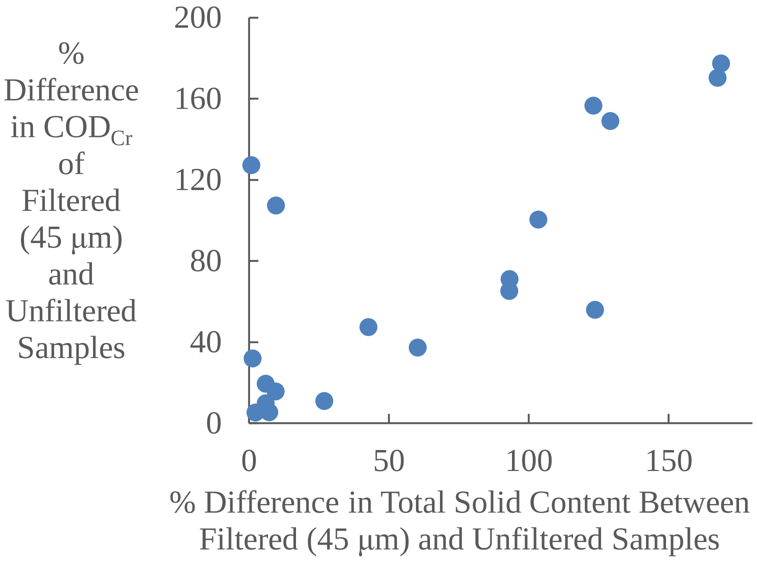


Figure 10- Comparison of % difference between Total COD_{Cr} and Filtered (45µm) COD_{Cr} to % difference between the TS content of filtered (45µm) and unfiltered samples for the untreated (incoming) wastewater samples

In the absence of a global correlation between peCOD and Total $COD_{Cr,}$ another strategy for application of PeCOD® Analyzer for organic pollution measurement of untreated (incoming) wastewater samples was investigated. The strategy was to obtain different correlations for different COD ranges instead of looking for a global correlation. The result of combining these two strategies is presented in Figure 12 and Figure 13. Figure 12 shows that for the subset of samples in the lower COD range (COD< 20,000 mg/L), a strong correlation ($R^2 = 0.78$) exists between peCOD and Filtered COD_{Cr} results. The correlation is much stronger for samples with Filtered COD_{Cr}<5000 mg/L. Outside that range (5000<COD_{Cr}<20,000 mg/L) the deviation between the results of the two methods is severe for several of the samples. As shown in Figure 8, for the subset of samples at the high COD range (COD>20,000 mg/L) the results of the two method are not correlated. While COD_{Cr} values of higher than 100,000 mg/L were observed, the PeCOD® method results did not go above 36,000 mg/L (marked with the dashed line in Figure 13).

The significant deviation between the results of the two methods is potentially mainly due to the fact that the PeCOD® Analyzer can only measure soluble COD as there is no digestion step in the PeCOD® method. As the filter pore size used for the pre-treatment of the sample is 100 times larger than the filter pore size (0.45 µm) used for sample pre-treatment when measuring soluble COD, particulate COD has also contributed to the Filtered COD_{Cr} readings. Additionally, the untreated (incoming) industrial wastewater samples used in this study contained high concentration of chloride, nitrogenous compounds, heavy metals and other inorganic compounds that potentially interfere with one or both measurement methods some of which have been investigated in the second phase of this work (chapters 3 and 4).

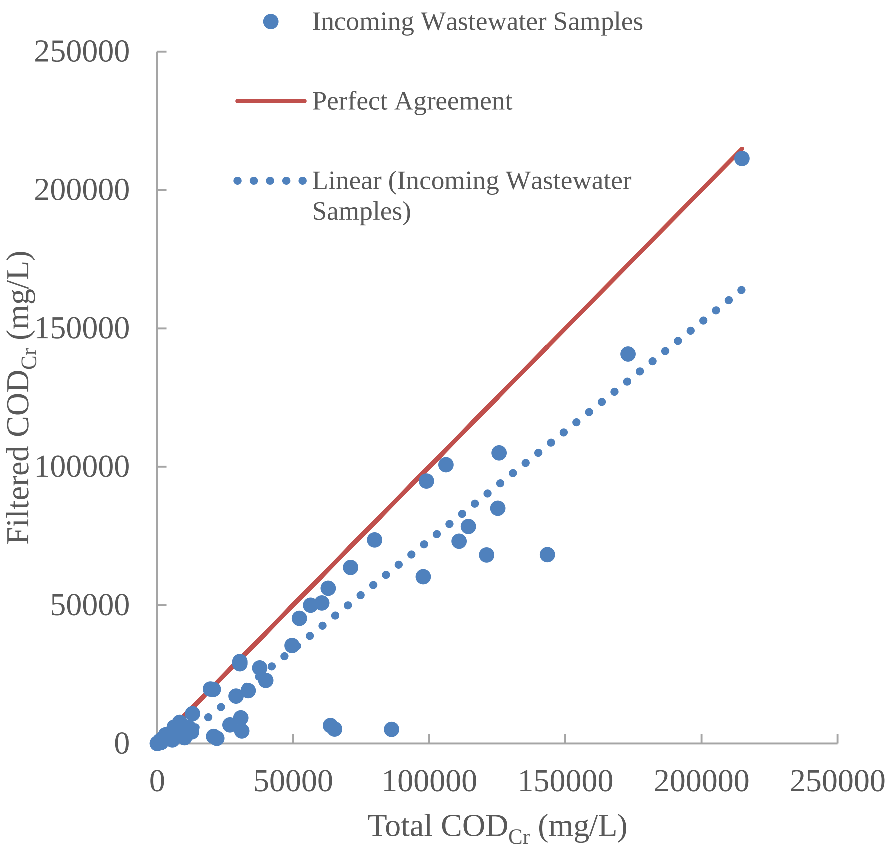


Figure 11- Correlation between Total COD$_{Cr}$ results and Filtered (45 µm) COD$_{Cr}$ results the untreated (incoming) wastewater samples (y= 0.78 x – 5748, R^2=0.84). The solid line is representing the condition of perfect agreement between the results of the two methods (i.e. peCOD= Total COD$_{Cr}$).

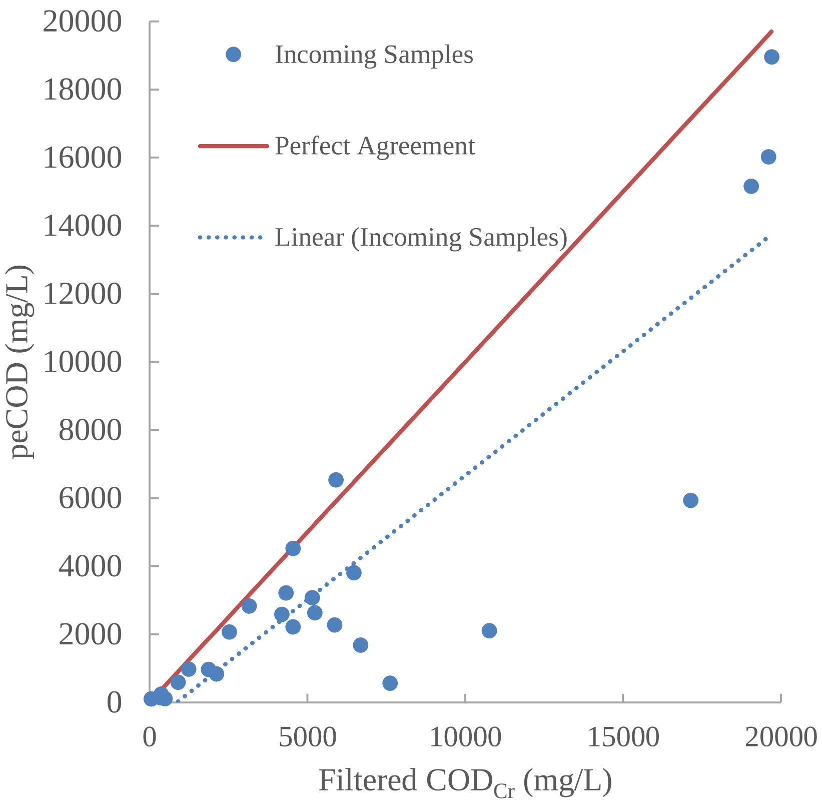


Figure 12- Correlation between peCOD results and filtered (45 µm) COD$_{Cr}$ results for the untreated (incoming) wastewater samples with filtered COD$_{Cr}$ < 20,000 mg/L (y= 0.733 x – 633, R^2=0.78). The solid line is representing the condition of perfect agreement between the results of the two methods (i.e. peCOD= Total COD$_{Cr}$).

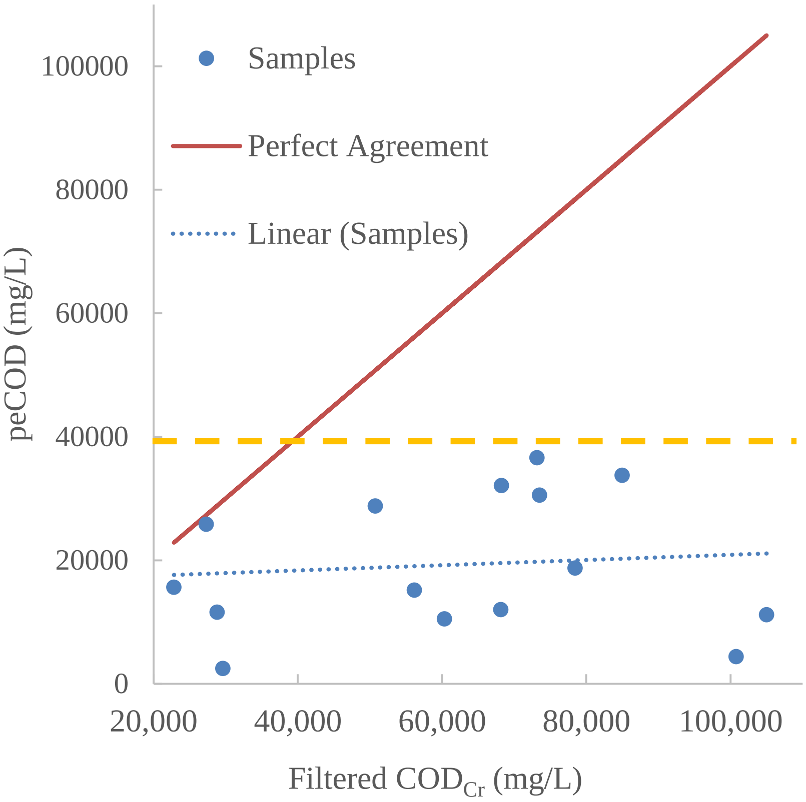


Figure 13- Correlation between peCOD results and Filtered (45 µm) COD$_{Cr}$ results for the untreated (incoming) wastewater samples with Filtered COD$_{Cr}$ >20,000 mg/L (y= 0.04 x +16671, R^2=0.01). The solid line is representing the condition of perfect agreement between the results of the two methods (i.e. peCOD= Total COD$_{Cr}$).

2.3.2 Treated (Effluent) Industrial Wastewater Samples

Thirty effluent samples were analyzed with both PeCOD® and dichromate methods to investigate the suitability of the PeCOD® method for organic pollution measurement of effluent samples. Figure 14 is showing the results obtained with the PeCOD® method plotted against the results obtained with the dichromate method. The PeCOD® and dichromate method results are strongly correlated (R^2= 0.92), however for the majority of the samples, PeCOD® method results are significantly lower (i.e. PeCOD® method results are on average 37% lower). Additionally, although the difference percentage between the results of two methods is in the 20-40 % range, for several of the samples differences greater than 60% are observed.

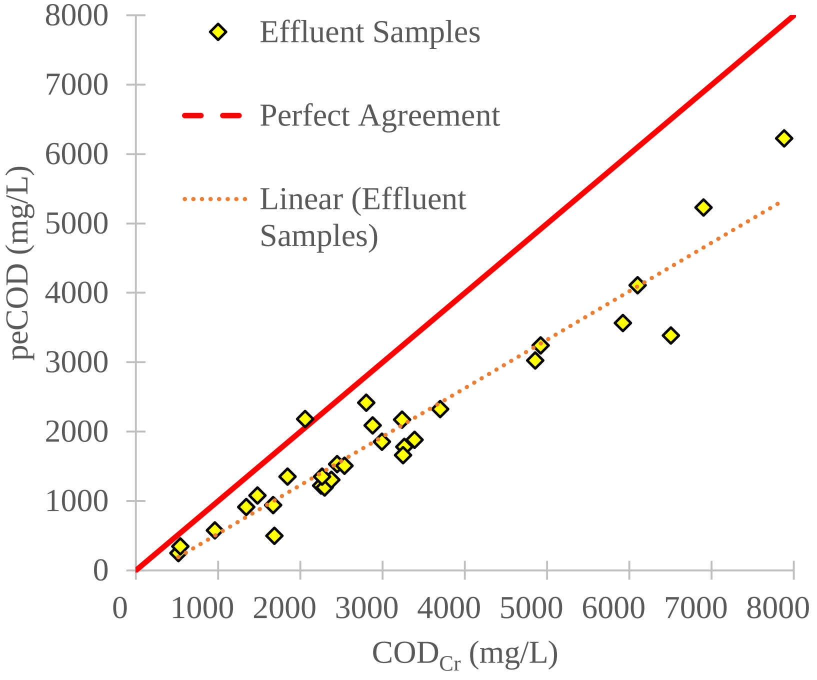


Figure 14- Correlation between peCOD results and COD_{Cr} results for the treated (effluent) wastewater samples (y= 0.70 x + 169.53, R^2= 0.92). The solid line is representing the condition of perfect agreement between the results of the two methods (peCOD=COD_{Cr}).

2.3.3 Assessment of PeCOD® Analyzer Analysis Speed

As discussed in the introduction, the PeCOD® technology analysis time is a fraction of the analysis time required for the dichromate method. However, in the dichromate method a large set of samples (typically between 9 to 25) can be analyzed simultaneously because the reactor block has multiple sample wells. For example, the

DRB 200 reactor block used in this study has 16. used for heating the samples has. On the other hand, with the current design of the PeCOD® Analyzer only one sample can be analyzed at a time. Additionally, in the PeCOD® method after analysis of several samples a quality control check must be run and recalibration of the system might also be required. The number of samples that can be analyzed before the need for system recalibration depends on the sample type (i.e. pollution level, pollution type, chloride concentration, etc.) and the age of the sensor.

To demonstrate which method is faster for applications that require analysis of a large set of samples in one batch, Figure 15 is provided. This figure has been developed under the following assumptions:

- Fixed analysis time for all samples (i.e. 20 minutes in the Red Range and 15 minutes in the Yellow Range).
- After running every five samples a quality control check is required which takes 20 minutes in the Red Range and 15 minutes in the Yellow Range.
- After running every five samples a recalibration and a subsequent quality control run is required which takes 60 minutes in the Red Range and 45 minutes in the Yellow Range.
- The analysis time of the dichromate method is 160 minutes (120 minutes for heating the COD vials and 40 minutes for the vials to cool down).
- The reactor used for heating the vials has over 16 wells (1 well is required for the blank vial).

Based on this assumptions, the PeCOD® method is the faster method for analysis of up to 5 samples when operating the system in the Red Range and up to 8 samples when operating the system in the Yellow Range. This is demonstrated in Figure 15 by the number of bars (dashed: Red Range, solid fill: Yellow Range) that are not intersected by the solid line which is representing the fixed analysis time of the dichromate method. It should be noted that for applications where only an estimate of COD is required and some error (> 5%) in the results is tolerated, the need for recalibration would be less frequent than what is assumed here.

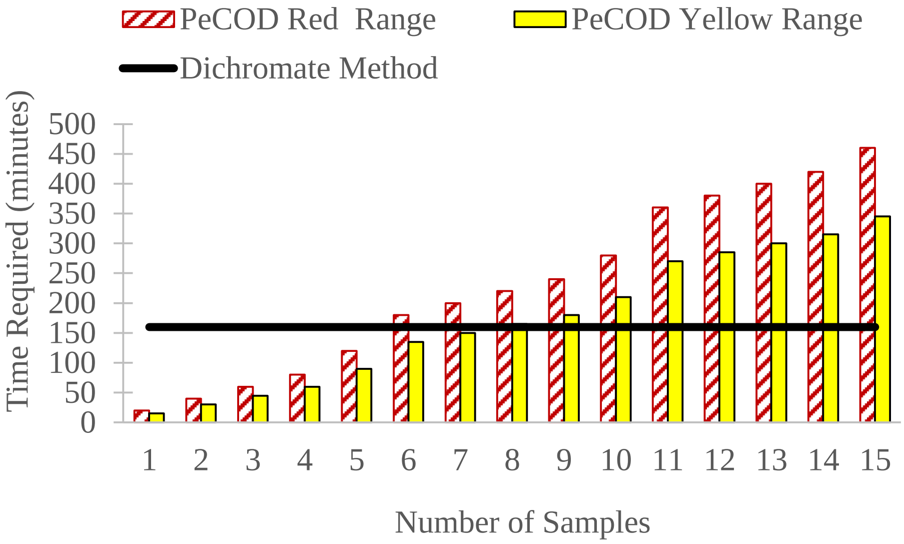


Figure 15- Comparison of the speed of analysis between the dichromate method (analysis time is demonstrated by the solid line) and the PeCOD® method (analysis time is demonstrated by dashed bars for the Red Range and by the solid fill bars for the Yellow Range) for different number (i.e. 1-15) of samples.

2.4 Conclusions

The streamlined substitution of the dichromate method with the PeCOD® method via application of a global correlation for converting the results of one method to the other was proven not to be feasible for applications where the quality and composition of the wastewater samples are constantly changing.

For the untreated (incoming) wastewater samples at the lower COD range, the results of the two methods seem to correlate, however, outliers with significant divergence were also observed. While the factors causing the divergence are unknown, correlations cannot be used with certainty as any sample from a new generator might turn out to be an outlier.

Correlations could be useful in applications where there is no significant variation in the organic and inorganic composition of the samples so the difference in the results of the two methods would always be in the same range. An example of such application would be the analysis of wastewater samples generated by a single industry. However, this was not the case for this study as wastewater loads from different generators were often shipped by a single truck to the treatment plant where the samples used in this study were received from.

For the treated (effluent) wastewater samples, despite the strong correlation obtained, the PeCOD® method cannot replace the dichromate method unless the factors causing the lower peCOD results are determined and accounted for. In the next phase of this study, a series of control experiments were conducted to investigate the potential causes leading to the lower peCOD results. Industrial wastewater characteristics that potentially interfere with one or both of the measurement methods were investigated which include: containing hard to oxidize materials (i.e. macromolecules) commonly present in industrial wastewater, high chloride and nitrogenous compound concentrations and high turbidity levels.

The PeCOD® method can generate results for a single sample in approximately 10-20 minutes which makes it suitable for inline applications. However, for applications where analysis of a batch of samples at once is required, it is only faster than the dichromate method when analyzing a small set of samples. The speed of analysis in the PeCOD® method is highly affected by the frequency of system recalibration needed.

Chapter 3: Oxidation of Macromolecules in the PeCOD® Method

3.1 Introduction

Larger molecules (referred to as macromolecules due to their large size) have many industrial applications as shown in Table 7 and thus are present in many industrial wastewater sources. The previous work by MANTECH and their academic partners has focused exclusively on the ability of the PeCOD® Analyzer to oxidize ‘small’ organic molecules (such as amino acids (tyrosine, tryptophan) and carboxylic acids (sodium acetate, sodium formate) that have molecular weights less than 300 Da [38]. Hence, the oxidative behaviour of different macromolecules in the PeCOD® method was investigated in this work. Four different macromolecules with different chemical structures and functional groups were chosen as model compounds: Polyethylene glycols/polyethylene oxides (PEG/PEO), dextran, polyvinylpyrrolidone (PVP) and polyacrylamide (PAM).

Table 7- Different categories of macromolecules, their examples and applications in industry

Category	Examples	Applications
Polysaccharides	dextran, starch, glycogen, levan, pullulan, xanthan, chitin	Manufacturing of paints, pigments, adhesives, latex emulsions, and various food products
Polyethers	polyethylene glycols, polyethylene oxides	Medical products (laxatives) and as industrial surfactants and lubricants
Other Water Soluble Polymers	polyvinylpyrrolidone	Industrial adhesives and thickening/binding agents
	polyacrylic acids	Thickening and emulsifying agents in pharmaceutical and cosmetic manufacturing
	Polyvinyl alcohol	Production of paper, textiles, and a variety of coatings

3.2 Materials and Methods

3.2.1 Model Compounds

Four macromolecules (dextran, polyethylene glycol, polyethylene oxide, polyvinylpyrrolidone and polyacrylamide) were purchased from Sigma Aldrich. The list of the materials used is provided in Table 8.

The concentration of the model compounds solutions was chosen to correspond to a Theoretical Oxygen Demand (ThOD) of 600 mg/L for all the molecular weights tested. ThOD was calculated using Equations (3) and (4) [39]:

$$C_n\, H_m O_e X_k N_j S_i P_h + bO_2 \rightarrow$$

$$nCO_2 + \frac{m-k-3j-2i-3h}{2} H_2O + kHX + jNH_3 + iH_2SO_4 + hH_3PO_4 \qquad (3)$$

X: Halogens

$$ThOD = b = n + \frac{m-k-3j-2i-3h}{2} - \frac{e}{2} + 2i + 2h \qquad (4)$$

Table 8- Compound name, chemical formula and the molecular weight (as reported by Sigma Aldrich) of the materials used as model compounds

Compound	Chemical Formula	Molecular Weight (MW)
Dextran	$(C_6H_{10}O_5)_n$	Average M_w (Da): 35000-45000 Da M_r (Da): 100000, 200000, 450000-650000 and 2000000
Polyethylene glycol	$H(OCH_2CH_2)_nOH$	M_r (Da): 300, 2000, 10000, 16000-24000,
Polyethylene oxide	$H(OCH_2CH_2)_nOH$	M_r (Da): 35000 Average M_v (Da): 100000, 200000, 600000, 2000000
Polyvinylpyrrolidone	$(C_6H_9NO)_n$	Average M_w (Da): 10000, 40000, 360000 and 1300000
Polyacrylamide	$(C_3H_5NO)_n$	Average M_n (Da): 40000,150000, 5000000-6000000

The solutions of the model compounds were filtered with 45 µm dissolution filters (Thermo Scientific™ SUN-SRi™ SunFlo™ Dissolution Filters) and were analyzed with both the dichromate and PeCOD® (Yellow Range) methods and the peCOD/COD_{Cr} ratio was calculated for each model compound. The peCOD measurements were done in duplicate.

3.2.2 Size Exclusion Chromatography (SEC)

Size Exclusion Chromatography (SEC) analysis was performed to provide a reference of molecular size for the materials used for the dextran and PEG/PEO model compounds. The SEC system used had three columns with the following specifications: Waters Ultrahydrogel-120, -250 and -500; 7.8 mm × 300 mm (length × ID); 6 µm particles. Their nominal MW range is 100 Da – 400 kDa. The solvent used was 0.5 M sodium nitrate plus 25 mM (2-Cyclohexylamino) ethanesulfonic acid (CHES) buffer (pH 10). The mode of detection was Refractive Index (RI). The system was calibrated with PEG standards up to molecular weight of 800 kDa. The injection volume was 20 µL. The concentration of the samples used for the SEC analysis was approximately 5-10 g/L. Samples were prepared with ultrapure water and filtered with a 0.45 µm Supor® polyethersulfone syringe filters (Pall Corporation) prior to analysis.

3.2.3 Liquid Chromatography-Organic Carbon Detection (LC-OCD)

The treated (effluent) industrial wastewater samples were passed through 0.45 µm Supor® polyethersulfone syringe filters (Pall Corporation) into TOC clean glass vials (VWR). The filters were pre-rinsed by passing approximately 20 mL of ultrapure water through them and then dried by passing air through them. Due to their high dissolved organic carbon (DOC) content, all samples had to be diluted 50-500 times with ultrapure water before the LC-OCD analysis. Samples were analyzed using the LC-OCD system (from DOC-LABOR) that is available at the University of Waterloo. A detailed description of the working principle and operation of the LC-OCD instrument has been well described in previous works [2][3]. As shown in Figure 6, the LC-OCD instrument uses a size exclusion column combined with an organic carbon detector (OCD), organic nitrogen detector (OND), and a UV absorption detector (UVD) to fractionate samples according to their size and hydrophobicity. PEG standards (Sigma Aldrich) were used to characterize the fractionation range of the size exclusion column according to the OCD signal. The chromatograms were analyzed using the ChromCALC software that is provided by the manufacturer of the LC-OCD instrument. Only the chromatograms from the OCD are presented here.

3.2.4 Serial Filtration

Hollow fiber membranes, modified polyethersulfone (mPES) MicroKros® filter modules (Spectrum Labs) were used to perform ultrafiltration on the treated (effluent) wastewater samples. The filter modules had an internal diameter (ID) of 0.5 mm and a surface area (SA) of 20 cm^2 and molecular weight cut-offs of 1 kDa, 5 kDa, 10 kDa and 30 kDa. An mPES MicroKros® filter module (Spectrum Labs) with a filter pore size of 0.2 µm, ID of 0.5 mm and SA of 20 cm^2 was also used. The filters were pre-rinsed by passing approximately 40 mL of ultrapure water through them and then dried by passing air through them. The filter module functioned by connecting three 20 ml syringes to it. Two of the syringes were used for pushing the sample back and forth in the membrane (cross-flow) and the permeate was collected in the third syringe. As the treated (effluent) industrial wastewater samples used for this segment of the study contained large particulates, before filtration they were first passed through a filter paper (Whatman™, Grade 1: 11 µm) to rapid fouling of the filtration modules.

The effluent sample was filtered with the different filter modules in series starting from the filter with the largest molecular weight cut-off (i.e. the permeate of each filter was passed through the next filter with the smaller molecular weight cut-off). A portion of the permeate from each filter was collected in a TOC clean glass vial and was sent for the LC-OCD analysis. Due to the high DOC content of the filtered samples they were diluted 500 times with ultrapure water before the LC-OCD analysis.

3.3 Results and Discussion

3.3.1 Oxidation of Macromolecules

3.3.1.1 Polyethylene Glycols/Polyethylene Oxides (PEG/PEO)

Polyethylene glycol (PEG) and polyethylene oxides (PEO) are linear chain polymers with an identical backbone structure featuring C-C, C-H and C-O bonds [40]; PEG refers to molecules with molecular weights less than 20 kDa while PEO refers to molecules with molecular weights greater than 20 kDa [41].

The ratio of the peCOD values to COD_{Cr} values obtained for the model compounds of PEG/PEO over a wide range of molecular weights (i.e. MW: 300 Da-2,000,000 Da) as reported by Sigma Aldrich is shown in Figure 16-a. The material used for several of the PEG/PEO model compounds was specified by the supplier to contain a range of molecular weights. Hence, the average of the provided molecular weight range was used for plotting the data in Figure 16-a. The same ratio has also been obtained for ethylene glycol (EG) which is the building block of PEG/PEO polymers. The dashed line is representing the condition of 'perfect agreement' between the results of the two methods (i.e. peCOD/COD$_{Cr}$ =1). As it can be seen in Figure 16-a, even for ethylene glycol (first data point from the left) which is a relatively small molecule (i.e. MW= 62.07 Da), the ratio of the results is slightly smaller than 1. (i.e. lower peCOD results). The ratio of the results significantly drops for PEG/PEO model compounds with MW ≥ 20,000 Da).

As the material used were of different analytical grades and several of them were specified by the supplier to contain a range of molecular weights, to provide a reference for comparison of the molecular weight distribution of the materials used, SEC analysis was done on the model compounds. Additionally, for the PEO model compounds with MW ≥ 100,000 Da, viscosity average molecular weights were provided by the supplier, while for all the PEG model compounds relative molecular mass was provided. The SEC chromatograms of the PEG/PEO model compounds are shown in Figure 17. The molecular weights of the two largest PEO model compounds tested (i.e. MW of 2,000,000 Da and 600,000 Da) were greater than the exclusion limit of the SEC column (i.e. 400,000 Da with reference to PEG calibration). However, the SEC analysis was performed for these two PEO model compounds to investigated whether they contain molecules of smaller than 400,000 Da. The chromatograms of the PEO model compounds with molecular weights of 600,000 Da and 2,000,000 Da are overlapping which was an expected outcome given that they are both larger than the column exclusion limit. Additionally, their chromatograms are also overlapping with that of the PEO model compounds with molecular weight of 100,000 Da and 200,000 Da, which indicates that a fraction of the two largest PEO model compounds tested, also contained smaller molecules. It can also be seen that chromatograms of the PEO model compounds with MW of 100,000 Da and 200,000 Da are overlapping which indicates that these model compounds contained a range of molecular weights and that is potentially why peCOD results have been similar for these PEOs. Another interesting observation in the SEC analysis results is the heavy right tail of the chromatogram belonging to the PEG with the average molecular weight of 10,000 Da. This heavy right tail which is overlapping with the chromatogram of the PEG sample with average molecular weight of 300 Da, indicates that a considerable portion of this PEG sample was composed of PEG polymers with molecular weights much smaller than 10,000 Da which is potentially the reason why the ratio of the results for this PEG samples is closer to 1 compared to the PEG samples with the average molecular weight of 20,000 Da.

The peCOD/COD_{Cr} ratio was also plotted against the peak retention times obtained via the SEC analysis for the PEG/PEO model compounds in Figure 16-b. A higher retention time indicates a lower molecular weight.

The lower peCOD results compared to the COD_{Cr} results is potentially an indication that in the PeCOD® method PEG/PEO polymers do not undergo complete oxidation. This conclusion is in agreement with results of a previous study done on the uncatalyzed oxidation of PEG which showed that the short-chain oligomers such as ethylene glycol formed in the oxidation of PEG polymers are very resistant to total oxidation [42]. Additionally, several studies have identified PEG to have a poor biodegradability [43][44].

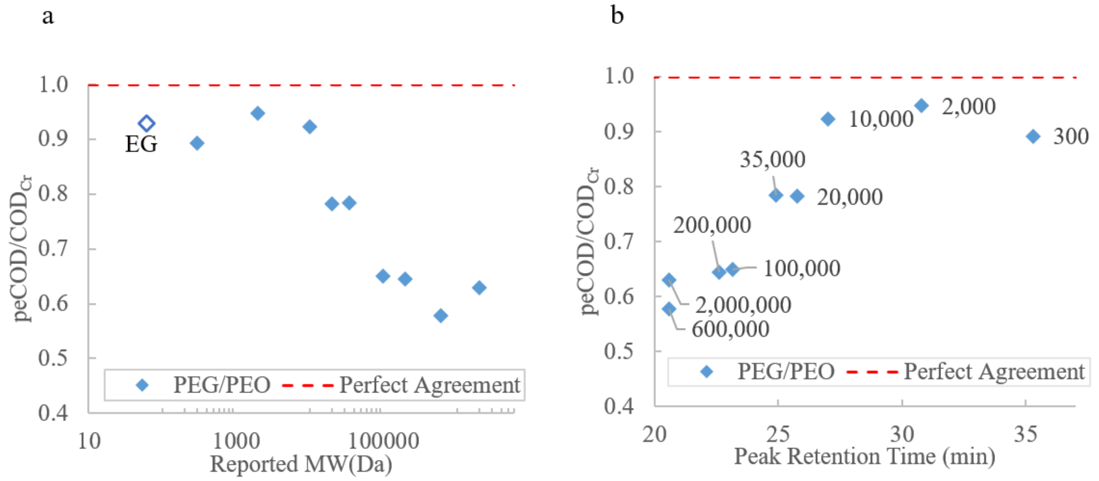


Figure 16- Panel a: peCOD/COD$_{Cr}$ ratio for PEG/PEO over a range of molecular weights (MW: 300 Da- 2,000,000 Da) as reported by Sigma Aldrich. The first data point from the left belongs to ethylene glycol (EG). Panel b: peCOD/COD$_{Cr}$ ratio for PEG/PEO plotted against the peak retention times obtained by SEC analysis (referrer to Figure 17) for the PEG/PEO model compounds. The reported MW in Da is shown besides each data point. The dashed line is representing the condition of 'perfect agreement' between the results of the two methods (i.e. peCOD/COD$_{Cr}$ =1) in both panels.

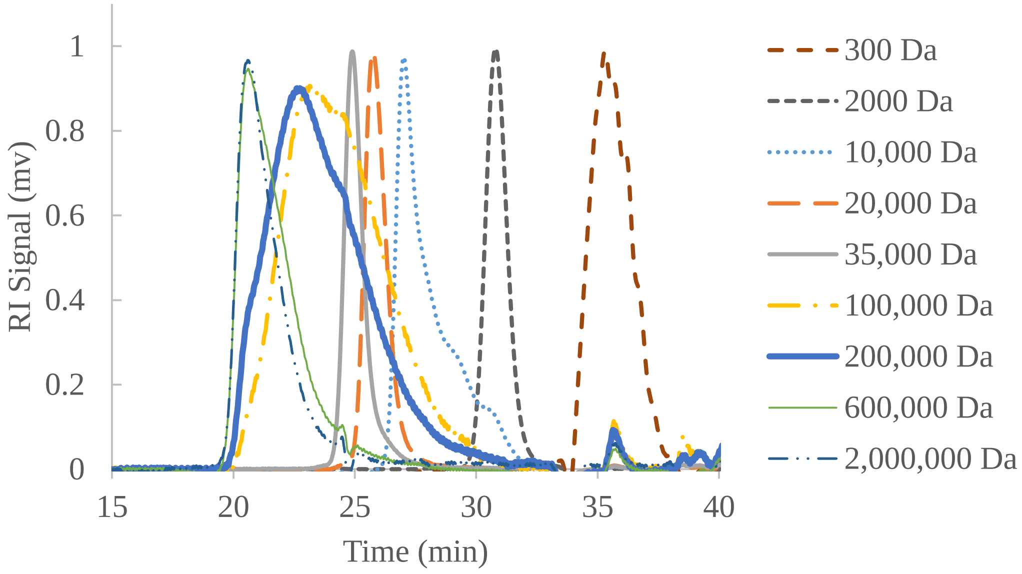


Figure 17- SEC results obtained for PEG/PEO over a range of molecular weights (MW: 300 Da- 2,000,000 Da).

3.3.1.2 Dextran

The ratio of the peCOD values to COD_{Cr} values obtained for the model compounds of dextran over a wide range of molecular weights (i.e. MW: 40,000 Da-2,000,000 Da) is shown in Figure 18-a. As it can be seen in Figure 18-a, for the relatively smaller dextrans (i.e. MW≤ 100,000 Da), the ratio of the results was greater than one (i.e. higher peCOD results) but for the larger dextrans the ratio dropped and was observed to be 0.7 for the largest dextran tested (MW=2,000,000 Da).

Dextran is composed of many glucose molecules chained together and glucose, a molecule with abundant hydroxyl functional groups, is reported to undergo easy oxidation in peCOD measurement [45]. This is potentially why the agreement between the results of the two methods is stronger for dextran compared to PEG.

As the material used as model compounds were of different analytical grades and several of them were specified by the supplier to contain a range of molecular weights, to provide a reference for comparison of the molecular weight distribution of the materials used, SEC analysis was done on the model compounds. The SEC chromatograms of the dextran model compounds are shown in Figure 19. The molecular weights of the two largest dextran model compounds tested (i.e. MW of 550,00 Da and 2,000,000 Da) were greater than the exclusion limit of the SEC column (i.e. 400,000 Da with reference to PEG calibration). However, the SEC analysis was performed for these two dextran model compounds to investigated whether they contained molecules of smaller than 400,000 Da. The chromatograms obtained for the two largest dextrans are overlapping with the chromatograms of the smaller dextrans which indicates that these model compounds contained a wide range of molecular weights. Additionally, the 200,000 Da and the 550,000 Da dextran model compounds have approximately the same peak retention time but very different breadths. The 'double peak' observed for dextran with molecular weight of 2,000,000, indicates that this model compound was composed of two main molecular weight fractions.

The peCOD/COD$_{Cr}$ ratio was also plotted against the peak retention times obtained via the SEC analysis for the dextran model compounds in Figure 18-b.

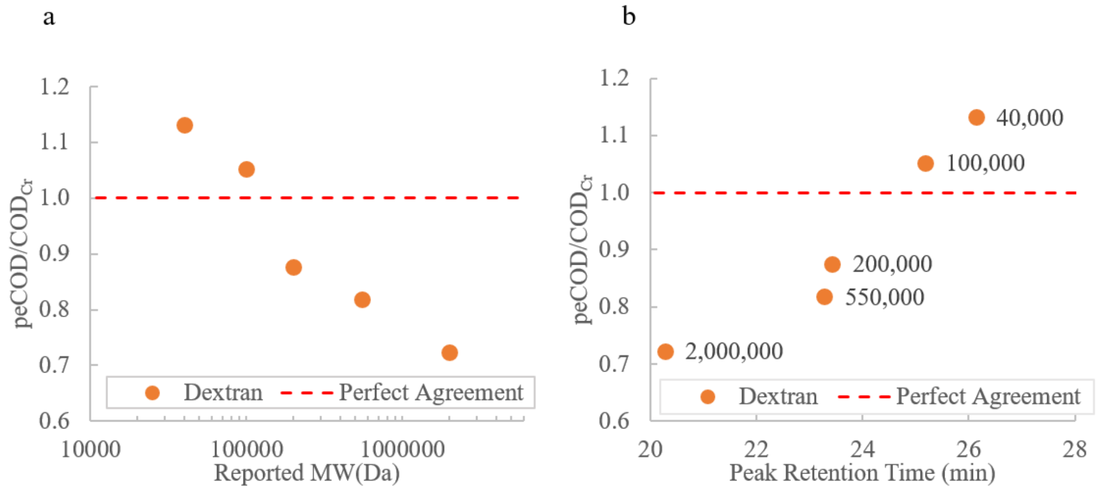


Figure 18- Panel a: peCOD/COD$_{Cr}$ ratio for Dextran over a range of molecular weights (MW: 40,000 Da- 2,000,000 Da) as reported by Sigma Aldrich. Panel b: peCOD/COD$_{Cr}$ ratio for dextran plotted against the peak retention times obtained by SEC analysis (referrer to Figure 19) for the dextran model compounds. The reported MW in Da is shown besides each data point. The dashed line is representing the condition of 'perfect agreement' between the results of the two methods (i.e. peCOD/COD$_{Cr}$ =1) in both panels.

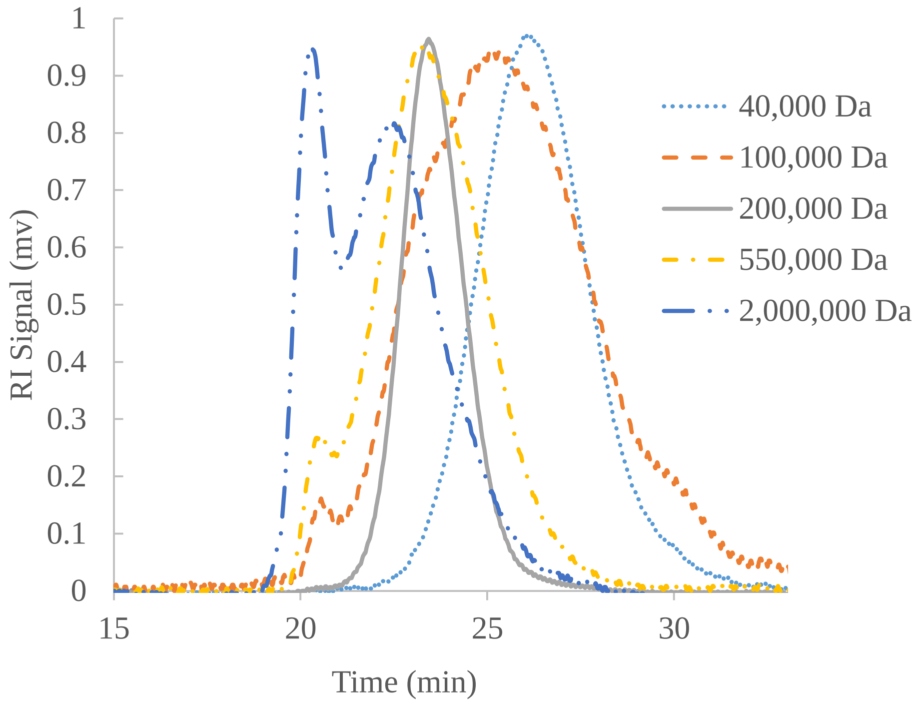


Figure 19- SEC results obtained for dextran over a range of molecular weights (MW: 40,000 Da- 2,000,000 Da).

3.3.1.3 Polyvinylpyrrolidone (PVP)

Polyvinylpyrrolidone (PVP) is a water-soluble polymer which its backbone is composed of C-C and C-H bonds and has a five-membered lactam ring as a pendant group [46]. As shown in Figure 20, peCOD results were significantly lower than the COD_{Cr} results for all the molecular weights tested for this polymer.

Horikoshi et al. [46] reported that in experiments done with TiO_2 aqueous dispersions, the photodecomposition of PVP is through adsorption of PVP onto the TiO_2 particulates through the N–C=O function of the pendant lactam ring which is a relatively slow process. The slow adsorption mechanism is potentially the cause of incomplete oxidation of PVP in the PeCOD® method.

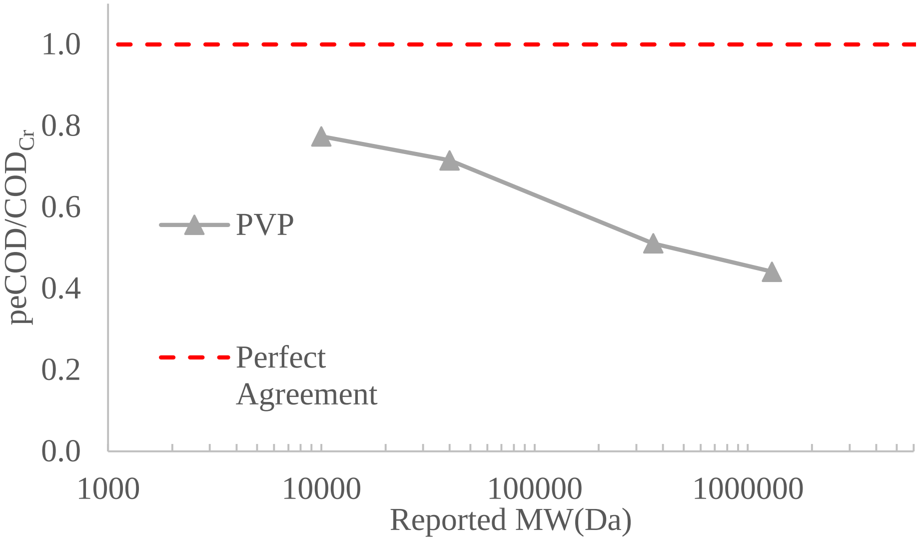


Figure 20- peCOD/COD$_{Cr}$ ratio for PVP over a range of molecular weights (MW: 10,000 Da- 1,300,000 Da). The dashed line is representing the condition of 'perfect agreement' between the results of the two methods (i.e. peCOD/COD$_{Cr}$ =1).

3.3.1.4 Polyacrylamide (PAM)

Polyacrylamide (PAM) is a water soluble polymer which its backbone is composed of C-C and C-H bonds and has an amide group as its pendant group [40]. As shown in Figure 21, peCOD results were significantly lower than the COD$_{Cr}$ results for all the molecular weights tested for this polymer. PAM photo-oxidation is potentially slower than PEO since dissociation of C-C bonds requires more energy compared to C-O bonds [40] [47].

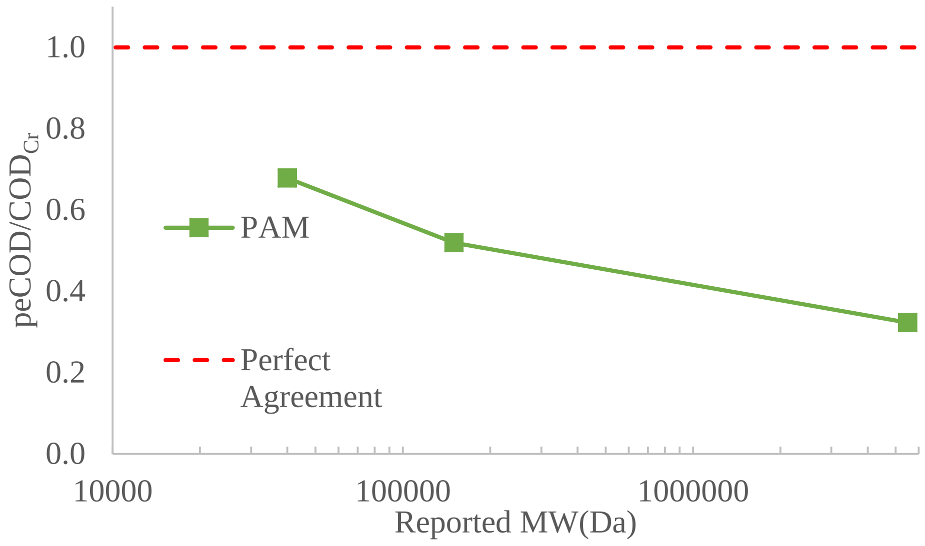


Figure 21- peCOD/COD$_{Cr}$ ratio for PAM with three different molecular weights (MW: 40,000 Da, 150,000 Da- 5,0000,000-,6000,000 Da). The dashed line is representing the condition of 'perfect agreement' between the results of the two methods (i.e. peCOD/COD$_{Cr}$ =1).

3.3.2 Application of the LC-OCD Analysis for Determination of Treated (Effluent) Industrial Wastewater Molecular Weight Distribution

It was shown in the previous parts that very large macromolecules do not undergo complete oxidation in the PeCOD® method which leads to lower peCOD results compared to COD$_{Cr}$ results. Hence, presence of macromolecules in the untreated (incoming) and treated (effluent) industrial wastewater samples studied in Chapter 2 of this work is potentially one of the factors that caused the lower peCOD results observed for those samples.

In this section, the presence of macromolecules in treated (effluent) industrial wastewater samples was investigated via LC-OCD analysis. This analysis method has been previously applied for obtaining an account of molecular weight distribution for Natural Organic Matter (NOM) present in natural water sources. However, its application for analysis of industrial wastewater is a novelty of this work. Calibration with PEG standards, in combination with serial filtration was used to provide an account of molecular weight distribution in the treated (effluent) industrial wastewater samples.

3.3.2.1 Comparison of LC-OCD Chromatograms for a Library of Treated (Effluent) Industrial Wastewater Samples

The Organic Carbon Detector (OCD) chromatograms of thirteen effluent samples are shown in Figure 22. It can be concluded by the comparison of these chromatograms that only one peak with retention time of approximately 50 minutes is shared between all the samples while all the other peaks are either unique to a certain sample or to a group of samples. The variation in the peak retention times and the peak areas for this library of samples is an indication of variation in the organic composition of these samples. Variation in the organic composition is potentially one of the main factors that causes the level of agreement between peCOD and COD_{Cr} results to vary from sample to sample.

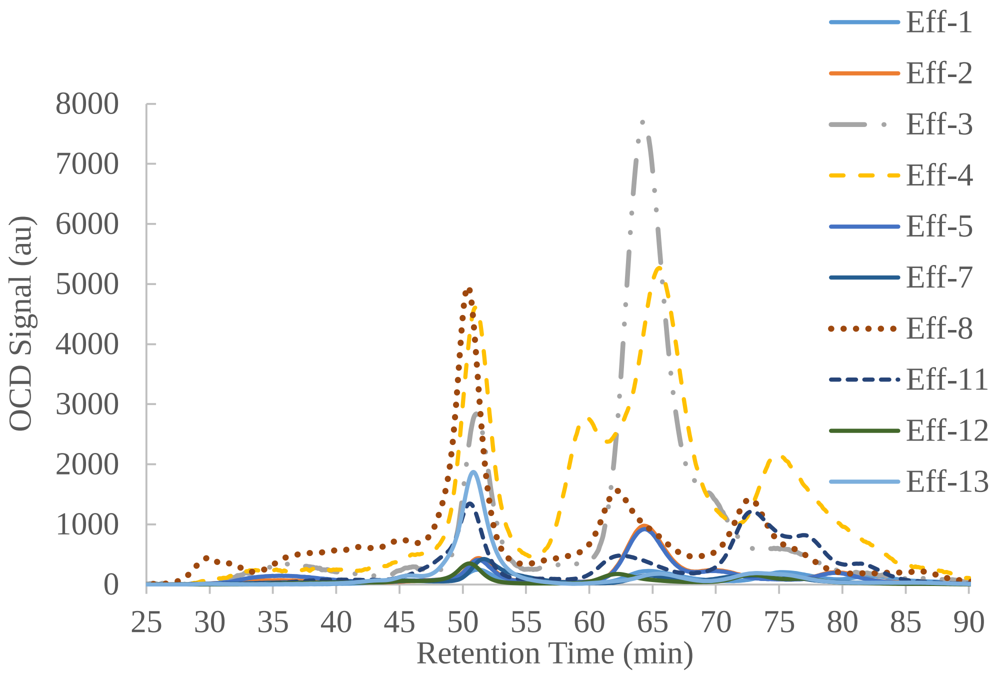


Figure 22- The OCD chromatograms for thirteen treated (effluent) industrial wastewater samples. The samples were filtered (0.45 µm) and diluted for the LC-OCD analysis. The dilution factors are accounted for in the presentation of the chromatograms.

3.3.2.2 Investigation of Presence of Macromolecules in Treated (Effluent) Industrial Wastewater via Combination of Serial Filtration and LC-OCD Analysis

The effect of serial filtration up to the molecular weight cut-off of 30 kDa on an effluent sample is demonstrated in Figure 23. When comparing the chromatogram of the effluent after serial filtration to that of the effluent after filtration with only a 0.2 µm filter, it is observed that peaks with retention times of up to approximately 50 minutes have been completely removed by the 30 kDa filter. This retention time corresponds to a molecular weight of approximately 1 kDa according to the PEG calibration.

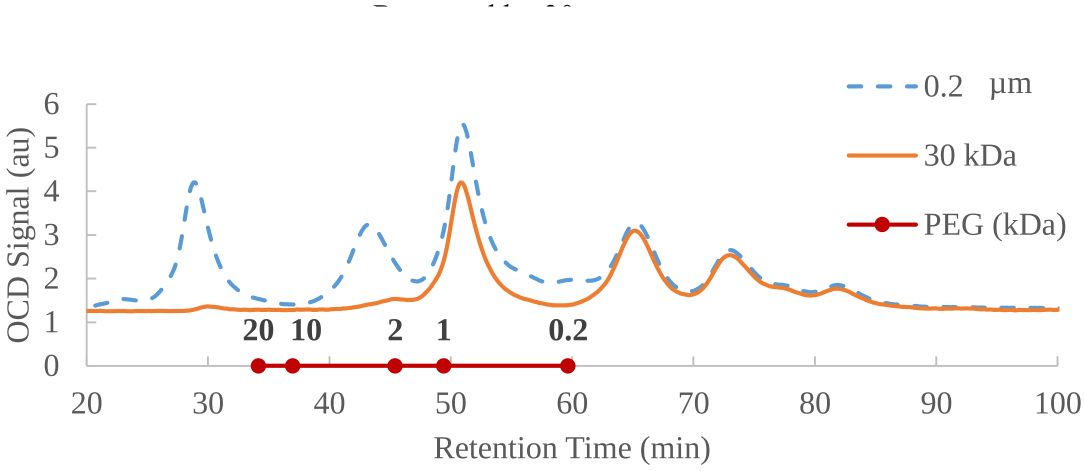


Figure 23- Comparison of the OCD chromatograms of an effluent sample with two different pre-filtrations: filtration with only a 0.2 µm filter and filtration with a 0.2 µm filter and a 30 kDa filter in series. Samples were diluted 500 times before analysis. The peak retention times associated with the molecular weight (kDa) of five PEG standards are shown on the x-axis for comparison; note that a total of eleven PEG standards were actually used to calibrate the LC-OCD system.

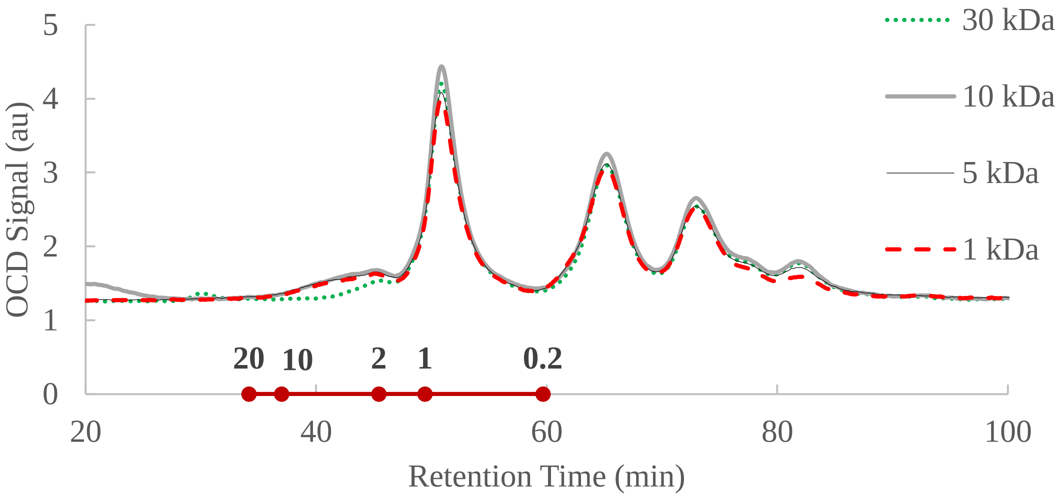


Figure 24- Comparison of the OCD chromatograms of an effluent sample after serial filtration. The legend is showing the molecular weight cut-off of the last filter used in the serial filtration of the sample. The peak retention times associated with the molecular weight (kDa) of five PEG standards are shown on the x-axis for comparison; note that a total of eleven PEG standards were actually used to calibrate the LC-OCD system.

The effect of serial filtration up to the molecular weight cut-off of 1 kDa on the same effluent sample is demonstrated in Figure 24. When comparing the chromatograms of the effluent sample after serial filtration with the final filter having a molecular weight cut-off of 30 kDa to that of the effluent samples after filtration with the final filter having a molecular weight cut-off of 10 kDa, 5 kDa and 1 kDa, it is observed that filtration with filters with molecular weight cut-off of smaller than 30 kDa has not had a significant effect on the effluent sample chromatogram. It can be concluded that these filters have not achieved a significant dissolved organic carbon removal for this sample. This observation agrees with the information provided with the PEG calibration which states that peaks appearing after the retention time of approximately 50 minutes correspond to organic species with molecular weights of smaller than 1 kDa which cannot be filtered out with the filters used in this study.

3.3.2.3 Effect of Macromolecules Present in a Treated (Effluent) Industrial Wastewater Sample on its peCOD Result

The effect of ultrafiltration was also studied on the agreement between peCOD and COD_{Cr} results. As shown in Table 9, although according to the LC-OCD results, filtration with the 30 kDa removed species with molecular weights of greater than 1 kDa with reference to the PEG calibration, no significant improvement was observed in the agreement between peCOD and COD_{Cr} results. It can be concluded that for this effluent sample the difference between the results of the two methods is not due to the presence of macromolecules with $MW \geq 1$ kDa.

Table 9- peCOD and COD_{Cr} results for an effluent sample with two different pre-filtrations: filtration with only a 0.2 µm filter and filtration with a 0.2 µm filter and a 30 kDa filter in series. The % difference between the results of the two methods is shown in the last column.

Filter Size	COD_{Cr} Result 1 (mg/L)	COD_{Cr} Result 2 (mg/L)	COD_{Cr} Result 3 (mg/L)	peCOD Result 1 (mg/L)	peCOD Result 2 (mg/L)	peCOD Result 3 (mg/L)	% Diff. (peCOD vs. COD_{Cr})
0.2 µm	4840	4830	4960	4042	3897	4023	18
30 kDa	4640	4690	4620	3937	3743	3979	16

3.4 Conclusions

A comparison of the peCOD/COD_{Cr} ratio trend of decreases with increase in molecular weight for all the macromolecules tested is shown in Figure 25. The results indicate that for all the macromolecules tested at high molecular weights complete oxidation was not achieved in the PeCOD® method, however, the molecular weight threshold for incomplete oxidation depends on the chemical structure and functional groups of the macromolecule. For instance, when comparing the different macromolecules at approximately equal molecular weights, the best agreement between peCOD and COD_{Cr} results is observed for the dextran samples and the greatest deviation between the results of the two methods is observed for PAM.

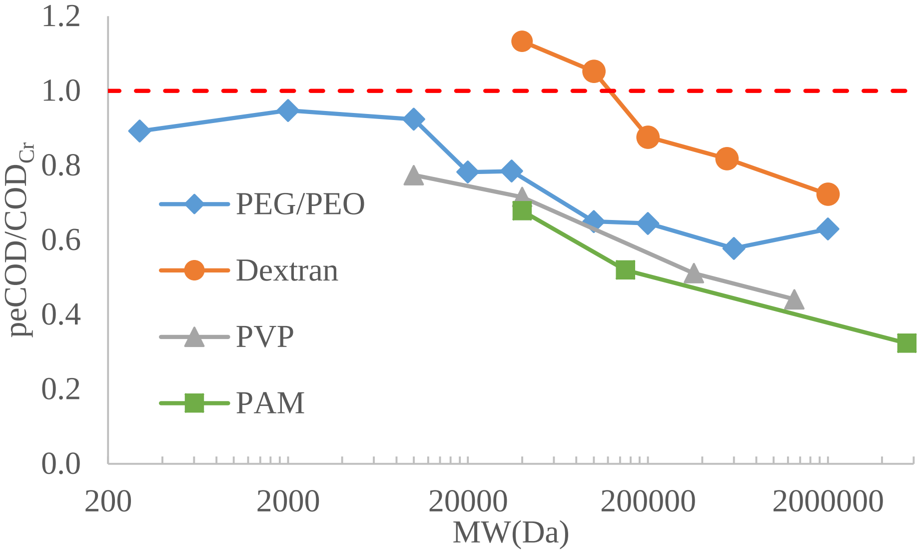


Figure 25- $peCOD/COD_{Cr}$ ratio for different macromolecules over a range of molecular weights. The dashed line is representing the condition of 'perfect agreement' between the results of the two methods (i.e. $peCOD/COD_{Cr} = 1$).

Three main conclusions can be made based on the results of section 3.3.2:

1- The variation in the effluent samples' organic composition which was speculated based on the fact that the effluent samples were collected from the treated wastewater loads generated by different industries and commercial facilities was verified by the variation observed in the effluent samples' LC-OCD chromatograms.

2- The 30 kDa filter used in this study is capable of removing species of approximately 3-5 times smaller than its molecular weight cut-off value as per its manufacturer's specification. The removal achieved with this filter corresponded to the disappearance of peaks with retention times that corresponded to the molecular weight of smaller than 1 kDa according to the PEG calibration. Based on the approximate agreement between the filter molecular weight cut-off and the

PEG calibration data, it can be concluded that the PEG calibration data is providing a good approximation of molecular weight distribution for the effluent samples at least for the range tested in this study.

3- Results of section 3.3.1 indicated that large macromolecules do not undergo complete oxidation in the PeCOD® method and hence their presence in the effluent samples was speculated to be the potential cause of the difference between the results of the two methods in the analysis of the effluent samples. Hence, it was expected that by removing macromolecules with ultrafiltration, an improvement between the results of the two methods to be observed. However, it was shown that for the sample used in this study this was not the case. As a result, smaller macromolecules and/or inorganic interferences are speculated to be the cause of the difference between the results of the two methods for this sample.

Chapter 4: Potential Causes of Interference in the PeCOD® and Dichromate Methods

4.1 Introduction

4.1.1 Inorganic Interferences in the PeCOD® and Dichromate Methods

A number of inorganic compounds are known to interfere with either one or both the dichromate and PeCOD® methods the interference caused by some of which can be overcome by addition of chemicals as summarized in Table 10 [7][48].

Table 10- Inorganic interferences of dichromate and PeCOD® methods and their prevention methods

	Dichromate Method		PeCOD® Method	
Inorganic Species	Interference	Prevention Strategy	Interference	Prevention Strategy
Chloride	Yes	Mercuric Sulfate Addition	Yes	Deposition of silver (I) oxide on sensors
Halides	Yes	Mercuric Sulfate Addition	Expected to behave similar to chloride	Deposition of silver (I) oxide on sensors
Ammonia	Yes (When in combination with chloride)	Application of lower concentrations of potassium dichromate	No	Not Needed
Nitrite	Yes	Sulfamic Acid	No	Not Needed
Reduced inorganics (Ferrous Iron, Sulfide, Manganous Manganese, etc.)	Yes	Not Available	Chromate, Sulfide, Sulfite, Ferrous Iron, Silver	Not Available

4.1.1.1 Chloride Interference in the PeCOD® and Dichromate Methods

Chloride is the main compound that interferes with both measurement methods causing high false readings in the dichromate method and false low readings in the PeCOD® method. Chloride interferes with the dichromate method in two ways:

1- Inhibiting the catalytic function of silver by producing silver chloride precipitates
2- Reacting with dichromate resulting in formation of chromium ions

The first interfering effect of chloride limits the oxidation potential of the method which should result in false low COD readings. However, as the final step of COD measurement is a colorimetric method based on the intensity of the green color of the chromium ions formed as the product of the reaction between the organic pollutants and dichromate, the main interfering effect of chloride is due to the second interfering mechanism which results in false high COD readings. The chloride interference can be partly overcome by addition of mercuric sulfate to the COD vials [7]. The HR HACH COD vials used in this study contained enough mercuric sulfate to inhibit chloride interference effects of up to a concentration of 2000 mg/L.

The chloride interference has been partly overcome in the PeCOD® method by deposition of silver (I) oxide on the titanium dioxide sensor as described in a 2010 patent [49]. The principles of how this deposition blocks the chloride interference are not well understood. It is believed that oxidation is more efficient for species that are adsorbed onto the TiO_2 surface. It was hypothesized that the deposition of silver (I) oxide on the sensor makes its surface more negatively charged which impedes adsorption of chloride to it and hence prevents the organic species from having to compete with chloride over the TiO_2 reaction sites. Sensors with silver (I) oxide deposited on them tolerate chloride in cell concentrations (i.e. concentration after dilution with electrolyte) of up to 200 mg/L which corresponds to a sample chloride concentration of 2000 mg/L when operating the system in the Yellow Range as in this range the samples is diluted ten times with lithium nitrate electrolyte before being introduced to the reaction cell.

As chloride concentration greater than 2000 mg/L is a known interference for both methods, chloride concentration was monitored for all the wastewater samples. For those samples that exceeded the 2000 mg/L tolerance limit, a dilution step was used to ensure that the results were not affected by the chloride interference.

4.1.1.2 Combined Interference of Chloride and Ammonia in the Dichromate Method

Ammonia cannot be oxidized in either the dichromate method or the PeCOD® method. However, ammonia and its derivatives react with elemental chlorine which results in the production of chloride via formation of chloramine in a series of cyclic changes [5]. Wastewater from many sources contains ammonia [50]. Additionally, ammonia is generated from organic amines and other nitrogen-containing organics in the oxidation step of the dichromate method [5]. The addition of mercuric sulfate cannot mask the combined effect of chloride and ammonia especially in the application of High Range COD vials due to the high strength of the dichromate solution [5].

Although high concentrations of chloride and nitrogenous compounds are one of the main characteristics of many wastewaters such as those generated by the fish canning industry, wet lime–gypsum desulphurisation process and tanneries [50], surprisingly no information is available on the extent and the tolerance limits of the interference caused by the simultaneous presence of chloride and ammonia. The effect of the simultaneous presence of chloride and ammonia is also unknown for the PeCOD® method.

4.1.1.3 Other Inorganic Interferences in the PeCOD® Method

A variety of inorganic anions and cations are present in the wastewater generated by different industries. The effect of the presence of several of which on the PeCOD® method has been reported and is provided in the Table A-2 of Appendix A. However, the reported results are for the condition where the sample only contains a single ion while, real samples often contain several different inorganic species. No studies to date have been done on the effect of presence of a combination of inorganic species on the PeCOD® method.

In this work zinc and boron were chosen for their individual and combined effects to be studied on the PeCOD® method. The choice of the inorganic species to study was based on the 2014 historical data provided by the industrial wastewater treatment plant where the samples were obtained (the summary of the historical data is provided in Table 2 of Chapter 1). Analysis of the historical data revealed that boron and zinc were among the top ten elements present in the wastewater loads and present in over 90% of the wastewater loads received.

4.1.2 Effect of Turbidity on the PeCOD® Method

Sample turbidity has also been investigated as a potential interference for the PeCOD® method as turbid samples have high UV absorptions and this may potentially decrease the intensity of UV illumination of the TiO_2 sensor and affect the peCOD results. Suspended matter such as clay, silt, fine organic and inorganic matter, soluble colored organic compounds, and etc. all contribute to the turbidity of wastewater [7]. Table 11 compares the turbidity value for a small set of the treated (effluent) industrial wastewater samples used in this study to provide a reference for the turbidity level that was of an interest in this study. As it can be seen in Table 11 turbidity values as low as 20 NTU and as high as over 3000 NTU were recorded for the actual effluent samples.

Table 11- Turbidity of a subset of effluent samples tested in this study

Sample ID	Turbidity (NTU)
Eff-12	20
Eff-6	33
Eff-7	37
Eff-1	83
Eff-2	173
Eff-5	268
Eff-13	301
Eff-11	906
Eff-3	2,350
Eff-4	3,400

Two different kinds of turbidity were tested in this study: Turbidity caused by kaolin particles and turbidity caused by formazin (a polymer formed by reacting hydrazine sulfate and hexamethylenetetramine [51]).

4.2 Materials and Methods

4.2.1 Chloride/Ammonia Interference in the PeCOD® and Dichromate Methods

COD_{Cr} measurements were done via HACH High Range COD vials and peCOD measurements were done in the Yellow Range (i.e. COD <1500 mg/L). Standard sorbitol solutions (ThOD= 600 mg/L) with different concentrations of chloride and nitrogen were prepared by dissolving the required amounts of sodium chloride (Sigma Aldrich) and ammonium sulfate (Sigma Aldrich) in the sorbitol solution. All samples were filtered by a 45 µm dissolution filter (Thermo Scientific™ SUN-SRi™ SunFlo™ Dissolution Filters) prior to analysis.

4.2.2 Zinc and boron Interference in the PeCOD® Method

Three surrogate samples with different concentrations of zinc and boron as shown in Table 15 were prepared by dissolving zinc nitrate hexahydrate (Sigma Aldrich) and boric acid (Sigma Aldrich) in a standard sorbitol solution (ThOD= 1200 mg/L). Zinc nitrate was chosen as the source of zinc ions since nitrate is reported not to interfere with the PeCOD® method [48]. The experiments were done in the Yellow Range (i.e. COD <1500 mg/L). All samples were filtered by a 45 µm dissolution filter (Thermo Scientific™ SUN-SRi™ SunFlo™ Dissolution Filters) prior to analysis.

4.2.3 Turbidity Interference

4.2.3.1 Sample Preparation

Kaolin (aluminum silicate hydroxide) obtained from Sigma Aldrich was mixed with ultrapure water at a concentration of 10 g/L and stirred for one hour. Then it was left to rest for one day to allow for the complete hydration of the particles. The kaolin stock solution was remixed before each set of experiments. Three different turbidity levels were obtained by diluting the kaolin stock solution with standard sorbitol solution (ThOD= 600 mg/L). The diluted kaolin solutions were filtered (45 µm dissolution filter) before peCOD measurement. The peCOD reading for the diluted kaolin solution was compared against the peCOD reading obtained for the sorbitol standard solution used for making the kaolin dilution. The turbid solution and the sorbitol reference used for making the turbid solution were tested with the PeCOD® Analyzer back to back to minimize the effect of time on the system's calibration. The recipes used for making the different kaolin dilutions referred to as KS1-KS4 are provided in Table 12.

Formazin (Mixture of hexamethylenetetramine (< 1.25 %), hydrazinium (2+) sulphate (< 0.13 %) and water > 98 %) was obtained as a turbidimeter calibration standard (turbidity= 1000 NTU) from Sigma Aldrich and was diluted 25 times with ultrapure water so its COD would be in the range of the PeCOD® and dichromate methods. The peCOD and COD_{Cr} measurements were done on the diluted formazin samples once with 45 µm pre-filtration (Thermo Scientific™ SUN-SRi™ SunFlo™ Dissolution Filters) and once with 0.45 µm pre-filtration (Supor® polyethersulfone syringe filter by Pall Corporation). All peCOD measurements were done in duplicate.

Table 12- Recipes, dilution ratios and ThOD of the kaolin samples

Sample ID	Recipe	Dilution Ratio	Final ThOD (mg/L)
KS1	kaolin stock solution diluted 200 times with sorbitol solution (600 mg/L)	1/200	600
KS2	kaolin stock solution diluted 20 times with sorbitol solution (600 mg/L)	1/20	600
KS3	5 ml kaolin stock solution +20 ml water + 25 ml sorbitol solution (1200 mg/L)	1/10	600
KS4	0.012 g sorbitol dissolved directly into 20 ml of kaolin stock solution	Not Diluted	600

4.2.3.2 Turbidity and UV Absorption Measurements

Turbidity measurements were done with a 2100Q / 2100Q IS Portable Turbidimeter (HACH) per the nephelometric method instructions. Measurements of the samples UV absorption at the wavelength of 400 nm (i.e. the wavelength of PeCOD® system LED lamp) were done with a spectrophotometer (DR 3900, HACH).

4.3 Results and Discussion

4.3.1 Chloride and Ammonia Mixture Interference

After confirming that samples containing only chloride up to a concentration of 2000 mg/L and only ammonium up to a concentration of 300 mg-N/L do not affect the dichromate and PeCOD® methods, a 2^2 full factorial was used to study the effect of the simultaneous presence of chloride and ammonium on both methods. Standard sorbitol solutions (ThOD= 600 mg/L) were mixed with different concentrations of sodium chloride and ammonium sulfate and were tested with both methods. The results are presented in Table 13 in terms of error percentage for each condition. The simultaneous presence of chloride and ammonium has resulted in false high COD_{Cr} results and false low peCOD results. However, the effect is much more severe on the dichromate method. In fact, the PeCOD® method was only significantly affected at the condition with the highest concentrations of chloride and ammonium (% Error = -17 %) and the error recorded for all the other conditions is below the accepted measurement error (i.e. ± 5 %).

The simultaneous presence of chloride and nitrogenous compounds is potentially one of the main factors that resulted in the significant deviation of peCOD and COD_{Cr} results obtained for the effluent samples in the first phase of this study. As an example, the chloride concentration and the concentration of nitrogenous compounds (obtained from the OND chromatogram of the LC-OCD analysis) for an effluent sample is shown in Table 14. The COD_{Cr} and peCOD results obtained for this sample are also presented in Table 14. It can be seen that there is nearly 40 % difference in the results of the two methods that is potentially partly caused by the high chloride concentration of this samples in combination with nitrogenous compounds. The sample was diluted five times prior to peCOD and COD_{Cr} measurements. The dilution ratio has been accounted for in the presentation of the results.

Table 13- COD_{Cr} and peCOD measurement error for a standard sorbitol solution (COD_{Cr} =600 mg/L) at different concentrations of chloride and nitrogen

Nitrogen Concentration (mg/L)	Chloride Concentration (mg/L)	% Error COD_{Cr}	% Error peCOD
30	1000	4	-4
30	2000	17	-3
300	1000	12	3
300	2000	32	-17

Table 14- Chloride concentration, nitrogen concentration, COD_{Cr}, peCOD and the % difference between peCOD and COD_{Cr} for an effluent sample. Dilution ratio (DR=1/5) has been accounted for in the presentation of the data.

Nitrogen Concentration (mg/L)	Chloride Concentration (mg/L)	COD_{Cr} (mg/L)	peCOD (mg/L)	% Difference (peCOD vs. COD_{Cr})
50	4000	1915	1231.5	36 %

4.3.2 Zinc and Boron

As shown in Table A-2 of Appendix A, previous work had indicated that zinc does not interfere with the PeCOD® method. However, pervious work had only investigated in-cell (i.e. after dilution with electrolyte) concentrations of 500 mg/L and lower. In this work the effect of a higher in-cell concentration (i.e. 1500 mg/L) of zinc was investigated. Additionally, although boron was present in over 90% of the incoming samples to the plant according to the 2014 historical data, previous work has not studied its effect on the PeCOD® method. Hence it was investigated in this work both individually for in-cell concentration of 800 mg/L and also in combination with zinc.

To study the individual and combined effect of presences of boron and zinc on the PeCOD® method, surrogate samples of sorbitol solution with ThOD of 1200 mg/L containing only boron with the concentration of 8000 mg/L, only zinc with the concentration of 15000 mg/L, and both boron (8000 mg/L) and zinc (15000 mg/L) were analyzed with the PeCOD® Analyzer and the results were compared against the peCOD reading for the standard sorbitol solution (ThOD=1200 mg/L) that was used for making the samples. The peCOD reading for the standard sorbitol solution was 1158.7 mg/L. The ratio of the surrogate samples' peCOD over the standard sorbitol solution peCOD is provided in Table 15. It can be seen that the peCOD results were not significantly affected (i.e. the ratios are close to 1) even though very high boron and zinc concentrations were used. It should be noted the pH of the individual solutions of zinc and boron is slightly outside the recommended range for the PeCOD® method (i.e. 4-10), however, it has not significantly affected the results.

Table 15- peCOD, pH and sample/standard peCOD ratio for surrogate samples containing different concentrations of zinc and boron

Inorganic Species	Concentration (mg/L)	peCOD (mg/L)	pH	Ratio (Sample/Sorbitol Standard-1200 mg/L)
Boron	8000	1045.9	3.40	0.90
Zinc	15000	1125.9	3.53	0.97
Boron + Zinc	Boron (8000), Zinc (15000)	1105.5	4.38	0.95

4.3.3 Kaolin Turbidity

The COD_{Cr} measured for the stock solution of kaolin was only 120 mg/L. Since for the experiments, the stock solution was at least 20 times diluted with the sorbitol solution, the contribution of kaolin to the final COD of the samples was considered negligible.

Sorbitol standard solutions (ThOD= 600 mg/L) with different turbidity levels were analyzed with PeCOD® and compared against a standard sorbitol solution. The results are provided in Table 16. It can be seen that even at the very high turbidity level of over 14000 NTU peCOD results were unaffected (i.e. the ratio of the peCOD result for the turbid sample to that of the sorbitol standard is close to 1). The UV absorbance at the wavelength of 400 nm was also recorded in Table 16 as 400 nm is the wavelength emitted by the PeCOD® system LED lamp. As it can be seen in Table 16, UV absorbance increased with the increase in sample turbidity.

Table 16- Turbidity, UV absorbance, peCOD, sample/standard peCOD ratio for the kaolin samples

Sample ID	Turbidity (NTU)	400 nm UV Absorbance	Sample peCOD Reading (mg/L)	Sorbitol Standard peCOD Reading (mg/L)	Ratio (Sample/Sorbitol Standard- 600 mg/L)
KS1	64	0.295	573.1	573.0	1.00
KS2	856	2.363	597.9	618.5	0.97
KS3	1,570	3.452	566.8	571.9	0.99
KS4	14,200	34.37	556	540.3	1.03

4.3.4 Formazin Turbidity

As formazin is a polymer, unlike kaolin it has a significant COD and a very high COD_{Cr} reading (~ 20,000 mg/L) was observed for the 1000 NTU turbidity standard used in this study. The peCOD result obtained for the diluted formazin mixture that was filtered with a 45 µm filter was 20 % lower than the COD_{Cr} result obtained for the same sample. However, it could not be concluded from the results of that experiment whether the difference in the peCOD and COD_{Cr} results is due to the turbidity of the sample since formazin is a macromolecule with a complex chemical structure that might not undergo complete oxidation in the PeCOD® method according to the findings of section 3.3.1. To further investigate the effect of formazin turbidity, the sample was filtered with a 0.45 µm filter. This filtration step reduced the turbidity of the sample to near zero. However, the difference between the peCOD and COD_{Cr} results remained unchanged which indicates that the lower peCOD results were not due to the turbidity of the sample (Table 17). Note that the peCOD measurement cannot be done for unfiltered samples as they may potentially clog the system. Hence, no peCOD results are shown for the unfiltered formazin sample. The COD_{Cr} result for the unfiltered formazin sample is provided for comparison with the COD_{Cr} results for the filtered formazin samples. It can be concluded that the effect of 45 µm filtration has been insignificant on the COD_{Cr} result, while the 0.45 µm filtration have had a significant effect on it.

Table 17- Effect of filtration on turbidity, peCOD and COD_{Cr} of 25 times diluted formazin sample

Starting Material	Dilution Ratio	Filter	Turbidity (NTU)	peCOD Result 1 (mg/L)	peCOD Result 2 (mg/L)	peCOD Average (mg/L)	COD_{Cr} (mg/L)	% Difference (peCOD vs. COD_{Cr})
Formazin (1000 NTU)	1/25	No Fil.	42	Not Tested	Not Tested	Not Tested	938	Not Tested
Formazin (1000 NTU)	1/25	45 µm	37	724.4	751.2	737.8	902	20
Formazin (1000 NTU)	1/25	0.45 µm	0.48	726.6	722.6	724.6	897	19

The experiments with the surrogate samples of kaolin and formazin indicated that samples turbidity does not affect peCOD results. This is in agreement with findings of Zhang et al. [52], who reported that sample color does not have a significant effect on peCOD measurement. They hypothesized this feature to be due to the application of the thin-cell (i.e. cell thickness=0.1 mm) since UV light absorption has a very small light path in that setting. According to the Beer-Lambert law as shown in Equation (5), the light path (distance between the inner faces of the sample cell) directly affects the sample UV-absorption and when it is sufficiently small, even samples containing UV-absorbing analytes at high concentrations would not have a significant UV-absorption. Reduction in absorption of UV light as the photoelectrocatalytic mineralization propagates was also identified as another potential explanation by Zhang et al. [52].

$$A = E \times b \times C \qquad (5)$$

A: Absorbance at a particular wavelength λ (AU)

E: Molar absorption coefficient of the analyte (L/(mol.cm))

b: Optical path length (cm)

C: Analyte concentration (mol/L)

4.4 Conclusions

It can be concluded that the dichromate method is not suitable for analysis of wastewater samples that contain high concentration of both chloride and ammonia. The PeCOD® method could potentially be used as an alternative that yields more accurate results. However, more experiments at different concentrations of chloride, nitrogen and organic pollution and also experiments with other nitrogenous compounds are required to confirm this.

Boron and zinc do not affect PeCOD® method neither when they are present in the samples individually or together. Future work should investigate the effect of other inorganic species commonly present in untreated (incoming) industrial wastewater samples such as iron and phosphorous.

The effect of sample turbidity on the PeCOD® method was investigated with two different sources of turbidity. It was shown that peCOD results were unaffected by the turbidity caused by kaolin and formazin. Turbidity measurement is often used for estimating the suspended solid concentration of wastewater samples. It should be noted that the results of this study do no indicated that PeCOD® is capable of measuring the COD contribution of wastewater samples' suspended solids. The results only indicate that turbidity caused by components that pass through a 45 µm filter that do not contribute to the COD content of the sample, do not interfere with the PeCOD® method.

Lastly it should be noted that other inorganic sources of turbidity not studied in this work might interfere with the PeCOD® method not due to their turbidity effect but by other mechanisms.

Chapter 5. Combining LC-OCD Analysis with Design-Of-Experiments Methods to Optimize an Advanced Oxidation Process for the Treatment of Industrial Wastewater

Declaration of academic achievement: The majority of this work has been submitted to the Canadian Journal of Chemical Engineering to be considered for publication. (K. Aghasadeghi, M. Csordas, S. Peldszus, D.R. Latulippe, The Canadian Journal of Chemical Engineering (CJCE-16-1052).

5.1 Introduction

Advanced oxidation (AO) is a non-selective treatment process that uses the strong oxidizing power of chemical radicals such as the hydroxyl radical for complete or partial mineralization of organic contaminants [53]. AO processes are frequently used in industrial wastewater treatment for breaking down the non-biodegradable contaminants as part of the pre-treatment and 'polishing' steps of biological treatment processes [53]. There are multiple types of AO processes including those based on Fenton's reaction such as photo-Fenton reaction [20][54], electro-Fenton reaction [55], and sono-Fenton reaction [56]. The Fenton process is based on the generation of hydroxyl radicals from hydrogen peroxide at acidic pH in the presence of ferrous ions [20]. The principal reaction of the Fenton's process is shown below as Equation (6):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot \qquad (6)$$

However, there is actually a total of nine reactions involved in the process [56]. The simplicity of the Fenton process reaction, in addition to no energy input requirements and short reaction time [57], has made it an attractive ‘polishing’ treatment step. Also, it is a robust process that can achieve a high treatment efficacy for many different compounds 58]. The main disadvantage of the Fenton process is the high operational costs due to the use of expensive reagents [56][57]. Thus, there exists a strong need to optimize the reaction conditions to obtain the best treatment for a given cost.

Maintaining the treatment process efficacy to meet discharge regulations is very challenging at the specialized treatment facilities that treat tanker truck shipments of wastewater from multiple industrial, manufacturing, and commercial facilities as typically the composition of the incoming feed to the process changes with each shipment from a different facility.

To the best of my knowledge, only one previous study has been done on optimizing the AO conditions for wastewater loads from multiple sources. Bianco et al. [58], studied COD removal via the Fenton’s reaction on wastewater samples which had a wide range of initial COD and were very diverse in composition. These samples were obtained from an industrial wastewater treatment plant that treated wastewater from different industries. The percent removal of COD was determined for different ratios of the reaction reagents.

One of the challenges faced in the optimization of AO processes for application in wastewater treatment plants with dynamically varying incoming loads is the initial characterization of the wastewater composition. Neither of the approaches in the two categories of studies mentioned above is appropriate; bulk measurements (e.g. COD, BOD, TOC) tell the researcher nothing about the initial composition or changes in composition post-treatment and it is not feasible to use advanced analytical techniques (e.g. GC, HPLC, LC-MS) to identify specific contaminants due to the high level of contamination and complex matrices of the incoming wastewater. Thus, an alternative method was sought for in this study.

Given the usefulness of the LC-OCD method as a characterization tool as discussed in the first chapter, it was used in this work to study the effect of sample composition on Fenton treatment COD removal efficiency for two industrial wastewater samples that are sufficiently distinct in composition. A statistical design-of-experiment (DOE) strategy was used to vary the Fenton reaction process conditions. It was found that the combination of LC-OCD and DOE methods is an effective strategy for optimizing AO treatment efficiency by providing information on the different mechanisms of COD removal that take place during the treatment.

5.2 Materials and Methods

5.2.1 Wastewater Sample Source

The experiments of this study were done on two industrial wastewater samples (hereafter referred to as wastewater 1 and wastewater 2) that were provided by the research team at Aevitas (Brantford, Ontario, Canada). Both of the samples had undergone a preliminary treatment for partial removal of large particulate matter and insoluble oils. The Aevitas facility receives and treats loads of wastewater that are generated by a wide variety of industrial and commercial facilities. In order to ensure that the two samples were of significantly different composition, they were collected from the plant approximately one month apart. Exact details on the original source of the two samples are not available. Basic properties of the two samples are listed in Table 18; the initial COD (COD_i) was measured using HACH High Range COD vials as per the manufacturer's instructions and the pH was measured using a sympHony™ SB20 meter (VWR). The samples were stored at 4 °C and the experiments were conducted in less than one week from the date of sample collection.

Table 18- Properties of the as-received industrial wastewater samples from Aevitas

Sample	COD (mg/L)	pH
Wastewater 1	2700	8.4
Wastewater 2	4000	6.0

5.2.2 Experimental Procedure

A schematic summary of the experimental procedure is shown in Figure 26. The advanced oxidation experiments were conducted at room temperature in 150 mL glass beakers using just 50 mL of the wastewater sample for each experimental condition. The vessel from which the sample was withdrawn was continuously stirred to ensure that a reproducible sample is aliquoted into each beaker. All treatment conditions were conducted in duplicates. The first step was to lower the pH of the as-received wastewater sample to 3.0 (± 0.1) via the addition of 1 M hydrochloric acid (Sigma Aldrich); it has been previously reported that the optimal results are achieved at this low pH condition [56].

The COD removal efficiency of the Fenton's reaction was determined using the two independent factors S and R that are defined by Equations (7) and Equation (8):

$$\text{S:}\ \frac{\mathrm{H_2O_2}\text{Molar Concentration (mM)}}{\text{W}astewater\ COD\ \text{(mg/L)}} \qquad (7)$$

$$\text{R:}\ \frac{\mathrm{H_2O_2}\ \text{Molar Concentration (mM)}}{\mathrm{Fe^{2+}}\ \text{Molar Concentration (mM)}} \qquad (8)$$

As shown in Figure 26, a central composite design (CCD) in the form of a 2^2 full factorial with two extra face points (at ±1,0) was used in this study; the axial points were located at (0, ±α) and (±α, 0) where α, the coded unit distance of the axial points from the center point, was chosen to be 1.4. Thus, a total of 11 different treatment conditions were investigated for both of the wastewater samples that were studied in this work. The coded and real values of the S and R factors and their associated molar concentrations of reagents used in different treatment conditions are presented in Table 19. The coded values represent the real values after being centered and scaled.

A fresh solution of 50 g/L ferrous sulfate heptahydrate (Sigma Aldrich) in ultrapure water (obtained from a Millipore Milli-Q system) was prepared for each set of oxidation tests. The ferrous sulfate heptahydrate solution was added to each beaker based on the corresponding S and R values – refer to Table 19. After the ferrous sulfate heptahydrate solution had been added to all of the beakers, 35 wt% hydrogen peroxide (BDH) was added to each beaker to begin the reaction. The volume of hydrogen peroxide added to each beaker was based on the corresponding S value – refer to Table 19. The molar concentrations of H_2O_2 and Fe^{2+} based on the moles of reagent available per volume of the sample are provided in Table 19.

The reaction time was kept fixed at one hour. A basic solution of 50 wt% sodium hydroxide (Sigma Aldrich) was added to each beaker until the contents had reached a pH greater than 8. This step was required for three different reasons: it stopped the oxidation reaction, it caused the iron to precipitate out into a sludge, and it deactivated any residual H_2O_2 that could potentially interfere with the subsequent analysis steps. The samples were again left for one hour to allow the iron precipitates to settle to the bottom of the beaker. Multiple aliquots of the clear supernatant layer were used for the final COD measurement (COD_f), using the same HACH High Range COD vials, and the LC-OCD analysis (see Figure 26); the COD measurements were done in duplicate. The dilution effect (dilution factor <1.7) associated with the addition of different volumes of the ferrous sulfate heptahydrate and hydrogen peroxide solutions was considered in the COD_f determination.

The percentage removal of COD, as defined by Equation (9), was chosen as the objective function.

$$\%\ \text{COD Removal} = \frac{\text{COD}_\text{i} - \text{COD}_\text{f}}{\text{COD}_\text{i}} \times 100 \qquad (9)$$

Table 19- Coding values and associated molar concentrations of reagents used in different treatment conditions

S		**R**		**Wastewater 1**		**Wastewater 2**	
Coded Value	Real Value: H_2O_2 (mM)/ COD(mg/L)	Coded Value	Real Value: H_2O_2 (mM)/ Fe^{2+} (mM)	H_2O_2 (mM)	Fe^{2+} (mM)	H_2O_2 (mM)	Fe^{2+} (mM)
-1	0.1	0	10	270	27	400	40
+1	0.2	+1	15	540	36	800	53
-1	0.1	+1	15	270	18	400	27
+1	0.2	0	10	540	54	800	80
-1	0.1	-1	5	270	54	400	80
+1	0.2	-1	5	540	108	800	160
0	0.15	0	10	405	41	600	60
0	0.15	1.4	17.05	405	24	600	35
0	0.15	-1.4	2.95	405	137	600	203
-1.4	0.080	0	10	216	22	320	32
1.4	0.22	0	10	594	59	880	88

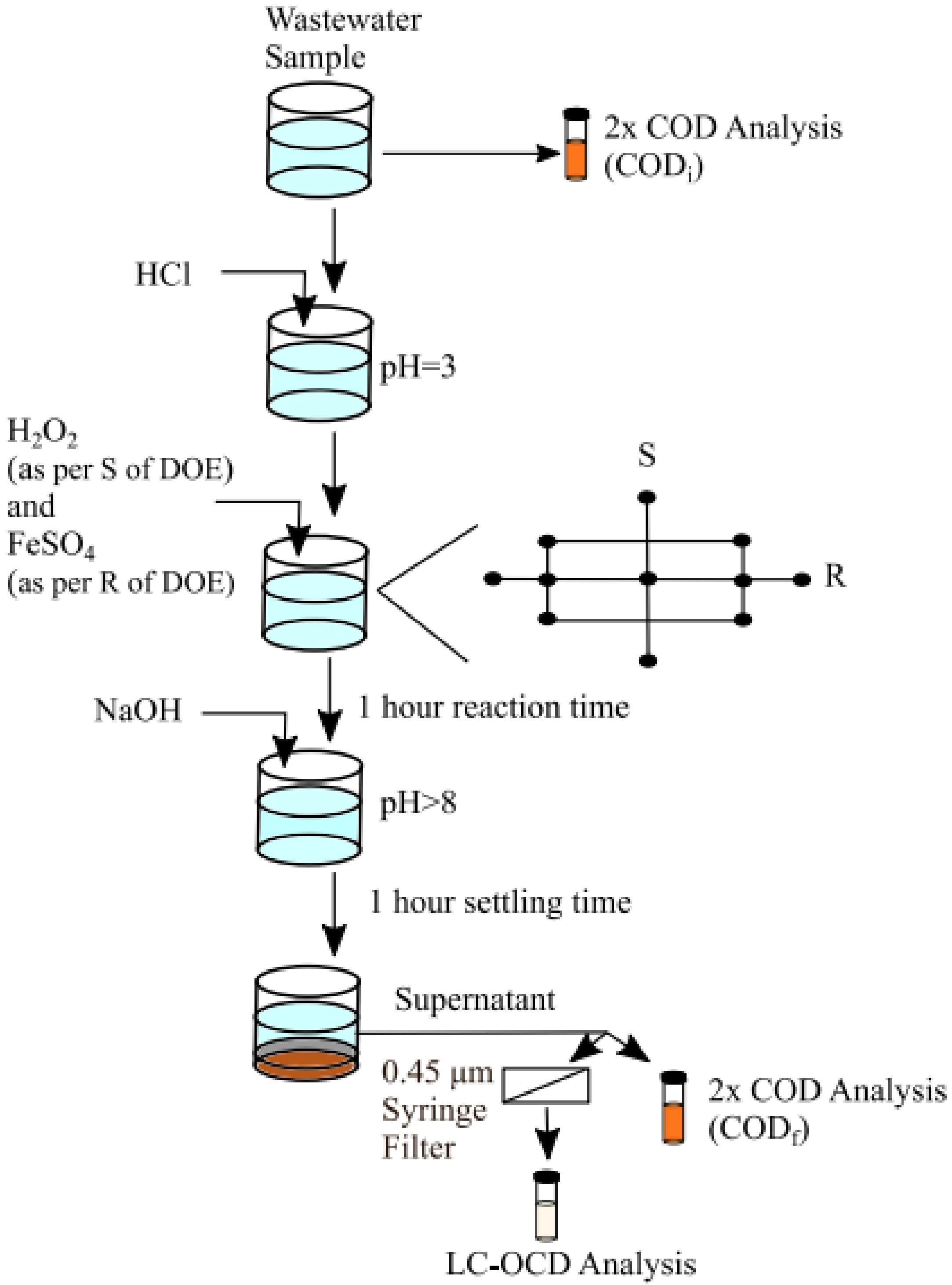


Figure 26- Schematic of the experimental workflow for the wastewater samples including the various analytical tests that were performed.

5.2.3 Liquid Chromatography – Organic Carbon Detection (LC-OCD)

The supernatant of the treated samples was collected in a plastic syringe and then passed through a 0.45 µm Supor® polyethersulfone syringe filter (Pall Corporation) into a TOC clean glass vial. The filters were pre-rinsed by passing approximately 20 mL of ultrapure water through them and then dried by passing air through them. Due to their high dissolved organic carbon (DOC) content all samples had to be diluted 50-500 times with ultrapure water before the LC-OCD analysis. Samples were analyzed using the LC-OCD system (from DOC-LABOR Huber) at the University of Waterloo. A detailed description of the working principle and operation of the LC-OCD instrument has been given in previous works [31][59]; see Figure 6 for a schematic illustration of the LC-OCD system. PEG standards from (Sigma Aldrich) were used to characterize the fractionation range of the size exclusion column according to the OCD signal. In this study, only the chromatograms from the OCD were analyzed since the study focused on COD reduction and not the removal of nitrogenous and aromatic compounds that can be studied via the OND and UVD chromatograms respectively.

The chromatograms were analyzed using the ChromCALC software that is provided by the manufacturer of the LC-OCD instrument. The software accounts for the dilution factor of each sample. The dilution effect (dilution factor <1.7) associated with the addition of different volumes of the ferrous sulfate heptahydrate and hydrogen peroxide solutions was also considered in the presentation of the chromatograms.

5.3 Results and Discussion

5.3.1 Comparison of LC-OCD Chromatograms for the Industrial Wastewater Samples

The organic carbon detector (OCD) chromatograms for the LC-OCD analysis of the two industrial wastewater samples as received from the research team at Aevitas (Brantford, Ontario, Canada) are shown in Figure 27. The chromatograms are quite different, especially at the longer retention times. For example, the large peak at a retention time of approximately 80 minutes for the wastewater 2 sample constitutes about 60% of its overall DOC content; no such peak was measured for the wastewater 1 sample. Thus, the two samples were good candidates for the optimization study of an advanced oxidation treatment process. The original development of the LC-OCD analytical method focused on water samples from natural sources and thus the regular occurrence of specific peak patterns in the resulting chromatograms were assigned to particular organic matter fractions (e.g. biopolymers, humic substances, low molecular weight acids) [31]. However, those categories are not suitable for the industrial wastewater samples used in this study given their radically different source. Therefore, the interpretation of the chromatograms was done by partial reliance on the LC-OCD calibration with PEG standards. The retention times of three of the PEG standards are shown on the x-axis of Figure 27 as a reference while the complete calibration data (for molecular weight range from 0.2 to 20 kDa) is provided as Appendix A (Table A-3). The retention time of the dominating peak in wastewater 2 is outside the PEG calibration range and based on the calibration it can only be concluded that the apparent molecular weight for this peak is smaller than 0.2 kDa. Ruhl et al. [60] demonstrated that the retention time of low molecular weight organics is not governed by the molecular weight but by the chemical structure and functional groups.

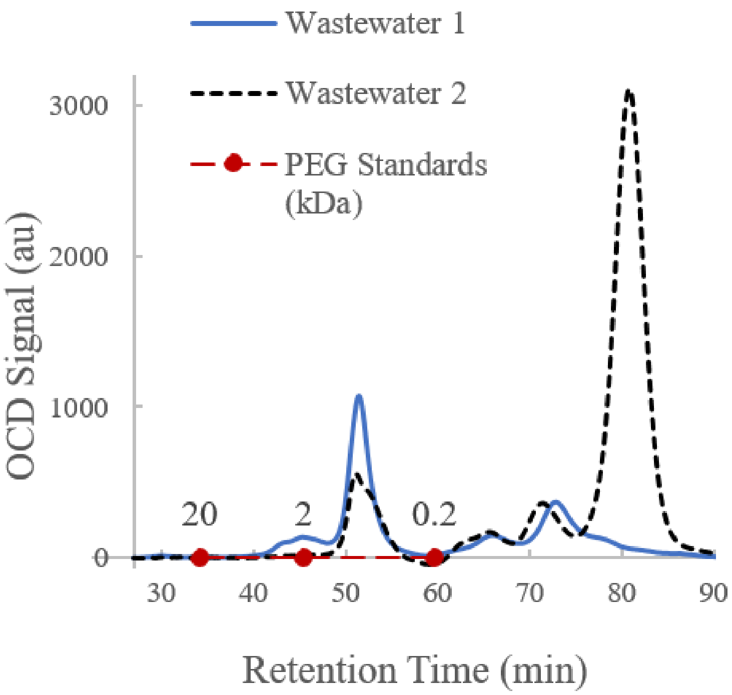


Figure 27- Comparison of the LC-OCD chromatograms for the two wastewater samples that were used in this study; the solid and dashed lines correspond to wastewater 1 and wastewater 2 respectively. Dilution factors are accounted for in the plot. The peak retention times associated with the molecular weight (kDa) of three PEG standards are shown on the x-axis for comparison; note that a total of eleven PEG standards were actually used to calibrate the LC-OCD system.

5.3.2 Statistical Analysis of COD Removal via Advanced Oxidation Treatment

The percent removal of COD was calculated for each of the eleven treatment conditions in the DOE method with the results shown in Figure 28 and Figure 29.

For wastewater 1 (Figure 28), the different treatment conditions resulted in a wide range of percent COD removals with the lowest COD removal (36%) at condition (-1, +1) and the highest COD removal (82%) at condition (+1, -1). For wastewater 2 (Figure 29), there is less variation in the percent COD removals achieved compared to wastewater 1 as some very different treatment conditions have resulted in similar COD removals. For this wastewater the lowest COD removal (31%) was at (-1.4, 0) and the highest COD removal (54%) was at condition (- 1, 0) and (-1.4, 0). Additionally, significantly different percent COD removals were achieved for the two wastewaters at the same treatment conditions. For instance, at (0, -1.4) the COD removal for wastewater 1 was 79% but for wastewater 2 it was only 48%. Comparison of the results at same treatment conditions for the two samples indicates that the optimum treatment conditions are significantly different for the two samples.

To further study the results a second order regression model was applied to both data sets and the suitability of each term in the model was determined using R software [61]. The statistical significance of the coefficients was determined based on their 95 % confidence interval (CI). If a coefficient's confidence interval did not span zero it was considered statistically significant and if it spanned zero symmetrically it was considered statistically insignificant. For coefficients that their confidence interval spanned zero asymmetrically, in order to determine their statistical significance more experimental results are required. As shown in Table 20, for the wastewater 1 sample both of the first order terms (i.e. S and R) have a significant effect on COD removal. The best treatment conditions in terms of COD removal were obtained at higher S values (i.e. higher H_2O_2

concentrations) and lower R values (i.e. lower H_2O_2/Fe^{2+}ratios). This observation is in good agreement with previous studies [23][62]. The second order term of S and the interaction term (i.e. S^2 and SR) have confidence intervals that span zero asymmetrically. The second order term of R (i.e. R^2) was determined to be statistically insignificant based on its relatively symmetric confidence interval. Therefore, a slightly simpler regression model without the second order term of R (i.e. R^2) was applied to the same set of COD removal results with the results shown in Table 21. The associated contour plots based on those model coefficients are displayed in Figure 28 with the contour line values shown in italics.

Table 20- Coefficients and 95 % confidence intervals of second order regression model of the COD removal results shown in Figure 28 and Figure 29.

	Wastewater 1		Wastewater 2	
Coefficient	Value	95% CI	Value	95% CI
Intercept	63.12	(59.02, 67.21)	47.80	(44.74, 50.86)
S	12.60	(11.06, 14.15	7.58	(6.43, 8.74)
R	-12.54	(-14.27, -1.82)	-0.81	(-2.1, 0.48)
SR	2.12	(-0.31, 4.54)	1.75	(-0.07, 3.57)
S^2	-2.71	(-5.48, 0.05)	-2.58	(-4.65, -0.51)
R^2	-0.65	(-3.11, 1.82)	0.66	(-1.18, 2.51)

Table 21- Coefficients and their 95% confidence intervals for the final regression model of the COD removal results shown in Figure 28 and Figure 29.

	Wastewater 1		Wastewater 2	
Coefficient	Value	95% CI	Value	95% CI
Intercept	60.27	(59.83, 64.69)	48.68	(46.85, 50.51)
S	12.61	(11.10, 14.11)	7.58	(6.45, 8.72)
R	-12.54	(-14.23, -10.86)	- 0.81	(-2.08, 0.46)
SR	2.12	(-0.25, 4.49)	1.75	(-0.04, 3.54)
S^2	-2.29	(-4.46, -0.11)	-3.02	(-4.66, -1.38)

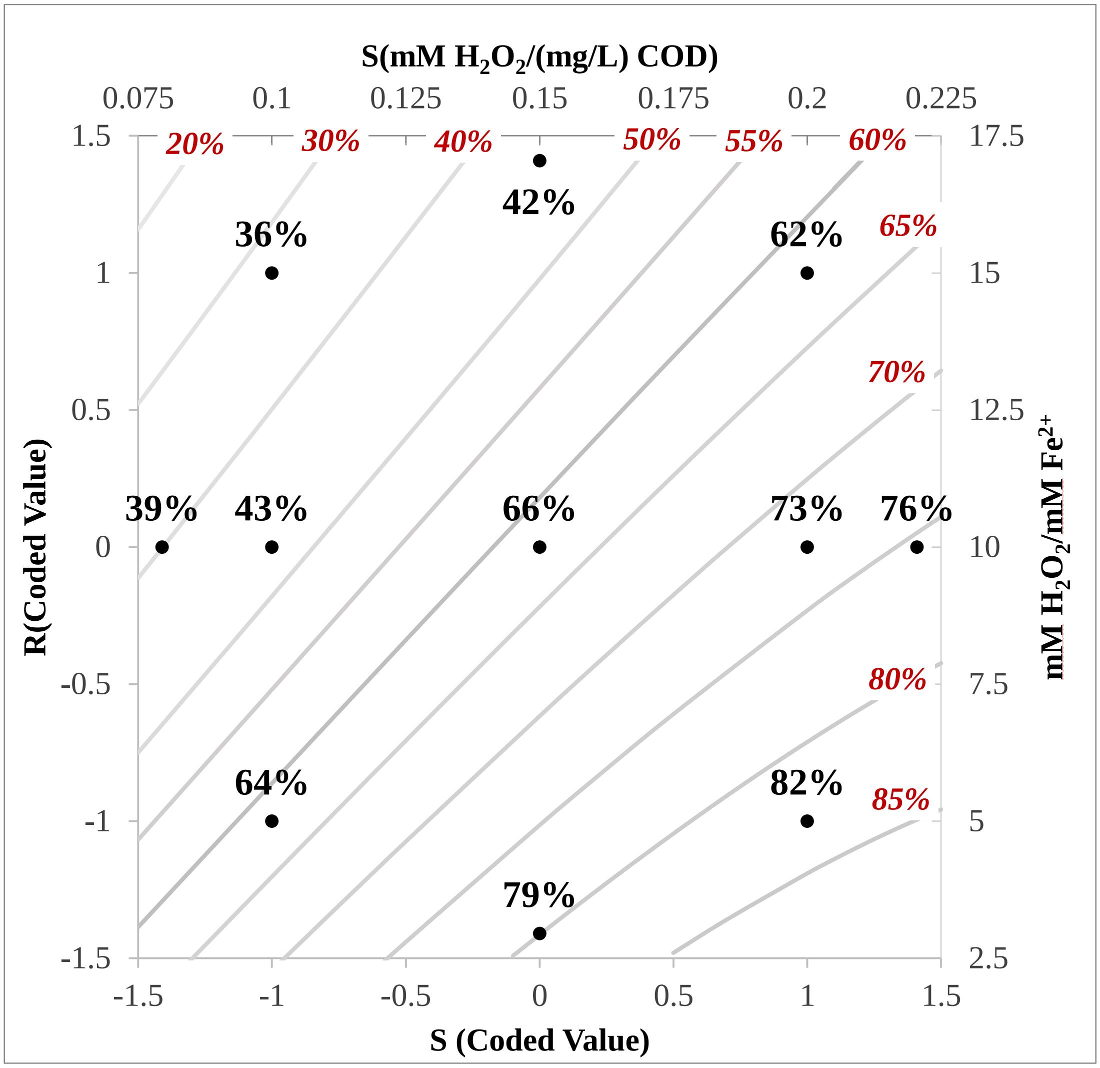


Figure 28- Contour plots of percent removal of COD as a function of the S and R coded values in the CCD (2^2 full factorial with two extra face points at (±1,0)) for wastewater 1. The associated contour plots were generated based on the model coefficients in Table 21 with the contour line values are shown in italics. The bottom x-axis and left side y-axis display the coded S and R values respectively; the top x-axis and right side y-axis display the ratios of reagents. The actual molar concentrations are given in Table 19.

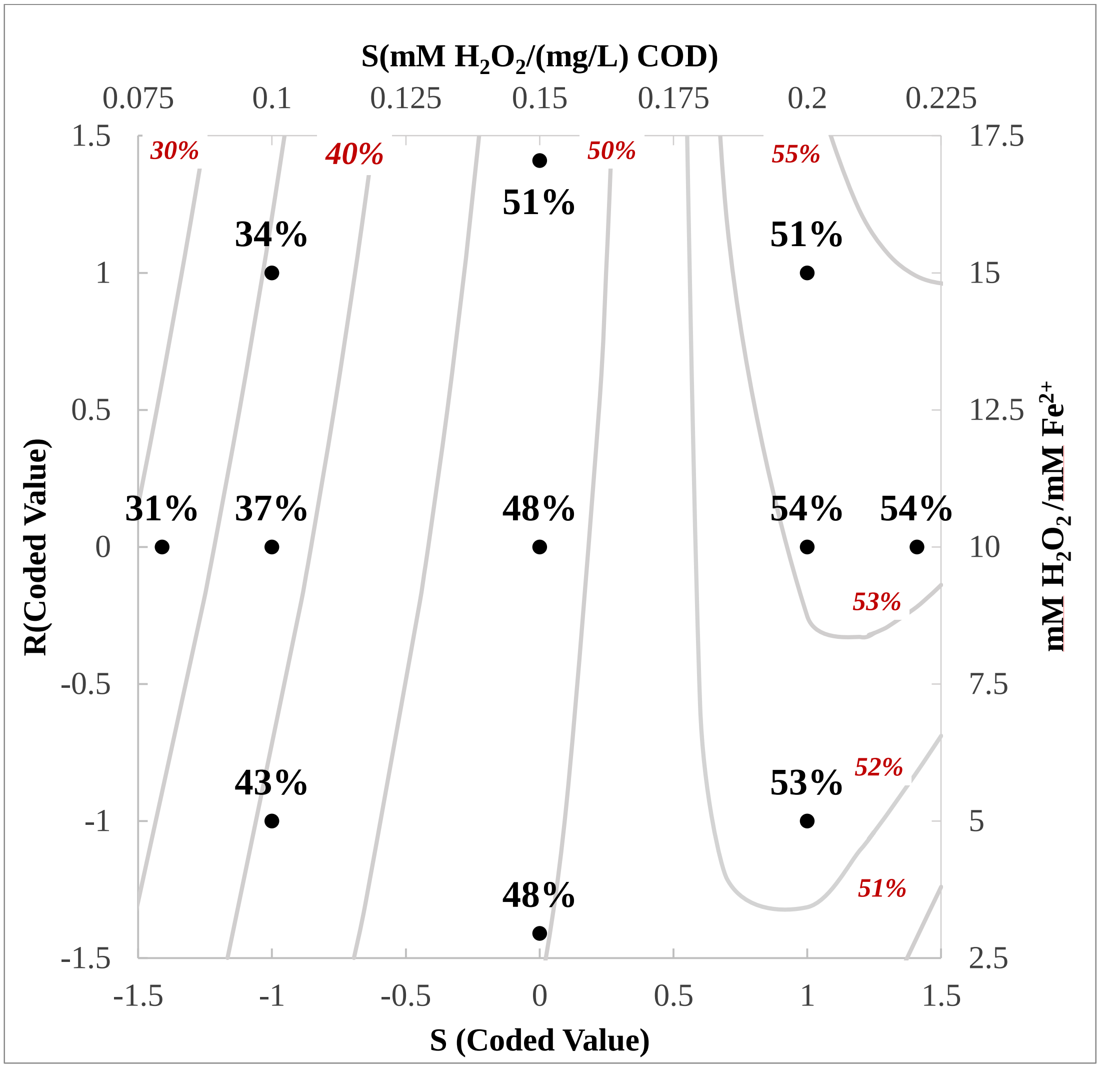


Figure 29- Contour plots of percent removal of COD as a function of the S and R coded values in the CCD (2^2 full factorial with two extra face points at (±1,0)) for wastewater 2. The associated contour plots were generated based on the model coefficients in Table 21 with the contour line values are shown in italics. The bottom x-axis and left side y-axis display the coded S and R values respectively; the top x-axis and right side y-axis display the ratios of reagents. The actual molar concentrations are given in Table 19.

As shown in Table 20, for the wastewater 2 sample, the first order term of S has a significant effect on COD removal and best treatment conditions in terms of COD removal were obtained at higher S values (i.e. higher H_2O_2 concentrations). However, the first order term of R has a confidence interval that spans zero asymmetrically and its magnitude is much smaller compared to that of S which indicates that the effect of H_2O_2/Fe^{2+}ratio is not as significant as the effect H_2O_2 concentration on the COD removal results. Similar to the wastewater sample 1 the second order term of S and the interaction term (i.e. S^2 and SR) have confidence intervals that span zero asymmetrically and the second order term of R (i.e. R^2) has an statistically insignificant effect. Therefore, similar to wastewater 1 sample a slightly simpler regression model without the second order term of R (i.e. R^2) was applied to the same set of COD removal results with the results shown in Table 21; the associated contour plots based on those model coefficients are displayed in Figure 29 with the contour line values shown in italics.

The main difference between the regression models obtained for the two wastewater samples is the magnitude of the first order term of R. The experimental results obtained for the wastewater 2 sample indicate that the R value had only affected the results at the low level of the S factor and unlike wastewater 1 sample at higher concentrations of H_2O_2 higher concentrations of Fe^{2+} have not enhanced the COD removal. This might be due the higher initial COD of the sample and/or the differences in the constituents of the two wastewaters as indicated by the LC-OCD chromatograms.

The statistical analyses presented above indicate that a universal model cannot be applied to predict treatment efficiency for wastewaters from different sources. Bianco et al. [58] addressed this issue by developing different models for different COD ranges. However, the two wastewater samples used in this study were in the same COD range and therefore LC-OCD analysis of the treated samples was integrated into the experimental workflow.

5.3.3 Comparison of LC-OCD Chromatograms for post-Advanced Oxidation Treatment

The key process steps involved in the Fenton reaction are to first adjust the pH to acidic conditions (pH ~ 3 to 4) and then to add the hydrogen peroxide and ferrous sulfate. The first step is important as it enables the activation of hydroxyl radicals and prevents the precipitation of ferric hydroxide out of solution [63]. A series of control experiments involving both of those process steps were conducted to determine their possible effects on the LC-OCD analysis.

Both of the as-received wastewater samples were subjected to the exact same pH-adjustment step (i.e. decrease pH to 3 for one hour then raise the pH to above 8) that was used for each treatment condition in the DOE setup. As shown in Figure 30, the LC-OCD analysis showed that the two samples had very different responses to the pH-adjustment step. For the wastewater 1 sample (shown in panel a of Figure 30), the positions of the peaks were the same but the size of the peaks increased. Specifically, the size of peak 1 increased by approximately 40%; it is hypothesized that this result is due to the transformation of particulate matter into dissolved DOC [37]. For the wastewater 2 sample (shown in panel b of Figure 30), the change in the chromatogram was much more drastic. Specifically, the pH-adjustment step transformed the one large peak at a retention time of 80 minutes into two peaks at lower retention times of 51 minutes (denoted as 1) and 62 minutes (denoted as 2). It is hypothesized that this result is due to the aggregation of small molecules as has been previously reported for humic substances [64]. Additionally, the pH-adjustment step resulted in a 15% increase in the DOC content of the sample. Thus, it is quite apparent that the pH adjustment step affects different samples in different ways; future work will explore in greater detail the exact mechanism of pH-adjustment effects. All of the subsequent comparisons of the different AO treatment conditions in the DOE setup will be made to the control pH-adjusted samples in order to isolate the effects of the actual AO treatment condition.

Control experiments were also carried out to determine whether hydrogen peroxide and ferrous sulfate cause any signal in the LC-OCD chromatograms. This was achieved by obtaining the LC-OCD chromatograms for each of these chemicals at the concentrations used in the center condition (i.e. S=0, R=0) of wastewater 1 respectively. It was observed that the signal caused by these chemicals in the OCD chromatograms is negligible.

Another control experiment was carried out to investigate whether the combination of all the treatment chemicals (i.e. hydrogen peroxide, ferrous sulfate, hydrogen chloride and sodium hydroxide) results in a signal in the LC-OCD chromatograms. The treatment chemicals were added to ultrapure water at the same concentrations used in the center condition (i.e. S=0, R=0) of wastewater 1 sample and the LC-OCD chromatogram was obtained for the mixture. A comparison the OCD chromatogram of the control experiment with the chromatogram of the center condition of wastewater 1 sample is provided in the Appendix B (Figure A-3). The two chromatograms seem to share a peak (i.e. peak 3) which is present in few of the treated chromatograms of wastewater 1 sample. It can be concluded that peak 3 is likely a signal caused by the treatment chemicals.

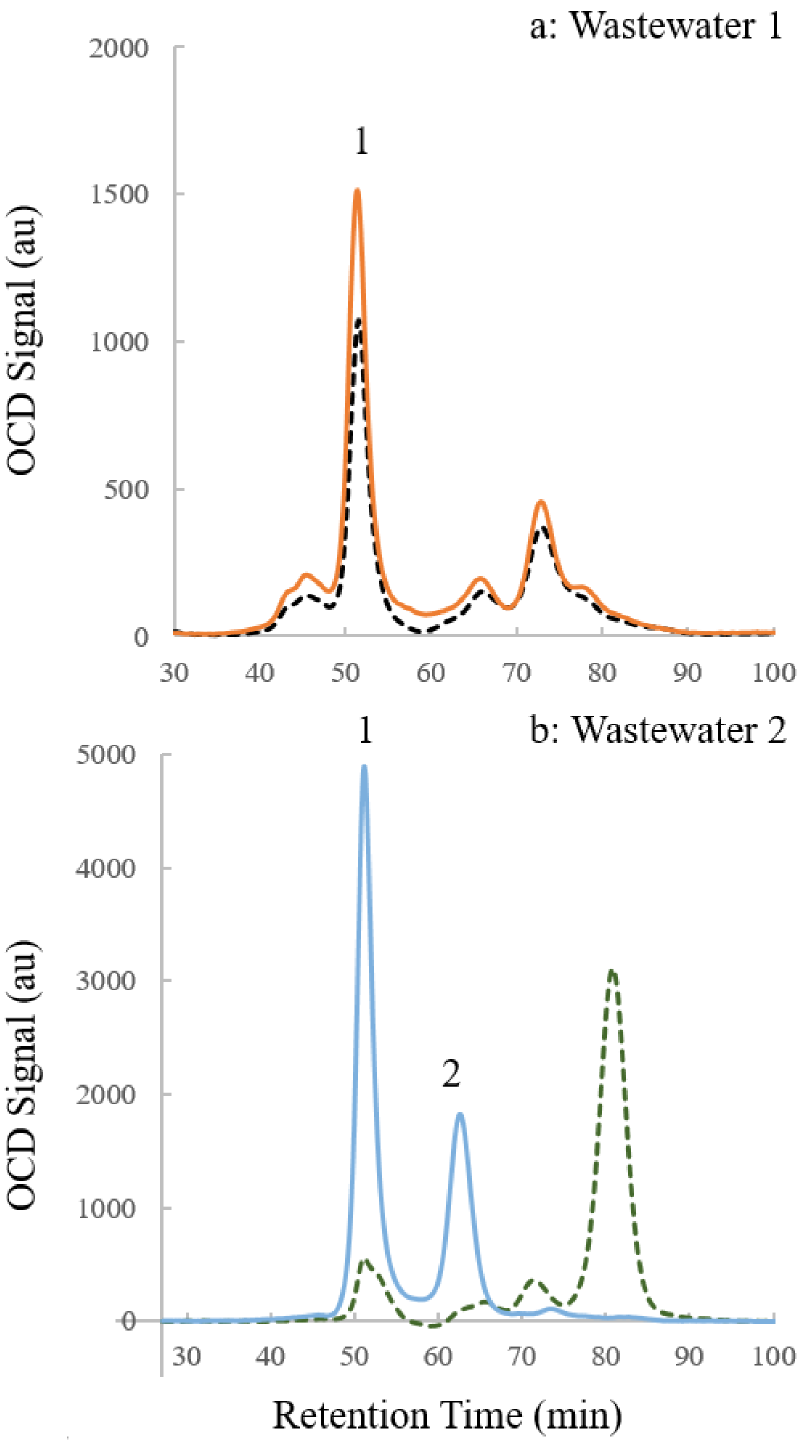


Figure 30- Comparison of LC-OCD chromatograms for the as-received samples (dashed line) and post-pH adjustment of the as-received samples (solid lines) for both wastewater 1 (panel a) and wastewater 2 (panel b).

As shown in Figure 26, the LC-OCD analysis was run for the supernatant from all eleven treatment conditions in the DOE method. However, I chose to present the LC-OCD chromatograms for a subset of the full experimental design. The LC-OCD chromatograms for wastewater sample 1 are shown in Figure 31. Each panel corresponds to a specific S and R condition as indicated in the panel legend; the percent COD removal is also given in the panel legend. The six panels are arranged strategically to match the arrangement of the S = 0.1 and S = 0.2 conditions in the DOE setup that was originally presented in Figure 28. Note that these six conditions actually span the full range of percent COD removal (36% to 82%) that was found over the entire DOE method.

The LC-OCD chromatogram for each treated sample was divided into two sections – peaks with retention times greater than 60 minutes and those with retention times less than 60 minutes.

For the first section, it was found that the peak size consistently decreased across all treatment conditions. However, the magnitude of the decrease in peak size varied across the different treatment conditions. As shown in Figure 32, it was found that the magnitude of this reduction (determined by LC-OCD analysis) was well correlated with the percent COD removal (determined via the HACH test kits). It should be noted that as the COD measurements were done on unfiltered samples, three different mechanisms contributed to the overall COD removals reported in this study: 1- Decomposition of particulate organics to dissolved organics 2. Decomposition of dissolved organics to products with higher oxidative levels compared to the original dissolved organics 3- Complete mineralization of the dissolved organics [63]. However, LC-OCD cannot measure particulate organic material since all samples had to be filtered (0.45 µm filter) prior to LC-OCD measurement. Additionally, only complete mineralization results in decrease in DOC.

For the second section, it was found that the peak sizes changed based on the specific treatment condition. For those conditions that achieved COD removals less than 70% (i.e. panels a, b, c, e), a ‘shoulder peak’ appeared on peak 1. The appearance of this peak was somewhat unusual as it was not present in the starting sample. In fact, this observation is supported by the other five LC-OCD analyses for the center point condition (0,0) and the four axial point conditions (0, ±1.4; ±1.4, 0) in the DOE method; refer to the Appendix B (Figure A-4). A previous study reported a similar observation related to the treatment of surface water containing natural organic matter and attributed it to the decomposition of particulate matter [37]. For those conditions that achieved COD removals greater than 70% (i.e. panels d, f), it is hypothesized that a two-stage process occurred during the AO treatment as follows – first the particulate matter was decomposed (as mentioned above) and then that material was further broken down. The extent of decomposition of the species represented by peaks 1 and 2 is also affecting the overall COD removal but the relationship is not as straightforward since two different COD removal mechanisms are affecting the size of these two peaks. At the treatment conditions that have yielded high COD removals, i.e. condition d and f, not only particulate matter has been decomposed into species represented by peaks 1 and 2 but these newly formed species have also been further decomposed to smaller species, hence smaller peaks 1 and 2 correspond to a higher COD removal (Compare conditions d and f). However, at the conditions with low COD removals, i.e. condition a and c, smaller peak 1 and peak 2 sizes indicate that less amount of particulate organics has been decomposed into soluble matter and hence the smaller peak sizes correspond to lower COD removal. (Compare conditions a and c)

Peak 3 is a signal caused by the treatment chemicals added to the sample. This was determined by obtaining the OCD chromatogram for a control experiment were the treatment chemicals were added to ultrapure water. The OCD chromatogram for the control experiment is provided as Appendix B (Figure A-3).

A schematic summary of the proposed mechanism of COD removal in wastewater 1 is provided in panel a of Figure 33. Clearly, the integration of the LC-OCD analysis into the optimization of AO treatment processes has yielded valuable information about the fate of different species involved in the treatment process, however further research is needed to validate the proposed mechanisms.

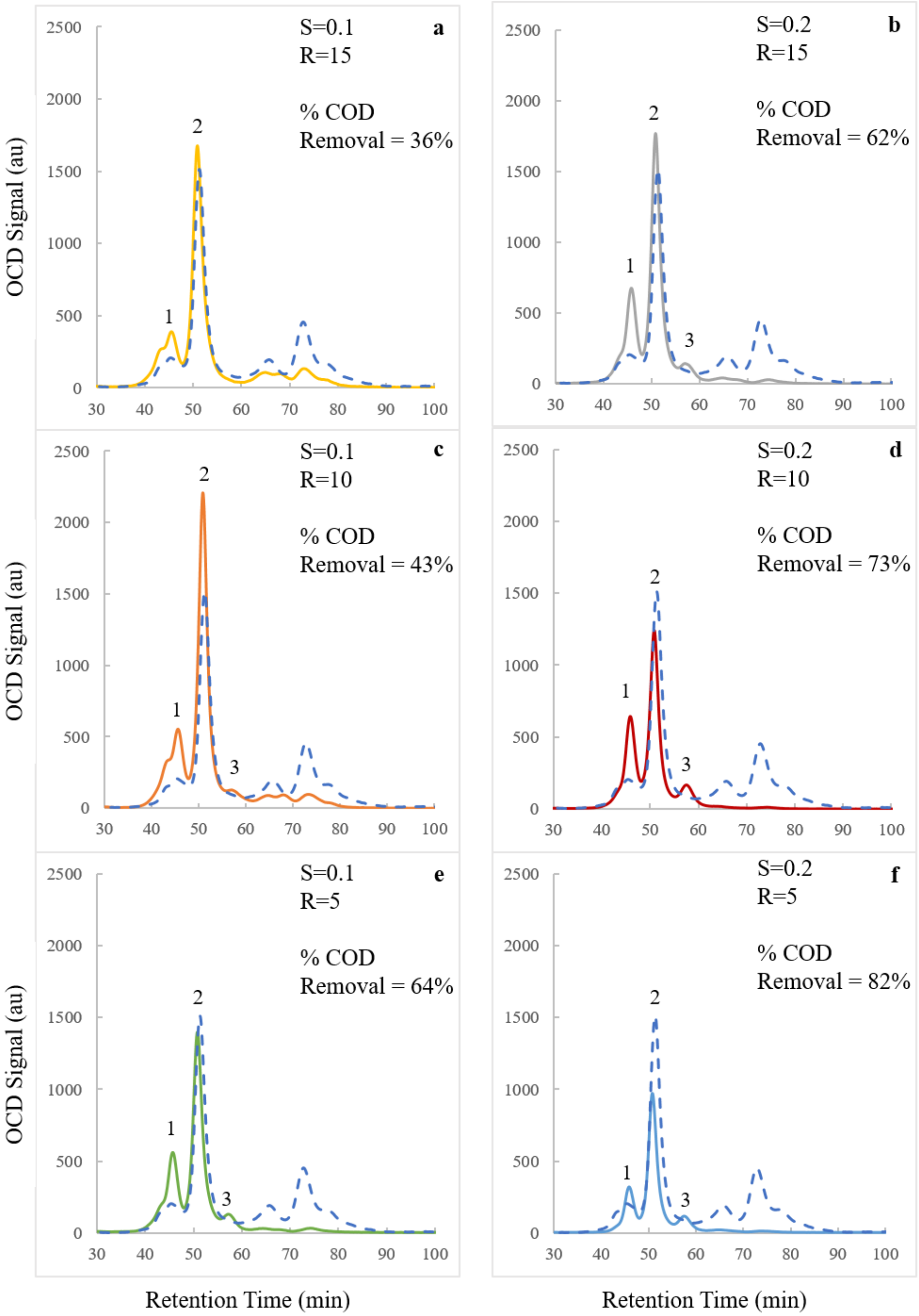


Figure 31- Comparison of LC-OCD chromatograms for a subset of the AO treated samples for wastewater sample 1; the six panels are arranged according to the S = 0.1 (panels a, c, e) and S = 0.2 (panels b, d, f) conditions in the DOE as originally shown in Figure 28. The dashed line in each panel corresponds to the control condition being pH adjustment of the as-received wastewater sample. The labels 1, 2, and 3 in each panel are used to identify peaks with different retention times.

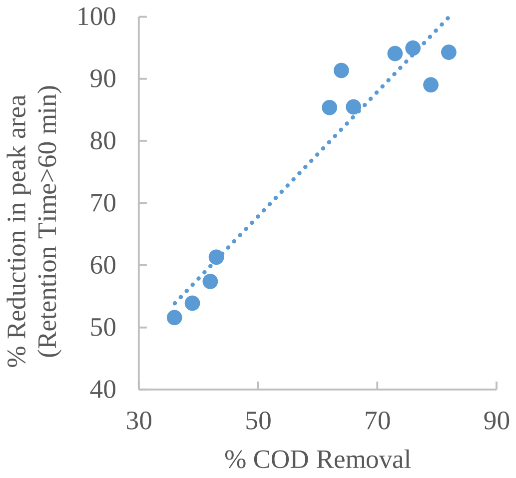


Figure 32- Comparison of LC-OCD analysis in terms of percent reduction in peak area for retention times greater than 60 minutes and percent COD removal.

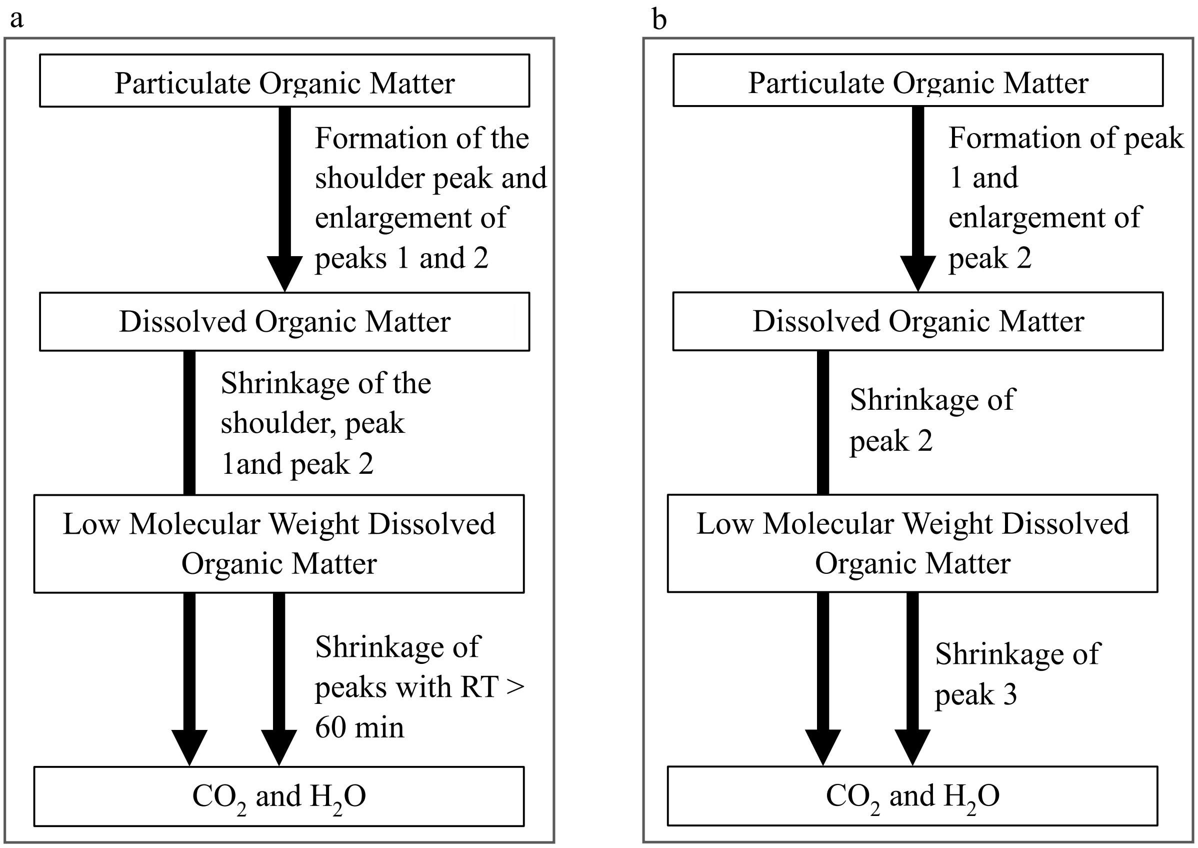


Figure 33- Schematic illustration of the proposed mechanism of COD removal for both wastewater 1 (panel a) and wastewater 2 (panel b).

As shown in Figure 34, the same presentation format was used for the LC-OCD chromatograms associated with the AO treatment of wastewater sample 2. Each panel corresponds to the same specific S and R conditions as indicated in the panel legend; the six panels are arranged strategically to match the arrangement of the S = 0.1 and S = 0.2 conditions in the DOE setup that was originally presented in Figure 29. Again, it is interesting to note that these six conditions nearly span the full range of percent COD removal that was found over the entire DOE method.

In the case of wastewater 2, formation of larger species caused by pH adjustment is likely one of the factors resulting in the lower COD removal efficiency for this wastewater compared to wastewater 1 as larger species are potentially harder to decompose. This is in accordance with the findings of Lipczynska-Kochany et al.[65] who reported that in the presence of humic substances, acidic pH had a negative effect on the organic removal of a coke plant wastewater heavily contaminated with ammonia. Peak 3 represents dissolved organic matter with low molecular weight that has originally been present in the as-received sample. At conditions with high COD removal this peak has been completely removed and in conditions with low COD removal it has shrunk.

A simple comparison to the chromatogram obtained for the pH-adjusted sample clearly shows that a new peak, identified as peak 1 (retention time of approximately 46 minutes), appeared in each LC-OCD chromatogram. It was found that the percent COD removal directly correlated with the portion of the DOC content of the samples represented by peak 1 (measured by the integration of peak 1 area). This correlation is shown in Figure 36.

Furthermore, a regression model for the peak 1 DOC as a function of S and R coded values, indicated that peak 1 DOC is directly correlated to the S factor and inversely correlated to the R factor, the interaction effect of S and R is not statistically significant (Table A-4)**.**

The enlargement of peak 2 is due to the decomposition of particulate organic matter into dissolved organic matter caused by the treatment. The extent of decomposition of the species represented by peak 2 is affecting the overall COD removal and the smaller this peak, the higher COD removal achieved.

Overall, a smaller area under peaks 2 and 3 corresponds to a higher COD removal. The DOC content of peaks 2 and 3 (measured by the integration of peaks 2 and 3 areas) correlates with the overall COD removal (Figure 35).

Also, a regression model for DOC content of peak 2 and 3 as a function of S and R coded values, indicated that peak 2 and 3 DOC is directly correlated to the S factor, however, it is not a function of R (Table A-5).

In summary, the DOC of peaks 1,2 and 3 are the factors that affected the COD removal. Peak 1 DOC is a function of both S and R, however, peak 2 and 3 DOC is only a function of S. This conclusion is in line with the results of the regression analysis which indicated that COD removal is a second order function of S, however, much less significantly affect by R. A schematic summary of the proposed mechanism of COD removal in wastewater 2 is provided in panel b of Figure 33.

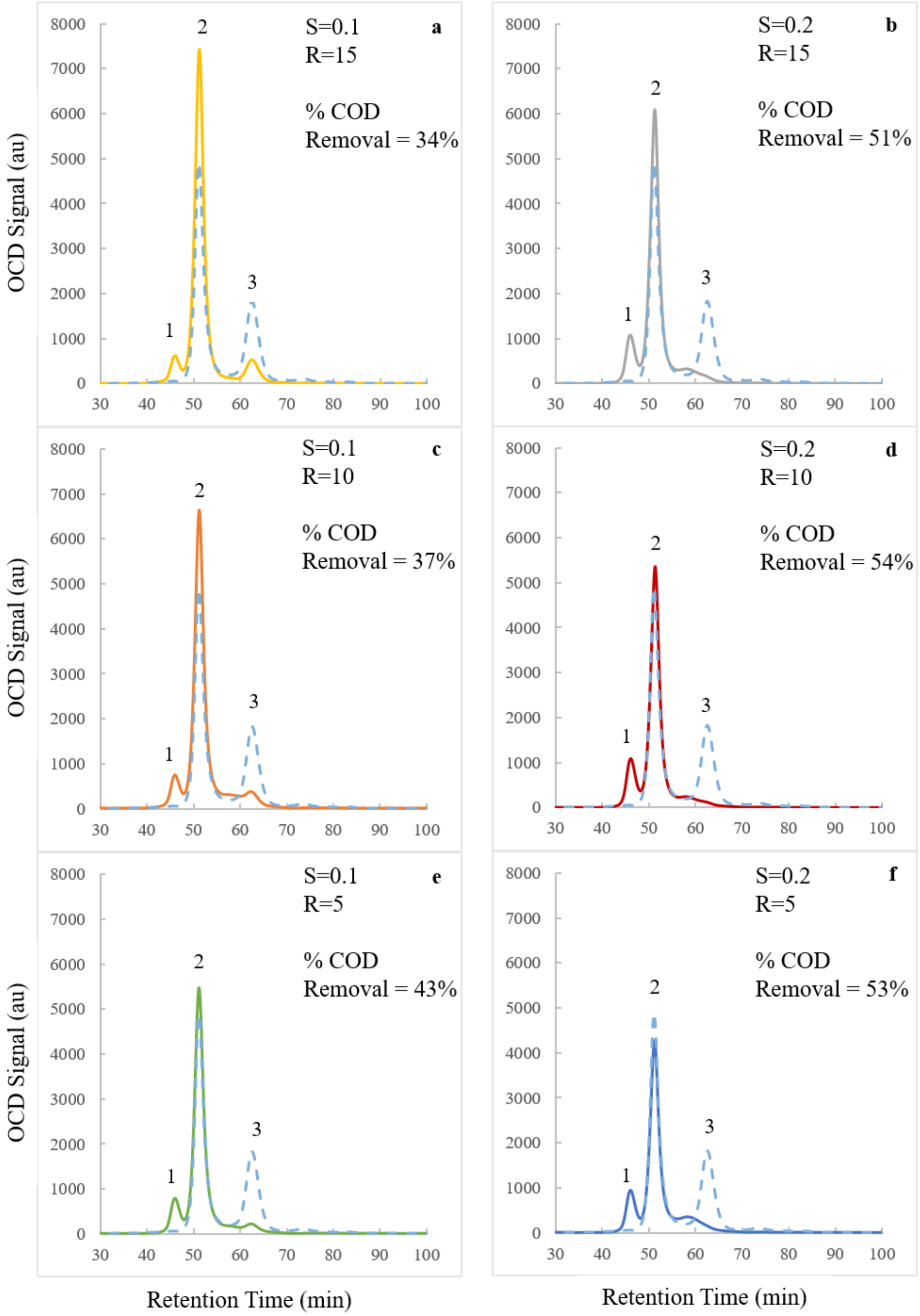


Figure 34- Comparison of LC-OCD chromatograms for a subset of the AO treated samples for wastewater sample 2; the six panels are arranged according to the S = 0.1 (panels a, c, e) and S = 0.2 (panels b, d, f) conditions in the DOE as originally shown in Figure 29. The dashed line in each panel corresponds to the control condition involving just a pH adjustment of the as-received wastewater sample. The labels 1, 2, and 3 in each panel are used to identify peaks with different retention times.

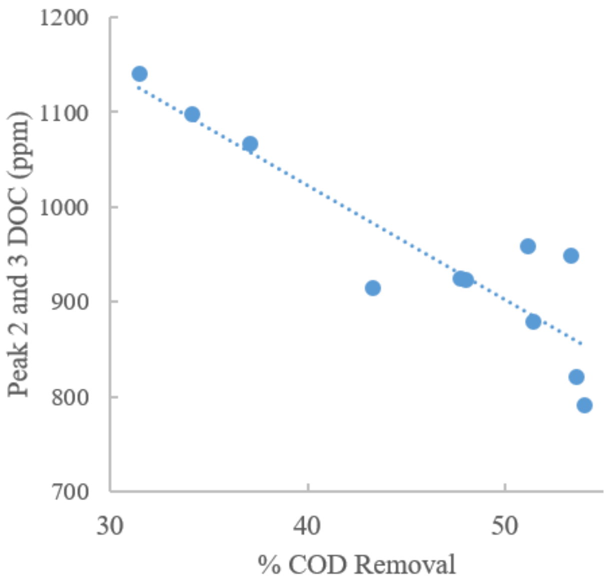


Figure 35- Correlation between peak 2 and 3 (wastewater 2) DOC and overall COD removal (Linear regression model: y= -12.05 x + 1505, R^2=0.81)

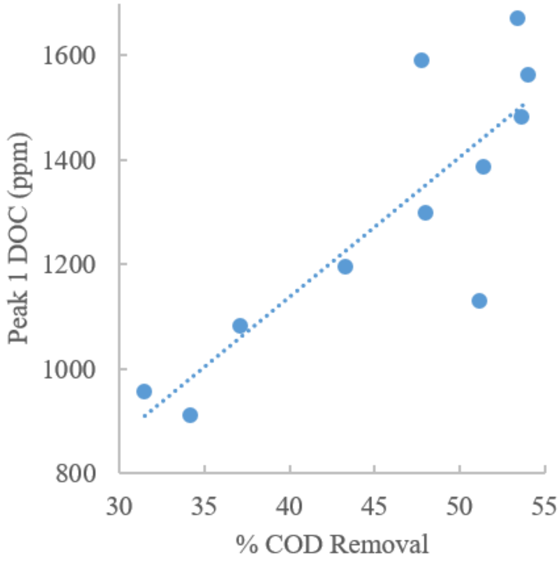


Figure 36- Correlation between peak 1 (wastewater 2) DOC and overall COD removal (Linear regression model: y= 26.75 x + 68.67, R^2=0.71)

5.4 Conclusions

It was demonstrated that LC-OCD analysis complements DOE methods based on bulk measurements (i.e. COD, TOC, BOD) for optimization of AO process in the treatment of industrial wastewater with dynamically varying composition. LC-OCD provides valuable information about the molecular weight distribution of the organic pollutants in the wastewater and the alteration of these organics in the different steps of treatment. This information can be utilized to better understand the effect of different treatment conditions on the different COD removal steps and also to study the dependence of optimum treatment conditions on the wastewater composition.

Chapter 6. Conclusions and Recommendations for Future Work

6.1 Conclusions

6.1.1 Application of PeCOD® for Inline Monitoring of Industrial Wastewater Organic Pollution

PeCOD® method application for quantifying organic pollution for both untreated (incoming) and treated (effluent) industrial wastewater samples was investigated. It was demonstrated that peCOD and COD_{Cr} correlate well for the treated (effluent) samples and also the untreated (incoming) samples under certain conditions. However, for applications where the composition of the samples is variable, correlation cannot be used with confidence not just due to the limitations of the PeCOD® method but also due to the overlooked limitations of the dichromate method.

Incomplete oxidation of macromolecules in the PeCOD® method and the severe chloride interference in samples containing ammonia in the dichromate method, were identified as limitations that rendered the correlations obtained between peCOD and COD_{Cr} unreliable unless there are no significant variations in the organic and inorganic composition of the samples.

It can be concluded that the suitability of PeCOD® method for inline monitoring of industrial wastewater should not be judged solely based on its agreement with COD_{Cr}. The feasibility of utilizing the PeCOD® method is dependent on its ability to detect changes in organic pollution level regardless of the wastewater organic and inorganic constituents. This was shown not to be possible in presence of large macromolecules. More studies like this one are required to identify species that do not undergo complete oxidation in the PeCOD® method or interfere with it so the method can be used confidently for samples that do not contain such species. Obtaining correction factors accounting for the effect of presence of such species might also be a feasible approach and should be investigated.

6.1.2 Optimization of Treatment Process for Dynamically Varying Wastewater

The need to consider the composition of wastewater in optimization of its treatment conditions is evident and the first requirement for achieving this goal is access to information about the sample composition. However, as discussed in this work the conventional analytical techniques are not suitable for obtaining information about organic composition of complex industrial wastewater samples.

In this work, LC-OCD analysis was combined with the DOE method of process optimization to study the importance of sample composition on the performance of the Fenton AO process. It was verified that sample composition has a significant effect on the efficacy of AO and process condition optimization based on bulk parameters (i.e. COD) is not sufficient. It was also demonstrated that the LC-OCD analysis can be used for understanding the alterations organic matter undergoes in the AO process and that in the Fenton process, these alterations are considerably affected by the pH adjustment step of the process and the transformation of particulate organics into dissolved matter.

6.2 Recommendations

6.2.1 Recommendations for Future Work with PeCOD® Analyzer

System calibration

Implementation of the following steps in addition to the calibration procedure described in this study is recommended for more confidence in peCOD results:

i. Quality control with standard sorbitol solution after each calibration

ii. Quality control with standard sorbitol solution containing chloride at the maximum tolerance level of the PeCOD® range being used after each calibration

The first recommended step was implemented in the control experiments done in this study but not in the first phase where actual samples were being studied. The reason these steps were not implement was that for the type of samples that were analyzed in this work due to their high organic and inorganic pollution level, PeCOD® only remained calibrated for analysis of about five samples. Doing to additional quality controls would limit the number of samples that could be analyze per each calibration even further. The next recommendation potentially would alleviate this problem.

Application of Green Range instead of the Yellow Range

The time required for system calibration is shorter in the Green Range (i.e. COD range: 0-150 mg/L). Additionally, it is reported by the manufacturer that when analyzing municipal wastewater samples, the system remains calibrated for longer periods of time when using the Green Range compared to when the Yellow Range (i.e. COD <1500 mg/L) is used. By diluting the samples more to fit into the COD range of less than 150 mg/L, the Green Range can be used in place of the Yellow Range for analysis of treated (effluent) industrial wastewater samples. However, the pollutants present in industrial wastewater might affect the capability of the system to remain calibrated in the Green Range as well. Hence as a first step the systems capability to remain calibrated when analyzing actual samples must be tested.

6.2.2 Recommendations for Future Work with LC-OCD Analysis

Filtration method

The 0.45 µm Supor® polyethersulfone syringe filters (Pall Corporation) and the mPES MicroKros® filter modules (Spectrum Labs) used in this study for the preparation of the samples for the LC-OCD analysis were not suitable for filtration of treated (effluent) industrial wastewater. Due to the high concentration of species larger than the molecular weight cut-off of these filters in the treated (effluent) industrial wastewater samples, the filters were frequently clogged and the permeate was collected at a very slow rate. Given that 40 ml of sample is required for the LC-OCD analysis the application of these filters was very cumbersome. Application of filter modules that operated with vacuum pumps or filtration after dilution of the sample is recommended.

Total Organic Carbon (TOC) measurement

The LC-OCD analysis is only capable of measuring samples' DOC. Studies that are concerned with degradation of organics should also TOC measurements of the samples in addition to LC-OCD analysis. This recommendation is based on the fact that conversion of particulate organics to dissolved organics is a crucial step of degradation and its occurrence can be confirmed when both DOC and TOC measurement data is available.

Duplicate LC-OCD analysis

It is recommended to do the LC-OCD analysis in duplicate for all samples when studying whether the small alterations in the chromatograms are due to treatment. Availability of duplicate results allows one to distinguish between measurement errors and real signals.

Application of an alternative analysis for lower molecular weight species

At low molecular weights (MW< 200 Da) the separation of organics in the LC-OCD method is reported to be affected by the chemical structure and functional groups of the species [60]. Hence, to obtain an account of molecular weight distribution at this range, an alternative analysis must be used.

6.3 Suggested Areas for Future Work

6.3.1 Future Research on the PeCOD® Analyzer

Future research should look more into the chloride interference exacerbation when nitrogenous compounds are present. In this study, only the effect of ammonia was studied and future research should investigate other nitrogenous compounds commonly present in industrial wastewater samples. Future work should also repeat analysis of actual samples but this time in addition to peCOD and COD_{Cr}, chloride and nitrogenous compounds should also be measured. This is to confirm if the difference in the results of the two methods is due to false high COD_{Cr} results caused by the chloride-nitrogen interference.

Investigation of the effect of presence of free radical scavengers such as dissolved oxygen and carbonate species in wastewater samples on the efficiency of the photoelectrocatalytic oxidation in the PeCOD method® is another suggested area of study for future research.

6.3.2 Future Research on the LC-OCD Analysis

Future research should use the LC-OCD analysis to study the effect AO on surrogate samples of different compounds. This control studies will help confirm the speculations that were made for the actual samples of unknown composition in this work. One of the main speculations that requires confirmation is the effect of the pH adjustment step of the Fenton treatment on the molecular weight distribution of the organics present in the wastewater. Studying the effect factors such as wastewater sample alkalinity and ionic strength on the transformation of the organic species in the pH adjustment step is recommended.

Also, the methods used in this study can be utilized to determine if AO is more effective in removal of particulate COD or soluble COD. It can also be used to study the molecular range where AO is the most effective.

Future research should extract information from the UVD and OND chromatograms. Ruhl et al.[60] have suggested that peaks representing the species that are hard to oxidize, appear with a lag in the OCD chromatogram compared to the UVD chromatogram. If this is verified it can be used as a method of identifying hard to oxidize species.

Removal of nitrogenous compounds is one of the main issues in wastewater treatment and OND chromatograms can be used in the same way that the OCD chromatograms were applied in this study, to investigate the effectiveness of a treatment in removing nitrogenous compounds.

Appendices

Appendix A: Additional Tables

Table A-1: Screening tests required for incoming wastewater loads

Test	Technique
TOX (Total Halogens)	Test Kit
Phenols	Test Kit
Formaldehyde	Test Strips
pH	pH Meter/Paper
Specific Gravity	Hydrometer
Chemical Oxygen Demand (COD)	COD Test Vials
Nitrate	Test Strips
Nitrite	Test Strips
Chloride	Test Strips
Ammonia	Test Kit
PCBs	GC-ECD
Flash Point	Closed Cap
Solids/Sludge	Centrifuge
Flammables (Gasoline, Diesel, Solvents)	Copper Flame Test
Heavy Metals	ICP-OES

Table A-2: PeCOD® Inorganic Interference Review [48]

Anions	Formula	Concentrations of < 500 mg/L (In the Cell)	Interference Concentration Threshold (In the Cell)
Ammonium	NH_4^+	No Interference	Not Applicable
Carbonate	CO_3^{2-}	No Interference	Not Applicable
Chlorate	ClO_3	No Interference	Not Applicable
Chloride	Cl^-	Interference	500
Nitrate	NO_3^-	No Interference	Not Applicable
Nitrite	NO_2^-	No Interference	Not Applicable
Perchlorate	ClO_4^-	No Interference	Not Applicable
Phosphate	PO_4^{3-}	No Interference	Not Applicable
Sulfate	SO_4^{2-}	No Interference	Not Applicable
Sulfide	S^{2-}	Interference	0
Sulfite	SO_3^{2-}	Interference	20
Cations			
Aluminium	Al^{3+}	No Interference	Not Applicable
Calcium	Ca^{2+}	No Interference	Not Applicable
Chromate	Cr^{3+}	Interference	2
Ferric	Fe^{3+}	No Interference	Not Applicable
Ferrous	Fe^{2+}	Interference	100
Magnesium	Mg^{2+}	No Interference	Not Applicable
Potassium	K^+	No Interference	Not Applicable
Silver	Ag^+	Interference	10
Sodium	Na^+	No Interference	Not Applicable
Zinc	Zn^+	No Interference	Not Applicable

Table A-3: PEG standards LC-OCD calibration data

Molecular Weight (kDa)	RT (min)
0.2	59.66
0.3	57.26
0.4	55.67
0.6	52.83
1	49.42
2	45.42
3	43.08
4	41.96
6	39.29
10	36.98
20	34.15

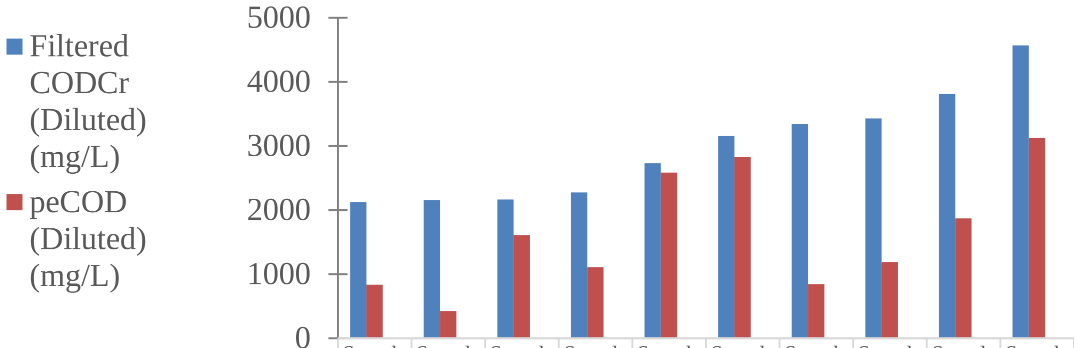
Table A-4: Regression model for peak 1 (wastewater 2) DOC as a function of S and R coded values

Coefficient	Value	95 % CI
Intercept	1298	(1265,1330)
S	222	(187, 256)
R	-153	(-192, -115)
SR	-0.5	(-55, 54)

Table A-5: Regression model for peak 2 and 3 (wastewater 2) DOC as a function of S and R coded values

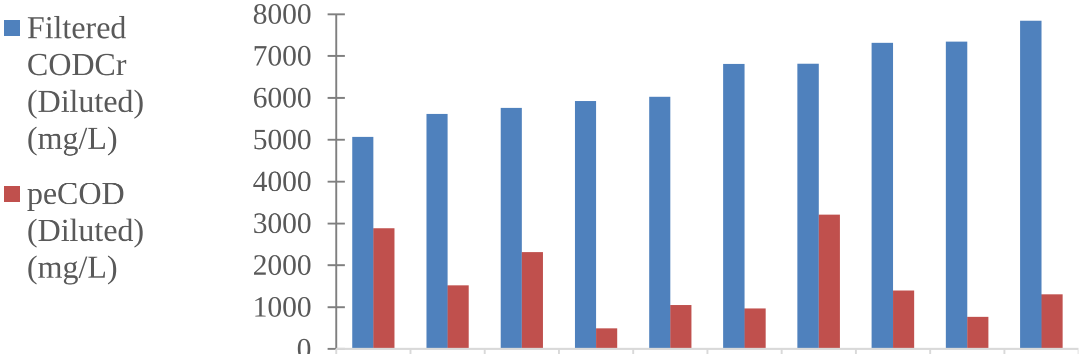
Coefficient	Value	95 % CI
Intercept	951	(916, 986)
S	-93	(-130, -56)
R	20	(-21, 62)
SR	-63	(-121, -5)

Appendix B: Additional Figures



	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Filtered CODCr (Diluted) (mg/L)	2122	2152	2163	2273	2730	3153	3340	3428	3810	4567
peCOD (Diluted) (mg/L)	834	422	1606.5	1109.8	2584.1	2824.2	842	1187	1867	3122
% Difference	61	80	26	51	5	10	75	65	51	32

Figure A-1: Comparison of Filtered COD_{Cr} and peCOD results for a subset of the incoming samples with diluted 2000 < COD_{Cr} < 5000 mg/L. Dilution factors are not accounted for in the presentation of the data.



	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Filtered CODCr (Diluted) (mg/L)	5072	5615	5765	5925	6030	6814	6820	7313	7350	7845
peCOD (Diluted) (mg/L)	2881	1518	2317.5	493	1049.6	969.8	3211.1	1400	768	1306
% Difference	43	73	60	92	83	86	53	81	90	83

Figure A-2: Comparison of Filtered COD_{Cr} and peCOD results for a subset of the incoming samples with diluted 5000 < COD_{Cr} < 8000 mg/L. Dilution factors are not accounted for in the presentation of the data.

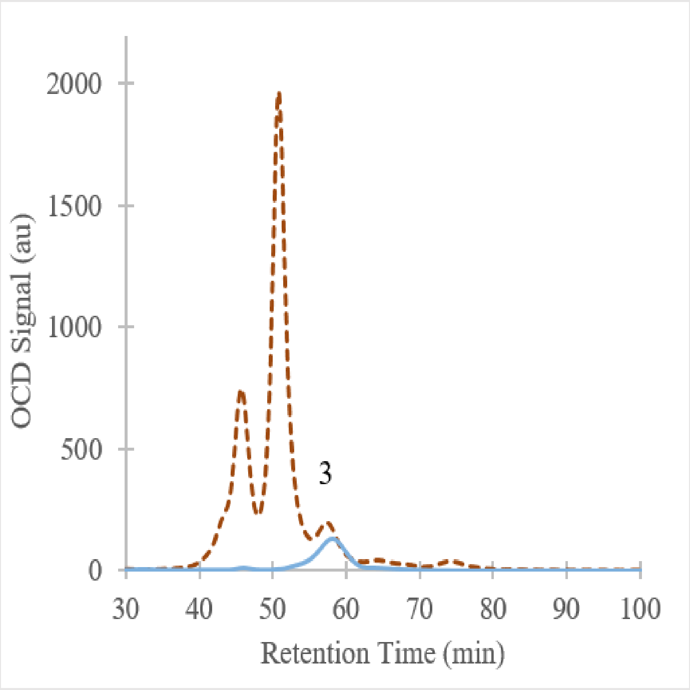


Figure A-3: Comparison of LC-OCD chromatograms for the center treatment condition (i.e. S=0, R=0) of wastewater 2 (dashed line) and a control sample (solid line) that was prepared by adding the same chemicals used for the treated sample to an equivalent volume of MQ water. The two chromatograms both show the same peak that is identified as ‘peak 3’ in the results and discussion section.

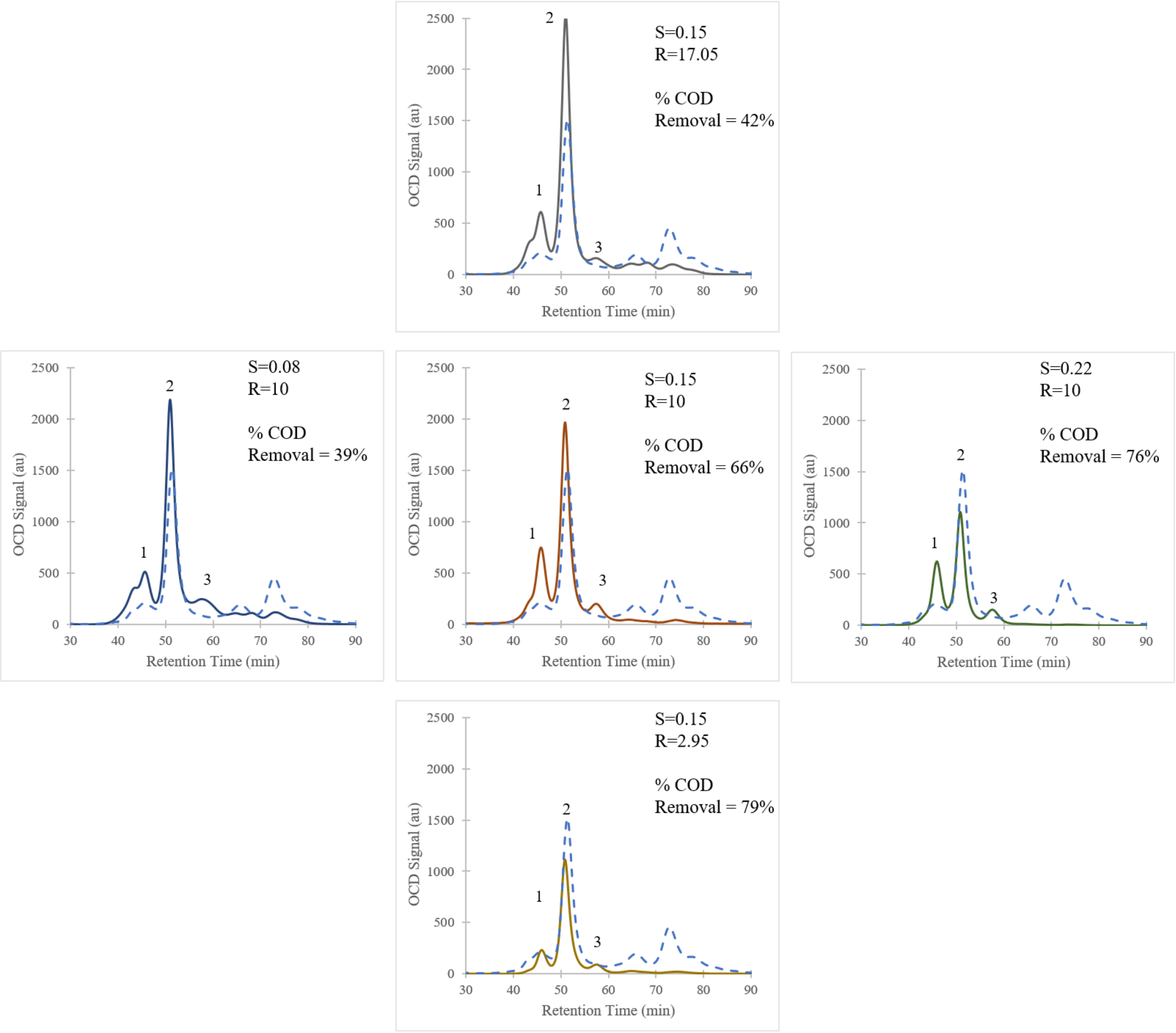


Figure A-4: Comparison of LC-OCD chromatograms for a subset of the AO treated samples for wastewater sample 1; the five panels are arranged according to the S and R conditions in the DOE as originally shown in Figure 28. The other six panels are shown in Figure 31. The dashed line in each panel corresponds to the control condition being pH adjustment of the as-received wastewater sample.

Appendix C: PeCOD® Analyzer Calibration Troubleshooting Guide

Failed calibrations are usually due to one of the following causes:

1- Old or damaged sensors

2- Clogged blank and/or sample ports

3- Clogged electrode block.

For the investigation of the cause of failed calibrations, the LabTerm software is provided by MANTECH for assessment of the oxidation curves. Flat oxidation curves usually indicated that the sensor is used up and cannot detect charge anymore. Jagged oxidation curves usually indicate a clogging has occurred in some part of the system. Examples of a normal oxidation curve (Figure A-5) and an abnormal oxidation Figure (A-6) curve are provided below.

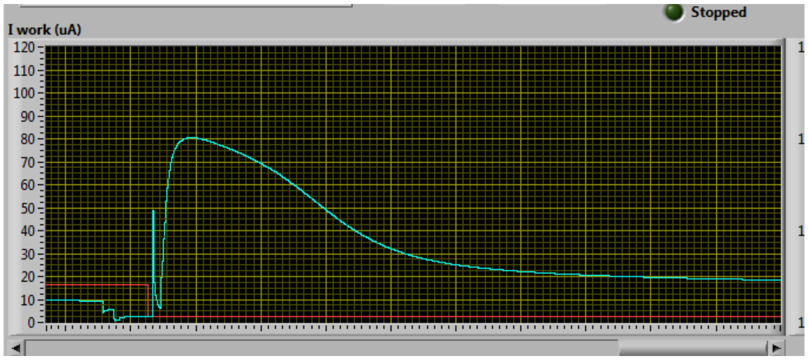


Figure A-5- A normal oxidation curve

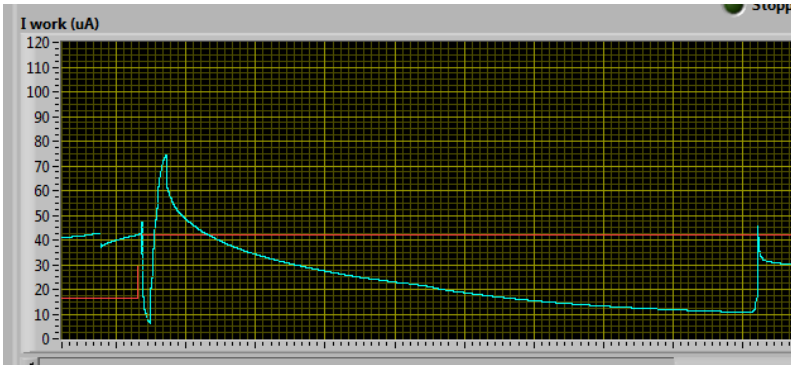


Figure A-6- An abnormal oxidation curve

The following sequence of steps is recommended for troubleshooting:

1- Investigate the oxidation curves via the LabTerm software. Determine whether only the Reference oxidation curves look abnormal or if the Blank curves are also flawed. If both the Reference and Blank curves are abnormal, the cause is more likely the sensor. However, if only the Reference curves are looking abnormal the cause is more likely a clogged part.

2- Check whether enough Blank and Reference solutions are available and whether the tubes are properly located in the solutions.

3- Manually prime both ports and check if the right volume of solution (1.8-2.5 ml) is pumped into the system with each prime. Lower volumes would indicate that the port is partially clogged.

4- Take out the electrode block and rinse all ports by flushing them with COD free water using a syringe with a pipet tip that fits into the electrode block holes placed on its top.

5- Backwash the internal parts of the system (instructions are available in the instruments manual).

6- If the previous steps did not resolve the issue install a new sensor.

7- If changing the sensor did not resolve the issue, install a new electrode block.

If the above steps did not resolve the issue the cause might be a clogging of the internal valves. In this case the analyzer must be opened and its internal valves should be investigated.

References

[1] Environment and Climate Change Canada, “Wastewater”, Environment and Climate Change Canada, http://www.ec.gc.ca/eu-ww/default.asp?lang=En&n=5F25AD10-1, [Accessed: 15-Feb-2017].

[2] G. Rae, “Enhancemnet of sewer use program,” City of Brantford Public Works Cumission, Report no. PW2014-032, pp.2-6, 2014.

[3] C. M. Bye, R. M. Jones, and P. L. Dold, “Pragmatic nitrification inhibition testing for robust plant design,” *Weftec*, 2012.

[4] W. Bourgeois, J. E. Burgess, and R. M. Stuetz, “On-line monitoring of wastewater quality: A review,” *J. Chem. Technol. Biotechnol.*, vol. 76, no. 4, pp. 337–348, 2001.

[5] W. Boyles, “The science of chemical oxygen demand", HACH Company Technical information Series, no. 9, pp.1-10, 1997.

[6] C. E. Domini, M. Hidalgo, F. Marken, and A. Canals, “Comparison of three optimized digestion methods for rapid determination of chemical oxygen demand: Closed microwaves, open microwaves and ultrasound irradiation,” *Anal. Chim. Acta*, vol. 561, no. 1–2, pp. 210–217, 2006.

[7] American Public Health, Water Environment Federation, and American Water Works Association, “Standard Methods for the Examination of Water and Wastewater, Part 4000", pp. 386-410, 1999.

[8] V. C. for S. D. K. Kinally, “European Chemicals Agency Formally Proposes 13 Substances for EU Ban,” http://ukbcsd.org.uk/2016/04/05/european-chemicals-agency-formally-proposes-13-substances-for-eu-ban/, [Accessed: 15-Feb-2017].

[9] E. Krakow, “Wastewater: PeCOD", http://watercanada.net/2015/wastewater-mantech-inc-pecod/, [Accessed: 15-Feb-2017].

[10] Sweden Ministry of Environment, “Sweden will ban the use of mercury on 1 June 2009", Information leaflet, 2009, http://www.government.se/contentassets/12c4d85c2ca64d05827fc131f1a47ab9/sweden-will-ban-the-use-of-mercury, [Accessed: 15-Feb-2017].

[11] Q. Mu, Y. Li, Q. Zhang, and H. Wang, “TiO_2 nanofibers fixed in a microfluidic device for rapid determination of chemical oxygen demand via photoelectrocatalysis,” *Sensors Actuators, B Chem.*, vol. 155, no. 2, pp. 804–809, 2011.

[12] H. Kong and H. Wu, “A rapid determination method of chemical oxygen demand in printing and dyeing wastewater using ultraviolet spectroscopy.,” *Water Environ. Res. a Res. Publ. Water Environ. Fed.*, vol. 81, no. 11, pp. 2381–2386, 2009.

[13] N. Yao, Z. Liu, Y. Chen, Y. Zhou, and B. Xie, “A Novel Thermal Sensor for the Sensitive Measurement of Chemical Oxygen Demand,” *Sensors*, vol. 15, no. 8, pp. 20501–20510, 2015.

[14] LAR, “COD Analyzer for Laboratories.”, https://www.lar.com/products/cod-analysis/cod-analyzer-quickcodlab.html, [Accessed: 15-Feb-2017].

[15] P. Westbroek and E. Temmerman, “In line measurement of chemical oxygen demand by means of multipulse amperometry at a rotating Pt ring - Pt/PbO2 disc electrode,” *Anal. Chim. Acta*, vol. 437, no. 1, pp. 95–105, 2001.

[16] B. Jin, Y. He, J. Shen, Z. Zhuang, X. Wang, and F. S. C. Lee, “Measurement of chemical oxygen demand (COD) in natural water samples by flow injection ozonation chemiluminescence (FI-CL) technique.,” *J. Environ. Monit.*, vol. 6, no. 8, pp. 673–8, 2004.

[17] Y.-C. Kim, S. Sasaki, K. Yano, K. Ikebukuro, K. Hashimoto, and I. Karube, “Photocatalytic sensor for the determination of chemical oxygen demand using flow injection analysis,” *Anal. Chim. Acta*, vol. 432, no. 1, pp. 59–66, 2001.

[18] J. Qiu, S. Zhang, and H. Zhao, “Recent applications of TiO_2 nanomaterials in chemical sensing in aqueous media,” *Sensors Actuators, B Chem.*, vol. 160, no. 1, pp. 875–890, 2011.

[19] I. P. Christos Comninellis, Agnieszka Kapalka, Sixto Malato, Simon A Parsons and and D. Mantzavinos5, “Advanced oxidation processes for water treatment:advances and trends for R&D,” *J. Chem. Technol. Biotechnol.*, vol. 82, no. May, pp. 1115–1121, 2007.

[20] M. A. Oturan and J.-J. Aaron, “Advanced oxidation processes in water/wastewater treatment: Principles and applications. A Review,” *Crit. Rev. Environ. Sci. Technol.*, vol. 44, no. 23, pp. 2577–2641, 2014.

[21] N. San Sebastián Martínez, J. F. Fernández, X. F. Segura, and A. S. Ferrer, “Pre-oxidation of an extremely polluted industrial wastewater by the Fenton’s reagent,” *J. Hazard. Mater.*, vol. 101, no. 3, pp. 315–322, 2003.

[22] I. Arslan-Alaton and S. Dogruel, “Pre-treatment of penicillin formulation effluent by advanced oxidation processes,” *J. Hazard. Mater.*, vol. 112, no. 1–2, pp. 105–113, 2004.

[23] F. Torrades, S. Saiz, and J. A. García-Hortal, “Using central composite experimental design to optimize the degradation of black liquor by Fenton reagent,” *Desalination*, vol. 268, no. 1–3, pp. 97–102, 2011.

[24] M. Ahmadi, F. Vahabzadeh, B. Bonakdarpour, E. Mofarrah, and M. Mehranian, “Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton’s

peroxidation," *J. Hazard. Mater.*, vol. 123, no. 1–3, pp. 187–195, 2005.

[25] M. Pérez, F. Torrades, X. Domènech, and J. Peral, "Fenton and photo-Fenton oxidation of textile effluents," *Water Res.*, vol. 36, no. 11, pp. 2703–2710, 2002.

[26] K. Barbusiński and K. Filipek, "Use of fenton's reagent for removal of pesticides from industrial wastewater," *Polish J. Environ. Stud.*, vol. 10, no. 4, pp. 207–212, 2001.

[27] M. A. Oturan, N. Oturan, M. C. Edelahi, F. I. Podvorica, and K. El Kacemi, "Oxidative degradation of herbicide diuron in aqueous medium by Fenton's reaction based advanced oxidation processes," *Chem. Eng. J.*, vol. 171, no. 1, pp. 127–135, 2011.

[28] R. Salazar, S. Garcia-Segura, M. S. Ureta-Zañartu, and E. Brillas, "Degradation of disperse azo dyes from waters by solar photoelectro-Fenton," *Electrochim. Acta*, vol. 56, no. 18, pp. 6371–6379, 2011.

[29] S. H. Yuan and X. H. Lu, "Comparison treatment of various chlorophenols by electro-Fenton method: Relationship between chlorine content and degradation," *J. Hazard. Mater.*, vol. 118, no. 1–3, pp. 85–92, 2005.

[30] S. Huber, "DOC-Labor-Introduction", http://www.doc-labor.de/Introduction.html, [Accessed: 15-Feb-2017].

[31] S. A. Huber, A. Balz, M. Abert, and W. Pronk, "Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND)", *Water Res.*, vol. 45, no. 2, pp. 879–885, 2011.

[32] Huber.S.A. and F. H. Frimmel, "Flow injection analysis of organic and inorganic carbon in the low-ppb range", *Anal.Chem.*, vol. 63, pp. 2122–2130, 1991.

[33] D. Metcalfe, P. Jarvis, C. Rockey, and S. Judd, "Pre-treatment of surface waters for ceramic microfiltration", *Sep. Purif. Technol.*, vol. 163, pp. 173–180, 2016.

[34] X. Zheng, R. Mehrez, M. Jekel, and M. Ernst, "Effect of slow sand filtration of treated wastewater as pre-treatment to UF," *Desalination*, vol. 249, no. 2, pp. 591–595, 2009.

[35] S. Jeong, Y. Okour, T. V. Nguyen, H. K. Shon, and S. Vigneswaran, "Ti-salt flocculation for dissolved organic matter removal in seawater," *Desalin. Water Treat.*, vol. 51, no. 16–18, pp. 3591–3596, 2013.

[36] S. Ciputra, A. Antony, R. Phillips, D. Richardson, and G. Leslie, "Comparison of treatment options for removal of recalcitrant dissolved organic matter from paper mill effluent," *Chemosphere*, vol. 81, no. 1, pp. 86–91, 2010.

[37] G. O. Bosire and J. C. Ngila, "Assessment of photo-oxidative alterations to natural

organic matter in water using fluorescence excitation emission matrices and liquid chromatography-organic carbon detection techniques," *Anal. Methods*, vol. 8, no. 6, pp. 1415–1424, 2016.

[38] A. K. Stoddart and G. a. Gagnon, "Application of photoelectrochemical chemical oxygen demand to drinking water," *J. Am. Water Works Assoc.*, vol. 106, no. 9, pp. E383–E390, 2014.

[39] J. R. Baker, M. W. Milke, and J. R. Mihelcic, "Relationship between chemical and theoretical oxygen demand for specific classes of organic chemicals," *Water Res.*, vol. 33, no. 2, pp. 327–334, 1999.

[40] S. P. Vijayalakshmi and G. Madras, "Photocatalytic degradation of poly(ethylene oxide) and polyacrylamide," *J. Appl. Polym. Sci.*, vol. 100, no. 5, pp. 3997–4003, 2006.

[41] J. K. Armstrong, R. B. Wenby, H. J. Meiselman, and T. C. Fisher, "The hydrodynamic radii of macromolecules and their effect on red blood cell aggregation.," *Biophys. J.*, vol. 87, no. 6, pp. 4259–70, 2004.

[42] D. Mantzavinos, R. Hellenbrand, A. Livingston, and I. Metcalfe, "Catalytic wet air oxidation of polyethylene glycol," *Appl. Catal. B Environ.*, vol. 11, no. 1, pp. 99–119, 1996.

[43] F. Kawai and T. Ueno, "Bacterial oxidation of polyethylene glycol," vol. 35, no. 4, pp. 679–684, 1978.

[44] J. Suzuki, "Study on ozone treatment of water-soluble polymers. I.Ozon degradation of polyethylene glycol in water ," *J. Appl. Polym. Sci*, vol. 20, pp. 93–103, 1976.

[45] L. Li, S. Zhang, G. Li, and H. Zhao, "Determination of chemical oxygen demand of nitrogenous organic compounds in wastewater using synergetic photoelectrocatalytic oxidation effect at TiO_2 nanostructured electrode," *Anal. Chim. Acta*, vol. 754, pp. 47–53, 2012.

[46] S. Horikoshi, H. Hidaka, and N. Serpone, "Photocatalyzed degradation of polymers in aqueous semiconductor suspensions: V. Photomineralization of lactam ring-pendant polyvinylpyrrolidone at titania/water interfaces," *J. Photochem. Photobiol. A Chem.*, vol. 138, no. 1, pp. 69–77, 2001.

[47] M. J. Caulfield, G. G. Qiao, and D. H. Solomon, "Some aspects of the properties and degradation of polyacrylamides," *Chem. Rev.*, vol. 102, no. 9, pp. 3067–3083, 2002.

[48] L. Peddle, "PeCOD Inorganic Interference Review", MANTECH Inc., Technical bulletin no. 2011-014, pp. 1, 2011.

[49] M. Esler (Aqua Diagnostic Holdingd Pty Ltd), "Water Analysis", World patent,

WO 2010132957 A1, 2010.

[50] J. L. Campos, A. Mosquera-Corral, M. Sánchez, R. Méndez, and J. M. Lema, “Nitrification in saline wastewater with high ammonia concentration in an activated sludge unit,” *Water Res.*, vol. 36, no. 10, pp. 2555–2560, 2002.

[51] M. J. Sadar (Hach Company), “Stabilized Formazin Composition”, United States patent, No. 5,777,011, 1998.

[52] S. Zhang, L. Li, H. Zhao, and G. Li, “A portable miniature UV-LED-based photoelectrochemical system for determination of chemical oxygen demand in wastewater,” *Sensors Actuators, B Chem.*, vol. 141, no. 2, pp. 634–640, 2009.

[53] I. Oller, S. Malato, and J. A. Sánchez-Pérez, “Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review,” *Sci. Total Environ.*, vol. 409, no. 20, pp. 4141–4166, 2011.

[54] I. N. Dias, B. S. Souza, J. H. O. S. Pereira, F. C. Moreira, M. Dezotti, R. A. R. Boaventura, and V. J. P. Vilar, “Enhancement of the photo-Fenton reaction at near neutral pH through the use of ferrioxalate complexes: A case study on trimethoprim and sulfamethoxazole antibiotics removal from aqueous solutions,” *Chem. Eng. J.*, vol. 247, pp. 302–313, 2014.

[55] P. V. Nidheesh and R. Gandhimathi, “Trends in electro-Fenton process for water and wastewater treatment: An overview,” *Desalination*, vol. 299, pp. 1–15, 2012.

[56] A. Babuponnusami and K. Muthukumar, “A review on Fenton and improvements to the Fenton process for wastewater treatment,” *J. Environ. Chem. Eng.*, vol. 2, no. 1, pp. 557–572, 2014.

[57] J. Bautista, P.;Mohedano, A. F.; Zazo, J.;Rodriguez, “An overview of the application of Fenton oxidation to industrial wastewater treatment,” *J. Chem. Technol. Biotechnol.*, vol. 83, no. May, pp. 1323–1338, 2008.

[58] B. Bianco, I. De Michelis, and F. Vegliò, “Fenton treatment of complex industrial wastewater: Optimization of process conditions by surface response method,” *J. Hazard. Mater.*, vol. 186, no. 2–3, pp. 1733–1738, 2011.

[59] F. Chen, S. Peldszus, A. M. Elhadidy, R. L. Legge, M. I. Van Dyke, and P. M. Huck, “Kinetics of natural organic matter (NOM) removal during drinking water biofiltration using different NOM characterization approaches,” *Water Res.*, vol. 104, pp. 361–370, 2016.

[60] A. Sebastian Ruhl and M. Jekel, “Elution behaviour of low molecular weight compounds in size exclusion chromatography.,” *J. Water Supply Res. Technol.*, vol. 61, no. 1, pp. 32–40, 2012.

[61] “R Core Team (2013). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL

http://www.R-project.org/." .

[62] H. Zhang, H. J. Choi, and C.-P. Huang, "Optimization of Fenton process for the treatment of landfill leachate.," *J. Hazard. Mater.*, vol. 125, no. 1–3, pp. 166–174, 2005.

[63] A. E. Papadopoulos, D. Fatta, and M. Loizidou, "Development and optimization of dark Fenton oxidation for the treatment of textile wastewaters with high organic load," *J. Hazard. Mater.*, vol. 146, no. 3, pp. 558–563, 2007.

[64] G. Yohannes, S. K. Wiedmer, M. Jussila, and M.-L. Riekkola, "Fractionation of humic substances by asymmetrical flow field-flow fractionation," *Chromatographia*, vol. 61, no. 7–8, pp. 359–364, 2005.

[65] E. Lipczynska-Kochany and J. Kochany, "Effect of humic substances on the Fenton treatment of wastewater at acidic and neutral pH.," *Chemosphere*, vol. 73, no. 5, pp. 745–750, 2008.