CONCURRENT REMOVAL OF ORGANIC AND HEAVY METAL CONTAMINANTS IN WASTEWATER: A CASE STUDY ON A PULP MILL EFFLUENT AND LEACHATE

By

Adekolapo Adeniran Adesida

Submitted in partial fulfillment of the requirements
for the degree of Master of Environmental Studies

at

Dalhousie University
Halifax, Nova Scotia
August 2020

DEDICATED TO MY WIFE AND FAMILY.

Table of Contents

List of Tables

List of Figures

Abstract

Wastewater, such as from the pulp and paper industry or landfill leachate, contains synthetic or naturally occurring organic pollutants (e.g., dioxins) and inorganic pollutants including heavy metals (metals with relatively high densities or atomic weight) like lead (Pb), which are difficult to eliminate by conventional wastewater treatment technique. In this thesis, an electrochemical method was designed to remove bio-refractory organic substances and heavy metals, concomitantly, from wastewater samples. An electrochemical filtration system (EFS) via a continuous flow reactor (CFR) was designed, and its application was tested for para-nitroaniline (PNA) degradation and real environmental wastewater (*i.e.,* Boat Harbour (BH) and leachate samples) treatment. BH is a former tidal lagoon within the Pictou Landing First Nation (PLFN) Nova Scotia, which is adjacent to the BH treatment facility (BHTF) that was built and operated by the provincial government to be used as receiving water body for the effluent discharge from a pulp mill company (PMC). The effluent from the PMC has contaminated the BH freshwater source thereby having an adverse effect on the health of the PLFN inhabitants. The CFR consists of cylindrical grade 316 stainless-steel, fitted with carbon felt electrodes, connected by a Perfluoroalkoxy (PFA) tubing in a vertical flow configuration, where oxidation of organic pollutants occurs on the anode and in the aqueous solution while heavy metals are removed on the cathode. Total organic carbon (TOC) mineralization efficiency of 73.2% and 92% discoloration was achieved at the optimized condition for PNA mineralization at a flow rate of 5mL min^{-1} (retention time of 20 min), applied potential of 2.5 V, sodium chloride (NaCl) concentration of 29 g L^{-1}, and using carbon felt electrodes. At this optimized experimental conditions, contaminated BH sample was passed through the CFR, and 76% degradation (initial TOC of 105.4 mg L^{-1}) was achieved and major organic compound (cresol) identified using gas chromatography-mass spectroscopy (GC-MS) was confirmed degraded. Also, a significant concentration reduction of heavy metals including arsenic (As), cadmium (Cd), and Pb, was achieved post-treatment at environmental pH, the energy consumption of 23 kWh (kg TOC)$^{-1}$, and overall operational cost of 0.66 USD g^{-1} of carbon removed.

In a second related project, hybrid processes including deodorization using permanganate, coagulation and flocculation using ferric chloride or Alum, chemical oxidation using hydrogen peroxide or persulfate, and the EFS, were investigated to treat a landfill leachate sample obtained from the Guysborough Waste Management Facility, Nova Scotia, Canada. The results revealed a significant reduction in TOC from 1520 to 131 mg L^{-1} (91.4% TOC removal) and compounds including acetaminophen and diethyltoluamide were degraded after applying the combined treatment processes. Additionally, application of the last stage of treatment, EFS, allowed for significant heavy metal removal. Overall, the combined cost was calculated and equates to \$0.06 g^{-1} of organic carbon removed.

In summary, economic viability and the energy consumptions of the treatment methods were calculated, and the EFS indicates a potential and future wastewater treatment method with active simultaneous removal of persistent organic pollutants and toxic heavy metals.

List of Abbreviations and Symbols Used

AOPs	Advanced Oxidation Processes
AOX	Adsorbable Organic Halides
BH	Boat Harbour
BHTF	Boat Harbour Treatment Facility
BOD	Biochemical Oxygen Demand
CEQG	Canadian Environmental Quality Guidelines
CFR	Continuous Flow Reactor
COD	Chemical Oxygen Demand
CWTP	Conventional Wastewater Treatment Plants
CWTT	Conventional Wastewater Treatment Technique
EFS	Electrochemical Filtration System
EO	Electrochemical Oxidation
GC-MS	Gas Chromatography-Mass Spectroscopy
ICPMS	Inductive Coupled Plasma Mass Spectroscopy
kWh L^{-1}	Kilowatt hour per liter
mg L^{-1}	milligram per liter (10^{-3})
mL min^{-1}	milliliter per minute
µM	Micromolar (10^{-6})
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PLFN	Pictou Landing First Nation
PME	Pulp Mill Effluent

PNA	para-Nitroaniline
POPs	Persistent Organic Pollutants
RS	Reactive Species
RSD	Relative Standard Deviation
SHE	Standard Hydrogen Electrode
TDS	Total Dissolved Solids
T_0	Initial Total Organic Carbon Analysis
TOC	Total Organic Carbon
TSS	Total Suspended Solids
T_t	Total Organic Carbon Analysis at time “t”
UV-Vis	Ultra-Violet Visible
WHO	World Health Organisation

Acknowledgments

I thank God for giving the opportunity, strength, wisdom, and adaptability to finishing this research successfully. I would like to express gratitude to the government of Nova Scotia for the Nova Scotia Government scholarship (NSGS) offer. I would like to thank the staff of Dalhousie University for the opportunity to study and finish well. I also acknowledge Cape Breton University for making the laboratory research convenient at the Verschuren center laboratory.

Further, I wish to express my acknowledgment to Dr. Michelle Adams, my supervisor, for her professional guidance, patience, and encouragement throughout the research. I also would like to appreciate the massive effort of Dr. Xu Zhang, as my co-supervisor, who made sure to attend to my professional and financial need which helped to stay focused and eventually triumph on this path. I would like to appreciate the effort of Dr. Tony Walker for his consistent effort, advice, and encouragement, especially during the writing of this thesis and on the road to the successful completion of this work. I would like to appreciate the effort of Dr. Ken Oakes for professional support and guidance throughout the study.

I wish to thank the SRES community for their support during the coursework at Halifax. Also, I would like to appreciate Mary MacGillivray who was very supportive during the application through to the completion of this program.

I acknowledge Xu Zhang group members who helped to make this research possible and convenient in the laboratory. I am indeed grateful to Dr. Albert C.N. Assonkeng, who guided me through this thesis and was there in terms of transportation back and forth to the laboratory every day. I cannot forget the immense advice and guidance from Dr. Andrew Carrier and Dr. Fahad Muhammad Hassan in practical research of this work, I really appreciate. I would like to also appreciate David Oakley, who is in the same boat with me, for being a friend more than a colleague throughout the program. I would like to thank Nick Driscoll who helped me to quickly adapt to a new community and drove me back and forth to the laboratory several times including during the harsh winter.

Lastly, I acknowledge the encouragement and prayers from my loving wife, parent (Mr. and Mrs. Adesida), siblings (Mr. Adeleke Adesida, Mrs. Ronke Oludare, and Mr. Adewale Adesida) and cousins, uncles, aunties and friends towards the successful completion of this degree. I am forever grateful.

Chapter I

1.0 Introduction

1.1 Background Study

Water, as a resource that is broadly distributed globally, plays a significant role in the survival of the environment, animal, and human life. Of the water sources, freshwater which constitutes about only 3% of planet earth water (Vörösmarty et al., 2015), is mostly preferred for human consumption because it contains less salt concentration than the saltwater and therefore relatively easily processed (Klemm et al., 2012). However, since the radical increase in global water consumption in the last five decades, because of development in technology and science and population growth, there has been depletion in quantity and quality of freshwater sources (Bolisetty et al., 2019). Quantity depletion of freshwater sources is due to the rapid growth in the world population which directly increases water demand (Dawadi & Ahmad, 2013). On the other hand, freshwater quality has been affected because of anthropogenic activities as a result of the industrial revolution (Tvedt, 2010). Daily, a huge amount of contaminated effluents from industry and municipal uses are released into water globally, without proper treatment, which results in a potential hazard to humans in the form of water-borne diseases (Beltrán et al., 1997; Chaudhary & Walker, 2019; Wilkinson et al., 2016).

One of the daunting challenges to the contemporary world is to conserve the quality of freshwater sources such as rivers, lakes, and ponds (Dudgeon et al., 2006). This is due to the exposure of such freshwater sources to various toxic synthetic organic and inorganic contaminants from industrial waste such as pulp mill effluent (Usha et al., 2016). The presence of toxic substances from industrial effluents in aquatic ecosystems can potentially lead to deteriorating human health, local environment, and economic activity (W.H.O, 2001).

An example of how an industrial activity has compromised a freshwater source is the improper effluent discharge from a pulp mill company (PMC) BHTF. BH is a freshwater lake within Pictou Landing First Nation (PLFN), Nova Scotia, Canada which is adjacent to BHTF, built and operated by the provincial government, and has been used as a receiving environment for wastewater effluent from a kraft pulp mill (Hoffman et al., 2015). The activities of the company reportedly compromise the quality of the freshwater source, thereby jeopardizing the health of PLFN inhabitants and the economic viability of the Harbour through recreation activities (Hoffman et al., 2015). The effluent discharge from the PMC consists of synthetic organic pollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans (PCDD/Fs), furans (Hoffman et al., 2019), and inorganic contaminants such as Pb and Cd (Hoffman et al., 2017b), which compromises the quality of the freshwater source.

Another example of occurrences that can affect the quality of freshwater sources, is the formation of leachate from a solid waste landfill. Leachate is formed by the percolation of landfill solid waste by water. The polluted solution formed, called leachate, contains high loads of organics and heavy metals that can contaminate nearby surface and groundwater sources (Lema et al., 1988).

Wastewater contamination, such as from the pulp and paper industry or landfill leachate, contains synthetic or naturally occurring organic pollutants (e.g., dioxins and furans) and inorganic pollutants including heavy metals like Pb and Cd, which are difficult to eliminate by conventional wastewater treatment techniques (CWTT), some, because of their bio-refractory (resistance to biodegradation) nature (Urtiaga et al., 2013). Some of these wastewaters are characterized by low biodegradability, high total organic carbon (TOC), high temperature and strong color (Urtiaga et al., 2013), and also consist of heavy metals present at a micro and nano level and not entirely treated by CWTT (Moreira et al., 2016). As a result, freshwater sources such as groundwater and surface water have been found contaminated, in pollutant dosages, and of high toxicity, capable of causing environmental and health issues (e.g., carcinogenicity) for aquatic organisms and humans (Moreira et al., 2017). For instance, the presence of heavy metal ions released into the environment can potentially bioaccumulate upon prolonged exposure, difficult to breakdown, and can pose a risk to human health through the food chain (Bolisetty et al., 2019).

CWTT, such as chemical coagulation (Wang et al., 2011), adsorption (Mohd Shaiful et al., 2014), and chemical and biological oxidation (Klauson et al., 2015) have been used individually in the past and results have led to incomplete oxidation of pollutants and partial removal of heavy metals (Saleem et al., 2018). For instance, biological treatment has been applied to treat pulp mill wastewater, but reports have shown it resulted in a low degradation rate because of biologically inactive molecules (Jaafarzadeh et al., 2017). Also, the physical adsorption method was used to treat leachate samples, and the result was found to be effective in removing non-biodegradable contaminants, but it was difficult and costly to regenerate adsorbents (Rivas et al., 2005).

Therefore, to protect natural water sources quality and prevent adverse effects of pollutants on the environment and eventually humans, efforts must be made to effectively treat industrial effluents within the discharge guidelines (W.H.O, 2018), before release into the receiving environment.

Hence, this thesis is to develop an efficient and environmentally friendly advanced technology to degrade persistent organic pollutants (POPs) such as para-nitroaniline (PNA) and reduce heavy metal concentration, concurrently. Thereafter, optimum condition attained can be applied to treat real wastewater samples from BH and landfill leachate samples from Guysborough Waste Management Facility, both in Nova Scotia, Canada. The advanced technology, an electrochemical filtration system (EFS) process, comprises a continuous flow reactor (CFR) whereby the oxidation of the organic pollutants occurs on the positive electrode (working electrode) while electroreduction of metals takes place on the negative electrode (counter electrode). To optimize the operating conditions including applied potential, catalyst concentration, pH, and electrolyte concentration, the EFS was used to degrade PNA. PNA is an organic compound used as an intermediate in the pharmaceutical and fertilizer industry. PNA discharge into the environment results in severe environmental issues because of its mutagenic and carcinogenic properties (Anotai et al., 2006). Additionally, to evaluate the efficiency of the EFS in terms of metal removal, a known concentration of Pb, Cd, Arsenic (As), and Chromium (Cr), was passed through the system for treatment and subsequent analysis was conducted.

Afterward, real wastewater (*i.e.*, BH samples) were passed through the EFS system to simultaneously remove organic pollutants and heavy metals. Also, the EFS system was used to treat landfill leachate samples after pretreatment by a combination of techniques including coagulation and chemical oxidation. The economic analysis with respect to energy consumption and cost-effectiveness of the system was analyzed in relation to alternative techniques.

1.2 Scopes and objectives

The main objectives of this research are as follows:

1. Develop an experimental prototype for an electrochemical filtration method to effectively oxidize POPs and reduce toxic heavy metals from the wastewater samples, simultaneously.
2. Develop an experimental setup to evaluate the performance of the electrochemical filtration method using model organic (*i.e.*, PNA) and inorganic metals (*i.e.*, Pb, Cd) contaminants,
    a. Analyze treated samples with TOC analyzer, Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), and Gas Chromatography-Mass Spectroscopy (GC-MS); to compare results of analysis before and after treatment for technique evaluation.

    b. Optimize the system parameters, including electrode material, nature of supporting electrolyte, pH, reaction time, and electrical potential difference; to achieve the optimum experimental conditions for high removal efficiency of contaminants.

3. Treat real wastewater from the industry using the optimized experimental condition from objective 2b.
4. Identify the reactive oxygen species generated in the system that is responsible for pollutant degradation to understand the mechanism of the treatment technique.

The objectives above were evaluated by testing the following hypotheses:

1. The Electrochemical filtration process can be used to oxidize model POPs.
2. The EFS can be applied to reduce model heavy metals from contaminated synthetic wastewater.
3. The application of EFS will oxidize POPs and remove heavy metals, concurrently, from real wastewater within discharge guideline for the protection of aquatic life.
4. The reactive species (*i.e.*, ozone, chlorine species) responsible for the degradation and mineralization of persistent organic pollutants in wastewater will be identified.

1.3 Methodology

To realize the research objectives, an electrochemical filtration set-up was developed in the laboratory and the following research methodology was followed (Fig. 1). Various model organic contaminants such as PNA and Toluene were introduced into the EFS for evaluation in terms of the removal of organic substances. TOC analyzer was used to quantitatively analyze the concentration of organics before and after treatment for comparison. Also, GC-MS was used to qualitatively analyze the type of organic before and after the electrochemical treatment process. Also, various model inorganic heavy metals such as Pb and Cd were passed through the EFS to evaluate the efficiency in terms of metal removal. ICP-MS was used to identify and quantify the presence of heavy metals pre- and post-treatment. Further, experimental conditions including flow rate, pH, voltage, and electrolyte concentration were optimized to achieve peak efficiency for the EFS. Then, applying the optimized conditions achieved while experimenting with the model contaminants, BH wastewater was passed through the EFS, and the experiment was done in triplicate and mean values and relative standard deviation were presented. Pre- and post-treatment analysis were carried out and the results was compared to evaluate the efficiency of the treatment method developed.

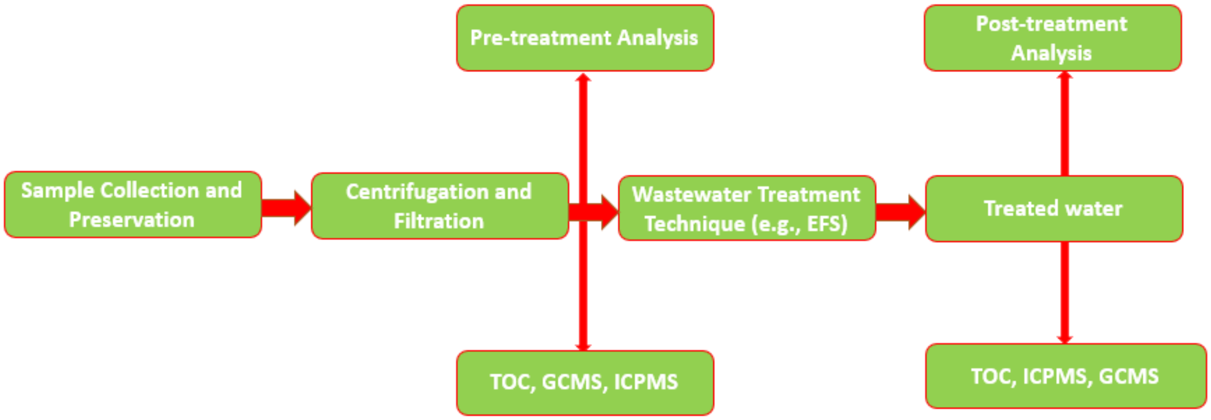


Fig. 1. Research Methodology.

1.4 Dissertation Layout

This dissertation consists of five chapters. The first chapter introduces the thesis background, whereby, the contamination of freshwater sources by human activities was discussed as a global water issue. Further, unsuccessful treatment by conventional wastewater methods to remove contaminants and the proposed new technique designed was talked about. Then, the thesis scopes and objectives were laid out. Finally, the thesis methodology and layout were discussed to wrap up the first chapter. The second chapter of the thesis deals with the literature review on the two wastewater (*i.e.,* BH and leachate sample) sources. Thereafter, various wastewater techniques and their advantages and drawbacks were discussed. In the third chapter, the design, principle, and application of the EFS were talked about. Further, the optimization of various experimental conditions was discussed. Subsequently, the application of the EFS, under optimum experimental conditions, on real wastewater from BH was investigated and reported. Chapter four entails another wastewater treatment project whereby the EFS was used in a combined technique with deodorization, coagulation and flocculation methods to decontaminate a leachate sample. The energy consumed and the cost was also investigated in this chapter. The last chapter summarizes a potential field application for the wastewater treatment methods used and the issues to consider before scale-up. Also, chapter five consist of the main conclusions and recommendations based on the thesis objectives and the results obtained.

Chapter II

2.0 Literature Review

2.1 Wastewater Sample

Wastewater, by definition, includes any water that has been polluted as a result of agricultural (Pimentel et al., 2004), industrial (Batista et al., 2016; Del Aguila Feijoo & Walker, 2018), domestic (Zaharia, 2016), commercial (Jeong, 2001), or human activities (Zornoza et al., 2012), individually or combined (Chaudhary & Walker, 2019; WEM, 1994). The characteristics of wastewater depend on the source of the pollution, as it is a by-product of the aforementioned activities. Depending on the source, wastewater can contain organic and inorganic contaminants in the biological, chemical, or physical forms of pollution (Larsen et al., 2016). The different types of wastewater include sewage (*i.e.*, wastewater from the community) (Lakshmanan & Kuttuva Rajarao, 2014), domestic wastewater (*i.e.*, from individual homes) (Zhou et al., 2018), and industrial wastewater (*i.e.*, from various industries) (Del Aguila Feijoo & Walker, 2018).

2.1.1 Pulp and Paper Mill Effluent: Boat Harbour

The pulp and paper industry involve the extraction of cellulose, an organic compound, from wood to produce paper. The pulp and paper industry has been culpable for causing significant effluent discharge in terms of wastewater containing synthetic organic and inorganic contaminants which result in pollution of the environment (Sibley et al., 2000). The chemical processes in the pulp and paper mill industry include wood preparation (e.g., wood debarking), pulping, pulp washing, kraft pulp bleaching by chlorine compounds, paper making, and chemical recovery (Chanworrawoot & Hunsom, 2012). These processes generate a large volume of wastewater containing wood debris and materials (*i.e.*, organic and inorganic) (Thompson et al., 2001). The large volume of water consumed during the paper production is largely converted into a huge quantity of wastewater, characterized by large amount of contaminants (organics and inorganics) loading (Pokhrel & Viraraghavan, 2004). For example, the Northern Pulp kraft mill at Pictou discharges approximately 80 million liters of wastewater daily (Campbell, 2019). Consequently, the large volume of wastewater requires advanced treatment techniques for complete contaminant elimination. The characteristics of wastewater from a pulp and mill industry include a high chemical oxygen demand (COD), high biochemical oxygen demand (BOD), high Total Suspended Solids (TSS), a high variety of adsorbable organic halides with low biodegradability, and inorganic compounds (Khansorthong & Hunsom, 2009). Some of the compounds that can be found include phenolic compounds, organic solvents, organic chlorides, additives, lignins, tannins, etc.; depending on the practiced paper producing process (Karrasch et al., 2006). These contaminants should typically be eliminated or reduced to within discharge guidelines before release into the environment. Various research reports have revealed the effect of the discharge of partly treated pulp and paper mill effluent on land, air, and water quality (Hoffman et al., 2017a; Khansorthong & Hunsom, 2009; Romo et al., 2019).

Since 1967, a pulp mill company, situated on Abercrombie Point in Pictou Landing Nova Scotia, Canada (Fig. 2), has operated and discharged its wastewater effluent into the Boat Harbour Treatment Facility (BHTF) over the years (Hoffman et al., 2015). BHTF is the facility built opposite a former lagoon called Boat Harbour (BH) for the stabilization and oxidation of the effluent from the pulp and paper industry (Fig. 3) (Hoffman et al., 2017b). The continuous wastewater effluent discharge to BHTF over the years has yielded an accumulation of organics such as PCDD/Fs, furans, PAHs (Hoffman et al., 2019), and inorganics such as As and Pb

(Hoffman et al., 2017b). The impact of the wastewater from the pulp mill industry has resulted in thermal effects, scum production, coloration, odor formation, and disappearance of the aesthetic beauty of the aquatic environment at BH (Lewis et al., 2020; Pictou Landing Native Women's Group (c/o Sheila Francis, 2016). The aggregate effect of the negative impacts of the effluent discharge in BH includes sediment and soil pollution on the environment, poor water and air quality for humans and aquatic organisms, and adverse effect on recreational activities for the local community dwellers (Romo et al., 2019). Hence, there is the need to remediate the BH and return it to its tidal status pre-1967.

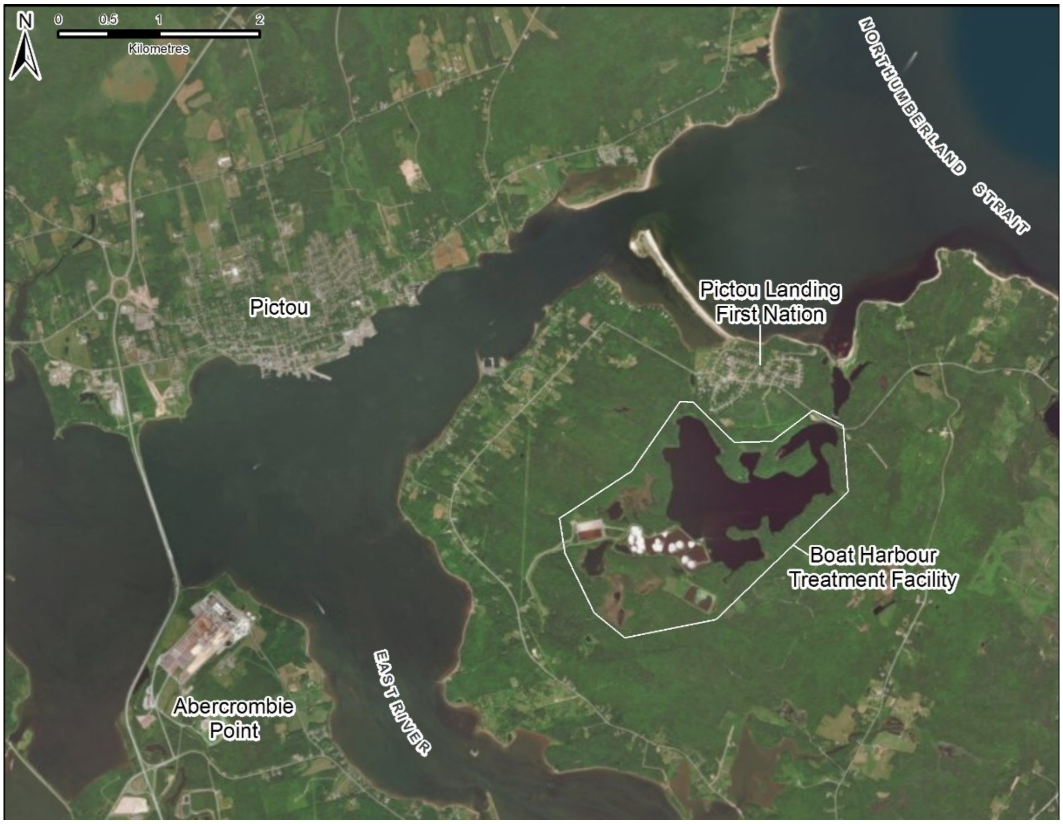


Fig. 2. Boat Harbour Treatment Facility position in relation to Abercrombie Point, Pictou Landing First Nation, and Pictou

(Romo et al., 2019).

Fig. 3. Aeration Stabilization Basin (ASB), Boat Harbour.

The typical wastewater treatment methods used in the pulp and paper mill industry consist of primary, secondary, and tertiary treatment techniques (Jaafarzadeh et al., 2017). The primary treatment consists of physicochemical processes such as sedimentation, filtration, and coagulation and flocculation. Pulp mill effluent (PME) largely consists of suspended solids and organic matter in high concentration (Chanworrawoot & Hunsom, 2012). These pollutants require physical methods including sedimentation, adsorption, or filtration to remove them. Thompson et al. (2001) achieved a 60% removal of suspended solids from PME using sedimentation (Thompson et al., 2001). Further, other researchers were able to remove total solid up to 87% from PME containing kraft black liquor (*i.e.*, a residual digesting liquor) using ultrafiltration method; however, it has a very high operational cost (Ashrafi et al., 2015). Lignin, a polymer that envelopes the cellulose framework in the wood, adds strong color to PME. Wang et al. (2011) reported 80% discoloration of PME using coagulation and flocculation, but the drawback of this process is the excess production of secondary waste in form of a slurry (Wang et al., 2011). On the other hand, secondary treatment including biological methods such as activated sludge and anaerobic digestion has been applied alone unsuccessfully to treat wastewater from the pulp and mill industry (Tarlan et al., 2002). This is due to the presence of non-biodegradable pollutants that cannot be oxidized by microbial activities (Wu et al., 2005). Also, when an activated sludge process was used to remove organic contaminants in pulp wastewater, more variable sludge was generated after the treatment (Thompson et al., 2001). Tertiary treatment method including ozonation (El-Din & Smith, 2002) and Fenton reaction (Lucas et al., 2012) process has also been applied to decontaminate PME without satisfactory pollutant removal efficiency. In addition, these treatment methods alone have not been able to yield satisfactory results within discharge guidelines (Pokhrel & Viraraghavan, 2004). Hence, efforts must be made to complement the aforementioned treatment methods with other advanced treatment processes such as electrochemical techniques to efficiently treat pulp and paper mill wastewater to meet ever-increasing stringent environmental discharge guidelines.

2.1.2 Landfill Leachate

Sanitary landfilling is the most common method of solid waste management (Ahmed & Lan, 2012). It allows for waste decomposition under controlled environmental conditions, which mitigates environmental problems associated with the dispersed waste (Lema et al., 1988).

However, landfills generate leachate formed by water permeating through solid waste, which extracts organic and inorganic matter through hydrolytic and extractive processes (Fernandes et al., 2015). Leachates can contaminate surface and ground waters, compromising local water quality. Leachates are complex solutions, containing huge loads of dissolved organic matter, heavy metals, and ammonia (Long et al., 2017). The toxicity of leachate samples depends on the waste composition and characteristics, hydrogeological factors, and age (young <5 years, intermediate 5–10 years, and mature >10 years old) of the landfill (Mandal et al., 2017).

A combination of treatment processes (e.g., biological processes followed by membrane technology) (Fernandes et al., 2015), have been applied to treat leachate. However, as leachate ages its biodegradability decreases, making biological treatment ineffective (Ahmed & Lan, 2012). However, the incorporation of other technologies, such as coagulation-flocculation (Yusoff et al., 2018), adsorption (Zhang et al., 2012), and chemical oxidation (Derco et al., 2010), is necessary to reduce the toxicity load to meet discharge standards.

2.2 Wastewater Treatment Techniques

The treatment techniques for various types of wastewater to be applied should assure complete pollutant removal within discharge guidelines before releasing into the environment. Generally, wastewater treatment methods are always in stages depending on the components of the mixture (Magdalena & Urszula, 2019). These stages involve the application of several techniques to eliminate or reduce all types of contaminants (organic, inorganic, and biological) from wastewater. On the other hand, the usage of one or other treatment methods depends on how concentrated the wastewater is and the flow volume (Rodríguez et al., 2012). It is imperative to apply the method that is suitable according to effluent characteristics (Heidari et al., 2018). The treatment methods frequently used for wastewater treatment include physiochemical (precipitation, coagulation/flocculation, adsorption, membrane separation, and reverse osmosis) (Wang et al., 2011), biological (activated sludge, aerobic, and anaerobic digestion) (Svensson et al., 2015), incineration (Won et al., 2010), and advanced oxidation processes (Leszczyński & Maria Jolanta, 2018). At times, a combination of one or more of these treatment methods is needed to eliminate contaminants from wastewater because of complex effluent composition (Hou et al., 2012).

The stages of wastewater treatment are classified into primary, secondary, and tertiary methods (Fig. 4). An example of primary wastewater treatment includes coagulation and flocculation, and chemical precipitation; while secondary treatment involves the biological application of microorganisms for remediation in terms of aerobic and anaerobic processes. Photocatalysis, oxidation, and membrane processes are few techniques that can be applied in the tertiary treatment stage.

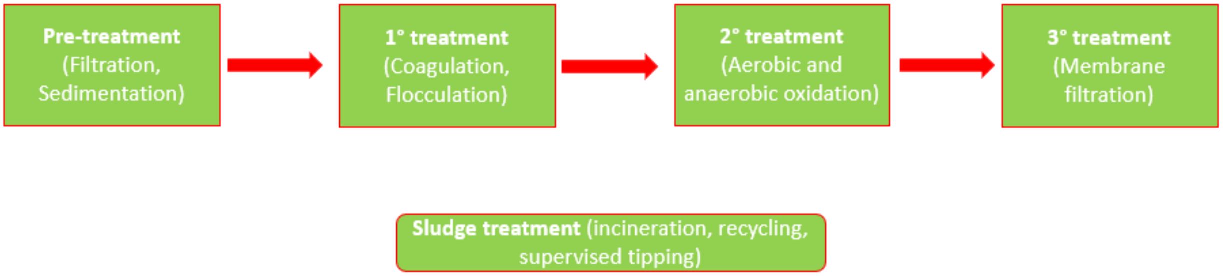


Fig. 4. Conventional Wastewater Treatment Methods.

2.2.1 Physiochemical Processes as Primary Wastewater Treatment

The primary stage of wastewater treatment involves the pre-treatment purification process before further advanced treatments are applied. The prior treatment method could include physicochemical techniques such as coagulation, flocculation, centrifugation, sedimentation, and screening and microfiltration. The physiochemical method involves the combined application of physical forces and chemical treatment of wastewater (Wang et al., 2011). Even though these methods do not entirely remove all the pollutants from the wastewater, a large amount can be extracted.

2.2.1.1 Coagulation and Flocculation

Coagulation involves the destabilization of suspended particles in the wastewater by the addition of coagulants such as Al and Fe salts. After the addition of positively charged coagulants, which attracts negatively charged organics, flocs are formed in a process known as flocculation (Yusoff et al., 2018). This is then followed by the sedimentation of the floc particles to form sludge which can be easily removed. The drawback of this wastewater treatment method is that the contaminants are removed instead of degraded (Gilpavas et al., 2017). Hence, treatment techniques that can degrade contaminants are further needed after the coagulation step. Also, the cost of chemical consumption and secondary waste (*i.e.*, slurry) is high (Wang et al., 2011).

2.2.1.2 Floatation

This is a treatment method based on the separation of tiny pollutant particles whose density is less than or close to that of water (French et al., 2000). It could be a liquid-liquid or solid-liquid separation method. This process involves creating microbubbles in water and having pollutants stick to similar pollutants to then float towards the water surface and be removed (George & Kostas, 2018). The generation of microbubbles can be achieved through various means which dictates several floatation methods such as dissolved air floatation (French et al., 2000), electro floatation (Jiang et al., 2002), and induced air floatation (Suarez et al., 2009). This method of wastewater treatment is simple and cheap to invest and maintain, but it does not remove large amounts of dissolved pollutants as desired (Bolisetty et al., 2019).

2.2.1.3 Chemical Precipitation

In this process, heavy metals in wastewater can be removed by pH regulation of the solution and the addition of chemical reagents such as hydroxides and sulfides to form insoluble particles that can be extracted by the sedimentation process (Bolisetty et al., 2019). The process is easy and inexpensive but the quality of the wastewater after does not meet discharge guidelines, which necessitates further treatment technique (Abolhasani et al., 2014). The drawback of this process includes a huge generation of secondary pollution in terms of sludge (Abolhasani et al., 2014).

2.2.2 Biological Processes as Secondary Wastewater Treatment

The secondary treatment techniques involve the application of naturally existing microorganisms such as bacteria and algae, to convert biological contaminants into less harmful substances (Deegan, 2011). However, some organic pollutants are difficult to breakdown by biological oxidation due to their high toxicity which can attack the microorganism and reduce its efficiency (El-Gohary et al., 1995). The biological treatment of wastewater is either achieved via aerobic or anaerobic processes.

2.2.2.1 Aerobic Oxidation

The aerobic treatment entails the treatment of wastewater by the addition of microorganisms to convert the pollutants into biomass and carbon dioxide in the presence of oxygen (O_2). Aerobic treatment of wastewater could be in the form of activated sludge process (Thompson et al., 2001), granular activated carbon (Frank et al., 2015), extended aeration activated sludge process (Afshin et al., 2016), and membrane bioreactors (Sun et al., 2016). Pokhrel and Viraraghan (2004) reported the use of activated sludge process and extended aerated lagoons for PME treatment, however huge sludge production was revealed as a drawback (Pokhrel & Viraraghavan, 2004). Further, certain microbes have also shown capabilities to remove heavy metals from wastewater (Frank et al., 2015). For instance, when immobilized yeast was applied on zeolites in the aerobic upflow process, efficient removal of Cu, Zn, and Fe was achieved (Karla Miriam Hernández et al., 2013). The advantages of the aerobic treatment method include relatively low-cost operation and the microorganism concentration can be scaled up as needed to meet the required amount, thereby increasing the degradation efficiency of large organic molecules in the bioreactor (Urase et al., 2005). However, water quality factors such as non-biodegradable organic matter, pH, BOD, and COD affect the efficiency of the aerobic biological process (El-Gohary et al., 1995).

2.2.2.2 Anaerobic Oxidation

Anaerobic treatment involves the application of microorganisms to convert pollutants into biogas without the presence of O_2. Anaerobic digestion treatment can be done via the use of reactors including a continuous stirred tank reactor (Hurtado et al., 2015), an up-flow anaerobic sludge reactor (Chelliapan et al., 2006), and fluidized bed reactors (Sponza & Çelebi, 2012). In a study by Singh (2007), 86% COD, 84% adsorbable organic halides (AOX), and 71% lignin was removed from a pulp mill effluent after a two-step sequential treatment (anaerobic first, then aerobic) in a bioreactor for eight days (Singh, 2007). Anaerobic treatment is often preferred to aerobic treatment due to the capacity to treat wastewater with high organic load using less energy input, yielding low sludge, operating at a lower cost, and the recovery of biogas (methane) as a valuable renewable energy source (Deegan, 2011). However, the drawback of the biology treatment technique (both aerobic and anaerobic) is the time taken for the microorganisms to breakdown the contaminants and also the instability of anaerobic bacteria to toxic material (Ashrafi et al., 2015).

2.2.3 Tertiary Treatment Techniques

This involves subjecting the wastewater sample, following primary and secondary treatment, to further advance treatment methods to meet strict environmental guidelines before discharge into a receiving environment (Abdullah et al., 2014). Some of the techniques which are often used as a tertiary treatment of wastewater are chemical oxidation, crystallization and distillation, adsorption, membrane technologies, and ion exchange resins.

2.2.3.1 Chemical Oxidation

This process involves the addition of oxidants to the wastewater to oxidize the organics through electron removal. Several oxidants are effective due to their oxidative potentials. The common ones are O_2, chlorine (Cl_2), permanganate, persulfate, and ozone (O_3). The advantage of this method is that these oxidants can be effective in degrading non-biodegradable compounds, however, the high cost of chemical consumed is a drawback (Herrmann, 1999). Table 1 shows the commonly used chemical oxidants (Beltrán et al., 1997). Ozonation is an example of a chemical oxidation process, whereby O_3, a strong oxidant, is applied to directly or indirectly attack an organic compound. Directly, O_3 attacks via electrophilic substitution mechanism under acidic medium or at basic pH, while indirectly in water it decomposes in a radical chain reaction step to yield hydroxyl radical, an oxidant stronger than O_3 (Eq. 1) (Asghar et al., 2015). Several recalcitrant nonbiodegradable contaminants such as nitroaniline (Tekle-Röttering et al., 2016) and nitrophenol (Kuosa et al., 2015) found in wastewater have been successfully treated using chemical oxidation by O_3. Ko et al. (2009) reported the application of ozonation to treat a kraft pulp mill effluent, and the result showed high removal efficiency for color and TOC. However, O_3 is limited in that certain organic compounds with amide linkages are resistant to its attack, as a drawback (Nakada et al., 2007).

$$O_3 + H_2O \rightarrow 2OH^{\cdot} + O_2 \qquad (1)$$

Table 1. Oxidative Potential of Selected Chemical Oxidants

(Watt, 2001)

Chemical Oxidants	Oxidative Potentials (V)	Order of Reactivity
Fluorine	3.03	Most reactive
Hydroxyl radical	2.80	↑
Atomic Oxygen	2.42	
Ozone	2.07	
Persulfate	2.01	
Hydrogen peroxide	1.77	
Permanganate	1.67	
Hypochlorous acid	1.49	
Chlorine	1.36	Least Reactive

2.2.3.2 Adsorption

This is a mass transfer process whereby the concentration of the pollutants is promoted towards the surface of the adsorbent for adsorption. One advantage of this technique is the possibility to regenerate adsorbent after adsorption for further reusability (Zhu et al., 2013). Common adsorbents used in wastewater treatment can be categorized into metal-based (Chao et al., 2019), carbon-based (Bach et al., 2008), or zeolite-based (Adam et al., 2018) adsorbents. For example, Othman et al. (2010) reported a successful application of silica sand as an adsorbent to achieve a removal efficiency of 51% and 44% for iron and zinc respectively from a stabilized leachate sample (Othman et al., 2010). The main factor that affects the efficiency of the adsorption method is the surface area of the adsorbent, hence, nanoparticles with large surface area and highly efficient chemical reactivity are useful to develop effective adsorption technologies (Chao et al., 2019).

2.2.3.3 Membrane Technology

Membrane technologies can be applied in various ways including reverse osmosis process, ultrafiltration, and nanofiltration processes. Ultrafiltration (Papageorgiou et al., 2012), nanofiltration (Al-Harahsheh et al., 2017), and microfiltration (Ding et al., 2016) membrane technologies have been successfully applied in wastewater recovery to eliminate micropollutant, total dissolved solids (TDS), bacteria and natural organic matters (Baruah et al., 2006). Çakmakcı & Özyaka (2013), in their research, applied a combination of ultrafiltration and nanofiltration to achieve a 98% total organic carbon removal efficiency of pollutants from organic loaded landfill leachate (Çakmakcı & Özyaka, 2013). The disadvantage of the membrane techniques is the retention of concentrate and disposal thereof on the membrane (Ding et al., 2016). Hence, further treatment is always required.

2.2.4 Advanced Oxidation Processes

The effective and total removal of bio-recalcitrant organic contaminants from wastewater in the last two decades has involved advanced treatment techniques such as advanced oxidation processes (AOPs) which makes use of very strong and highly reactive oxidants (*e.g.*, hydroxyl radical ($^{\cdot}OH$)) to degrade most organic compound non-selectively (Moreira et al., 2017). AOPs are chemical treatment techniques that involve the generation of reactive oxygen species (ROS) such as $^{\cdot}OH$, hydroperoxyl ($HO_{2}{}^{\cdot}$), superoxide radical ($O_{2}{}^{\cdot}$-), O_3, hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$) (Ikehata et al., 2006) to chemically oxidize contaminants in the aqueous phase.

Examples of such methods are photocatalysis (Gondal et al., 2015), Fenton reaction (Shan et al., 2016), and electrooxidation (Garcia-Segura et al., 2018). Various AOPs have been used in water treatment such as ozone-based (O_3, O_3/UV, O_3/ H_2O_2, O_3/ H_2O_2/UV (Li et al., 2010), Fenton-based (photo-Fenton (H_2O_2/Fe^{2+}/UV), Electro-Fenton (H_2O_2/Fe^{2+}) (Nidheesh & Gandhimathi, 2012), and titanium dioxide (TiO_2)-based (TiO_2/UV, TiO_2/ H_2O_2, TiO_2/ H_2O_2/UV) (Moreira et al., 2017), treatment methods. AOPs are reportedly more efficient in comparison to biological processes due to the eventual mineralization of organic pollutants into less harmful compounds (Kanakaraju et al., 2018). Also, AOP processes do not generate as much secondary waste as biological processes (Paździor et al., 2018). However, they are relatively expensive due to the large energy demand to yield a large number of reactive species to degrade heavily contaminated wastewater (Paździor et al., 2018).

2.2.4.1 Photocatalysis

Photochemical AOPs, especially photocatalysis, are efficient in wastewater treatment, because of the ability to generate highly reactive species (Gondal et al., 2016). The solar-powered photocatalysis, a green detoxification technique, involves the conversion of light energy into chemical energy by a semiconductor material (e.g., TiO_2) to generate reactive oxidative species such as $^{\cdot}OH$ for the complete mineralization of organic pollutants (Fujishima et al., 2008; Lettmann et al., 2001). Hassan et al. (2016) reported an application of TiO_2 based photocatalysis for the pretreatment of landfill leachate, however, the slow reaction rate was observed and the method could only be a pretreatment strategy instead of standalone approach (Hassan et al., 2016). The method is cost-effective because of the potential usage of sunlight as an energy source (Gondal et al., 2015). The advantages include low temperature and pressure operational conditions, no addition of costly oxidizing agents and less transportation and storage of oxidizing agents to generate oxidizing species (Neppolian et al., 2003). The drawback of this type of treatment is the non-availability of the energy source (sun) all year round which makes it a non-suitable process for large-scale use and also slow reaction rate (Fang et al., 2007).

2.2.4.2 Fenton Reaction

The Fenton process has been researched since it was discovered in 1894 as a reliable way to generate reactive oxygen species (Fenton, 1894). Fenton reactions have been applied for organic pollutant mineralization in wastewater, and it involves the production of $\cdot OH$ from the reaction of iron (II) (Fe^{2+}) and H_2O_2 (Eq. 2) to mineralize organic contaminants in effluents. The efficiency of the Fenton reaction can be determined by the right balance between the Fe^{2+} and H_2O_2 (Nihal Oturan, 2018). Further, an increase in the reactants` concentration to yield more $\cdot OH$ might not lead to higher efficiency due to the complexity of the effluent which may contain a lot of salts (i.e., chlorides and carbonates) (Blanco et al., 2011). The chloride salt can react with the radicals produced to form other radicals that are less reactive than $\cdot OH$, hence, reduced overall efficiency (Ledakowicz, 2012). Also, pH is another factor that influences the efficiency of Fenton reaction in effluent treatment. This is because the optimal pH for Fenton reaction is in the narrow acidic medium (3-3.5) which means a high concentration of strong acid is needed to achieve the perfect condition for Fenton treatment (Paździor et al., 2018). The addition of strong acids can cause precipitation, while the addition of organic acids will increase the organic load and mineral acid addition will increase the concentration of electrolytes such as chlorides and sulfates in the wastewater (Ledakowicz, 2012). Hence, Fenton treatment is better used to pre-treat wastewater to convert nonbiodegradable compounds so they can be further treated using biological methods (Radjenovic & Sedlak, 2015).

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

2.2.5 Electrochemical Treatment Methods

The electrochemical treatment has also been used to treat various kinds of wastewater. This involves processes that are driven by electricity. Electrochemical methods have been considered as an option to combine with conventional techniques for complete removal of recalcitrant contaminants (Pulgarin et al., 1994), and have been applied in several dimensions, for example, electrocoagulation (Khansorthong & Hunsom, 2009), electroreduction (Ghosh et al., 2011), electrooxidation (Moreira et al., 2017), electro-Fenton (Nihal Oturan, 2018), and electrodeposition (Issabayeva et al., 2006).

2.2.5.1 Electrochemical Oxidation

Electrochemical oxidation (EO) has been well researched in terms of water treatment (Särkkä et al., 2015). Electrochemical oxidation processes (EOPs) involve the electron transfer between the electrodes and electrolyte driven by the applied voltage in an electrochemical cell (Fernández-Castro et al., 2015). In EOPs, reactive species including $^{\cdot}OH$ and chlorine species are electro-generated to oxidize organic pollutants in wastewater (Martínez-Huitle & Ferro, 2006).

EOPs are used to degrade organic pollutants based on anodic oxidation (direct oxidation) and mediated oxidation (indirect oxidation) (Labiadh et al., 2016).

Direct EO occurs through electrolysis either by the pollutant diffusing from the bulk of the electrolyte to the electrode or oxidation at the anodic surface by electron transfer reaction (Eq. 3) (Martínez-Huitle & Ferro, 2006). Anodic oxidation occurs when the electrochemical reaction is operated at a lower voltage than the voltage of water splitting into hydrogen and oxygen (*i.e.*, oxygen evolution) (Marco & Giacomo, 2009). Hence, the rate at which the pollutant is degraded in direct EO is low or there is incomplete mineralization, because of competitive oxygen reduction reaction (Martínez-Huitle & Ferro, 2006). Also, the nature of anode material and electrocatalytic activity can favor anodic oxidation over oxygen evolution, however, this often leads to electrode fouling (*i.e.*, deactivation) as a drawback (Feng et al., 2016). For instance, in the result of the degradation of tetracycline antibiotics by anodic oxidation, Wu et al. (2005) reported the production of quinone as intermediates which proved to be more difficult to degrade further (Wu et al., 2005).

$$\mathrm{RH} \rightarrow \mathrm{R}^{+} + \mathrm{e}^{-} \qquad (3)$$

Where “RH” represents organic pollutant and “R^{+}” is the degraded product

The indirect EO involves oxidation of water to release oxygen and the formation of intermediate species on the anode surface where oxidation occurs (Moreira et al., 2017). The indirect EO of organic pollutants can take place on the surface of the electrode via the $\cdot OH$ produced from anodic water discharge or in the bulk of the solution by electrogenerated oxidants from electrolytes including chlorides and sulfates (Marco & Giacomo, 2009). For instance, the use of chloride as the electrolyte can yield chlorine species which can degrade organic pollutants (Eq. 4-7).

$2\mathrm{Cl}^- \rightarrow \mathrm{Cl}_2 + 2\mathrm{e}^-$ (4)

$\mathrm{Cl}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{H}^+ + \mathrm{Cl}^- + \mathrm{HOCl}$ (5)

$\mathrm{HOCl} \leftrightarrow \mathrm{H}^+ + \mathrm{OCl}^-$ (6)

$\mathrm{OCl}^- + \mathrm{R} \rightarrow \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} + \mathrm{Cl}^- + \mathrm{P}$ (7)

Where "R" represents organic pollutant and "P" is the degraded product

In the EOP, oxidation could be partial in which more biodegradable products are formed with further bio-processing method still needed, or the oxidation could lead to eventual mineralization of the organic into non-harmful inorganic carbon dioxide and water with no further treatment needed (Nidheesh & Gandhimathi, 2012). An example of an EOP is the electro Fenton (E-Fenton) reaction. This is a Fenton reaction driven by electricity to generate reactive oxygen species (ROS). The E-Fenton processes involve indirect oxidation of organic contaminants by $^{\cdot}\mathrm{OH}$. This occurs when the H_2O_2 generated through the cathodic reduction of oxygen in the presence of water (Eq. 8) reacts with iron (II) (Fe^{2+}) to yield $^{\cdot}\mathrm{OH}$ (Eq. 9). The $^{\cdot}\mathrm{OH}$ formed can oxidize organic pollutants (Eq. 10), whereas the iron (III) (Fe^{3+}) formed from the oxidation of Fe^{2+} is reduced on the cathode to complete the catalytic cycle (Eq. 11). Moreira et al. 2015 researched and observed a partial degradation of trimethoprim antibiotics by using the E-Fenton process which yielded oxidizable products in need of further treatment (Moreira et al., 2015).

$\mathrm{O}_2 + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2\mathrm{O}_2$ (8)

$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^- + \mathrm{OH}^{\cdot}$ (9)

$\mathrm{RH} + \mathrm{OH}^{\cdot} \rightarrow \mathrm{R}^{\cdot} + \mathrm{H}_2\mathrm{O}$ (10)

$\mathrm{R}^{\cdot} + \mathrm{Fe}^{3+} \rightarrow \mathrm{R}^+ + \mathrm{Fe}^{2+}$ (11)

Where “RH” represents organic pollutant

EOP efficiency for wastewater treatment depends on the optimization of various experimental parameters including electrode material, supporting electrolyte type and concentration, voltage, and current (Martínez-Huitle & Ferro, 2006).

Electrode (*i.e.*, cathode and anode) materials, as a factor, play a significant role in the efficiency of the EOP and must be chemically stable and highly conductive (Moreira et al., 2017). This is because an unstable anode material can deteriorate during an electrolytic process (Moreira et al., 2015). Various forms of Platinum (Pt) electrode including Pt sheet, foil, and plate, have been found useful and efficient for pollutant removal in EOP because they are chemically stable and conducts efficiently at high voltage and in harsh media (Nidheesh & Gandhimathi, 2012). Also, boron-doped diamond has been reportedly efficient as the anode in the decay of a landfill leachate sample (Panizza & Martinez-Huitle, 2013).

Another operational factor for an EOP process to be efficient is the concentration and nature of the supporting electrolyte. Supporting electrolytes are used in the degradation of model contaminants to aid the current flow (Nihal Oturan, 2018). Also, supporting electrolytes such as sodium chloride (NaCl) have been added to real wastewater sample to generate strong reactive species such as hypochlorite for further pollutant mineralization (Moreira et al., 2017). Other supporting electrolytes include sodium nitrate, potassium chloride, and sodium sulfate.

Applied potential is another factor that could be used to optimize the effect of the EOP. Moreira et al. (2017) observed a high amount of organic pollutant removal from a PME as the voltage applied increased, however to an extent (Moreira et al., 2017). This is because at high voltage, the production rate of reactive species increases. However, at a very high voltage, the process is slow because of electrode wearing (Fernández-Castro et al., 2015). Other conditions to be optimized include pH, the distance between electrodes (Nidheesh & Gandhimathi, 2012), and reaction time increase.

The advantages of the EOP include being environmentally compatible, versatile, easily automatable (Fernandes et al., 2015), and *in situ* electro generation of ·OH to avoid error in storage and transportation of reagent in the case of traditional Fenton reaction (Moreira et al., 2016).

The drawbacks of the electro-oxidation process include the production of a high concentration of organic chlorides or sulfates as secondary contaminants (Ghanbari & Moradi, 2015). This residue requires additional cost in the form of chemicals and manpower for further treatment or disposal (Nihal Oturan, 2018). Also, there have been reports on the pH limitation of this technique; for instance, in acidic medium, the concentration of carbonates (*i.e.*, electrolyte), which are known to scavenge ·OH in the solution, will be reduced, hence there will be an increased oxidation reaction (Anglada et al. 2010). Further, at higher pH (>3), there is an occurrence of unwanted oxygen evolution instead of oxidation which reduces the efficiency of the EOP (Mandal et al., 2017). Further, since EOP depends on electricity, the operational cost could be high except if integrated with existing water treatment techniques as a pre-treatment or polish stage (Moreira et al., 2017).

2.2.5.2 Electroreduction

Electroreduction as a wastewater treatment method includes electrodeposition whereby metal contaminants from wastewater can be removed (*i.e.*, deposited) on the cathode electrode, as used in electroplating industries (Feng et al., 2016). The reduction of metals electrochemically on the cathode depends on some factors including metal activity, pH value, and the current density. For example, if two or more metals are in the wastewater, the order of deposition depends on the position of the metals on the galvanic series (Zheng et al., 2013). Further, wastewaters loaded with organohalides (*i.e.*, organochlorine) which can be harmful if discharged into the environment, can be treated using electro reductive dechlorinated method (Bolisetty et al., 2019). Here, this method is largely dictated by the nature of the electrode used, especially silver-based electrodes (Feng et al., 2016). Shen et al. (2020) successfully achieved complete removal of halogenated organic polluted water applying electro reduction using a carbon bulk composite (Shen et al., 2020). However, the kinetic rate is reportedly slow (Oldham et al., 2012).

2.2.6 Hybrid Techniques

The need for the application of hybrid technology to treat wastewater arises due to the incomplete decontamination with single or standalone treatment technique (Ternes et al., 2002). The application of a combination treatment approach has attracted valid attention to improve treatment efficiency and remove contaminants within safe discharge limits from the environment to prevent potential harm to aquatic organisms and humans (Deegan, 2011). The integrated treatment approach could be a physiochemical method combined with a biological method or an AOP as a pretreatment in combination with a biological process. The common combined treatment methods entail having advanced oxidation processes as pre-treatment, to convert nonbiodegradable refractory substances into biodegradable ones (De et al., 2019). Hence, having improved the biodegradability of the wastewater, it can be effectively treated using biological methods. Also, advanced oxidation processes can be used as post-treatment after the wastewater has been treated using biological methods. Tripathi and Tripathi (2011) applied ozonation followed by biofiltration to a PME. Results revealed an improved efficiency of 80% organic removal, 70% heavy metal removal, and 95% microbial removal after the combined treatment (Tripathi & Tripathi, 2011). The removal efficiency without the ozonation step is 45%, 32%, and 15% for organics, heavy metals, and microbial load, respectively (Tripathi & Tripathi, 2011).

Conclusively, emphasis should be to understand the waste components and characteristics to proffer effective combined treatment solutions to eliminate pollutants to meet discharge guidelines before disposal to the environment.

Chapter III

3.0 Simultaneous Degradation of Persistent Organic Pollutants and Heavy Metal Removal via an Electrochemical Filtration System (EFS): Boat Harbour as a Case Study

Abstract: An electrochemical filtration system via a continuous flow electrochemical reactor was designed, and its application was tested for para-nitroaniline (PNA) degradation and environmental wastewater. The continuous flow reactor consists of cylindrical stainless-steel electrodes connected by a Perfluoroalkoxy (PFA) tubing in a vertical flow configuration. Optimization of the various operational parameters was performed for the electrochemical treatment of synthetic and real wastewater (obtained from the Boat Harbour (BH) remediation site, Nova Scotia (NS), Canada). Total organic carbon (TOC) removal efficiency of 73.2% and 92% discoloration was achieved at an optimized condition for PNA mineralization at a flow rate of 5mL min^{-1} (retention time of 20 min), applied potential of 2.5 V, NaCl concentration of 29 g L^{-1}, and using carbon felt electrodes. At the optimized conditions, 76% degradation of BH wastewater (initial TOC of 105.4 mg L^{-1}) with significant concentration reduction of heavy metals including As, Cd, and Cr, was achieved at natural pH, the energy consumption of 23 kWh (kg TOC)$^{-1}$, and overall operational cost of \$0.05 L^{-1}. Economic viability and the energy consumption of the reactions were calculated. The continuous flow reactor is an improvement in the batch reactor treatment approach, with active simultaneous removal of organic pollutants and toxic heavy metals.

3.1 Introduction

The modern world has experienced accelerated industrial growth during the past two decades. Several industries such as oil and gas, textile, power, fertilizer, and mining have developed exponentially in terms of the volume and characteristics of raw materials needed for operations (Bolisetty et al., 2019). For instance, industries use a large volume of water as a solvent, for cooling, cleaning, and transportation during their processes (Klemm et al., 2012). The large volume of process water used for various industrial and municipal uses is released as wastewater into the environment, most of the time, partially treated (Shiklomanov, 2000). On the other hand, a huge amount of raw material containing various inorganic and organic compounds is the backbone of the industrial sector; in turn, these materials are converted into hazardous wastes being dumped directly into the environment without proper remediation (Schwarzenbach et al., 2010). The release of contaminated industrial effluent without adequate treatment into the environment has unavoidably resulted in severe pollution in water, atmosphere, and human health (Martínez-Huitle & Ferro, 2006).

Industrial effluent containing refractive (non-biodegradable) organic compounds such as from the pulp and paper mill and pharmaceutical industries, for instance, can accumulate and agglomerate easily once discharged into a water body. The existence and toxicity of these persistent organic pollutants (POPs) (*e.g*., polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans (PCDD/Fs) in the environment, is well reported in the literature (Hoffman et al., 2019; Lapworth et al., 2012); and their removal is arguably one of the main challenges for scientists (Götz et al., 2010). These untreated POPs pose an imminent threat to human health if allowed to persist in the aquatic environment above permissible limits and, therefore, require adequate treatment. Hence, to comply with regulations and meet discharge guidelines imposed by the government to ensure the less polluted environment, effective innovative ideas for industrial wastewater treatment is required.

Typically, in conventional wastewater treatment plants (CWTP), remediation is performed in stages of primary, secondary, and tertiary treatment methods according to pollutant characteristics (Michael-Kordatou et al., 2015). The treatment methods frequently used in CWTP include physiochemical (precipitation, coagulation/flocculation, adsorption, membrane separation, and reverse osmosis) (Al-Obaidi et al., 2017), biological (activated sludge, aerobic, and anaerobic digestion) (Schultz, 2005), incineration (Nakatsuka et al., 2020), and advanced oxidation processes (ozonation and oxidation) (Miklos et al., 2018). With regards to POPs in wastewater, conventional wastewater treatment technique such as biological treatment has been ineffective perhaps because of the bio-refractory nature of the substrate (Bolisetty et al., 2019). As such, CWTP has become a major source through which these types of pollutants are discharged into water bodies because of incomplete treatment (Beltrán et al., 1997). Hence, as a result of the possible detrimental effects of POPs such as carcinogenicity (Haritash & Kaushik, 2009), reproductive and immune system damage (Karimi et al., 2013), on human health by their improper discharge into freshwater sources, developing an effective wastewater treatment technique is of great concern (Vecoli et al., 2016).

In addition to organic pollutants, inorganic contaminants in the form of heavy metals like Pb, Cd, and As are also concomitantly discharged as effluent by industries (for example, pulp mill companies) without adequate treatment. These heavy metals are mostly non-biodegradable, lethal at high concentration, and can be absorbed and agglomerated in living organisms because they are highly soluble in marine environments (Bolisetty et al., 2019). At high concentrations in living organisms, toxic metals can induce health issues such as cancer and hormonal disorders (Mitchell et al., 2011). For instance, excessive concentration of Pb in living organism tissue can result in brain malfunctioning and kidney damage (Pokorska-Niewiada et al., 2018). The treatment of heavy metals from the environment has been done in the past using methods such as absorption, chemical precipitation, and ion exchange process, but not efficiently (Feng et al., 2016). Hence, there is a need to develop an efficient technology to degrade POPs and remove toxic metals from wastewater prior to discharge into the environment.

Recently, advanced oxidation processes (AOP) have been reported as an efficient tool to address the aforementioned challenges. Different techniques including photocatalysis, Fenton process, electrochemical oxidation, are examples of AOPs, which involve the generation of strong oxidants such as $\cdot OH$ (Li et al., 2016), chlorine (Cl_2) (de Vera et al., 2017), hypochlorite (OCl^-)

(Al-Qaim et al., 2015), H_2O_2 (Guinea et al., 2008), and O_3 (García-Morales et al., 2013) for the mineralization of organic contaminants into carbon dioxide and water (Martínez-Huitle & Brillas, 2008). Some AOPs have proven to not be entirely effective in degrading POPs with various disadvantages (Muruganandham et al., 2014). For instance, using photocatalysis as a treatment method results in time consumption and solar energy is not always available. Also, applying Fenton reaction as a treatment plan involves the cost of chemicals and safety in transporting reagents which makes it unattractive (Kanakaraju et al., 2018; Martínez-Huitle & Ferro, 2006). Out of the AOPs, electrochemical treatment methods have been found to have more advantages (*e.g.*, environmentally adaptable, relative inexpensiveness, and versatileness) (Martínez-Huitle & Ferro, 2006). Additionally, electrochemical treatment methods have been reportedly efficient in reducing metals (Feng et al., 2016).

Lately, electrochemical methods have been considered as an option to combine with conventional techniques for the complete removal of recalcitrant contaminants (Pulgarin et al., 1994). Electrochemical treatment methods have been applied in several dimensions for contaminant removal, for example, electrocoagulation (Khansorthong & Hunsom, 2009), electroreduction (Ghosh et al., 2011), electrooxidation (Moreira et al., 2017), electro-Fenton (Nihal Oturan, 2018), and electrodeposition (Issabayeva et al., 2006). These methods have already been successfully tested to remove either organic or inorganic contaminants from various types of wastewaters including pharmaceutical (Bocos et al., 2015), textile (Sánchez-Sánchez et al., 2018), paper mill (Qu et al., 2012), landfill leachate (Moreira et al., 2015), tannery (Szpyrkowicz et al., 2005), and distillery (Manisankar et al., 2003).

However, the design for the electrochemical treatment of water can either be in a batch or continuous mode. The batch mode depicts a time-consuming approach for treatment with low reaction rate and efficiency, mass transfer constraints, and less attractiveness in terms of potential field application (Pillai & Gupta, 2015). On the other hand, the continuous flow systems approach allows for reduced reaction residence time which drastically improves the potential field applicability (Körbahti & Tanyolaç, 2009). There have been few electrochemical treatment studies with various continuous flow design in the literature. For instance, a group reported low efficiency while using a continuous stirred flow reactor to remediate wastewater samples (Ling et al., 2015). Another group reported the use of a concentric tubular flow electrochemical reactor, however, non-uniformity of current density was experienced which led to low efficiency in the system (Wang et al., 2015). Also, a continuous serpentine flow reactor has been used in another research, and it shows a high mass transfer rate to the electrodes and efficiency, however, the reactor was only applied to organic pollutant removal (Oduoza & Wragg, 2002).

However, in this study, the simultaneous removal of both organic pollutants and heavy metals in the electrochemical filtration system (EFS) via a vertically configured tubular electrochemical continuous flow reactor (CFR), was explored. The design and configuration allow for more reaction resident time for pollutant degradation at the electrode. Moreover, electrooxidation for POPs degradation, which involves the electro generation of the aforementioned reactive oxidants of high oxidative potentials capable of degrading organics, was applied. Simultaneously, charged heavy metal ions are attracted to the negatively charged cathode and reduced to an insoluble state in the EFS through the electroreduction process. Thus, the EFS has the advantage of fast reaction rate, more effectiv than conventional treatment techniques, and bifunctional by removing both organic and inorganic contaminants.

3.1.1 para-Nitroaniline as a Model Contaminant

A model contaminant, para-nitroaniline, was used to evaluate the efficiency of the technique to degrade organic compounds. p-Nitroaniline (PNA) is an organic compound (Fig. 5), highly stable, soluble, and used as a precursor or intermediate in the synthesis of antioxidants, pharmaceuticals, azo dyes, fuel additives, and corrosive inhibitors (Gautam et al., 2005). PNA discharge into the environment results in severe environmental issues because of its mutagenic and carcinogenic properties (Anotai et al., 2006). Herein, we use PNA as a model contaminant which we attempt to degrade via a continuous flow reactor (CFR) in an EFS by evaluating various operational parameters (*e.g.*, electrolyte species and concentration, potential difference, flow rate, initial pH, catalyst and electrode).

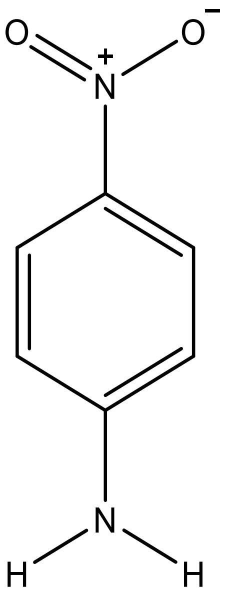


Fig. 5. para-Nitroaniline Structure.

In like manner, contaminated water sample individually containing metals such as Pb, Nickel (Ni), and Chromium (Cr) were used as model inorganic compounds to evaluate the technique for the removal of heavy metals from wastewater. After the evaluation of the EFS with model contaminants, at optimized operational conditions, real wastewater, a pulp mill effluent, from Boat Harbour (BH), was treated.

3.1.2 Case Study: Pulp mill effluent from Boat Harbour

BH, located within the Mi'kmaq Pictou Landing First Nation (PLFN) community in Nova Scotia (NS), Canada, is a former tidal estuary, which is adjacent to the BH Treatment Facility (BHTF), built and operated by the provincial government, and has been used as a receiving environment for wastewater effluent from a Kraft pulp mill since 1967 (Hoffman et al., 2015). The pulp mill effluent has been found to contain refractory organic pollutants including PAHs, furans, and PCDD/Fs (Hoffman et al., 2019), and heavy metals including Pb and Cd (Hoffman et al., 2017b), with an adverse effect on water quality and aquatic life (Romo et al., 2019). Owing to the characteristics and concentration of the aforementioned pollutants in the pulp mill effluent, conventional treatment technique such as biological methods have been found inefficient to effectively eliminate the contaminants. The aggregate effect of the pollution from the company has necessitated a remediation strategy that involves developing an efficient wastewater treatment plan. A sample of pore water was obtained from the BH remediation site and treated with the EFS. Also, the economic analysis of the EFS with respect to energy consumption and cost-effectiveness was analyzed in relation to alternative techniques. With 3V energy applied and low chemical cost, this electrochemical technique can be deployed in remote areas at a relatively inexpensive cost.

3.2 Experimental, Materials, and Methods

3.2.1 Reagents and Wastewater

All chemicals used in this research project were of analytical grade and applied without further purification. The PNA used as model organic contaminants to evaluate the EFS for organic degradation was obtained from Sigma Aldrich with >98% purity. Toluene (C_7H_8), also used as a model organic compound, and acetonitrile (C_2H_3N) used as the elution solvent for sample preparation by solid-phase extraction (SPE), were both obtained from VWR with >99.5% purity. Sodium chloride (NaCl), Sodium Bromide (NaBr), Sodium Nitrate ($NaNO_3$), and Potassium Chloride (KCl) used as supporting electrolytes, were of reagent grade, provided from Sigma Aldrich with >99% purity. Copper chloride ($CuCl_2$), used as a catalyst in this study was of reagent grade and purchased from Acros Organics. Iron Chloride ($FeCl_2$), Cobalt Chloride ($CoCl_2$), and Manganese Chloride ($MnCl_2$), used as metal catalysts for PNA degradation, were obtained from Sigma Aldrich with >99.9% trace metal basis. Sodium hydroxide (NaOH) and Hydrochloric acid (HCl), applied to adjust the pH of the solution, were obtained from Sigma Aldrich. Lead nitrate ($(Pb(NO_3)_2$), Chromium (III) Chloride hexahydrate ($CrCl_3.xH_2O$), and Nickel Chloride ($NiCl_2$), used as model inorganic compounds to evaluate the effectiveness of EFS for metal removal, were purchased from Sigma Aldrich with >99.99% trace metal basis. Carbon and graphite felt electrodes were purchased from Fuel Cell Store and used as procured. Fresh nano water was obtained daily from a Barnstead Nanopure water system and was used to prepare experiment solutions.

Real wastewater samples from BH were collected for investigation. The sample represents the raw wastewater from the PMC without prior treatment. Samples were collected in glass bottles and maintained under 4 °C until needed for the experiment. The composition of the real wastewater sample is shown in Table 2.

Table 2. Characteristics of Real Wastewater.

Parameter	**Water**
Colour	Brownish
pH	7-8
TOC (mg L^{-1})	105

3.2.2 Wastewater Sample Preparation

The real wastewater sample (Fig. 6) was prepared for qualitative analysis by GC-MS, using solid phase extraction (SPE). SPE cartridges [6*cc* Oasis® HLB extraction cartridge (150 mg, 30 µm)], were pre-conditioned with C_2H_3N and nano pure water before extracting 1000 ml of the wastewater sample, then washed with water, dried, and eluted with 1.5 ml of C_2H_3N. Samples were then transferred into 2ml glass vials for GC-MS analysis. Also, samples were prepared for metal analysis by dissolving a 10% sample in 1% Nitric acid solution before analysis by ICP-MS.

Fig. 6. Contaminated environmental wastewater from Boat Harbour before pretreatment.

3.2.3 Experimental Device (Continuous Flow Reactor (CFR)

A labelled photo of the electrochemical continuous flow reactor, where experiments were conducted, is displayed in Fig. 7, and the schematic is represented in Fig. 8. The CFR, designed in the laboratory at Cape Breton University, NS, Canada, consists of cylindrical grade 316 stainless-steel electrodes connected by a Perfluoroalkoxy (PFA) tubing in a vertical flow configuration with a total volume of 120 ml. The cathode and anode are carbon/graphite felt of the same dimensions (12.5 cm x 2 cm x 0.5 cm) inserted into the cylindrical stainless steel nipple (12.5 cm long), placed vertically and separated by a PFA tubing (28 cm long) of high chemical resistance (the immersed portion of each electrode was 64.5 cm^2). A tube connected to the stainless steel was fixed to a peristaltic pump equipped with cartridges used to transport water samples through the electrochemical filtration device. The desired voltage was supplied by a Tenma 72-685 digital control DC power supply (0-30 V) in connected to a Keithley 2000 Multimeter (0-1 A). The samples were collected post-treatment and analysis (e.g., Total Organic Analyzer (TOC) was performed in triplicate and mean results with relative standard deviation are presented).

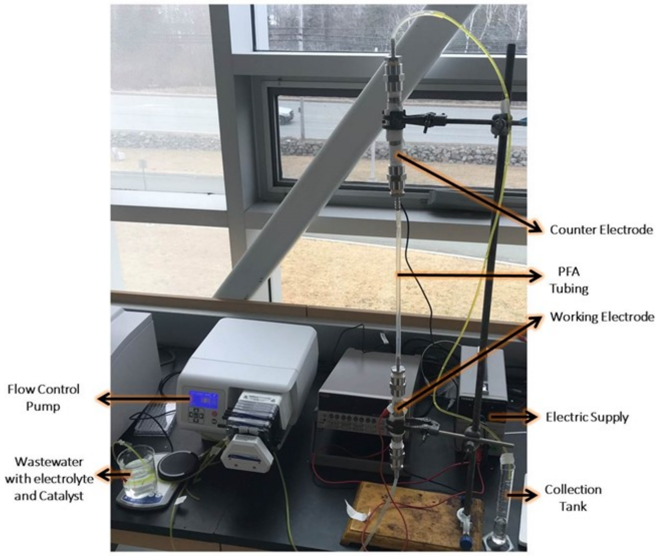


Fig. 7. Continuous Flow Reactor.

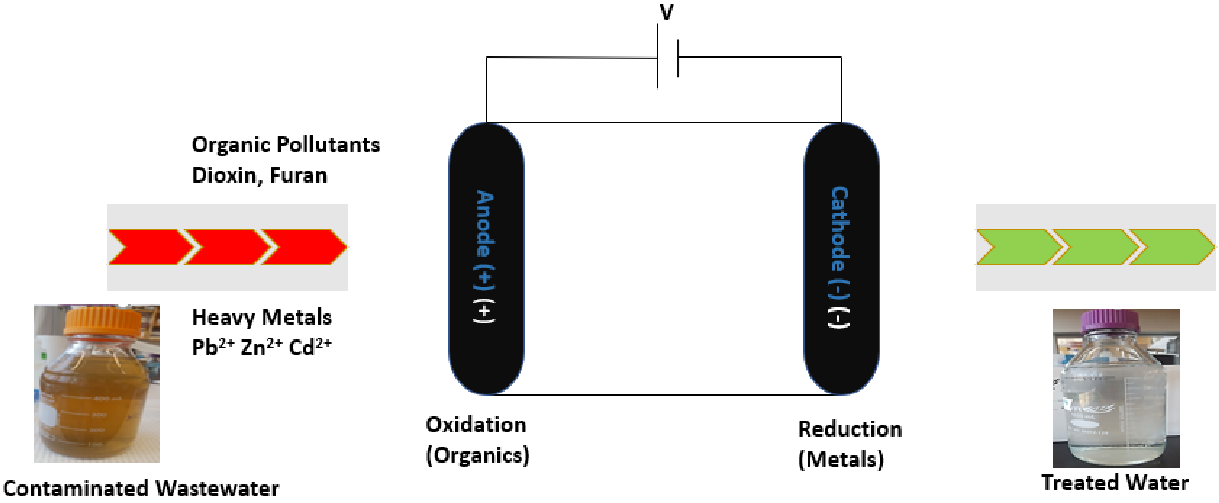


Fig. 8. Electrochemical Filtration Scheme.

3.2.4 Electrochemical Filtration Setup

The electrochemical filtration of samples was performed in the built CFR described earlier. For the laboratory experiment, with the peristaltic pump in the continuous process mode, 100 ml of a sample containing electrolyte, catalyst, and wastewater, stirred at 500 rpm to avoid concentration gradient, was fed into the reactor under varying voltage (0-3 V) from the power supply. Samples were fed into the reactor at different flow rates (5, 10, 25, 50, 100 ml min^{-1}). The pH of the samples was adjusted with 0.1 M HCl or NaOH to evaluate the effect of pH on the system. The carbon felt electrodes were changed after each run and the stainless-steel nipple washed with 0.1 M oxalic acid and dried prior to subsequent experiments. After each experiment, the treated sample was centrifuged at 3600 rpm and the supernatant was collected for TOC/ICP-MS analysis. Operational parameters were optimized, one factor at a time for the degradation of the model contaminant (PNA) at voltage (0-3 V), NaCl (10-1000 mM), $CuCl_2$ (10-1000 µM), and pH (3, 5, 6.5, 8 and10). Subsequently, optimized parameters were applied for the electrochemical filtration of real wastewater from BH at 2.5 V, 10 ml min^{-1} flowrate, 500 mM NaCl, and 200 μM $CuCl_2$. Treated samples were collected post-treatment and analysis was conducted.

3.2.5 Characterization and Analytical Techniques

3.2.5.1 Total Organic Carbon Analysis (TOC)

The oxygen demand of each sample solution is one of the ways to quantify the pollutants in the solution. This analytical method measures indirectly the oxygen demand of a pollutant by measuring the amount of carbon dioxide produced using the infrared spectroscopy. The TOC analysis involves the oxidation of the organic compounds in the sample to carbon dioxide and water by the action of ultraviolet light, heat, and persulfate. The mineralization progress was monitored by measuring the TOC of the samples by using a MULTI N/C UV HS Analytikjena (Germany) analyzer. The experiments were performed at 25 ±1 ºC. The experiments were done in triplicate and the average TOC values with relative standard deviations were obtained. The result of this TOC analysis reflects the degree of pollutant mineralization in the sample achieved after the electrochemical filtration treatment. The efficiency of the EFS was determined in terms of TOC analysis using the following equation (Eq. 12):

$$\%\ \text{TOC Efficiency} = \frac{T_0 - T_t}{T_0} \text{ X } 100 \qquad (12)$$

Where "T_0" and "T_t" are the TOC values of the samples measured in mg L^{-1} pre and post treatment respectively.

3.2.5.2 Ultraviolet-Visible (UV-Vis) Spectrophotometry

The ultraviolet-visible (UV-Vis) spectrometer analytical instrument was used to determine the degree of decolorization of the samples at different operation conditions. The UV-Vis analysis involves the number of light photons absorbed (absorbance) by a sample when a monochromatic source of light is passed through it. A UV-Vis spectrometer equipped with a spectrometric quartz cell (pathlength = 1 cm) and a detector were used for the analysis. The UV-Vis data was obtained using a DR-500 Hach spectrophotometer. The absorbance of the sample before and after an experiment was scanned over a 250-600 nm wavelength region. The concentration of the solution can be determined by measuring the absorbance of the solution and relating it to the concentration using Beer-Lambert`s law (Eq. 13). The Beer-Lamberts law states that the absorbance of a sample is directly proportional to its concentration. Mathematically,

$$A = Ebc \qquad (13)$$

Where “A” is the Absorbance, “E” is the molar absorptivity constant, “b” is the cell pathlength, and “c” is the concentration of the sample.

The decolorization efficiency was calculated following the reduction in absorbance at the same wavelength expressed in % terms as calculated as follow (Eq. 14):

$$\% \text{ Color} = \frac{C_0 - C}{C_0} \text{X } 100 \qquad (14)$$

where “C_0” is the initial absorbance of the dye and “C” is the final absorbance value at the same wavelength.

3.2.5.3 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The ICP-MS is an instrument, with an ionization source, capable of decomposing a sample into its constituent elements and converts the elements into ions. Specifically, ICP-MS is used to qualitatively and quantitatively analyze the presence of metals in a sample. The ICP-MS analysis in this research was performed with Perkin-Elmer inductively coupled plasma spectrometer coupled with NexION 300D with S10 Autosampler, with detection limit at parts per billion levels.

3.2.5.4 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

The GC-MS was used to qualitatively identify the type of compounds in the BH wastewater before and after the treatment using the electrochemical filtration system. The GC-MS analysis was performed with Aglient Technologies 6890N gas chromatograph coupled with a 5973-inert mass spectrum detector (Santa Clara, USA). A nano stationary phase (NSP)-5 Inert capillary column (15 m x 0.25 mm x 0.30 μm, J&K Scientific, Edwardsville Canada) was used for separation.

3.2.5.5 Differential Pulse Voltammetry (DPV) Analysis

The differential pulse voltammetry (DPV) was used to analyze the reactive species (ozone, hypochlorite), responsible for organic pollutant degradation in the EFS. The DPV analysis was conducted using a two-channel electrochemical workstation from CorrTest Instrument. The DPV analysis of the experiment was scanned over a 0-3 V potential difference region to evaluate the reaction of each reactive species while the voltage was measured against the current density.

3.2.5.6 Energy Consumption

The Energy Consumption (EC) is a measure of the electric power used up when 1kg of the pollutant is degraded as measured by TOC. The EC provides a platform to compare the efficiency of the EFS to other wastewater treatment methods. The EC is calculated as follows (Eq. 15):

$$EC = \frac{UIt}{\Delta TOC \text{ X } V} \qquad (15) \qquad \text{(Pillai \& Gupta, 2017)}$$

Where "U" is the voltage applied in volts (V), "I" represents the current in amperes (A), "t" is the time in hours (hr), "ΔTOC" is the TOC reduction in g L^{-1}, and "V" is the volume of the solution.

3.3 Results and Discussion

3.3.1 Parameter Optimization using Nitroaniline as a Model Contaminant

3.3.1.1 Supporting Electrolyte Effect

The effect of supporting electrolytes on PNA degradation was determined by varying the NaCl concentration from 10-1000 mM at 2.5 V, and pH 6.5 (natural pH without adjustment). The mineralization and decolorization rate increased NaCl concentration (Fig. 9, Fig. **10**, and Fig**. 11**) with up to 73.2% and 92% mineralization and bleaching, respectively at [NaCl] = 500 mM, which we suspect results from an increase in reactive species (RS) generation. However, a further increase to [NaCl]= 1000 mM results in the decrease of the efficiency of the system, which we believe results from electrode degradation by increased chlorine product. This was evident with the presence of the electrode particles in the treated solution (Miao Li a, 2010; Mussa et al., 2015). Without NaCl, no bleaching and only 2.7% mineralization was observed. This indicates a lack of direct anodic oxidation as without electrolyte (Current, I=1 mA), and no or limited RS generation (Cameselle et al., 2005).

In the EFS, chloride ion (Cl^-) is oxidized to form hypochlorite ion (ClO^-) (via Cl_2) at the anode, which subsequently oxidizes organic pollutants (Eq. 4-7).

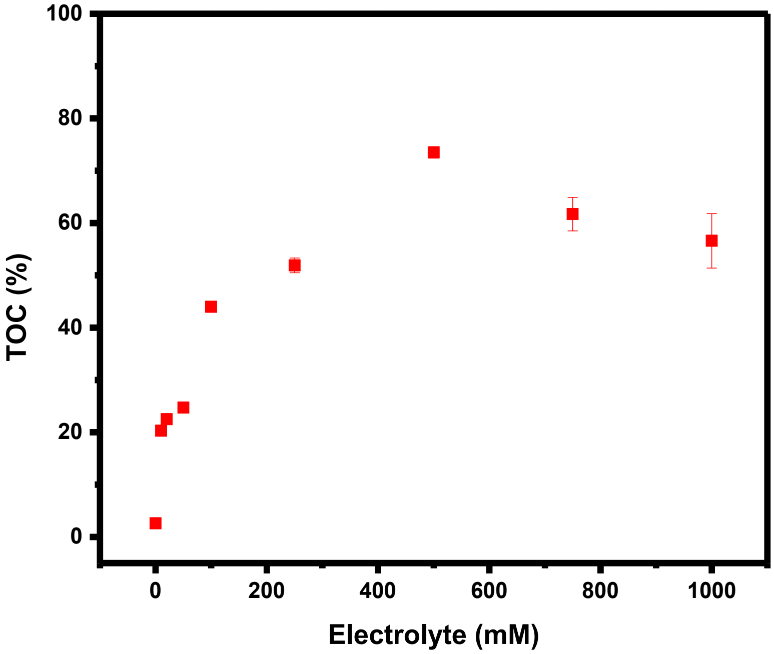


Fig. 9. [NaCl] effect on mineralization p-Nitroaniline (PNA) (TOC Analysis).

Experiment at 2.5 V, $[Cu^{2+}]$ = 200 µM, 5 mL min^-1, carbon felt electrode, pH 6.5 in triplicate. Vertical bars denote relative standard deviation (±RSD).

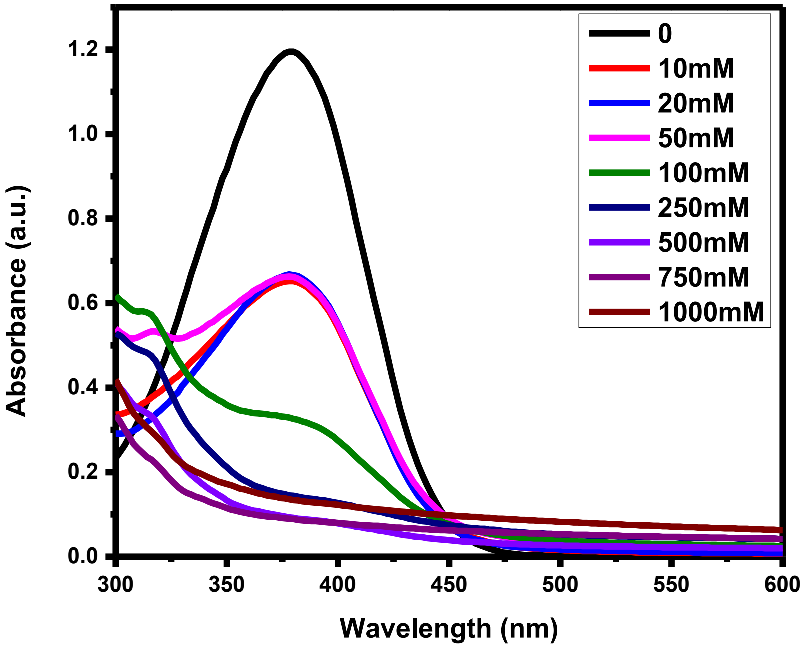


Fig. 10. [NaCl] effect on decolorization of PNA (UV-Vis Analysis).

Experiment at 2.5 V, $[Cu^{2+}]$ = 200 µM, 5 mL min^{-}1, carbon felt electrode, pH 6.5 in triplicate.

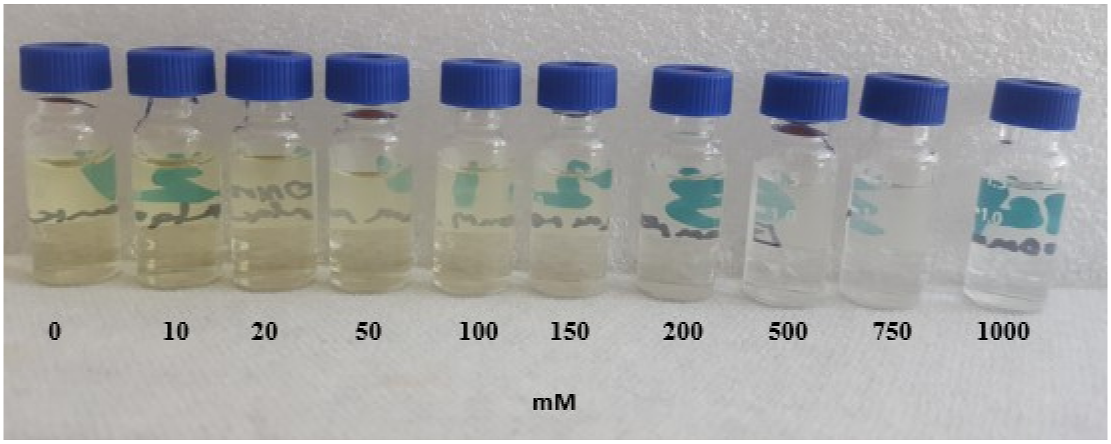


Fig. 11. [NaCl] effect on decolorization of PNA.

Experiment at 2.5 V, $[Cu^{2+}]$ = 200 µM, 5 mL min^{-}1, carbon felt electrode, pH 6.5.

Other electrolytes, *i.e.*, $NaNO_3$, NaBr, and KCl at equal ionic strength were tested, which revealed the necessity of having an oxidizable halide present in the system (Fig. 12). Mixtures of $NaNO_3$ and NaCl with constant ionic strength yielded mineralization and decolorization linearly correlated to [Cl^-] (Fig. 13 and Fig. 14).

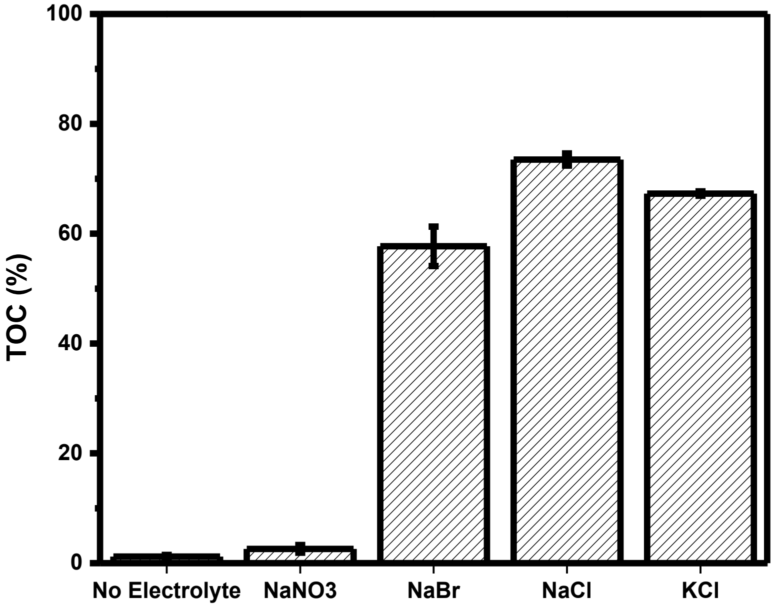


Fig. 12. Various Salt (Concentration = 500 mM) effect on PNA mineralization.

Experiment at 2.5 V, [Cu^{2+}] = 200 μM, 5 mL $min^{-}1$, carbon felt electrode, and pH 6.5. (*n*=3, ±RSD).

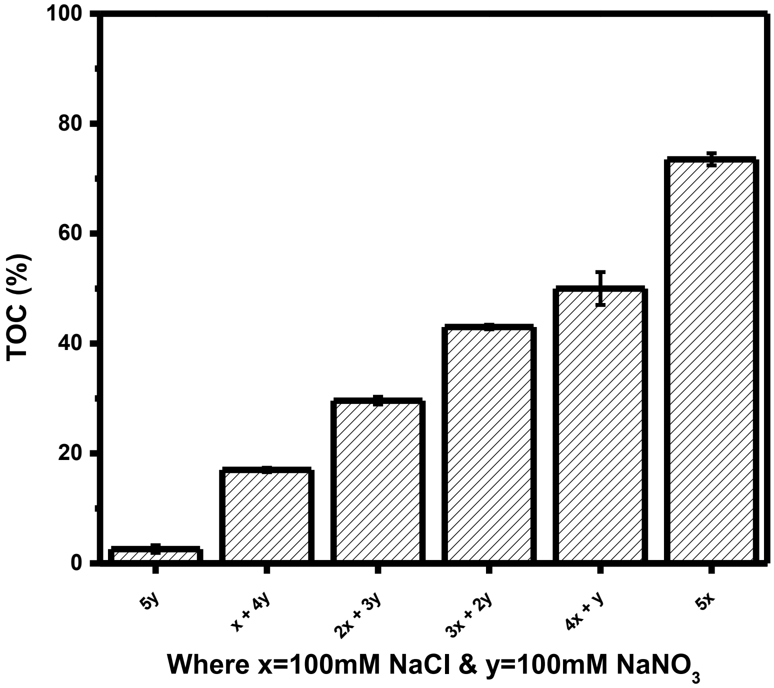


Fig. 13. Mixed salt ([NaCl] + [$NaNO_3$] = 500 mM) effect on PNA mineralization. Experiment at 2.5 V, [Cu^{2+}] = 200 μM, 5 mL min⁻1, carbon felt electrode, pH 6.5 (*n*=3, ±RSD).

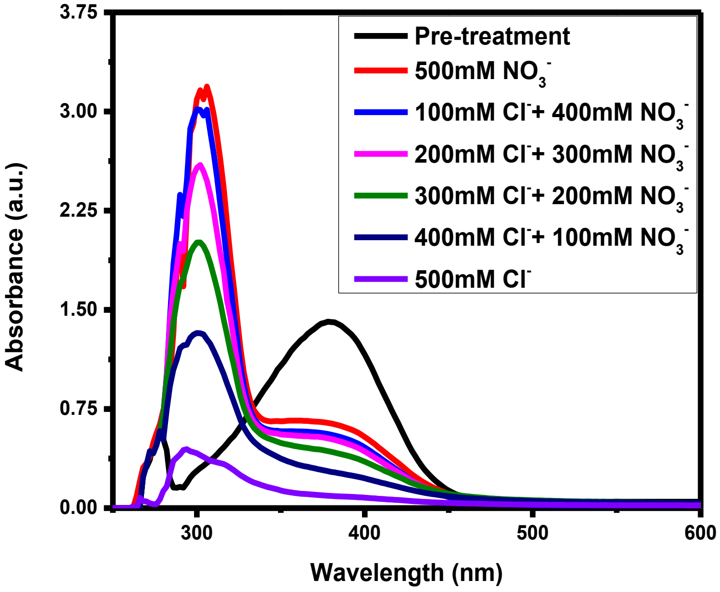


Fig. 14. Mixed salt ([NaCl] + [$NaNO_3$] = 500 mM) effect on PNA decolorization. Experiment performed at 2.5 V, [Cu^{2+}] = 200 μM, pH 6.5, 5 mL min^{-1}, carbon felt electrode.

3.3.1.2 Voltage Influence

The applied potential is the most important factor to optimize to maximize efficiency while reducing energy consumption (Särkkä et al., 2015). Without potential, removal is limited to electrode adsorption; however, we observed increasing mineralization and decolorization (Fig. 15, Fig. 16, and Fig. 17) up to 2.5 V with no further improvement, beyond that which only increases the cost, electrode wear, and oxygen generation.

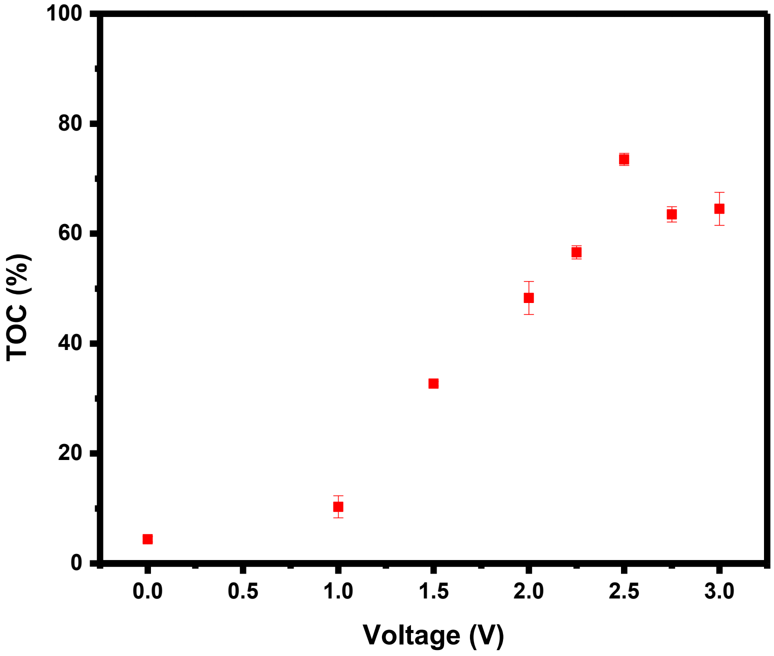


Fig. 15. PNA mineralization in the continuous flow reactor (CFR) as a function of the voltage. Experiment performed at [NaCl] = 500 mM, [Cu^{2+}] = 200 µM, pH 6.5, 5 mL min^{-1}, and carbon felt electrode. (*n*=3, ±RSD).

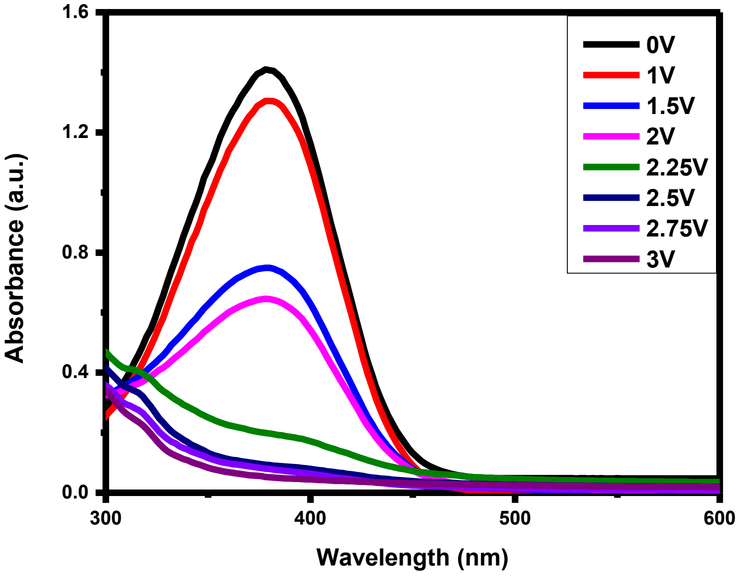


Fig. 16. PNA decolorization in the CFR as a function of the voltage (UV-Vis Analysis).

Experiment performed at [NaCl] = 500 mM, [Cu^{2+}] = 200 µM, pH 6.5, 5 mL min^{-1}, and carbon felt electrode.

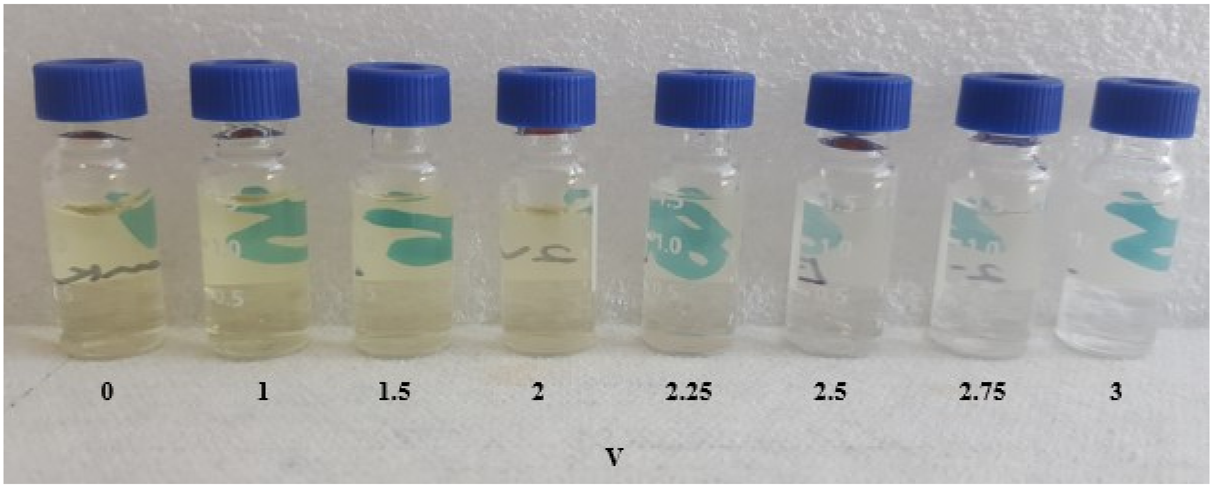


Fig. 17. PNA decolorization in the CFR as a function of the applied potential.

Experiment performed at [NaCl] = 500 mM, [Cu^{2+}] = 200 µM, pH 6.5, 5 mL min^{-1}, carbon felt electrode.

3.3.1.3 Catalyst Effect

Soluble transition metal redox couples, e.g., Cu^{2+}/Cu^{+}, Fe^{3+}/Fe^{2+} can catalyze electro-oxidation reactions in the form of mediated oxidation (Nihal Oturan, 2018). In mediated oxidation, metal ions such as Cu^{2+} can undergo redox reaction to a more reactive oxidation state (Eq. 16) where they can oxidize organic pollutants (Eq. 17 and 18) (Oturan, 2014).

$$\mathrm{Cu^{2+} + e^{-} \rightarrow Cu^{+}} \qquad (16)$$

$$\mathrm{M^{z+} \rightarrow M^{(z+1)+} + e^{-}} \qquad (17)$$

$$\mathrm{M^{(z+1)+} + organics \rightarrow M^{z+} + CO_2 + H_2O} \qquad (18)$$

Where “M” is a transition metal catalyst.

Although 55% mineralization was achieved without the addition of a transition metal catalyst, the efficiency was increased with increasing Cu^{2+} addition, up to 200 μM (Fig. 18), beyond which no increase in the efficiency was observed at $[Cu^{2+}]$ = 1000 μM. This can be attributed to the excess Cu^{+} scavenging the ROS in the system (Eq. 23) (Barhoumi et al., 2017).

$$\mathrm{Cu^{+} + OH^{\cdot} \rightarrow Cu^{2+} + OH^{-}} \qquad (19)$$

Other transition metals, *i.e.*, Co^{2+}, Fe^{2+}, and Mn^{2+}were compared to Cu^{2+} with decreasing effectiveness in the order $Cu^{2+}>Co^{2+}> Fe^{2+}> Mn^{2+}$ (Fig. 19). If these metals participated through mediated oxidation, their activity is in the order of their standard reduction potential (Table 3). Additionally, the Fe^{2+}activity was limited by the solution pH, since it reportedly performs better in acidic media (Nihal Oturan, 2018).

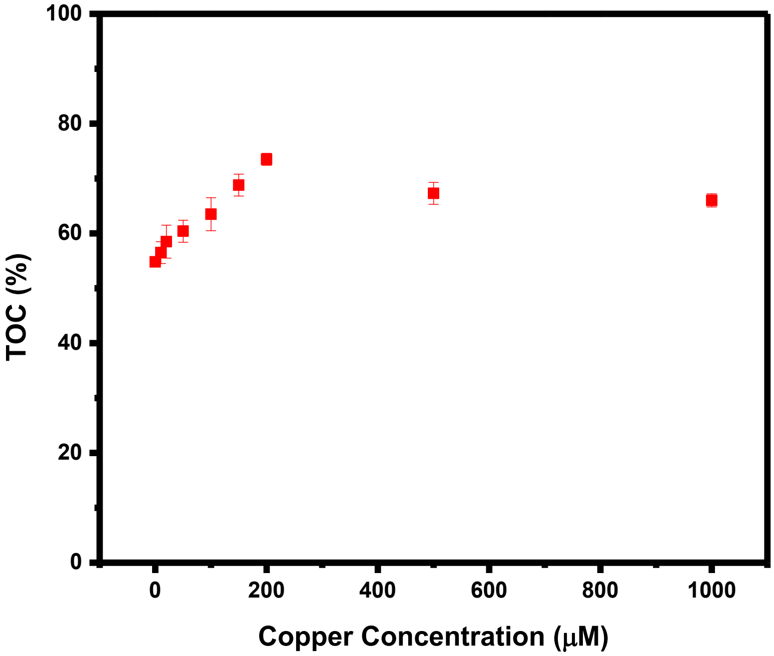


Fig. 18. PNA mineralization as a function of [Cu^{2+}].

Experiment performed at [NaCl] = 500 mM, 2.5 V, 5mL min^{-1}, pH 6.5, carbon felt electrode (*n*=3, ±RSD).

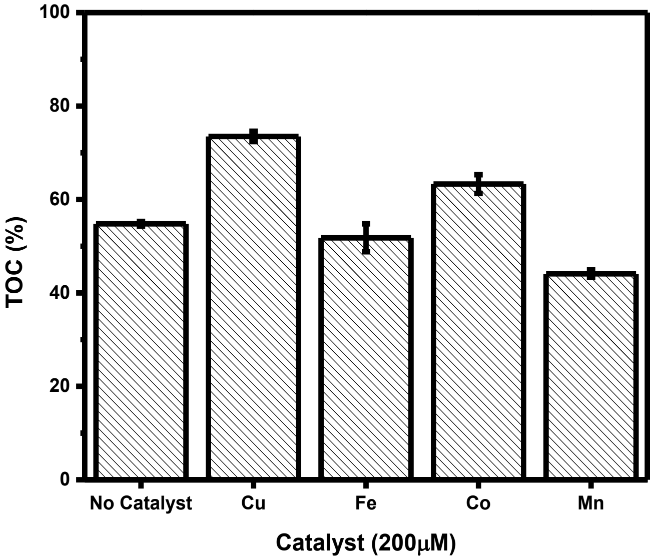


Fig. 19. PNA mineralization as a function of 200 μM of different M^{2+}ions (n=3, ±RSD).

Experiment performed at [NaCl] = 500 mM, 2.5 V, 5mL min^{-1}, pH 6.5, carbon felt electrode (*n*=3, ±RSD).

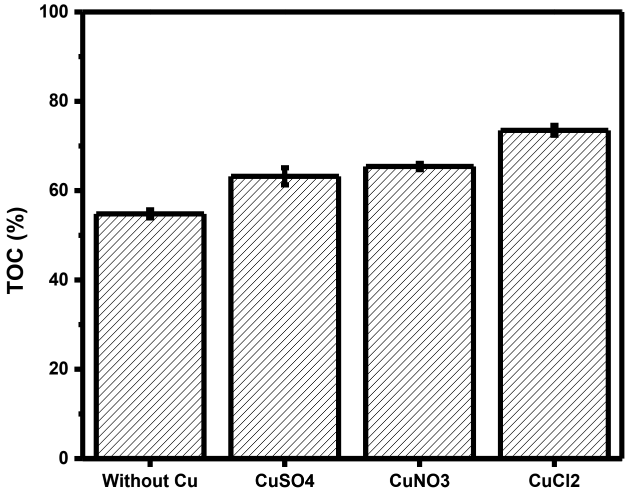


Fig. 20. PNA mineralization as a function of different Cu^{2+} salts.

Experiment performed at [NaCl] = 500 mM, 2.5 V, 5mL min^{-1}, pH 6.5, carbon felt electrode (*n*=3, ±RSD).

Additionally, several Cu^{2+}salts were evaluated where the relative activities were in the order $CuCl_2>Cu(NO_3)_2 \approx CuSO_4$ (Fig. 20). $CuCl_2$ as a supporting electrolyte shows better efficiency than other salts, perhaps, because of slightly higher conductivity of chloride anions (Barry & Lynch, 1991).

Table 3. Standard Reduction Potentials of Transition Metal Catalysts (Park et al., 2018)

Reduction reaction	E^0 **(V vs SHE)**
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.19
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.45
$Co^{2+} + 2e^- \rightarrow Co$	-0.28
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34

3.3.1.4 Flow Rate Influence

The EFS is a continuous flow reactor, and as such the flow rate affects the residence time of reactants on and between the porous electrodes, where longer residence times allow more ROS-based oxidation. The flow rate of the system was varied from 2.5–50 mL min^{-1} to optimize the efficiency and processing time (Fig. 21, Fig. 22, and Fig. 23). The most efficient mineralization and decolorization efficiencies were reached at a flow rate of 5 mL min^{-1}.

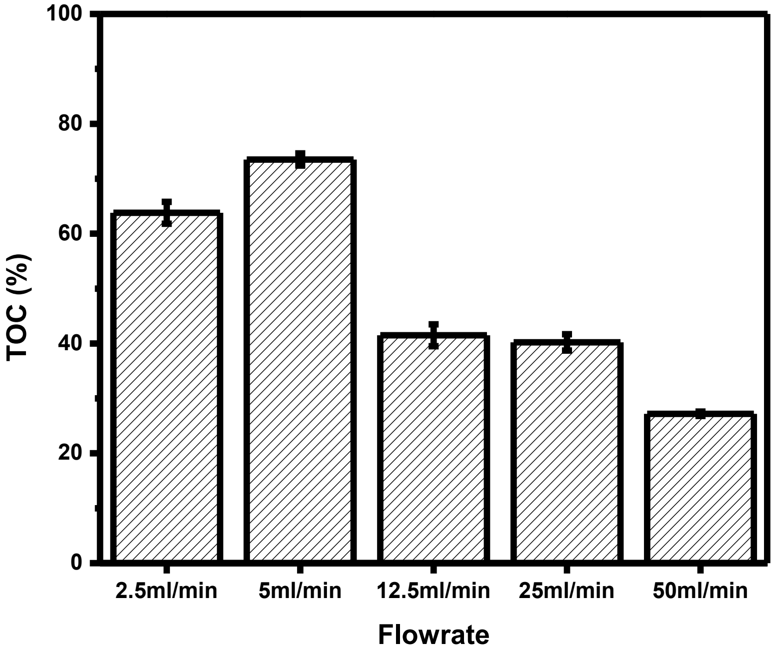


Fig. 21. PNA mineralization as a function of flow rate.

Experiment performed at 2.5 V, [Cu^{2+}] = 200 μM, [NaCl] = 500 mM, pH 6.5, carbon felt electrode. (*n*=3, ±RSD).

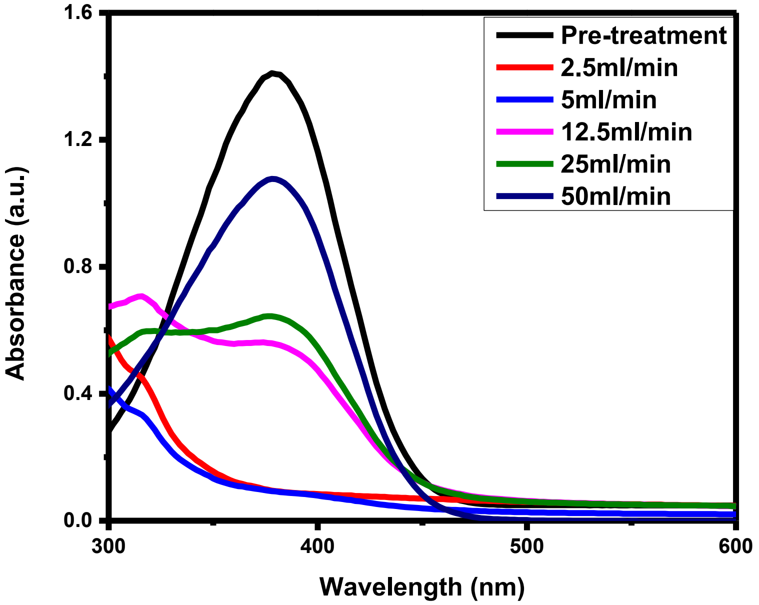


Fig. 22. PNA decolorization as a function of flow rate.

Experiment performed at 2.5 V, [Cu^{2+}] = 200 µM, [NaCl] = 500 mM, pH 6.5, carbon felt electrode.

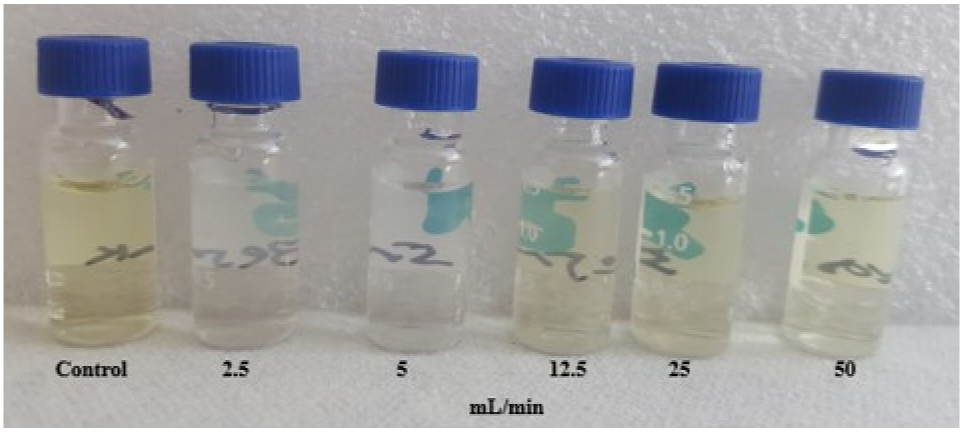


Fig. 23. PNA decolorization as a function of flow rate.

Experiment performed at 2.5 V, [Cu^{2+}] = 200 µM, [NaCl] = 500 mM, pH 6.5, carbon felt electrode.

3.3.1.5 Nature of Electrode

The EFS uses porous electrodes to allow the reaction mixture to continuously flow through. Two felt electrodes were compared, composed of either glassy carbon or graphite, with respect to their efficiencies. The glassy carbon felt electrode was superior for both mineralization and decolorization (Fig. 24 and Fig. 25). It also yielded a higher current density at identical potential as the graphite felt electrode, which indicates that it is more easily able to generate ROS.

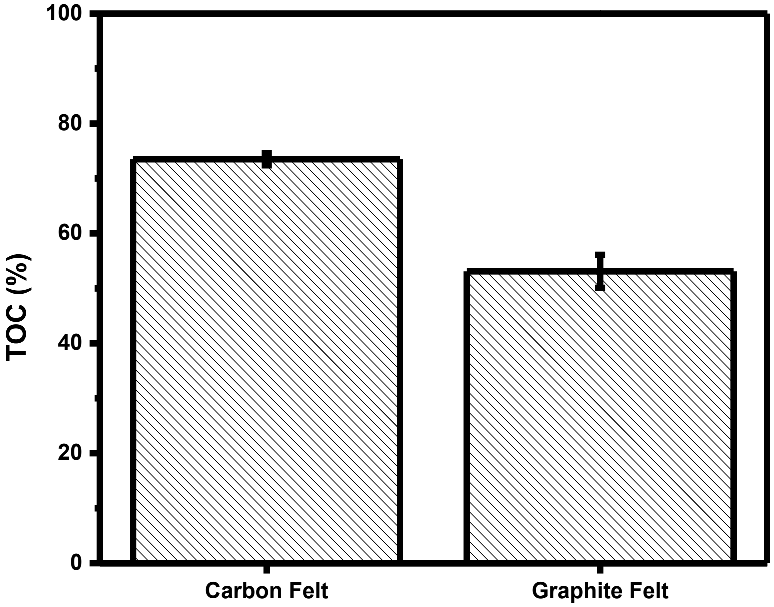


Fig. 24. PNA mineralization using either carbon (CF) or graphite (GF) felt electrodes. Experiment performed at 2.5 V, [Cu^{2+}] = 200 µM, [NaCl] = 500 mM, 5mL min^{-1}, pH 6.5 (*n*=3, ±RSD).

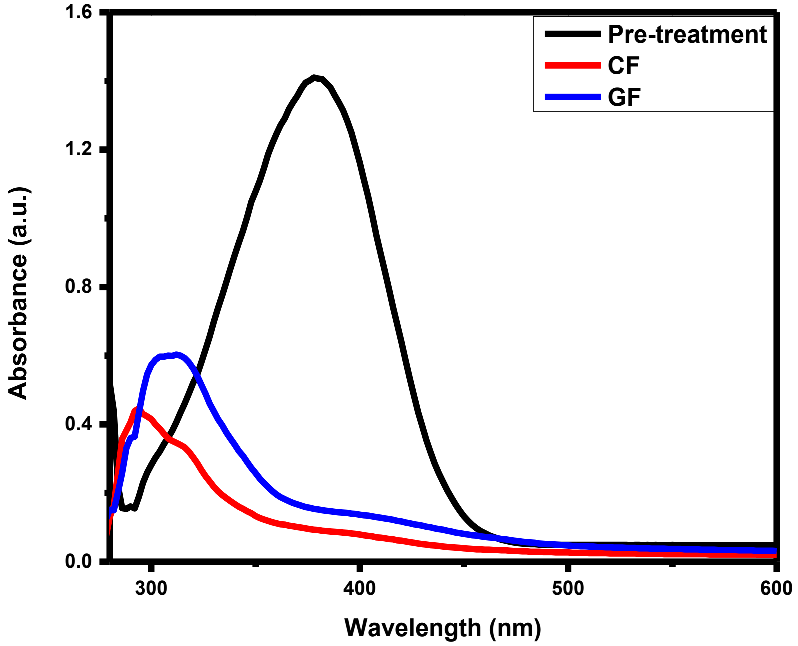


Fig. 25. PNA decolorization by the EFS using either glassy carbon (CF) or graphite (GF) felt electrodes. Experiment performed at 2.5 V, $[Cu^{2+}]$ = 200 µM, [NaCl] = 500 mM, 5mL min^{-1}, pH 6.5 (*n*=3, ±RSD).

3.3.1.6 pH Influence

Initial solution pH significantly affects oxidative processes in the electro-oxidation processes (Mussa et al., 2015). It was observed that maximum and minimum mineralization was achieved at pH 6.5 and 10, respectively (Fig. 26), with efficiency, dropping as pH was altered from neutral to either acidic or basic conditions. In the EFS, the chloride species present in the acidic and neutral medium is in the form of hypochlorous acid and hypochlorite (Eq. 5 & 6) (Boxall & Kelsall, 1992). These chlorine species in neutral and acidic medium possess sufficiently high oxidative potential to oxidize PNA (Pillai & Gupta, 2017), which agrees with an earlier study (Ma & Zhou, 2009). In basic medium, TOC removal efficiency is reduced, perhaps due to the low formation of hypochlorite ions but high formation of chlorate and perchlorate, the latter with low oxidative potential and relatively lower oxidizing capabilities (Eq. 20 and 21) (Marco & Giacomo, 2009; Moreira et al., 2016).

$$\mathrm{Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e^-} \qquad \mathrm{E^0 = +0.89V} \qquad (20)$$

$$\mathrm{ClO^- + 2OH^- \rightarrow ClO_2 + H_2O + 2e^-} \qquad \mathrm{E^0 = +0.67V} \qquad (21)$$

Further, more decolorization at pH 3 and 5 was observed, due to the high production of hypochlorite, a bleaching agent, in the acidic medium (Fig. 27) (Brillas & Martínez-Huitle, 2015). At pH 3 & 5, decolorization was higher than at neutral pHs but TOC removal efficiency was reduced. This result suggests the additional effect of the copper catalyst is stronger at neutral pHs than in acidic mediums. Therefore, the optimal pH for the electrochemical oxidation process for high TOC removal efficiency is near-neutral pH (without adjustment). Identical conclusions have been made in a research study where copper was used as a catalyst in pollutant degradation (Zhan et al., 2010). Hence, the EFS can easily be applied to real wastewater conditions at neutral pH without necessary adjustment, thereby, cost-saving.

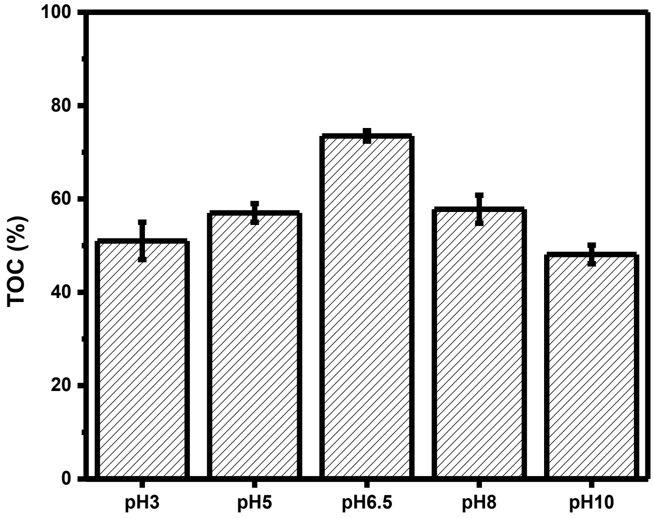


Fig. 26. PNA mineralization as a function of pH.

Experiment performed at 2.5 V, [Cu^{2+}] = 200 µM, [NaCl] = 500 mM, 5 mL min^{-1}, carbon felt electrode. (*n*=3, ±RSD).

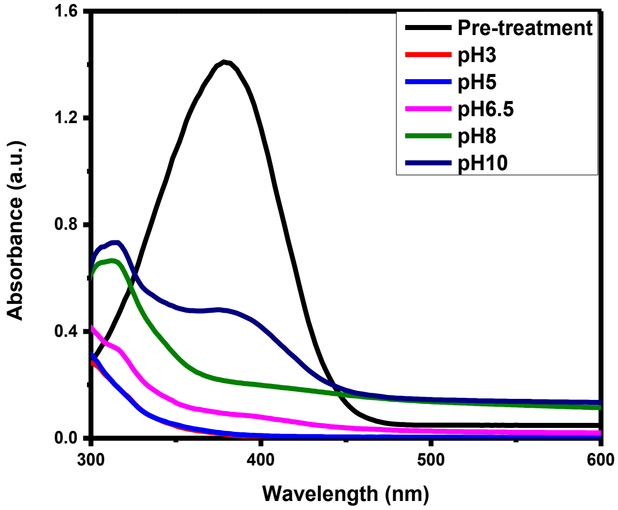


Fig. 27. PNA decolorization as a function of pH.

Experiment performed at 2.5 V, [Cu^{2+}] = 200 µM, [NaCl] = 500 mM, 5 mL min^{-1}, carbon felt electrode.

3.3.2 Reactive Species Identification

Reactive species, e.g., Cl_2 and O_3 have contributed to the indirect oxidation of organic pollutants (Martínez-Huitle & Ferro, 2006; Särkkä et al., 2015). Cl^- in the supporting electrolyte leads to anodic Cl_2 production, which can be converted into a series of reaction to ClO^- (Eq. 16-19). Organic pollutants are oxidized by chlorine species in the form of HOCl (E = 1.63 V), ClO^- (E = 0.9 V), and Cl_2 (E = 1.359 V).

O_3 can also be generated electrolytically (Eq. 22) but is disfavored because of the thermodynamic stability of O_2 (Honda et al., 2013) (Eq. 23). It can be successfully formed using electrodes with high oxygen evolution overpotentials. O_3-based water treatment is advantageous because of its high redox potential (E = 2.07 V) and benign byproduct, O_2 (Marco & Giacomo, 2009).

$$3H_2O \rightarrow O_3 + 6e^- + 6H^+ \qquad E^0 = 1.51V \quad Vs \quad SHE \qquad (22)$$

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+ \qquad E^0 = 1.23V \quad Vs \quad SHE \qquad (23)$$

At an optimum high applied potential of 2.5 V, water splitting occurs from 1.23 V where oxygen is formed, beyond that voltage, some oxygen molecules formed dissociate to form oxygen atoms which can subsequently react with oxygen molecules to form ozone (Marco & Giacomo, 2009). The O_3 produced can then oxidize organic pollutants and decompose to O_2 (Särkkä et al., 2015).

Differential pulse voltammetry (DPV) was performed to identify the reactive species produced in the EFS, which yields current density peaks for the species at their oxidation potentials. Four experiments were performed to identify the reactive species and their influence (Fig. 28, Fig. 29, Fig. 30, Fig. 31, and Table 4), and samples were scanned from 0-3V. Each experiment contained NaCl (500 mM) electrolyte and consisted of either the blank, $CuCl_2$ (200 μM), PNA (100 μM), or both. O_2, Cl_2, HOCl, and O_3 were observed in each reaction mixture (and Cu^{2+} in Cu-containing reactions), but the HOCl and O_3 peaks were significantly increased in the presence of Cu^{2+} only, and the Cl_2 peak disappeared in both PNA-containing reactions. The PNA appeared to quench the more reactive species, Cl_2 and O_3, as it was degraded. Notably, the electrodes were visibly unstable beyond 2.5 V.

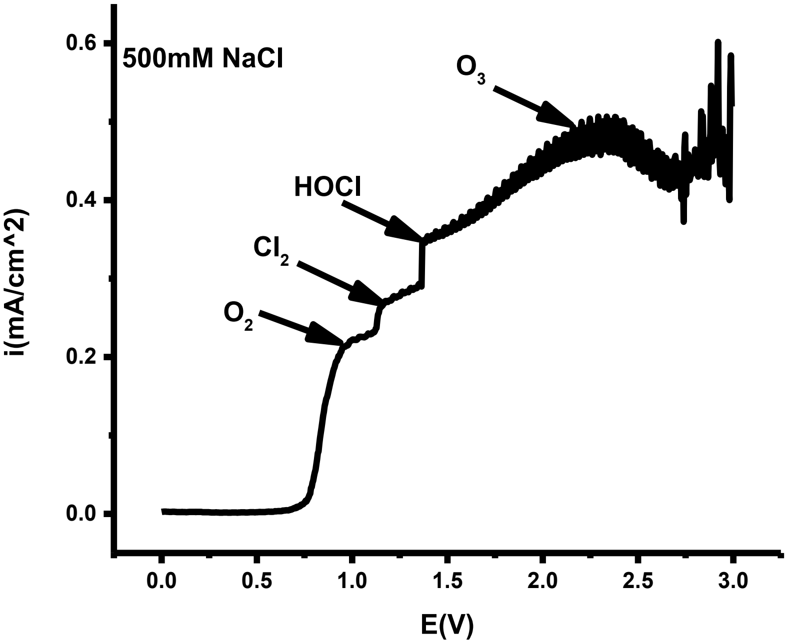


Fig. 28. Differential pulse voltammetry (DPV) Analysis of [NaCl] = 500 mM over 0-3 V scan.

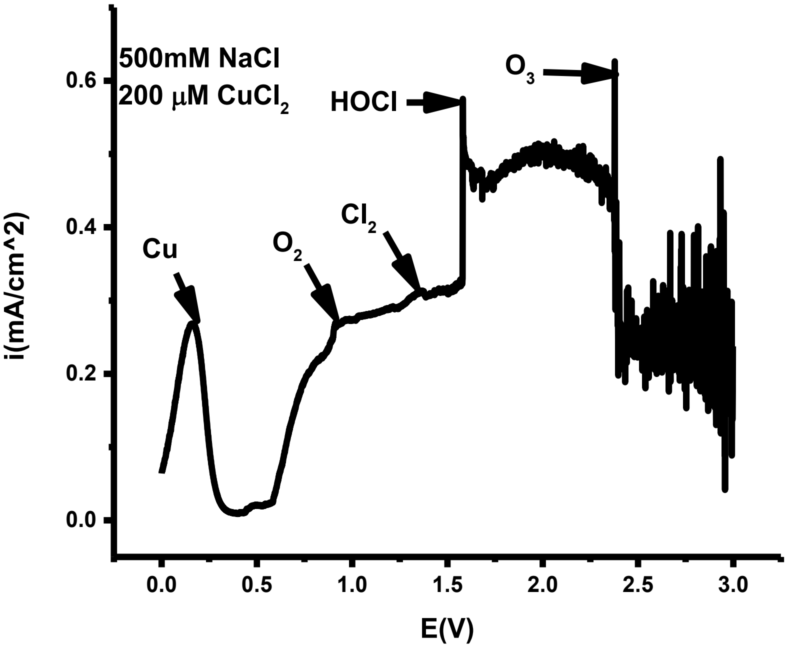


Fig. 29. DPV Analysis of [NaCl] = 500 mM and [$CuCl_2$] = 200 μM, over 0-3 V scan.

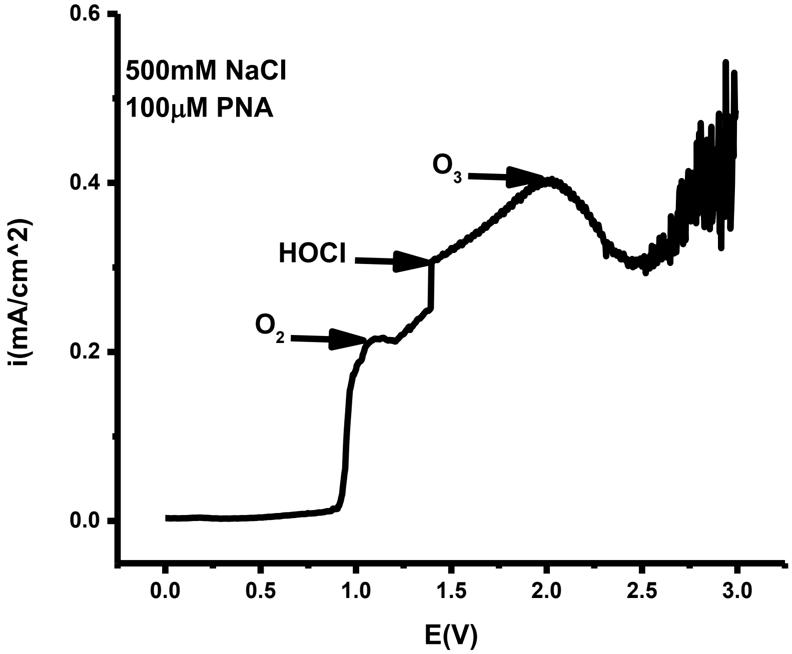


Fig. 30. DPV Analysis of [NaCl] = 500 mM and [PNA] = 100 μM, over 0-3 V scan.

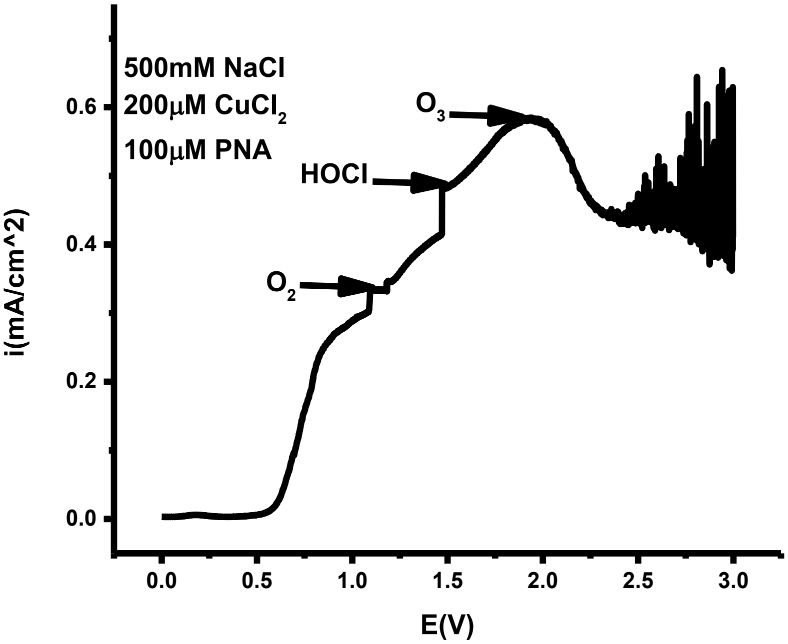


Fig. 31. DPV Analysis of [NaCl] = 500 mM, $[CuCl_2]$ = 200 µM and [PNA] = 100 µM , 0-3 V scan.

Table 4. Differential Pulse Voltammetry Analysis for Reactive Species Identification.

Experiment Condition	**Current Intensity Peak O_2 ($mA_{\_}cm^{-2}$)**	**Current Intensity Peak O_3 ($mA_{\_}cm^{-2}$)**	**Current Intensity Peak HOCl ($mA_{\_}cm^{-2}$)**
NaCl	0.23	0.51	0.35
NaCl + $CuCl_2$	0.27	0.62	0.58
NaCl + PNA	0.23	0.4	0.31
NaCl + $CuCl_2$ + PNA	0.26	0.58	0.49

3.3.3 Toluene Oxidation

To evaluate the treatment scope of the EFS, 0.1% *w/v* Toluene contaminated water was treated under the optimized reaction conditions. Without applied voltage, 8.8% adsorption on the electrode was observed, while at optimized parameters, a TOC reduction of 578 mg L^{-1} (pretreatment was 603.9 mg L^{-1} and post treatment was 52 mg L^{-1}) was achieved (Fig. 32). The GC-MS analysis of the sample pre and post treatment showed complete removal of toluene with no residual volatile compounds (Fig. 33).

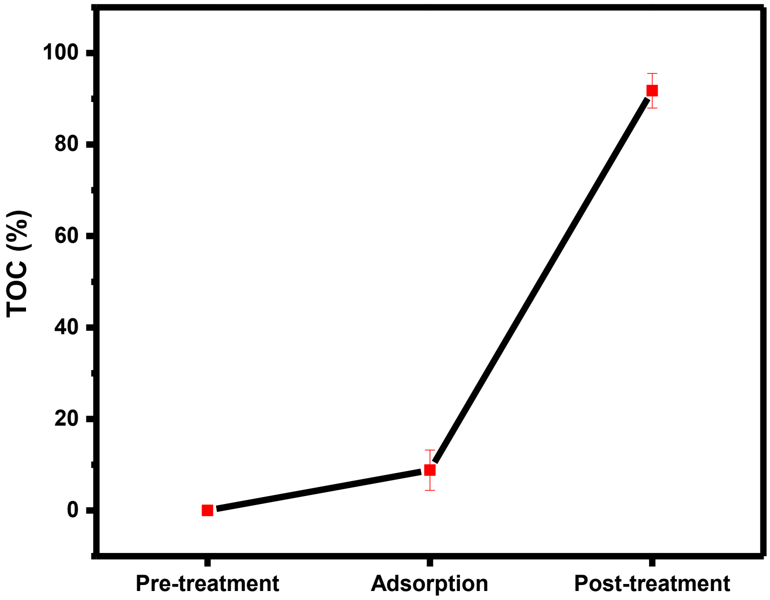


Fig. 32. Treatment of 0.1% Vol Toluene contaminated water by the EFS.

Experiment performed at 2.5 V, [Cu^{2+}] = 200 μM, [NaCl] = 500 mM, 5 mL min^{-1}, glassy carbon electrode. (*n*=3, ±RSD).

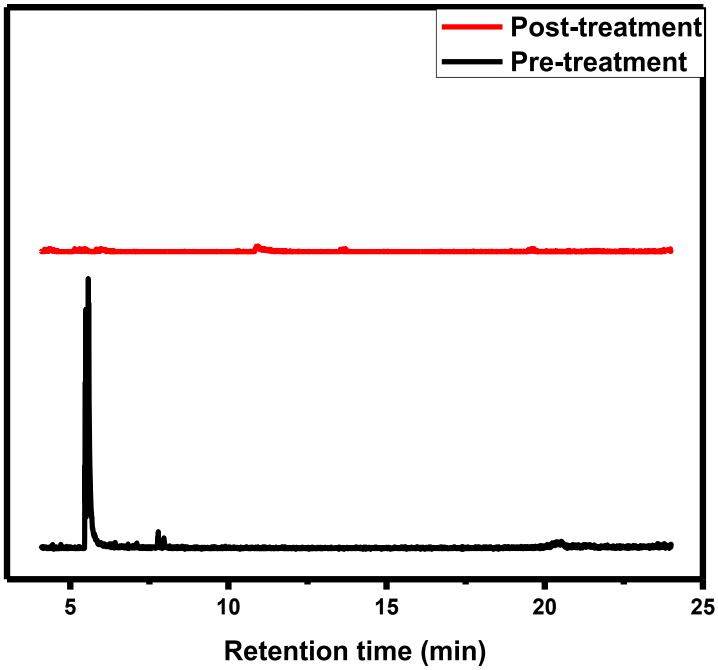


Fig. 33. Gas Chromatogram of extracted toluene contaminated water pre and post treatment. Experiment performed at 2.5 V, $[Cu^{2+}]$ = 200 µM, [NaCl] = 500 mM, 5 mL min^{-1}, glassy carbon electrode.

3.3.4 Reduction of Heavy Metals

In addition to oxidizing organic pollutants, in the EFS, heavy metals (*i.e.*, Pb, Cd, and Cr) are simultaneously reduced when a wastewater sample is passed through. Prior to passing BH wastewater through the EFS, 50 mg L^{-1} concentration of Cr, Pb, and Ni were individually investigated as a model. The result showed metal concentrations reduced post-treatment. In a control experiment, the individual metals were passed through the CFR without applied voltage to evaluate for adsorption. Thus, of the reduction in metal concentration, 13% Pb, 21% Ni, and 16% Cr, were recovered via adsorption on the reactor walls and electrode surface when the voltage was not applied to the system (Table 5). The remaining removal efficiency can be attributed to electroreduction (*i.e.*, gain of electrons by metallic atoms on the cathodic surface) when the voltage was applied (Fig. 34) (Issabayeva et al., 2006).

Table 5. ICP-MS of Metal-contaminated Water.

Treatment	Pb	Ni	Cr
Adsorption (%)	13	21	16
Electroreduction (%)	24	44	70

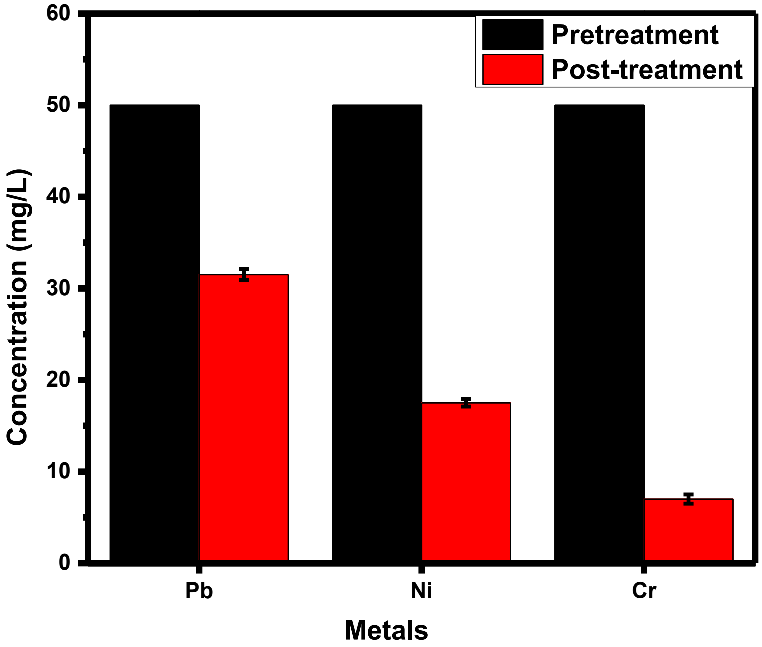


Fig. 34. Treatment of metal-contaminated water by the EFS pre and post treatment.

Experiment performed at 2.5 V, $[Cu^{2+}] = 200\ \mu M$, [NaCl] = 500 mM, 5 mL min^{-1}, carbon felt electrode (*n*=3, ±RSD).

The order of reduction did not follow the increase in the reducing strength of the metals (*i.e.*, $Pb^{2+} < Ni^{2+} < Cr^{3+}$) (Table 6). This perhaps indicate that more of the metal reduction is attributable to adsorption rather than electro reduction (Liu et al., 2019).

Table 6. Standard Reduction Potential of Metals.

Reduction reaction	**E^0 (V vs Standard Hydrogen Potential)**
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.26
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73

3.4 Electrochemical Treatment of Environmental Wastewater from Boat Harbour

We evaluated the effectiveness of the EFS for the real contaminated BH water sample. The EFS treatment of this real wastewater sample resulted in mineralization of 76 mg L^{-1} total organic carbon and the major contaminants were removed (Fig. 35 and Fig. 36).

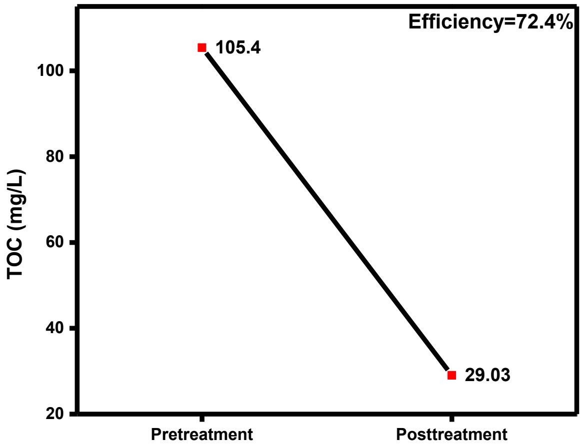


Fig. 35. Treatment of Boat Harbour wastewater by the EFS, mineralization (*n*=3, ±RSD). Experiment performed at 2.5 V, $[Cu^{2+}]$ = 200 μM, [NaCl] = 500 mM, 5 mL min^{-1}, natural pH, carbon felt electrode.

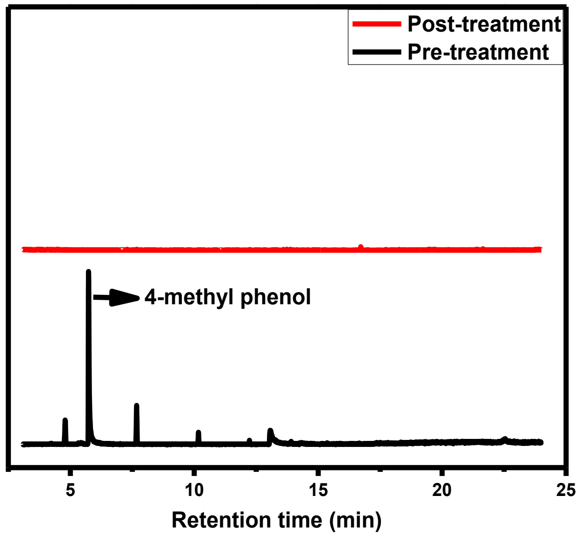


Fig. 36. Gas Chromatogram of contaminated water pre and post treatment.

Experiment performed at 2.5 V, [Cu^{2+}] = 200 μM, [NaCl] = 500 mM, 5 mL min^{-1}, natural pH, carbon felt electrode.

Simultaneously, a reduction in the metal concentration of the real wastewater from BH was observed, perhaps, via both adsorption and electroreduction. Adsorption of heavy metals can occur by movement of ions through binding sites on the cathodic surface; while electrodeposition can occur as a result of migration of ions to the cathodic surface thereby forming an electrical double layer and reduced to zerovalent metal form (Liu et al., 2019). After the treatment using the EFS, all five metals of concern including [As], [Cd], [Cr], [Ni], and [Pb] were significantly reduced in concentration, with As, Cd, and Cr close to the WHO drinking water standards (W.H.O, 2018) and the Canadian Council of Ministers of the Environment (CCME) Protection for Freshwater Aquatic Guidelines (CCME, 2019) (Table 7). It is suspected that the competition among metal atoms for limited electrons on the cathodic surface limits electroreduction efficiency. This is because when more than two metal atoms are present in an electrolytic solution, they compete for electrons to be deposited on the cathode (Martínez-Huitle & Brillas, 2008). The order of electrodeposition depends on their reducing strength reflected by the position of the metals on the electrochemical series (Zheng et al., 2013).

Table 7. Concentration of Metals Pre and Post EFS Treatment.

Metals	**Pretreatment (mg/L)**	**Posttreatment (mg/L)**	**WHO Drinking Water Standards (mg/L)**	**CCME Guidelines (mg/L)**
Cr	8.26	0.097	0.05	0.009
Ni	8.4	0.85	0.07	NA
As	21.38	0.036	0.01	0.005
Cd	7.44	0.0073	0.003	NA
Pb	8.11	0.49	0.01	NA

3.5 Energy Efficiency

In the EFS, as the applied potential difference increases, the energy consumed increases, however as flow rate increase the energy consumed decreases since less time is spent per unit volume (Fig. 37 and Fig. 38). Under the optimized conditions (*i.e.*, 2.5 V and 5 mL min^{-1}) the EFS consumes 23 kWh per kg of organic carbon removal. To make a comparison of energy consumption obtained in other projects or reports where variables such as real wastewater sample matrix, anode material, treatment time, and sample volumes are different, seems unreasonable. For instance, a study by a group revealed the energy consumption obtained after treating a leachate sample by electrochemical technique to be 90.1 kWh per kg (Annabel et al., 2013). In another study, where the group made use of boron-doped diamond (BDD) electrodes in the treatment of a leachate sample, 140 kW/h per litre of the sample was reported as energy consumption (Panizza & Martinez-Huitle, 2013). Also, in comparison to another group where a tubular electrochemical reactor was applied for industrial textile wastewater, a COD removal efficiency of 53% was achieved with an energy consumption of 193.1 kWh per kg (Körbahti & Tanyolaç, 2009).

Further, we revealed that the energy consumed without electrolyte was high because of the absence of ions for conductivity. Also, when $NaNO_3$ was used as the electrolyte, the energy consumption was high relative to NaCl, KCl, and NaBr, with NaCl being the most energy efficient electrolyte, perhaps due to relatively high ion mobility (Barry & Lynch, 1991) (Fig. 39).

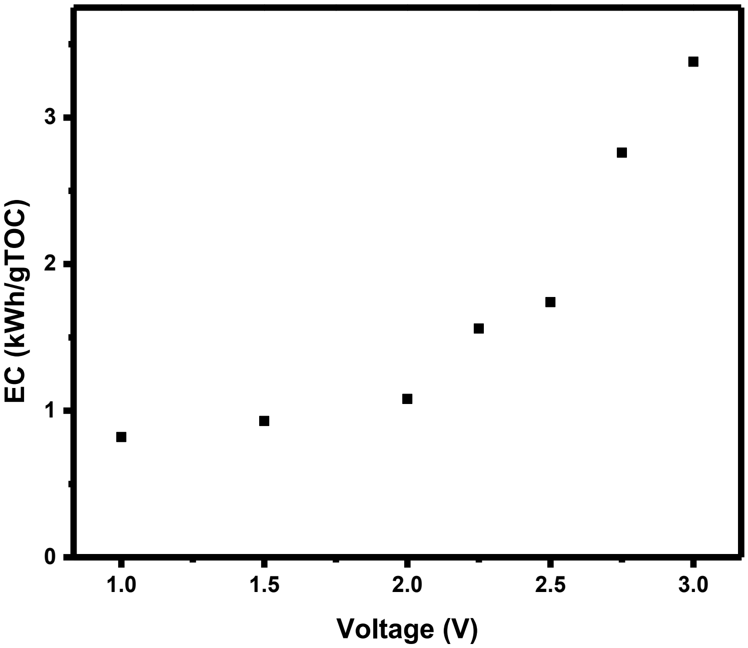


Fig. 37. Energy Consumption (EC) as a function of applied potential.

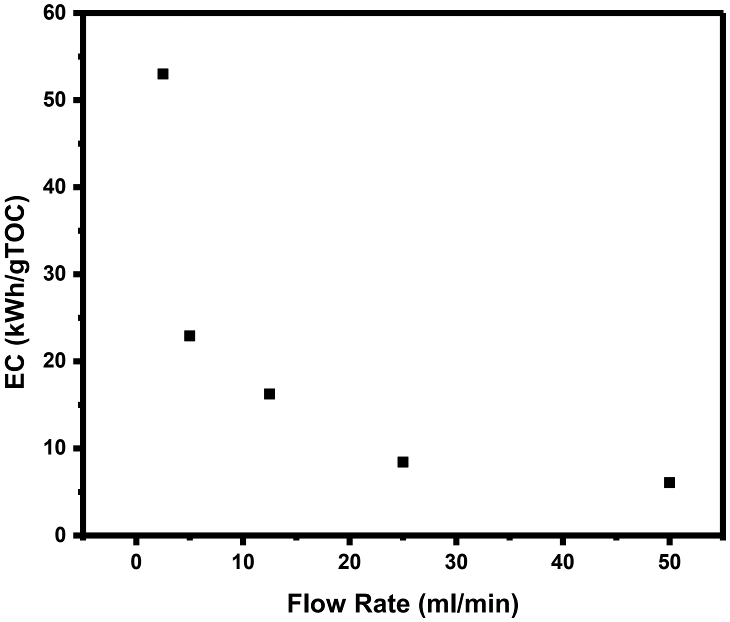


Fig. 38. Energy Consumption (EC) as a function of flow rate.

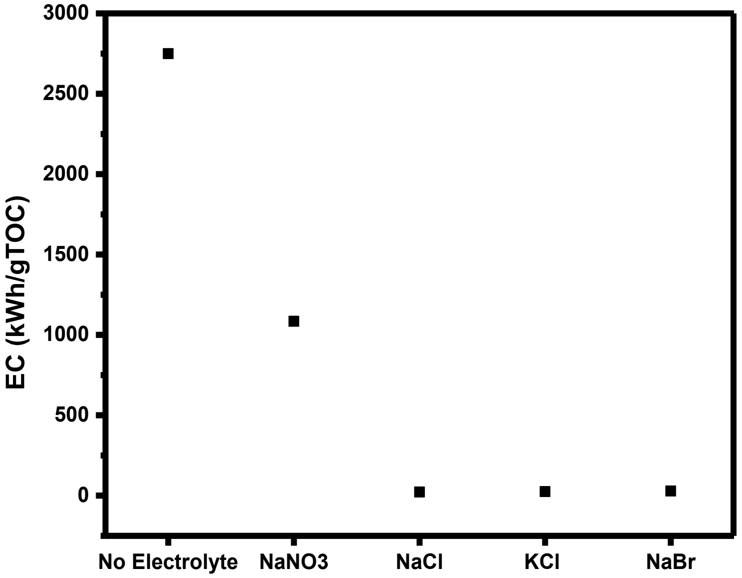


Fig. 39. Energy Consumption (EC) as a function of supporting electrolyte.

Unless specified [electrolyte] = 500 mM, 2.5 V, 5 mL min^{-1}, pH 6.5 [Cu^{2+}] = 200 μM, carbon felt electrode.

3.6 Economic Viability

The practicability and feasibility of any technology are determined by the operational cost (*i.e.*, materials and electricity, and capital cost) relative to alternative approaches. The laboratory-grade copper chloride cost 4.8 USD kg^{-1} while the sodium chloride cost 1 USD kg^{-1}. The electricity cost was calculated using the industrial tariff rate for Nova Scotia at 0.08 USD kWh^{-1} (Jane, 2019).

Under optimum operating conditions, the environmental water samples from Boat Harbour at the optimal removal efficiency (*i.e.*, simultaneous 76 mg L^{-1} organic carbon and significant heavy metal removal), would cost ~ 0.03 USD and ~0.02 USD L^{-1}, for chemical and electricity inputs, respectively. This equates to 0.66 USD g^{-1} of carbon removed in addition to heavy metals removal (Table 8). Low energy usage and operational cost of 0.2 kWh L^{-1} and 0.05 USD L^{-1} were achieved, respectively. This seems inexpensive relative to another study where a similar technique was used to remediate pulp mill effluent at energy consumption and operational cost of 1.2 kWh L^{-1} and 0.29 USD L^{-1} obtained, respectively (Khansorthong & Hunsom, 2009). This implies with 78 mg L^{-1} TOC removed, it would cost the group 3.7 USD to remove 1 g of TOC. This is relatively expensive compared to 0.66 USD required to remove the same amount of TOC if EFS were applied.

Table 8. Cost Estimate- Boat Habour Bulk Water Remediation using the EFS.

Item	**Cost (USD)**
Chemical (Electrolyte and catalyst) consumables per litre of sample	0.03
Energy input (0.2 kWh L^{-1}) per litre of sample	0.02
Removal of 76 mg TOC, 8 mg Cr, 7.5 mg Ni, 21 mg As, 7.4 mg Cd, and 7.6 mg Pb, per litre of sample treated	0.05
To remove 1 g TOC, 0.1 g Cr, 0.1 g Ni, 0.28 g As, 0.98 g Cd, and 0.1 g Pb, from wastewater sample	0.66

In relation to the remedial option decision document proposed for the clean-up of BH by GHD water engineering company, which include the use of low technology system (*i.e.* coarse filtration, coagulation, clarification, and adsorption-based processes) to remove contaminants of concern from bulk water; the estimated cost of treatment proposed is 6 USD per m^3 (1000 litres) (GHD, 2018), which is 5 times cheaper than the treatment cost using the EFS. This value represents only the chemicals and consumables cost, without the utility cost, using the low technology system mentioned earlier (GHD, 2018). Although the estimated cost using the EFS is 30 USD per m^3, it is important to note that NaCl claims 99% of the cost , whereas if we used seawater, which contains 35 g salts per litre (USGS, 2015), the chemical and consumable cost would drastically reduce. In addition, since the cost estimate does not include the utility cost, perhaps the usage of the EFS, whereby renewable energy such as solar panel could be applied, provides better efficient system with reduced utility cost than the alternative treatment technique by GHD. Further, it is important to consider sludge production and treatment cost after the BH water treatment using the proposed treatment methods by GHD, whereby significant associated sludge treatment cost will increase the overall operational cost. Another disadvantage of the proposed GHD remediation treatment design is the inability of the geotube filtration system to eliminate biologically active contaminants. This implies additional biological treatment would be required for complete wastewater treatment, hence, additional cost.

3.7 Conclusions and Recommendations

3.7.1 Conclusions

The results obtained in this study lead to the following conclusions:

1. The EFS, applied in a continuous flow reactor was effectively applied to degrade PNA as a model contaminant, whereby various operational parameters were optimized.
2. The optimized experimental condition was applied to degrade environmental wastewater from BH.
3. Simultaneous organic pollutants and heavy metals removal from BH wastewater were achieved.
4. The identification of reactive species in the EFS via DPV analysis indicated chlorine species and ozone were largely responsible for the organic pollutant mineralization via mediated electro-oxidation.
5. The use of copper as a catalyst was found to activate more the influence of the reactive species (hypochlorous acid and ozone) indicated by the DPV analysis.
6. The pH of the system was investigated, and it was revealed that there was no need for acidity or alkalinity adjustment of a sample, since the optimum condition which yielded the highest TOC mineralization was neutral. Hence, no cost incurred for pH adjustment.
7. Heavy metal removal was achieved through adsorption on the electrode surface and electroreduction process.
8. Energy consumption of the EFS was investigated and at 0.2 kWhr L^{-1} of a sample, it was found energy efficient relative to alternatives.
9. The economic analysis which was carried out at optimum operating conditions shows that at 0.05 USD L^{-1}, the EFS is relatively inexpensive compared to alternative treatment technique.

3.7.2 Recommendations

In consequence of the obtained results, the following recommendations should be considered to further this research:

1. The unidentified intermediates and products after the degradation of PNA via the EFS should be identified qualitatively to propose a reaction mechanism.
2. To evaluate the effect of the EFS on real wastewater samples and monitor toxic by-products, for example, organo halides, toxicity study should be conducted. This determines the toxicity of the treated effluent, which is an important parameter to propose a wastewater treatment strategy and approach.
3. In terms of electroreduction of metals, more research is needed to establish electrodeposition of metals on the surface of the cathode and formation of metallic oxides using energy dispersed x-ray spectroscopy (EDS).
4. In terms of scaling up the continuous reactor flow, more experiments must be performed to evaluate the number of runs needed before electrode wear, since there will be constant electro generation of active chlorine species which attacks them.
5. Finally, the biodegradability of the treated effluent should be evaluated to find the fit for EFS in a combined wastewater treatment strategy.

Chapter IV

4.0 Effective Hybrid Treatment Technique for Landfill Leachate

Abstract: Leachate, a liquid that has percolated through a landfill and extracted organic and inorganic compounds, is high strength wastewater which is difficult to treat by conventional treatment techniques and demand advanced methods to achieve environmental guidelines. Hybrid processes including deodorization using potassium permanganate ($KMnO_4$), coagulation and flocculation using ferric chloride or Alum, chemical oxidation using hydrogen peroxide or persulfate, and electrochemical filtration system (EFS), were investigated to treat landfill leachate samples from the Guysborough Waste Management Facility, Nova Scotia (NS), Canada. The comparison of various coagulants and chemical oxidants used were studied on total organic carbon (TOC) removal for optimum efficiency. The results revealed a significant reduction in TOC removal achieved from 1520 to 131 mg L^{-1} (91.4% TOC removal) after applying the combined treatment processes. Additionally, application of the last stage of treatment, EFS, allowed for heavy metal removal including As, Cd, and Pb close to WHO drinking water guidelines. The financial and environmental costs of the integrated processes were evaluated. The result showed Ferric Chloride as coagulant was more effective than Alum. Also, results revealed that persulfate as oxidant degraded more organics in the leachate than hydrogen peroxide. Overall, the combined cost was calculated and equates to \$0.06 g^{-1} of organic carbon removed.

4.1 Introduction

The eradication of solid urban waste is usually done through incineration, composting, or landfilling (Mussa et al., 2015). Studies have revealed that sanitary landfilling serves as the most common and inexpensive method of solid waste management (Lema et al., 1988). Landfilling allows for waste decomposition under controlled environmental conditions, which mitigates environmental problems associated with the dispersed waste (Lema et al., 1988). However, landfills generate leachate, a type of wastewater formed by water permeating through solid waste, which extracts organic and inorganic matter through hydrolytic and extractive processes. Further, depending on the characteristics and degree of deterioration of the debris, leachates can contaminate local surface and ground waters, thereby compromising local water quality. Leachates are complex solutions, containing high loads of dissolved organic matter, heavy metals, and ammonia (Long et al., 2017). The toxicity of leachate samples depends on the waste composition and characteristics, hydrogeological factors, and age (young <5 years, intermediate 5–10 years, and mature >10 years old) of the landfill (Mandal et al., 2017). Various treatment techniques including biological processes (Trois et al., 2010), ozone oxidation (Leszczyński & Maria Jolanta, 2018), Fenton reaction (Aftab et al., 2018), and photocatalysis (Hassan et al., 2016) have been investigated for leachate treatment. However, the huge total organic load and complex sample matrix of leachate has made it difficult for a single treatment method to meet discharge guidelines (Zhong et al., 2017). Hence, incorporation of other technologies in a combined strategy, which is a fundamental approach in wastewater treatment, is necessary to reduce the leachate toxicity load to meet discharge standards (Jaafarzadeh et al., 2017). For instance, biological processes followed by membrane technology (Fernandes et al., 2015), has been applied to treat leachate samples in the past. However, as the leachate samples age, biodegradability decreases and reduces the effectiveness of biological treatment (Ahmed & Lan, 2012). Other combined treatment techniques such as ozonation and biological method (Svensson et al., 2015), coagulation-flocculation and oxidation (Wang et al., 2011), adsorption and chemical oxidation (Abdullah et al., 2014), have also been investigated in leachate treatment.

This study demonstrates heavily contaminated landfill leachate samples, *e.g.*, with a total organic carbon (TOC) content of >1000 mg L^{-1} and pharmaceutical pollutants, can be treated using a combination of chemical and electrochemical filtration processes. The objective of this research is to apply a combination of processes including deodorization, coagulation, and oxidation, to decontaminate heavily contaminated leachate samples. Pre-treatment of heavily contaminated leachate to remove odor-producing compounds can be achieved through chemical oxidation by oxidants such as $KMnO_4$. $KMnO_4$ has an oxidative potential of 1.7 V, capable of oxidizing organic compounds via electron abstraction, hydrolysis, or hydroxylation (Xie et al., 2019). $KMnO_4$, as an electrophile, oxidizes organic compounds by attracting electrons from their electron-rich functional group (*e.g.*, carbon to carbon double bond) and forming MnO_2, which easily precipitates out of the sample (Maxwell, 1986).

The coagulation and flocculation method has been used in the past to treat leachate samples (Amokrane et al., 1997) and has also been used in this work. This process can be applied to remove some of the suspended particles from solution, by utilizing the addition of coagulants such as potassium aluminum sulfate (Alum or $KAl(SO_4)_2.12H_2O$) or iron (III) chloride ($FeCl_3$) to the leachate sample. The positively charged metal ions of the coagulants (*i.e.*, Al^{3+} and Fe^{3+}), attracts negatively charged organic compounds in the sample, allowing particulates to agglomerate and form flocs that settle to the bottom of the solution (Amokrane et al., 1997). Additional treatment technique (i.e., chemical oxidation), involves using strong oxidants, such as hydrogen peroxide (H_2O_2) or sodium persulfate ($Na_2S_2O_8$) to further mineralize residual dissolved organic matter and reduce the toxicity load of the leachate. H_2O_2 is an oxidant with an oxidative potential of 1.8 V which has been used to oxidize organic pollutants in wastewater (Abdullah et al., 2014; Zhou et al., 2013). Also, H_2O_2 can generate hydroxyl radical ($OH^\cdot$), a powerful oxidant, when reacted with iron in a Fenton reaction (Blanco et al., 2012). Furthermore, $Na_2S_2O_8$ has been successfully investigated for organic compound oxidation in water remediation (Abu Amr et al., 2013). $Na_2S_2O_8$ is a strong oxidant with an oxidative potential of 2.01 V, and capable of oxidizing organic substances. On activation, $SO4^{\cdot -}$ with a redox potential 2.6 V, can be generated by persulfate and applied to degrade persistent organic substances (Zhong et al., 2017). $Na_2S_2O_8$ is readily water-soluble, safe to handle, and stable at room conditions (Alizadeh Fard & Barkdoll, 2018).

Finally, a new electrochemical filtration technique was introduced to further treat the leachate sample after coagulation and oxidation processes. The electrochemical filtration process involves the passage of the sample through a continuous flow reactor (CFR), whereby the organic pollutants in the sample are further oxidized on the anode by electrogenerated reactive species in the solution. Simultaneously, heavy metals including Pb and Cd, are reduced on the cathodic surface in the electrochemical process. The oxidation of pollutants occurs by the reactive species generated electrolytically, while the heavy metal removal is attributed to electroreduction on the cathode in the CFR. The influence of various dosages of coagulants and oxidants were investigated using the landfill leachate samples to maximize total organic carbon removal efficiency at optimum operational conditions. Additionally, comparisons of coagulants and chemical oxidants were studied in terms of financial and environmental costs. The economic viability of the combined treatment methods was also investigated in this research.

This study is intended to develop a combination treatment method to effectively remove persistent organic pollutants and heavy metals, which are otherwise difficult to eliminate by conventional techniques, from leachate sample.

4.2 Materials and Methods

4.2.1 Leachate Sampling

The landfill leachate treated in this report was obtained from the Guysborough Waste Management Facility, NS, Canada (The Municipality of the District of Guysborough, 151 Waste Management Rd., Boylston, NS). The leachate was collected in plastic containers and stored at

4°C before and during experiments, to reduce potential changes to the sample matrix. The characteristics of the leachate sample are shown in Table 9 and the pictorial representation in Fig. 40.

Table 9. Composition of Leachate.

Parameter	**Leachate**
Appearance	Dark
pH	7-8
TOC (mg L^{-1})	1520

Fig. 40. Landfill leachate sample from the Guysborough Waste Management Facility, NS, Canada.

4.2.2 Chemical and Reagent

All the chemicals used in this research project were of analytical grade and applied without further purification. The ferric chloride ($FeCl_3$) used as a coagulant in this study was obtained from Sigma Aldrich with >97% grade. Potassium Aluminum sulfate (alum) was bought from Dollar Store, Canada. Potassium permanganate ($KMnO_4$) and sodium persulfate ($Na_2S_2O_8$), applied as oxidants, were purchased from Sigma Aldrich with 99% purity. Hydrogen peroxide (H_2O_2, 30% w/w), used as a chemical oxidant was bought from EMD Millipore, USA. Copper (II) Chloride ($CuCl_2$) as a catalyst, and sodium chloride (NaCl) as an electrolyte, were obtained from Sigma Aldrich with >99.9% purity. The carbon felt electrodes used in this research were purchased from Fuel Cell Store and used as procured. Fresh nano water obtained daily from a Barnstead Nanopure water system was used to prepare solutions for all experiments.

4.2.3 Sample Preparation: Solid-Phase Extraction (SPE)

Solid-phase extraction (SPE) cartridges [6*cc* Oasis® HLB extraction cartridge (150 mg, 30 µm)] were pre-conditioned with acetonitrile and nano pure water before extracting 1000 ml of leachate or treated leachate sample, then washed with water, dried, and eluted with 1.5 ml of acetonitrile. Samples were then transferred into 2 ml glass vials for Gas Chromatography-Mass Spectroscopy (GC-MS) analysis. In addition, samples were prepared for metal analysis by dissolving a 10% sample in 1% Nitric acid solution before analysis by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

4.3 Experimental Setup

The sequence of the integrated treatment processes applied to the leachate is shown in Fig. 41.

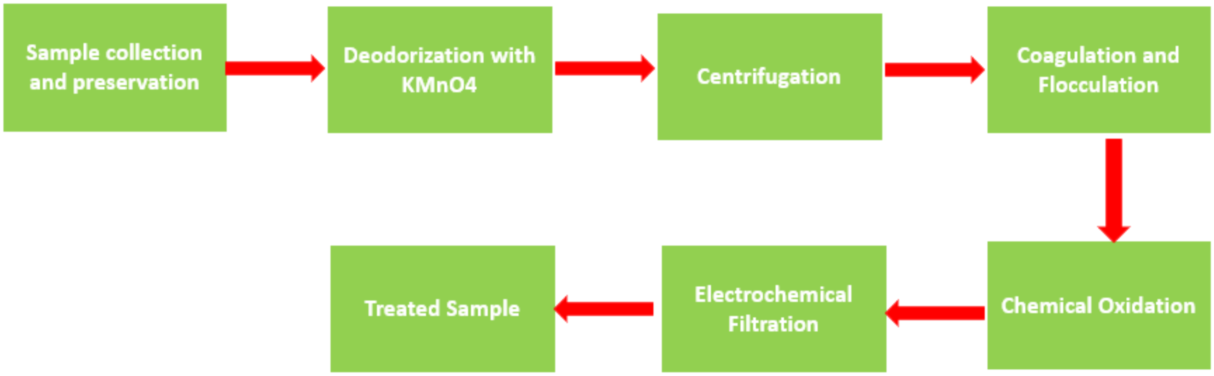


Fig. 41. Schematic flowchart displaying the integrated treatment stages applied to the leachate sample.

4.3.1 Deodorization

This involves the addition of chemicals to eliminate odorous compounds such as sulfide from the leachate sample (Amokrane et al., 1997). $KMnO_4$ is needed for sample pretreatment, to oxidize the chemicals generating offensive odor in the sample. The raw leachate samples were deodorized with $KMnO_4$ (200 mg/L) to oxidize the compounds responsible for the offensive odor (*e.g.*, amines and thiols). Then the samples were centrifuged at 4200 rpm to separate the slurry from the solution, and then the supernatant was decanted and further subjected to treatment methods including coagulation and oxidation.

4.3.2 Coagulation and Flocculation

Various concentration of solid coagulant (*i.e.*, $FeCl_3$ or Alum) was added to the leachate sample while stirring at 500 rpm under ambient temperature (Fig. 42). Each solution was mixed for 1 h followed by a 1 h settling period before collecting the supernatant, which was then centrifuged, and the supernatant obtained for total organic carbon (TOC) analysis.

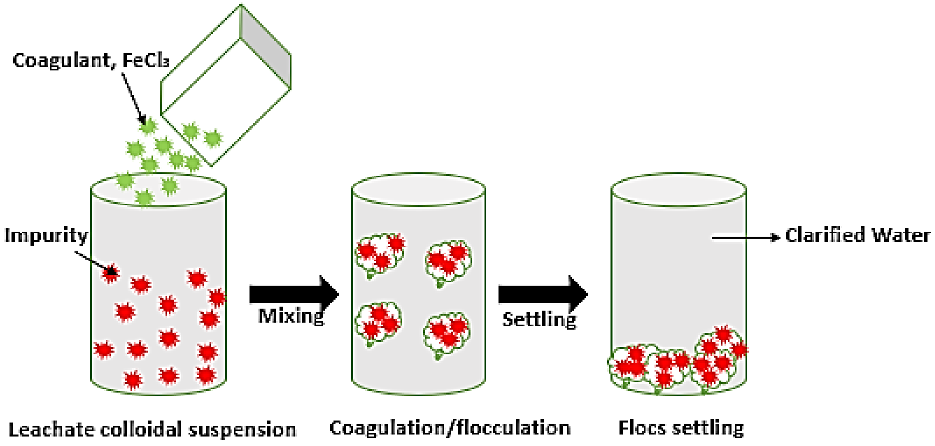


Fig. 42. Coagulation Mechanism scheme for Leachate sample.

4.3.3 Chemical Oxidation

After choosing the appropriate coagulant based on TOC removal efficiency, various dosages of oxidants (H_2O_2 or $Na_2S_2O_8$) were added to the sample immediately after coagulant addition. The solution was mixed at 500 rpm for 1 h and allowed to settle for 1 h. Supernatants were collected afterward for TOC analysis.

4.3.4 Electrochemical Filtration System (EFS)

The details of the setup, the principle, and the instruments used for the continuous flow reactor (CFR) in the electrochemical filtration process has been described in chapter three of this thesis. Post coagulation and oxidation samples could alternatively be treated through the electrochemical filtration device where dissolved organic matter is oxidized on the anode with concurrent reduction of heavy metals on the cathode with the aid of an electrocatalyst. At 3 V, using $CuCl_2$ as the catalyst, NaCl as the electrolyte, carbon felt as electrodes and stirring at 500 rpm, the post-oxidized sample is passed through the CFR with the aid of a peristaltic pump, for further treatment.

4.4 Characterization and Analytical Techniques

Quantitatively, a total organic carbon analyzer (TOC) was used to evaluate the overall removal of organic pollutants, and values before and after each treatment were compared. A MULTI N/C 3100 Analytikjena (Germany) analyzer was used to collect the TOC data. The TOC analyzer was used to measure samples collected before and after the experiment to compare their results, and the experiments were done in triplicates. The result from this analysis reflects the TOC removal achieved after each treatment stage (*i.e.*, after coagulation, chemical oxidation, and EFS). The TOC removal efficiency was determined using the TOC equation (Eq. 12).

The GC-MS analysis was performed with Aglient Technologies 6890N gas chromatograph coupled with a 5973-inert mass spectrum detector (Santa Clara, USA). An NSP-5 capillary column (15 m x 0.25 mm x 0.30 μm, J&K Scientific, Edwardsville Canada) was used for separation. The

GC-MS was used to qualitatively identify the type of compounds in the leachate before and after the combined treatment.

ICP-MS was applied to evaluate the reduction in heavy metal concentration pre and post treatment. The ICP-MS analysis was performed with Perkin-Elmer inductively coupled plasma spectrometer coupled with NexION 300D with S10 Auto sampler, with detection limit at parts per billion levels.

4.5 Results and Discussion

4.5.1 Deodorization

To carry out an experiment on the leachate sample, odor removal was necessary via oxidation. 200 mg L^{-1} $KMnO_4$ was applied to the sample for deodorization. A yield of 22.5% TOC removal (Fig. 43) was observed and the elimination of the strong odor confirmed via nasal perception. It is suspected that the odor-causing organic substances in the leachate were oxidized by the permanganate radical by attracting electrons from the electron-rich organic pollutants and forming MnO_2, which easily precipitates out of the sample (Eq. 29) (Maxwell, 1986).

$$\mathrm{MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-} \qquad \mathrm{E^0 = 1.7V} \qquad (25)$$

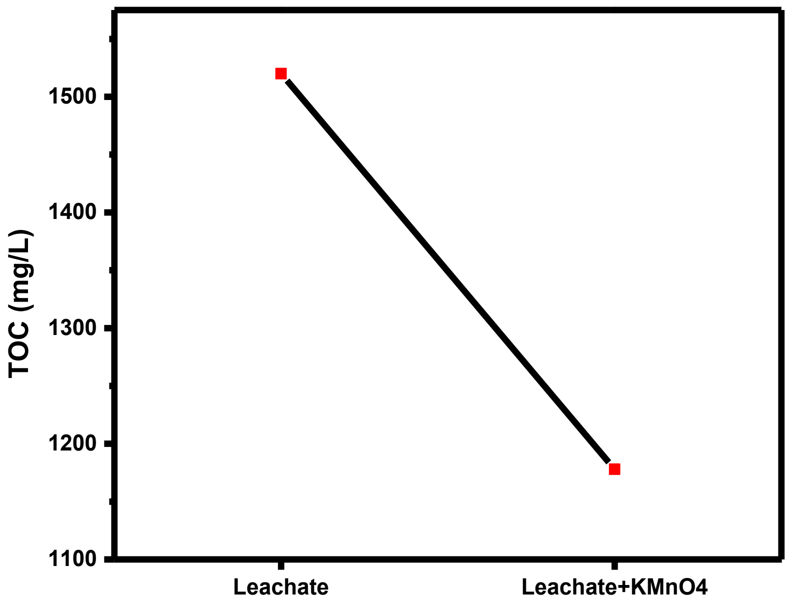


Fig. 43. Leachate Pretreatment (Deodorization) with 1.3 mM $KMnO_4$.

4.5.2 Coagulation and Flocculation

The effect of coagulants on the leachate sample was determined by varying $[FeCl_3]$ from 10-200 mM. The TOC removal rate increased with increasing $[FeCl_3]$ with up to 68.8% of the suspended organic carbon removed through precipitation, as measured by TOC analysis at $[FeCl_3]$ = 50 mM (Fig. 26). However, a further increase beyond $[FeCl_3]$ = 50 mM results in a decrease in TOC removal efficiency (to be explained later).

Similarly, alum was used to coagulate suspended organic particles also in the form of charge neutralization like iron (Fig. 27). Both coagulants (Alum and $FeCl_3$) achieve optimum TOC removal at different concentrations, Alum at 100mM and $FeCl_3$ at 50 mM when used individually as described before. Hence, $FeCl_3$ was more effective at a lower concentration than Alum.

Further, an increase in both Alum and $FeCl_3$ dosage beyond the concentration with the optimal effect resulted in a decrease in TOC removal efficiency (Fig. 45 and Fig. 47). This is also indicated in the decolorization of the sample. As the coagulant concentration increased toward the optimum dosage, the color of the leachate, after the settling down of the sludge, changed from dark brown to pale brown and then colorless, reflecting high TOC removal efficiency. Then, as the coagulant dosage increased the color turned darker brown again, indicating a reduction in the efficiency (Fig. 46 and Fig. 48). This can be related to the electrostatic imbalance in the solution after the optimal concentration is exceeded. Further increases in coagulant concentration beyond the optimal dose creates imbalance and leads to dissociation of the agglomerated flocs back into the solution, thereby increasing TOC values (Amokrane et al., 1997).

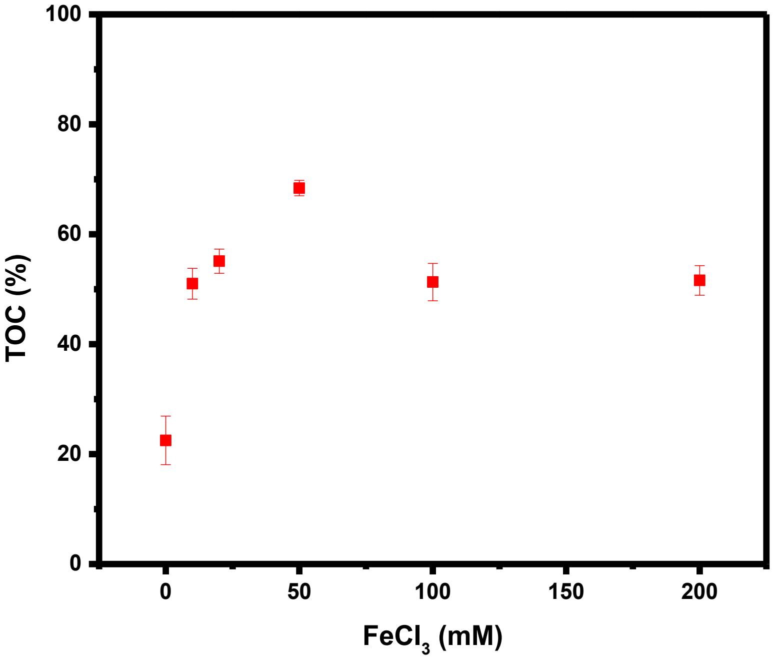


Fig. 44. Coagulant effect on leachate using $FeCl_3$ (TOC removal).

Experiments were performed at neutral pH. Stirring for 1 h at 500 rpm and 1 h settling period. Vertical bars denote the relative standard deviation (±RSD) (*n*=3).

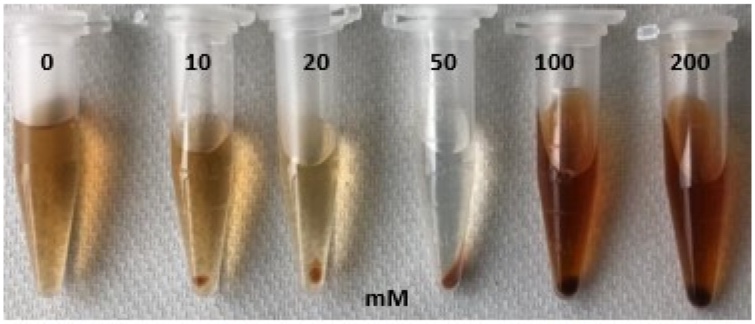


Fig. 45. Coagulant effect on leachate using $FeCl_3$ (Decolorization).

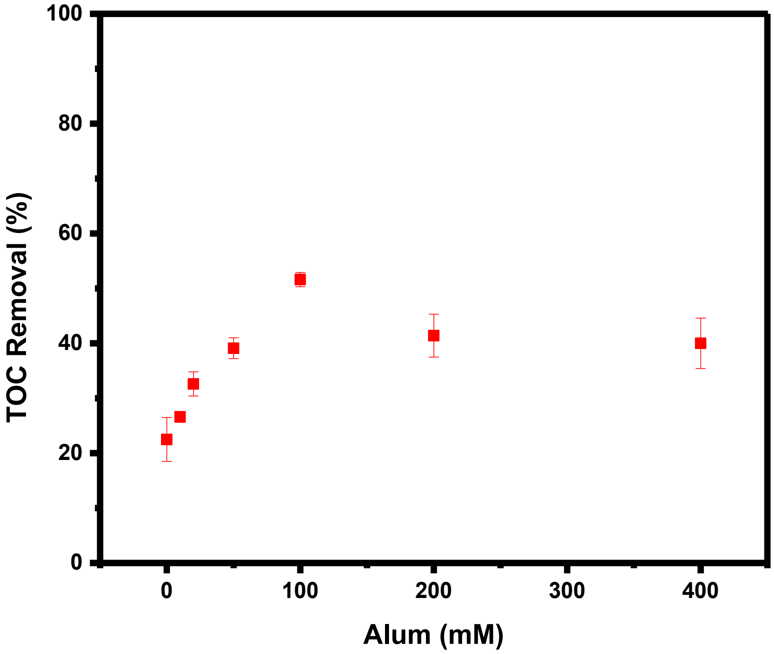


Fig. 46. Coagulant effect on leachate using Alum (TOC removal).

Experiments were performed at neutral pH. Stirring for an hour at 500 rpm and 1 h settling period. (n=3, ±RSD).

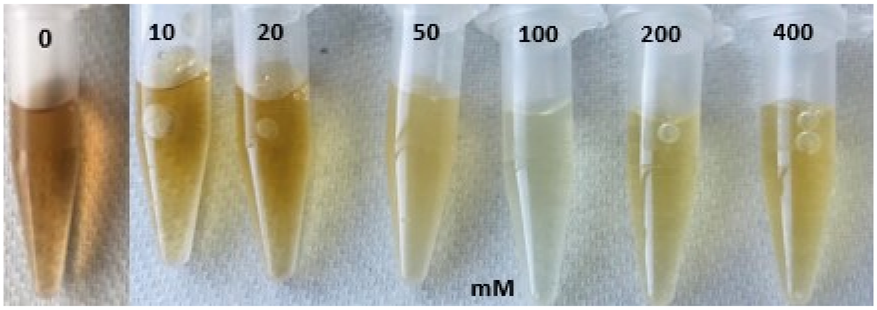


Fig. 47. Coagulant effect on leachate using Alum (decolorization).

4.5.3 Coagulant Comparison

We compared the two coagulants in Table 10, and we show that $FeCl_3$ was more effective at achieving higher TOC removal than Alum and at a less expensive rate per g of TOC removed from a liter of sample. Further, in terms of environmental footprint, both coagulants generate high volumes of slurry as a secondary contaminant (Ratnayaka, 2017). This slurry must go through a dewatering process after coagulation, hence, additional cost is incurred for sludge treatment (Teh et al., 2016). Biologically, it has been advised that the presence of aluminum in drinking water may be related to neurological disorders and Alzheimer's disease and not good for renal dialysis users (Nandy et al., 2003). In brief, the advantages of using $FeCl_3$ as coagulant supersedes that of Alum.

Table 10. Comparison of Coagulants.

	Alum $KAl(SO_4)_2.12H_2O$)	**Iron (III) Chloride ($FeCl_3$)**
Optimum TOC removal achieved (%)	51.6	68.8
Concentration required (mM)	100	50
TOC Removed after Combined Treatment (mg L^{-1})	784	1046
Coagulant Quantity L^{-1} (g)	25	8.1
Cost L^{-1} (¢)	1.25	0.5
To remove 1g TOC L^{-1} Cost (¢)	1.59	0.48

Therefore, $FeCl_3$ was used as a coagulant for subsequent experiments. Collectively, a total TOC removal of 68.8% has been achieved using combined treatment (Fig. 48). This implies that with the combined treatments, the TOC load value of the raw leachate sample was reduced from 1520 mg L^{-1} to 474 mg L^{-1}, similar to earlier studies on landfill leachate using similar combined treatment methods (Amokrane et al., 1997).

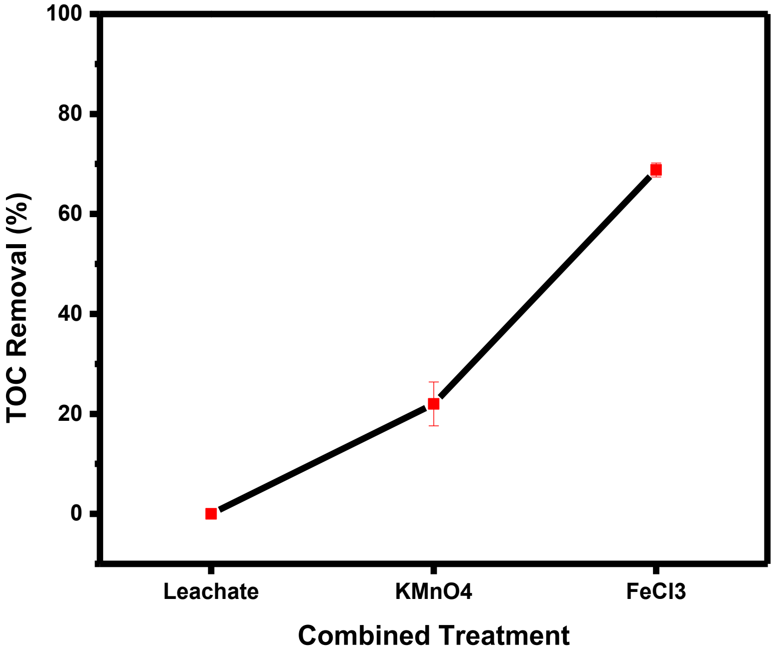


Fig. 48. % TOC removal from leachate sample after application of combined treatment (deodorization and coagulation). [$KMnO_4$] = 1.3 mM, [$FeCl_3$] = 50 mM (*n*=3, RSD).

4.5.4 Chemical Oxidation

A known amount of oxidant (H_2O_2 or $Na_2S_2O_8$) was added to 50 ml of the leachate sample right after the addition of 50 mM $FeCl_3$ (dosage of coagulant with optimal effect) and the solution stirred for an hour. The addition of H_2O_2 slightly oxidizes some of the dissolved organic matter with [H_2O_2] =100 mM, being the concentration with the optimal effect (Fig. 49). Hydrogen peroxide was able to mineralize 79% of the remaining TOC, most likely by undergoing a Fenton reaction (Eq. 26) with the remaining dissolved Fe^{3+} from the coagulation step, resulting in the generation of hydroxyl radical.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \qquad (26)$$

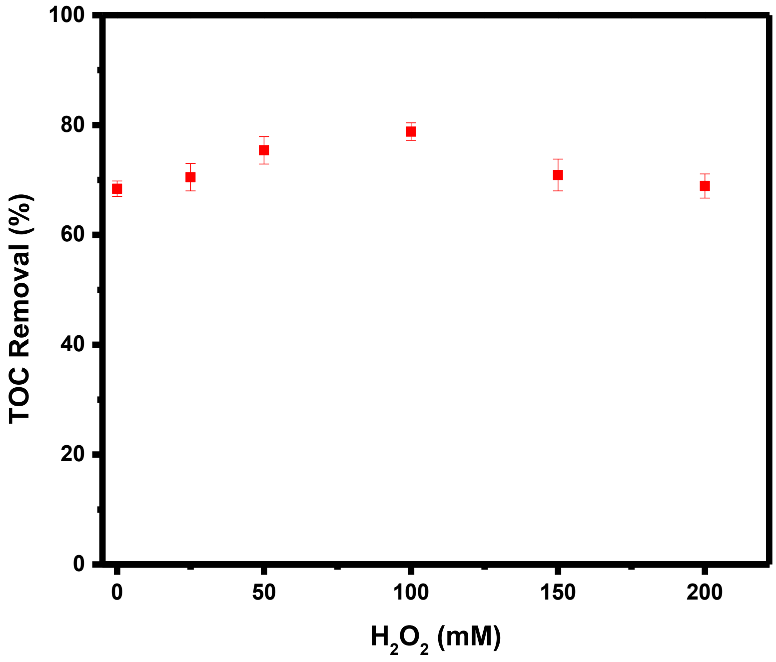


Fig. 49. Oxidation effect on leachate using H_2O_2 after coagulation with [$FeCl_3$] = 50 mM. Experiments were performed at neutral pH. Stirring for an hour at 500 rpm and 1 h settling period. (*n*=3, RSD).

Similarly, a varying concentration of $Na_2S_2O_8$ (10-200 mM) was added to a 50 ml leachate sample right after coagulation with 50 mM $FeCl_3$ (coagulant dosage with optimal effect). $Na_2S_2O_8$ further degraded the residual sample with a 100 mM concentration yielding the optimal effect of 85% TOC removal (Fig. 50). We suspect that chemical oxidation using $Na_2S_2O_8$ was activated by the production of sulfate radicals of high oxidizing potential to degrade organic contaminants (Eq. 27) (Abu Amr et al., 2013).

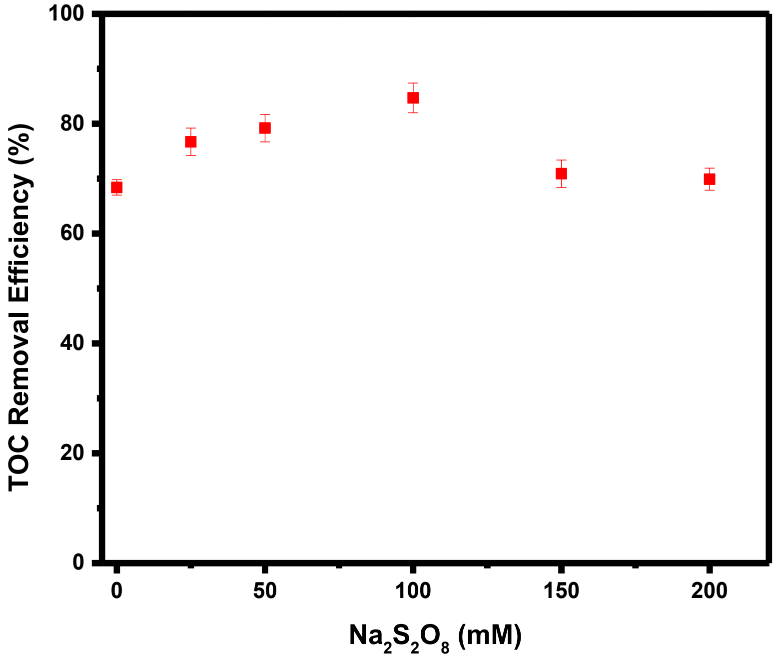


Fig. 50. Oxidation effect on leachate using $Na_2S_2O_8$ after coagulation with $[FeCl_3]$ = 50 mM. Experiments were performed at neutral pH. Stirring for an hour at 500 rpm and a 1hour settling period. (*n*=3, RSD).

$$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^{-\cdot} \qquad (27)$$

Furthermore, it was observed that when $Na_2S_2O_8$ was added to the sample alone, without coagulation by Ferric chloride, only 26% TOC removal was achieved (Fig. 51), we suspect this is because of the absence of iron to activate the persulfate to generate sulfate radicals (Anipsitakis & Dionysiou, 2003). Moreover, the improved performance of persulfate can be attributed to activation in the presence of Fe^{3+} according to the following equation (Eq. 28), similar to what has been proposed in another study (Abu Amr et al., 2013).

$$Fe^{3+} + S_2O_8^{2-} \rightarrow 2SO_4^{-\cdot} + Fe^{2+} \qquad (28)$$

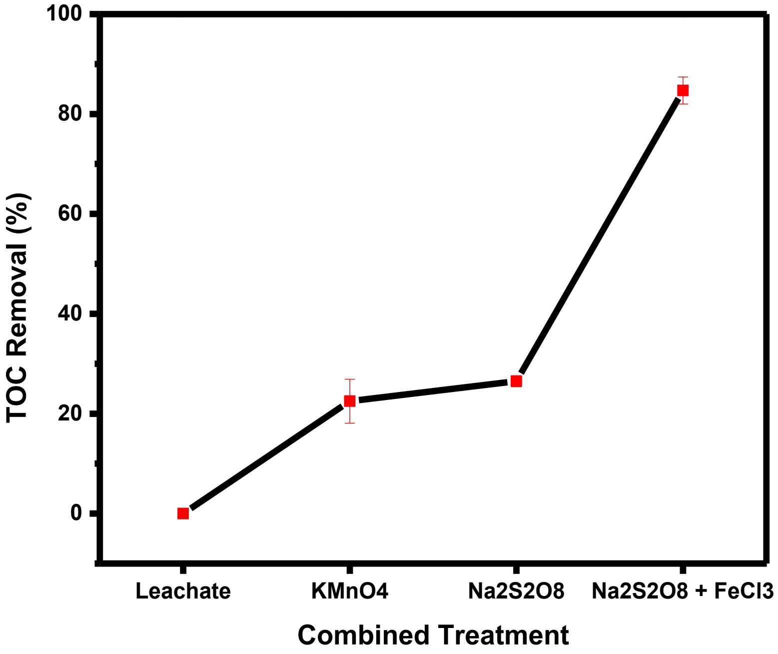


Fig. 51. Application of combined treatment with $Na_2S_2O_8$ only and then, $FeCl_3$ coagulant. $[KMnO_4]$ = 1.3 mM, $[FeCl_3]$ = 50 mM, $[Na_2S_2O_8]$ = 100 mM (*n*=3, RSD).

4.5.5 Chemical Oxidant Comparison

In comparison, chemical oxidation using $Na_2S_2O_8$ was more efficient than H_2O_2 at the same concentration with optimal dosage (100 mM) added to the pre-treated leachate sample, perhaps because $Na_2S_2O_8$ possesses a higher oxidative potential (2.1 V) compared to H_2O_2 (1.8 V), hence, a stronger oxidizing strength. Further, the TOC removal efficiency could have improved when H_2O_2 was used, if the pH of the solution was acidic since the Fenton reaction is more effective under such conditions (Mandal et al., 2017). However, adjusting the pH of the sample to an acidic medium before treatment would be a disadvantage in terms of the amount of acid required, and the need to neutralize the wastewater post-treatment prior to discharge. Furthermore, $Na_2S_2O_8$ is efficient across a broad range of pH values (Abu Amr et al., 2013). Finally, both oxidants are relatively inexpensive to remove 1 g of TOC per liter of leachate sample (Table 11).

Table 11. Comparison of Chemical Oxidants.

	Hydrogen Peroxide	**Sodium Persulfate**
Optimum efficiency achieved (%)	78.8	85
Oxidative Potential (V)	1.8	2.1
Optimum concentration required (mM)	100	100
Total TOC Removed after Combined Treatment (mg L^{-1})	1198	1292
Quantity of oxidant/L of Leachate sample	10ml	23.8g
Cost L^{-1} (¢)	0.35	2.4
To remove 1g TOC L^{-1} Cost (¢)	0.29	1.86

Therefore, after combined treatment, a TOC removal efficiency of 85% has been achieved. That is, the TOC value of the raw leachate was reduced from 1520 mg L^{-1} to 228 mg L^{-1}, after a series of combined treatment techniques (Fig. 52).

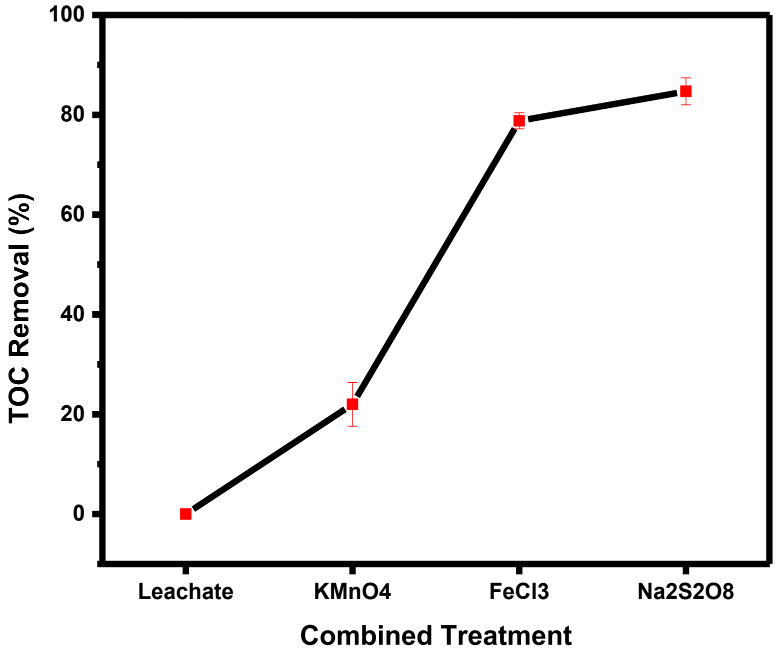


Fig. 52. Showing the % TOC removal from leachate sample after application of combined treatment (deodorization, coagulation, and chemical oxidation).

[$KMnO_4$] = 1.3 mM, [$FeCl_3$] = 50 mM. [$Na_2S_2O_8$] = 100 mM. (*n*=3, RSD).

4.5.6 Electrochemical Filtration (EF)

Post-coagulation samples could alternatively be treated through an electrochemical filtration device whereby dissolved organic matter is oxidized on the anode with concurrent reduction of heavy metals on the cathode with the aid of an electrocatalyst. It is important to note that the dissolved organic compounds which remained after the combined treatments (coagulation and oxidation) are the persistent and recalcitrant compounds that are, mostly, difficult to degrade. In the EFS, reactive species such as ozone and hypochlorite ions (as explained in chapter three) are generated to further degrade the leachate sample by oxidizing the refractory organic substances. As a component of a complete water treatment process, applying the EFS after the other treatment

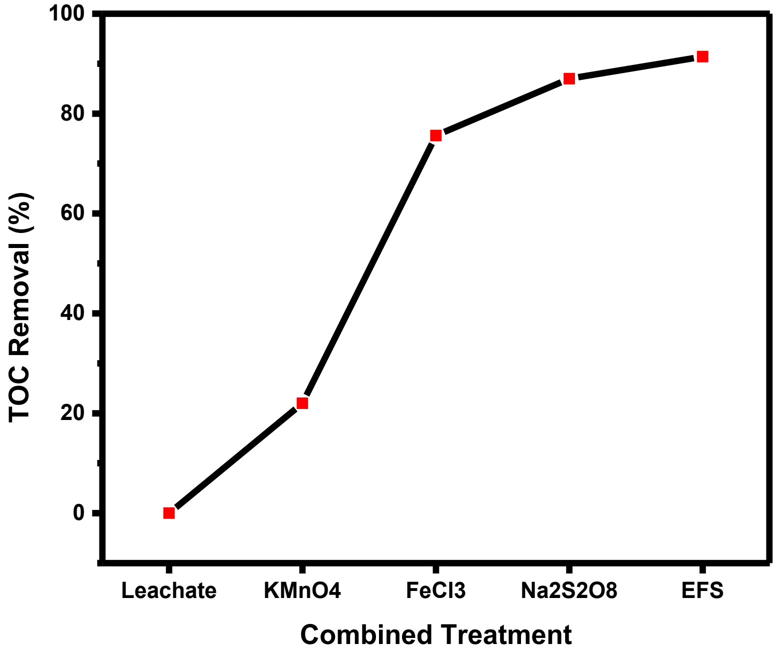


Fig. 53. Combined treatment result on leachate sample (TOC removal).

Experiments were performed at neutral pH, $KMnO_4$] = 1.3 mM, [$FeCl_3$] = 50 mM. [$Na_2S_2O_8$] = 100 mM, [$CuCl_2$] = 200 µM, [NaCl] = 500 mM. (*n*=3, ±RSD).

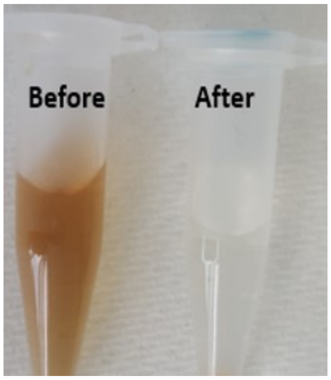


Fig. 54. Decolorization pre and post combined treatment of Landfill Leachate Sample.

methods, the TOC of the leachate sample was reduced by up to 91.4% (Fig. 53). Further, the dark brown color of the raw leachate was completely turned colorless after the effective combined treatments (Fig. 54). The GC-MS qualitative analysis of the leachate sample before treatment showed the presence of pharmaceutical and personal care compounds (*i.e.*, acetaminophen and Diethyl-toluamide (DEET)). After the combined treatment, which leads to the degradation of dissolved organics into smaller fragments, partial mineralization, and removal of compounds of concern was observed (*i.e.*, the big peak for DEET was significantly reduced while the peak for acetaminophen disappeared (Fig. 55).

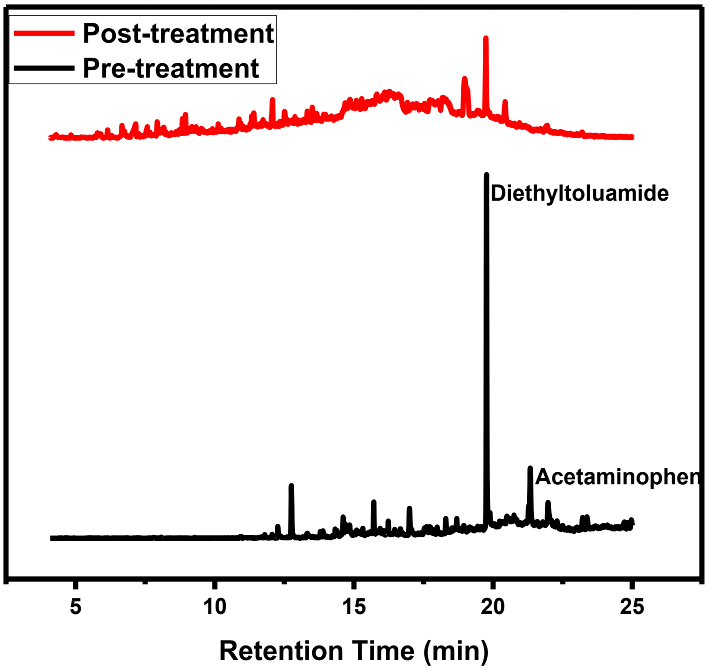


Fig. 55. Gas chromatogram of the leachate sample before and after combined treatment.

Experiments were performed at neutral pH, 2.5 V, [$KMnO_4$] = 1.3 mM, [$FeCl_3$] = 50 mM. [$Na_2S_2O_8$] = 100 mM, [$CuCl_2$] = 200 µM, [NaCl] = 500 mM.

Furthermore, we observed a significant reduction in the metal concentration, perhaps via electroreduction (gain of electrons) and adsorption on the cathodic surface. The concentration of metals of interest such as [As], [Cd], [Cr], [Ni], and [Pb] were reduced in concentration close to the WHO drinking water standards (W.H.O, 2018) and the CCME Protection for Freshwater Aquatic Guidelines (CCME, 2019) (Table 12).

In brief, after the combination treatment of the leachate sample, 91.4% TOC removal was achieved (Table 13), and toxic metals including As, Cd, Pb, Cr, and Ni were significantly reduced concurrently at the last stage of the hybrid process.

Table 12. Metal concentration pre and post EFS stage of the combined treatment process.

Metals	**Pretreatment (mg/L)**	**Posttreatment (mg/L)**	**WHO Drinking Water Standards (mg/L)**	**CCME Guidelines (mg/L)**
Cr	1.13	0.64	0.05	0.009
Ni	0.72	0.28	0.07	NA
As	0.66	0.05	0.01	0.005
Cd	0.42	0.009	0.003	NA
Pb	0.57	0.04	0.01	NA

Table 13. TOC Removal Efficiency at each Treatment Stage.

	Average TOC Residual (mg L^{-1})	**Cumulative TOC Removal Efficiency (%)**
Raw Leachate Sample	1520	
Sample + $KMnO_4$	1178	22.5
Residual Sample + $FeCl_3$ + $Na_2S_2O_8$	228	85
Residual Sample + Electrochemical filtration	131	91.4

4.5.7. Combined Treatment Cost

The economic viability of a wastewater treatment strategy is a significant factor to consider when determining its feasibility. This involves the total operational cost relative to other wastewater treatment alternatives (*i.e.*, material and operative cost). The permanganate for deodorization cost 0.8 USD $kg^{-1}$and the rest of the chemicals have been mentioned earlier. At optimum operational condition, to remove TOC of 1389 mg L^{-1} from leachate sample will require deodorization at 0.00016 USD, coagulation at 0.0044 USD, chemical oxidation at 0.024 USD, and electrochemical treatment at 0.05 USD (calculated in the previous chapter), per liter of leachate sample. This equates to 0.06 USD g^{-1} of organic carbon removed in addition to the heavy metals significantly reduced.

4.6 Conclusions and Recommendations

4.6.1 Conclusions

The results obtained in this study lead to the following conclusions:

1. The integrated coagulation/chemical oxidation/electrochemical treatment process displayed an interesting result for the treatment of heavily contaminated landfill leachate, whereby concurrent organic pollutant and heavy metal removal was achieved.
2. In the combined treatment, permanganate was applied as an oxidant to oxidize odor-causing organic substances in the sample. Ferric chloride was applied as a coagulant to remove a significant amount of suspended organic pollutants via flocculation. Sulfate radicals, from persulfate, was applied to further oxidize dissolved organic substances in the sample through activation by dissolved iron. Finally, reactive species including ozone and hypochlorite were generated in the EFS to further degrade the organic pollutant while heavy metals were simultaneously reduced on the cathode via electroreduction and adsorption.
3. A TOC of 1389 mg L^{-1} was removed after the combined treatment of the leachate. In addition, the concentrations of metals of interest including Pb, As, Cr, Cd, and Ni were reduced via the EFS stage of the combined treatment.
4. In terms of economic viability, it will cost 0.06 USD per g organic carbon removed, which implies a relatively inexpensive approach compared to alternatives.

4.6.2 Recommendations

The following recommendations were made to further this research:

1. The deodorization stage in the combined treatment can be optimized.
2. Also, other iron compounds with less slurry potential than ferric chloride can be applied as a coagulant (*e.g.*, poly ferric sulfate).
3. The toxicity of the residual sample after the combined treatment should be evaluated.
4. A pilot scale study should be done to understand the limitations in the field, modelling field conditions.
5. The life cycle analysis of the treatment process should also be evaluated and integrated while upscaling the technology to minimize environmental footprint.

Chapter V

5.0 Conclusions

5.1 Potential Field Application

The applied combined treatment method for the leachate sample in this study can be implemented onsite for field application. However, a thorough study is required for the design to factor in leachate characteristics and discharge options. Even though the combined cost for the landfill leachate treatment is relatively inexpensive; the coagulation and chemical oxidation treatment stages involve high consumption of chemicals and environmental cost for use in case of field application. Additionally, for field applications, a huge amount of slurry should be expected after the coagulation and flocculation stage. Hence, plans must be made for sludge treatment, either dewatering and landfilling or incineration (Ashrafi et al., 2015). Also, there is the risk of safety in handling while transporting reagents for coagulation and chemical oxidation processes.

On the other hand, the electrochemical method offers an advantage; as the oxidants needed for pollutant degradation are generated *in situ*. Therefore, encouraged by the laboratory results, a continuous flow reactor for EFS application to treat a large volume of wastewater (~180 L^{-1} day) was built for scale-up and applied at the BH remediation site (Fig. 56). The scaled-up reactor was applied to a treated BH wastewater sample, as a post-treatment method, after dewatering by Geotube filters. Geotube dewatering involves the treatment of raw BH wastewater using polymers inside a geotube textile (Alimohammadi, 2019). The treated water was further subjected to EFS to remove recalcitrant organic pollutants and heavy metals. Experiment conditions including, flowrate, electrode size, and treatment time, were scaled up accordingly on the Boat Harbour remediation site.

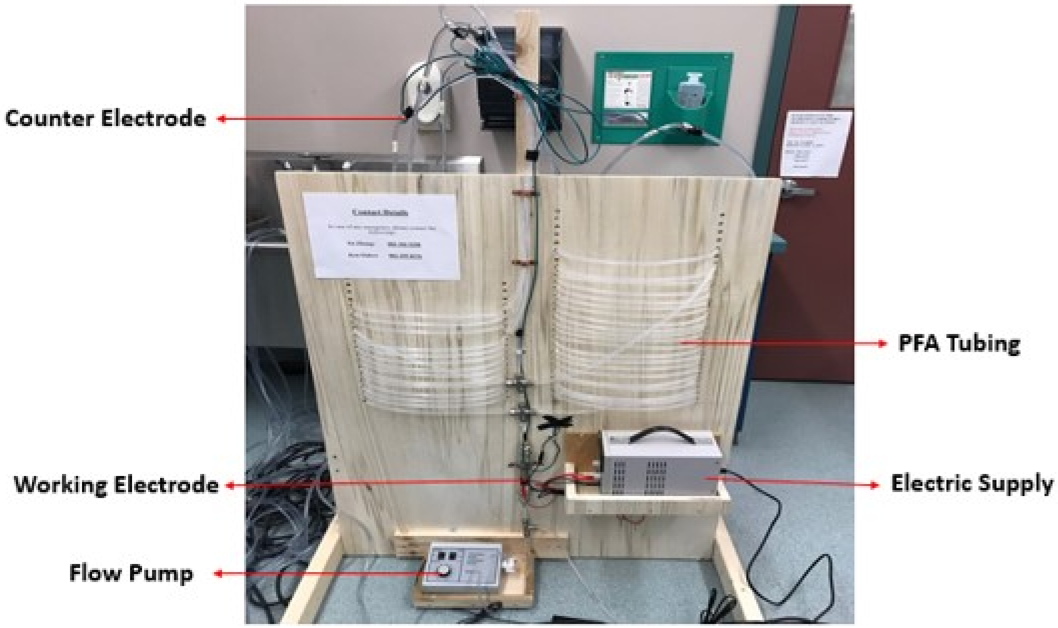


Fig. 56. Scaled-up Continuous Flow Reactor.

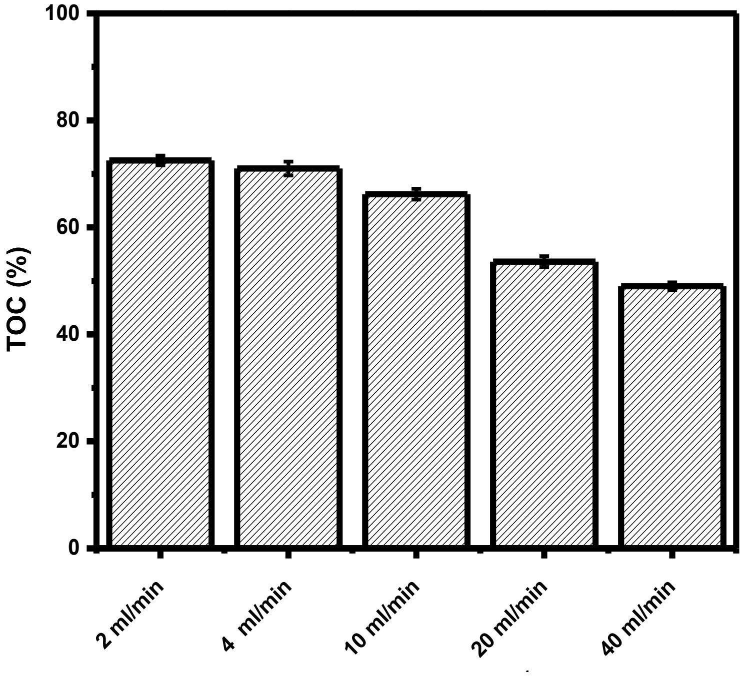


Fig. 57. Field treatment of Boat Harbour wastewater by the EFS at varying flow rate.

Experiment performed at [NaCl] = 500 mM, [Cu^{2+}] = 200 μM, pH 6.5, glassy carbon electrode (*n*=3, ±RSD).

The flow reactor applied at the BH site is a scaled-up replica, in components, to the reactor used in the laboratory, albeit with five counter electrodes (cathodes) of different distances from the working electrode, indicating varying hydraulic resident times of BH water samples during treatment. The result obtained on the field is similar to the laboratory yield in terms of TOC efficiency (Fig. 57). Organic compound removal efficiencies increased as the flow rate decreased, corresponding to what was obtained in the laboratory. Hence, the optimization of reaction parameters including applied voltage potential, catalyst, and supporting electrolyte concentration, achieved in the laboratory are transferable to the scale-up of the EFS for field application. However, further experiments including more study of the metal removal property, toxicity test for treated sample, and electrochemical oxidation mechanism, must be carried out before full field application.

5.2 Conclusions and Recommendations

5.2.1 Conclusions

Conclusively, the objectives of this research thesis (Section 1.2) was addressed, which are:

- An experimental prototype EFS that concurrently oxidized organic pollutants and removed heavy metals from wastewater (synthetic or real) samples was developed.
- A laboratory experiment was set up to evaluate the performance of the EFS using model organic (*i.e.*, PNA) and inorganic (*i.e.*, Pb, Cr, Ni) contaminants.
- The system parameters including electrode material, nature of supporting electrolyte, pH, catalyst concentration, flow rate, and applied voltage potential differences, were optimized to achieve the experimental conditions for the high removal efficiency of contaminants.

- At the optimum conditions of 2.5 V, [Cu^{2+}] = 200 µM, [NaCl] = 500 mM, 5 mL min^{-1}, glassy carbon electrode, and natural pH, using TOC and UV-Vis analysis, 73% mineralization and 92% discoloration, respectively, of PNA was achieved. In addition, at optimum conditions, a TOC reduction of 578 mg L^{-1} (92% mineralization efficiency) of Toluene was achieved and the GC-MS analysis of the sample pre- and post-treatment showed complete removal of the compound with no residual volatile compounds.
- Although the electrochemical oxidation mechanism is complex using differential voltammetry analysis, reactive species (*i.e.*, O_3 and HOCl) were found to be the major ROS responsible for pollutant degradation. Additionally, the DPV analysis revealed the effect of the catalyst (Cu^{2+}) on the activation of the reactive species.
- Also, metal-contaminated water (*i.e.*, 50 mg L^{-1} concentration of Cr, Pb, and Ni), as model inorganic pollutants were individually investigated using the EFS. Without applied voltage, 13% Pb, 21% Ni, and 16% Cr, were recovered via adsorption on the reactor walls and electrode surface, while 24%, 44%, and 70% reduction, respectively, can be attributed to electroreduction when the voltage was applied.
- Thereafter, a real contaminated water sample (*i.e.*, Boat Harbour water) was evaluated and TOC mineralization of 76 mg L^{-1} (72.4% efficiency) of total organic carbon and the major contaminants were removed. The GC-MS analysis showed that cresol, a compound which can be found as waste during pulp digestion, which was detected before the treatment was not found post-analysis. Also, [As], [Cd], [Cr], [Ni], and [Pb] were significantly reduced.
- In another project, where the EFS was applied as a post-treatment in a hybrid process including deodorization using permanganate, coagulation and flocculation using ferric chloride or Alum, and chemical oxidation using hydrogen peroxide or persulfate, leachate

sample obtained from the Guysborough Waste Management Facility, Nova Scotia, Canada was treated.

- After the combined treatment, in the order of deodorization-coagulation-chemical oxidation-EFS, a significant reduction in TOC removal from 1520 to 131 mg L^{-1} (91.4% efficiency) was achieved and compounds including acetaminophen and diethyltoluamide were mineralized, as revealed by the GC-MS analysis. Additionally, the application of the last stage of treatment, EFS, allowed for heavy metal removal including Pb and Cd close to discharge guidelines for protection of aquatic life.

5.2.2 Recommendations

Based on the results presented, the application of EFS as a wastewater treatment plan for contaminant removal shows some advantages including high TOC removal efficiency, relatively inexpensive financial cost, and high energy efficiency. Nevertheless, there are factors to consider before a scale-up for field applications. The EFS is designed to mineralize dissolved organic and reduce inorganic pollutants. Hence, it will be effective to apply EFS as a post-treatment plan in a hybrid strategy with another treatment technique for wastewater with high suspended solids. Furthermore, the high generation of chlorine species will result in non-selective oxidation thereby attacking the electrodes as observed in the laboratory scale experiments. The high production of chlorine species can also lead to the formation of adsorbable organic halides, which are difficult compounds to degrade further. These unwanted side reactions need to be factored in when developing the EFS for field applications. Additionally, further experiments need to be conducted to study the metal removal property of the system. Finally, the various operating parameters must be optimized for different wastewater content and concentration.

In conclusion, a relatively inexpensive and effective advanced electrochemical filtration system has been designed and conducted on a model and real wastewater in the laboratory. The EFS has been scaled-up and applied at the Boat Harbour remediation site with a capacity of treating 180 L^{-1} day. The EFS is a promising potential future wastewater treatment technique, which can complement other methods to mineralize refractory dissolved organic pollutants. Finally, at <3 V applied voltage, EFS can be applied in remote areas for water treatment using solar power, thereby reducing environmental footprint.

References

Abdullah, N., Aziz, H., Yusuf, N., Umar, M., & Amr, S. (2014). Potential of KMnO 4 and H 2 O 2 in treating semi-aerobic landfill leachate. *Applied Water Science, 4*(3), 303-309. doi: 10.1007/s13201-013-0146-6

Abolhasani, J., Khanmiri, R. H., Ghorbani-Kalhor, E., Hassanpour, A., Asgharinezhad, A. A., Shekari, N., & Fathi, A. (2014). An Fe 3 O 4 @SiO 2 @polypyrrole magnetic nanocomposite for the extraction and preconcentration of Cd(ii) and Ni(ii). *Anal. Methods, 7*(1), 313-320. doi: 10.1039/c4ay01991a

Abu Amr, S. S., Aziz, H. A., Adlan, M. N., & Bashir, M. J. K. (2013). Pretreatment of stabilized leachate using ozone/persulfate oxidation process. *Chemical Engineering Journal, 221*, 492-499. doi: 10.1016/j.cej.2013.02.038

Adam, M. R., Salleh, N. M., Othman, M. H. D., Matsuura, T., Ali, M. H., Puteh, M. H., . . . Jaafar, J. (2018). The adsorptive removal of chromium (VI) in aqueous solution by novel natural zeolite based hollow fibre ceramic membrane. *Journal of Environmental Management, 224*, 252. doi: 10.1016/j.jenvman.2018.07.043

Afshin, T., Bahareh, K., Abdolkazem, N., & Reza Jalilzadeh, Y. (2016). Study of Operational and Maintenance Problems and Parameters of Extended Aeration Activated Sludge Process in Golestan Hospital Wastewater Treatment Plant, Ahvaz, and Their Solutions. *Muhandisī-i Bihdāsht-i Muḥīṭ, 3*(4), 270-279. doi: 10.18869/acadpub.jehe.3.4.270

Aftab, B., Shin, H.-S., & Hur, J. (2018). Exploring the fate and oxidation behaviors of different organic constituents in landfill leachate upon Fenton oxidation processes using EEM-PARAFAC and 2D-COS-FTIR. *Journal of Hazardous Materials, 354*, 33-41. doi: 10.1016/j.jhazmat.2018.04.059

Ahmed, F. N., & Lan, C. Q. (2012). Treatment of landfill leachate using membrane bioreactors: A review. *Desalination, 287*, 41-54. doi: 10.1016/j.desal.2011.12.012

Al-Harahsheh, M., Hussain, Y. A., Al-Zoubi, H., Batiha, M., & Hammouri, E. (2017). Hybrid precipitation-nanofiltration treatment of effluent pond water from phosphoric acid industry. *Desalination, 406*, 88-97. doi: 10.1016/j.desal.2016.06.014

Al-Obaidi, M. A., Kara-Zaïtri, C., & Mujtaba, I. M. (2017). Wastewater treatment by spiral wound reverse osmosis: Development and validation of a two dimensional process model. *Journal of Cleaner Production, 140*, 1429-1443. doi: 10.1016/j.jclepro.2016.10.008

Al-Qaim, F., Mussa, Z. H., Othman, M. R., & Abdullah, M. P. (2015). Removal of caffeine from aqueous solution by indirect electrochemical oxidation using a graphite-PVC composite electrode: A role of hypochlorite ion as an oxidising agent. *Journal of Hazardous Materials, 300*, 387-397. doi: 10.1016/j.jhazmat.2015.07.007

Alimohammadi, M., Tackley, H. A., Lake, C. B., Jamieson, R., Spooner, I., Walker, T. R., … Bossy, K. (2019). Effect of different sediment dewatering techniques on subsequent particle sizes in industrial derived effluent. doi: https://doi.org/10.1139/cjce-2019-0269

Alizadeh Fard, M., & Barkdoll, B. (2018). Effects of oxalate and persulfate addition to Electrofenton and Electrofenton-Fenton processes for oxidation of Ketoprofen: Determination of reactive species and mass balance analysis. *Electrochimica Acta, 265*, 209-220. doi: 10.1016/j.electacta.2018.01.153

Amokrane, A., Comel, C., & Veron, J. (1997). Landfill leachates pretreatment by coagulation-flocculation. *Water Research, 31*(11), 2775-2782. doi: 10.1016/S0043-1354(97)00147-4

Anipsitakis, G. P., & Dionysiou, D. D. (2003). Degradation of organic contaminants in water with sulfate radicals generated by the conjunction of peroxymonosulfate with cobalt. *Environmental science & technology, 37*(20), 4790. doi: 10.1021/es0263792

Annabel, F., Edite, C., Lurdes, C., Maria, J. P., & Lopes, A. N. A. (2013). Electrochemical treatment of leachates from sanitary landfills. *Journal of electrochemical science and engineering, 3*(3), 125-135. doi: 10.5599/jese.2013.0034

Anotai, J., Lu, M.-C., & Chewpreecha, P. (2006). Kinetics of aniline degradation by Fenton and electro-Fenton processes. *Water Research, 40*(9), 1841-1847. doi: 10.1016/j.watres.2006.02.033

Asghar, A., Abdul Raman, A. A., & Wan Daud, W. M. A. (2015). Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: a review. *Journal of Cleaner Production, 87*(1), 826-838. doi: 10.1016/j.jclepro.2014.09.010

Ashrafi, O., Yerushalmi, L., & Haghighat, F. (2015). Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission. *Journal of Environmental Management, 158*, 146-157. doi: 10.1016/j.jenvman.2015.05.010

Bach, A., Zelmanov, G., & Semiat, R. (2008). Cold catalytic recovery of loaded activated carbon using iron oxide-based nanoparticles. *Water Research, 42*(1-2), 163-168. doi: 10.1016/j.watres.2007.07.044

Barhoumi, N., Olvera-Vargas, H., Oturan, N., Huguenot, D., Gadri, A., Ammar, S., . . . Oturan, M. A. (2017). Kinetics of oxidative degradation/mineralization pathways of the antibiotic tetracycline by the novel heterogeneous electro-Fenton process with solid catalyst chalcopyrite. *Applied Catalysis B: Environmental, 209*, 637-647. doi: 10.1016/j.apcatb.2017.03.034

Barry, P. H., & Lynch, J. W. (1991). Liquid junction potentials and small cell effects in patch-clamp analysis. *The Journal of Membrane Biology, 121*(2), 101-117. doi: 10.1007/BF01870526

Baruah, G. L., Nayak, A., & Belfort, G. (2006). Scale-up from laboratory microfiltration to a ceramic pilot plant: Design and performance. *Journal of Membrane Science, 274*(1), 56-63. doi: 10.1016/j.memsci.2005.07.046

Batista, N. J. C., de Carvalho Melo Cavalcante, A. A., de Oliveira, M. G., Medeiros, E. C. N., Machado, J. L., Evangelista, S. R., . . . Da Silva, J. (2016). Genotoxic and mutagenic evaluation of water samples from a river under the influence of different anthropogenic activities. *Chemosphere, 164*, 134. doi: 10.1016/j.chemosphere.2016.08.091

Beltrán, F. J., Encinar, J., & González, J. F. (1997). Industrial wastewater advanced oxidation. Part 2. Ozone combined with hydrogen peroxide or UV radiation. *Water Research, 31*(10), 2415-2428. doi: https://doi.org/10.1016/S0043-1354(97)00078-X

Blanco, J., Torrades, F., De, l. V., & García-Montaño, J. (2012). Fenton and biological-Fenton coupled processes for textile wastewater treatment and reuse. *Desalination, 286*, 394-399.

Blanco, J., Torrades, F., Varga, D. L., & García-Montaño, J. (2011). Fenton and biological-Fenton coupled processes for textile wastewater treatment and reuse. *Desalination, 286*. doi: 10.1016/j.desal.2011.11.055

Bocos, E., Alfaya, E., Iglesias, O., Pazos, M., & Ángeles Sanromán, M. (2015). Application of a new sandwich of granular activated and fiber carbon as cathode in the electrochemical advanced oxidation treatment of pharmaceutical effluents. *Separation and Purification Technology, 151*, 243-250. doi: 10.1016/j.seppur.2015.07.048

Bolisetty, S., Peydayesh, M., & Mezzenga, R. (2019). Sustainable technologies for water purification from heavy metals: review and analysis. *Chemical Society Reviews, 48*(2), 463-487. doi: 10.1039/C8CS00493E

Boxall, C., & Kelsall, G. H. (1992). Hypochlorite Electrogeneration. . *Thermodynamics and Kinetic 560 model of the Anode Reaction Layer, Institution of Chemical Engineers, Rugby, United 561 Kingdom. , 2*, pp. 59-70.

Brillas, E., & Martínez-Huitle, C. A. (2015). Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Applied Catalysis B: Environmental, 166-167*(C), 603-643. doi: 10.1016/j.apcatb.2014.11.016

Çakmakcı, M., & Özyaka, V. Ş. (2013). Aerobic composting leachate treatment by the combination of membrane processes. *Waste Management & Research, 31*(2), 187-193. doi: 10.1177/0734242X12462283

Cameselle, C., Pazos, M., & Sanromán, M. A. (2005). Selection of an electrolyte to enhance the electrochemical decolourisation of indigo. Optimisation and scale-up. *Chemosphere, 60*(8), 1080-1086. doi: 10.1016/j.chemosphere.2005.01.018

Campbell, F. (2019). N.S. wants more information about Northern Pulp wastewater plan, *theguardian*. Retrieved from https://www.theguardian.pe.ca/news/provincial/ns-wants-more-information-about-northern-pulp-wastewater-plan-296125/

CCME. (2019). Water Quality Guidelines for the Protection of Freshwater Aquatic Life.

Chanworrawoot, K., & Hunsom, M. (2012). Treatment of wastewater from pulp and paper mill industry by electrochemical methods in membrane reactor (Vol. 113, pp. 399-406).

Chao, Y., Jin, Y., Jiang, W., Chen, L., Li, X., Luo, J., . . . Zhu, W. (2019). Metal-based ionic liquid assisted synthesis of highly dispersed mesoporous Fe(III)/SiO2 for enhanced adsorption of antibiotics. *Journal of Chemical Technology & Biotechnology, 94*(12), 3815-3824. doi: 10.1002/jctb.6130

Chaudhary, M., & Walker, T. R. (2019). River Ganga pollution: Causes and failed management plans (correspondence on Dwivedi et al. 2018. Ganga water pollution: A potential health threat to inhabitants of Ganga basin. Environment International 117, 327–338). *Environment International, 126*, 202-206. doi: https://doi.org/10.1016/j.envint.2019.02.033

Chelliapan, S., Wilby, T., & Sallis, P. J. (2006). Performance of an up-flow anaerobic stage reactor (UASR) in the treatment of pharmaceutical wastewater containing macrolide antibiotics. *Water Research, 40*(3), 507-516. doi: 10.1016/j.watres.2005.11.020

Dawadi, S., & Ahmad, S. (2013). Evaluating the impact of demand-side management on water resources under changing climatic conditions and increasing population. *Journal of Environmental Management, 114*, 261-275. doi: 10.1016/j.jenvman.2012.10.015

De, S., Hazra, T., & Dutta, A. (2019). Treatment of landfill leachate by integrated sequence of air stripping, coagulation–flocculation and adsorption. *Environment, Development and Sustainability, 21*(2), 657-677. doi: 10.1007/s10668-017-0053-3 de Vera, G. A., Gernjak, W., & Radjenovic, J. (2017). Predicting reactivity of model DOM compounds towards chlorine with mediated electrochemical oxidation. *Water Research, 114*, 113-121. doi: 10.1016/j.watres.2017.01.038

Deegan, A. M. S., B.; Nolan, K.; Urell, K.; Tobin, J.; Morrissey, A. . (2011). Treatment options for wastewater effluents from pharmaceutical companies. . *Int. J. Environ. Sci. Technology., 8,*, 649−666.

Del Aguila Feijoo, M., & Walker, T. R. (2018). Correspondence to the Editor Re: Artisanal and small-scale gold mining impacts in Madre de Dios, Peru: Management and mitigation strategies. *Environment International, 111*, 133-134. doi: https://doi.org/10.1016/j.envint.2017.11.029

Derco, J., Gotvajn, A., Zagorc-Končan, J., Almásiová, B., & Kassai, A. (2010). Pretreatment of landfill leachate by chemical oxidation processes. *Chemical Papers, 64*(2), 237-245. doi: 10.2478/s11696-009-0116-5

Ding, Q., Yamamura, H., Murata, N., Aoki, N., Yonekawa, H., Hafuka, A., & Watanabe, Y. (2016). Characteristics of meso-particles formed in coagulation process causing irreversible membrane fouling in the coagulation-microfiltration water treatment. *Water Research, 101*, 127-136. doi: 10.1016/j.watres.2016.05.076

Dudgeon, D., Arthington, A. H., Gessner, M. O., Kawabata, Z. I., Knowler, D. J., Lévêque, C., . . . Sullivan, C. A. (2006). Freshwater biodiversity: importance, threats, status and conservation challenges. *Biological Reviews, 81*(2), 163-182. doi: 10.1017/S1464793105006950

El-Din, M. G., & Smith, D. W. (2002). Ozonation of kraft pulp mill effluents: process dynamics. *Journal of Environmental Engineering and Science, 1*(1), 45-57. doi: 10.1139/s01-001

El-Gohary, F. A., Abou-Elela, S. I., & Aly, H. I. (1995). Evaluation of biological technologies for wastewater treatment in the pharmaceutical industry. *Water Science and Technology, 32*(11), 13-20. doi: https://doi.org/10.1016/0273-1223(96)00112-6

Fang, Y.-F., Huang, Y.-P., Liu, D.-F., Huang, Y., Guo, W., & David, J. (2007). Photocatalytic degradation of the dye sulforhodamine-B: A comparative study of different light sources. *Journal of Environmental Sciences, 19*(1), 97-102. doi: 10.1016/S1001-0742(07)60016-3

Feng, Y., Yang, L., Liu, J., & Logan, B. E. (2016). Electrochemical technologies for wastewater treatment and resource reclamation. *Environmental Science: Water Research & Technology, 2*(5), 800-831. doi: 10.1039/C5EW00289C

Fenton, H. J. H. L.-. (1894). Oxidation of tartaric acid in the presence of iron. *J.Chem. Soc. Trans., 65,*, 899-910.

Fernandes, A., Pacheco, M. J., Ciríaco, L., & Lopes, A. (2015). Review on the electrochemical processes for the treatment of sanitary landfill leachates: Present and future. *Applied Catalysis B: Environmental, 176-177*, 183-200. doi: 10.1016/j.apcatb.2015.03.052

Fernández-Castro, P., Vallejo, M., San Román, M. F., & Ortiz, I. (2015). Insight on the fundamentals of advanced oxidation processes. Role and review of the determination methods of reactive oxygen species. *Journal of Chemical Technology & Biotechnology, 90*(5), 796-820. doi: 10.1002/jctb.4634

Fernández-Castro, P., Vallejo, M., San Román, M. F., & Ortiz, I. (2015). Insight on the fundamentals of advanced oxidation processes. Role and review of the determination methods of reactive oxygen species. *Journal of Chemical Technology & Biotechnology, 90*(5), 796-820. doi: 10.1002/jctb.4634

Frank, J., Ruhl, A. S., & Jekel, M. (2015). Impacts of backwashing on granular activated carbon filters for advanced wastewater treatment. *Water Research, 87*, 166-174. doi: 10.1016/j.watres.2015.09.020

French, K., Guest, R. K., Finch, G. R., & Haas, C. N. (2000). Correlating Cryptosporidium removal using dissolved air flotation in water treatment. *Water Research, 34*(16), 4116-4119. doi: 10.1016/S0043-1354(00)00164-0

Fujishima, A., Zhang, X., & Tryk, D. A. (2008). TiO 2 photocatalysis and related surface phenomena. *Surface Science Reports, 63*(12), 515-582. doi: 10.1016/j.surfrep.2008.10.001

García-Morales, M. A., Roa-Morales, G., Barrera-Díaz, C., Bilyeu, B., & Rodrigo, M. A. (2013). Synergy of electrochemical oxidation using boron-doped diamond (BDD) electrodes and ozone (O3) in industrial wastewater treatment. *Electrochemistry Communications, 27*, 34-37. doi: 10.1016/j.elecom.2012.10.028

Garcia-Segura, S., Ocon, J. D., & Chong, M. N. (2018). Electrochemical oxidation remediation of real wastewater effluents — A review. *Process Safety and Environmental Protection, 113*, 48-67. doi: 10.1016/j.psep.2017.09.014

Gautam, S., Kamble, S. P., Sawant, S. B., & Pangarkar, V. G. (2005). Photocatalytic degradation of 4-nitroaniline using solar and artificial UV radiation. *Chemical Engineering Journal, 110*(1), 129-137. doi: 10.1016/j.cej.2005.03.021

George, Z. K., & Kostas, A. M. (2018). Flotation in Water and Wastewater Treatment. *Processes, 6*(8), 116. doi: 10.3390/pr6080116

Ghanbari, F., & Moradi, M. (2015). A comparative study of electrocoagulation, electrochemical Fenton, electro-Fenton and peroxi-coagulation for decolorization of real textile wastewater: Electrical energy consumption and biodegradability improvement. *Journal of Environmental Chemical Engineering, 3*(1), 499-506. doi: 10.1080/19443994.2015.1005144

GHD. (2018). Remedial Option Decision Document. *11148275, 5*, i.

Ghosh, P., Samanta, A. N., & Ray, S. (2011). Reduction of COD and removal of Zn 2+ from rayon industry wastewater by combined electro-Fenton treatment and chemical precipitation. *Desalination, 266*(1), 213-217. doi: 10.1016/j.desal.2010.08.029

Gilpavas, E., Dobrosz-Gómez, I., & Gómez-García, M. Á. (2017). Coagulation-flocculation sequential with Fenton or Photo-Fenton processes as an alternative for the industrial textile wastewater treatment. *Journal of Environmental Management, 191*, 189-197. doi: 10.1016/j.jenvman.2017.01.015

Gondal, Adesida, A., Rashid, S., Shi, S., Khan, R., Yamani, Z., . . . Chang, X. (2015). Preparation of WO 3 /g-C 3 N 4 composites and their enhanced photodegradation of contaminants in aqueous solution under visible light irradiation. *Reaction Kinetics, Mechanisms and Catalysis, 114*(1), 357-367. doi: 10.1007/s11144-014-0787-y

Gondal, Adesida, A. A., Rashid, S. G., Hameed, A., Aslam, M., Ismail, I. M. I., . . . Rehman, A. U. (2016). Facile synthesis, characterization and photocatalytic performance of Au-Ag alloy nanoparticles dispersed on graphitic carbon nitride under visible light irradiations. *Journal of Molecular Catalysis. A, Chemical, 423*, 114-125. doi: 10.1016/j.molcata.2016.06.013

Götz, C., Stamm, C., Fenner, K., Singer, H., Schärer, M., & Hollender, J. (2010). Targeting aquatic microcontaminants for monitoring: exposure categorization and application to the Swiss situation. *Environmental science and pollution research international, 17*(2), 341-354. doi: 10.1007/s11356-009-0167-8

Guinea, E., Arias, C., Cabot, P. L., Garrido, J. A., Rodríguez, R. M., Centellas, F., & Brillas, E. (2008). Mineralization of salicylic acid in acidic aqueous medium by electrochemical advanced oxidation processes using platinum and boron-doped diamond as anode and cathodically generated hydrogen peroxide. *Water Research, 42*, 499-511.

Haritash, A. K., & Kaushik, C. P. (2009). Biodegradation aspects of Polycyclic Aromatic Hydrocarbons (PAHs): A review. *Journal of Hazardous Materials, 169*(1 3), 1. doi: 10.1016/j.jhazmat.2009.03.137

Hassan, M., Zhao, Y., & Xie, B. (2016). Employing TiO2 photocatalysis to deal with landfill leachate: Current status and development. *Chemical Engineering Journal, 285*, 264-275. doi: 10.1016/j.cej.2015.09.093

Heidari, E. A., Alidadi, H., Najafpoor, A. A., Mohseni, S. M., Dehghan, A., Sheibani, A., & Sarkhosh, M. (2018). Data on assessment of physical, chemical and biological characteristics of effluent from wastewater treatment in Torbat Heydarieh, Iran. *Data in Brief, 19*, 1287-1290. doi: 10.1016/j.dib.2018.05.086

Herrmann, J.-M. (1999). Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants (Vol. 53, pp. 115-129).

Hoffman, E., Alimohammadi, M., Lyons, J., Davis, E., Walker, T., & Lake, C. (2019). Characterization and spatial distribution of organic-contaminated sediment derived from historical industrial effluents. *An International Journal Devoted to Progress in the Use of Monitoring Data in Assessing Environmental Risks to Man and the Environment, 191*(9), 1-19. doi: 10.1007/s10661-019-7763-y

Hoffman, E., Bernier, M., Blotnicky, B., Golden, P., Janes, J., Kader, A., . . . Walker, T. (2015). Assessment of public perception and environmental compliance at a pulp and paper facility: a Canadian case study. *Environmental Monitoring and Assessment, 187*(12), 1-13. doi: 10.1007/s10661-015-4985-5

Hoffman, E., Guernsey, J., Walker, T., Kim, J., Sherren, K., & Andreou, P. (2017a). Pilot study investigating ambient air toxics emissions near a Canadian kraft pulp and paper facility in Pictou County, Nova Scotia. *Environmental Science and Pollution Research, 24*(25), 20685-20698. doi: 10.1007/s11356-017-9719-5

Hoffman, E., Lyons, J., Boxall, J., Robertson, C., Lake, C., & Walker, T. (2017b). Spatiotemporal assessment (quarter century) of pulp mill metal(loid) contaminated sediment to inform remediation decisions. *An International Journal Devoted to Progress in the Use of Monitoring Data in Assessing Environmental Risks to Man and the Environment, 189*(6), 1-17. doi: 10.1007/s10661-017-5952-0

Honda, Y., Ivandini, T. A., Watanabe, T., Murata, K., & Einaga, Y. (2013). An electrolyte-free system for ozone generation using heavily boron-doped diamond electrodes. *Diamond & Related Materials, 40*, 7-11. doi: 10.1016/j.diamond.2013.09.001

Hou, Y., Liu, H., Zhao, X., Qu, J., & Chen, J. P. (2012). Combination of electroreduction with biosorption for enhancement for removal of hexavalent chromium. *Journal of colloid and interface science, 385*(1), 147-153. doi: 10.1016/j.jcis.2012.05.056

Hurtado, F. J., Kaiser, A. S., & Zamora, B. (2015). Fluid dynamic analysis of a continuous stirred tank reactor for technical optimization of wastewater digestion. *Water Research, 71*, 282-293. doi: 10.1016/j.watres.2014.11.053

Ikehata, K., Jodeiri Naghashkar, N., & Gamal El-Din, M. (2006). Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. *Ozone: Science & Engineering, 28*(6), 353-414. doi: 10.1080/01919510600985937

Issabayeva, G., Aroua, M. K., & Sulaiman, N. M. (2006). Electrodeposition of copper and lead on palm shell activated carbon in a flow-through electrolytic cell. *Desalination, 194*(1), 192-201. doi: 10.1016/j.desal.2005.09.029

Jaafarzadeh, N., Ghanbari, F., Ahmadi, M., & Omidinasab, M. (2017). Efficient integrated processes for pulp and paper wastewater treatment and phytotoxicity reduction: Permanganate, electro-Fenton and Co3O4/UV/peroxymonosulfate. *Chemical Engineering Journal, 308*, 142-150. doi: 10.1016/j.cej.2016.09.015

Jane, L. (2019). Rate and Tariffs. Nova Scotia. Retrieved from https://www.nspower.ca/about-us/electricity/rates-tariffs.

Jeong, C. H. (2001). Effect of land use and urbanization on hydrochemistry and contamination of groundwater from Taejon area, Korea. *Effect of land use and urbanization on hydrochemistry and contamination of groundwater from Taejon area, Korea, 253*(1-4), 194-210. doi: 10.1016/S0022-1694(01)00481-4

Jiang, J.-Q., Graham, N., André, C., Kelsall, G. H., & Brandon, N. (2002). Laboratory study of electro-coagulation–flotation for water treatment. *Water Research, 36*(16), 4064-4078. doi: 10.1016/S0043-1354(02)00118-5

Kanakaraju, D., Glass, B. D., & Oelgemöller, M. (2018). Advanced oxidation process-mediated removal of pharmaceuticals from water: A review. *Journal of Environmental Management, 219*, 189-207. doi: 10.1016/j.jenvman.2018.04.103

Karimi, H., Farmany, A., & Noorizadeh, H. (2013). Chemometrics analysis for investigation of retention behavior of hazardous compounds in effluents. *An International Journal Devoted to Progress in the Use of Monitoring Data in Assessing Environmental Risks to Man and the Environment, 185*(1), 473-483. doi: 10.1007/s10661-012-2568-2

Karla Miriam Hernández, M., Onofre Monge, A., María Teresa Certucha, B., Francisco Javier Almendariz, T., & Evelia Acedo, F. (2013). Metallic Biosorption Using Yeasts in Continuous Systems. *International Journal of Photoenergy, 2013*, 1-4. doi: 10.1155/2013/578729

Karrasch, B., Parra, O., Cid, H., Mehrens, M., Pacheco, P., Urrutia, R., . . . Zaror, C. (2006). Effects of pulp and paper mill effluents on the microplankton and microbial self-purification capabilities of the Biobío River, Chile. *Science of the Total Environment, 359*(1-3), 194-208. doi: 10.1016/j.scitotenv.2005.03.029

Khansorthong, S., & Hunsom, M. (2009). Remediation of wastewater from pulp and paper mill industry by the electrochemical technique. *Chemical Engineering Journal, 151*(1), 228-234. doi: 10.1016/j.cej.2009.02.038

Klauson, D., Kivi, A., Kattel, E., Klein, K., Viisimaa, M., Bolobajev, J., . . . Trapido, M. (2015). Combined processes for wastewater purification: treatment of a typical landfill leachate with a combination of chemical and biological oxidation processes. *Journal of Chemical Technology & Biotechnology, 90*(8), 1527-1536. doi: 10.1002/jctb.4484

Klemm, O., Schemenauer, R., Lummerich, A., Cereceda, P., Marzol, V., Corell, D., . . . Fessehaye, G. (2012). Fog as a Fresh-Water Resource: Overview and Perspectives. *A Journal of the Human Environment, 41*(3), 221-234. doi: 10.1007/s13280-012-0247-8

Körbahti, B. K., & Tanyolaç, A. (2009). Continuous electrochemical treatment of simulated industrial textile wastewater from industrial components in a tubular reactor. *Journal of Hazardous Materials, 170*(2-3), 771-778. doi: 10.1016/j.jhazmat.2009.05.032

Kuosa, M., Kallas, J., & Häkkinen, A. (2015). Ozonation of p-nitrophenol at different pH values of water and the influence of radicals at acidic conditions. *Journal of Environmental Chemical Engineering, 3*(1), 325-332. doi: 10.1016/j.jece.2014.10.015

Labiadh, L., Fernandes, A., Ciríaco, L., Pacheco, M. J., Gadri, A., Ammar, S., & Lopes, A. (2016). Electrochemical treatment of concentrate from reverse osmosis of sanitary landfill leachate. *Journal of Environmental Management, 181*, 515-521. doi: 10.1016/j.jenvman.2016.06.069

Lakshmanan, R., & Kuttuva Rajarao, G. (2014). Effective water content reduction in sewage wastewater sludge using magnetic nanoparticles. *Bioresource Technology, 153*, 333-339. doi: 10.1016/j.biortech.2013.12.003

Lapworth, D. J., Baran, N., Stuart, M. E., & Ward, R. S. (2012). Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. *Environmental Pollution, 163*, 287-303.

Larsen, T. A., Hoffmann, S., Lüthi, C., Truffer, B., & Maurer, M. (2016). Emerging solutions to the water challenges of an urbanizing world. *Science (New York, N.Y.), 352*(6288), 928. doi: 10.1126/science.aad8641

Ledakowicz, S., L. Bilińska, R. Żyłła. (2012). Application of Fenton's Reagent in the Textile Wastewater Treatment Under Industrial Conditions. *Ecol. Chem. Eng. S., 19*, 163–174. . doi: doi:10.2478/v10216-011-0013-z

Lema, J., Mendez, R., & Blazquez, R. (1988). Characteristics of landfill leachates and alternatives for their treatment: A review. *Water, air, and soil pollution, 40*(3), 223-250. doi: 10.1007/BF00163730

Leszczyński, J., & Maria Jolanta, W. (2018). The removal of organic compounds from landfill leachate using ozone-based advanced oxidation processes. *E3S Web of Conferences, 45*, 00046. doi: 10.1051/e3sconf/20184500046

Lettmann, C., Hinrichs, H., & Maier, W. F. (2001). Combinatorial Discovery of New Photocatalysts for Water Purification with Visible Light. *Angewandte Chemie International Edition, 40*(17), 3160-3164. doi: 10.1002/1521-3773(20010903)40:17<3160::AID-ANIE3160>3.0.CO2-Z

Lewis, D., Francis, S., Francis-Strickland, K., Castleden, H., & Apostle, R. (2020). If only they had accessed the data: Governmental failure to monitor pulp mill impacts on human health in Pictou Landing First Nation. *Social Science & Medicine*, 113184. doi: https://doi.org/10.1016/j.socscimed.2020.113184

Li, W., Zhou, Q., & Hua, T. (2010). Removal of Organic Matter from Landfill Leachate by Advanced Oxidation Processes: A Review. *International Journal of Chemical Engineering, 2010*(2010). doi: 10.1155/2010/270532

Ling, Y., Xu, H., & Chen, X. (2015). Continuous multi-cell electrochemical reactor for pollutant oxidation. *Chemical Engineering Science, 122*, 630-636. doi: 10.1016/j.ces.2014.10.031

Liu, C., Wu, T., Hsu, P.-C., Xie, J., Zhao, J., Liu, K., . . . Cui, Y. (2019). Direct/Alternating Current Electrochemical Method for Removing and Recovering Heavy Metal from Water Using Graphene Oxide Electrode. *ACS Nano, 13*(6). doi: 10.1021/acsnano.8b09301

Long, Y., Xu, J., Shen, D., Du, Y., & Feng, H. (2017). Effective removal of contaminants in landfill leachate membrane concentrates by coagulation. *Chemosphere, 167*, 512-519. doi: 10.1016/j.chemosphere.2016.10.016

Lucas, M. S., Peres, J. A., Amor, C., Prieto-Rodríguez, L., Maldonado, M. I., & Malato, S. (2012). Tertiary treatment of pulp mill wastewater by solar photo-Fenton. *Journal of Hazardous Materials, 225-226*(C), 173-181. doi: 10.1016/j.jhazmat.2012.05.013

Ma, X., & Zhou, M. (2009). A comparative study of azo dye decolorization by electro-Fenton in two common electrolytes. *Journal of Chemical Technology & Biotechnology, 84*(10), 1544-1549. doi: 10.1002/jctb.2218

Magdalena, Z., & Urszula, A.-K. (2019). Wastewater Treatment Methods for Effluents from the Confectionery Industry – an Overview. *Journal of Ecological Engineering, 20*(9), 293-304. doi: 10.12911/22998993/112557

Mandal, P., Dubey, B. K., & Gupta, A. K. (2017). Review on landfill leachate treatment by electrochemical oxidation: Drawbacks, challenges and future scope. *Waste Management, 69*, 250-273. doi: 10.1016/j.wasman.2017.08.034

Manisankar, P., Viswanathan, S., & Rani, C. (2003). Electrochemical treatment of distillery effluent using catalytic anodes. *Green Chemistry, 5*(2), 270-274. doi: 10.1039/b208424b

Marco, P., & Giacomo, C. (2009). Direct And Mediated Anodic Oxidation of Organic Pollutants. *Chemical Reviews, 109*(12), 6551.

Martínez-Huitle, C. A., & Ferro, S. (2006). Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. *Chemical Society Reviews, 35*(12), 1324-1340. doi: 10.1039/B517632H

Martínez-Huitle, C. A., & Brillas, E. (2008). Electrochemical Alternatives for Drinking Water Disinfection. *Angewandte Chemie International Edition, 47*(11), 1998-2005. doi: 10.1002/anie.200703621

Maxwell, D. (1986). The Principles and Practice of Electron Microscopy . By Ian M. Watt. Pp. 303. (Cambridge University Press, 1985.) £40.00. *Quarterly Journal of Experimental Physiology, 71*(3), 492-492. doi: 10.1113/expphysiol.1986.sp003010

Miao Li a, C. F. a. Z. Z. b. S. Y. a. N. S. b. (2010). Treatment of nitrate contaminated water using an electrochemical method. *Bioresource Technology*.

Michael-Kordatou, I., Michael, C., Duan, X., He, X., Dionysiou, D. D., Mills, M. A., & Fatta-Kassinos, D. (2015). Dissolved effluent organic matter: Characteristics and potential implications in wastewater treatment and reuse applications. *Water Research, 77*, 213-248. doi: 10.1016/j.watres.2015.03.011

Miklos, D. B., Remy, C., Jekel, M., Linden, K. G., Drewes, J. E., & Hübner, U. (2018). Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review. *Water Research, 139*, 118-131. doi: 10.1016/j.watres.2018.03.042

Mitchell, E., Frisbie, S., & Sarkar, B. (2011). Exposure to multiple metals from groundwatera global crisis: Geology, climate change, health effects, testing, and mitigation. *Metallomics, 3*(9), 874-908. doi: 10.1039/c1mt00052g

Mohd Shaiful, S., Chin Hua, C., Sarani, Z., & Mika, S. (2014). Removal of Organic Pollutants and Decolorization of Bleaching Effluents from Pulp and Paper Mill by Adsorption using Chemically Treated Oil Palm Empty Fruit Bunch Fibers. *BioResources, 9*(3), 4517-4527. doi: 10.15376/biores.9.3.4517-4527

Moreira, F. C., Boaventura, R. A. R., Brillas, E., & Vilar, V. J. P. (2017). Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. *Applied Catalysis B: Environmental, 202*, 217-261. doi: 10.1016/j.apcatb.2016.08.037

Moreira, F. C., Soler, J., Alpendurada, M. F., Boaventura, R. A. R., Brillas, E., & Vilar, V. (2016). Tertiary treatment of a municipal wastewater toward pharmaceuticals removal by chemical and electrochemical advanced oxidation processes. *Water Research, 105*, 251-263. doi: 10.1016/j.watres.2016.08.036

Moreira, F. C., Soler, J., Fonseca, A., Saraiva, I., Boaventura, R. A. R., Brillas, E., & Vilar, V. J. P. (2015). Incorporation of electrochemical advanced oxidation processes in a multistage treatment system for sanitary landfill leachate. *Water Research, 81*, 375-387. doi: 10.1016/j.watres.2015.05.036

Muruganandham, M., Suri, R. P. S., Jafari, S., Sillanpää, M., Lee, G.-J., Wu, J. J., & Swaminathan, M. (2014). Recent Developments in Homogeneous Advanced Oxidation Processes for Water and Wastewater Treatment. *International Journal of Photoenergy, 2014*. doi: 10.1155/2014/821674

Mussa, Z. H., Othman, M. R., & Abdullah, M. P. (2015). Electrochemical Oxidation of Landfill Leachate: Investigation of Operational Parameters and Kinetics Using Graphite-PVC Composite Electrode as Anode. *Journal of the Brazilian Chemical Society, 26*(5), 939-948. doi: 10.5935/0103-5053.20150055

Nakada, N., Shinohara, H., Murata, A., Kiri, K., Managaki, S., Sato, N., & Takada, H. (2007). Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. *Water Research, 41*(19), 4373-4382. doi: https://doi.org/10.1016/j.watres.2007.06.038

Nakatsuka, N., Kishita, Y., Kurafuchi, T., & Akamatsu, F. (2020). Integrating wastewater treatment and incineration plants for energy-efficient urban biomass utilization: A life cycle analysis. *Journal of Cleaner Production, 243*. doi: 10.1016/j.jclepro.2019.118448

Nandy, T., Shastry, S., Pathe, P., & Kaul, S. (2003). Pre-Treatment of Currency Printing Ink Wastewater through Coagulation-Flocculation Process. *An International Journal of Environmental Pollution, 148*(1-4), 15-30. doi: 10.1023/A:1025454003863

Neppolian, B., Kanel, S. R., Choi, H. C., Shankar, M. V., Arabindoo, B., & Murugesan, V. (2003). Photocatalytic degradation of reactive yellow 17 dye in aqueous solution in the presence of with cement binder. *International Journal of Photoenergy, 5*(2). doi: 10.1155/S1110662X03000126

Nidheesh, P. V., & Gandhimathi, R. (2012). Trends in electro-Fenton process for water and wastewater treatment: An overview. *Desalination, 299*, 1-15. doi: 10.1016/j.desal.2012.05.011

Nihal Oturan, M. A. O. (2018). Electro-Fenton Process: Background, New Developments, and Applications. Electrochemical Water and Wastewater Treatment https://doi.org/10.1016/B978-0-12-813160-2.00008-0. *Chapter.*

Oduoza, C. F., & Wragg, A. A. (2002). Local mass-transfer distribution in the channels of a serpentine flow baffled parallel plate cell. *Chemical Engineering Journal, 85*(2), 119-126. doi: 10.1016/S1385-8947(01)00215-7

Oldham, K. B., Myland, J. C., & Bond, A. M. (2012). *Electrochemical Science and Technology*. West Sussex, England: John Wiley & Sons.

Othman, E., Mohd, S. Y., Hamidi, A. A., Mohd, N. A., Mohammed, J. K. B., & Yung-Tse, H. (2010). The Effectiveness of Silica Sand in Semi-Aerobic Stabilized Landfill Leachate Treatment. *Water, 2*(4), 904-915. doi: 10.3390/w2040904

Oturan, M. (2014). Electrochemical advanced oxidation technologies for removal of organic pollutants from water. *Environmental Science and Pollution Research, 21*(14), 8333-8335. doi: 10.1007/s11356-014-2841-8

Panizza, M., & Martinez-Huitle, C. A. (2013). Role of electrode materials for the anodic oxidation of a real landfill leachate – Comparison between Ti–Ru–Sn ternary oxide, PbO_2 and boron-doped diamond anode. *Role of electrode materials for the anodic oxidation of a real landfill leachate – Comparison between Ti–Ru–Sn ternary oxide,* PbO_2 *and boron-doped diamond anode, 90*(4), 1455-1460.

Papageorgiou, S. K., Katsaros, F. K., Favvas, E. P., Romanos, G. E., Athanasekou, C. P., Beltsios, K. G., . . . Falaras, P. (2012). Alginate fibers as photocatalyst immobilizing agents applied in hybrid photocatalytic/ultrafiltration water treatment processes. *Water Research, 46*(6), 1858-1872. doi: 10.1016/j.watres.2012.01.005

Park, J., Kwon, T., Kim, J., Jin, H., Kim, H. Y., Kim, B., . . . Lee, K. (2018). Hollow nanoparticles as emerging electrocatalysts for renewable energy conversion reactions. *Chem. Soc. Rev., 47*(22), 8173-8202. doi: 10.1039/c8cs00336j

Paździor, K., Bilińska, L., & Ledakowicz, S. (2018). A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment. *Chemical Engineering Journal*. doi: 10.1016/j.cej.2018.12.057

Pictou Landing Native Women's Group (c/o Sheila Francis, P. P., Castleden, H., Lewis, D., Jamieson, R., Gibson, M., Rainham, D., Russell, R., Martin, D., & Hart, C. . (2016). "Our Ancestors Are in Our Land, Water, and Air": A Two-Eyed Seeing Approach to Researching Environmental Health Concerns with Pictou Landing First Nation-Final Report.

Pillai, I. M. S., & Gupta, A. K. (2015). Batch and continuous flow anodic oxidation of 2,4-dinitrophenol: Modeling, degradation pathway and toxicity. *Journal of Electroanalytical Chemistry, 756*(C), 108-117. doi: 10.1016/j.jelechem.2015.08.020

Pillai, I. M. S., & Gupta, A. K. (2017). Performance analysis of a continuous serpentine flow reactor for electrochemical oxidation of synthetic and real textile wastewater: Energy consumption, mass transfer coefficient and economic analysis. *Journal of Environmental Management, 193*, 524-531. doi: 10.1016/j.jenvman.2017.02.046

Pimentel, D., Berger, B., Filiberto, D., Newton, M., Wolfe, B., Karabinakis, E., . . . Nandagopal, S. (2004). Water Resources: Agricultural and Environmental Issues. *BioScience, 54*(10), 909-918. doi: 10.1641/0006-3568(2004)054[0909:WRAAEI]2.0.CO2

Pokhrel, D., & Viraraghavan, T. (2004). Treatment of pulp and paper mill wastewater—a review. *Science of the Total Environment, 333*(1-3), 37-58. doi: 10.1016/j.scitotenv.2004.05.017

Pokorska-Niewiada, K., Rajkowska-Myśliwiec, M., & Protasowicki, M. (2018). Acute Lethal Toxicity of Heavy Metals to the Seeds of Plants of High Importance to Humans. *Bulletin of Environmental Contamination and Toxicology, 101*(2), 222-228. doi: 10.1007/s00128-018-2382-9

Pulgarin, C., Adler, N., Péringer, P., & Comninellis, C. (1994). Electrochemical detoxification of a 1,4-benzoquinone solution in wastewater treatment. *Water Research, 28*(4), 887-893. doi: 10.1016/0043-1354(94)90095-7

Qu, X., Gao, W. J., Han, M. N., Chen, A., & Liao, B. Q. (2012). Integrated thermophilic submerged aerobic membrane bioreactor and electrochemical oxidation for pulp and paper effluent treatment – towards system closure. *Bioresource Technology, 116*, 1-8.

Radjenovic, J., & Sedlak, D. L. (2015). Challenges and Opportunities for Electrochemical Processes as Next-Generation Technologies for the Treatment of Contaminated Water. *Environmental science & technology, 49*(19), 11292-11302. doi: 10.1021/acs.est.5b02414

Ratnayaka, D. D. (2017). *Twort's water supply* (Seventh edition.. ed.). Amsterdam: Amsterdam : Elsevier, Butterworth-Heinemann is an imprint of Elsevier.

Rivas, F. J., Beltrán, F., Carvalho, F., Gimeno, O., & Frades, J. (2005). Study of Different Integrated Physical−Chemical + Adsorption Processes for Landfill Leachate Remediation. *Industrial & Engineering Chemistry Research, 44*(8), 2871-2878. doi: 10.1021/ie049066j

Rodríguez, A., Muñoz, I., Perdigón-Melón, J. A., Carbajo, J. B., Martínez, M. J., Fernández-Alba, A. R., . . . Rosal, R. (2012). Environmental optimization of continuous flow ozonation for urban wastewater reclamation. *The Science of the total environment, 437*, 68. doi: 10.1016/j.scitotenv.2012.07.084

Romo, J., Chaudhary, M., & Walker, T. R. (2019). Baseline assessment of contaminants in marine biota prior to remediation of industrial effluent impacted sediments in a former tidal estuary in Nova Scotia, Canada. *Marine Pollution Bulletin, 145*, 641-648. doi: 10.1016/j.marpolbul.2019.06.055

Saleem, M., Spagni, A., Alibardi, L., Bertucco, A., & Lavagnolo, M. C. (2018). Assessment of dynamic membrane filtration for biological treatment of old landfill leachate. *Journal of Environmental Management, 213*, 27-35. doi: 10.1016/j.jenvman.2018.02.057

Sánchez-Sánchez, A., Tejocote-Pérez, M., Fuentes-Rivas, R., Linares-Hernández, I., Martínez-Miranda, V., & Fonseca-Montes de Oca, R. M. G. (2018). Treatment of a Textile Effluent by Electrochemical Oxidation and Coupled System Electooxidation–. *International Journal of Photoenergy, 2018*. doi: 10.1155/2018/3147923

Särkkä, H., Bhatnagar, A., & Sillanpää, M. (2015). Recent developments of electro-oxidation in water treatment — A review. *Journal of Electroanalytical Chemistry, 754*, 46-56. doi: 10.1016/j.jelechem.2015.06.016

Schultz, T. (2005). Biological Wastewater Treatment. *Chemical Engineering, 112*(10), 44-46,48-51.

Schwarzenbach, R. P., Egli, T., Hofstetter, T. B., von Gunten, U., & Wehrli, B. (2010). Global Water Pollution and Human Health. *Annual Review of Environment and Resources, 35*(1), 109-136. doi: 10.1146/annurev-environ-100809-125342

Shan, Z., Lu, M., Wang, L., Macdonald, B., Macinnis, J., Mkandawire, M., . . . Oakes, K. D. (2016). Chloride accelerated Fenton chemistry for the ultrasensitive and selective colorimetric detection of copper. *Chem. Commun., 52*(10), 2087-2090. doi: 10.1039/c5cc07446k

Shen, X., Xiao, F., Zhao, H., Chen, Y., Fang, C., Xiao, R., . . . Zhao, G. (2020). In Situ-Formed PdFe Nanoalloy and Carbon Defects in Cathode for Synergic Reduction–Oxidation of Chlorinated Pollutants in Electro-Fenton Process. *Environmental science & technology, 54*(7), 4564. doi: 10.1021/acs.est.9b05896

Shiklomanov, I. A. (2000). Appraisal and Assessment of World Water Resources. *Water International, 25*(1), 11-32. doi: 10.1080/02508060008686794

Sibley, P., Dixon, D. G., & Barton, D. R. (2000). Impact of bleached kraft pulp mill effluent on benthic community structure in relation to environmental factors. *Journal of Aquatic Ecosystem Stress and Recovery, 7*(3), 229-246. doi: 10.1023/A:1009987123319

Singh, P. (2007). Sequential anaerobic and aerobic treatment of pulp and paper mill effluent in pilot scale bioreactor. *Journal of Environmental Biology, 28*(1), 77.

Sponza, D. T., & Çelebi, H. (2012). Removal of oxytetracycline (OTC) in a synthetic pharmaceutical wastewater by sequential anaerobic multichamber bed reactor (AMCBR)/completely stirred tank reactor (CSTR) system: biodegradation and inhibition kinetics. *Journal of Chemical Technology & Biotechnology, 87*(7), 961-975. doi: 10.1002/jctb.3706

Suarez, S., Lema, J. M., & Omil, F. (2009). Pre-treatment of hospital wastewater by coagulation–flocculation and flotation. *Bioresource Technology, 100*(7), 2138-2146. doi: https://doi.org/10.1016/j.biortech.2008.11.015

Sun, Y., Shen, Y.-X., Liang, P., Zhou, J., Yang, Y., & Huang, X. (2016). Multiple antibiotic resistance genes distribution in ten large-scale membrane bioreactors for municipal wastewater treatment. *Bioresource Technology, 222*, 100-106. doi: 10.1016/j.biortech.2016.09.117

Svensson, H., Hansson, H., & Hogland, W. (2015). Combined Ozone and Biological Treatment of Oak Wood Leachate. *CLEAN – Soil, Air, Water, 43*(4), 598-604. doi: 10.1002/clen.201400141

Szpyrkowicz, L., Kaul, S. N., Neti, R. N., & Satyanarayan, S. (2005). Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater. *Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater, 39*, 1601-1613.

Tarlan, E., Dilek, F. B., & Yetis, U. (2002). Effectiveness of algae in the treatment of a wood-based pulp and paper industry wastewater. *Bioresource Technology, 84*(1), 1-5. doi: https://doi.org/10.1016/S0960-8524(02)00029-9

Teh, C. Y., Budiman, P. M., Shak, K. P. Y., & Wu, T. Y. (2016). Recent Advancement of Coagulation–Flocculation and Its Application in Wastewater Treatment. *Industrial & Engineering Chemistry Research, 55*(16), 4363-4389. doi: 10.1021/acs.iecr.5b04703

Tekle-Röttering, A., Von Sonntag, C., Reisz, E., Eyser, C. V., Lutze, H. V., Türk, J., . . . Schmidt, T. C. (2016). Ozonation of anilines: Kinetics, stoichiometry, product identification and elucidation of pathways. *Water Research, 98*, 147-159. doi: 10.1016/j.watres.2016.04.001

Ternes, T., Meisenheimer, M., McDowell, D., & Sacher, F. (2002). Removal of pharmaceuticals during drinking water treatment. *Environmental science & technology, 36*(17), 3855-3863. doi: 10.1021/es015757k

Thompson, G., Swain, J., Kay, M., & Forster, C. F. (2001). The treatment of pulp and paper mill effluent: a review (Vol. 77, pp. 275-286). England: Elsevier Ltd.

Tripathi, S., & Tripathi, B. D. (2011). Efficiency of combined process of ozone and bio-filtration in the treatment of secondary effluent. *Bioresource Technology, 102*(13), 6850-6856. doi: 10.1016/j.biortech.2011.04.035

Trois, C., Coulon, F., de Combret, C. P., Martins, J. M. F., & Oxarango, L. (2010). Effect of pine bark and compost on the biological denitrification process of non-hazardous landfill leachate: Focus on the microbiology. *Journal of Hazardous Materials, 181*(1-3), 1163-1169. doi: 10.1016/j.jhazmat.2010.05.077

Tvedt, T. (2010). Why England and not China and India? Water systems and the history of the Industrial Revolution *. *Journal of Global History, 5*(1), 29-50. doi: 10.1017/S1740022809990325

Urase, T., Kagawa, C., & Kikuta, T. (2005). Factors affecting removal of pharmaceutical substances and estrogens in membrane separation bioreactors. *Desalination, 178*(1), 107-113. doi: https://doi.org/10.1016/j.desal.2004.11.031

Urtiaga, A. M., Pérez, G., Ibáñez, R., & Ortiz, I. (2013). Removal of pharmaceuticals from a WWTP secondary effluent by ultrafiltration/reverse osmosis followed by electrochemical oxidation of the RO concentrate. *Desalination, 331*, 26-34. doi: 10.1016/j.desal.2013.10.010

USGS. (2015). Saline Water and Salinity.

Usha, M. T., Sarat Chandra, T., Sarada, R., & Chauhan, V. S. (2016). Removal of nutrients and organic pollution load from pulp and paper mill effluent by microalgae in outdoor open pond. *Bioresource Technology, 214*, 856-860. doi: 10.1016/j.biortech.2016.04.060

Vecoli, C., Montano, L., & Andreassi, M. (2016). Environmental pollutants: genetic damage and epigenetic changes in male germ cells. *Environmental Science and Pollution Research, 23*(23), 23339-23348. doi: 10.1007/s11356-016-7728-4

Vörösmarty, C. J., Hoekstra, A. Y., Bunn, S. E., Conway, D., & Gupta, J. (2015). Fresh water goes global. *Science, 349*(6247), 478-479. doi: 10.1126/science.aac6009

W.H.O, W. H. O. (2001). Arsenic and arsenic compounds, 2nd ed. Geneva, World Health Organization. *(Environmental Health Criteria, 224*.

W.H.O, W. H. O. (2018). A global overview of national regulations and standards for drinking-water quality. from https://www.who.int/water_sanitation_health/publications/national-regulations-and-standards-for-drinking-water-quality/en/

Wang, J.-P., Chen, Y.-Z., Wang, Y., Yuan, S.-J., & Yu, H.-Q. (2011). Optimization of the coagulation-flocculation process for pulp mill wastewater treatment using a combination of uniform design and response surface methodology. *Water Research, 45*(17), 5633-5640. doi: 10.1016/j.watres.2011.08.023

Wang, J., Li, T., Zhou, M., Li, X., & Yu, J. (2015). Characterization of hydrodynamics and mass transfer in two types of tubular electrochemical reactors. *Electrochimica Acta, 173*, 698-704. doi: 10.1016/j.electacta.2015.05.135

Watt, C. (2001). BIOE 4322 Aquacultural Engineering Course Notes Handbook. Faculty of Biological Engineering, Dalhousie University, Halifax, NS. 276 pp.

WEM. (1994). Wastewater. *Water Engineering & Management, 141*(12), 19.

Wilkinson, J. L., Swinden, J., Hooda, P. S., Barker, J., & Barton, S. (2016). Markers of anthropogenic contamination: A validated method for quantification of pharmaceuticals, illicit drug metabolites, perfluorinated compounds, and plasticisers in sewage treatment effluent and rain runoff. *Chemosphere, 159*, 638. doi: 10.1016/j.chemosphere.2016.06.039

Won, S. W., Mao, J., Kwak, I.-S., Sathishkumar, M., & Yun, Y.-S. (2010). Platinum recovery from ICP wastewater by a combined method of biosorption and incineration. *Bioresource Technology, 101*(4), 1135-1140. doi: 10.1016/j.biortech.2009.09.056

Wu, J., Xiao, Y.-Z., & Yu, H.-Q. (2005). Degradation of lignin in pulp mill wastewaters by white-rot fungi on biofilm. *Bioresource Technology, 96*(12), 1357-1363. doi: https://doi.org/10.1016/j.biortech.2004.11.019

Xie, X., Zhao, W., Hu, Y., Xu, X., & Cheng, H. (2019). Permanganate oxidation and ferric ion precipitation (KMnO4-Fe(III)) process for treating phenylarsenic compounds. *Chemical Engineering Journal, 357*, 600-610. doi: 10.1016/j.cej.2018.09.194

Yusoff, M. S., Aziz, H. A., Zamri, M. F. M. A., Suja, F., Abdullah, A. Z., & Basri, N. E. A. (2018). Floc behavior and removal mechanisms of cross-linked Durio zibethinus seed starch as a natural flocculant for landfill leachate coagulation-flocculation treatment. *Waste Management, 74*, 362-372. doi: 10.1016/j.wasman.2018.01.016

Zaharia, C. (2016). EVALUATION OF WATER POLLUTION STATUS IN BAHLUI RIVER (IASI TOWN AREA) DUE TO DOMESTIC AND URBAN WASTEWATER TREATMENT ACTIVITIES. *Journal of Engineering Studies and Research, 21*(4). doi: 10.29081/jesr.v21i4.11

Zhan, Y., Li, H., & Chen, Y. (2010). Copper hydroxyphosphate as catalyst for the wet hydrogen peroxide oxidation of azo dyes. *Journal of Hazardous Materials, 180*(1), 481-485. doi: 10.1016/j.jhazmat.2010.04.055

Zhang, Y., Liu, J., Li, R., Zeng, X., Xue, Y., Liu, J., & Nie, Y. (2012). Determining the Biodegradability of Leachate Through XAD-8 Adsorption. *Procedia Environmental Sciences, 16*(C), 3-8. doi: 10.1016/j.proenv.2012.10.002

Zheng, J., Wu, K.-L., Shi, T.-H., & Xu, Y. (2013). A series of novel ferrocene-based dipeptide receptors for electrochemistry and biological activity: Electrochemical sensing of zinc group metals. *Applied Organometallic Chemistry, 27*(12), 698-703. doi: 10.1002/aoc.3042

Zhong, H., Tian, Y., Yang, Q., Brusseau, M. L., Yang, L., & Zeng, G. (2017). Degradation of landfill leachate compounds by persulfate for groundwater remediation. *Chemical Engineering Journal, 307*, 399-407. doi: 10.1016/j.cej.2016.08.069

Zhou, H., Li, X., Xu, G., & Yu, H. (2018). Overview of strategies for enhanced treatment of municipal/domestic wastewater at low temperature. *Science of the Total Environment, 643*, 225-237. doi: 10.1016/j.scitotenv.2018.06.100

Zhou, L., Hu, Z., Zhang, C., Bi, Z., Jin, T., & Zhou, M. (2013). Electrogeneration of hydrogen peroxide for electro-Fenton system by oxygen reduction using chemically modified graphite felt cathode. *Separation and Purification Technology, 111*, 131-136.

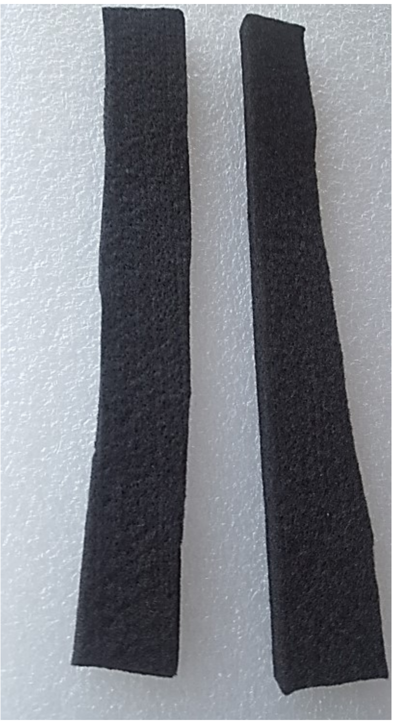
Zhu, D., Zhang, J., Song, J., Wang, H., Yu, Z., Shen, Y., & Xie, A. (2013). Efficient one-pot synthesis of hierarchical flower-like α-Fe2O3 hollow spheres with excellent adsorption performance for water treatment. *Applied Surface Science, 284*(C), 855-861. doi: 10.1016/j.apsusc.2013.08.022

Zornoza, R., Carmona, D., Acosta, J., Martínez-Martínez, S., Weiss, N., & Faz, Á. (2012). The Effect of Former Mining Activities on Contamination Dynamics in Sediments, Surface Water and Vegetation in El Avenque Stream, SE Spain. *An International Journal of Environmental Pollution, 223*(2), 519-532. doi: 10.1007/s11270-011-0879-5

Appendix A: Filtration System for the pretreatment of raw wastewater.

Appendix B: Solid phase extraction (SPE) for the pretreatment of wastewater.

Appendix C: Carbon/Graphite felt electrode used in the CFR.



Appendix D: Performing SPE of wastewater sample before Analysis.

Appendix E: Geotextile tube (a filtration system) for wastewater dewatering.

Appendix F: Processing the electrolyte via blending at the BH site.

Appendix G: Scaled-up CFR for field application at the BH site.