PHOTOCHEMICAL DEGRADATION OF ORGANIC POLLUTANTS IN WASTEWATERS

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Declaration form

DECLARATION

I hereby, declare that this manuscript, entitled “*Photochemical degradation of organic pollutants in wastewaters”,* is the result of my own work except for quotations and citations which have been duly acknowledged.
I also declare that, to the best of my knowledge and belief, it has not been previously or concurrently submitted, in whole or in part, for any other degree or diploma at Nazarbayev University or any other national or international institution.

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Abstract

In the present work, the photochemical treatment of a synthetic wastewater in a batch recycle photochemical reactor using ultraviolet irradiation (254 nm, 6 W), hydrogen peroxide and ferric ions was studied. The wastewater was composed of peptone, lab lemco, glucose, ammonia hydrogen carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate and had initial total carbon 1080 mg L^{-1}. Its volume was 250 mL, and the active (irradiated) volume in the annular photoreactor was 55.8 mL. The effect of initial total carbon, initial hydrogen peroxide amount, and Fe(III) added, on total carbon removal was studied aiming at optimizing operating parameters. Each experiment lasted 120 min, and the process was attended via pH, total carbon and HPLC analysis (for determination of phenolic compounds conversion). The results obtained showed that the addition of Fe(III) markedly increased the mineralization of the wastewater, especially during the first 60 min. Specifically, for initial carbon concentration 528 mg L^{-1}, hydrogen peroxide 2664 mg L^{-1}, without any Fe(III) added, the total carbon removal achieved after two hours was 50%, whereas after adding 240 mg L^{-1} Fe(III) the total carbon removal observed was 87%. The difference was even more pronounced during the first 60 min since the total carbon removal was increased from 19% in the absence of Fe(III) to 79% in the presence of 240 mg L^{-1} Fe(III). The effect of phenol presence (0-100 mg L^{-1}) on total

carbon removal was also examined. In all experiments, complete removal of phenol was observed, whereas TC removal was around 75%. The results obtained were applied for the treatment of real wastewater (landfill leachate) with initial carbon concentration 2650 mg L^{-1}, and pH 8.3. It was observed that pH adjustment markedly increased the percentage of carbon removal. With pH adjustment from 8 to 5 the results for total carbon removal improved from 3% (using only 13320 mg L^{-1} H_2O_2) to 75% after pH adjustment with HCl (using 13320 mg L^{-1} H_2O_2, 400 mg L^{-1} Fe(III)).

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List of Abbreviations & Symbols

AOP	Advanced Oxidation Processes
WW	Wastewater
WWT	Wastewater treatment
WWTP	Wastewater treatment plant
MWW	Municipal wastewater
TC	Total carbon
TIC	Total inorganic carbon
TOC	Total organic carbon
TN	Total nitrogen
NDIR	Non-dispersive infrared absorption detector
CLD	Chemiluminescence detector
ChD	Electrochemical detector
HPLC	High-performance liquid chromatography
MCT	Multicolumn thermostat
DAD	Diode array detectors
MBR	Membrane bioreactor
RO	Reverse osmosis
PCO	Photocatalytic oxidation
SS	Suspended solids
UV	Ultraviolet light
ppm	Parts per million
ppb	Parts per billion
PCO	Photocatalytic oxidation
AC	Activated Carbon
LCMS	Liquid chromatography mass spectroscopy

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Chapter 1 - Introduction

1.1 An overview of master thesis topic

Among environmental problems, water related issues have the highest impact on people’s everyday life. The water problems come from the wrong water management and pollution. These problems lead to the water scarcity. However, it should be noted, that the problem of water scarcity is not associated with insufficiency of resources to fulfill people’s needs; it relates to imprudent water use regarding pollution. In addition, sending the discharge of untreated wastewater into water bodies is another problem associated with water management, which contributes to the ecological issues. One of the strategies to manage previously mentioned issues is to introduce the sophisticated wastewater treatment (WWT) technologies. Installation of such equipment can help to decrease the water demand for industrial or agricultural purposes because the high-quality effluent from the wastewater treatment plants (WWTP) could replace the use of fresh water, by merely recycling the treated water back to the process. WWT is a procedure that recovers utilized water stream by removing chemicals, bacteria, and other contaminants before it is recycled back into the process or discharged to the environment.

A lot of research has been devoted to study and enhance the wastewater remediation techniques. One of the recent and most effective methods to treat contaminated water is to apply Advanced Oxidation Processes (AOPs).

AOPs are classified as useful methods used for degradation of toxic organic compounds [1]. The processes are classified as “AOPs” when hydroxyl radicals (•OH) are formed and used for oxidation of organic pollutants. Hydrogen peroxide (H_2O_2) can play the role of a source for hydroxyl radicals after being irradiated with ultraviolet (UV) light.

1.2 Aims & Objectives

The primary research objective is to study the degradation of organic pollutants in synthetic wastewater using photochemical treatment with hydrogen peroxide with and without ferric ions. The overall conversion of organic wastes during the experiments will be identified based on the percentage of carbon removal. Moreover, as a part of this thesis, the addition of phenol to the initial synthetic solution will be studied. The efficiency of the conducted experiments will be identified by the concentration of phenol in the provided samples. Furthermore, the obtained results from synthetic wastewater will be examined on a real wastewater, which is a landfill leachate.

This thesis aims to test different sets of experiments based on the objective mentioned above and to identify the best scenario for degradation of organic pollutants in WW for each set of experiments.

1.3 Thesis structure

The current thesis is structured into five chapters. The first one is an introduction. The first section is focused on providing general information of the research problem, describing the primary objectives of the thesis, and presenting the overall structure of the following chapters given in this master thesis.

The second chapter is dedicated to a literature review. This section presents the necessary background on different wastewater technologies used and covers the conducted research published in the area of Advanced Oxidation Processes.

Chapter 3 follows with the methodology of conducted experiments. This chapter includes the explanation of the initial wastewater composition, reagents used, and how the experiments were performed. Moreover, comprehensive description of the equipment used for analysis is described.

The next section focuses on the obtained results and their discussion. Depending on the type of experiment conducted, a different set of results are presented. There are mainly three sets of experiments that are analyzed. The first one is the set of tests performed with synthetic wastewater. The results of these experiments are analyzed based on the TC analysis, which shows the percentage of carbon removal. The second set of experiments is focused on synthetic WW with different initial concentrations of phenol addition. These results are analyzed for TC removal, as well as at HPLC equipment for phenol removal. The third set of experiments is based on the real wastewater – leachate solution. The obtained results will identify not only the TC removal but also the concentration of TIC as well as TN.

Finally, the fifth chapter is dedicated to the conclusion of the work presented in this thesis. The possible recommendations and future work are stated in this section.

Chapter 2 - Literature review

2.1 Conventional treatment methods

Each year there is a significant amount of organic pollutants that are being produced in large volumes of wastewater by various processes, such as chemical plants, oil refining, and those produced in our everyday lives [2]. This statement raises the concern about organic pollutants that might bring the hazards to people's health as well as to the environment. Thus, the focus of this literature review will be given to a detailed analysis of several water remediation techniques considered in industry, providing their advantages and possible limitations.

A general scheme of wastewater remediation for any process consists of primary, secondary and tertiary steps [3]. The primary treatment is mostly associated with sedimentation and coagulation processes. During the sedimentation, suspended solids are physically removed by gravity, density, and buoyancy. According to David [4], to accelerate the process of settling, the special chemicals, known as coagulants, are used. The use of coagulants helps to aggregate the particles; thus, they are removed together [4].

The secondary treatment includes the processes used to remove the dissolved organic matter from the coming flow that primary treatment technique could not capture [5]. A variety of different biological treatment techniques in combination with secondary sedimentation unit can be used to remove the pollutants from the mixture [3]. For the biological treatment part, such processes as the flotation, filtration, chemical reaction processes, or membrane bioreactor (MBR) can be used [3].

Finally, there is a tertiary treatment step that is needed to decrease the concentration of dissolved organic and inorganic matter by implementing one of the following processes: reverse osmosis, evaporation, adsorption by activated carbon [3]. Generally, the tertiary treatment step, which can bring the effluent quality to 99%, is optional because this step can be costly [6]. Therefore, this step is performed if only the process, where the treated water is recycled, has a particular specification of high discharge quality standards that must be maintained. In addition, in case of MWW plats, this step is vital only if water should have the quality to be further used for drinking purposes. Thus, in the case when water is used for the industrial and agricultural processes, this step can be simplified to simple disinfection process. Several authors observed that the use of combined chlorine for disinfection purposes is the most common and cheapest way to treat the effluent fully [7, 8].

Secondary treatment is an essential step in water recovery because it helps to remove approximately from 80 to 90% of all pollutants [9]. However, conventional treatment methods might be inefficient for complete removal of hazardous organic matter [10, 11]. For that reason, there is a need for detailed analysis of different technologies that could be applied to the secondary treatment step.

2.2 Advanced Oxidation Process

The problem with a conventional scheme of wastewater treatment rises if the influent to the wastewater treatment plant is highly toxic, or it has resistant organic compounds [10-12]. In this case, the conventional way of wastewater remediation fails to address the problem adequately. In such cases, the proposal is to replace the biological treatment in the secondary step by one of the advanced oxidation processes (AOP) or to add this step to tertiary treatment. The general term of AOP presents the process, where the hydroxyl radicals are formed and used for degradation purposes of toxic organic compounds found in wastewater [13]. These radicals are highly reactive as well as they are non-selective for almost all electron-reach organic compounds, which makes them very efficient for the treatment processes [13]. The treatment process with hydroxyl radicals is based on the reaction (2.1).

$$R - H + \bullet OH \rightarrow H_2O + \bullet R \qquad (2.1)$$

A hydrogen atom from an organic compound (R – H) is taken away by the hydroxyl radical to form the organic radical (•R) and water [11]. This organic radical goes further through a set of reactions to create its products and by-products. Theoretically, it is possible to oxidize organic pollutants to water and carbon dioxide [14].

2.2.1 Classification of different methods of AOP

AOP is based on the hydroxyl radical formation with the help of oxidizers. Therefore, various oxidizing species and their relative oxidation power were analyzed in *Table 2.1*.

Table 2.1: Oxidation power of different oxidizers [15]

Oxidizer	**Oxidation power**
Chlorine	1.00
Hypochlorous acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged titanium dioxide, TiO_2^+	2.35

According to *Table 2.1*, the best results are obtained for the hydroxyl radical (•OH) and positively charged TiO_2 oxidizers. The working principle of •OH radicals is as follows: in the presence of oxygen source, the hydroxyl radical starts the series of complex reactions that initiates the organic compound mineralization [16]. It was observed that by applying AOP technologies, it is possible to reduce the concentration of toxic organic compounds to the value that varies approximately from several hundred ppm to less than 5 ppb [16].

There are numerous methods available to form hydroxyl radicals. These methods are classified as non-photochemical and photochemical technologies [16]. There are three most common methods, which are used as non-photochemical processes: ozonation at elevated pH level (higher than 8.5), a combination of ozone with hydrogen peroxide (O_3/H_2O_2) as well as the Fenton system, which uses the combination of hydrogen peroxide with Fe^{2+} ions (H_2O_2/Fe^{2+}) [16]. With the development in the field of advanced oxidation processes, it was observed that non-photochemical technologies do not achieve a complete oxidation of organic compounds into water and carbon dioxide [17]. Moreover, these methods can form undesired intermediate products that could be even more toxic than the compounds from the influent stream [16]. For these reasons, scientists developed a new branch of AOPs, known as photochemical treatment technologies that are based on the use of UV radiation [16]. There are five most common methods, which are used as photochemical processes: a combination of ozone with UV radiation (O_3/UV), a combination of hydrogen peroxide with UV radiation (H_2O_2/UV), a combination of ozone with hydrogen peroxide and UV radiation (O_3/H_2O_2/UV), the photo-Fenton system as well as a photocatalytic process based on the combination of titanium dioxide with UV radiation (TiO_2/UV) [15].

2.2.2 Photochemical treatment by UV/O_3

The driven force for any of the introduced treatment methods is the chemical reactions that occur during the process. Thus, it is necessary to discuss the nature of the chemicals that are used and the reaction that will proceed with the experiments.

This method presents the modification for the simple ozone treatment. The advantage of this treatment technique is that the use of UV light helps to avoid the formation of dangerous undesired products [16]. The suitable wavelength for the ozonation process is 254 nm [16].

$$O_3 + hv \rightarrow O_2 + O(^1D) \tag{2.2}$$

$$O(^1D) + H_2O \rightarrow H_2O_2 \rightarrow 2°OH \tag{2.3}$$

During this process, the ozone under the UV radiation forms the intermediate product, hydrogen peroxide, which is then decomposed into hydroxyl radicals.

However, wastewater treatment by ozone and UV light is energy and cost-intensive [18]. Moreover, bromate, that affects the absorption of UV radiation can be formed as a by-product of ozone reaction under UV light [18].

2.2.3 Photochemical treatment by UV/TiO_2

This method is more commonly known as photocatalytic oxidation (PCO) [16]. During this process, there is a reaction happening between media and solid semiconductor (in this case it is TiO_2) under the UV radiation. The working principle of TiO_2 under the UV-light is taking place based on the following reactions (2.4) – (2.7). First, negative electrons (e^-) in the conduction band and positive holes (hv^+) in the valence band are produced.

$$TiO_2 \overset{hv}{\rightarrow} e_{cb}^- + hv_{vb}^+ \tag{2.4}$$

Then, these electrons and holes undergo further reactions on the surface of titanium dioxide to form hydroxyl radical [19].

$$hv_{vb}^{+} + OH^{-}(surface) \rightarrow \bullet\, OH \tag{2.5}$$

$$hv_{vb}^{+} + H_2O(absorbed) \rightarrow \bullet\, OH + H^{+} \tag{2.6}$$

$$e_{cb}^{-} + O_2(absorbed) \rightarrow O_2^{\bullet -} \tag{2.7}$$

Based on the use of semiconductor and its properties, such as flat-band potential, surface state, it was concluded that the change in pH level of the process has the most dramatic effect on the process [16]. Weichgrebe [20] performed several experiments on two processes (treatment by H_2O_2/UV and combinational method of treatment by TiO_2/H_2O_2/UV) by varying the value of pH. The tests were conducted for pH of 3, 5, 7 and 11 [20]. The procedure of the experiments is the same as for all wastewater remediation techniques: the oxidant is fed to the process, and the resultant mixture is treated in the reactor under the UV light. The optimum result for these experiments corresponded to the case with pH of 3 [20].

2.2.4 Photochemical treatment by UV/H_2O_2

This method presents the modification for the simple hydrogen peroxide treatment. There is a considerable amount of experiments on this homogeneous photochemical treatment based on H_2O_2 working under UV light. The treatment principle of this method is based on the following chemical reactions:

$$H_2O_2 \leftrightarrow HO_2^{-} + H^{+} \tag{2.8}$$

$$HO_2^{-} \overset{hv}{\rightarrow} {}^{\circ}OH + O^{\circ -} \tag{2.9}$$

Placing H_2O_2 under the direct light of UV leads to the formation of HO_2^- anions that produce the desired hydroxyl radicals [16]. The overall reaction for this process is presented in the following form:

$$H_2O_2 \overset{hv}{\rightarrow} 2°OH \tag{2.10}$$

From reaction (2.7) it is seen that one molecule of hydrogen peroxide forms two •OH radicals.

Based on the study performed by Stasinakis [13], it was observed that higher the rate of formation for •OH radicals, the better the decomposition of the toxic organic matter is. As it can be found from the reaction (2.10), the rise of H_2O_2 initial concentration in the process will result in the increased formation rate for hydroxyl radical. However, there is a limit to the initial concentration of H_2O_2, as the excess amount of this chemical might favor the process towards the formation of hydroperoxyl radical, which is the undesired product of this method [13].

The effect of the change in the ratio between organic compounds present in the system and initial concentration of H_2O_2 was examined in the study performed by Dincer et al. [21]. Three experiments with different initial concentrations of organic matter in the wastewater (1050, 4200, and 21000 mg L^{-1}) were analyzed [21]. The initial concentration of H_2O_2 in all experiments remained the same (2100 mg L^{-1}) [21]. The results showed the 90% efficiency in the first experiment, 55% in the second, and 39% in the third. Thus, it was concluded that the optimum ratio of organic matter to H_2O_2 is 1:2, and that with an increase of organic compounds in the influent, the rate of their degradation decreases [21].

2.2.5 Photochemical treatment by Fenton "like" systems

This method is based on the H_2O_2/UV with the addition of Fe(III). Fenton reactions are the most straightforward method for •OH radical formation. It does not require special operation conditions (temperature or pressure), and reactions can happen even without UV light [22]. However, the mineralization rate of organic pollutants and reduction of Fe^{3+} to Fe^{2+} is strongly accelerated with a presence of UV light [19, 22].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \qquad (2.11)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \qquad (2.12)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (2.13)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \qquad (2.14)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2H^{+} \qquad (2.15)$$

$$Fe^{2+} + HO_2^{\bullet} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \qquad (2.16)$$

$$HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (2.17)$$

The photo-Fenton "like" process using Fe(III) is similar to photo-Fenton system (Fe(II)). The photo-Fenton process starts with reaction (2.11), whereas photo-Fenton “like” starts with reaction (2.12). Further, they undergo the same reactions. However, the initial rate of mineralization of organic matter with Fe(II) is much faster compared to a system with Fe(III)/H_2O_2 [11]. The reason might be due to higher reactivity of ferric ions towards hydrogen peroxide, and direct formation of H_2O_2 from Fe(II) by reaction [22]. The scavenging effect of Fenton reagents on hydroxyl radical is shown in reactions (2.13) and (2.14). A major drawback of this process is the formation of iron sludge [11, 19, 23]. This leads to the necessity of treatment from iron sludge and a further increase in operational cost.

There is a considerable amount of research that has been done on this treatment method. Neyens and Baeyens [24] studied the effect of oxidant concentration change. The experiment was conducted by the same procedure several times based on different H_2O_2 concentrations. It was observed that with an increase of initial oxidant concentration, there is a rise in degradation rate. However, there is a limitation that excess amount of H_2O_2 does not enhance the efficiency of the process. This might be explained by auto-decomposition of H_2O_2 in the presence oxygen and water [24]. Also, the relation between H_2O_2 concentration and temperature of the experiment at pH of 3 was studied. The results showed that at low temperatures (<40℃), there is a need for high oxidant concentrations; whereas for high temperatures (80-90℃), a minimum amount H_2O_2 was required [24].

From the abovementioned study, it can be noticed that the optimum value of pH is 3. Several other researchers conducted a study on the effect of pH level on the rate of degradation. Pignatello et al. [25] and Coelho et al. [26] performed the similar experiments on classical Fenton reagents varying the pH from 2 to 6. The optimum efficiency of the processes corresponded to pH 3, and pH 2.8 respectively [25, 26].

2.3 Landfill leachate

Despite the development of different technologies on solid waste management, the most widespread practice is to apply the sanitary landfilling [27]. When the waste deposits are received in the landfills, they start to undergo the aerobic and anaerobic microbial decomposition [27-29]. These biodegradation processes lead to the formation of leachate and biogas [29]. Landfill leachate is usually composed of nutrients, toxic organics, high level of total ammonium nitrogen and inorganic salts [28-30]. It is highly essential to treat the leachate solution because there is a concern about the negative impact that it is giving on people’s health and surrounding environment [26, 31]. Previous studies showed that landfill leachate contains organic compounds that are highly resistant to degradation by conventional treatment methods [27-29, 31].

Depending on the age of the leachate, it is divided into young and mature [19, 32-40]. It is much easier to treat the young leachate rather than the mature one. The young leachate is known to have a higher ratio of BOD_5/COD than the mature leachate. Therefore, young leachate solutions can be treated by biological methods [34]. Characterization of leachate is presented in *Table 2.2*.

Table 2.2: Characteristics of leachates as a function of landfill age

Parameter	Young	Mature	Reference
Age (years)	<1-2	>5-10	[41]
	<2	>10	[42]
	<2	>6.5	[43]
pH	4.5-7.5	7.5-9.0	[41]
	4.5-7.5	6.6-7.5	[42]
	5.8	8.0	[43]
	6.2	7.5	[44]
	5.6-7.3	7.9-8.1	[45]
	4.5-7.5	7.5-9.0	[46]
COD (mg L^{-1})	3000-60000	100-500	[41, 42]
	62000	3000	[43]
	23800	1160	[44]
	6610	1700	[45]
	6000-60000	500-4500	[46]
BOD_5/COD	0.6-1	0-0.3	[41]
	0.05-0.67	0.04-1	[42]
	0.39	0.05	[43]
	0.5	0.2	[44]
	0.24	0.09	[45]
COD/TOC	4.1	2.7	[45]
	3.3	1.2	[47]
	4.0	1.2	[48]

The leachate used during the experiments were collected from Municipal Solid Waste landfill of Astana city. This landfill can be considered as mature because it has been received for ten years.

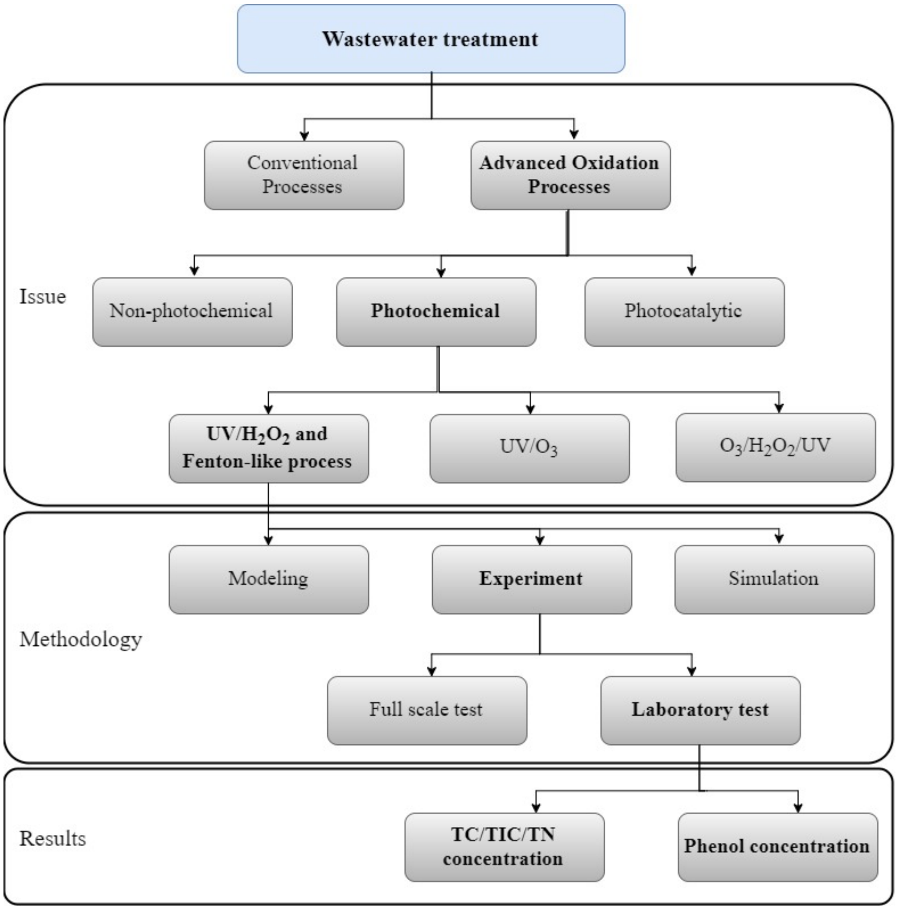
Chapter 3 - Materials and Methods

3.1Experimental targets

Based on the performed literature review, the lack of scientific knowledge in existing studies was identified. For instance, regarding the experiments with phenol, all previously conducted research was focused on the treatment of wastewater containing only phenol with no other pollutants. The current work is performed on the combination of synthetic wastewater and the phenol. Moreover, compared with already existing scientific knowledge on this topic, the work is extended by applying the results obtained from synthetic wastewater to treat the real landfill leachate. This could help to cover and enhance the knowledge on the threatment method more completely.

The scope of this work was to use the photochemical treatment process to mineralize synthetic and real wastewater. The main objective was to achieve the high percentage of removal efficiency regarding the organic carbon. The schematic representation of the scope of this thesis is depicted in *Figure 3.1* in the form of K-chart.

Figure 3.1: K-chart for the research



In total 31 experiments were conducted. Firstly, simple, direct photolysis using only UV light was tested. Secondly, the photochemical treatment based on hydrogen peroxide working under UV light was analyzed. The optimum concentration of initial TC and dosage of hydrogen peroxide was selected. This method was additionally checked for the effect of pH adjustment. Thirdly, enhancement of photochemical treatment with H_2O_2 and UV light was made by addition of ferric ions. Additionally, the treatment of synthetic wastewater was also examined for phenol removal. Finally, the photo-Fenton "like" process was tested with real wastewaters. For the real wastewater (leachate solution) the effect of pH change was identified.

3.2 Materials

Hydrogen peroxide solution (37.6% w/w) was used as a source of hydroxyl radicals, whereas iron (III) chloride anhydrous (Cl_3Fe, ≥97% w/w) was used as a source of ferric ions. H_2O_2 was purchased from SKAT-REACTIV company, whereas Fe(III) was received from FISHER-CHEMICAL.

For pH adjustment purposes two chemicals were used: hydrochloric acid (HCl, 37% w/w) and sodium hydroxide (NaOH, ≥97% w/w). When it was necessary to decrease pH of the solution, HCl solution was used. To increase the pH, NaOH purchased from FISHER-CHEMICAL was used.

During the TC/TIC/TN and HPLC analyses, the ultra-pure water generated from Direct-Q 3UV equipment was used for washing purposes inside the analyzer.

For the HPLC analyzer, acetonitrile (C_2H_3N) solution (99.8% w/w) in combination with ultra-pure water were used as carrier liquid phase through the equipment and for needle wash. Acetonitrile was purchased from SIGMA-ALDRICH.

3.3 Synthetic wastewater composition

The photochemical degradation of organic compounds was tested for two different types of wastewater: for synthetic and real (leachate) wastewater. Experiments were first conducted using synthetic wastewater, and then the results obtained were applied to actual leachate solution from the solid disposal area. The composition of the synthetic WW solution is provided in *Table 3.1*.

Table 3.1: Composition of synthetic wastewater with given characteristics

Compound	**Assay**	**Concentration [mg L^{-1}]**	**Molar weight [g/mol]**	**Total carbon [mg L^{-1}]**
D-Glucose anhydrous ($C_6H_{12}O_6$)	≥97.5%	1600	180	639.4
Bacterial peptone		480		
Lab Lemco		320		
Ammonia hydrogen carbonate (CH_5NO_3)	≥99%	160	79	24.3
Potassium hydrogen carbonate ($CHKO_3$)	≥99%	80	100	9.6
Sodium hydrogen carbonate ($CHNaO_3$)	≥99.7%	80	84	11.4

The synthetic solution is composed of D-Glucose anhydrous, bacterial peptone, lab lemco, ammonia hydrogen carbonate, potassium hydrogen carbonate and sodium hydrogen carbonate. All reagents, except lab lemco, were purchased from FISHER-CHEMICAL. Lab lemco was received from OXOID LTD. All chemicals were used without any further purification. For dilution purposes, only deionized water was used.

Theoretical total carbon was estimated as 684.7 mg L^{-1}, excluding the unknown compositions of bacterial peptone and lab lemco. The actual concentration of TC in the solution was 1080 mg L^{-1}. The rest 395.3 mg L^{-1} of total carbon should correspond to bacterial peptone and lab lemco. Bacterial peptone refers to the reagent that is made from an enzymatic digest of meat tissue, and it is used to increase the process of bacterial growth [49]. It is composed of casein peptone (27% w/w), yeast extract (13.5% w/w), sodium chloride (27% w/w) and agar (32.4% w/w). Since, peptone granules contain agar ($C_{14}H_{24}O_9$, MW 336 g mol^{-1}), it theoretically accounts for 77.8 mg L^{-1} of total carbon in the solution. Experimental analysis showed that peptone accounts for 134.23 mg L^{-1} of total carbon.

Lab lemco is a specially made meat extract that comes in a fine powder form. It is used in biological treatment step to accelerate the growth of bacteria [50]. Lab lemco is composed of total nitrogen (12.4% w/w), amino nitrogen (2.5% w/w) and chloride (1.1% w/w). Experimental analysis obtained that 197.93 mg L^{-1} of lab lemco is present in total carbon of the stock solution. Thus, peptone and lab lemco account for 332.16 mg L^{-1} of TC, which is close to the theoretical value of 395.3 mg L^{-1}.

3.4 Landfill leachate characterization

The leachate that was used for the experiments was collected on 25th of October 2017, from the municipal solid disposal area in Astana. The initial concentration of leachate solution had around 2750 mg L^{-1} of total initial carbon, among which approximately 1200 mg L^{-1} was coming from inorganic carbon. This results in the ratio of TIC to TC in the initial raw leachate solution as 44%. The initial pH of raw, real wastewater was around 8. This TIC composition correlates with observations by other authors, stating that the solution is highly concentrated with inorganic salts [24].

Additional experiments using the bio-treated leachate with initial TC concentration around 990 mg L^{-1}, with 32 mg L^{-1} being inorganic carbon, were conducted. Thus, the pretreatment of raw leachate lowered the ratio of inorganic carbon to total carbon in the leachate from 44 to 3%.

Firstly, the wastewater, which contains 250 mL of leachate and 150 mL of tap water, was pretreated for 17 hours for ammonia removal by air stripping at pH 12. The initial pH of the solution was 8.5. The concentrated solution of potassium hydroxide (KOH) was used to increase the pH to the required value. Air stripping refers to the process, where a considerable amount of gas, most commonly air, passes through the solution to remove the undesired substances by carrying them away with the gas [51]. For biological treatment step, the leachate with mixed with activated sludge collected from “Astana Su Arnasy” wastewater treatment plant in Astana. The reactor with 600 mL solution was used (250 mL of leachate, 200 mL of activated sludge and 150 mL of tap water). With the addition of activated sludge to the reactor, 9 g L^{-1} of activated carbon (AC) and natural zeolite with the same concentration as AC were injected. Adsorption by activated carbon is usually used for the removal of organic carbon, whereas the zeolite is used to reduce the ammonium-N content in the solution [52]. Three different conditions of biological treatment method were tested: aerobic, anaerobic and the combination of both treatment conditions. When the experiment was conducted under aerobic biological treatment, the constant stirring and air supply by air pumps were applied. On the contrary, during the anaerobic mode of biological treatment, the reactor was sealed by parafilm and only left with constant mixing without any air supply. Biological treatment experiments were conducted with 24 hours of residence time. For this treatment step, pH was manually reduced to 7 by addition of concentrated HCl. The optimum combination of treatment mentioned above techniques resulted in 95% of ammonium removal, 96% of TIC conversion as well as 31% degradation of organic pollutants.

3.5 Reactor configuration

All experiments were conducted with apparatus illustrated in *Figure 3.2*. A reactor with 250 mL solution was operated in batch recycle mode, where wastewater was continuously pumped through the cylindrical vessel with an active volume of 55.8 mL. The ultraviolet light of 254 nm was produced from the ultraviolet lamp of

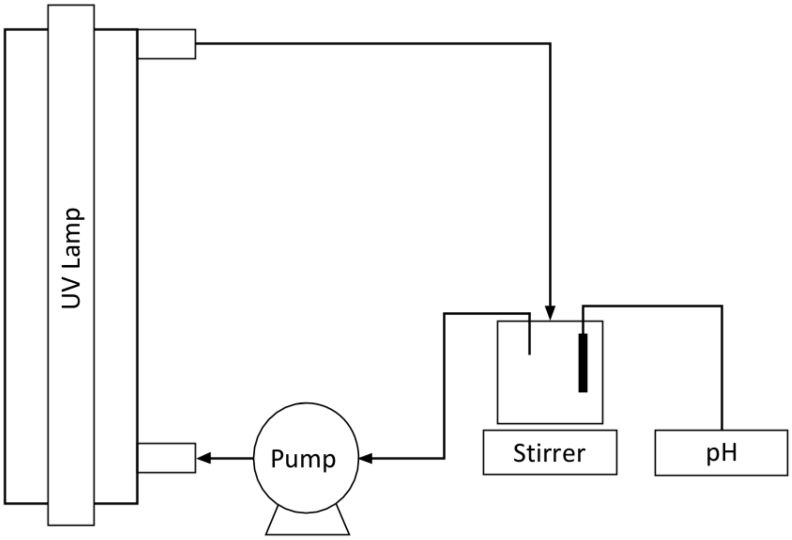
6 W placed inside the cylindrical vessel of the reactor. The Osram lamp specifications are given in *Table 3.2*.

Table 3.2: Osram PURITEC HNS G5 6W UV lamp specifications

Electrical data	
Nominal wattage [W]	6
Nominal voltage [V]	42
Construction voltage [V]	42
Nominal current [A]	0.16
Lamp current [A]	0.16
Photochemical date	
Radiated power 200…280 nm (UVC) [W]	1.7
Dimensions & weight	
Diameter [mm]	16
Length [mm]	212
Additional product data	
Base (standard designation)	G5
Capabilities	
Burning position	s180

A peristaltic Pump drive 5006 by Heidolph with a rate of 175 mL min^{-1} was used to circulate the wastewater solution continuously. A magnetic stirrer was used to constantly mix the part of the solution that was not directly irradiated by UV-lamp. Throughout the whole duration of each experiment, the pH was measured via pH electrode LE409 by Mettler Toledo. Each experiment lasted 120-150 minutes.

Figure 3.2: The experimental setup



For each experiment, several samples were taken at the specific point of time and sent for analysis: TC/TIC/TN measurements and HPLC (for determination of phenol in the solution).

3.6 Experimental procedure

Each experiment was performed using the 250 mL solution. The solution was prepared by diluting the initially prepared stock solution of synthetic wastewater with distilled water, and with the presence of hydrogen peroxide with/without ferric ions. The optimum initial concentration of total carbon was checked in the range of 136-1080 mg L^{-1}, while the concentration of H_2O_2 was kept constant at 2664 mg L^{-1}. An automated pipette 1000 µL by Vitlab was used.

The start of the experiment was considered immediately as the UV-lamp with the pump was turned on. All test samples were directly sent to analysis to avoid further reactions.

For the experiments that were focused on analyzing the presence of phenols in the solution in the range 0-100 mg L^{-1}, additional samples for HPLC analysis were collected. Samples were also immediately sent to analysis. Prior filtration with disposable syringe filters (Chromafil Xtra RC-20/25) with 0.20 µm pore size was applied. Those HPLC certified filters were purchased from Macherey-Nagel company.

3.7 Analytical equipment

3.7.1 Multi N/C 3100

The Multi N/C 3100 equipment (*Figure 3.3*) by Analytik Jena AG was used to derive the values for total carbon, total inorganic carbon as well as total nitrogen from the aqueous samples taken during the experiments. The apparatus is equipped with sample rack with up to 72 positions.

Figure 3.3: Multi N/C 3100 equipment [53]

The analysis is performed by thermocatalytic high-temperature oxidation in the presence of a special catalyst. The platinum catalyst is recommended for the use. Depending on the catalyst, digestion temperatures can go up to 950℃. The equipment takes 250 µL from the sample per each repetition. The injection is taken by syringe pump with the 2-port valve. The sample is directly transferred to a combustion furnace. A combustion is taking place in a furnace with tube (reactor) made from quartz glass. The combustion tube is filled with catalyst and auxiliary material. Oxygen was used as an oxidation agent and carrier gas. At this zone of the equipment, the pyrolysis and oxidation of the injected sample were performed. The process is presented in reactions (3.1) – (3.3), where symbol R represents a carbonic substance.

$$R + O_2 \rightarrow CO_2 + H_2O \tag{3.1}$$

$$R - N + O_2 \rightarrow NO + CO_2 + H_2O \tag{3.2}$$

$$R - Cl + O_2 \rightarrow HCl + CO_2 + H_2O \tag{3.3}$$

Then the flow is transferred to the condensation coil, where measuring gas is being cooled. As condensed water is separated, it goes to the TIC condensation vessel. As this step, corrosive acting gases are removed, and CO_2 is added to the NDIR (non-dispersive infrared absorption detector) detector. The concentration of total carbon is detected during the combustion step, by measuring generated CO_2 amount. Inorganic carbon is measured by placing the sample into the acidic TIC reactor. The CO_2 is purged and thus the concentration of TIC is measured. In parallel to carbon measurements, it is also possible to detect the concentration of total nitrogen in the samples. During the combustion, nitrogen oxides are produced, that can be further detected by CLD (chemiluminescence detector) or ChD (electrochemical detector).

The results are obtained by apparatus performing two repetitions of the measurement. The results are retrieved as an average value from those two measurements.

The analysis that equipment performed was based on the following calibration curves. Each method had its own calibration curve. TC calibration curve (*Figure 3.4*) was set for samples from 5 to 500 mg L^{-1}. TIC calibration curve (*Figure 3.5*) was done for the range from 5 to 25 mg L^{-1}. TN calibration curve (*Figure 3.6*) was created for the range from 10 to 50 mg L^{-1}.

Figure 3.4: TC calibration curve for Multi N/C 3100 equipment

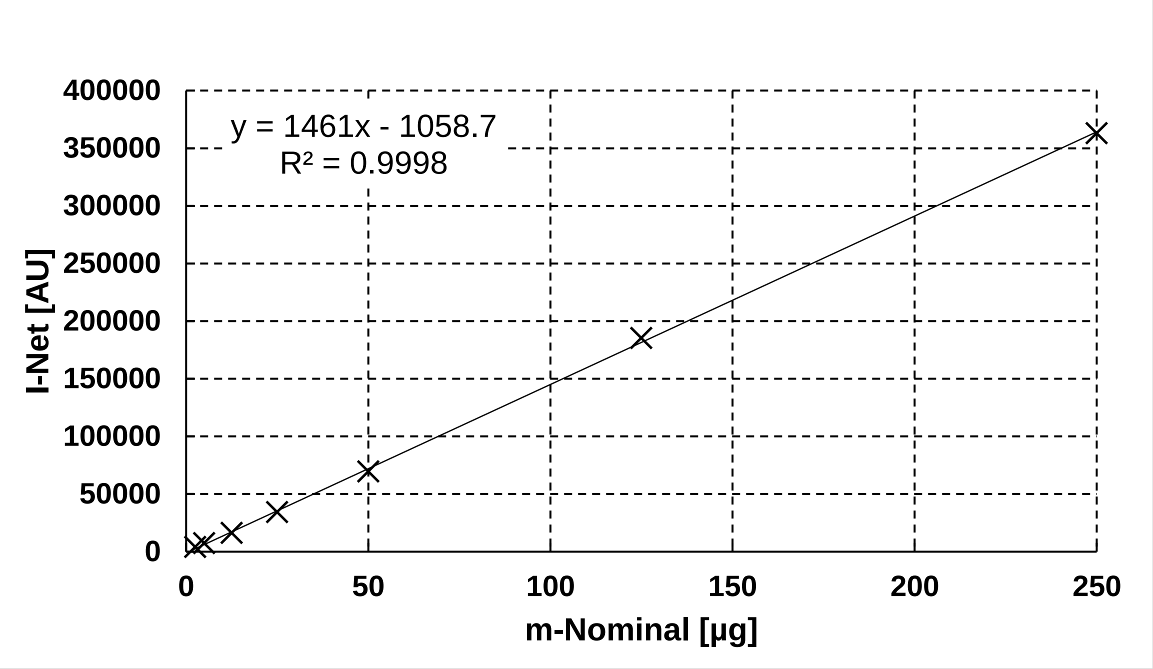


Figure 3.5: TIC calibration curve for Multi N/C 3100 equipment

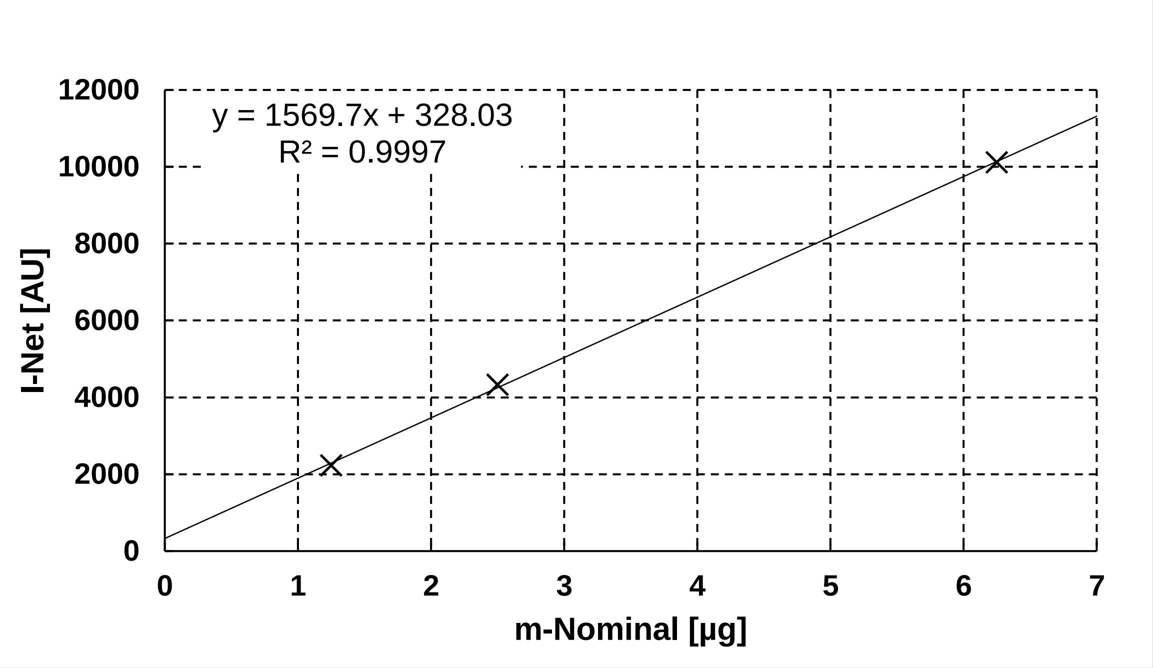
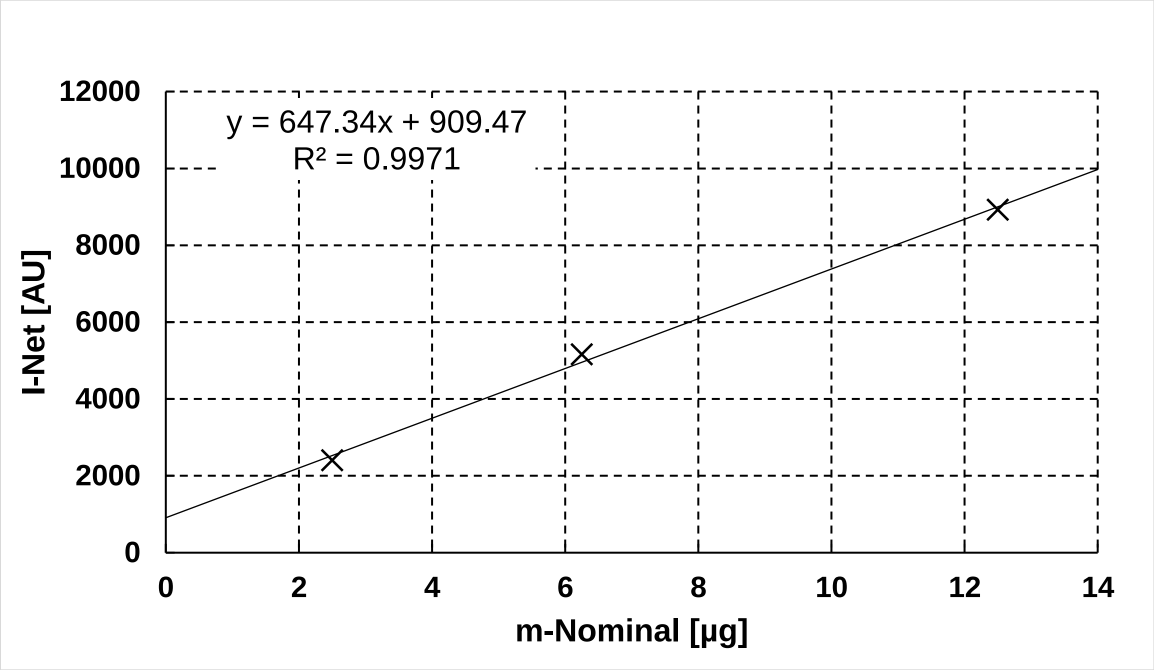


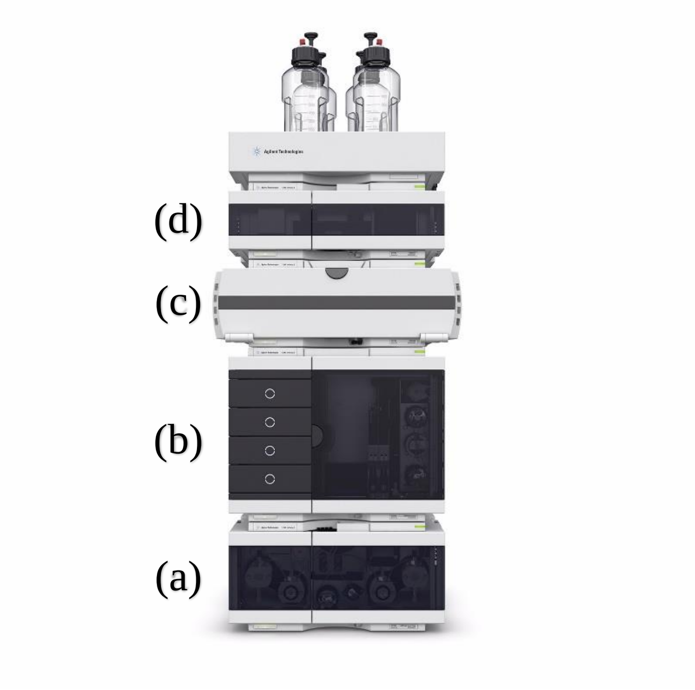
Figure 3.6: TN calibration curve for Multi N/C 3100 equipment



3.7.2 HPLC Infinity II

The HPLC analyzer 1290 Infinity II by Agilent Technologies was used to identify the presence of phenols from the samples provided throughout the experiment. This equipment is presented in *Figure 3.7*, and it consists of four vital parts [54].

Figure 3.7: HPLC equipment (a) high speed pump (b) multisampler (c) multicolumn thermostat (d) diode array detector



The first part of the analyzer is a high-speed pump (G7120A). This section is designed with a dual pump head (A & B). Each pump head is attached to two solvents located at the top of whole HPLC configuration. Before the start of the analysis, the two required channels (A1/A2 and B1/B2) are specified. Each pump head is operated by two independent pistons working in series. The process begins with a movement of a piston two, as it drives the solvent to the flow path. The speed of the piston determines the flow rate for the process (settable flow range: 0.001-5 mL min^{-1} with 0.001 mL min^{-1} increments). At the same time, piston one retrieves the solvent from its bottle, closes the piston chamber and compresses the solvent to operating pressure of the equipment (up to 1300 bar at rate 0-2 mL min^{-1}, up to 800 bar at 5 mL min^{-1}).

As the piston one starts to deliver the solvent to the flow path, piston two reverses the direction and re-fills its chamber. Thus, the solvent delivery cycle starts over [55].

The second part of the equipment is multisampler (G7167B). The system can analyze samples introduces in any of the following: vials or microtiter plates. The drawers can hold inside up to 6144 vial samples, or 16 microtiter plates. All internal movement of the samples and plates are performed automatically by a Cartesian robot. It uses X-Y-Z drive for taking and placing the module drawers, as well as to handle the needle movement inside the equipment. Before each sample analysis, the injection needle is washed with a solution of 50% (w/w) ultra-pure water and 50% (w/w) acetonitrile. Washing of the needle reduces the carryover between the runs to less than 9 ppm. The standard needle injection configuration from the samples can be set up from 0.1 µL to 20 µL in 0.1 µL increments. The equipment for this research is taking 5 µL from each sample for analysis. During the injection, the sample is retrieved from the vial and sent through the multisampler unit to the column. However, if the sample is not being taken, the valve unit bypasses the multisampler and connects the pump directly with column [56].

The third part is the multicolumn thermostat (MCT G7116B). Single MCT can contain up to eight columns of 100 mm length. It has two separate temperature zones that are capable of cooling to 20 degrees below ambient temperature and heating up to 110℃ (with 0.05℃ temperature precision). As solvent with injected sample flows to this section of HPLC equipment, it initially being preheated or cooled to specified temperature before entering the column. As equilibrium is reached, mobile phase enters the column inlet and goes through the stationary phase. A special packing material can separate the mobile phase into different compound bands [57].

The fourth part of the equipment is diode array detectors (DAD G7117B). This detector can work with sampling rates up to 240 Hz to perform the spectral detection. The UV-lamp is used as an optical system of the detector. It can emit the light with the wavelength range 190-800 nm. The UV light is focused on the entrance of a flow cell cartridge by a lamp mirror. The light leaves the flow cell from the other side and is being focused by the second mirror through the slit assemble to the grating, where the light is being dispersed on the diode array. This equipment allows identifying the wavelength in the range 190-640 nm [58].

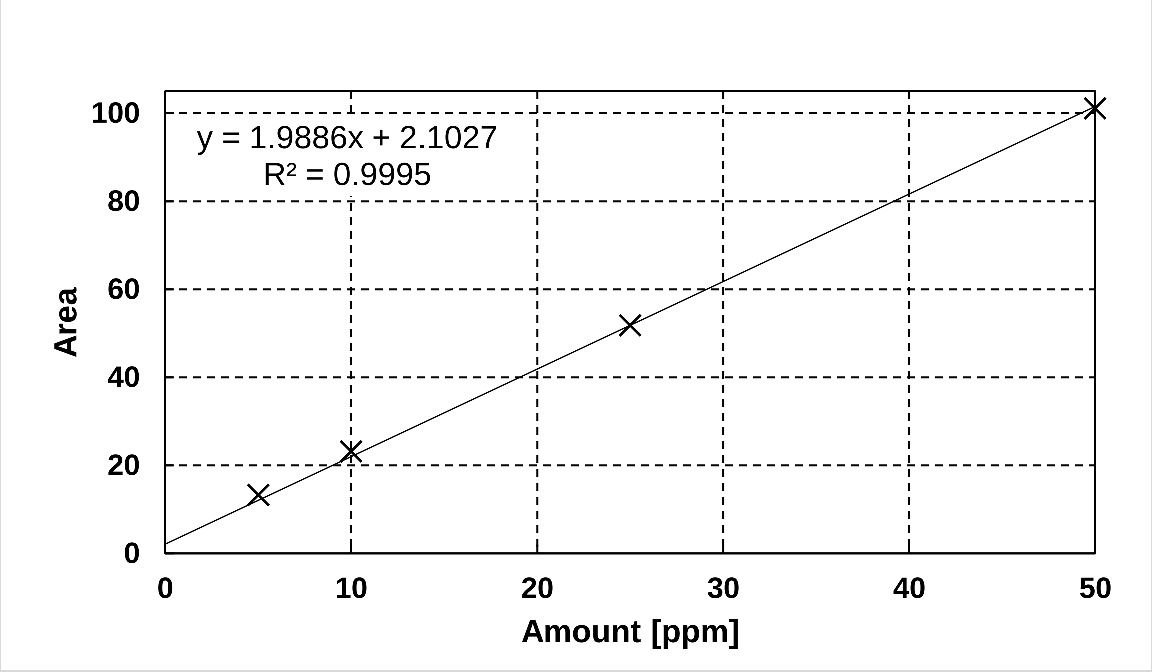
Combining all the parts of equipment, here is the working principle of high-performance liquid chromatographer:

1. As the pump starts delivering solvent with specific flow rate and using it as a mobile phase for the whole equipment, the process is initiated.
2. The autosampler is used to inject the sample and introduce it to the mobile phase.

3. The sample is carried to the column, where it goes through the stationary phase with a special packing material. During this step, the mobile phase is separated into different compound bands.
4. The detector is used to analyze and identify the compound bands. As compound is detected, the data signal is sent to a computer for data collection.
5. Finally, the mobile phase leaves the system as a waste.

Before the start of phenol measurements in the samples, an appropriate calibration curve of phenol in water was created. A calibration curve was set from 5 to 50 ppm of phenol.

Figure 3.8: Calibration curve of phenol in water for HPLC

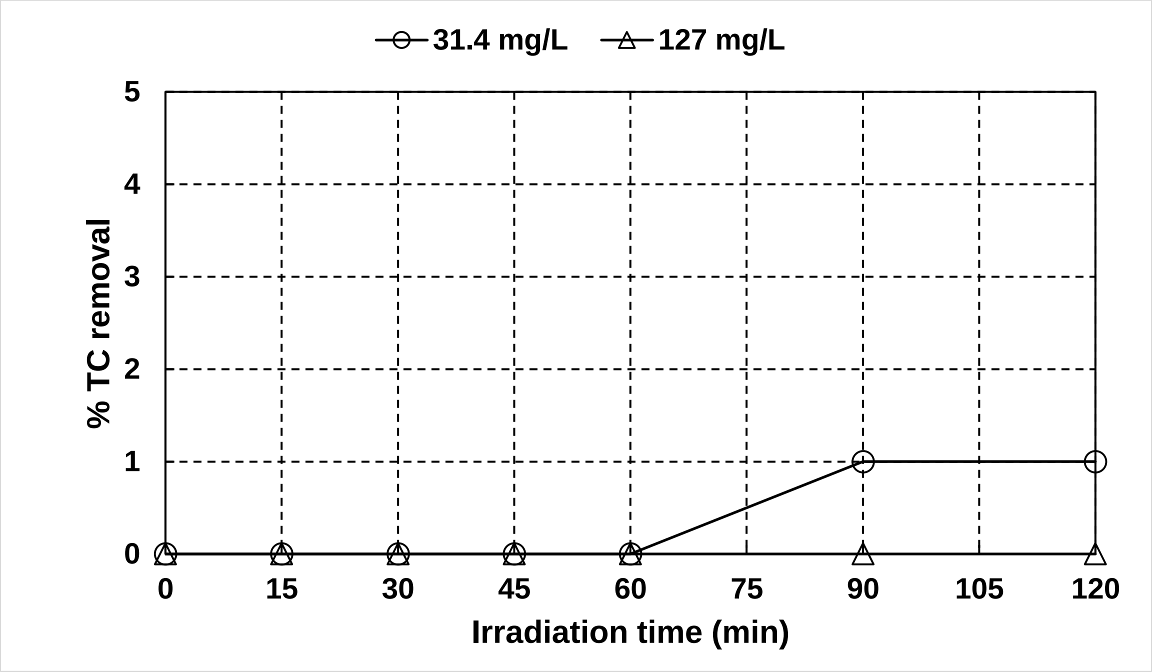


Chapter 4 - Results and Discussion

4.1Direct photolysis using UV light

Firstly, the direct effect of UV light on the treatment process was examined. The initial concentration of total carbon was around 127 mg L^{-1}. The results obtained are depicted in *Figure 4.1.* After two hours of treatment with direct photolysis, the results showed 0% conversion for TC removal. The same process was checked for the smaller concentration of initial TC of the solution (31.4 mg L^{-1}) as well. However, the results showed only 1% TC conversion after two hours of the experiment. Results of these experiments showed that components of the initial stock solution are resistant to UV-light.

Figure 4.1: Efficiency of direct photolysis on treatment of synthetic solution



The same trend was observed in other studies [59, 60]. Therefore, it is essential to modify this process to achieve the removal of total carbon from the solution. Degradation of organic pollutants can be made by AOPs, where the use of specific chemicals will follow the oxidation route focused directly on the elimination of non-degradable and biologically harmful substances [60].

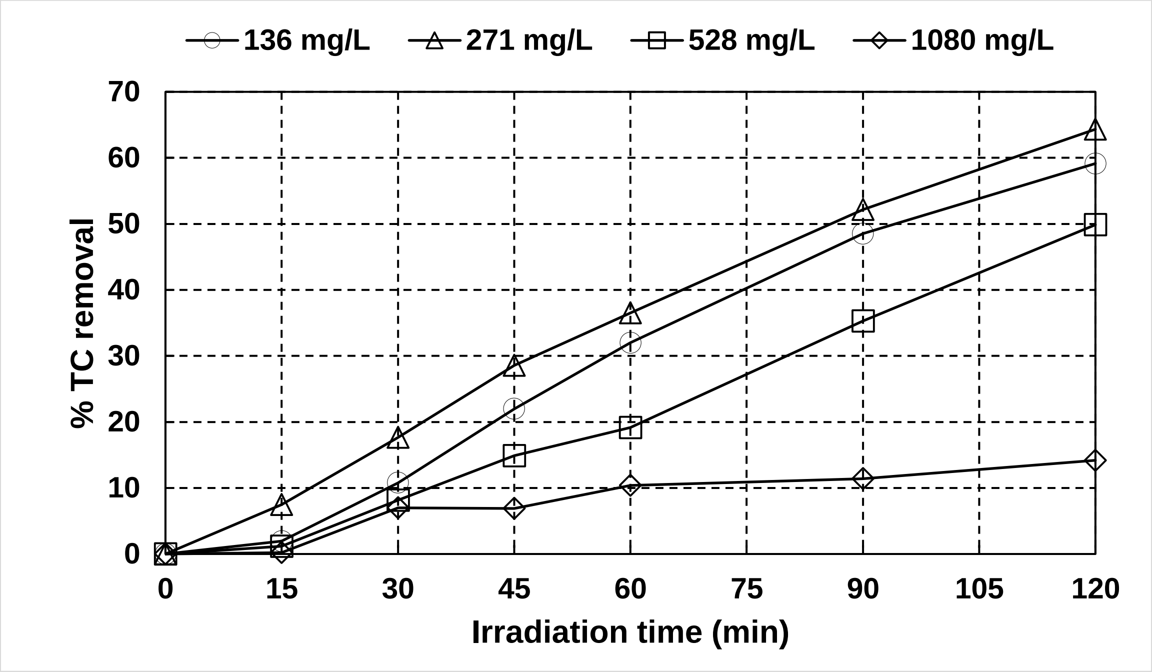
The effect of direct photolysis was not examined on wastewater containing only phenol. However, based on the literature, it is possible to degrade 11% of initial 0.1 mM (9.4 ppm) phenol using one 6W UV light (λ_{max}=352 nm) for three hours [61]. Nevertheless, the decrease in TOC values was less than 3% was observed as phenolic intermediate compounds might be formed. Another author [62] conducted an experiment with 100 ppm of phenol. The treatment process was examined with three 15W mercury lamps (λ_{max}=365 nm) as a UV light source. Results obtained 20% of phenol oxidation in two hours, and 36% in four hours. However, no significant TOC removal was achieved.

4.2 Photochemical treatment using H_2O_2 and UV light

4.2.1 Effect of initial TC

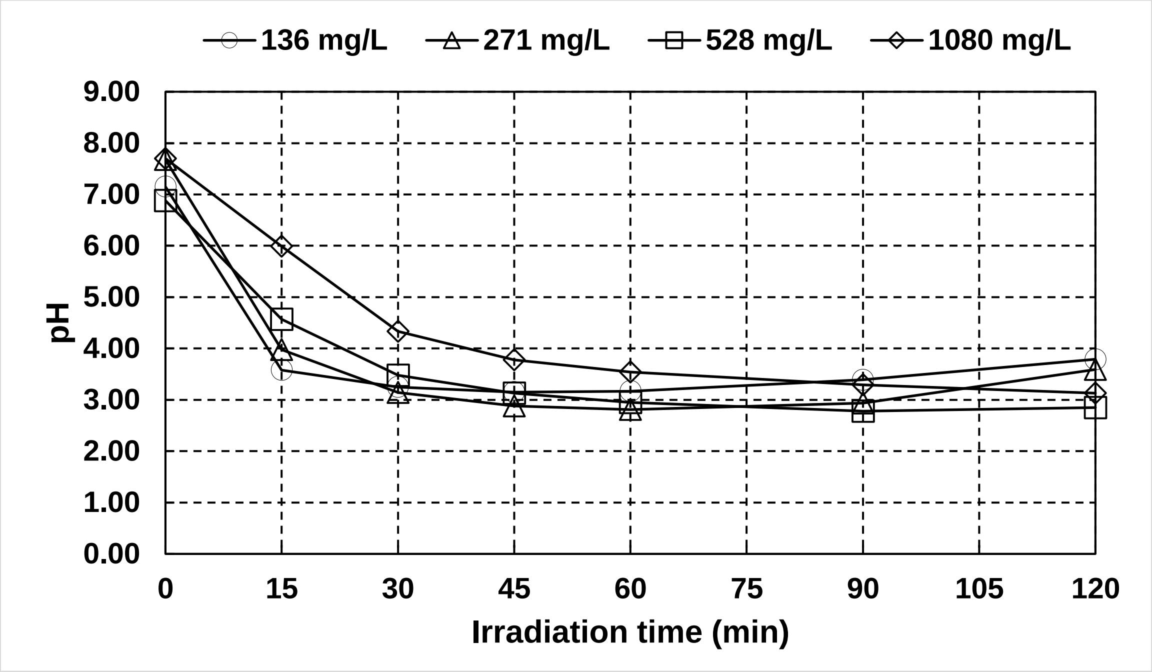
Secondly, the degradation of total carbon in synthetic wastewater under UV light in the presence of H_2O_2 was studied. The initial concentration of compounds plays a significant role in the effectiveness of the degradation process. To obtain the optimal values, the initial concentration of TC was first varied, keeping constant the initial concentration of hydrogen peroxide (2664 mg L^{-1} or 78 mmol L^{-1}). It was observed that with an initial concentration of 136 and 271 mg L^{-1} TC, around 60% conversion was achieved directly (*Figure 4.2*).

Figure 4.2: Effect of initial [TC]$_o$ in terms of conversion with constant H_2O_2 (2664 mg L^{-1})



When initial TC was increased to 528 mg L^{-1}, the TC conversion was observed as 50%. A further increase in TC to 1080 mg L^{-1}, the conversion achieved was of no practical use, showing only 14% of total carbon removal. As a result of these observations, 528 mg L^{-1} was used as initial TC concentration for next experiments. Moreover, it is essential to emphasize the consistency of pH readings throughout all tests. Observations are illustrated in *Figure 4.3*.

Figure 4.3: Effect of initial $[TC]_o$ in terms of pH with constant H_2O_2 (2664 mg L^{-1})



It can be noted that all experiments start approximately at pH 7. Then, pH values begin to drop, implying that organic compounds degrade to organic acids, which in turn are decomposed to carbon dioxide. At the last step, pH is expected to increase, as CO_2 leaves the solution. According to the results obtained, the same behavior in pH values was observed.

Hydrogen peroxide under UV light irradiation decomposes to highly reactive •OH radicals, which then react with organic compounds leading to the degradation of total carbon in solution.

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \quad (4.1)$$

$$HO_2^- \overset{hv}{\rightarrow} {}^\circ OH + O^{\circ -} \quad (4.2)$$

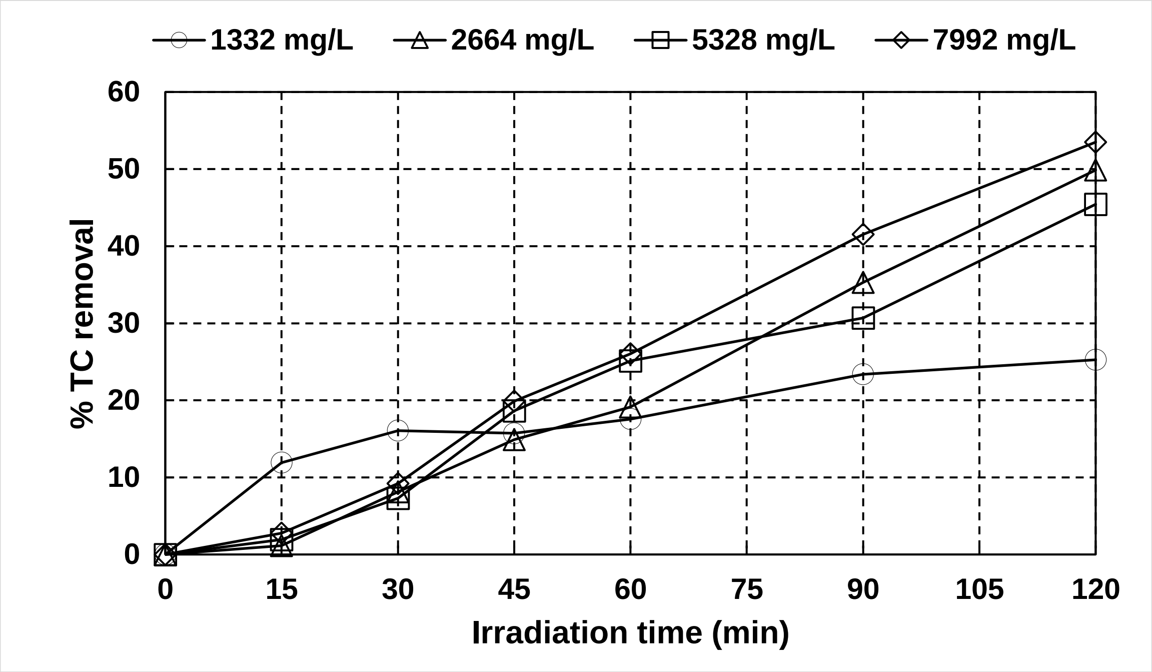
$$H_2O_2 \overset{hv}{\rightarrow} 2°OH \qquad (4.3)$$

During the first step of these reactions, the hydrogen peroxide breaks down into two ions (HO_2^- anion and H^+ cation). HO_2^- anion under the direct UV light leads to the desired formation of hydroxyl radicals [16]. The process behind this experiment can also be expressed in terms of overall reaction (4.3), which shows that two hydroxyl radicals are formed from using one molecule of hydrogen peroxide. Previous studies showed that higher formation rates of hydroxyl radicals result in more efficient decomposition of total carbon [13]. However, it has its limitation as an excessive amount causes generation of hydroperoxyl radicals, which decrease the effectiveness of the degradation process [13].

4.2.2 Effect of initial H_2O_2

The next step was to evaluate the optimum amount of H_2O_2 keeping constant the initial total carbon concentration. Specifically, the experiments were conducted for 1332, 2664, 5328 and 7992 mg L^{-1} of hydrogen peroxide, and the mean TC value was kept at 528 mg L^{-1}. The results obtained are shown in *Figure 4.4*.

Figure 4.4: Effect of H_2O_2 in terms of conversion for constant initial TC (528 mg L^{-1})



When 1332 mg L^{-1} of hydrogen peroxide was used, resulting in 25% TC conversion, too low to be of any practical use. The increase in the concentration of initial H_2O_2 to 2664 mg L^{-1}, doubled the removal efficiency. Further increase in hydrogen peroxide dosage, achieved almost similar conversions as for 2664 mg L^{-1} of H_2O_2. Thus, considering that concentrations of 2664, 5326 and 7992 mg L^{-1} of hydrogen peroxide obtained close results in mineralization of organic compounds from wastewater, it was more practical to use 2664 mg L^{-1} as an optimum concentration of hydrogen peroxide for next experiments.

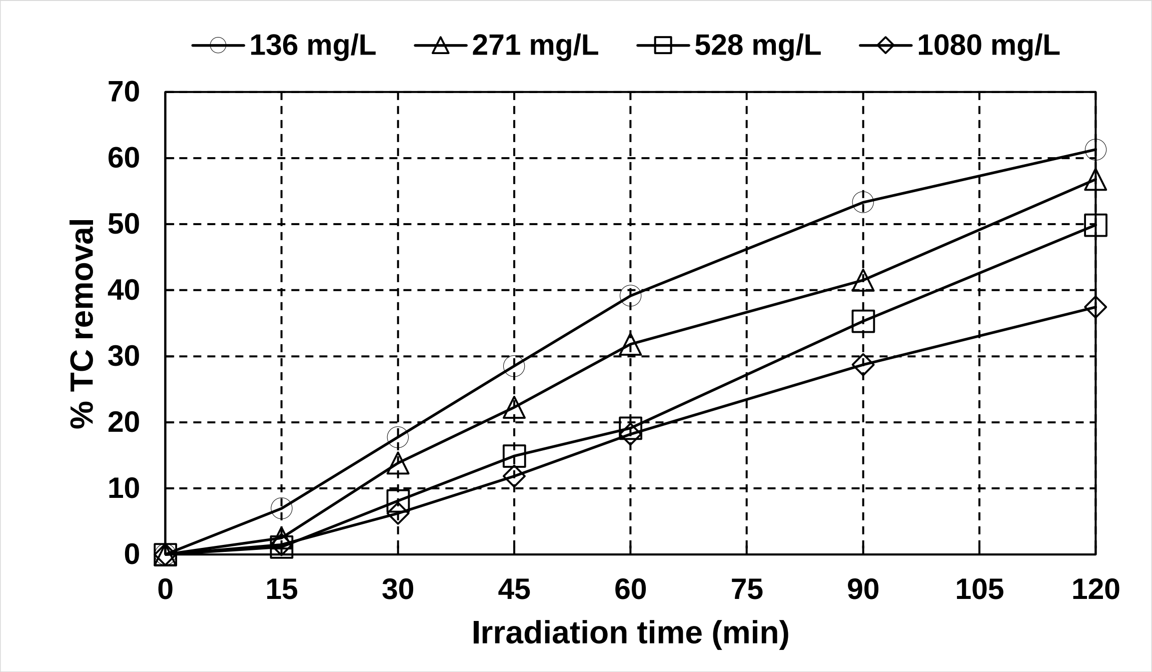
Moreover, as it was observed by other researchers, an excess amount of hydrogen peroxide can result in scavenging effect of H_2O_2 on hydroxyl radicals [19, 59]. This results in a decline of treatment efficiency. The scavenging effect is presented in reaction (4.4).

$$H_2O_2 + 2HO^{\bullet} \rightarrow H_2O + \frac{3}{2}O_2 + H_2 \tag{4.4}$$

On the contrary, insufficient H_2O_2 dosage results in a decrease of treatment efficiency, as there is less amount of hydroxyl radicals being produced [63]. This could be the reason behind the low conversion value with 1332 mg L^{-1} of H_2O_2.

A series of experiments were conducted for varying amounts of initial TC and H_2O_2 concentrations to examine whether the reaction follows a different pathway depending on the initial TC and H_2O_2 concentrations. The H_2O_2/TC ratio was kept at 4.9-5.0 (*Figure 4.5*). Thus, for 136 mg L^{-1} of initial TC, 666 mg L^{-1} of hydrogen peroxide was used. The same ratio was kept for other initial TC values: 1332 mg L^{-1} of H_2O_2 for 271 mg L^{-1} of TC, 2664 mg L^{-1} of H_2O_2 for 528 mg L^{-1} of TC, and 5328 mg L^{-1} of H_2O_2 for 1080 mg L^{-1} of TC.

Figure 4.5: Effect of [TC]$_o$ in terms of conversion for constant [H_2O_2]$_o$/[TC]$_o$ optimum ratio



4.2.3 Effect of initial pH

The effect of initial pH value of the synthetic solution on the photochemical degradation of organic pollutants using only H_2O_2 was investigated. Without any pH adjustment, the initial pH of the solution is around 7. In this case, after two hours 50% removal is achieved. However, if the initial pH is lowered by addition of HCl to pH around 5, the TC conversion drops to 45%. Finally, by addition of NaOH, it is possible to increase the pH of the solution to 8. Nevertheless, even if pH is initially raised to 8 after hydrogen peroxide is introduced into the system and process is started, pH instantly drops back to values around 5. This scenario with pH adjustment corresponds to the highest percentage of total carbon removal – 54%. Summary of these experiments is depicted *Figures 4.6* and *4.7.*

Figure 4.6: Effect of pH adjustment on process with H_2O_2 in terms of TC removal

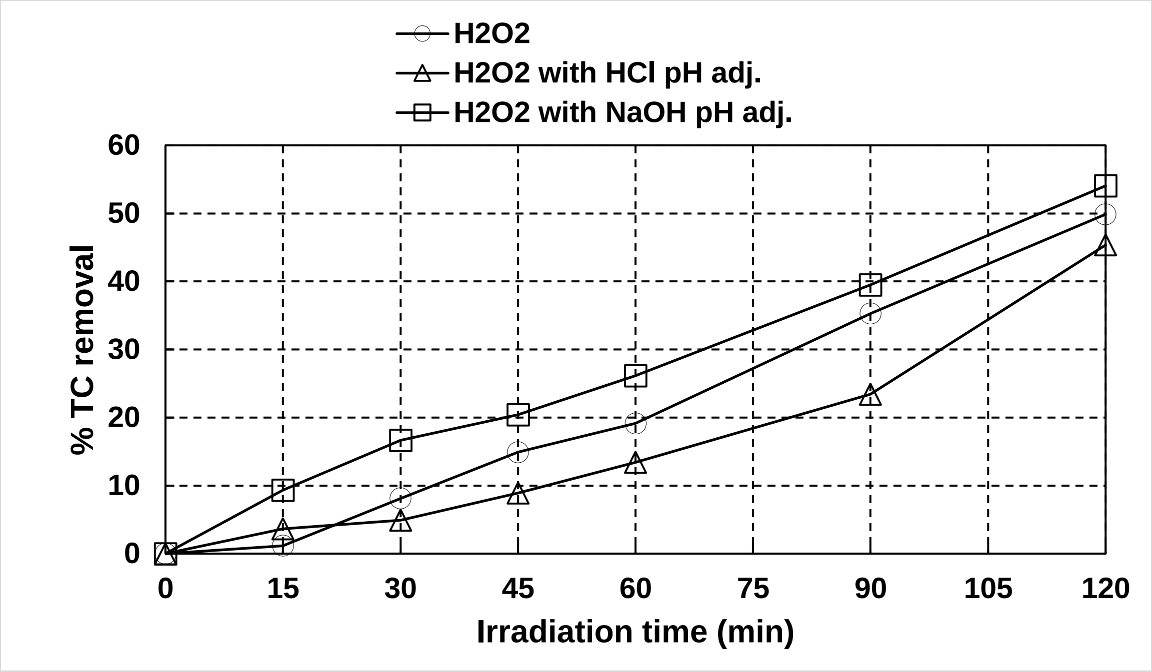
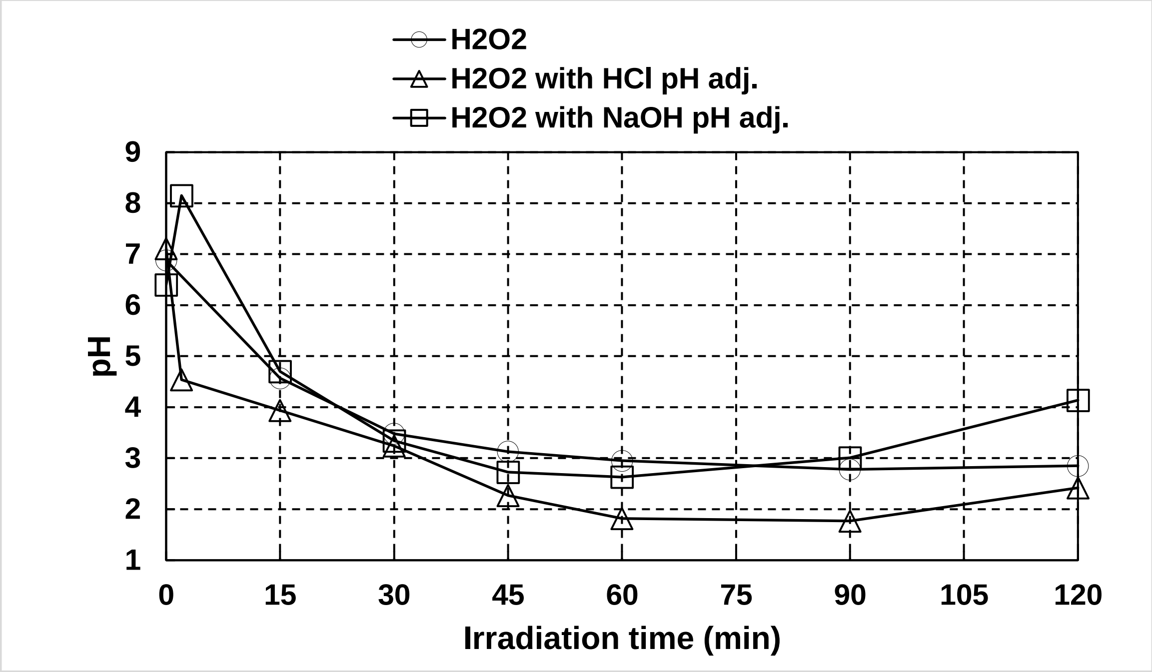


Figure 4.7: Effect of pH adjustment on process with H_2O_2 in terms of pH



The same trend was observed by other authors that the photochemical oxidation by hydrogen peroxide is a pH-dependent process [64]. It was claimed that with higher pH, at alkaline conditions, the rate of photolysis using H_2O_2 is higher. This observation may be explained due to the higher molar absorption coefficient (240 M^{-1} cm^{-1} at 254 nm) of the peroxide anion HO_2^- [64].

Wang et. al. [63] concluded that optimum pH corresponds to the range of 2.5-3. It was proposed that at lower pH, the scavenging effect of the hydroxyl radical becomes higher (reaction 4.5).

$$HO^{\bullet} + H^+ + e^- \rightarrow H_2O \tag{4.5}$$

4.3 Photo-Fenton "like" process with synthetic wastewater

This method is based on the H_2O_2/UV with further enhancement by addition of Fe(III). No pH adjustment was made because the process works without it, obtaining 50% reduction of organic carbon. The focus of these experiments was given on the effect of ferric ions concentration on the process. All experiments were conducted using the same initial TC (528 mg L^{-1}) and H_2O_2 (2664 mg L^{-1}) concentrations and different initial Fe(III) amounts (0-320 ppm). It was observed that with an increase of initial Fe(III) concentration, there is a rise in degradation rate. For the base case with no addition of Fe(III), a conversion of 50% was achieved. The highest percentage of TC removal of 87% was observed at 240 ppm of ferric ions. However, even if a further increase in the dosage of ferric ions to 320 ppm showed better TC conversion throughout first 1.5 hours of the experiment, the final rate of TC removal was almost the same as for 240 ppm. Thus, there was no need to examine higher concentrations of Fe(III). Comparison of all results in this series of experiments is given in *Figure 4.8* and *4.9*.

Figure 4.8: Effect of Fe(III) in terms of conversion for constant initial TC (528 mg L^{-1}) and constant H_2O_2 (2664 mg L^{-1})

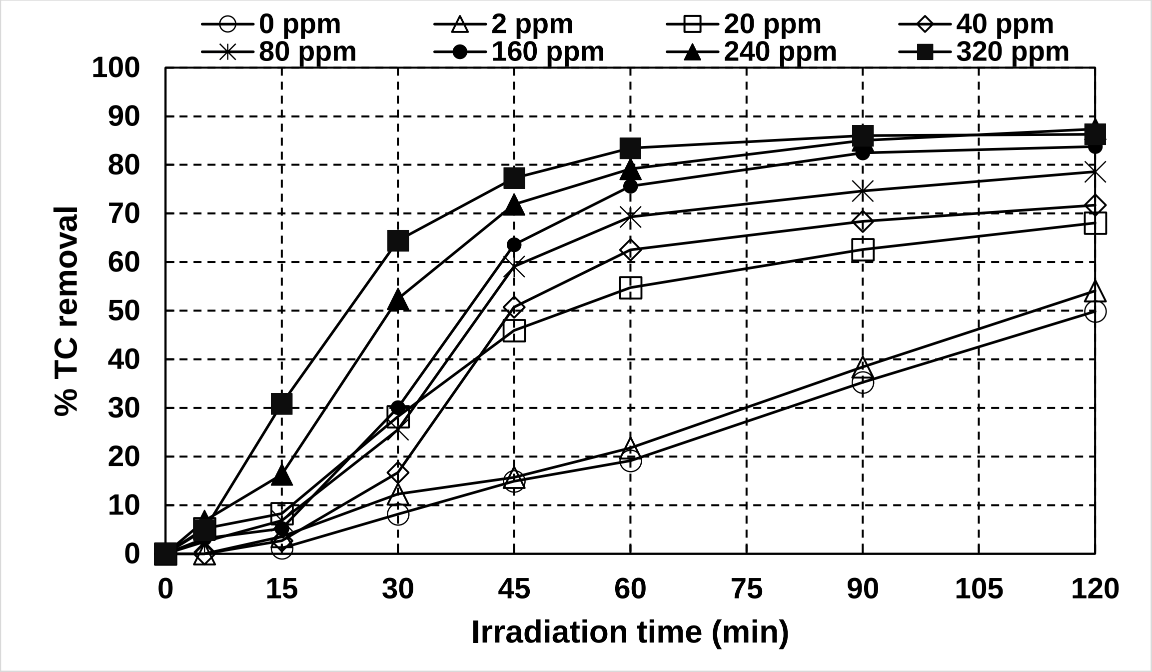
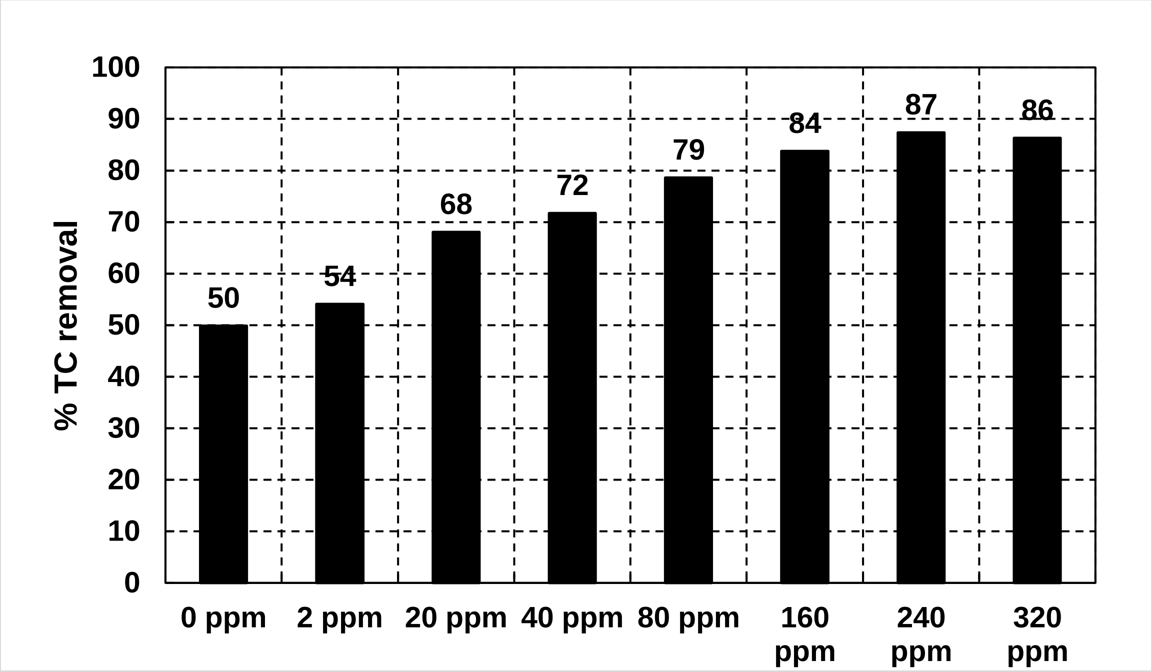


Figure 4.9: Effect of Fe(III) in terms of final conversions after two hours



Results obtained shows that even if the Fe(III) concentration is doubled from 160 to 240 ppm, conversion of the process increases only by 3%. Comparing the results of ferric ions addition of 80 and 160 ppm illustrates that it is still efficient to add just 80 ppm of Fe(III) as the TC removal for this case was 79%, whereas at 160 ppm of Fe(III) conversion increased only to 84%.

In addition, it is more practical to choose 80 ppm of Fe(III) for further experiments with photo-Fenton “like” because it would be more cost efficient to use less amount of chemical. Also, it would be required to treat less amount of iron sludge, as there is the 2 ppm limit that is allowed to be discharged with a wastewater by European Unit (EU) [24, 65].

As it was discussed in the literature review, treatment process with Fe(III) is initially slower than the photo-Fenton process with Fe(II) [11, 19, 22, 66]. This is primarily due to the following reactions (4.6) and (4.7), where it is clearly shown that photo-Fenton "like" process, first, requires the formation of Fe^{2+}, and only then the production of hydroxyl radicals takes place.

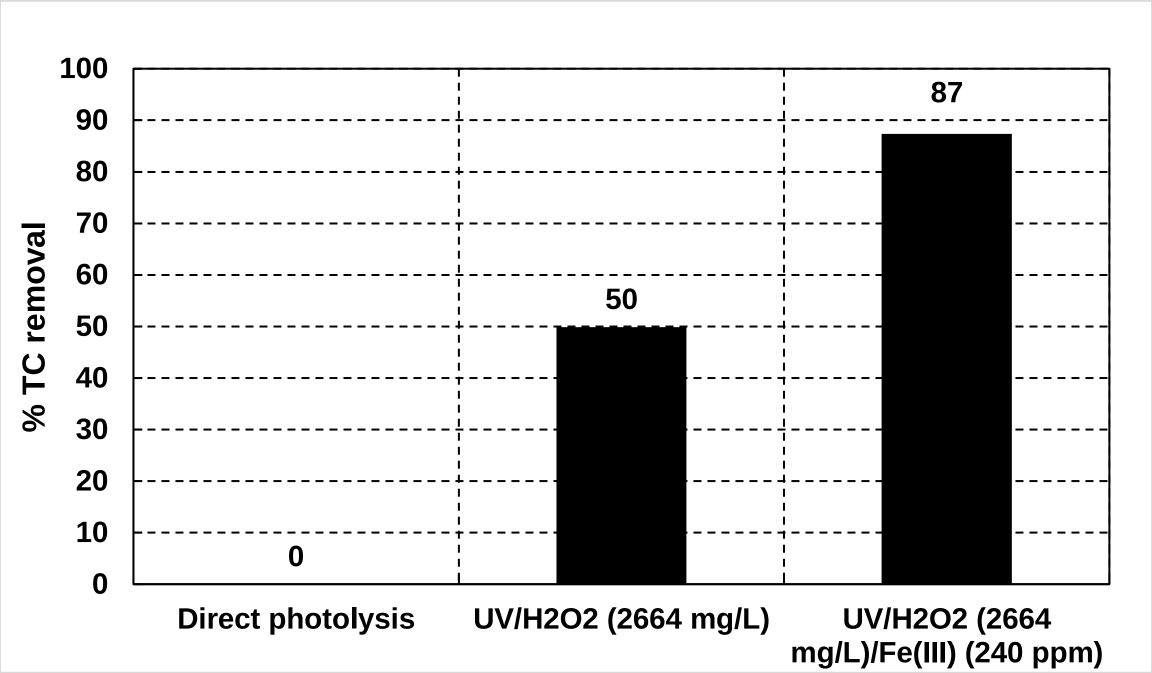
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \tag{4.6}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \tag{4.7}$$

4.4 Efficiency removal of synthetic wastewater under different processes

In total, three remediation techniques were examined for the treatment of synthetic wastewater. Summary of treatment methods in terms of mineralization of total carbon is depicted in *Figure 4.10*. Based on the results obtained, direct photolysis working only under UV light showed 0% conversion, meaning that components in wastewater are resistant to UV light. Addition of 2664 mg L^{-1} of hydrogen peroxide to the process significantly increased the degradation rate of total carbon, resulting in 50% conversion. The final enhancement to the process was made by injection of 240 ppm of ferric ions. This method achieved 87% of TC removal.

Figure 4.10: TC removal from synthetic wastewater under different processes



4.5 Photo-Fenton "like" process with synthetic wastewater for phenol removal

The treatment process with 2664 mg L^{-1} of H_2O_2 and 80 ppm of Fe(III) was additionally examined for the spikes in phenol (C_6H_5OH) concentration in the influent stream for the photo-reactor in the range of 0-100 mg/l was treated.

Phenols are a class of chemical compounds that have aromatic hydrocarbon group bonded to a hydroxyl group (-OH). The source of the phenols in wastewater can be the coking plant, the chemical plant producing different types of phenols, refining, paper and insulation material producing plants [67, 68]. Phenols are highly carcinogenic compounds that can negatively impact humans' health, even at low concentrations [67].

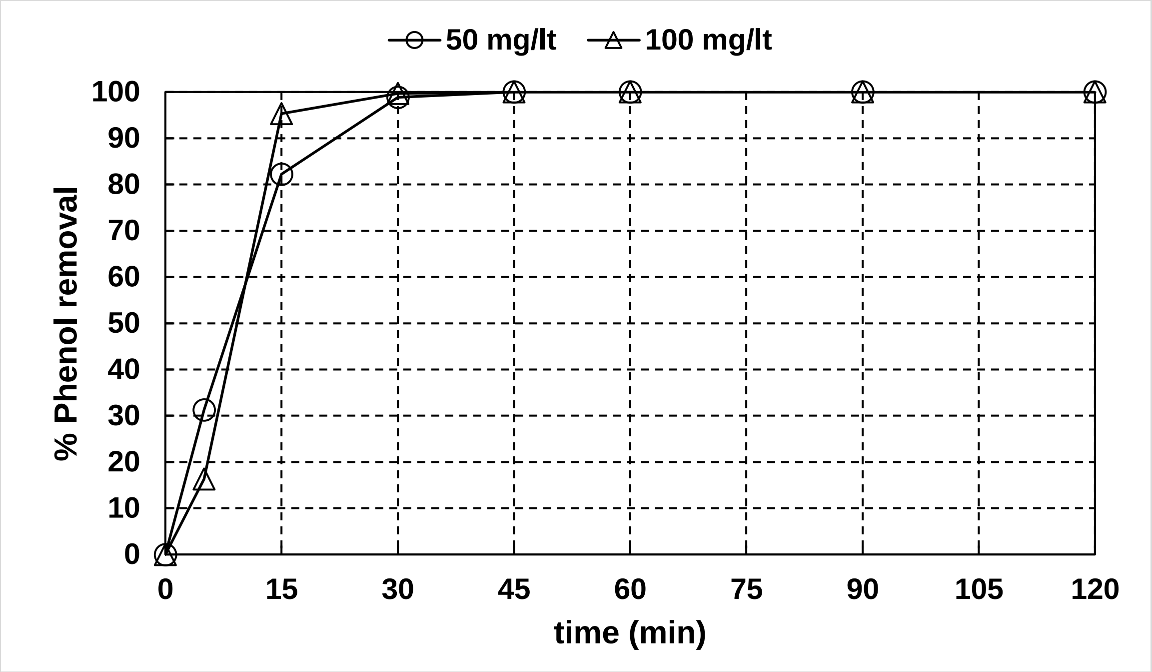
Two experiments were performed. Initially, 50 mg L^{-1} of phenol was added to the solution. Then, the same treatment process was checked on wastewater containing 100 mg L^{-1} of phenol. For both experiments, the initial TC of the synthetic solution was adjusted considering the theoretic concentration of carbon in phenol, so that the total initial TC will be around 528 mg L^{-1}. Theoretical concentration of carbon in phenol was calculated by the following equation:

$$\frac{MW\ of\ C\ in\ C_6H_5OH\ (\ g\ mol^{-1})}{MW\ of\ C_6H_5OH\ (\ g\ mol^{-1})} * C_6H_5OH\ in\ solution\ (mg\ L^{-1}) = \frac{12*6}{94.113} * 50\ or\ 100\ (mg\ L^{-1}) \qquad (4.8)$$

Therefore, for the case, when 50 mg L^{-1} of phenol was used, there was 38.25 mg L^{-1} of theoretic carbon. Consequently, there was 76.5 mg L^{-1} of carbon in 100 mg L^{-1} of phenol.

The results from the experiments were derived from two analytical equipment: Multi N/C 3100 and HPLC. Both trials obtained 100% of phenol removal after 45 minutes (*Figure 4.11*). It would be expected that lower concentration of phenol would have better results in terms of phenol removal.

Figure 4.11: Comparison of phenol removal (%) of different experiments



However, comparing both experiments at the point of 15 minutes, a higher percent of removal is obtained for 100 mg L^{-1} of phenol. This could be explained by the faster intermediate formation at higher concentrations of phenol, which was observed as a sudden color change of the solution at 15 minutes. Then, improvement in color was obtained with degradation of those intermediate compounds after 45 minutes from the start of the experiment. These observations are illustrated in *Figure 4.12*. Regarding the solution with 50 mg L^{-1} of phenol, such dramatic color changes were not observed. Only slight improvement in the final color of the solution was recorded. This observation is presented in *Figure 4.13*.

Figure 4.12: Color change during experiment with 100 mg L^{-1} of phenol: (a) at 0 minutes, (b) at 15 minutes, (c) in 45 minutes

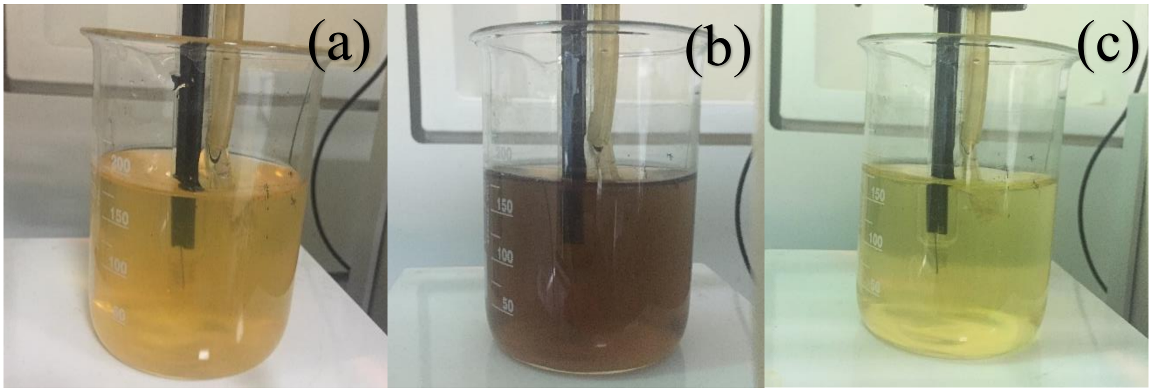
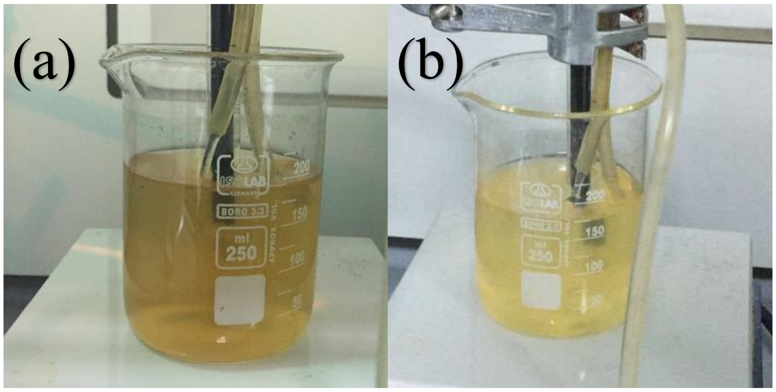
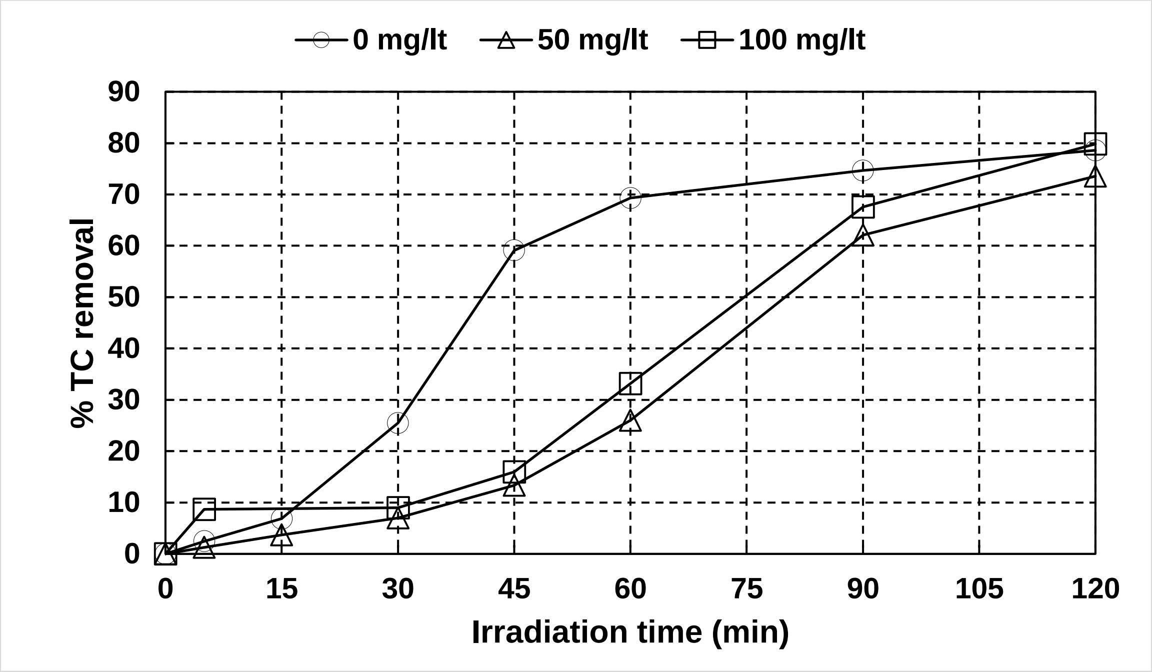


Figure 4.13: Color change during experiment with 50 mg L^{-1} of phenol: (a) at 0 minutes, (b) at 120 minutes



As the HPLC was programmed to identify phenol only, at time of 15 minutes, it was almost entirely transformed into phenolic intermediates, and high conversions for phenol removal are observed (82% for 50 mg L^{-1} of phenol and 95% for 100 mg L^{-1} of phenol). However, this does not mean that the degradation of organic matter took place. For that reason, it is necessary to perform analysis for TC simultaneously with HPLC. It can be noticed from the *Figure 4.14* that at 15 minutes, both experiments resulted in less than 10% mineralization of total carbon.

Figure 4.14: Results of TC removal for 0-100 mg L^{-1} of phenol

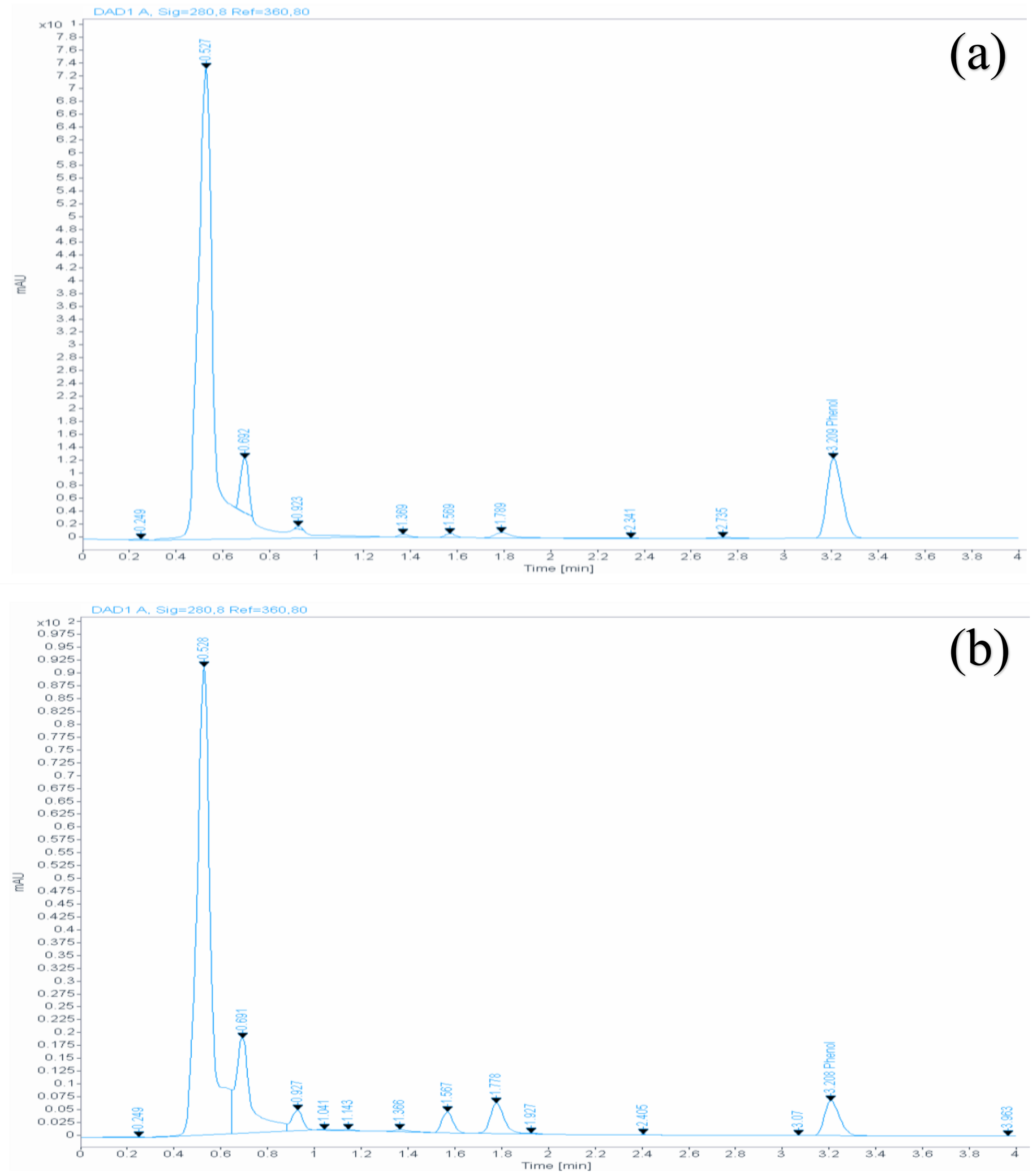


Based on TC results, it is also observed that experiment, which is more concentrated with phenol, has better results in terms of conversion. This observation could be due to the reason that in this wastewater composition (phenol with organic matter), phenol is more chemically oxidizable than the rest organic compounds. Thus, when more phenol is used, it has a higher amount of carbon that is ready to be oxidized.

Even the slight changes in operational conditions can change the pathway of reaction [69]. With phenol addition to wastewater containing organic compounds, there is a possibility of different intermediates formation. According to the literature, there are two types of intermediates [62, 69, 70]. The first group is organic acids like acetic acid, maleic acid, formic acid, and fumaric acid. The second group is the aromatic intermediates, such as benzoquinone and hydroquinone-like compounds (catechol and hydroquinone). During the Fenton “like” reactions [19], the first step is the reduction of Fe^{3+} to Fe^{2+} by H_2O_2. This reaction is slow having the rate constant of $0.001–0.01 M^{-1} s^{-1}$ [69]. Therefore, the complete mineralization of phenol in terms of total carbon in the initiation period is slow. Thus, this statement correlates to the results observed that at time of 15 minutes, there was less than 10% of TC mineralization. As proposed by several authors, the hydroquinone-like intermediates are formed during the reduction of Fe^{3+} to Fe^{2+} [62, 69, 71-74]. A complete mineralization of phenol requires the breaking of all C-C bonds. Each bond breaking represents the process of formation of carbon dioxide and shorter chain organic acids [62]. As benzoquinone is created, its further oxidation gives mucinic acid. Following reaction of the mucinic acid with •OH forms maleic acid [74]. For complete TC removal, all six C-C bonds of the phenol must be broken.

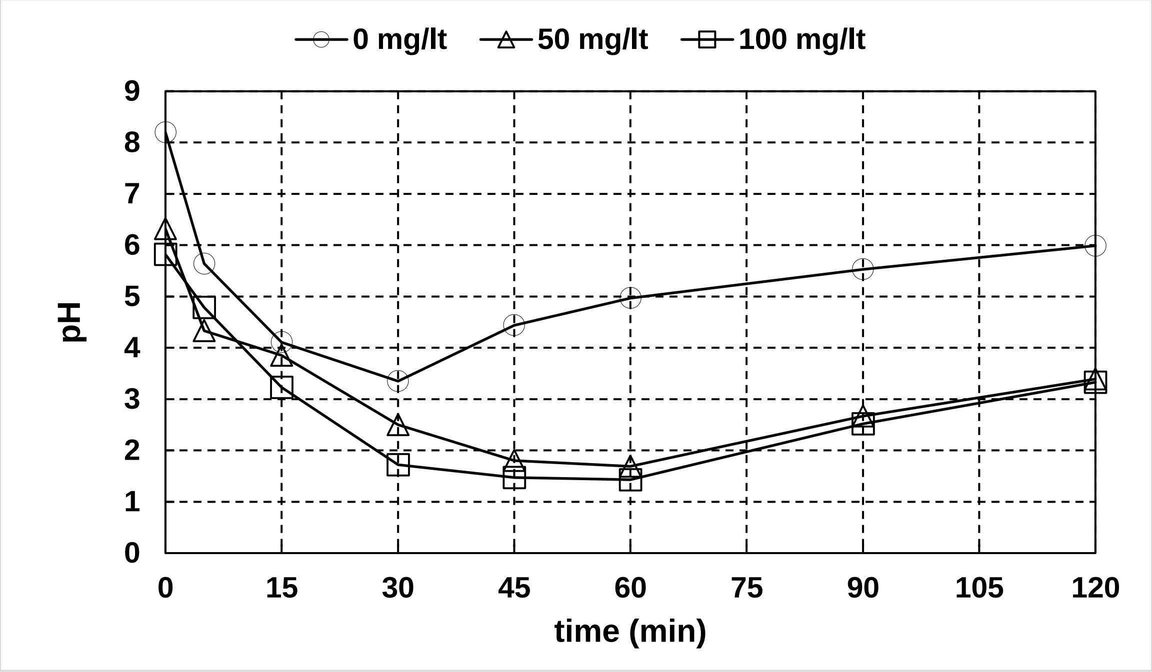
HPLC equipment that was used to analyze the amount of phenol present in the samples was able to detect the presence of phenolic intermediates as well. However, to identify the specific phenolic intermediates found in the samples, another, more sophisticated analytical equipment should be used. For instance, LCMS (Liquid chromatography mass spectroscopy) could be used. *Figure 4.15* shows the comparison in HPLC chromatogram between 50 and 100 mg L^{-1} at 15 minutes sample. It can be observed that for the sample with 100 mg L^{-1} of phenol, more intermediates were formed.

Figure 4.15: Comparison of HPLC chromatogram between 50 and 100 mg L^{-1} at 15 minutes sample: (a) for 50 mg L^{-1}, (b) for 100 mg L^{-1}



The initial pH for solutions with phenol varied as 6.07±0.25. No change to the initial pH values was made. The pH readings from the performed experiments are depicted in *Figure 4.16*.

Figure 4.16: pH results for 0-100 mg L^{-1} of phenol



Based on the literature, for phenol removal by direct photolysis, the neutral pH between 6 and 7 are preferred [75, 76]. Way and Wan [75] conducted a study based on this treatment method for phenol degradation. The wide range of pH values tested showing the results that the optimum condition, when the rate of phenol degradation is maximum, corresponds to pH of 6.5 [75]. In addition, the experiment presented that the process does not work adequately if pH is less than 2 [75]. Moreover, phenol degradation rate drops as pH is increased from 6.5 to 11 [75]. Another study on phenol degradation based on different pH values was performed by Preis et al. [76].

This experiment was based on the work of Way and Wan [75] and showed similar results for the rate of phenol decomposition. In addition to prior studies, this work presented that the further increase of pH (>11) will result in the second rise in phenol degradation rate [75]. However, the optimum case will still correspond approximately to pH of 6.5 [75].

However, for the treatment process by UV and hydrogen peroxide, several studies stated that initial pH lower than 8-9 does not affect phenol removal efficiency [77, 78]. Kusic [78] indicated that for a pH range of 3 to 9, degradation of >98% of 100 mg L^{-1} of phenol was achieved. The decline in phenol removal process to 65.7% was recorded only at pH 11. The highest TOC removal was observed at pH 8-9, resulting in 38.7 and 37.1% of organic carbon degradation [78]. However, it should be noted that the processes can behave differently depending on the composition of wastewater. Examples given from the literature were performed with wastewaters containing only phenol, whereas the experiments in this thesis were focused on a combination of synthetic wastewater with phenol.

The effect of hydrogen peroxide dosage was studied by Thind, Thomas & John [79]. It was identified that for 50 mg L^{-1} of phenol it is optimum to keep the H_2O_2/phenol ratio at 50, whereas for 100 mg L^{-1} of phenol, the H_2O_2/phenol ratio should be at 20 [79]. Comparing these results to the values used in this thesis, 2664 mg L^{-1} of H_2O_2 was used for both concentrations of phenol. Therefore, the for 50 mg

L^{-1} of phenol the ratio was 53.28, and for 100 mg L^{-1} of phenol, the ratio was 26.64. These values are close to what was observed as optimum values by other authors. Another observation made by authors is that the 50-200 mg L^{-1} of phenol has close removal efficiencies, the effect of the process declines at 300-500 mg L^{-1} of phenol [79]. The same trend was observed during this master thesis, where phenol removal in the range of 50-100 mg L^{-1} had similar results.

4.6 Photo-Fenton "like" process with real wastewater (leachate)

The best base scenario identified during experiments with synthetic wastewater was applied for treatment of actual wastewater – landfill leachate. Eight experiments were conducted. As it was mentioned earlier, leachate solution had around 2650 mg L^{-1} of total initial carbon with 1126 mg L^{-1} coming from inorganic carbon. Thus, TIC accounted for around 42% of total carbon in the initial raw leachate solution. The initial total nitrogen was estimated as 1017 mg L^{-1}, and the initial pH was around 8.

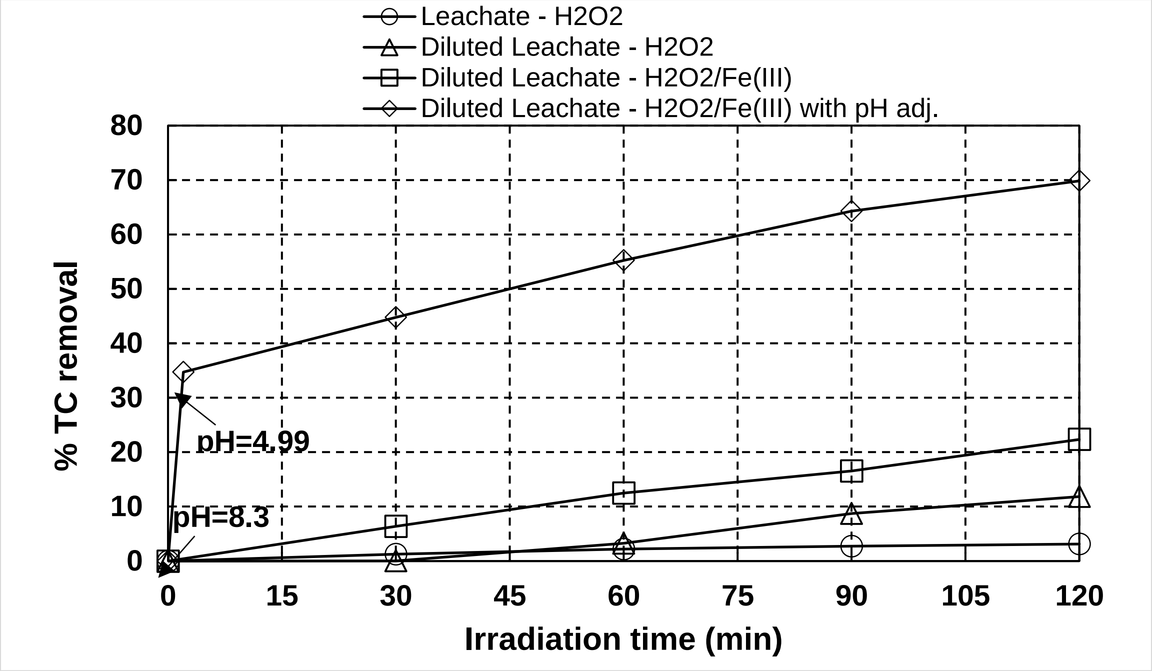
Initially, the photochemical process with UV/H_2O_2 was checked for the concentrated raw leachate solution without any dilution with distilled water. The experiment was conducted with 13320 mg L^{-1} of H_2O_2. The process had the initial pH of 8.3, and throughout the whole test, that pH was remaining around 7.9. As shown in *Figure 4.17*, the results did not show the significant removal of total carbon.

Then, the same process was examined with diluted raw leachate solution. The initial TC was diluted to 553 mg L^{-1}. The initial amount of hydrogen peroxide in the solution was kept at 2664 mg L^{-1}. Initial pH of diluted real wastewater was at 7.62, and during the experiment reduced only up to pH of 7.1. At a dilution of TC to 553 mg L^{-1}, the conversion achieved was of no practical use, showing just 12% of total carbon removal. Additional analyses for TIC and TN were conducted. The results showed only 4% of inorganic carbon removal. The TN value was unchanged throughout experiment approximately at 235 mg L^{-1}.

The last process was enhanced by the addition of 80 mg L^{-1} of Fe(III). The pH of the solution remained around 6.7 throughout the whole duration of the experiment. After two hours of the test, the TC analyzed showed the efficiency of total carbon degradation as 22%. However, the previous experiment with synthetic wastewater with same initial TC concentration achieved 79% of conversion under the identical conditions.

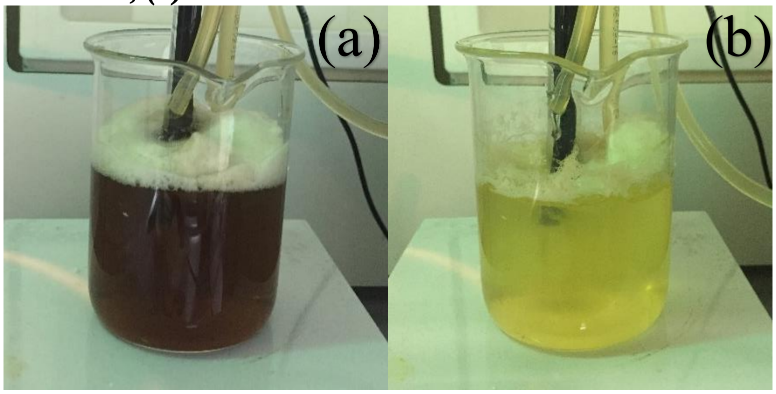
Since the previous experiment was only capable of degrading 22% of organic pollutants, it was decided to try to reduce pH value of the solution under the same initial conditions of chemical dosage. Significant impact on the remediation process occurred due to the pH adjustment by hydrochloric acid (HCl, >37% (w/w)). The initial pH of 8.3 was adjusted to pH of 5. This change in pH value considerably affected the treatment of raw diluted leachate solution from 22 to 70% of total carbon removal. At the same time, degradation of inorganic carbon enhanced from 4 to 75%.

Figure 4.17: Results of TC removal for leachate



The concentration of total nitrogen was not affected by pH adjustment and remained at 218 mg L^{-1} during the experiment. Also, significant color change of the solution before and after the experiment was achieved. The results are illustrated in *Figure 4.18*.

Figure 4.18: The color change observed for treatment of diluted leachate by pH adjustment: (a) at 0 minutes, (b) at 120 minutes



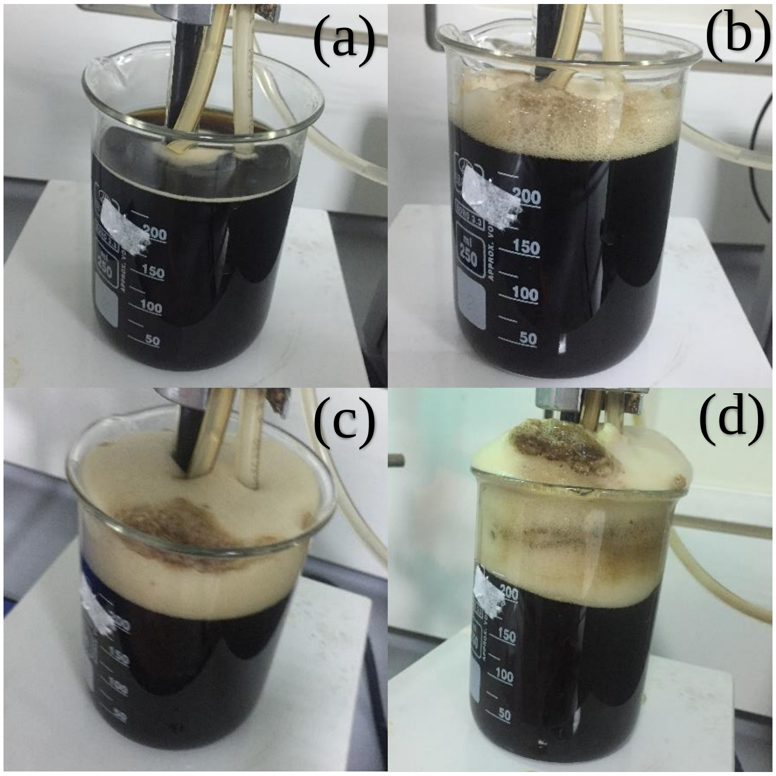
Since the diluted wastewater achieved such remarkable results only by a change in the initial pH value of the solution, the same process with pH adjustment by HCl was checked on the concentrated landfill leachate. The dosage of hydrogen peroxide and ferric ions was calculated based on the base case, where for 528 mg L^{-1} of initial TC, 2664 mg L^{-1} of H_2O_2 (2 mL, 78 mmol L^{-1}) and 80 mg L^{-1} of Fe(III) were used:

$$Amount\ of\ H_2O_2 = 2\ mL * \frac{TC}{528\ mg\ L^{-1}} \tag{4.9}$$

$$Amount\ of\ Fe(III) = 80\ mg\ L^{-1} * \frac{TC}{528\ mg\ L^{-1}} \tag{4.10}$$

Considering that used leachate is mature, it practically acceptable to apply the photo-Fenton process because, in case of young leachate, the organic pollutants can be easily degraded using biological treatment [34]. Taking into account that initial total carbon of the raw leachate was approximately 2650 mg L^{-1}, 10 mL (13320 mg L^{-1}, 392 mmol L^{-1}) of hydrogen peroxide and 400 mg L^{-1} of ferric ions were used for the treatment of real wastewater. Initially, before the experiment, the solution had pH of 8.21. By the addition of 2.5 mL of hydrochloric acid, the pH value was reduced to 4.82. *Figure 4.19* represents four stages of the solution before the start of the experiment. Initially, photo (a) shows raw leachate without any manipulations. Secondly, photo (b) illustrates the solution after the addition of HCl. It can be noticed that at this moment the foam starts to appear. Then, photo (c) presents the solution when hydrogen peroxide was also added to the solution. Finally, picture (d) indicates the solution right when the experiment was started after the addition of Fe(III).

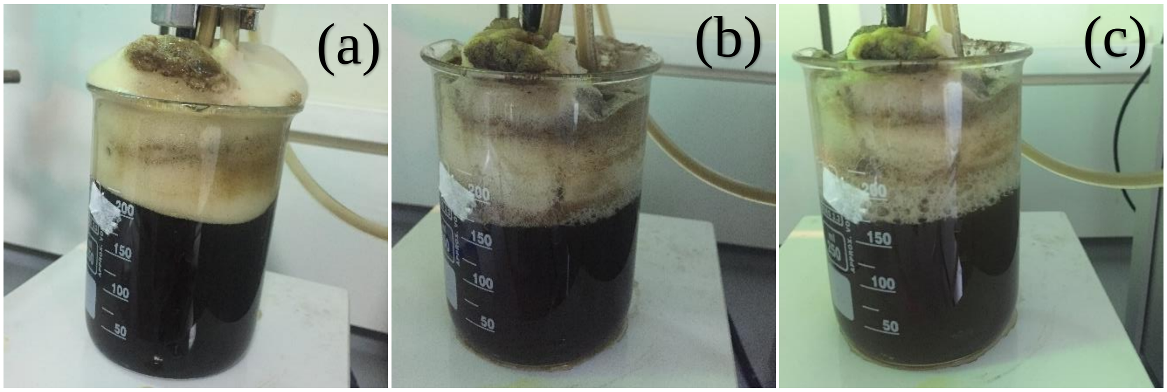
Figure 4.19: Effect on pH adjustment on initial solution of concentrated leachate: (a) raw leachate without any addition, (b) after the addition of HCl, (c) after the addition of H_2O_2, (d) after the addition of Fe(III)

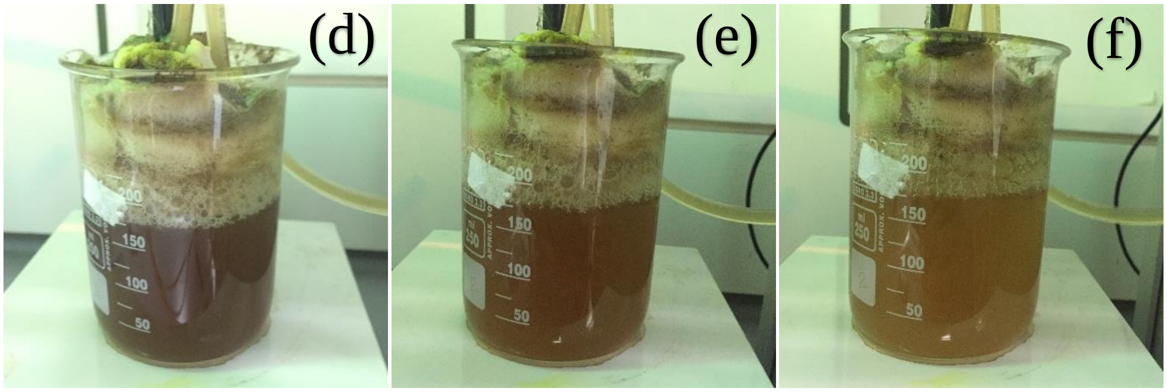


According to TC analysis, the 56% of initial total carbon was removed only using the chemical process by pH adjustment, having the drop in TC concentration from 2651 mg L^{-1} to 1179 mg L^{-1}. At the same time, performing the TIC analysis identified that this reduction in total carbon was coming only from degradation of inorganic compounds. Initially, the solution had 1126 mg L^{-1} of TIC. The foam from the pH adjustment decreased this value to 65 mg L^{-1}, resulting in 94% for TIC conversion.

The color change of the solution was noticed after 90 minutes from the start of the experiment. For that reason, the experiment was extended to additional 30 minutes. The illustration of color change of the treated leachate can be seen from *Figure 4.20*.

Figure 4.20: The color change observed for treatment of concentrated leachate by pH adjustment: (a) at 0 minutes, (b) 30 minutes, (c) 60 minutes, (d) 90 minutes, (e) 120 minutes, (f) 150 minutes

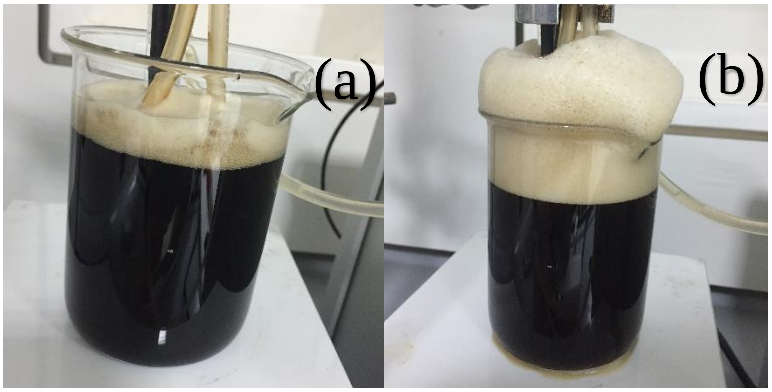




Comparing the results of this test with concentrated leachate with the previous experiment, where no ferric ions were added, and no pH adjustment was conducted to the process, shows the significant difference. The last test resulted only in 3% degradation of total carbon from the solution. This result was enhanced to 69% of TC conversion at two hours, and additional 6% conversion at the point of two and a half hours. Regarding the results of inorganic carbon, final conversion for TIC after 2.5 hours of the experiment was 98%. This effect means that after the initial TIC removal by HCl addition there was 1525 mg L^{-1} of total organic carbon. The remediation of wastewater resulted in 58% degradation of organic pollutants. Thus, the final TOC value in the leachate after the experiment was 643 mg L^{-1}. Concerning the TN measurement, the initial total nitrogen concentration in the solution was at 1017 mg L^{-1}. This value declined to 4% after the formation of the foam and remained unchanged after that throughout the whole duration of the experiment.

The last experiment was also put on test with another acid – sulfuric acid (H_2O_4S, 95-97% (w/w)). The goal was to achieve only the pH reduction, without the formation of foam that chemically removes the TIC from the solution. However, the addition of H_2O_4S resulted in the creation of foam as well. Thus, this solution was terminated from further use and experiment was canceled. The observed foam is illustrated in *Figure 4.21*. Photo (a) shows the foam formation after the addition of H_2O_4S. Photo (b) presents the increase in the foam layer after the introduction of hydrogen peroxide to the system.

Figure 4.21: The foam formation after the pH adjustment with H_2O_4S on concentrated leachate: (a) after the addition of H_2O_4S, (b) after the addition of H_2O_2



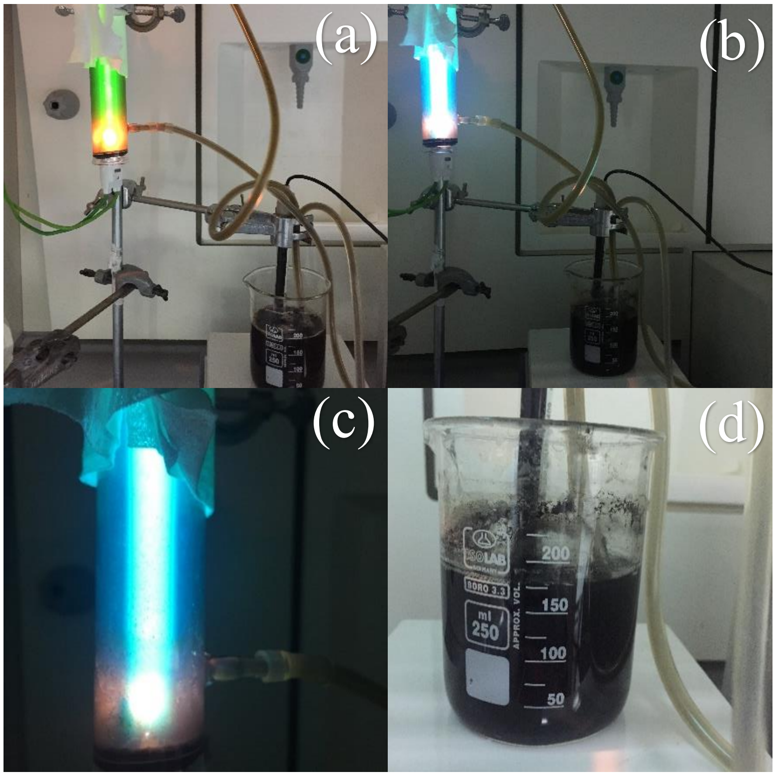
Finally, there were two experiments performed on undiluted landfill leachate that was initially bio-treated. It can be noted that application of air stripping, adsorption, and biological treatment can remarkable reduce the TIC and TN content in the wastewater. However, further reduction of non-biodegradable organic carbon is required.

The further step was chosen to be the treatment by UV light in the presence of hydrogen peroxide and ferric ions. According to the literature, the photo-Fenton process is the best technique among other AOP process for leachate treatment [80].

This process is stated to be effective in COD removal; the used chemicals are nontoxic; the process is simple and cost-effective [80]. The dosage of H_2O_2 and Fe(III) in the solution was again derived by equations (4.9) and (4.10). Considering the initial TC of pretreated leachate is around 928 mg L^{-1}, 4662 mg L^{-1} (3.5 mL, 137 mmol L^{-1}) of hydrogen peroxide and 140 mg L^{-1} of ferric ions were used. In addition, taking into account that the initial pH of treated leachate was 7.98, the pH adjustment with 0.1 mL of HCl (>37% (w/w)) was applied. The pH of the solution before the start of the experiment was reduced to 4.88. The duration of the experiment was kept as 2.5 hours, to be consistent with the previous test with concentrated raw leachate. Considering that the initial TC of fresh landfill leachate was approximately 2650 mg L^{-1}, the pretreatment of the wastewater resulted in 65% TC conversion. Application of additional remediation technique by photo-Fenton process resulted in further 29% of total carbon degradation. Moreover, the initial concentration of inorganic carbon in the solution was 32 mg L^{-1}, whereas in the raw, untreated wastewater there was approximately 1126 mg L^{-1} of IC. This result means that pretreatment achieved 97% of inorganic carbon removal. Application of additional treatment with H_2O_2 and Fe(III) under UV light is not designed to remove inorganic carbon from the solution. Nevertheless, a small reduction in TIC value was observed due to the pH adjustment by hydrochloric acid. Therefore, it can be summarized that after the further remediation process of already pretreated leachate, additional 29% of organic carbon can be degraded from the solution. Furthermore, the concentration of total nitrogen was reduced by pretreatment from 1017 mg L^{-1} to 158 mg L^{-1}. The total nitrogen was reduced using air stripping used for ammonium removal. However, further treatment of this solution by photo-Fenton “like” process did not enhance the TN removal.

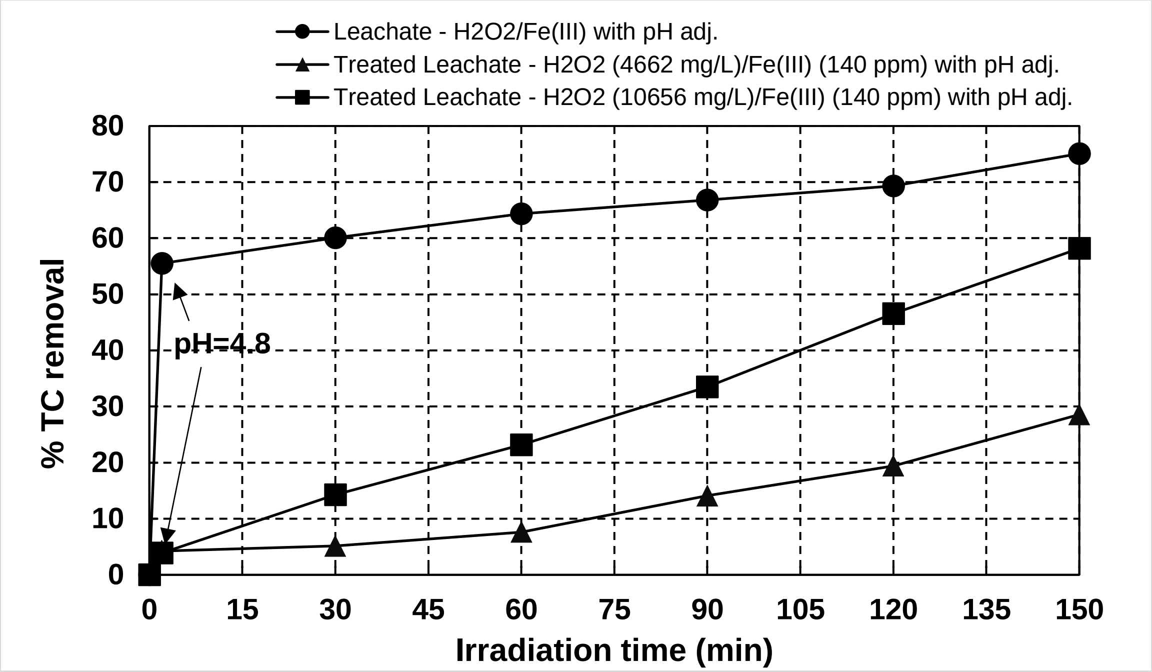
Finally, the previous experiment was enhanced by the increase of hydrogen peroxide dosage into the solution. At this time, 8 mL (10656 mg L^{-1}, 313 mmol L^{-1}) of H_2O_2 was used, whereas the concentration of ferric ions in the solution remained the same as 140 mg L^{-1}. Initial pH of the solution was 7.71, which was later adjusted to 4.82 by addition of 0.14 mL of HCl. It was observed that the concentration of total carbon in the solution declined from 930 mg L^{-1} to 389 mg L^{-1}, giving the 58% of TC conversion. The results for TIC and TN showed the same behavior as the previous test for treated leachate. Thus, the achieved conversion of TC implies that it was only the degradation of organic carbon from the solution. Finally, none of the experiments performed with pretreated leachate reached much of a color change. The change in color was only noticed in the cylindrical part of the reactor, where the solution was irradiated continuously by UV lamp. The final solution (after 2.5 hours of the experiment) it was mostly contaminated with dark solid particles. The illustration of these observations can be seen from *Figure 4.22*.

Figure 4.22: Observations throughout the experiment: (a) color in the lamp at 0 minutes, (b) color in the lamp at 150 minutes, (c) close-up of the lamp at 150 minutes, (d) final solution at 150 minutes



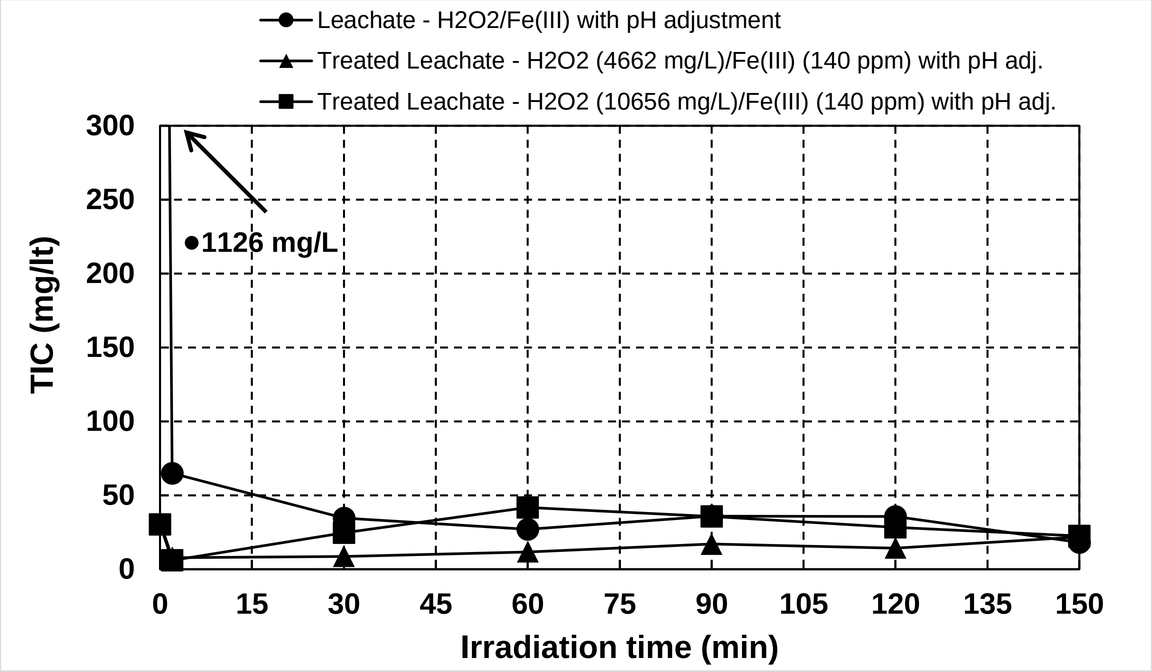
Comparison of results obtained for concentrated leachate and bio-treated leachate with initial pH adjustment is given in *Figure 4.23*. It can be noted that since 96-97% of inorganic carbon was removed with the help of pretreatment by air stripping, the significance of pH adjustment was only considerably noticed during the experiments with raw leachate.

Figure 4.23: Results of TC removal of leachate and bio-treated leachate with initial pH adjustment



The TIC analyses were performed only for the processes that achieved high results in oxidizing the organic pollutants and for the experiments conducted on pretreated wastewater. It can be noted that not depending on the initial TIC of the untreated wastewater (diluted leachate – 240 mg L^{-1}, concentrated leachate – 1126 mg L^{-1}), right after the pH adjustment both wastewaters showed the concentration of inorganic carbon in the range of 61-65 mg L^{-1}. These values continued to decrease through the experiment slightly. Regarding the pretreated leachate, the initial TIC was at 32 mg L^{-1}, and this amount, with slight fluctuations in the results, was remained throughout the tests. Therefore, it can be summarized that no additional TIC removal was observed for the experiments with already pretreated leachate solution. Graphical summary of above-mentioned experimental observations is presented in *Figure 4.24*.

Figure 4.24: Comparison of TIC concentrations of different experiments

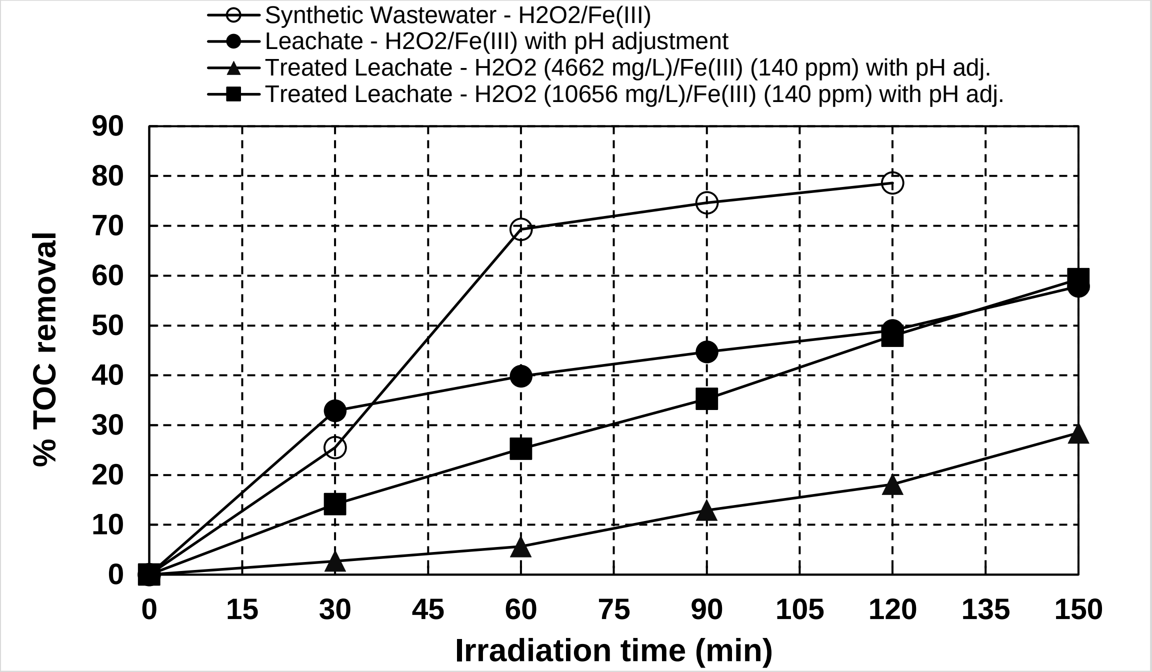


As the focus of this thesis is given for the degradation of organic pollutants from the wastewater, it is essential to study the effect of treatment method on oxidation of organic carbon. The concentration of total organic carbon was calculated manually as in equation (4.11).

$$TOC\ (mg\ \ L^{-1}) = TC\ (mg\ L^{-1}) - TIC\ (mg\ L^{-1}) \qquad (4.11)$$

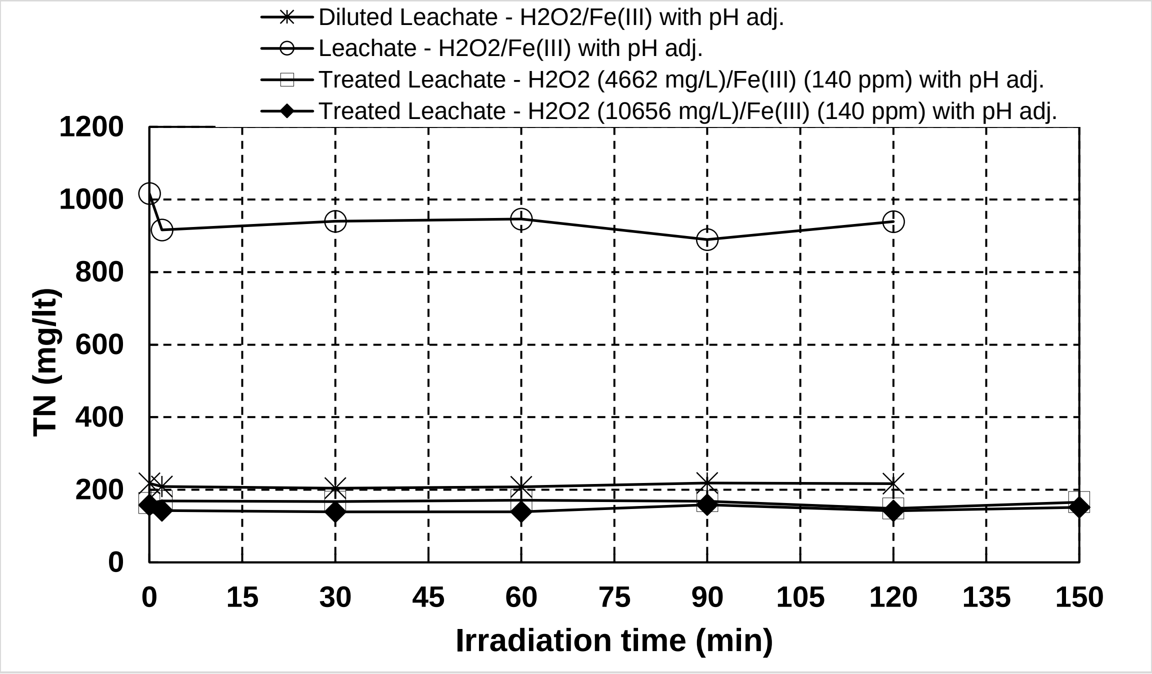
The highest concentration of organic carbon was obtained from concentrated raw leachate having 1525 mg L^{-1} of TOC. After applying the treatment with pH adjustment, 13320 mg L^{-1} of H_2O_2 and 400 mg L^{-1} of Fe(III), 58% conversion was achieved. Diluting the initial TC of raw leachate, that contains 318 mg L^{-1} of TOC, and treating it by an appropriate amount of hydrogen peroxide and ferric ions (2664 mg L^{-1}, 80 mg L^{-1}) resulted in 52% of TOC removal. Comparing the same dosage of chemicals on synthetic wastewater with higher initial TOC (568 mg L^{-1}) gave 79% of degradation of organic compounds. This statement could be explained by the fact that real wastewater is mature, and has more complicated composition. Regarding the results for treated leachate, the initial TC concentration was around 928 mg L^{-1}. The removal efficiency was based on the dosage of hydrogen peroxide used. The higher percent of degradation of organic compounds is achieved with 10656 mg L^{-1} of H_2O_2 (313 mmol L^{-1}) resulting in 59% TC removal, whereas at 4662 mg L^{-1} of H_2O_2 (137 mmol L^{-1}) only 29% TC conversion was observed. The results for organic carbon in terms of percentage removal are shown in *Figure 4.25.*

Figure 4.25: Comparison of TOC conversion of different experiments



The analysis performed on total nitrogen concentration showed that the photo-Fenton "like" process does not affect the removal of nitrogen (*Figure 4.26*). In case of concentrated raw leachate, the small initial reduction in TN value corresponds to the removal of nitrogen by pH adjustment. In all other cases, the concentration results for total nitrogen remains stable throughout all experiments.

Figure 4.26: Comparison of TN concentrations of different experiments



As it was noted from the experiments with leachate, initial pH value is one of the essential characteristics of the remediation process. Other authors also emphasize the effect of pH adjustment [81, 82, 83-87]. According to Steensen [82], H_2O_2 is only capable of degrading the organic pollutants at acceptable reaction rates by the use of radical formation. The pH reduction helps to decrease the concentration of carbonate, simultaneously increasing the oxidizing potential. Preferably the pH value should be kept between 2 and 4.5. Working at a lower pH (below 2) could lead the reaction to go through an undesired pathway that would cause the formation of $[Fe(H_2O)]^{2+}$ that slowly reacts with hydrogen peroxide [88]. Therefore, there would be fewer hydroxyl radicals produced. In addition, at a lower pH, the scavenging effect of H^+ on hydroxyl radicals becomes more noticeable, reducing the efficiency of the treatment process

[68, 83]. On the other hand, working with pH above 5 could trigger the decomposition of hydrogen peroxide due to the absence of H^+ [85]. Thus, the production of •OH radicals would be limited. Moreover, at high pH (>5) the reaction could undergo the undesired path that would result in the formation of ferric oxyhydroxide [81, 86, 87]. The formation of this unwanted byproduct might accumulate as a sludge inside the reactor, and disturb UV light from penetration through the solution. Furthermore, at pH higher than 5, there is a risk of decomposition of hydrogen peroxide to water and oxygen [86]. In such case, no formation of hydroxyl radicals would be expected. Finally, at high pH values, the reduction of oxidation potential of •OH radicals could be observed [87].

Before the pH adjustment, there were no significant results in degradation of organic pollutant. This is related to the presence of inorganic carbon in leachate [19]. More specifically, the presence of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) disturbs the treatment process by scavenging effect on hydroxyl radicals [19]. This problem is eliminated by lowering the pH values to acidic conditions. Under the appropriate pH, CO_3^{2-} and HCO_3^- combine with H^+ to produce unstable H_2CO_3 that is further reduced to CO_2 and water [19]. Hence, the pH adjustment results in CO_2 bubbles formation. Thus, the problem with foaming was indicated as one of the common side effects of pH lowering [19, 89]. The possible solution to overcome this problem is to add antifoaming agents, for instance, amyl alcohol [89].

Young leachates are mostly composed of volatile fatty acids (80%), whereas the composition of mature leachate comes from humic and fumic substances [90]. The presence of organic substances like humic acids results in the initial dark color of the leachate [90]. With increasing landfilling age, the molecular weight of humic substances also increases [91]. As treatment process begins, these large organic substances are reduced into smaller and simpler molecules, which result in discoloration of initial leachate. Based on studies of other authors showed that treatment by the photo-Fenton process can achieve tremendous results in color improvement [81, 92]. Kim and Huh [81] performed experiments on mature leachate, which resulted in 92% of decolorization efficiency.

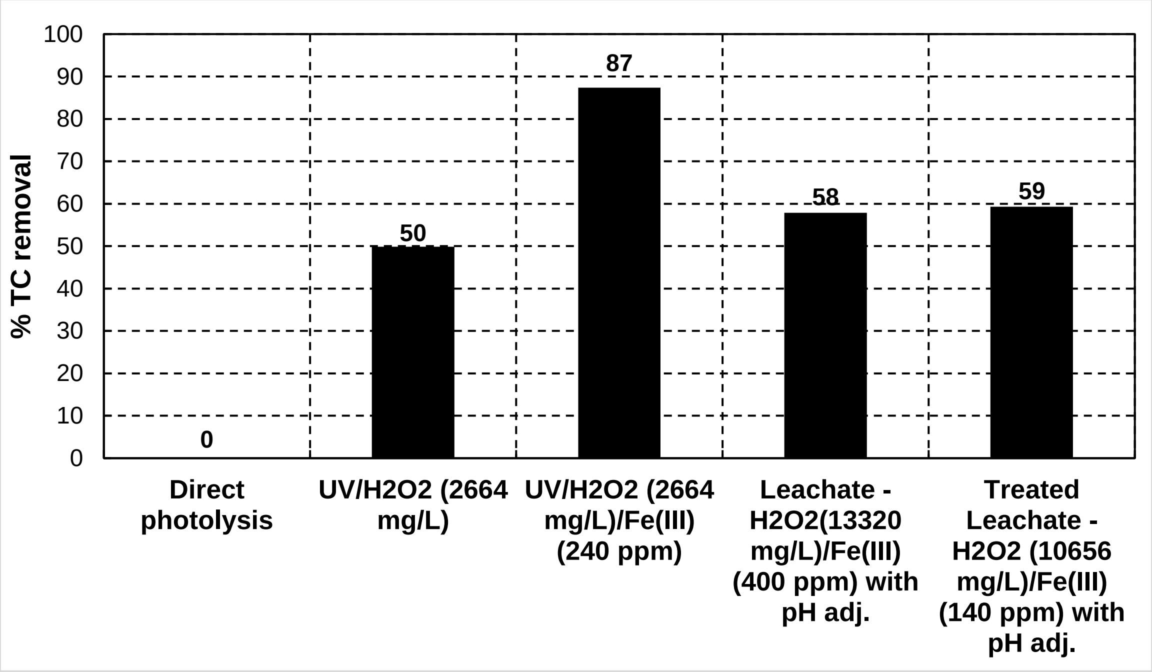
As it was mentioned earlier, the photo-Fenton “like” process did not affect the concentration of total nitrogen. The same trend was observed during several other experiments conducted by other studies [66, 92-94]. The results showed that photo-Fenton process had an impressive performance regarding oxidizing capacity; however, it was not capable of degrading ammonia.

A similar combination of treatment methods by AOP and biological treatment was also performed by other authors [82, 95-102]. Firstly, leachate was pretreated by biological treatment, where the ammonia and biodegradable organic matter were removed. Then, the photochemical process with H_2O_2 under the UV light was applied to remove the non-biodegradable organic compounds. Also, it was claimed that the photochemical oxidation changes the structure of organic matter. Initially, after the biological treatment, there are hardly biodegradable long-chain molecules, which after the treatment by H_2O_2 and UV light are broken to short-chain organic acids, which are more biodegradable [95, 98]. At this point, it is hard to remove this compound by AOP. However, recirculation of the effluent back to the biological reactor might help to biodegrade those short-chain organic acids [82, 96, 101]. Such recirculation procedure can increase the efficiency of the treatment process by 10-15% [82].

4.7 Summary of main results

For the experiments with synthetic wastewater, three treatment techniques were examined. Then, the best of them was applied for remediation of real wastewater (a landfill leachate). Summary of the main results is depicted in *Figure 4.27*. The results showed that components present in synthetic wastewater are resistant to UV light, having 0% of conversion. Enhancement of this process is achieved by the addition of 2664 mg L^{-1} of hydrogen peroxide to the process. In this case, it was possible to degrade 50% of organic carbon. Addition of 240 ppm of ferric ions resulted in further improvement of the process. The removal efficiency was increased to 87%. Examining the photo-Fenton “like” process on real wastewater with 13320 mg L^{-1} of H_2O_2 and 400 ppm of Fe(III) was capable of degrading 58% of the total carbon from the leachate. The experiment on bio-treated leachate with 10656 mg L^{-1} of H_2O_2 and 140 ppm of Fe(III) achieved 59% of TC removal.

Figure 4.27: Summary of main results



Chapter 5 - Conclusion

In this work, the photochemical process was applied for the treatment of a synthetic wastewater containing mainly organic carbon. Also, the presence of phenol in the process was examined. Finally, the results obtained for synthetic wastewater were applied to the real wastewater to see how the treatment process will deal with pollutants found in leachate solution. The main conclusions are:

(a) The photochemical treatment using UV and H_2O_2 was effective in the mineralization of the wastewater for initial TC concentration of 528 mg L^{-1} and 2664 mg L^{-1} of H_2O_2, resulting in 50% TC removal.

(b) The process can be significantly enhanced by the addition of ferric ions. Adding 240 ppm Fe(III) resulted in 87% conversion.

(c) Adjustment of pH resulted in better TC conversion when the initial pH was adjusted from 7 to 8. Total carbon removal increased from 50% to 54%.

(d) Both experiments with phenol (50 and 100 mg L^{-1}) achieved 100% of phenol degradation from the synthetic solution. Regarding the TC removal, the results were comparable with previous observations on an experiment with synthetic wastewater with 79% of TC mineralization. The TC oxidation achieved with 50 mg L^{-1} of phenol was 74%, whereas 80% of total carbon was degraded when 100 mg L^{-1} of phenol was used.

(e) Application of the photo-Fenton “like” process on real wastewater showed that the treatment method is not working unless the pH is adjusted approximately to 5.

(f) Removal of 75% TC from the leachate was achieved after 2.5 hours by addition of 13320 mg L^{-1} of H_2O_2 and 400 ppm or Fe(III).

(g) Additional treatment of initially bio-treated leachate resulted in 58% TC elimination in 2.5 hours by addition of 10656 mg L^{-1} of H_2O_2 and 140 ppm or Fe(III).

Future work will include the study on the effectiveness of the optimized processes when other phenolic compounds; such as 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-nitrophenol, are also present in the synthetic wastewater. Moreover, further experiments with bio-treated leachate could be performed. For instance, the effluent from the AOP could be sent back to the biological treatment to see the additional effect of biodegradation of organic compounds.

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Appendix

All experimental results are presented in this section.

Date: 20.09.17

Solution	250	ml
H2O2	2	ml
Stock solution	248	ml

Sample	Time (min)	TC (mg/l)	Correction of TC (mg/l)	TOC*Dilution ratio (20) (mg/l)	pH	Conversion
1	0	38.37	54	1080.1	7.7	0
2	15	38.3	53.9	1078.1	5.99	0
3	30	35.5	49.8	996.3	4.33	8
4	45	35.82	50.3	1005.7	3.78	7
5	60	34.52	48.4	967.7	3.54	10
6	90	34.16	47.9	957.2	3.29	11
7	120	33.12	46.3	926.9	3.13	14

Date: 21.09.17

Solution	250	ml
H2O2	2	ml
Stock solution	125	ml
DI water	123	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	TOC*Dilution ratio (10) (mg/l)	pH	Conversion
1	0	37.52	52.8	527.6	6.88	0
2	15	37.1	52.2	521.5	4.57	1
3	30	34.58	48.5	484.7	3.48	8
4	45	32.13	44.9	449.0	3.13	15

5	60	30.6	42.7	426.7	2.95	19
6	90	24.76	34.1	341.4	2.78	35
7	120	19.49	26.5	264.5	2.85	50

Date: 25.09.17

Solution	250	ml
H2O2	2	ml
Stock solution	62.5	ml
DI water	185.5	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.37 ± 0.42%					
1	0	38.47 ± 0.04%	54.2	2/10	270.8	7.68	0
2	15	35.7 ± 0.36%	50.1	2/10	250.5	3.98	7
3	30	31.92 ± 0.38%	44.6	2/10	223.0	3.14	18
4	45	27.88 ± 0.74%	38.7	2/10	193.5	2.88	29
5	60	24.93 ± 0.65%	34.4	2/10	172.0	2.81	36
6	90	19.11 ± 0.67%	25.9	2/10	129.5	2.94	52
7	120	14.60 ± 1.18%	19.3	2/10	96.6	3.59	64

Date: 26.09.17

Solution	250	ml
H2O2	2	ml
Stock solution	31.25	ml
DI water	216.75	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
1	0	38.7± 0.99%	54.5	4/10	136.2	7.15	0
2	15	37.98 ± 1.18%	53.4	4/10	133.6	3.58	2
3	30	34.67 ± 2.19%	48.6	4/10	121.5	3.25	11

4	45	30.49 ± 1.62%	42.5	4/10	106.3	3.15	22
5	60	26.76 ± 1.08%	37.1	4/10	92.7	3.17	32
6	90	20.59 ± 1.47%	28.1	4/10	70.1	3.39	49
7	120	16.62 ± 1.22%	22.3	4/10	55.7	3.79	59

Date: 27.09.17

Solution	250	ml
H2O2	0	ml
Stock solution	31.25	ml
DI water	218.75	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.34 ± 7.63%					
1	0	36.24 ± 0.92%	50.9	4/10	127.2	7.25	0
2	15	37.66 ± 0.63%	53.0	4/10	132.4	4.07	0
3	30	37.7 ± 0.41%	53.0	4/10	132.6	4.05	0
4	45	38.61 ± 0.57%	54.4	4/10	135.9	4.04	0
5	60	37.46 ± 0.24%	52.7	4/10	131.7	4.03	0
6	90	38.74 ± 0.16%	54.5	4/10	136.4	4.01	0
7	120	39.72 ± 0.28%	56.0	4/10	139.9	4	0

Date: 28.09.17

Solution	250	ml
H2O2	1	ml
Stock solution	125	ml
DI water	124	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		1.96 ± 0.95%					
1	0	37.87 ± 0.54%	53.3	1/10	532.7	7.12	0
2	15	33.52 ± 1.02%	46.9	1/10	469.3	3.81	12

3	30	32.00 ± 0.55%	44.7	1/10	447.1	3.76	16
4	45	32.13 ± 0.41%	44.9	1/10	449.0	3.7	16
5	60	31.46 ± 0.60%	43.9	1/10	439.2	3.67	18
6	90	29.33 ± 1.11%	40.8	1/10	408.1	3.64	23
7	120	28.65 ± 1.70%	39.8	1/10	398.2	3.66	25

Date: 29.09.17

Solution	250	ml
H2O2	4	ml
Stock solution	125	ml
DI water	121	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.04 ± 6.18%					
1	0	35.15 ± 1.10%	49.3	1/10	493.1	6.83	0
2	15	34.49 ± 0.30%	48.3	1/10	483.4	3.76	2
3	30	32.69 ± 0.27%	45.7	1/10	457.2	3.65	7
4	45	28.85 ± 0.19%	40.1	1/10	401.1	3.7	19
5	60	26.66 ± 0.99%	36.9	1/10	369.2	3.78	25
6	90	24.78 ± 0.80%	34.2	1/10	341.7	3.83	31
7	120	19.80 ± 1.58%	26.9	1/10	269.0	3.85	45

Date: 02.10.17

Solution	250	ml
H2O2	6	ml
Stock solution	125	ml
DI water	119	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.10 ± 0.31%					
1	0	38.49 ± 1.57%	54.2	1/10	541.8	7.41	0

2	15	37.46 ± 0.12%	52.7	1/10	526.8	5.21	3
3	30	35.07 ± 0.55%	49.2	1/10	491.9	3.45	9
4	45	31.11 ± 0.53%	43.4	1/10	434.1	3.03	20
5	60	28.83 ± 1.11%	40.1	1/10	400.8	2.84	26
6	90	23.08 ± 1.62%	31.7	1/10	316.9	2.72	42
7	120	18.63 ± 0.31%	25.2	1/10	252.0	2.79	53

Date: 03.10.17

Solution	250	ml
H2O2	1	ml
Stock solution	62.5	ml
DI water	186.5	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.56 ± 6.20%					
1	0	35.73 ± 1.60%	50.2	2/10	250.8	7.02	0
2	15	34.87 ± 0.40%	48.9	2/10	244.5	3.71	3
3	30	30.97 ± 0.43%	43.2	2/10	216.0	3.47	14
4	45	28.07 ± 0.28%	39.0	2/10	194.9	3.28	22
5	60	24.80 ± 0.18%	34.2	2/10	171.0	3.22	32
6	90	21.46 ± 0.95%	29.3	2/10	146.6	3.38	42
7	120	16.22 ± 0.06%	21.7	2/10	108.4	3.71	57

Date: 04.10.17 (a)

Solution	250	ml
H2O2	0.5	ml
Stock solution	31.25	ml
DI water	218.25	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.04 ± 3.41%					
1	0	34.75 ± 0.5%	48.7	4/10	121.8	6.86	0
2	15	32.42 ± 0.95%	45.3	4/10	113.3	3.68	7
3	30	28.82 ± 0.68%	40.1	4/10	100.2	3.48	18
4	45	25.23 ± 0.26%	34.8	4/10	87.1	3.4	29
5	60	21.68 ± 1.35%	29.6	4/10	74.1	3.44	39
6	90	16.95 ± 0.43%	22.7	4/10	56.9	3.66	53
7	120	14.29 ± 0.06%	18.9	4/10	47.2	3.95	61

Date: 04.10.17 (b)

Solution	250	ml
H2O2	4	ml
Stock solution	246	ml
DI water	0	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water							
1	0	33.55 ± 0.8%	47.0	1/20	939.4	6.81	0
2	15	33.07 ± 0.53%	46.3	1/20	925.4	3.61	1
3	30	31.54 ± 0.11%	44.0	1/20	880.7	3.66	6
4	45	29.73 ± 0.33%	41.4	1/20	827.9	3.7	12
5	60	27.69 ± 0.27%	38.4	1/20	768.4	3.69	18
6	90	24.30 ± 0.16%	33.5	1/20	669.4	3.7	29
7	120	21.50 ± 0.55%	29.4	1/20	587.7	3.74	37

Date: 09.10.17

Solution	250	ml
H2O2	2	ml

Stock solution	125	ml
DI water	123	ml
Fe (III)	0.0003	g

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		1.99 ± 1.05%					
1	0	38.42 ± 0.12%	54.1	1/10	540.8	10.18	0
2	5	39.87 ± 0.64%	56.2	1/10	561.9	6.86	0
3	15	37.1 ± 1.87%	52.2	1/10	521.5	5.12	4
4	30	33.86 ± 0.24%	47.4	1/10	474.2	3.59	12
5	45	32.60 ± 0.32%	45.6	1/10	455.8	3.22	16
6	60	30.36 ± 0.18%	42.3	1/10	423.1	3.06	22
7	90	24.19 ± 0.19%	33.3	1/10	333.1	3.12	38
8	120	18.38 ± 2.24%	24.8	1/10	248.3	3.88	54

Date: 10.10.17

Solution	250	ml
H2O2	2	ml
Stock solution	125	ml
DI water	123	ml
Fe (III)	0.005	g

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.38 ± 18.60%					
1	0	35.34 ± 1.24%	49.6	1/10	495.8	7.83	0
2	5	33.58 ± 0.11%	47.0	1/10	470.1	3.84	5
3	15	32.53 ± 0.70%	45.5	1/10	454.8	3.97	8
4	30	25.76 ± 2.16%	35.6	1/10	356.0	4.27	28
5	45	19.74 ± 2.87%	26.8	1/10	268.2	4.59	46
6	60	16.73 ± 2.65%	22.4	1/10	224.2	4.84	55
7	90	14.07 ± 0.47%	18.5	1/10	185.4	5.26	63

8	120	12.22 ± 0.68%	15.8	1/10	158.4	5.68	68

Date: 11.10.17

Solution	250	ml
H2O2	2	ml
Stock solution	125	ml
DI water	123	ml
Fe (III)	0.01	g

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.23 ± 4.62%					
1	0	37.34 ± 1.55%	52.5	1/10	525.0	7.75	0
2	5	39.20 ± 0.11%	55.2	1/10	552.2	6.35	0
3	15	36.37 ± 0.40%	51.1	1/10	510.9	4.97	3
4	30	31.32 ± 1.15%	43.7	1/10	437.2	3.7	17
5	45	19.08 ± 1.99%	25.9	1/10	258.5	4.49	51
6	60	14.85 ± 3.51%	19.7	1/10	196.8	5.11	63
7	90	12.74 ± 0.52%	16.6	1/10	166.0	5.55	68
8	120	11.54 ± 0.38%	14.8	1/10	148.5	5.92	72

Date: 12.10.17

Solution	250	ml
H2O2	2	ml
Stock solution	125	ml
DI water	123	ml
Fe (III)	0.02	g

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		1.80 ± 3.26%					
1	0	40.31 ± 0.75%	56.8	1/10	568.4	8.2	0
2	5	39.35 ± 0.14%	55.4	1/10	554.3	5.64	2

3	15	37.64 ± 0.50%	52.9	1/10	529.4	4.11	7
4	30	30.38 ± 1.11%	42.3	1/10	423.4	3.35	25
5	45	17.29 ± 2.87%	23.2	1/10	232.4	4.44	59
6	60	13.32 ± 1.07%	17.4	1/10	174.5	4.97	69
7	90	11.24 ± 1.81%	14.4	1/10	144.1	5.53	75
8	120	9.70 ± 0.52%	12.2	1/10	121.6	5.99	79

Date: 13.10.17

Solution	250	ml
H2O2	2	ml
Stock solution	125	ml
DI water	123	ml
Fe (III)	0.04	g

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.19 ± 7.83%					
1	0	38.81 ± 0.28%	54.6	1/10	546.5	5.06	0
2	5	37.64 ± 0.51%	52.9	1/10	529.4	4.31	3
3	15	36.87 ± 0.61%	51.8	1/10	518.2	3.64	5
4	30	27.54 ± 2.07%	38.2	1/10	382.0	2.87	30
5	45	15.01 ± 6.08%	19.9	1/10	199.1	3.71	64
6	60	10.49 ± 5.11%	13.3	1/10	133.2	4.35	76
7	90	7.93 ± 0.70%	9.6	1/10	95.8	5.03	82
8	120	7.44 ± 0.12%	8.9	1/10	88.7	5.44	84

Date: 16.10.17

Solution	250	ml
H2O2	2	ml
Stock solution	125	ml
DI water	123	ml
Fe (III)	0.08	g

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.06 ± 4.39%					
1	0	44.20 ± 0.66%	62.5	1/10	625.1	3.26	0
2	5	42.10 ± 1.73%	59.4	1/10	594.5	2.83	5
3	15	30.99 ± 3.14%	43.2	1/10	432.3	2.33	31
4	30	16.61 ± 7.41%	22.2	1/10	222.5	2.52	64
5	45	11.10 ± 6.84%	14.2	1/10	142.1	3.53	77
6	60	8.46 ± 4.72%	10.4	1/10	103.5	3.4	83
7	90	7.36 ± 0.39%	8.7	1/10	87.5	3.13	86
8	120	7.24 ± 0.70%	8.6	1/10	85.7	2.92	86

Date: 17.10.17

Solution	250	ml
H2O2	2	ml
Stock solution	125	ml
DI water	123	ml
Fe (III)	0.06	g

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.20 ± 1.45%					
1	0	38.25 ± 0.10%	53.8	1/10	538.3	3.26	0
2	5	35.76 ± 0.88%	50.2	1/10	502.0	1.86	7
3	15	32.23 ± 1.19%	45.0	1/10	450.4	1.61	16
4	30	18.9 ± 6.25%	25.6	1/10	255.9	1.7	52
5	45	11.75 ± 2.04%	15.2	1/10	151.6	2.42	72
6	60	9.05 ± 1.04%	11.2	1/10	112.2	3.4	79
7	90	6.89 ± 0.61%	8.1	1/10	80.6	3.13	85
8	120	6.02 ± 0.91%	6.8	1/10	67.9	2.92	87

Date: 25.10.17

Solution	250	ml
H2O2	0	ml
Stock solution	7.8	ml
DI water	242.2	ml
TiO2	0	g

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TOC*Dilution ratio (mg/l)	pH	Conversion
DI water		2.09 ± 8.19%					
1	0	18.58 ± 1.57%	25.1	8/10	31.4	8.64	0
3	30	18.57 ± 2.81%	25.1	8/10	31.4	5.42	0
4	60	18.74 ± 4.45%	25.4	8/10	31.7	5.32	0
5	90	18.45 ± 1.29%	24.9	8/10	31.2	5.2	1
6	120	18.47 ± 0.83%	25.0	8/10	31.2	4.94	1

Date: 04.11.17 Leachate

Solution	270	ml
H2O2	10	ml
Leachate	185	ml
DI water	75	ml
TiO2	0	g
Fe (III)	0	g

Sample	Time (min)	TC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TC*Dilution ratio (mg/l)	270/185	pH	Conversion
DI water		1.06 ± 14.30%						
1	0	23.19 ± 1.05%		0.02	1692.6	2470.3	8.3	
2	15	24.61 ± 0.30%	33.9	0.02	1671.4	2439.4	7.95	0
3	30	24.33 ± 0.16%	33.4	0.02	1654.8	2415.1	7.89	1
4	60	24.11 ± 0.05%	33.1	0.02	1646.5	2402.9	7.89	2
5	90	24.00 ± 0.13%	32.9	0.02	1639.6	2393.0	7.94	3
6	120	23.91 ± 0.23%	32.8	0.02	1692.6	2470.3	7.96	3

Date: 07.11.17 Leachate

Solution	250	ml
H2O2	2	ml
Leachate	53	ml
DI water	195	ml
TiO2	0	g
Fe (III)	0	g

Sample	Time (min)	TC (mg/l)	Dilution ratio	Correction of TC (mg/l)	TC*Dilution ratio (mg/l)	pH	TC Conversion	TIC (mg/l)	TIC*Dilution ratio (mg/l)	TIC Conversion	TN (mg/l)	TN*Dilution ratio (mg/l)	TN Conversion
DI water		1.64 ± 48.83%											
1	0	39.31 ± 0.58%	0.10	56.1	561.1	7.62	0						
2	8	38.67 ± 0.02%	0.10	55.1	551.4	7.5	2				42.62 ± 0.29%	422.90	0
3	30	39.29 ± 0.03%	0.10	56.1	560.8	7.27	0	24.44 ± 0.36%	244.40	0	42.19 ± 0.48%	421.90	0
4	60	38.10 ± 0.12%	0.10	54.3	542.8	7.1	3	23.50 ± 2.78%	235.00	4	41.65 ± 1.17%	416.50	2
5	90	36.07 ± 0.06%	0.10	51.2	512.0	7.1	9	23.39 ± 0.77%	233.90	4	43.06 ± 0.06%	430.60	-2
6	120	34.92 ± 0.21%	0.10	49.5	494.6	7.19	12	23.49 ± 0.05%	234.90	4	43.94 ± 0.28%	439.40	-4

Date: 08.11.17 Leachate

Solution	250	ml
H2O2	2	ml
Leachate	53	ml
DI water	195	ml
TiO2	0	g
Fe (III)	0.02	g

Sample	Time (min)	TC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TC*Dilution ratio (mg/l)	pH	Conversion
DI water		1.39 ± 26.01%					
1	0	34.07 ± 0.91%	48.2	0.10	481.8	6.52	0
2	30	32.03 ± 0.22%	45.1	0.10	450.9	6.68	6
3	60	30.09 ± 0.56%	42.1	0.10	421.5	6.7	13
4	90	28.81 ± 0.74%	40.2	0.10	402.1	6.76	17
5	120	26.96 ± 0.59%	37.4	0.10	374.1	6.87	22

Date: 10.11.17 Leachate

Solution	250.53	ml
H2O2	2	ml
Leachate	53	ml
DI water	195	ml
TiO2	0	g
Fe (III)	0.02	g
HCl	0.53	ml

Sample	Time (min)	TC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TC*Dilution ratio (mg/l)	pH	TC Conversion	TIC (mg/l)	TIC*Dilution ratio (mg/l)	TIC Conversion	TN (mg/l)	Correction of TN (mg/l)	TN*Dilution ratio (mg/l)
DI water		2.18 ± 2.81%											
Initial TC		37.24 ± 0.71%	53.0	0.02	2648.8								
1	0	26.10 ± 0.31%	55.3	0.10	553.2	4.99	0	6.09 ± 2.89%	60.90	0	38.78 ± 1.73%	21.8	217.6
2	2		36.1	0.10	361.1		35					20.9	208.7
3	30	22.44 ± 0.93%	30.6	0.10	305.7	4.77	45	4.57 ± 5.93%	45.70	25	37.96± 0.59%	20.4	204.3
4	60	18.60 ± 0.59%	24.8	0.10	247.5	4.45	55	2.28 ± 6.60%	22.80	63	38.73 ± 0.06%	20.8	208.5
5	90	15.31 ± 0.42%	19.8	0.10	197.7	4.56	64	1.16 ± 6.89%	11.60	81	40.63 ± 0.59%	21.9	218.7
6	120	13.27 ± 0.17%	16.7	0.10	166.8	4.88	70	1.51 ± 4.14%	15.10	75	40.35 ± 0.52%	21.7	217.2

Date: 11.11.17 Leachate

Solution	252.5	ml
H2O2	10	ml
Leachate	240	ml
DI water	0	ml
TiO2	0	g
Fe (III)	0.1	g
HCl	2.5	ml

Sample	Time (min)	TC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TC*Dilution ratio (mg/l)	pH	TC Conversion	TIC (mg/l)	TIC*Dilution ratio (mg/l)	TIC Conversion	TN (mg/l)	Correction of TN (mg/l)	TN*Dilution ratio (mg/l)
DI water		1.67 ± 16.45 %											
0 min no HCl		37.27 ± 0.40%	53.0	0.02	2651.1	8.21	0	22.52 ± 0.15%	1126	0	37.77 ± 0.47%	20.3	1016.5
0 min with HCl		22.57 ± 0.82%	30.8	0.02	1538.2	4.82	42	3.67 ± 3.37%	183.5	84	36.25 ± 0.77%	19.5	975.6
1	0	17.83 ± 0.09%	23.6	0.02	1179.4	4.49	56	1.30 ± 5.18%	65.00	0	34.05 ± 0.44%	18.3	916.4
2	30	16.23 ± 1.10%	21.2	0.02	1058.2	3.33	60	0.6905 ± 2.80%	34.53	47	34.93 ± 0.05%	18.8	940.1
3	60	14.73 ± 3.14%	18.9	0.02	944.7	2.82	64	0.5404 ± 2.93%	27.02	58	35.16 ± 0.09%	18.9	946.3
4	90	13.87 ± 1.01%	17.6	0.02	879.6	2.59	67	0.7191 ± 13.43%	35.96	45	33.05 ± 0.48%	17.8	889.5
5	120	13.00 ± 0.35%	16.3	0.02	813.7	2.58	69	0.7152 ± 4.03%	35.76	45	34.89 ± 0.23%	18.8	939.0
6	150	10.98 ± 1.71%	13.2	0.02	660.8	2.74	75	0.363 ± 5.58%	18.15	72	34.58 ± 0.09%	18.6	930.6
Foam		265.6 ± 15.18 %		0.25	1605.2								

Date: 13.11.17 Treated leachate

Solution	250.1	ml
H2O2	3.5	ml
Leachate	246.5	ml
DI water	0	ml
TiO2	0	g
Fe (III)	0.035	g
HCl	0.1	ml

Sample	Time (min)	TC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TC*Dilution ratio (mg/l)	pH	TC Conversion	TIC (mg/l)	TIC*Dilution ratio (mg/l)	TIC Conversion	TN (mg/l)	Correction of TN (mg/l)	TN*Dilution ratio (mg/l)
DI water		0.9683 ± 18.45%											
0 min no HCl		32.84 ± 0.69%	46.3	0.05	926.3	7.98	0	1.60 ± 0.08%	32		11.11 ± 0.87%	8.2	163.5
0 min with HCl		31.54 ± 0.95%	44.3	0.05	886.9	4.88	4	0.3907 ± 7.71%	7.814	0	11.49 ± 1.04%	8.5	169.1
1	30	31.27± 0.08%	43.9	0.05	878.7	4.11	5	0.4327 ± 0.80%	8.654	-11	11.36 ± 1.23%	8.4	167.2
2	60	30.51 ± 0.15%	42.8	0.05	855.7	3.86	8	0.5877 ± 11.42%	11.754	-50	11.64 ± 0.29%	8.6	171.3
3	90	28.53 ± 0.45%	39.8	0.05	795.8	3.55	14	0.8496 ± 3.89%	16.992	-117	11.47 ± 0.78%	8.4	168.8
4	120	26.90 ± 1.19%	37.3	0.05	746.4	3.34	19	0.7173 ± 0.66%	14.346	-84	10.09 ± 0.83%	7.4	148.5
5	150	24.10 ± 0.60%	33.1	0.05	661.6	3.24	29	1.09 ± 8.04%	21.8	-179	11.27 ± 0.83%	8.3	165.9

Date: 14.11.17 Phenol

Solution	250	ml
H2O2	2	ml
Stock	112.2	ml
DI water	135.8	ml
TiO2	0	g
Fe (III)	0.02	g
Phenol	0.0125	g

Sample	Time (min)	TC (mg/l)	Dilution ratio	Correction of TC (mg/l)	TC*Dilution ratio (mg/l)	pH	Conversion	Phen. Conversion
DI water		2.26 ± 11.16%						
1	0	35.20 ± 1.51%	0.1	49.4	493.8	6.32	0	0
2	5	34.77 ± 0.29%	0.1	48.8	487.5	4.33	1	31
3	15	33.95 ± 0.16%	0.1	47.6	475.5	3.85	4	82
4	30	32.84 ± 0.37%	0.1	45.9	459.3	2.5	7	99
5	45	30.69 ± 0.87%	0.1	42.8	428.0	1.8	13	100
6	60	26.41 ± 1.16%	0.1	36.6	365.5	1.69	26	100
7	90	14.19 ± 1.79%	0.1	18.7	187.2	2.67	62	100
8	120	10.31 ± 0.99%	0.1	13.1	130.5	3.39	74	100

Date: 15.11.17 Phenol

Solution	250	ml
H2O2	2	ml
Stock	99.5	ml
DI water	148.5	ml
TiO2	0	g
Fe (III)	0.02	g
Phenol	0.025	g

Sample	Time (min)	TC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TC*Dilution ratio (mg/l)	pH	Conversion	Phen. Conversion
DI water		1.64 ± 3.97%						
1	0	33.51 ± 1.32%	46.9	0.1	469.1	5.82	0	0.0
2	5	30.71 ± 12.11%	42.8	0.1	428.3	4.79	9	16.3
3	15	-	-	0.1	-	3.23	-	95.4
4	30	30.61 ± 1.75%	42.7	0.1	426.8	1.72	9	99.7
5	45	28.38 ± 0.86%	39.4	0.1	394.3	1.47	16	100.0
6	60	22.85 ± 2.14%	31.4	0.1	313.5	1.43	33	100.0
7	90	11.78 ± 4.55%	15.2	0.1	152.0	2.52	68	100.0
8	120	7.85 ± 1.86%	9.5	0.1	94.6	3.33	80	100.0

Date: 16.11.17

Solution	250	ml
H2O2	2	ml
Stock solution	125	ml
DI water	123	ml
HCl	0.02	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	TOC*10 (mg/l)	pH	Conversion
1 no HCl	0	36,82 ± 1,32%	51.7	517.4	7.11	0
2 with HCl	0	36,33 ± 0,07%	51.0	510.3	4.54	1
3	15	35,52 ± 0,04%	49.8	498.5	3.94	4
4	30	35,07 ± 0,03%	49.2	491.9	3.24	5
5	45	33,66 ± 0,47%	47.1	471.3	2.27	9
6	60	32,06 ± 0,25%	44.8	448.0	1.82	13
7	90	28,52 ± 1,15%	39.6	396.3	1.77	23
8	120	20,74 ± 3,19%	28.3	282.8	2.42	45

Date: 20.11.17

Solution	253.3	ml
H2O2	2	ml
Stock solution	125	ml
DI water	123	ml
NaOH	3.3	ml

Sample	Time (min)	TOC (mg/l)	Correction of TC (mg/l)	TOC*10 (mg/l)	pH	Conversion
1 no NaOH	0	39.05 ± 0.94%	55.0	550.0	6.4	0
2 with NaOH	0	36.32 ± 0.35%	51.0	510.1	8.15	7
3	15	35.54 ± 0.19%	49.9	498.7	4.7	9
4	30	33.77 ± 0.63%	45.8	458.3	3.34	17
5	45	31.36 ± 0.66%	43.8	437.7	2.73	20
6	60	29.19 ± 1.27%	40.6	406.1	2.63	26
7	90	24.16 ± 2.23%	33.3	332.7	3.01	40
8	120	18.68 ± 2.62%	25.3	252.7	4.14	54

Date: 21.11.17 Treated leachate

Solution	251.14	ml
H2O2	8	ml
Leachate	243	ml
DI water	0	ml
TiO2	0	g
Fe (III)	0.035	g
HCl	0.14	ml

Sample	Time (min)	TC (mg/l)	Correction of TC (mg/l)	Dilution ratio	TC*Dilution ratio (mg/l)	pH	TC Conversion	TIC (mg/l)	TIC*Dilution ratio (mg/l)	TIC Conversion	TN (mg/l)	Correction of TN (mg/l)	TN*Dilution ratio (mg/l)	TN Conversion	TOC	TOC convertion
0 min no HCl		32.95 ± 0.58%	46.5	0.05	659	7.71	0	1.51 ± 3.96%	30.2	0	10.74 ± 0.47%	7.9	214.8	0	899.4	0
0 min with HCl		31.76 ± 1.50%	44.7	0.05	635.2	4.82	4	0.3004 ± 20.84%	6.008		9.69 ± 0.26%	7.1	193.8	10		
1	30	28.56 ± 5.20%	39.8	0.05	571.2	3.27	13	1.23 ± 3.39%	24.6	19	9.46 ± 1.22%	7.0	189.2	12	772.1	14
2	60	25.84 ± 0.30%	35.7	0.05	516.8	2.68	22	2.09 ± 1.03%	41.8	-38	9.49 ± 0.50%	7.0	189.8	12	672.5	25
3	90	22.66 ± 0.88%	30.9	0.05	453.2	2.47	31	1.78 ± 1.83%	35.6	-18	10.78 ± 0.27%	7.9	215.6	0	582.4	35
4	120	18.66 ± 1.28%	24.8	0.05	373.2	2.71	43	1.42 ± 1.40%	28.4	6	9.63 ± 0.57%	7.1	192.6	10	468.5	48
5	150	15.09 ± 1.24%	19.4	0.05	301.8	3.21	54	1.13 ± 3.05%	22.6	25	10.29 ± 0.73%	7.6	205.8	4	366.2	59