Photocatalytic Degradation of Organic Pollutants in Wastewater

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DECLARATION

I hereby declare that this manuscript, entitled “Photocatalytic Degradation of Organic Pollutants in Wastewater”, 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

This work presents experimental results on the treatment of a synthesized wastewater by means of photocatalytic Advanced Oxidation Process (AOPs) constituted by a combination of a single oxidant. The experiment was conducted with the presence of UV light, TiO_2 catalyst and H_2O_2 oxidant in a batch recycle reactor. The total volume of the reactor was 250 mL with 55.8 mL of the effective annular volume of a photoreactor. Fluid inside photoreactor was irradiated by 254 nm, 6W ultraviolet light. Each experiment was conducted for 120 min accompanied by total carbon and HPLC analysis. The feed wastewater was prepared from D – Glucose anhydrous ($C_6H_{12}O_6$), Sodium hydrogen carbonate ($CHNaO_3$), Potassium hydrogen carbonate ($CHKO_3$), Ammonium hydrogen carbonate (CH_5NO_3), Peptone and Lab Lemco, with initial total carbon 1080 mg L^{-1}. The effect of reagents' initial concentration on total carbon removal was studied to derive the optimum operating conditions. As a result, obtained initial total carbon concertation was found to be 32 mg L^{-1}. The optimum amount for TiO_2 loading was 0.5 g L^{-1} with 58% TC removal and 53% with 66.6 mg L^{-1} H_2O_2. Addition of both reagents to process, catalyst, and oxidant, did not result in better performance, only 52% total carbon removal was observed. Besides, the effect of phenolic compound presence on the photocatalytic treatment of synthesized wastewater was examined. Experiments were conducted for phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-nitrophenol at 5

ppm and 10 ppm concentrations. The conversion of the model compound was always higher than corresponding total organic carbon removal, whereas introduction of H_2O_2 led to higher total carbon removal and higher phenolic compound decomposition. Synthetic wastewater with 10 ppm phenol, keeping 32 mg L^{-1} initial TC concentration, treated by UV/TiO_2 showed 48% TC and 98% phenol removal, while the H_2O_2 addition markedly enhanced the process obtaining 100% phenol removal after 45 minutes and 80% TC removal. Results for 10 ppm 2-chlorophenol with the only TiO_2 demonstrated 81% total carbon removal with the complete decomposition of 2-chlorophenol. Results of TC removal were also obtained for 2,4-Dichlorophenol at 5 ppm, 10 ppm and with the addition of H_2O_2, 40%, 59%, and 88%, respectively. 2,4-DCP oxidation was 91% at 5 ppm concentration, 95% at 10 ppm and 100% in the presence of hydrogen peroxide. For 2,4,6-Trichlorophenol, TC conversion at 5 ppm was 36%, at 10 ppm was 44% and 83% with H_2O_2, and 100% of 2,4,6-TCP oxidation by the end process. 4-Nitrophenol also degraded entirely after 120 minutes and resulted in 84% conversion of TC at 10 ppm concentration with process containing H_2O_2 and catalyst.

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Chapter 1 – Introduction

Water pollution and lack of clean drinking water are among the most significant problems worldwide. The significant part of this issue refers to the pollution caused by disposal of industrial wastewater. The industrial growth and rise in population have resulted in high demand for resources, whereas the release of toxic materials and wastes to the environment has posed a risk to natural ecosystems and human health. Therefore, it is essential to make sure that disposed water is appropriately treated so that it has minimal impact on aquatic life and the environment. Moreover, treated water can be converted to a potential profit stream for the industry by reusing it in the domestic area, or for agricultural purposes. The concentration of typical wastewater contaminates is presented *Table 1.1*.

Table 1.1: Composition of pollutants in wastewater [1]

Parameter	**Industrial Effluent**
COD [mg L^{-1}]	6000 to 11000
BOD [mg L^{-1}]	1000 to 6000
TDS [mg L^{-1}]	28000
TSS [mg L^{-1}]	100
BOD_5/COD	0.2-0.5
pH	5.5-6
Free hydrocarbons	Up to 1000
Suspended Solids	Up to 500
Phenol	10 to 100
Benzene	5 to 15
Sulphides	Up to 100
Ammonia	Up to 100

The main objective of wastewater treatment is to allow produced or used water from industry or agriculture, or municipal usage to be disposed of without danger to human health or unacceptable damage to the environment. Currently, three principal steps in treating wastewater are available, which are preliminary, secondary and tertiary steps. The purpose of the *preliminary step* is to remove coarse solids and other large substances that can be easily done by coarse screening and grit removal, to eliminate damage to process units. After that additional *primary* treatment is applied to remove settable organic and inorganic compounds/solids from sludge by sedimentation of solids and skimming of material that floats. In this step up to 50% of biochemical oxygen demand (BOD), 50% to 70% of total suspended solids and approximately 60% of oil and grease can be removed [2]. In *secondary treatment,* the target is to remove residual inorganic and organic compounds from primary treatment. Exist various methods of secondary treatment including physical, chemical, mechanical, biological and combined techniques [2-3]. It can be stated that secondary step is the most important part of wastewater treatment. Therefore, the majority of prior research focused on the development of the most favorable secondary treatment technique. *Tertiary treatment* is used to remove nitrogen, phosphorous, additional solids, dissolved solids, heavy metals and refractory organics. It is also called advanced treatment process and usually used with or instead of secondary treatment. However, a challenging problem which arises in this is that conventional water treatments are not able to completely remove toxic compounds. Besides, they also perform the long-time operation and requires a high cost for implementation [4]. A number of works have shown that this problem can be overcome by using Advanced Oxidation Process (AOPs). AOPs was developed specifically for cleaning water from highly toxic pollutants. Moreover, it is used as additional treatment after biological treatment, as biological reactors are not able to remove some toxic organic pollutants [5]. The general principle of AOPs treatment is a generation of the very high oxidative •OH radicals that has potential to mineralize the organic substances in aqueous media [6]. Although there are many studies, the research in AOPs techniques has limitations, which addressed in the following sections.

The aim of this thesis was to investigate the performance of photocatalytic AOPs technique, with TiO_2, on the degradation of organic compounds in synthesized wastewater. As one of the goal, research focused on finding optimal conditions for photocatalytic process treatment. These operating conditions further applied for photocatalytic degradation process of organic pollutants combined with phenolic compounds in aqueous media.

Chapter 2 – Literature Review

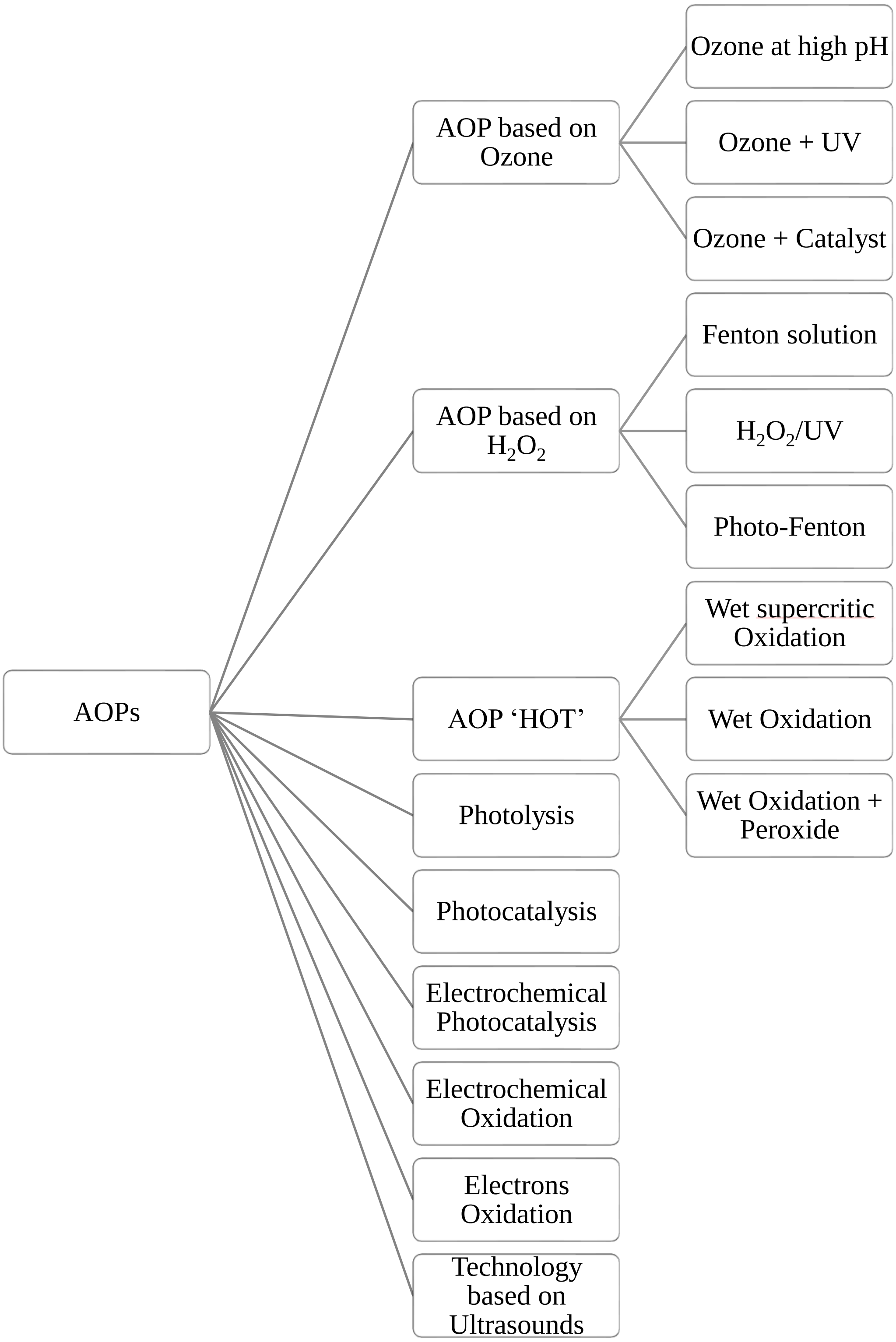
AOPs for wastewater treatment is used globally due to its ability to remove small amounts of hazardous health pollutants. Moreover, AOP treatment used in treating industrial and municipal wastewater, as this procedure is based on the generation of highly oxidative hydroxyl radicals which can break complex toxic molecules in wastewater, thus making them more biologically degradable. The AOPs method was firstly introduced in 1980 and designed to treat potable water [7]. AOPs involve two stages of oxidation, the first is a generation of the strong oxidizing agent, and the second is the reaction of oxidant with organic contaminants in water. The common oxidizing agent for AOPs is hydroxyl radicals (•OH). These radicals, when AOPs applied for wastewater treatment, acts as powerful oxidizing agents, and have enough potential to efficiently destruct pollutants and make wastewater less toxic, even eliminate their toxicity [7-9]. In *Table 2.1*, is presented the oxidants used in different wastewater techniques with the corresponding potential, and among all of them •OH has the highest potential. It is essential to understand, that efficiency of treatment depends on the selected type of AOPs, physical and chemical properties of pollutants and operating parameters of the process. A great number of techniques are classified under the broad definition of AOPs. The most widely used methods are presented in classification *Figure 2.1*.

Table 2.1: The oxidation potential of various oxidants [11]

Reactive species	Potential (V)
Hydroxyl radicals (•OH)	2.86
Oxygen (O_2)	2.42
Ozone molecule (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.78
Chlorine (Cl_2)	1.36
Chlorine dioxide (ClO_2)	1.27
Oxygen molecule (O_2)	1.23

AOPs can be divided into two main categories, depending on reagents used: homogeneous and heterogeneous.

Figure 2.1: AOP classifications [10]



2.1 Homogeneous AOPs.

The principle work of homogeneous AOPs depends on the presence of UV or visible light and oxidants, which generates •OH radicals. Mostly, Ozone (O_3), O_2 and hydrogen peroxide (H_2O_2) is used as source of these radicals.

2.1.1 Photochemical AOPs

The photochemical process by UV light and H_2O_2 were investigated on its organic pollutant oxidation efficiency. *Equation 2.1 and 2.2* shows the reaction of •OH generation. When H_2O_2 is irradiated by UV light, it forms HO_2^- anions, which in turn generates hydroxyl radicals.

$$H_2O_2 \rightleftarrows HO_2^- + H^+ \tag{2.1}$$

$$HO_2^- + H_2O \xrightarrow{hv} 2HO^{\bullet} + OH^- \tag{2.2}$$

The •OH radicals react almost immediately with targeted compounds and decompose them to intermediate compounds. Some compounds can be mineralized towards CO_2 and H_2O. The significant factors affecting the effectiveness of the process are the ratio between H_2O_2 and organic pollutants concentration and pH of the solution.

2.1.2 AOPs based on Ozone

The Ozone based AOPs is found to be eco-friendly treatment process, as ozone oxidizes into oxygen without forming by-products. Moreover, Ozone is readily provided one atom of oxygen, thus providing active oxidizing agent. Ozonation process can go through two paths: the first method involves a reaction between ozone dissolved compounds, while second implies the reaction between the dissolved compound and hydroxyl radicals formed by ozone decomposition [12]. In order to increase the effectiveness of ozonation, H_2O_2 or UV light is induced into the process and it follows the reaction presented by *Equation 2.3* and *2.4* [10, 12].

O_3/H_2O_2 process:

$$H_2O_2 + 2O_3 \rightarrow 2HO^{\bullet} + 3O_2 \tag{2.3}$$

O_3/UV process:

$$O_3 + H_2O \overset{hv}{\rightarrow} 2HO^{\bullet} + O_2 \tag{2.4}$$

The combined method of O_3/UV/H_2O_2 is found to be the most effective process for highly polluted wastewater, as it has various ways to form hydroxyl radicals. Moreover, pH of solution plays also a significant role. Ozone reacts with a compound in a molecular form at low pH, while with high pH ozone is decomposed before it reacts with organic substrate [13]. The main disadvantages of ozonation process are high energy cost for implementation in industrial scale.

2.1.3 AOPs based on Fenton

Wastewater was also treated by using iron salt and hydrogen peroxide called Fenton process. This process started to attract attention in 1894 when ferric ions in combination with H_2O_2 had significantly improved oxidation of tartaric acid

[14]. Addition of H_2O_2 to wastewater containing ferrous salts generates strong oxidants that readily oxidizes organic compounds. [11, 14, 15]. Non-toxicity of ferric ions and easy handling of hydrogen peroxide, makes photo-Fenton process suitable for wastewater treatment. The presence of ferric ions, which acts as a catalyst, initiates the decomposition of H_2O_2. The process generates the hydroxyl radicals that responsible for the decomposition of organic pollutants. Irradiation with UV light improves the process, additional hydroxyl radicals are formed, and it also leads to regeneration of catalyst [12-16]. Fe^{2+} is used for the formation of hydroxyl radicals. As long as H_2O_2 is present, the concentration of Fe^{2+} remains low, as it generates Fe^{3+}. After H_2O_2 entirely consumed, Fe^{3+} regenerates Fe^{2+} as shown in *Equation 2.5*. Photo-Fenton is two-step removal process, which involves oxidation and coagulation [16].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \tag{2.5}$$

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + H^+ + HO^\bullet \tag{2.6}$$

The regeneration process of Fe^{2+} in the reaction allows adding a small amount of reagent, thus making it beneficial for industrial use. However, the regeneration and separation of ferric ions from treated wastewater is difficult on a large scale, and it produces additional sludge.

2.2 Heterogenous AOPs

Heterogenous AOPs requires the presence of semiconductors as a photocatalyst, which has already proved their efficiency in removing the organic compounds from wastewater [17]. Photocatalytic degradation process is found to be sustainable treatment technology with “zero” waste after process [18]. Also, for degradation of phenols and chlorinated phenols, the photocatalytic technique is found to be favorable, as no oxidant is required during the reaction and no need for further separation than with other AOPs techniques.

According to studies, the metal oxide nanoparticles more preferred catalyst for water purification, due to high surface areas and better photolytic properties. The most widely used ones are TiO_2, ZnO, CeO2, CdS, etc. They demonstrated high effectiveness in organic degradation in aqueous streams [18, 19]. Moreover, this process is driven by different sources of light, like UV, solar or visible light. The main characteristics of the catalyst are its photocatalytic activity, resistance to photo-corrosion, biological immunity and cost. Photocatalytic activity is dependent on the structural properties, band gap, surface area, particle size distribution, porosity and surface hydroxyl density [20].

2.2.1 TiO_2 catalyst

Among research on many semiconductors as photocatalysts, the general conclusion is that TiO2 is more effective because of its characteristics. Comparing to other semiconductor powders, TiO_2 has maximum quantum yields due to high photocatalytic activity, photo-corrosion resistance, and low cost and toxicity [21-23]. In 1972, Honda and Fujshima first demonstrated the potential of using TiO_2 based semiconductor in water purification. Compared to CdS catalyst, photocatalytic activity for TiO_2 in phenol decomposition demonstrated better performance [22]. Sakthivel observed that TiO_2 had greater photocatalytic efficiency than α-Fe2O3, ZrO_2, CdS, WO_3 and SnO_2 under similar conditions [21]. ZnO demonstrated better results than TiO_2, but Augugliaro argued that despite the higher activity of ZnO, TiO_2 is more photochemically stable [23]. The same conclusion was withdrawn during experiments done by Wu, who compared TiO_2 with ZnO and SnO_2 [24]. Also, a study by Xiang et al. illustrates that titanium TiO_2 performs better than other semiconductors in producing •OH [24]. The experiment based on the production of •OH in water solution under UV lamp irradiation using a number of different semiconductors (ZnO, BiOCl, CdS, WO_3, rutile $TiO_{2,}$ etc.) to see which of catalyst could give the best performance. The photoluminescence (PL) technique with coumarin (COU) as a probe molecule were used to compare those. As a result, the characteristic of TiO_2 including the pH values and phase structure is identified to be the most efficient in producing the •OH. Moreover, the paper states that the product can be boosted with the addition of anatase and rutile.

Many research was conducted on investigating the impact of crystal structure and size on photocatalytic activity of TiO_2 [26, 27]. Two crystal structure, anatase, and rutile have been studied the most, whereas studies on the third type of structure, brookite, are still rare [23, 27-30]. The difference between anatase and rutile structure based on the position of oxygen and titanium ions. In case of anatase structure, oxygen ion position shows triangular arrangement on the exposed catalyst surface. It allows better absorption of organic pollutants which further reacts with titanium ion, which position creates favorable conditions for the reaction. This type arrangement does not occur in rutile structure, thus anatase has relatively higher photocatalytic activity [30-32]. Augugliaro also suggested that difference in performance between two structures is upon electronic and chemical properties [23]. Studies have shown that photochemical activity of the catalyst can be improved by adding rutile rather than using pure anatase phase [33-35]. Introduction of rutile provides wider pore size distribution and mesoporosity, which can increase the effectiveness of the catalyst. It was reported that mixture of both crystal structures results in maximum photocatalytic activity [33-35]. The Degussa P25 that composed of 70% of anatase and 30% of rutile structure gives the better performance compared to other combinations [33, 35]. The main factor that impacts on photocatalytic activity is a surface area, larger the surface better the performance. Anatase has 10 m^2/g, rutile 20 m^2/g, while Degussa P25 corresponds to 50 m^2/g of surface area. Large surface area results from the small size of particles, as it, in turn, gives more active sites, consequently providing with greater adsorbability of the organic pollutants on the surface [37]. The most critical factors of a photocatalytic reactor configuration are light distribution and a total surface area of irradiated catalyst per unit volume within the reactor.

TiO_2 has a wide bandgap, 3.2 eV and its radiation in the near UV range, which is a material advantage compared to other semiconductors. At the same time, this wide band gap limits light adsorption to only UV light and decreases the potential of using TiO_2 with visible light [38]. When the UV light is irradiated on the TiO_2 surface, it gets excited and generates a pair of electrons and holes in the conduction (e^-_{cb}) and valence band (hv^+_{vb}) with reductive and oxidative capacity, respectively. The hole adsorbs the surrounding water molecules and gets oxidized to form a hydroxyl radical [3, 20].

$$TiO_2 + hv \rightarrow e^-_{cb} + hv^+_{vb} \tag{2.7}$$

$$hv^+_{vb} + OH^-{}_{surface} \rightarrow HO^\bullet \tag{2.8}$$

$$hv^+_{vb} + H_2O_{absorbed} \rightarrow \ HO^\bullet + H^+ \tag{2.9}$$

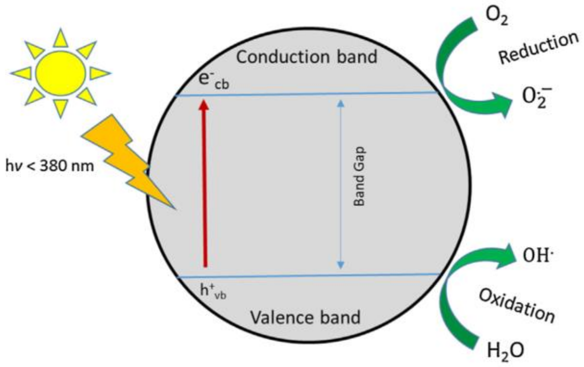
$$e^-_{cb} + O_{2_{absorbed}} \rightarrow O_2^\bullet \tag{2.10}$$

$$hv^+_{vb} + Organic \ \rightarrow \ CO_2 \tag{2.11}$$

$$HO^\bullet + Organic \ \rightarrow \ CO_2 \tag{2.12}$$

OH^-, H_2O and $O_2^\bullet$ react with electrons and holes on the surface of catalyst leading to the generation of hydroxyl radicals. The generation of hydroxyl radical is a cyclic process and initiates the series of reactions on the TiO_2 surface as shown in the schematic representation in *Figure 2.2* [3].

Figure 2.2: Schematic mechanism of TiO_2 photocatalysis [38]



2.2.2 Wastewater treatment by UV/TiO_2 process

Kositzi et. al. studied the effect of photocatalytic degradation of synthetic municipal wastewater with initial 200 mg L^{-1} dissolved organic carbon (DOC) and 250 mg L^{-1} of chemical oxygen demand (COD) characteristics [40]. Experiment with use of TiO_2 P-25 as photocatalyst resulted in 18% of DOC reduction, while in the presence of additional oxidant H_2O_2 reduction of DOC was 55% and with $Na_2S_2O_8$ lead to 73%. The process was also investigated on the treatment of wastewater with high concentration of organic carbon. As an example, Ghaly conducted an experiment with the use of the photocatalytic process with the addition of H_2O_2 under solar irradiation for 2000 mg L^{-1} COD value mill wastewater. 0.75 g L^{-1} of TiO_2 loading removed COD by 70.5%, whereas addition of H_2O_2 enhanced the process up to 78% [41]. It was also revealed that high photocatalytic activity occurs at pH around 6-10. The effect of pH tested on wastewater form agriculture with initial pH of 9 and high content of organic matter. However, adjustment of pH to 6, 7 and 8 did not lead to enhancement of process on COD removal [42]. Significant removal of COD was observed to occur at low pH, around 2-4, specifically for wastewater containing dyes [43-45]. However, it is difficult to conclude with optimal pH from literature, due to difference in treated wastewater composition.

2.2.3 Kinetics in TiO_2 photocatalyst

The kinetics of photocatalytic oxidation of organics can be described by Langmuir-Hinshelwood (L-H) approach [18]. The following *Equation 2.13* derives the rate reaction:

$$r = k_{overall}(\frac{K_A K_D C_A C_D}{1+K_A C_A+K_D C_D}) \tag{2.13}$$

Where r is the reaction rate, the $k_{overall}$ kinetic rate constant, K_i Langmuir adsorption constants, C_i concentrations, A and D for the reactants. The photocatalytic process starts with the interaction of oxygen and water with generated charge carriers on the photoinduced surface of the catalyst. The L-H approach implies that first step is adsorbance of reactants on the catalyst surface. It follows with the reaction that generates products that eventually desorb from the surface.

Advantages of the photocatalytic process with TiO_2 semiconductor are as follows:

- UV/TiO_2 can perform at a higher wavelength, 300 to 380 nm, than other UV assisted oxidation processes [44, 45].
- This process has been studied for many organic compounds degradation.

However, this process has also some drawbacks such as:

- The full-scale application has not been realized, yet.
- Pre-treatment of feedstock is required to avoid the fouling of active TiO_2 sites and inhibition of catalyst [46]. Fouling is occurred due to the presence of inorganic particulates and non-organic materials. Presence of alkalinity and anionic species observed to inhibit catalyst activity.
- With the initially low concentration of dissolved oxygen in feedstock additional oxygen sparging will be required to increase the efficiency of process performance [46].

2.3 Intermediate by-products

Photocatalytic degradation of phenols has two phases, phenols transform to by-products in intermediate compound phase, and then these by-products are removed in mineralization phase by transformation to carbon dioxide and water [49]. According to literature, the possible by-products of phenol during an intermediate phase are catechol(1,2-dihydroxybenzene), benzoquinones, hydroquinone (1,4-dihydroxybenzene) resorinone (1,3-dihydroxybenzene), biphenyl diol, muconic acid, maleic acid, fumaric acid, oxalic acid and formic acid [51-53]. These intermediate products have C-H, H-O, C-O bonds that are weak, thus, they can be easily oxidized further to CO_2 and H_2O (*Figure 2.3*). The decomposition tendency of phenol to by-products presented in *Figure 2.4.*

Figure 2.3: By-products of phenol decomposition [49]

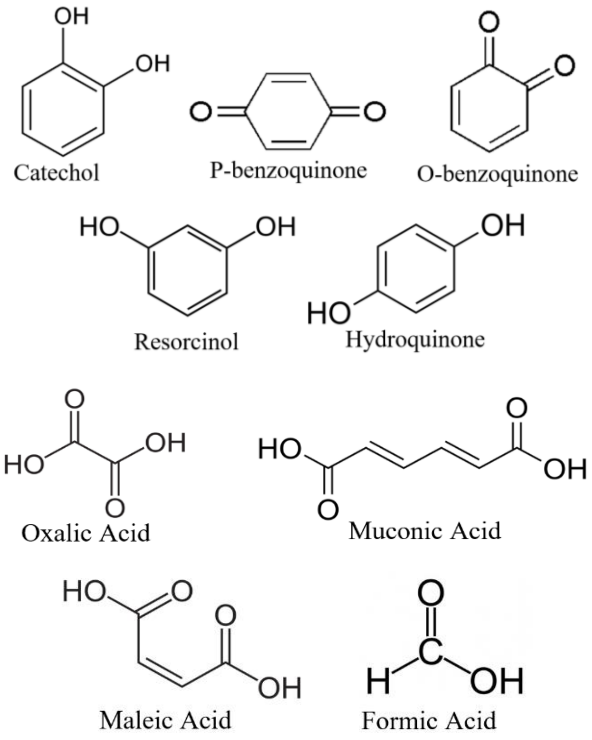
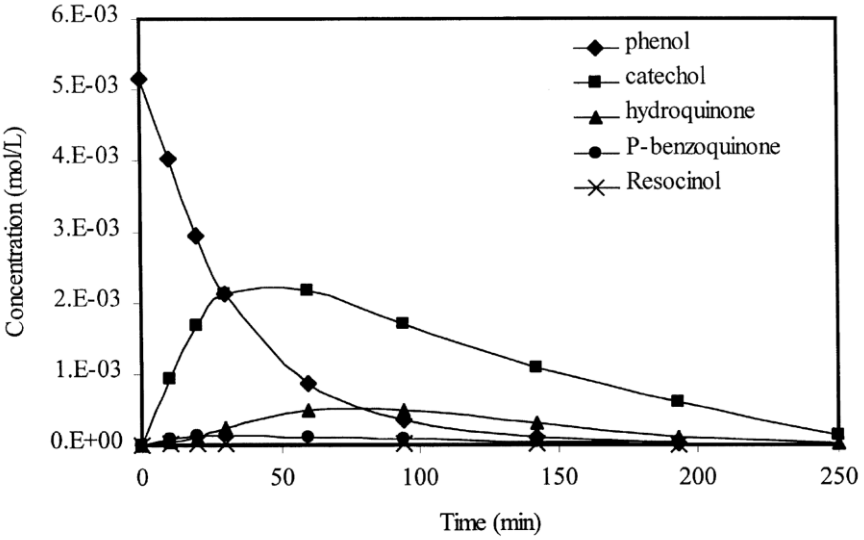


Figure 2.4: Phenol degradation to intermediate products [53]



According to previously conducted research, the possible intermediates of 2-CP degradation are almost the same as for phenol: catechol, hydroxyhydroquinone (HHQ) and additionally chlorohydroquinone (CHQ), only chlorinated detected intermediate [54]. Moreover, the formation of intermediates with higher carbon atoms as 2-hydroxy benzaldehyde (HB) and [1,1’-biphenyl]-2,2’-diol (BPD) was reported and corresponding HPLC peaks observed at 4.20 and 11.99 minutes, respectively [52]. Degradation of 2,4-DCP also goes through intermediate and mineralization phase as phenol, leading to the formation of 4-chlorophenol, phenol, 3,5-dichlorocatechol, HHQ, 4-hydroxybenzaldehyde [55]. Also, maleic and acetic acid presence was reported during 2,4-DCP decomposition, and the retention time of intermediates detected in chromatography used to be lower than for parent compound [56]. In terms of 4-Nitrophenol, the most probable intermediates in the photodegradation are 1,2-dihydroxy-4-nitro-cyclohexadienyl radical which then transforms to 4-nitrocatechol [57].

2.4 Scope of the work

There is a considerable amount of existing studies on photocatalytic treatment of wastewater, however, they have almost exclusively focused on mineralization of only one model component in aqueous solution. No study to date has examined the treatment of municipal synthesized wastewater containing both organic pollutants and phenolic compounds. Therefore, this paper delivers the results of photocatalytic AOPs treatment of typical industrial wastewater with organic compositions containing small concentrations of phenols, so far lacking in the scientific literature.

This work presents results of photocatalytic degradation of synthesized wastewater with TC concentration in the range of 30-500 mg L^{-1}. Firstly, the effect of TiO_2 loading and H_2O_2 concentration was investigated on total carbon removal efficiency aiming to obtain optimal operating condition for the process. Further, results obtained were applied on the treatment of organic wastewater containing phenols. Compounds as phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-nitrophenol at 5ppm and 10 ppm concentration were added to stock solution. Moreover, the applicability of combined process on total carbon removal and mineralization of phenolic compounds was examined.

Chapter 3 - Materials and Methods

3.1 Methodology

The main objective of the research was to demonstrate the feasibility of photocatalytic AOPs processes on treatment of synthetic wastewater. In order to achieve this, the work was organized in following steps:

- Determine optimal conditions for UV/TiO_2 and UV/H_2O_2 processes.
- Evaluate the combination of TiO_2 and H_2O_2 on organic compound degradation.
- Investigate the effect of phenolic compounds present on the efficacy of the photocatalytic process.

3.2 Materials

D – Glucose anhydrous ($C_6H_{12}O_6$), Sodium hydrogen carbonate ($CHNaO_3$), Potassium hydrogen carbonate ($CHKO_3$), Ammonium hydrogen carbonate (CH_5NO_3) and Peptone (a mixture of peptides and amino acids) were purchased from Fisher Scientific. Lab Lemco, which contains total nitrogen 12.4%, amino nitrogen 2.5%, and chloride 1.1%, was supplied by Oxoid. 2-Chlorophenol (≥99%), with a molecular weight of 128.56 mg L^{-1} and 1.24 g mol^{-1} density, 2,4,6-Trichlorophenol (≥98%), 4-Nitrophenol (≥99%) were supplied by Sigma Aldrich. 2,4-Dichlorophenol (≥99%) was purchased from Acros Organics. Mentioned chemicals were used to synthesize feedstock wastewater for the reactor. Titanium (IV) Dioxide P-25 (≥99%) used as photocatalyst and Hydrogen Peroxide (37.6%), the source of hydroxyl radicals, were obtained from Sigma-Aldrich and "Фирма Скат", respectively. All reagents were used without additional purification and deionized water was used.

3.3 Synthetic Wastewater Characterization

The experimental initial concentration of carbon of the stock solution was 1080 mg L^{-1}. Total inorganic carbon (TIC) present in solution was approximately 4% of TC. Synthesized wastewater had the following characteristics as shown in *Table 3.1.*

Table 3.1: Composition of synthesized wastewater

Component	**Molecular Weight [g mol^{-1}]**	**Concentration [mg L^{-1}]**	**Total Carbon [mg L^{-1}]**
D – Glucose anhydrous	180.16	1600	640
Bacterial Peptone		480	198*
Lab Lemco		320	134.2*
Ammonium Hydrogen Carbonate	79.06	160	24
Potassium Hydrogen Carbonate	100.12	80	9.5
Sodium Hydrogen Carbonate	84	80	11.4
Total Carbon (theoretical)			1017

*Measured by TC analysis.

The initial carbon concentration of reactor solution was partially substituted by phenolic compounds with 5 ppm and 10 ppm concentrations. 2-chlorophenol (500 ppm), 2,4-dichlorophenol (20 ppm), 2,4,6 – trichlorophenol (500 ppm) and 4 – nitrophenol (100 ppm) were prepared in a distilled water in a flask with 500 mL volume. The phenols characterization and concentrations added are presented in *Table 3.2.* They were further diluted with distilled water to obtain the desired concentration and then added to reactor solution. Both, stock and phenolic solutions, kept in the refrigerator at 3.4°C, and degradation of any components was not observed.

Table 3.2: Phenolic compound characterization

Component	Molecular Weight [g mol^{-1}]	Present Carbon [w/w%]	TC in 5 ppm [mg L^{-1}]	TC in 10 ppm [mg L^{-1}]	Solubility in water at 20 °C [g L^{-1}]
Phenol	94.11	76.5	3.83	7.65	82.8
2 – Chlorophenol	128.56	56	2.8	5.6	10
2,4 - Dichlorophenol	163	44.2	2.21	4.42	10
2,4,6 - Trichlorophenol	197.45	36.5	1.83	3.66	0.5
4 – Nitrophenol	139.11	52	2.6	5.2	11.6

3.4 Reactor Configuration

The experiment was performed in a batch recycled reactor with an ultraviolet lamp that had 6W input power and 254 nm irradiated wavelength, more detailed description of the lamp is presented in *Table3.3.*

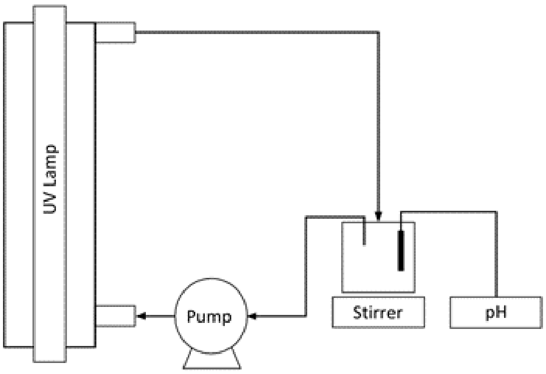
Table 3.3: Osram HNS 6W G5 Putitec HNS Lamp specification

Electrical Data	
Nominal wattage	6 W
Nominal voltage	42 V
Construction voltage	42 V

Nominal current	0.16 A
Lamp current	0.16 A
Photometrical data	
Radiated power 200…280 nm (UVC)	1.7 W
Dimension and Weight	
Diameter	16 mm
Length	212 mm
Additional product data	
Base (standard designation)	G5
Burning position	S180

The schematic representation of apparatus is shown in *Figure 3.1*. The reactor was open to air and non-irradiated part of solution were stirred continuously with a magnetic stirrer that was placed at the bottom with the stirring level at 3. The total volume of the reactor was 250 mL with 55.8 mL effective volume of annular photoreactor. UV lamp was placed inside the annular photoreactor, and fluid flow was from bottom to top. A Pumpdrive 5006 by Heidolph was used to ensure 175 mL min^{-1} flow rate.

Figure 3.1: Schematic representation of reactor unit



An electrode LE409 by Mettler Toledo was immersed in the aqueous solution for pH measurements. The reaction process continued for 120 min and samples were taken periodically for further quantification of total carbon and phenolic compounds. Prior to HPLC and TC analysis, samples were filtrate by the filter

Chromofil Xtra RC-20/25) with a pore size of 0.20 μm, purchased from Macherey-Nagel.

3.5 Experimental Procedure

Standard reaction was done with 250 mL of aqueous solution, which composed of deionized distilled water and stock solution, and added the predetermined amount of TiO_2. The effect of initial TC, initial TiO_2 amount and H_2O_2 concentration were investigated to optimize the operating conditions. The initial TC concentration of the stock solution was in the range of 30 – 500 mg L^{-1} with fixed 1 g L^{-1} TiO_2 concentration. When optimal concentration of TC was found, the effects of TiO_2 loading in a range [0.1-1] g L^{-1} and H_2O_2 concentration from 27 to 266 mg L^{-1}, individually, was investigated. Moreover, the combined effect of catalyst and H_2O_2 was observed.

The experiment proceeded further to observe the effect of phenolic compounds present on process efficiency. In this part of experimental work, phenolic compounds added to reactor feedstock partially substituted the amount of initial total carbon in the solution. The concentration of added phenolic compounds was 5 ppm and 10 ppm. The theoretical amount of carbon present in phenolic compounds was calculated, and considering this, the required initial amount of stock solution was derived, by giving in total the desired initial TC concentration. Also, specifically for 10 ppm of phenolic compounds concentration, an additional experiment conducted with a combination of hydrogen peroxide (66.6 mg L^{-1}) and catalyst (0.5 g L^{-1}).

The experiment lasted for 120 minutes and samples were withdrawn every 30 minutes. For the experiments containing H_2O_2, samples were taken every 15 minutes during the first hour, and then every 30 minutes. At 0 minutes the first sample and pH value were taken, and then stopwatch immediately started with turning on the ultraviolet light, while fluid continued mixing by the stirrer. Periodically, pH value was recorded and samples (8 mL) were withdrawn from the reactor by pipette, filtrated from the catalyst and stored in 20 mL glass vials and was diluted with distilled water in 8/10 range for TC analysis. For the experiments containing phenolic compounds, additional 1 mL of samples, with prior filtration, were stored in 2 mL glass vials for further HPLC analysis.

3.6 Analytical Procedures

Total carbon analysis was performed using Multi N/C 3100 analyzer from Analytik Jena AG. Thermostatic high-temperature oxidation for TC digestion ensures detection of even very stable complex carbon and it works with the presence of a special catalyst. The 250 microliters of sample are dosed into the combustion tube, where, due to the catalyst, combustion and pyrolysis of the sample in carrier gas flow take place. The temperature in combustion furnace goes up to 950 ^{o}C. Moreover, a carrier gas (Oxygen) also acts as the oxidation agent, and reaction between oxidant and carbonic subtance shown in *Equation 3.1*.

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

R – carbonic substances

Heated gas then cooled and dried in condensation coil, where condensed water is separated from the measuring gas. Further, NDIR detector measures the CO_2 gas with the aid of an infrared light and according to the absorbed amount of light, the concentration of TC in the sample is then calculated. Analyzer operates at calibration line from 1 to 100 ppm obtained from standards and corresponding calibration curves for TC and TIC is presented in *Figures 3.2* and *3.3.*

Figure 3.2: TC calibration curve

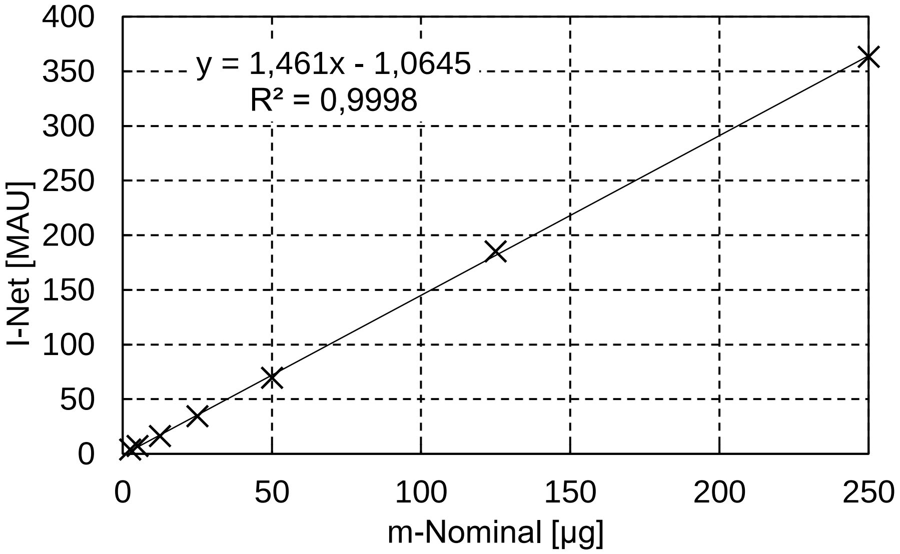
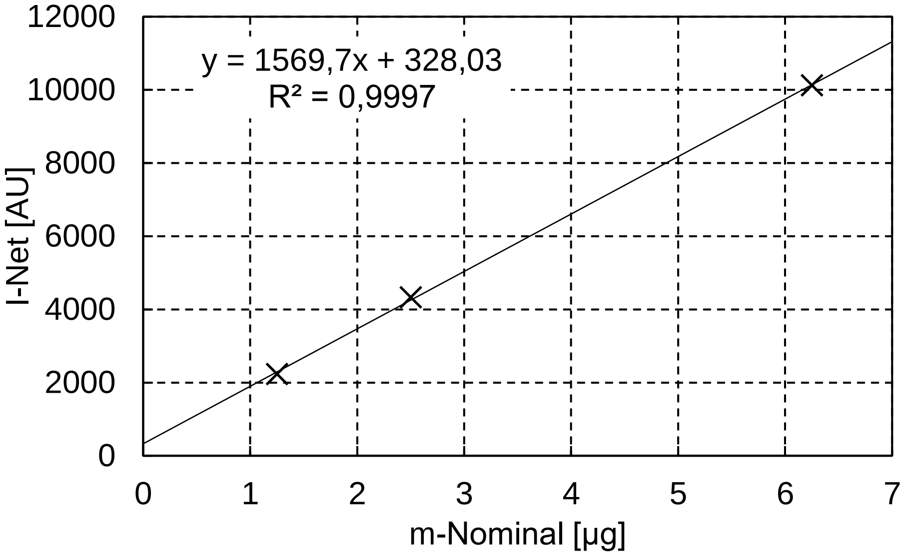


Figure 3.3: TIC calibration Curve



Phenolic compounds were identified by high-pressure liquid chromatography (HPLC). It contains a reservoir for solvent, high-pressure pump that generates a flow rate of solvent, an injector that introduces the sample into the solvent stream, which in turn delivers it to HPLC column. This column is equipped with chromatographic packing material that is responsible for separation process after that solvent flows to the detector for compound evaluation. Sample injected to mobile phase flows through the column, and different compounds start to form a band with chromatograph material. Depending on attraction level of compounds, some of them more attracted with a chromatograph, and another one with mobile phase, compounds will have different speed. Thus, the attraction of stable phase and mobile phase causes separation process. The separated sample passes further to the detector, where with aid of UV light, fluorescence or an evaporate-light-scattering detector samples are analyzed, and results are sent to the computer. In this work, Agilent 1290 Infinity HPLC was used. Equipment has HPLC grade water in channel A, and HPLC grade acetonitrile in channel B. Its columns packed with 2 Sub-2-micron particles, which allows faster sample analyzes than in the previous series and provides results with higher efficiency and higher resolution. Prior to measurements, a calibration curve was plotted for a different aromatic ring containing compounds. Phenol calibration curve was plotted from 4 concentrations, 0.5, 1, 2 and 5 ppm. Whereas calibration curve for 2–chlorophenol, 2,4–dichlorophenol, 2,4,6–trichlorophenol and 4–nitrophenol were prepared with 1, 3, 5, 10 and 20 ppm concentrations (*Figures 3.4 – 3.8*).

Figure 3.4: Phenol Calibration Curve

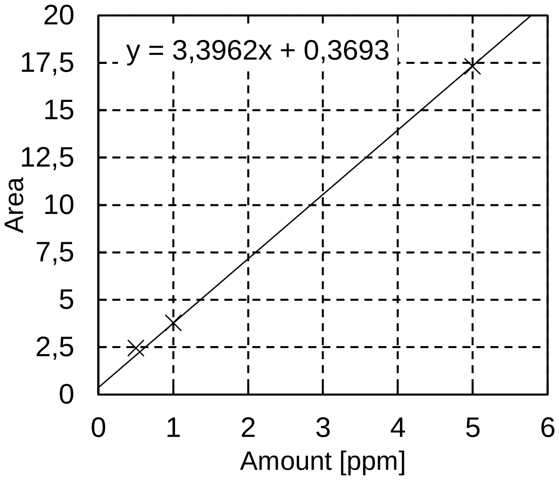


Figure 3.5: 2-Chlorophenol Calibration Curve

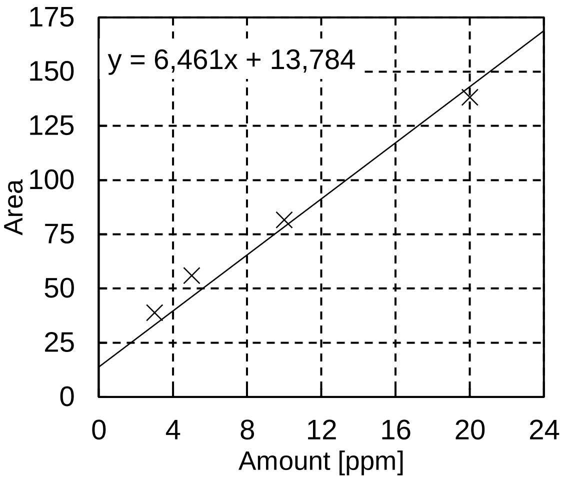


Figure 3.6: 2,4-Dichlorophenol Calibration Curve

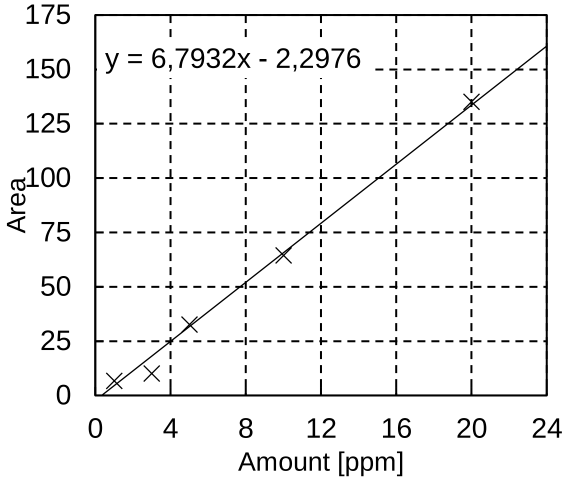


Figure 3.7: 2,4,6-Trichlorophenol Calibration Curve

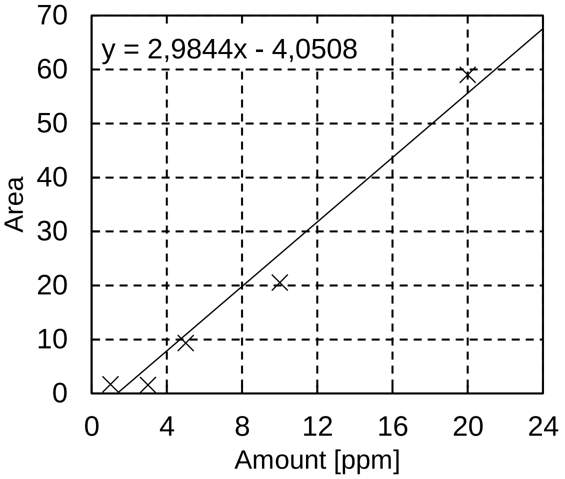
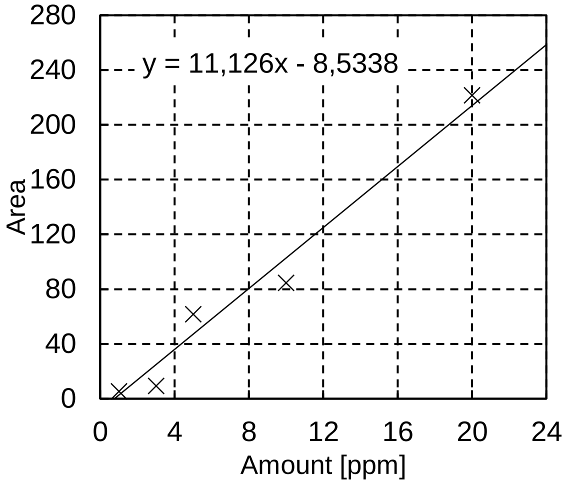


Figure 3.8: 4-Nitrophenol Calibration Curve

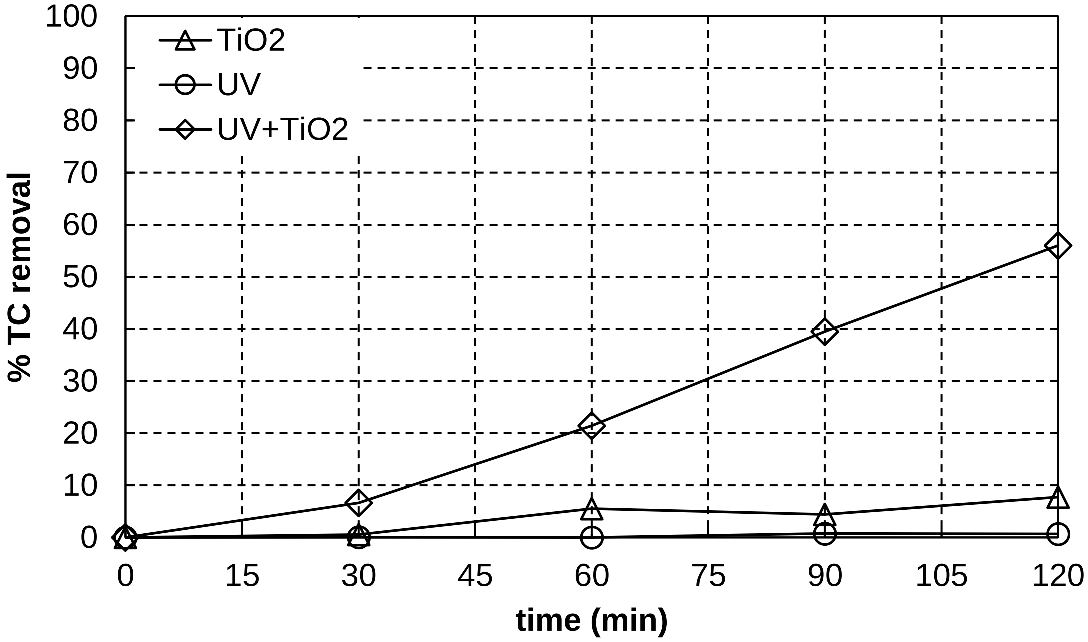


Chapter 4 - Results and Discussion

4.1 UV/TiO_2 photocatalytic process

Initially, a solution with 32 mg L^{-1} of total carbon (no phenolic compounds) was loaded into the reactor and was irradiated by UV light for 120 min. As a result, the degradation rate of organic carbon occurred at a slow rate. Moreover, the presence of only 1 g L^{-1} catalyst, without UV irradiation, also did not result in significant degradation of total carbon. In *Figure 4.1,* UV/TiO2 process demonstrates better performance, resulting in 56% TC removal.

Figure 4.1: Process Efficiency of UV/TiO₂ ($[TC]_o$= 32 mgL^{-1}, $[TiO_2]_o$= 1gL^{-1})

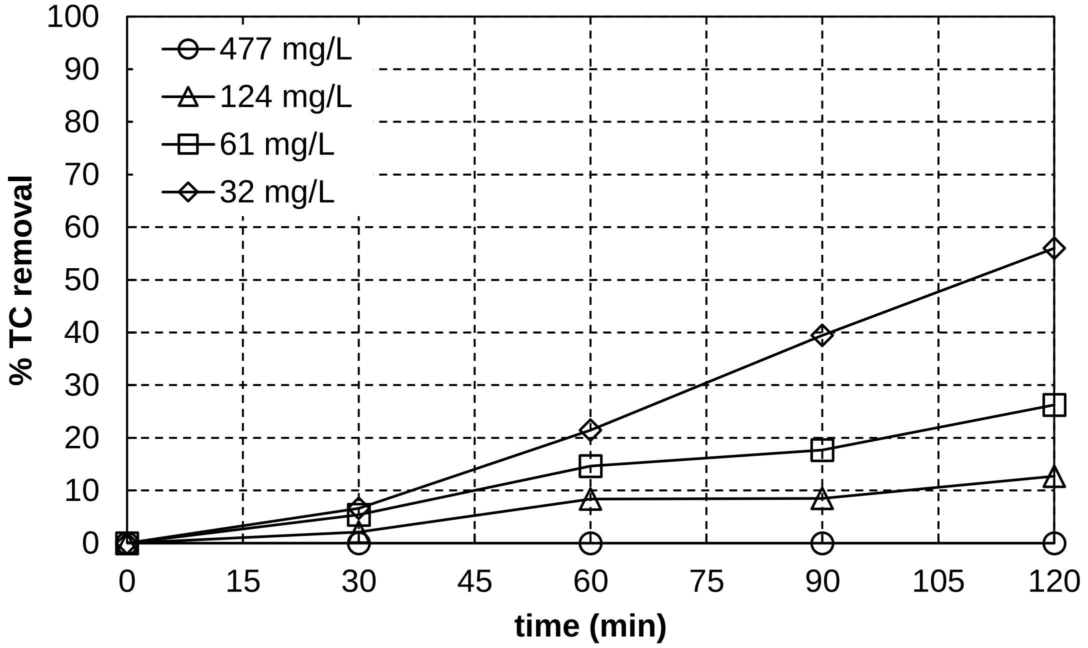


During the photocatalytic process, hydroxyl radicals are formed due to the presence of light source and photocatalyst, as shown in *Equations 2.7 to 2.12*. Therefore, it is essential to have both main factors, semiconductor and light.

4.1.1 Effect of Initial Total Carbon

Secondly, the effect of initial TC concentration on process efficiency was examined. Set of experiments at a different range of TC (30-500 mg L^{-1}) with fixed catalyst load (1 g L^{-1}) were performed. By comparing the results, it is evident from *Figure 4.2* that the optimum concentration for initial TC was 32 mg L^{-1} with 56% obtained conversion.

Figure 4.2: Effect of TC initial concentration ([TiO2]o= 1gL-1)

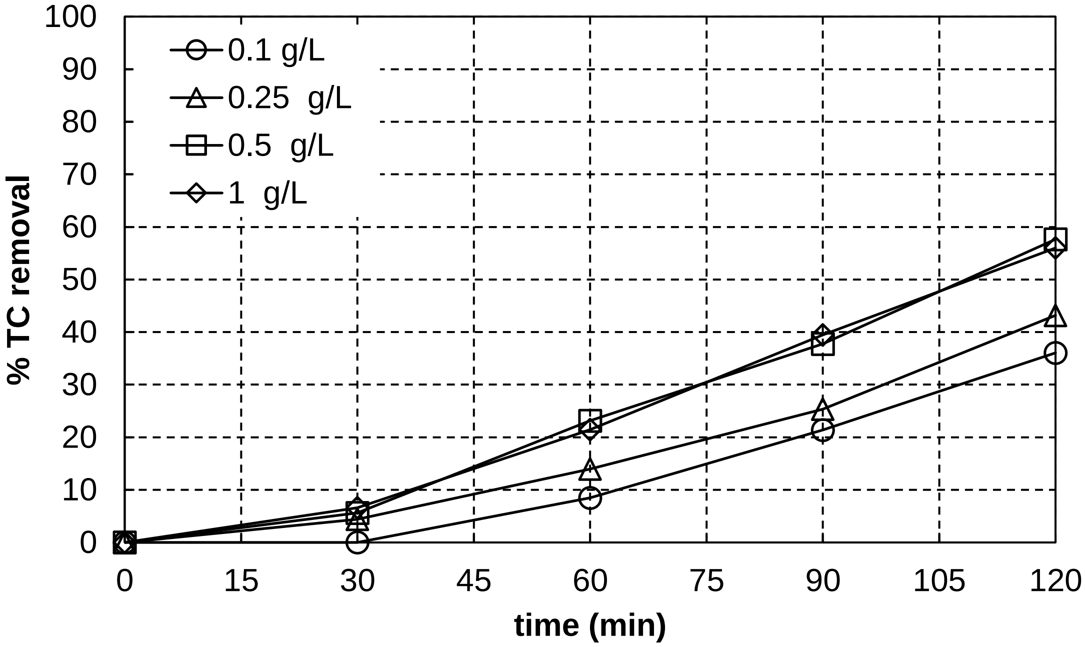


It was observed that effect of the photocatalytic process increases with a decrease in pollutant concentration and it follows the first order kinetics. Overall these findings are in accordance with previous reports [42, 46, 58-62]. Excess concentration of pollutants has a negative impact on process efficiency. As the amount of catalyst loaded in the reactor remains the same, the active sites on the TiO_2 also fixed. Thus, the high concentration decreases the photocatalytic degradation rate due to the shortage of generated reactive species [58]. At high concentration light photons might intercept with pollutants before reacting with catalyst surface. Moreover, already adsorbed pollutant molecules can occupy the active site of catalyst, thus, decreasing overall mineralization of organic substances.

4.1.2 Effect of TiO_2 loading

Under various TiO_2 loading of 0.1-1g L^{-1}, the effect of TiO_2 on total carbon removal was investigated. The result was 36% with 0.1 g L^{-1} TiO_2 loading and increased to 56% at higher loading of 1 g L^{-1}. The results presented in *Figure 4.3,* showed that there was no significant deviation in total carbon removal with TiO_2 concentration at 0.5 g L^{-1} and 1 g L^{-1}. Thus, a further increase in catalyst loading was not considered. The experiment demonstrated that 0.5 g L^{-1} shows the best removal of total carbon with obtained total carbon conversion of 58%.

Figure 4.3: Effect of TiO_2 loading ($[TC]_o$= 32 mgL^{-1})



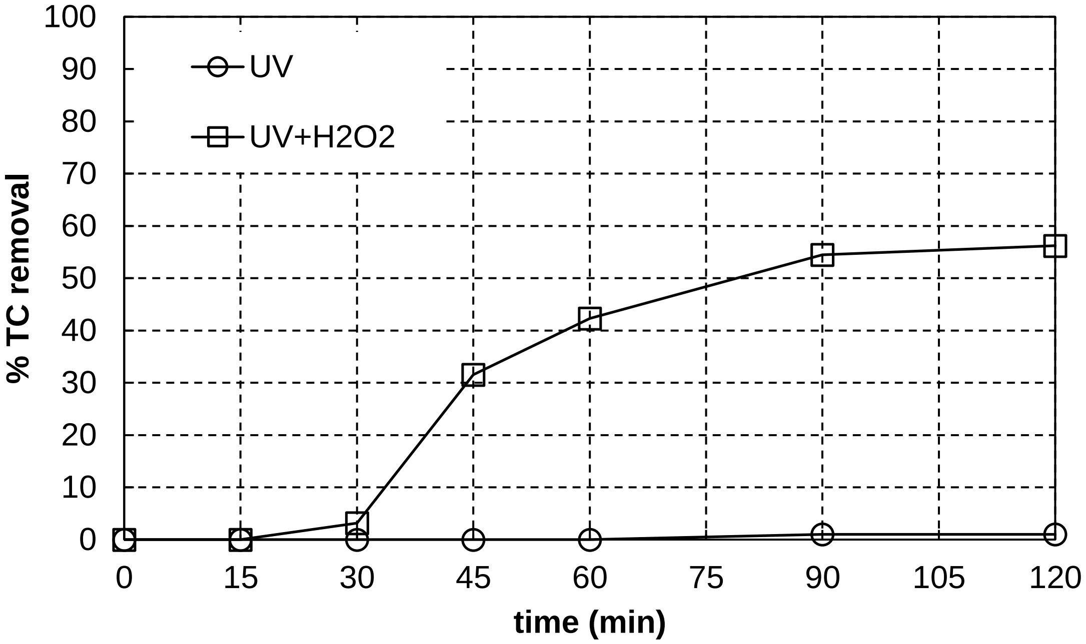
Other studies reported that at higher loading the process will not be enhanced [15-20, 26]. The explanation of this is that particles of TiO_2 decrease the light penetration, thus inhibits the generation of oxidizing agents. Besides, the effect of TiO_2 catalyst loading on process efficiency has been studied widely, direct comparison of results was not made as different reactor configuration and reagent concentrations were used [3, 54, 65].

However, outcomes of research demonstrated the existence of the optimum amount of catalyst that can be added to photocatalytic process [61-64]. According to previous studies, the optimal TiO_2 was found in the range of 0.5-1 g L^{-1}[40, 65]. Moreover, at some point, reaction losses linear dependency on TiO_2 and starts to deteriorate [3]. When the amount of catalyst transcends the saturation level, it leads to a high turbidity state. Excess TiO_2 particles generate light screening effect, which decreases the surface area of catalyst that exposed to UV light. Additionally, it also impedes the penetration of UV light due to strong scattering of light photons [3, 63].

4.2 UV/H_2O_2 process

As the next step, the direct photolysis (only UV) process on the conversion of organic pollutants in aqueous solution was studied. The absence of degradation of organic matter only by UV absorbance was experimentally proved. The present findings confirm the enhancement of process by introducing H_2O_2 oxidant into the process, resulting in 53% TC removal. The comparison plots of direct photolysis and UV/H_2O_2 processes are presented in *Figure4.4.* After 30 minutes of the process, the achieved TC removal was only 3%, while previous findings report faster decomposition of organic pollutants by the H_2O_2 oxidant. Even though, the similar pattern of results was obtained with different H_2O_2 concentrations, which presented in paragraph 4.2.1.

Figure 4.4: Process efficiency with UV and UV/H_2O_2
($[TC]_o$= 32 mgL^{-1}, $[H_2O_2]_o$=66.6 mgL^{-1})

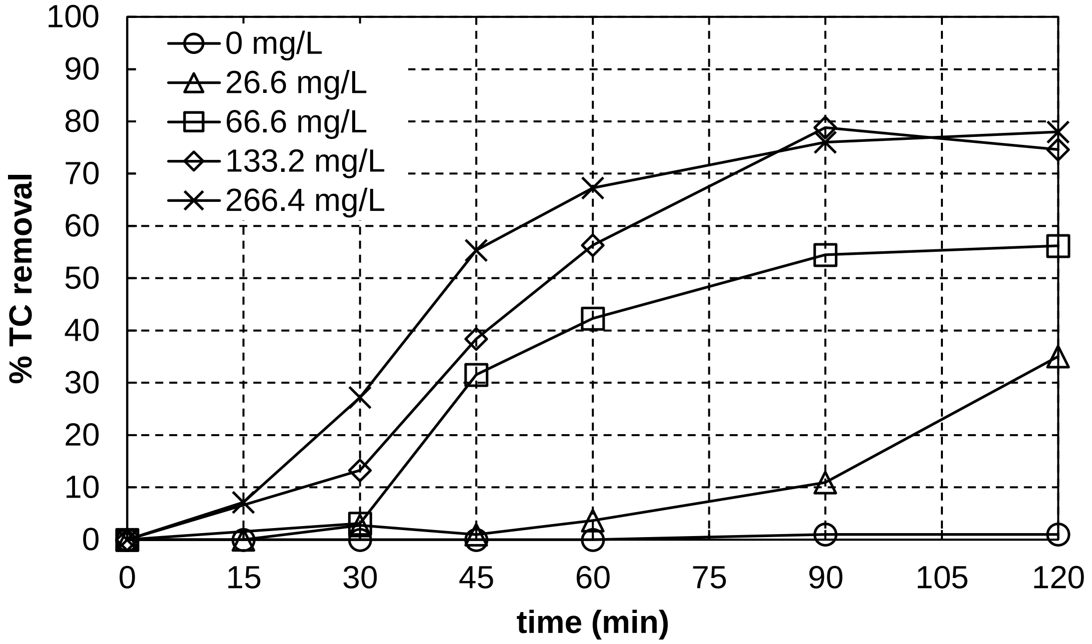


4.2.1 Effect of initial H_2O_2 concentration

Hydrogen peroxide is found to be an efficient oxidant, and its presence in the photocatalytic process increases the rate of reaction. In this work, experiments were performed to find the optimum concentration of H_2O_2. Thus, the process was conducted at different concentrations of H_2O_2, in the range from 27 to 266 mg L^{-1}, with fixed initial concentrations of total carbon. Obtained results of the process are shown in *Figure 4.5*. The significant changes have occurred, when the concentration was increased from 27 to 67 mg L^{-1}, and further to 133 mg L^{-1}. Difference between 133 and 266 mg L^{-1} concentration was negligible, 75% and 78% conversion, respectively. H_2O_2 at a concentration of 66.6 mg L^{-1} had 53%

conversion, and from an economic point of view, this concentration was chosen to be the optimum one for this process, as a double increase in concentration gives only 20% improvement in efficiency.

Figure 4.5: Effect of H_2O_2 concentration ($[TC]_o$= 32 mgL^{-1})



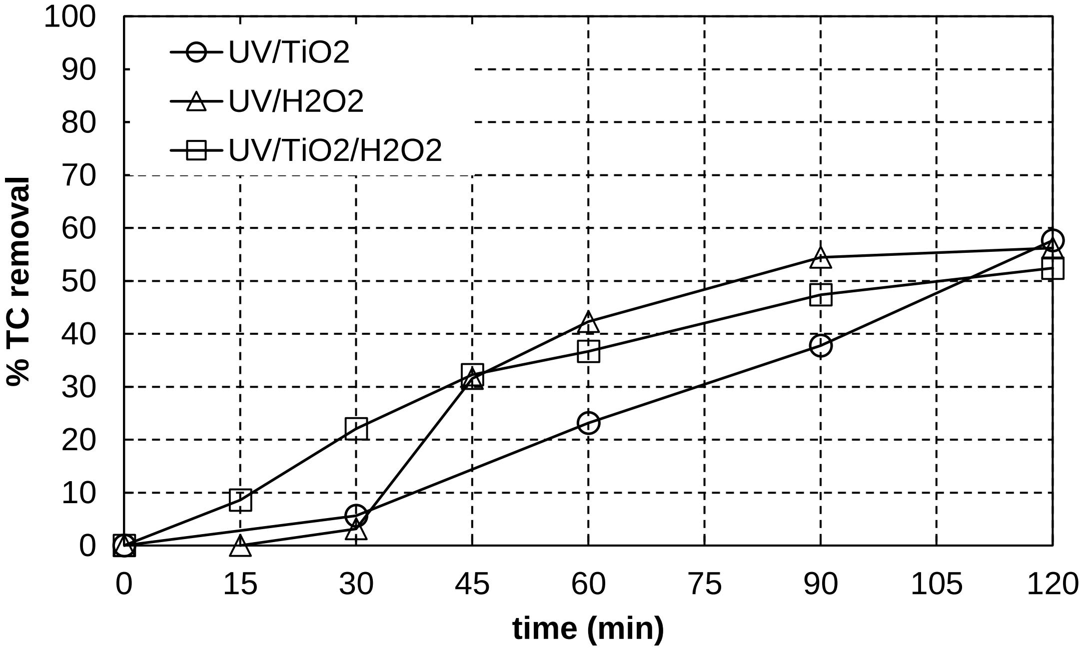
It was observed that increase in concertation of oxidants leads to higher total carbon removal. A similar conclusion was reached by previous studies [51]. When an excess amount of hydrogen is added, it oppositely lowers the degradation rate. This is the reason, why there was no change in removal efficiency with 133 and 266 mg L^{-1} concentrations. This trend has been reported in other studies as well and explained by the fact that excess H_2O_2 reacts with already generated hydroxyl radicals, hence acts as an inhibitor [52]. The reaction is presented in *Equation 4.1.*

$$H_2O_2 + 2HO^{\bullet} \rightarrow H_2O + \frac{3}{2}O_2 + H_2 \qquad (4.1)$$

4.3 UV/H_2O_2/TiO_2 process

The process efficiency was evaluated on the removal of organic carbon and phenolic components. For the first scenario, no phenolic constituents, the concentration of H_2O_2 (66.6 mg L^{-1}), initial TC (32 mg L^{-1}) and TiO_2 loading (0.5 g L^{-1}) kept at previously obtained optimum value. The main aim of this experiment was to see if the combination of catalyst and oxidant results in better decomposition of organic pollutants. The results showed that addition of oxidant into photocatalytic AOPs does not seem to improve process performance. The combined method removes only 52% of TC. Presented results in *Figure 4.6* demonstrates that total carbon mineralized faster by UV/H_2O_2/TiO_2 first 30 minutes, 32%, compared to UV/TiO_2 and UV/H_2O_2, 6%, and 1%, respectively. It can be stated that effect of H_2O_2 at small concentrations do not provide with significant enhancement of process, as final conversion remains similar.

Figure 4.6: Effect of different photocatalytic processes ($[TC]_o$= 32 mgL^{-1}, $[TiO_2]_o$=66.6 mgL^{-1}, $[H_2O_2]_o$=66.6 mgL^{-1})



Nevertheless, other research has shown that addition of oxidant improves the degradation of parent compound. Combined method increases the process efficiency, as ultraviolet rays coupled with oxidant and photocatalyst [50].

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \tag{4.2}$$

$$TiO_2(e^{-}) + O_2 \rightarrow O_2^{\bullet} \tag{4.3}$$

H_2O_2 is the source of active species on the catalyst surface, thus, this process should have resulted in higher conversion than UV/TiO_2 and UV/H_2O_2 processes alone [50, 66]. On the other hand, the ratio of TiO_2 loading and amount of H_2O_2 added to process differs between presented work and literature. In Lopez work, H_2O_2 at 0.25 and 0.5 g L^{-1} with TiO_2 at 0.2 g L^{-1}, achieved TOC conversions were 46.81% and 73.85%, respectively. Also, they used textile wastewater with TOC around 200 mg L^{-1}, which is 10 times higher than in presented work [66].

There are can be two scenarios explaining the absence of improvement after the combination: a) As the concentration of hydrogen peroxide is too small, it has been consumed in first 30 minutes of reaction, and another removal process was conducted with aid of a catalyst. Hence it explains 20% TC removal the first 30 minutes; b) Competition for the UV absorbance between catalyst and hydrogen peroxide might be contributed to the performance of the process [66].

In experiments containing phenolic compounds, the effect of the combination had a remarkable increase in aromatic rings degradation and TC removal, which will be explained later in this work.

4.4 UV/H_2O_2/TiO_2/Fe(III)

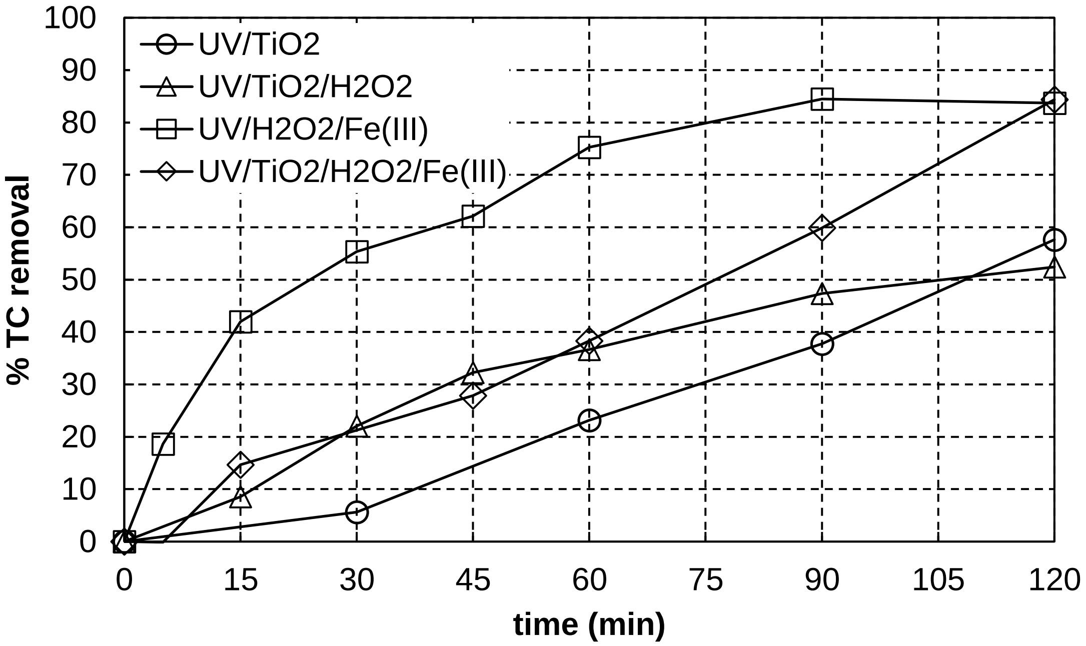
In this work, the performance of UV/H_2O_2/Fe(III) and UV/H_2O_2/TiO_2/Fe(III) processes was observed. The compositions of treatment techniques are presented in *Table 4.1.* In the photo – Fenton oxidation process, hydrogen peroxide, and Fe(III) ions react stoichiometrically, thus it provides with an equivalent amount of iron salt that produces the required amount of •OH radicals. In photo-Fenton, •OH radicals were used efficiently, if an excess amount of Fe(III) is added it acts as an inhibitor for oxidation of organic carbons [67].

Table 4.1: Concentration of added reagents

Reagents	UV+H_2O_2+TiO_2	UV+H_2O_2+Fe(III)	UV+H_2O_2+TiO_2+Fe(III)
TiO_2 [g/L]	0.5	0	0.5
H_2O_2 [mg/L]	67	67	67
Fe(III) [ppm]	0	10	10
TC Conversion	52%	84%	84%

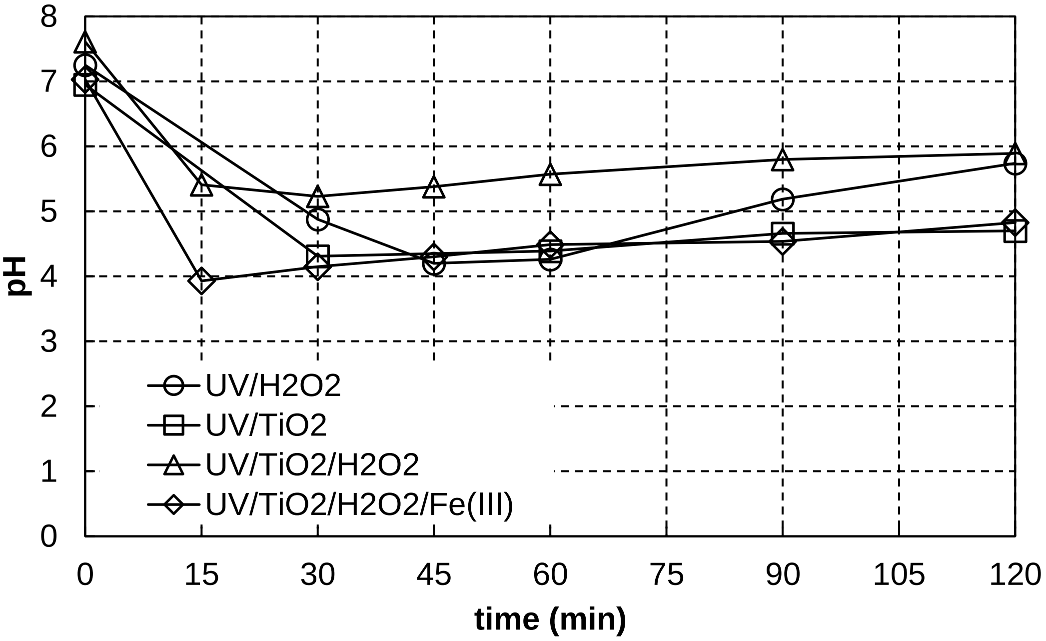
As it can be seen from *Figure 4.7*, the total carbon removal by UV/H_2O_2/TiO_2/Fe(III) and UV/H_2O_2/Fe(III) has similar results in terms of overall TC removal. The reaction rate of the first process follows the first-order kinetics, while the second process has exponential behavior. For the first hour, UV/H_2O_2/Fe(III) process mineralized two times more amount of total carbon comparing to UV/H_2O_2/TiO_2/Fe(III), 75% and 38% TC removal, respectively. The first process slows down next hour, while the second one follows constant rate. Nevertheless, both processes reach 84% removal of TC. UV/H_2O_2/TiO_2 process removed only 52% of the total carbon from the aqueous solution after two hours. The process containing all three reagents did not demonstrate the better result than photo – Fenton process. The explanation of this could be the fact that there exists competition for UV light within reagents, or H_2O_2 entirely consumed for oxidation of Fe(III) and thus it did not generate active hydroxyl radicals on catalyst surface or excess amount of Fe(III) act as scavenger of HO• radicals and excess TiO_2 loading had scattering effect of UV light, thus inhibiting the performance of the process. Introduction of catalyst to process had negligible effect. Possibly due to the fact that all radiated UV light was absorbed in the liquid for H_2O_2 oxidation and did not reach the catalyst surface [66].

Figure 4.7: Effect of Fe(III) on TC removal



According to experimental results, change in pH value throughout all experiments had the same behavior. *Figure 4.8* presents the pH measurements of processes at their optimal conditions. The pH readings of the solution in the reactor at 0 minute was around 7, then it starts to drop as the process goes on. The decrease in pH value occurs due to the transformation of organic carbons to organic acids [51]. During the last step, organic acids degrade to CO_2 which in turn leaves the solution, thus increasing the pH values as expected [51].

Figure 4.8: pH values for different AOPs techniques

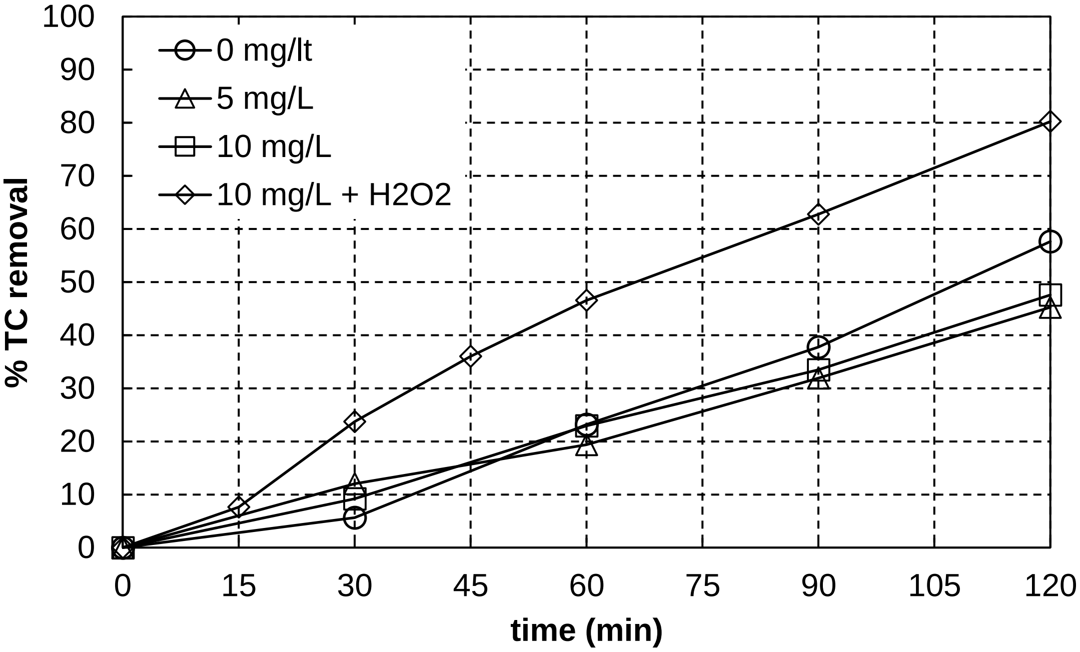


4.5 Degradation of Phenolic compounds

4.5.1 Removal of Phenol

Photocatalytic degradation process was conducted for synthesized water containing a small concentration of phenol, 5 ppm, and 10 ppm and results are presented in *Figure 4.9*. According to obtained results for 5 ppm, after 2 hours 94% of phenol has been decomposed. The total carbon in solution was removed by 45%, while without phenol, the same initial carbon concentration has been removed by 58%. In the case of 10 ppm, TC conversion was obtained to be 48% with 98% of phenol removal. However, the results of 5 ppm and 10 ppm did not differ from each other significantly.

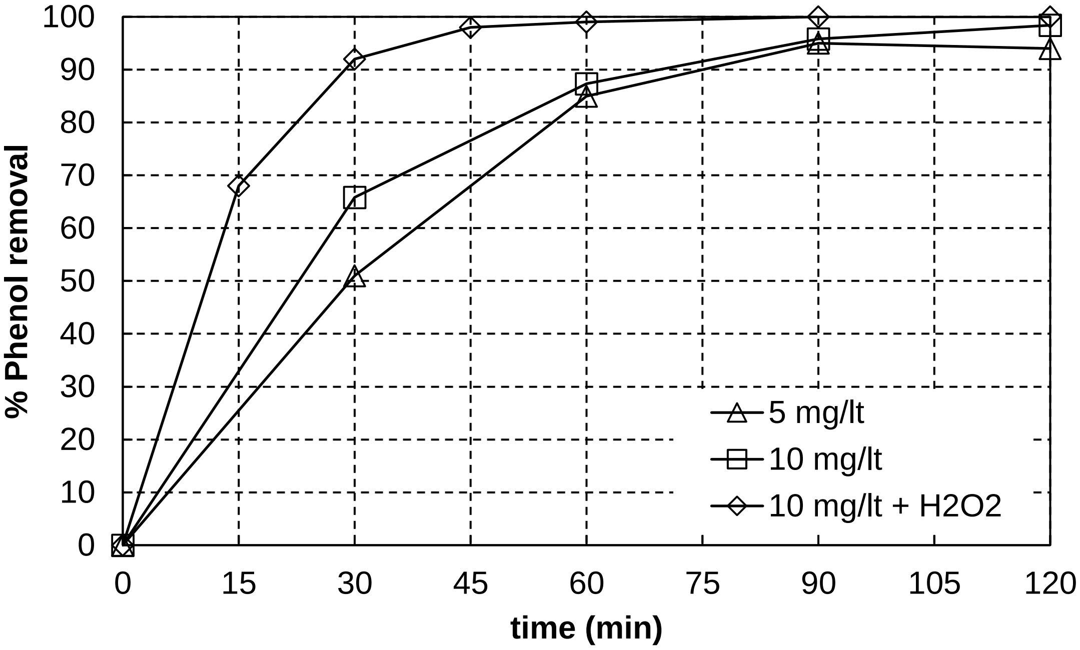
Figure 4.9: Effect of phenol on TC removal



As discussed in paragraph 2.3, phenol degrades to intermediate compounds. This explains the obtained high values for HPLC analysis, shown in *Figure 4.10*. However, by-products were not completely degraded to carbon dioxide and water, which explains low total carbon removal. In the first hour, phenol tends to degrade readily, due to the presence of high concentration of oxidants. After formation of intermediates, and considering already existing organic carbon constituents in the solution, competition between pollutants occurs for oxidizing agents. This decreases the degradation rate of phenol and total carbon removal; same findings were observed in other research [66].

The addition of hydrogen peroxide forms more active hydroxyl radicals with catalyst thus increases the rate of degradation. Presence of H_2O_2 forms additional oxidants and increases the conversion of TC to 80% with 100% phenol mineralization. Comparing process efficiency of UV/H_2O_2/TiO_2 with and without phenolic compound in solution, for phenol (80%) it works better than for only organic carbon (52%) in terms of TC removal.

Figure 4.10: Decomposition of phenol



According to HPLC analysis presented in *Figure 4.11* and *4.12,* it can be seen that with the presence of H_2O_2, after 2 hours, the less possible intermediate peaks were detected. The explanation could be that intermediate compounds of phenol are readily degradable than initial organic compounds in solution [9]. Dixit et. al. have performed similar research, where they achieved 100% decomposition of phenol by combined method [51]. The overall reaction of phenol degradation follows the Equation 4.4 [68].

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O \qquad (4.4)$$

Figure 4.11: HPLC analysis of 10 ppm phenol at (a) 0 min and (b) 120 min

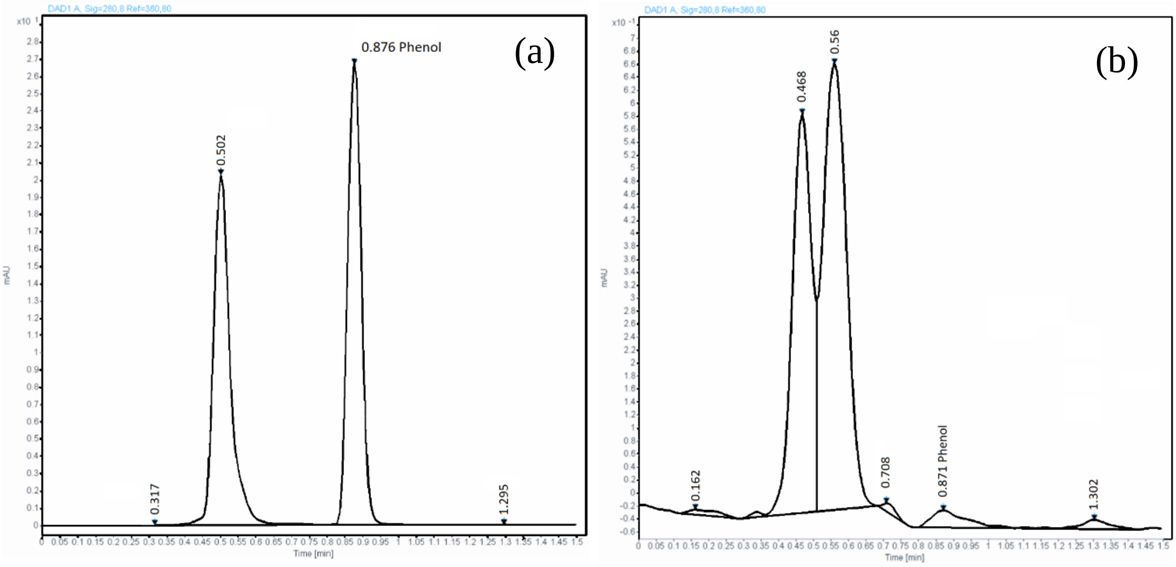
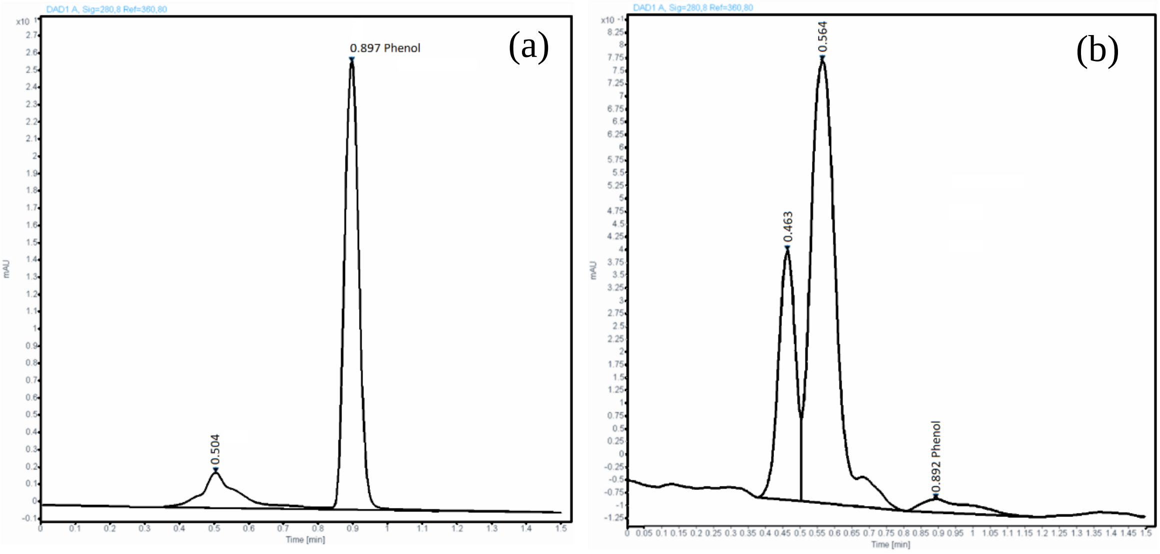
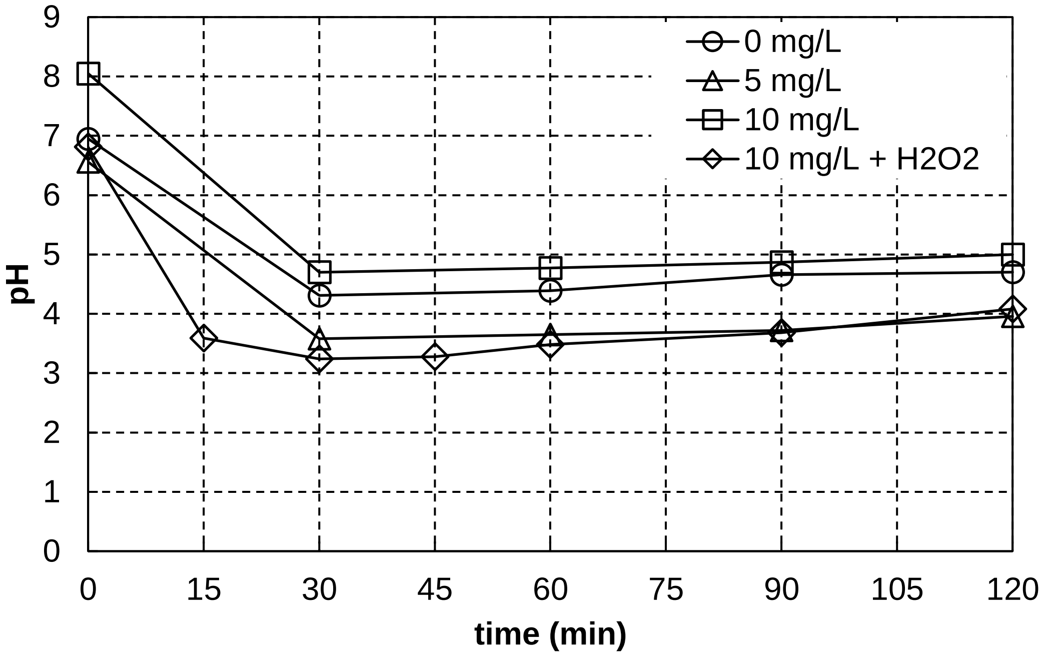


Figure 4.12: HPLC analysis of 10 ppm phenol with H_2O_2 at (a) 0 min and (b) 120 min



According to *Figure 4.13,* the initial pH of the solution was between 6.5 and 8. The presence of acidic intermediate was justified by the pH measurements, as it tends to decrease from an initial value and during the mineralization phase it increases. Phenol degradation rate increases with increasing pH and it was previously reported that degradation of phenol has its maximum at pH around 6.5 [1].

Figure 4.13: pH measurements for phenol



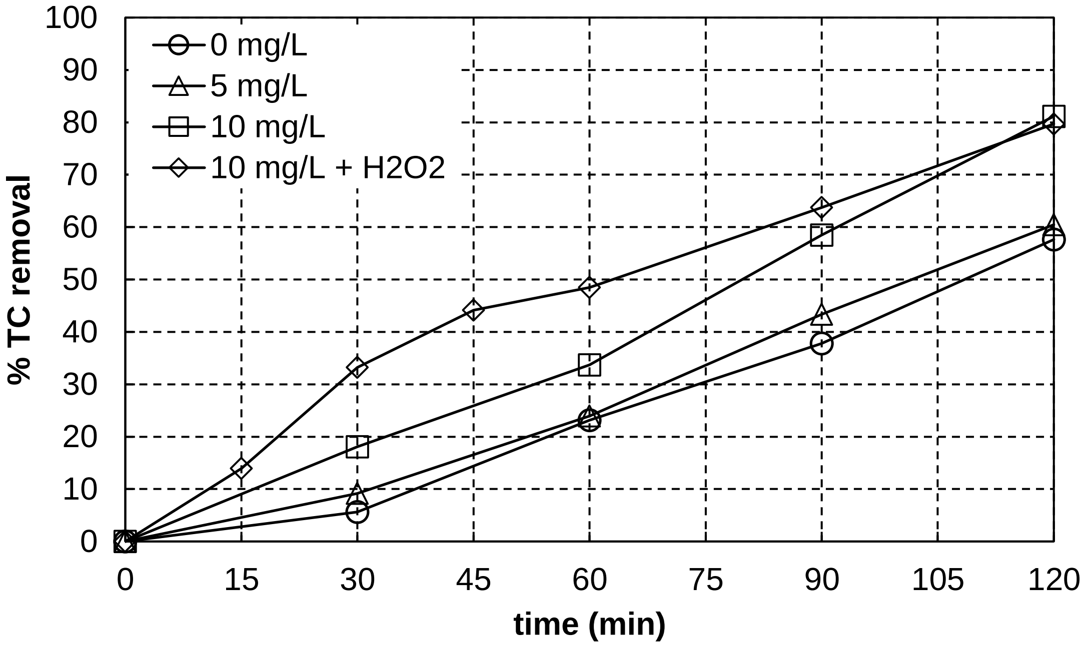
It was experimentally proved that phenol degradation has higher removal under UV/TiO_2 process than by only TiO_2 or UV irradiation. UV light irradiation alone used for oxidation of phenol can remove about 20% after 1.5 hours with 200 ppm initial concentration [53]. Other research has shown that degradation of phenol with initial 300 ppm concentration by only UV or H_2O_2 barely reached 10% after 2 hours of illumination [54]. Degradation of 100 ppm with aid of the only TiO_2 after 24 hours of experiment resulted in also approximately 10% removal [52]. The combined method had resulted in a complete removal of phenol from aqueous solution.

4.5.2 Removal of 2-Chlorophenol

2-Chlorophenol (2-CP) was added to the system at 5 ppm and 10 ppm concentration, partially substituting the initial total carbon concentration. Base case process, without the addition of H_2O_2, removed TC by 59% for 5 ppm and

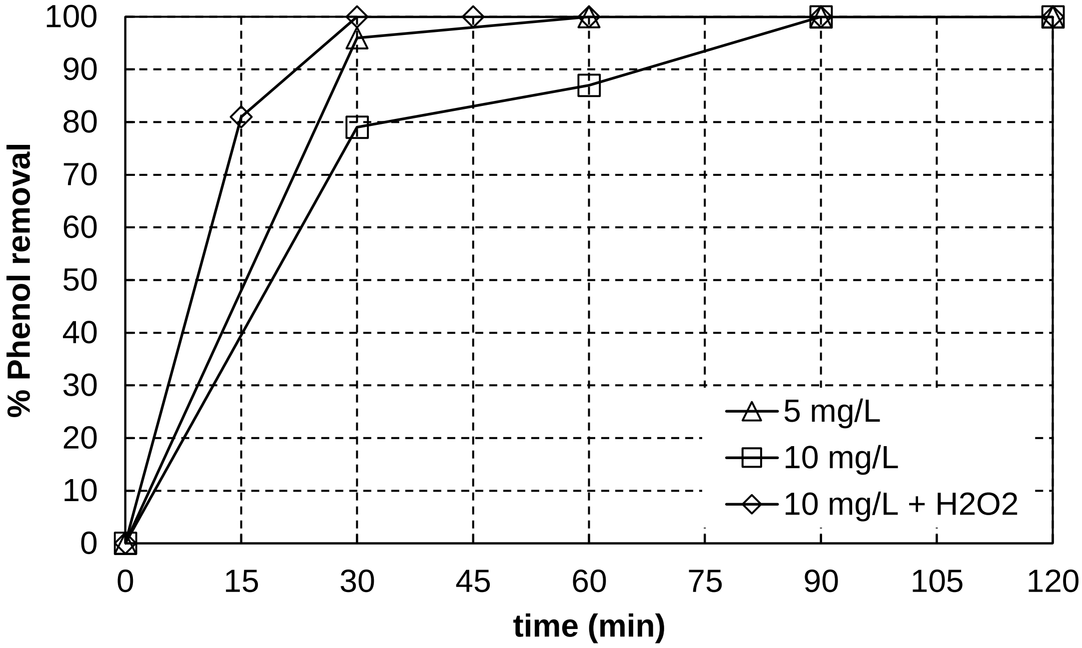
82% for 10 ppm. It can be seen in *Figure 4.14* that TC removal is higher for 10 ppm in comparison with 5 ppm. Moreover, the introduction of H_2O_2 did not markedly improve the process. The obtained results for UV/TiO_2 for 10 ppm was 80% as well as for the process containing an oxidant. A by-product of chlorinated phenols is difficult to oxidize, especially intermediates that contain Cl^-. Nevertheless, there is an assumption that Cl^- might positively impact on the process, which is discussed in paragraph 4.6.

Figure 4.14: Effect of 2-chlorophenol on TC removal



For 10 ppm, the decomposition of 2-CP is slower in comparison with 5 ppm, which results in the slower formation of intermediates, thus fewer compounds are in competition for hydroxyl radicals at the same time. According to *Figure 4.15*, 2-CP at higher concentration achieved 100% conversion after 90 minutes, while 5 ppm fully converted after 60 minutes. It shows that dechlorination of aromatic rings depends on the initial concentration of chlorinated phenol. This was also reported in previous research, where the concentration of 2-CP ranged from 150 – 3000 mg L^{-1}, resulting in lower dichlorination rate for high concentration [71]. Introduction of hydrogen peroxide into process enhances the dechlorination rate, as after 30 minutes 100% of 2-CP was removed.

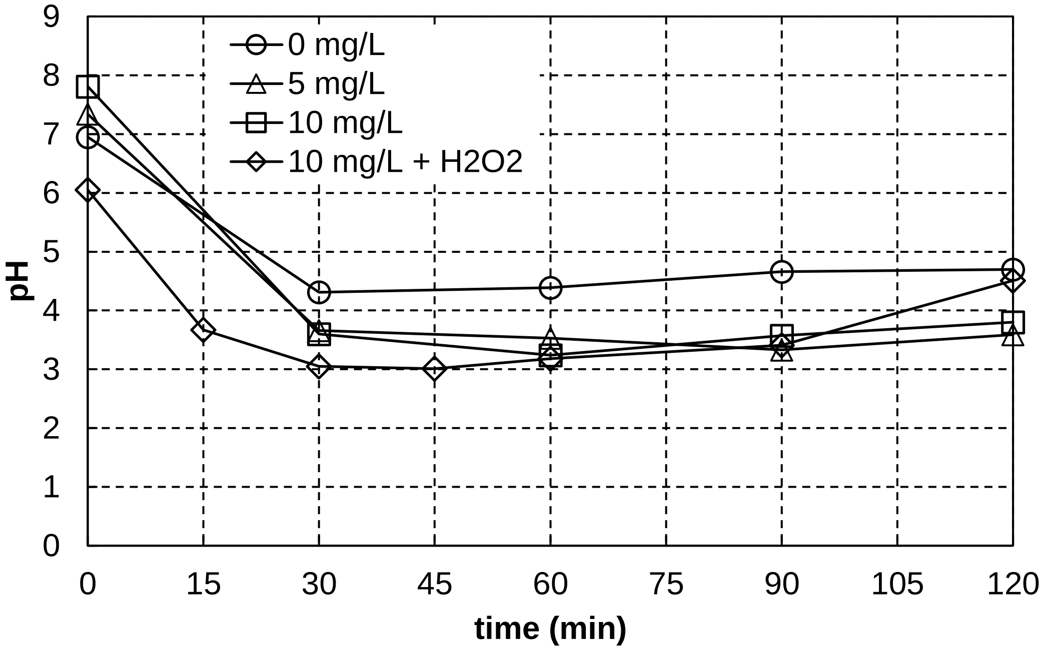
Figure 4.15: Decomposition of 2-chlorophenol



In all three scenarios, 2-CP decomposed faster in first 30 minutes, then it starts to slow down. The reason for this can be that after 30 minutes surface of TiO_2 reaches its threshold coverage due to the absorbance of pollutants on it. Thus, at the beginning it has enough active sites, which are then occupied by organic matter, explaining the decrease in the reaction rate [69]. Also, the multicomponent system creates competitive inhibition between chlorophenols and organic carbons for hydroxyl radicals [70]. The advantage of the photocatalytic process is that after oxidation on photocatalyst surface only mineral products are formed. *Figure 4.16* presents the pH measurements of process treating wastewater with 2-CP. In case of chlorinated phenols, the product is used to be CO_2, H_2O_2, and Cl^-. The overall reaction of photocatalytic degradation of 2-CP can be presented by *Equation 4.5*.

$$ClC_6H_4OH + \frac{13}{2}O_2 \rightarrow 6CO_2 + 2H_2O + HCl \qquad (4.5)$$

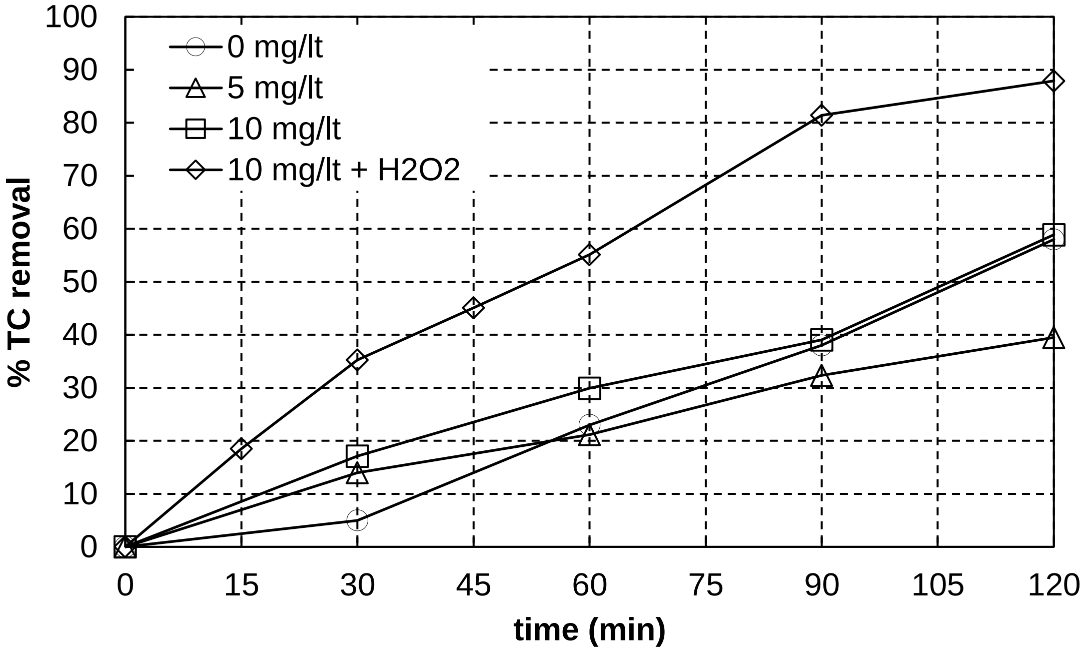
Figure 4.16: pH measurements for 2-chlorophenol



4.5.3 Removal of 2,4 - Dichlorophenol

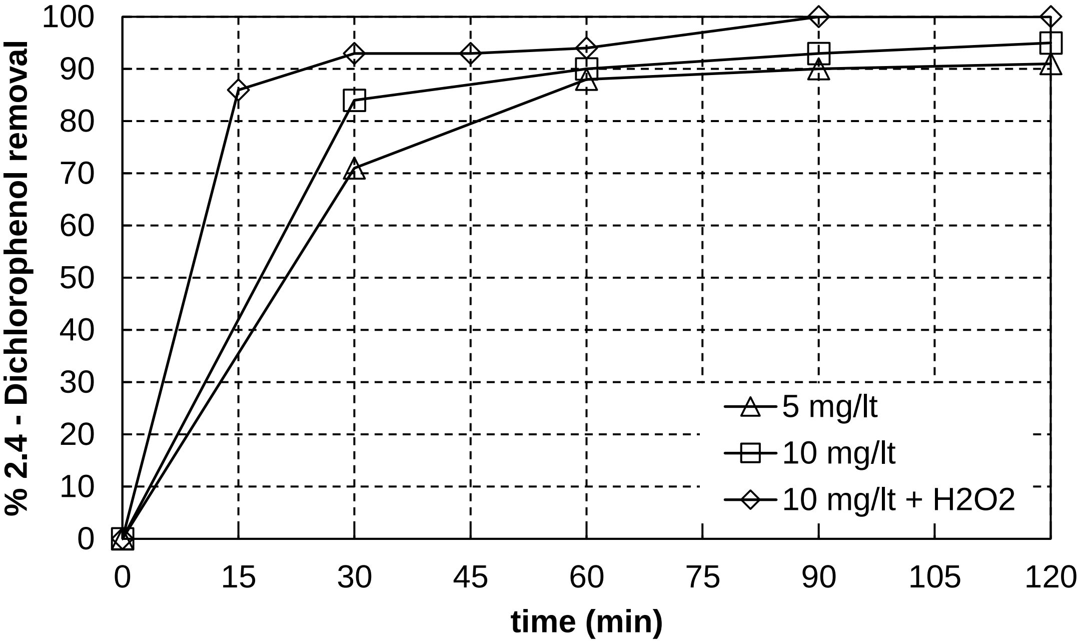
The total carbon concentration in synthetic wastewater remained 32 mg L^{-1}. Based on experimental results, the concentration of 2,4-DCP at 5 ppm and 10 ppm showed TC conversion of 38% and 57%, respectively, *Figure 4.17*. Increase in concentration of 2,4-DCP resulted in higher TC removal. Also, the presence of an oxidant in process increased TC removal up to 88%, as H_2O_2 provides the system with more active radicals.

Figure 4.17: Effect of 2,4-dichlorophenol on TC removal



Degradation of 2,4-DCP at 5 and 10 ppm had almost similar results, 91%, and 95%, respectively. 2,4-DCP was completely converted after the introduction of hydrogen peroxide into the system, achieving 100% after 90 minutes. *Figure 4.18* presents the obtained results of 2-CP decomposition by mean of photocatalytic AOPs. A system with H_2O_2 has shown the complete removal of 2-DCP, and no intermediate peaks have been detected by HPLC. Thus, by UV/H_2O_2/TiO_2 the synthesized water with 2,4-DCP went through mineralization phase, forming CO_2 and water, and achieving higher conversion of TC. However, without H_2O_2 compound removal in both scenario did not achieve 100% as it was achieved for 2-CP. This supports the statement that degradation of chlorinated compounds depends on the concentration of chlorine atom on the aromatic ring.

Figure 4.18: Decomposition of 2,4-dichlorophenol

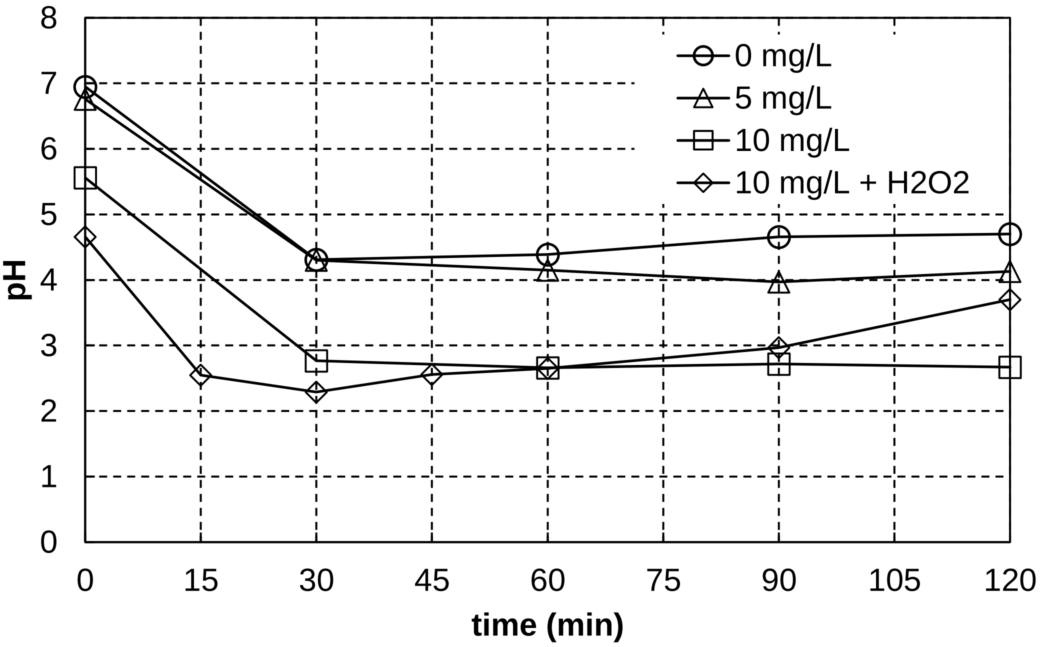


2-DCP mineralization is consistent with stoichiometry and shown in *Equation 4.6*.

$$Cl_2C_6H_3OH + 6O_2 \rightarrow 6CO_2 + H_2O + 2HCl \qquad (4.6)$$

As in previous parts, pH measurements of the process were recorded periodically, and results are presented in *Figure 4.19.*

Figure 4.19: pH measurements of 2,4-dichlorophenol



4.5.4 Removal of 2,4,6-Trichlorophenol

The same set of experiments were performed for 2,4,6-Trichlorophenol (2,4,6-TCP). 5 ppm and 10 ppm 2,4,6-TCP were added to the synthesized wastewater. The *Figures 4.20* and *4.21* present the results of TC removal and 2,4,6-TCP removal at different concentrations. It is evident from the result that maximum conversion of TC and model compound degradation was observed when wastewater was exposed to UV/H_2O_2/TiO_2 process, reaching 83% and 100%, respectively. 100% decomposition of 5 ppm compound with the only catalyst occurred after 60 minutes, and after 2 hours 36% of TC was removed. In the case of 10 ppm, complete removal of compound observed at 90 minutes and TC was removed by 44% by the end of the process. It can be noticed that with an increase in the concentration of 2,4,6-TCP, the conversion of TC also increased. However, 2,4,6-TCP degraded faster at low concertation.

Figure 4.20: Effect of 2,4,6-trichlorophenol on TC removal

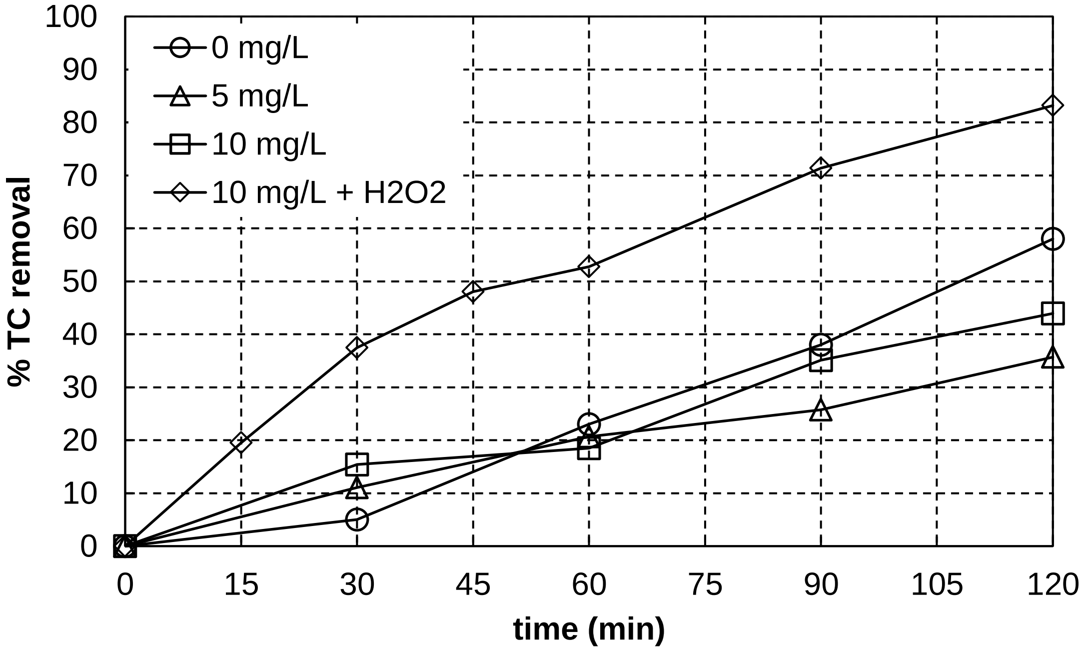
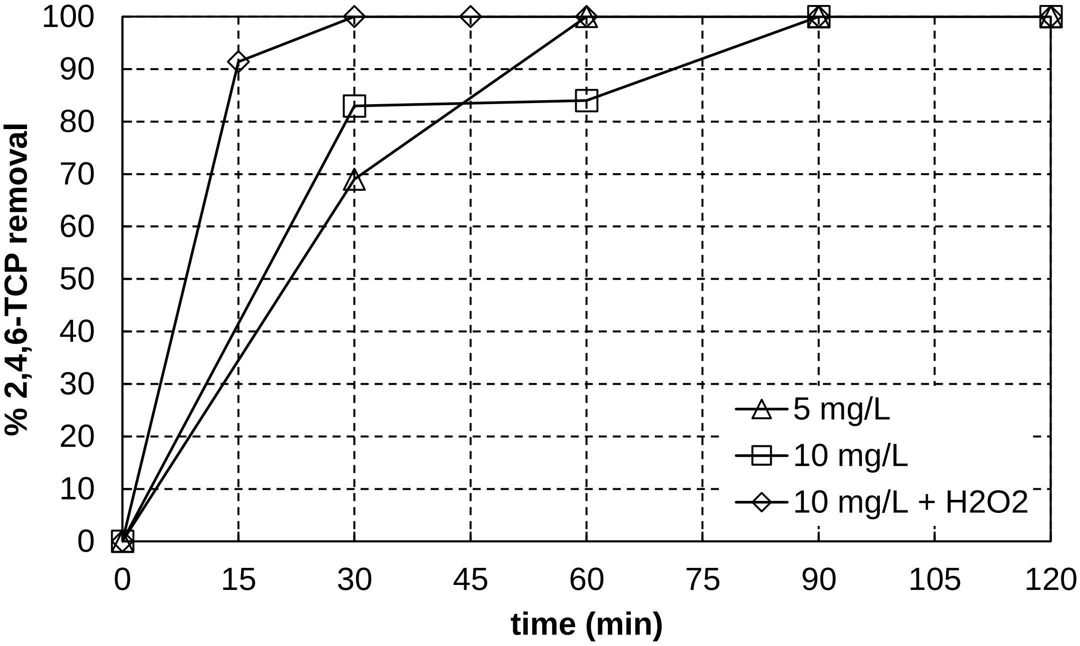


Figure 4.21: Decomposition of 2,4,6-trichlorophenol



According to HPLC results, the process can completely convert 2,4,6-TCP after 120 minutes, but possible peaks of intermediate products were detected. Addition of H_2O_2 results in enhancement of 2,4,6-TCP removal, as it achieves 100% in 30 minutes. Moreover, no by-product peaks were indicated after 120 minutes.

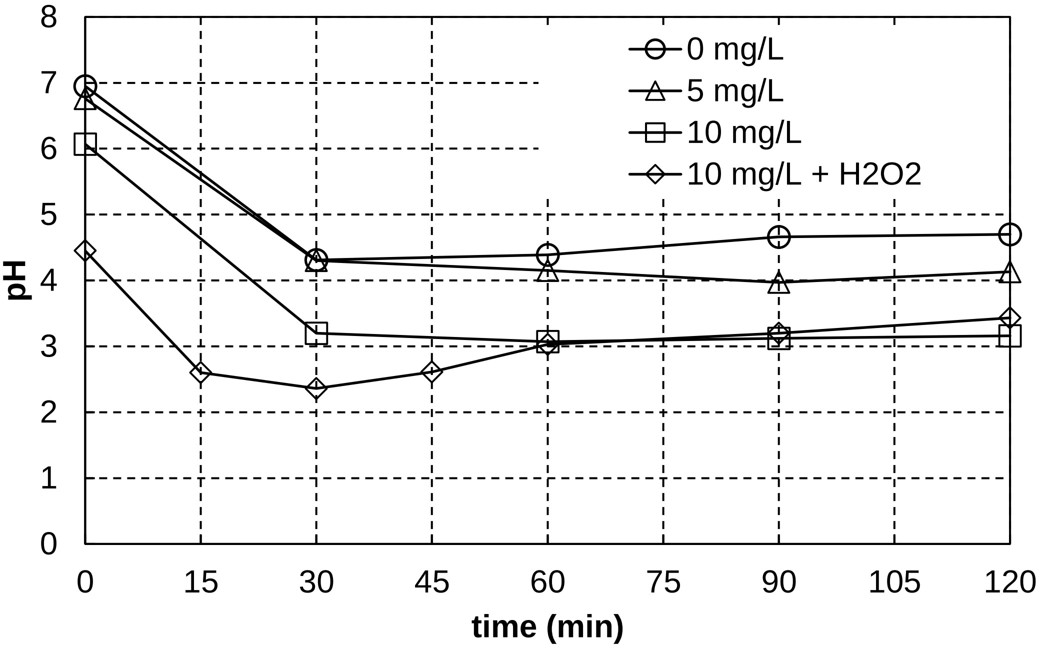
The overall photocatalytic reduction of 2,4,6-DCP is presented by *Equation 4.7*.

$$Cl_3C_6H_2OH + O_2 \rightarrow CO_2 + H_2O + HCl \qquad (4.7)$$

According to literature, the intermediate products of 2,4,6-TCP are similar as for 2-CP, with 6-CHQ [72].

The pH measurements over the process are presented in *Figure 4.22*. It can be noticed that with the addition of H_2O_2 the change in pH value is higher than in other scenarios. Thus, it might indicate that the more parent compounds were transformed to organic acids, which then readily oxidized to CO_2, HCl and water.

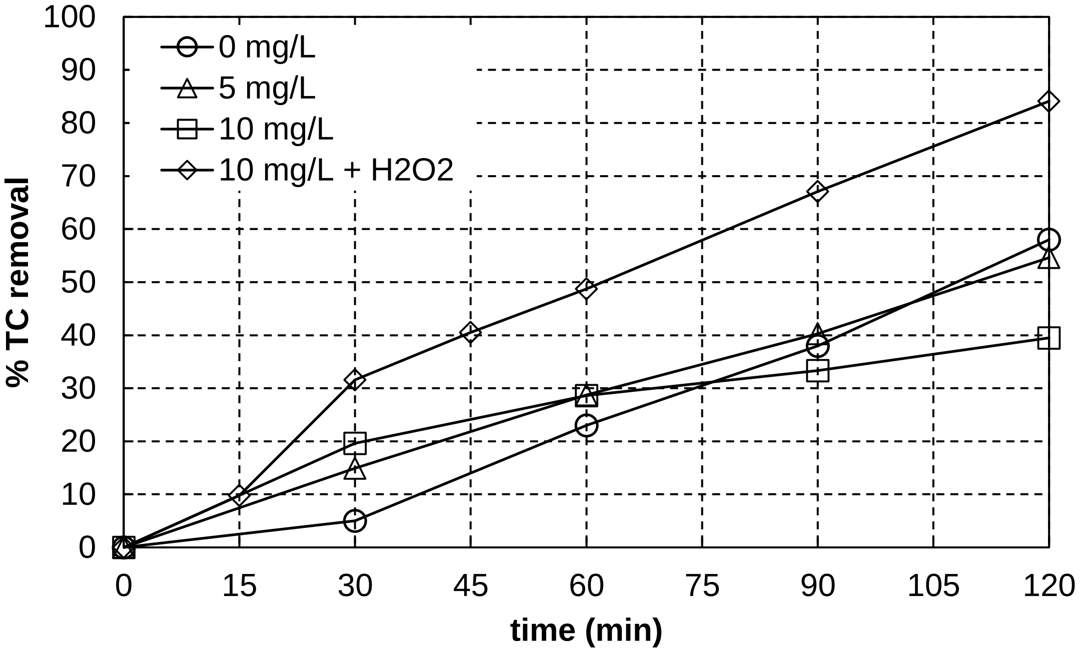
Figure 4.22: pH measurement of 2,4,6-trichlorophenol



4.5.5 Removal of 4 - Nitrophenol

Degradation of 4-Nitrophenol (4-NP) was studied with an initial concentration of 5 ppm and 10 ppm. The total initial concentration of TC (32 mg L^{-1}) and TiO_2 (0.5 g L^{-1}) loading remained at the optimum value. From *Figure 4.23*, it can be seen that with an increase in the concentration of 4-NP the TC removal efficiency decreases. 55% of total carbon was removed, when wastewater contained 5 ppm on 4-NP, whereas 10 ppm decreased TC removal to 39%. The higher initial concentration might result in the formation of more intermediates that could aggregate the surface of the catalyst, consequently leading to decrease of catalyst active sites [73].

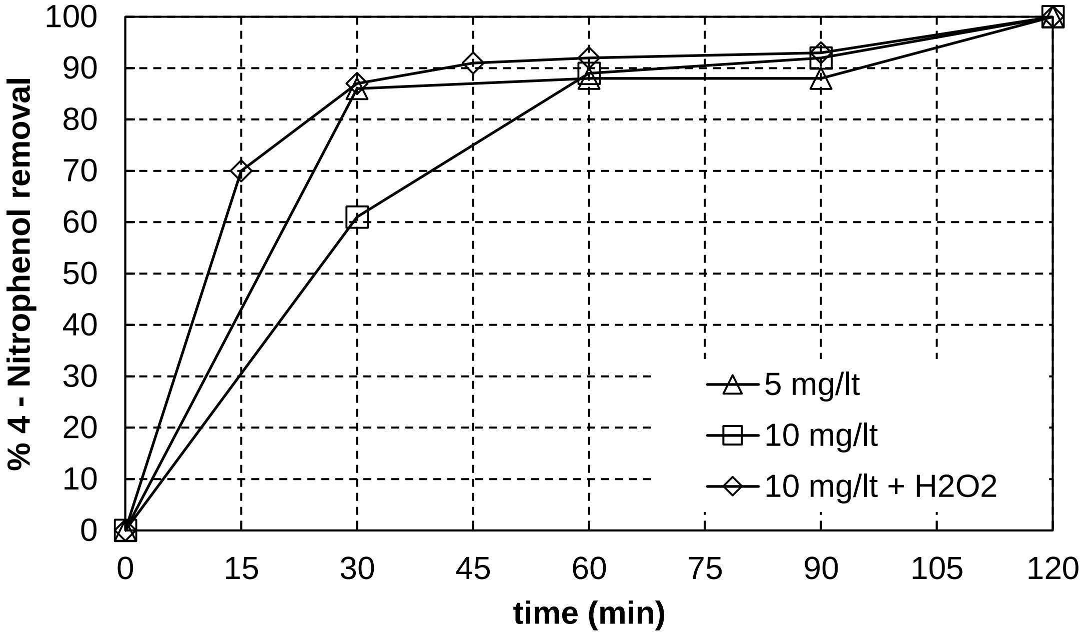
Figure 4.23: Effect of 4-nitrophenol on TC removal



Regarding decomposition of 4-NP itself, HPLC analysis indicated 100% removal of the compound from solution at 5 and 10 ppm (*Figure 4.24*). After 30 minutes, 5 ppm of 4-NP was removed for 87%, whereas 10 ppm for 61%. However, even better results were achieved by introducing H_2O_2 into the system, 84% of TC was removed. This finding ties well with previous studies wherein the combination of H_2O_2 and TiO_2 showed the improvement in degradation of pollutants [23, 73].

Analysis of UV/TiO_2 process with 10 ppm 4-NP, obtained from HPLC after 120 minutes, did not show 4-NP, however, it presented other peaks differing from the initial graph. Thus, it can be assumed, that those peaks correspond to formed intermediates. Combination of catalyst and oxidant on removal 4-NP showed better results, as there were significantly fewer detected intermediates. Moreover, the occurred peaks can belong to the primary organic pollutants.

Figure 4.24: Decomposition of 4-nitrophenol

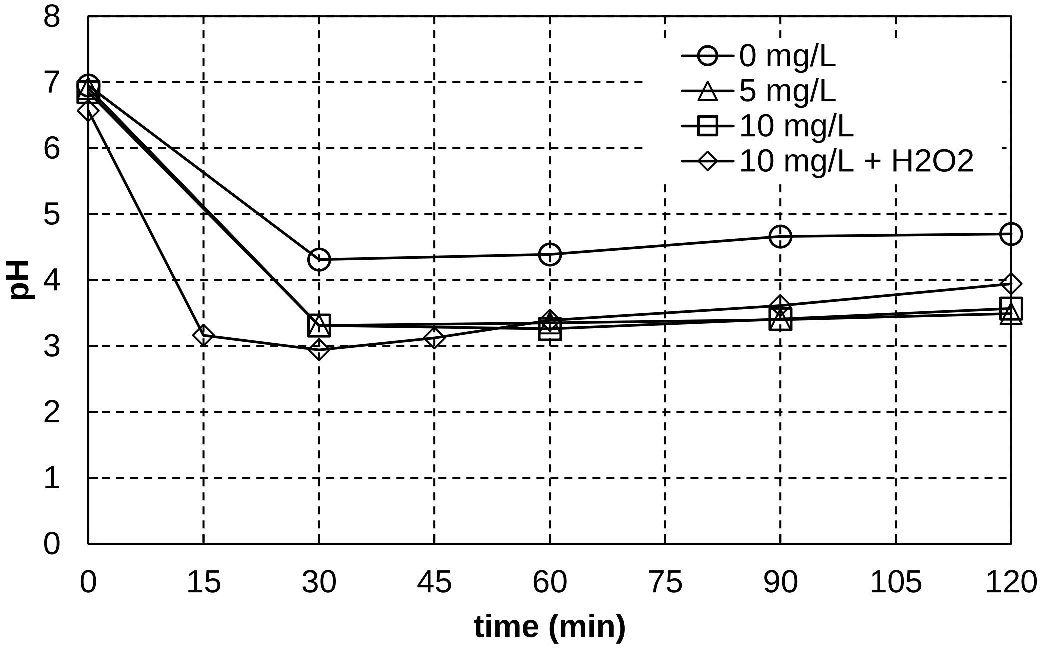


As hydroxyl radicals attack 4-NP, NO_2^- oxidizes to NO_3^-, eventually, all parent compounds and intermediates degrade to CO_2 [23]. Therefore, after the introduction of hydrogen peroxide more radicals were formed, thus, resulting in the higher conversion of TC.

$$C_6H_4OHNO_2 + 7O_2 \rightarrow 6CO_2 + 2H_2O + HNO_3 \qquad (4.8)$$

Also, pH aqueous solution has changed during the process. It can be seen from *Figure 4.25* that pH measurement tends to decrease in the first 30 minutes. As discussed previously, the possible reason for this is the formation of intermediate products like organic acids, which makes the solution more acidic.

Figure 4.25: pH measurement of 4-nitrophenol



4.5.6 Effect of ion species

The TC conversion in case of 2-CP, 2,4-DCP, and 2,4,6-DCP followed a different path than with phenol and 4-NP. It was noted that with an increase in the concentration of chlorophenols, the TC conversion also increases. While for phenol and 4-NP, increase in concentration lead to opposite result. Presence of ions in solution can impact on the performance of photocatalytic degradation [75]. Generation of inorganic radicals comes from the interaction of holes and hydroxyl radicals, and they adsorb on the TiO_2 surface, thus decreasing the photocatalytic activity [38]. Moreover, studies were done on the investigation of the influence of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and chloride (Cl^-)ions. The reaction of all three inorganic ions are presented in the following equations:

$$CO_3^{2-} + HO^{\bullet} \rightarrow OH^- + CO_3^- \qquad (4.9)$$

$$HCO_3^- + HO^\bullet \rightarrow H_2O + CO_3^- \qquad (4.10)$$

$$Cl^- + HO^\bullet \rightarrow Cl^\bullet + OH^- \qquad (4.11)$$

Studies on 4-chlorophenol, 2,4-DCP, and 2,4,6-DCP have suggested that formed chloride radicals ($Cl^\bullet$) can assist in the promotion of organic pollutant degradation [74]. If it forms a prior generation of chloride anions (Cl^-), which in turn, inhibits the catalyst activity and solubility of organic substances [74].

$$Cl^- + h_{vb}^+ \rightarrow Cl^\bullet \qquad (4.12)$$

$$Cl^- + Cl^\bullet \rightarrow Cl_2^\bullet \qquad (4.13)$$

Chloride anions in comparison to other inorganic ions have a more detrimental effect on photocatalytic treatment. As shown in the equation, it forms less reactive chloride ($Cl^\bullet$) and dichloride radicals ($Cl_2^\bullet$) [20]. These generated chloride radicals might react with organic matter by one-electron oxidation, depending on the characterizations of the substrate. The reaction can go by H-abstraction and addition to unsaturated C-C bonds [74]. Chloride radicals show lower reactivity than hydroxyl radicals, but it can efficiently oxidize substituted aromatic rings. Theoretically, the first step in these multi-phase process can be •OH attack, and then chloride radicals proceed reactions with organic molecule [75].

4.5.7 Comparison of phenolic compounds effects

The all experimental results on TC removal of wastewater containing phenols are presented in *Table 4.2*. One of the main findings was that phenol and 4-NP effect on process differently than chlorophenols. The possible explanation of this might be the fact that they have different properties of molecules and by-products, thus, they might have different adsorption on catalyst surface or UV light absorption.

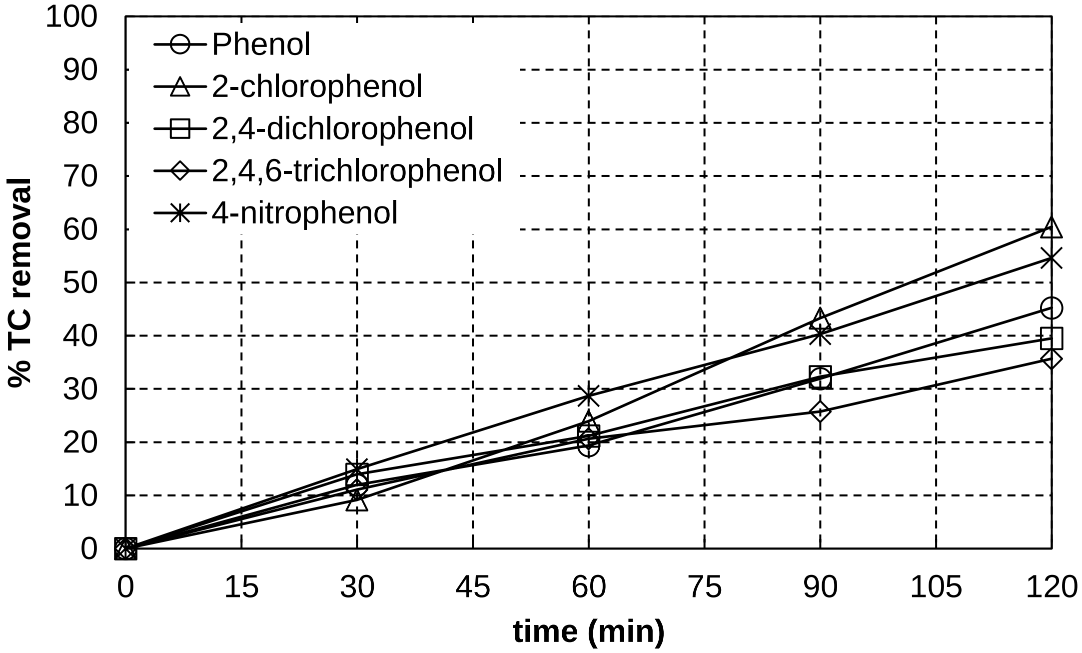
Table 4.2: Effect of phenols on TC removal

Concentration	Phenol	2-CP	2,4-DCP	2,4,6-TCP	4-NP
5 ppm	45%	60%	40%	36%	55%
10 ppm	48%	81%	59%	44%	39%
10 ppm + H_2O_2	80%	80%	88%	83%	84%

Figures 4.26 and *4.27* present the TC removal and model component conversion of a solution containing 5 ppm phenols. In this case, phenol had reduced the performance of photocatalytic process from 58% to 45%, whereas 4-NP did not have a significant impact. After HPLC analysis, 6% of phenol was remained in solution, while 4-NP had 100% removal. In terms of chlorophenols, the process efficiency on TC removal decreased with the increase of chlorine atoms in the molecule, the same pattern also occurred with 10 ppm concentration (*Figure 4.28*). The number and position of chlorinated atoms have its effect on oxidation potential of the compound. The reason that chlorine atoms may block the favorable positions on the aromatic ring for hydroxyl radicals [5, 76]. However, obtained results for chlorophenols decomposition by the photocatalytic process at 5 ppm and 10 ppm showed that 2,4-DCP did not convert entirely, while 2-CP and 2,4,6-TCP had 100% conversion (*Figure 4.27* and *4.29*). Explanation of this results can be attributable to by-products of the parent compound. It might be that by-products of 2,4-DCP are difficult to oxidize [77]. One of the limitations of the

present study was that intermediates were not identified, due to the absence of required laboratory equipment.

Figure 4.26: TC removal with 5ppm phenolic compounds



It was observed an increase in the concentration of 4-NP to 10 ppm reduced the total carbon removal, while the increase in phenol concentration did not change treatment efficiency. Chlorophenols, in turn, had controversial results than 4-NP, as the presence of 10 ppm chlorophenols boosted the conversion of total carbon by UV/TiO_2 process. Moreover, treatment was able to oxidize all phenolic compounds more than 95%.

Figure 4.27: Component removal at 5 ppm concentration

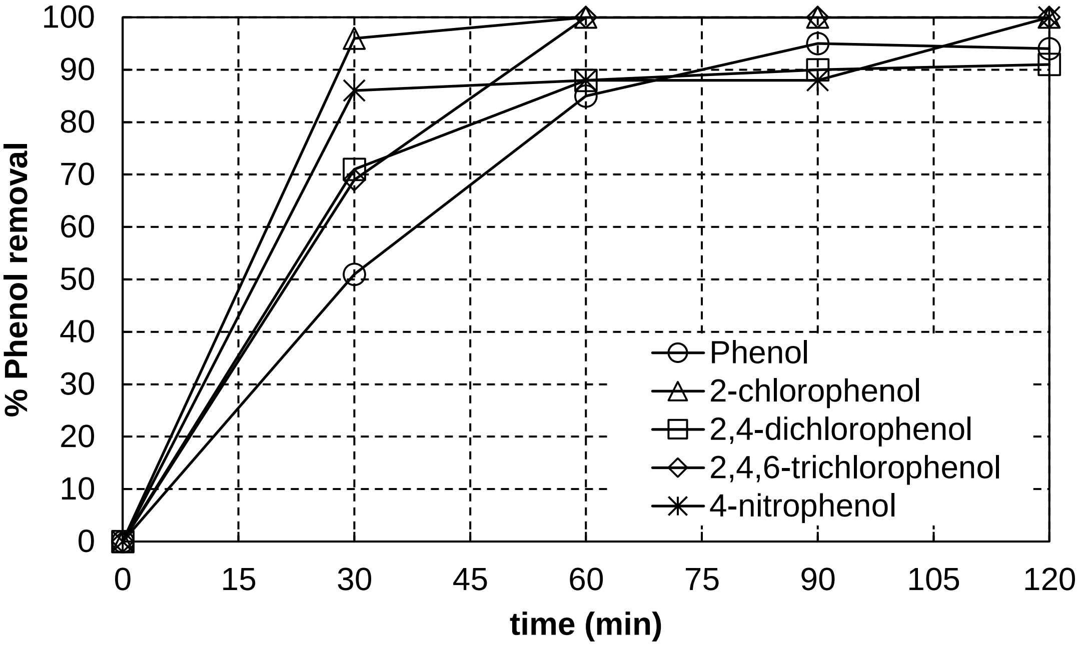


Figure 4.28: TC removal with 10 ppm phenolic compounds

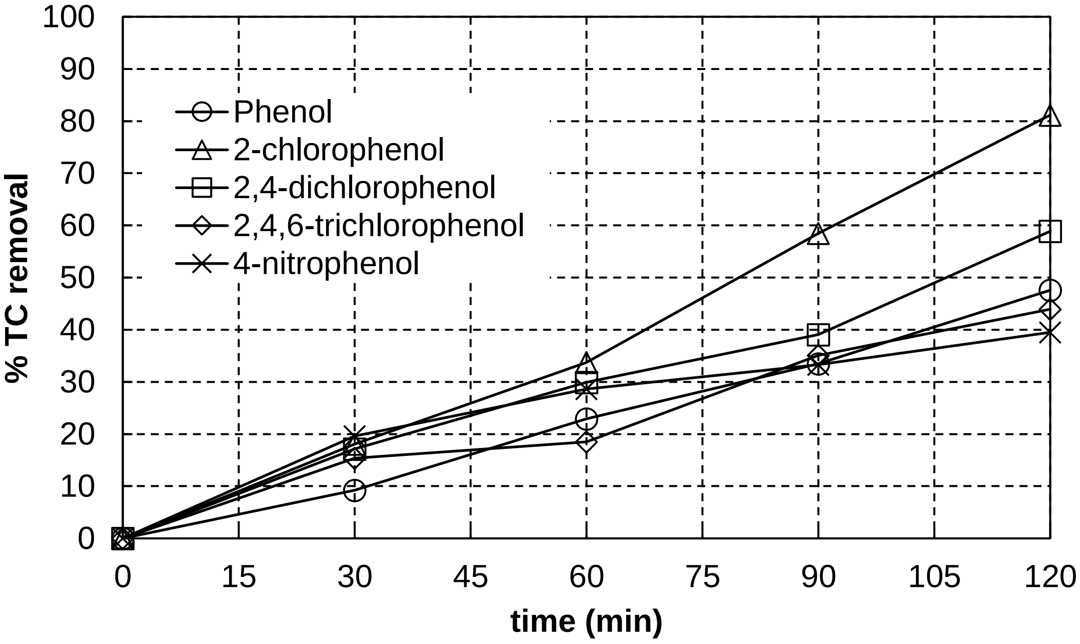
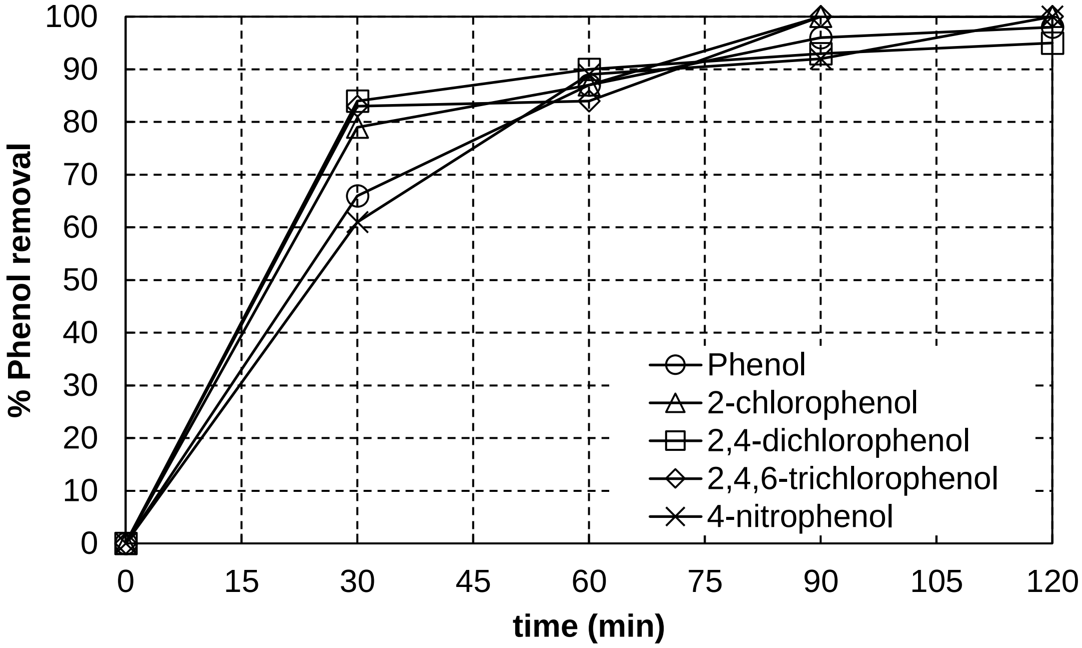


Figure 4.29: Component removal at 10 ppm concentration



Even better results were achieved when H_2O_2 oxidant was added to the treatment process. As it was discussed, the sequence of degradation rates for chlorophenolslike compounds was 2-CP>2,4-DCP>2,4,6-TCP regarding TC removal, whereas addition of H_2O_2 changes sequence to 2,4-DCP>2-CP>2,4,5-TCP (*Figure 4.30*). Also, the oxidant markedly increased the conversion of phenolic compounds, 100% of decomposition for all components was achieved after two hours, as shown in *Figure 4.31*.

Figure 4.30: TC removal with 10 ppm phenolic compounds and H_2O_2

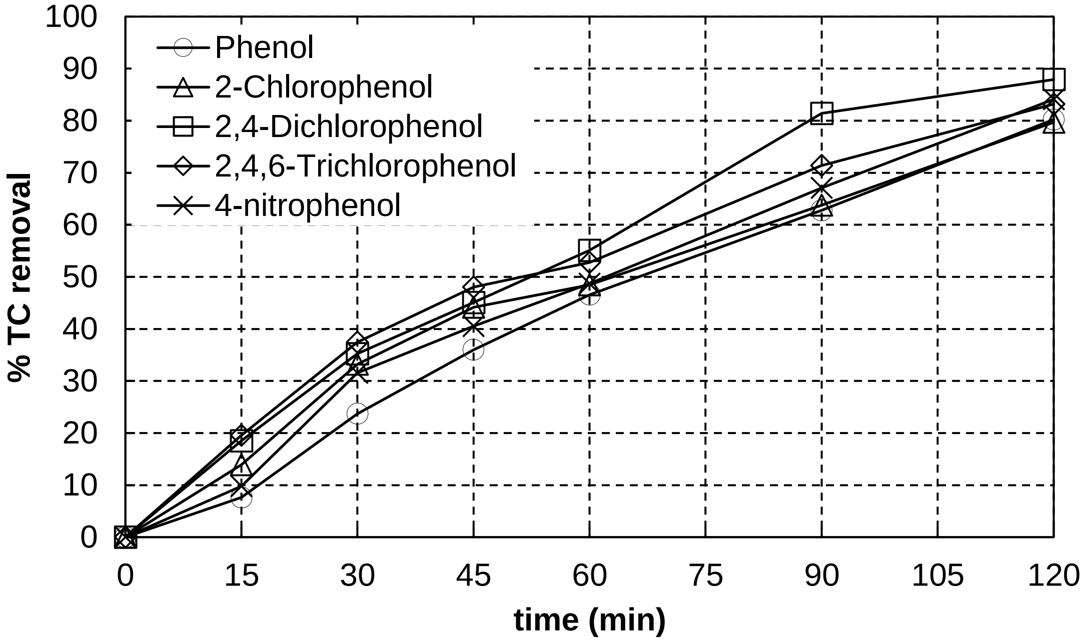
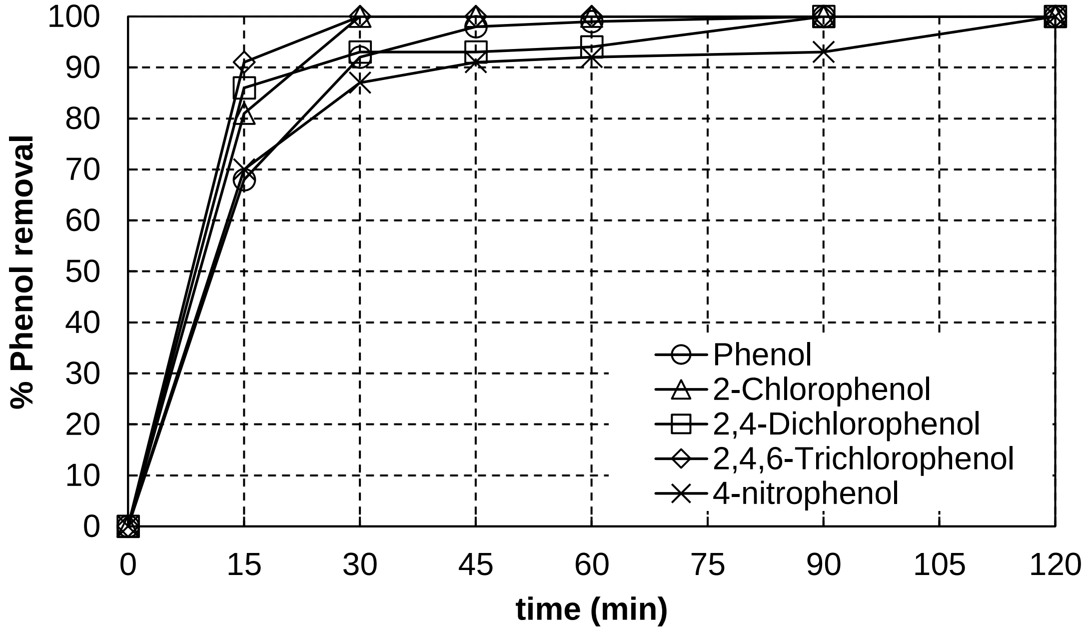


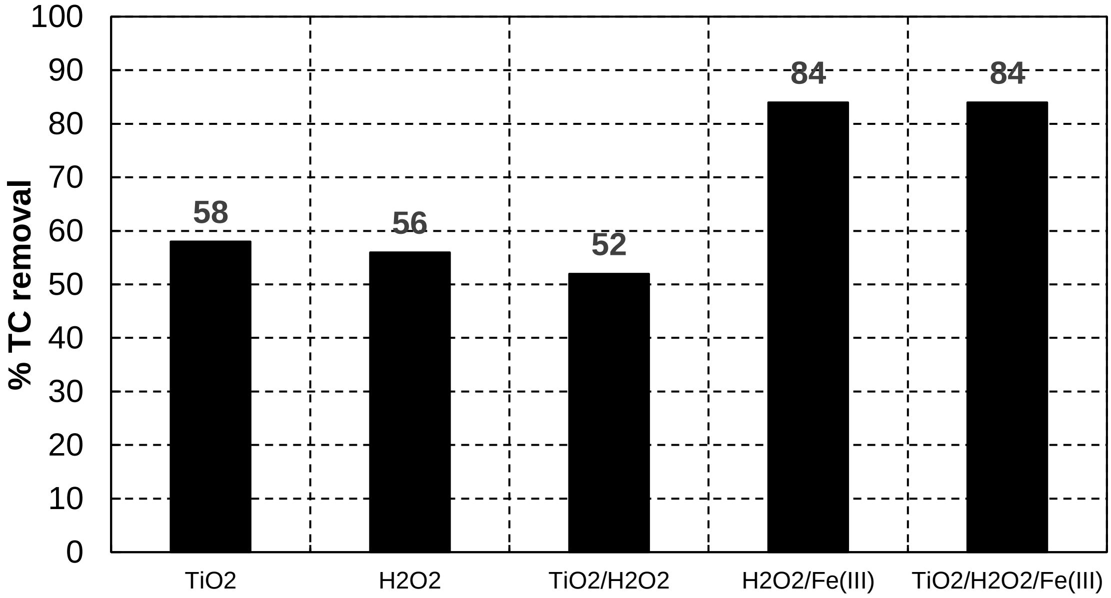
Figure 4.31: Component removal at 10 ppm concentration with H_2O_2



4.6 Summary of findings

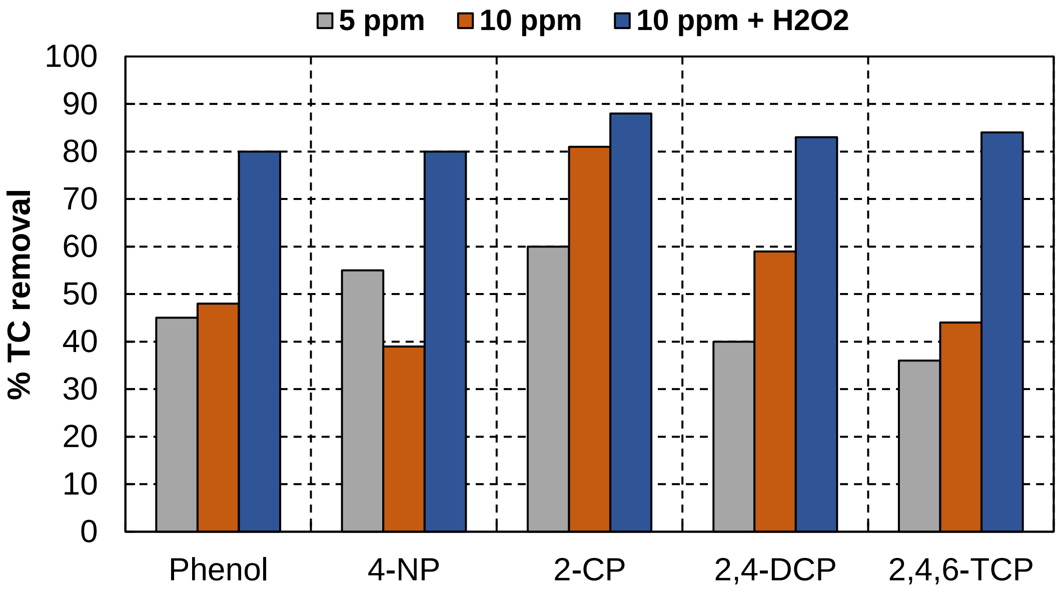
Heterogeneous photocatalytic reaction with TiO_2 has shown sufficient efficiency in degradation of organic molecules from synthesized wastewater. *Figure 4.32* presents the results obtained by different techniques that were applied to treat synthesized water with 32 mg L^{-1} total carbon concentration. UV/TiO_2 process performance was better than it was combined with an H_2O_2 oxidant. Results were also obtained for methods containing ferric ions aiming to compare its performance with the photocatalytic process. It is evident that presence of Fe(III) markedly improved the TC removal. The maximum achieved conversion of TC was 84% by UV/H_2O_2/Fe(III) and UV/TiO_2/H_2O_2/Fe(III).

Figure 4.32: Efficiency of different AOPs methods



After optimal operating conditions of photocatalytic AOPs were identified, these findings were applied on the treatment of wastewater that contains a low concentration of the phenolic compound. From the *Figure 4.33,* it is clear that photocatalytic AOPs constituted by H_2O_2 is able to effectively treat wastewater containing a small concentration of phenolic compounds. UV/TiO_2/H_2O_2 process was able to remove more than 80% of total carbon from wastewater composed of organic carbon pollutant and phenolic compound.

Figure 4.33: Results of %TC removal in wastewater with phenolic compounds



Chapter 5 – Conclusion

In this study, the photocatalytic process was applied to treat synthesized wastewater with a typical composition of industrial wastewater. The target was to compare the performance of photocatalytic AOPs process with the photochemical and photo-Fenton processes and evaluate the efficiency of their combination on total carbon removal. Moreover, the UV/TiO_2 and UV/H_2O_2/TiO_2 processes were examined on phenolic compounds removal from wastewater. The main results are:

- The UV/TiO_2 (58%) and UV/H_2O_2 (56%) processes are effective in the treatment of synthesized wastewater at the following conditions: TC=32 mg L^{-1}, TiO_2 = 0.5 g L^{-1} and H_2O_2=66.6 mg L^{-1}.

- Photocatalytic AOPs constituted with a combination of H_2O_2 does not result in higher removal of total carbon from synthesized wastewater. Only 52% of TC was removed by this process.
- UV/H_2O_2 can be enhanced by the addition of ferric ions into the process, resulting in 84% conversion. However, in comparison, a combination of all reagents, TiO_2, H_2O_2 and Fe(III) did not result in higher TC removal.
- Application of UV/TiO_2 on treatment wastewater, containing organic pollutants combined with phenolic compounds, showed that the conversion of the model compound was always higher than corresponding total organic carbon removal.
- Total carbon and model compound removal increases with increase in concentrations of 2-CP, 2,4-DCP and 2,4,6-TCP.
- Photocatalytic AOPs constituted by H_2O_2 is able to effectively treat phenolic compounds present wastewater, achieving more than 80% of TC removal.

The conducted research presents important findings in the understanding of the treatment of wastewater, which contains organic pollutants combined with phenolic compounds. Regardless, future studies could continue to investigate the effect of intermediate by-products on overall process performance. In addition, research should be conducted on testing the applicability of presented process in real industrial wastewater.

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Appendix

Table A. 1: Results of experiment conducted on 17.10.2017

17.10 Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**TOC*DR**	**Correction**	**pH**	**Conversion**
Water		3.81 ± 41.54%					
1	0	34.03 ± 1.20%	1/10	340.3	476.7088	7.05	0
2	15	34.62 ± 0.08%	1/10	346.2	485.3193	5.57	-2
3	30	37.99 ± 0.47%	1/10	379.9	534.5011	5.41	-12
4	45	37.04 ± 0.76%	1/10	370.4	520.6368	5.34	-9
5	60	36.20 ± 0.79%	1/10	362	508.3778	5.32	-7
6	90	36.05 ± 0.70%	1/10	360.5	506.1887	5.34	-6
7	120	34.77 ± 0.12%	1/10	347.7	487.5084	5.35	-2
H2O2	0	ml					
Stock	125	ml					
Water	125	ml					
TiO2	0.25	g					

Table A. 2: Results of experiment conducted on 18.10.2017

18.10 Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction factor**	**TC*DR**	**pH**	**Conversion**
DI		3.04 ± 52.87%					
1	0	35.35 ± 0.24%	4/10	49.59729	123.99	6.85	0
3	30	34.63 ± 0.35%	4/10	48.546522	121.37	4.5	2
4	60	32.51 ± 1.63%	4/10	45.452594	113.63	4.31	8
5	90	32.47 ± 0.37%	4/10	45.394218	113.49	4.21	8
6	120	31.03 ± 0.26%	4/10	43.292682	108.23	4.19	13
H2O2	0ml						
Stock	31.25ml						
water	218.75ml						
TiO2	0.25ml						

Table A. 3: Results of experiment conducted on 19.10.2017

19.10a Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction factor**	**TC*DR**	**pH**	**conversion**
Water		2.19 ± 5.88%					
1	0	26.32 ± 0.10%	6/10	36.419	60.70	7.66	0
3	30	24.97 ±0.35%	6/10	34.449	57.41	3.84	5
4	60	22.66 ± 2.35	6/10	31.078	51.80	4.1	15
5	90	21.91 ± 0.08%	6/10	29.983	49.97	4.38	18
6	120	19.77 ± 0.95%	6/10	26.860	44.77	4.67	26
H2O2	0	ml					
Stock	15.625	ml					

Water	234.375	ml
TiO2	0.25	g

19.10b Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**TC*DR**	**pH**	**conversion**
Water		2.06 ± 16.79%					
1	0	25.77 ± 1.75%	6/10	35.616	59.36	7.77	0
3	30	26.08 ± 0.06%	6/10	36.069	60.11	4.75	-1
4	60	24.75 ± 0.69%	6/10	34.128	56.88	4.54	4
5	90	23.21 ± 0.59%	6/10	31.880	53.13	4.66	10
6	120	21.97 ± 0.81	6/10	30.071	50.12	4.72	16

H2O2	0	ml
Stock	15.625	ml
Water	234.375	ml
TiO2	0.0625	g

Table A. 4: Results of experiment conducted on 20.10.2017

20.10 Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**TC*DR**	**pH**	**conversion**
Water		2.04 ± 12.19%					
1	0	18.17 ± 0.11%	8/10	24.525	30.66	7.46	0
3	30	17.06 ± 0.33%	8/10	22.905	28.63	4.35	7
4	60	14.57 ± 2.21%	8/10	19.271	24.09	4.57	21
5	90	11.54 ± 0.50%	8/10	14.849	18.56	4.79	39
6	120	8.76 ± 4.74%	8/10	10.792	13.49	4.96	56

H2O2	0	ml
Stock	7.8125	ml
Water	242.1875	ml
TiO2	0.25	g

Table A. 5: Results of experiment conducted on 23.10.2017

23.10 Dark Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**TC*DR**	**pH**	**conversion**
Water		2.10 ± 1.82%					
1	0	17.90 ± 0.07%	8/10	24.131	30.16	6.96	0
3	30	17.81 ± 1.41%	8/10	23.999	30.00	6.62	1
4	60	16.99 ± 0.50%	8/10	22.803	28.50	6.75	6
5	90	17.17 ± 0.56%	8/10	23.065	28.83	6.8	4
6	120	16.62 ± 1.01%	8/10	22.263	27.83	6.85	8

H2O2	0	ml
Stock	7.8	ml
Water	242.2	ml
TiO2	0.25	g

23.10 Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**correction**	**TC*DR**	**pH**	**conversion**
Water		2.10 ± 1.82%					
1	0	17.26 ± 1.82%	8/10	23.197	29.00	7.08	0
3	30	18.29 ± 0.20%	8/10	24.700	30.87	4.31	0
4	60	15.91 ± 0.17%	8/10	21.227	26.53	4.42	8
5	90	13.86 ± 2.16%	8/10	18.235	22.79	4.52	21
6	120	11.53 ± 0.92%	8/10	14.834	18.54	4.6	36
H_2O_2	0	ml					
Stock	7.8	ml					
Water	242.2	ml					
TiO_2	0.025	g					

Table A. 6: Results of experiment conducted on 24.10.2017

24.10 Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**correction**	**pH**	**TC*DR**	**conversion**
Water		2.55 ± 11.52%					
1	0	17.17 ± 0.08%	8/10	23.065	6.95	28.83	0
3	30	16.28 ± 0.07%	8/10	21.767	4.31	27.21	6
4	60	13.51 ± 1.57%	8/10	17.724	4.39	22.15	23
5	90	11.20 ± 1.14%	8/10	14.353	4.66	17.94	38
6	120	8.06 ± 1.59%	8/10	9.770	4.7	12.21	58
H_2O_2	0	ml					
Stock	7.8	ml					
Water	242.2	ml					
TiO_2	0.125	g					

Table A. 7: Results of experiment conducted on 25.10.2017

25.10a Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**pH**	**TC*DR**	**conversion**
Water		2.31 ± 11.79%					
1	0	18.27 ± 0.34%	8/10	24.671	7.06	30.84	0
3	30	17.53 ± 0.30%	8/10	23.591	4.14	29.49	4
4	60	15.91 ± 2.05%	8/10	21.227	4.29	26.53	14
5	90	13.99 ± 1.85%	8/10	18.425	4.42	23.03	25
6	120	10.97 ± 0.76%	8/10	14.017	4.58	17.52	43
H_2O_2	0	ml					
Stock	7.8	ml					
Water	242.2	ml					
TiO_2	0.0625	g					
25.10b Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**pH**	**TC*DR**	**conversion**
Water		2.09 ± 8.19%					
1	0	18.58 ± 1.57%	8/10	25.123	8.64	31.40	0

3	30	18.57 ± 2.81%	8/10	25.109	5.42	31.39	0
4	60	18.74 ± 4.45%	8/10	25.357	5.32	31.70	-1
5	90	18.45 ± 1.29%	8/10	24.933	5.2	31.17	1
6	120	18.47 ± 0.83%	8/10	24.963	4.94	31.20	1

H2O2	0	ml
Stock	7.8	ml
Water	242.2	ml
TiO2	0	g

Table A. 8: Results of experiment conducted on 26.10.2017

26.10 Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**correction**	**pH**	**TC*DR**	**conversion**
Water		2.10 ± 5.62%					
1	0	17.12 ± 1.85%	8/10	22.99	8.05	28.74	0
3	30	15.03 ± 0.68%	8/10	19.94	3.88	24.93	13
4	45	11.07 ± 0.26%	8/10	14.16	4.44	17.70	38
5	60	8.25 ± 2.98%	8/10	10.05	5.44	12.56	56
6	90	4.87 ± 35.85%	8/10	6.09	6.13	6.09	79
7	120	5.36 ± 19.51%	8/10	5.83	6.29	7.29	75

H2O2	0.1	ml
Stock	7.8	ml
Water	242.1	ml
TiO2	0	g

Table A. 9: Results of experiment conducted on 27.10.2017

27.10a Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**pH**	**TC*DR**	**conversion**
Water		1.76 ± 1.93%					
1	0	17.98 ± 0.99%	8/10	22.48	7.25	28.09	0
2	15	18.09 ± 2.12%	8/10	24.41	6.15	30.51	-9
3	30	17.46 ± 2.42%	8/10	23.49	4.88	29.36	-5
4	45	12.74 ± 39.24%	8/10	16.60	4.2	20.75	26
5	60	10.95 ± 1.56%	8/10	13.99	4.26	17.48	38
6	90	8.93 ± 15.69%	8/10	11.04	5.19	13.80	51
7	120	8.64 ± 0.89%	8/10	10.62	5.74	13.27	53

H2O2	0.05	ml
Stock	7.8	ml
Water	242.15	ml
TiO2	0	g

27.10b Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**pH**	**TC*DR**	**conversion**
Water		1.76 ± 1.93%					
1	0	16.73 ± 0.51%	8/10	22.42	7.85	28.03	0
2	15	15.63 ± 0.78%	8/10	20.82	3.98	26.02	7

3	30	12.55 ± 0.78%	8/10	16.32	3.85	20.40	27
4	45	8.23 ± 3.50%	8/10	10.02	5.18	12.52	55
5	60	6.39 ± 0.85%	8/10	7.33	5.64	9.17	67
6	90 [1]	5.02 ± 1.65%	8/10	5.33	6.47	6.67	76
7	90 [2]	5.09 ± 0.94%	8/10	5.44	6.47	6.79	76
8	120 [1]	5.07 ± 0.65%	8/10	5.41	6.49	6.76	76
9	120 [2]	4.95 ± 0.33%	8/10	6.19	6.49	6.19	78
H2O2	0.2	ml					
Stock	7.8	ml					
Water	242	ml					
TiO2	0	g					

Table A. 10: Results of experiment conducted on 30.10.2017

30.10a Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**pH**	**TC*DR**	**conversion**
Water		2.31 ± 5.16%					
1	0	17.91 ± 1.93%	8/10	24.15	7.45	30.18	0
2	15	18.03 ± 4.69%	8/10	24.32	6.4	30.40	-1
3	30	17.46 ± 4.12%	8/10	23.49	6.06	29.36	3
4	45	17.75 ± 0.64%	8/10	23.91	5.58	29.89	1
5	60	17.30 ± 0.68%	8/10	23.26	5.17	29.07	4
6	90	16.10 ± 0.04%	8/10	21.50	4.77	26.88	11
7	120	12.11 ± 22.00%	8/10	15.68	4.8	19.60	35
H2O2	0.02	ml					
Stock	7.8	ml					
Water	242.18	ml					
TiO2	0	g					

30.10b Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**pH**	**TC*DR**	**conversion**
Water		2.31 ± 5.16%					
1	0	16.55 ± 4.26%	8/10	22.16	7.61	27.70	0
2	15	15.25 ±1.26%	8/10	20.26	5.41	25.33	9
3	30	13.20 ± 20.85%	8/10	17.27	5.23	21.59	22
4	45	11.65 ± 5.02%	8/10	15.01	5.38	18.76	32
5	60	10.98 ± 5.13%	8/10	14.03	5.57	17.54	37
6	90	9.36 ± 0.64%	8/10	11.67	5.8	14.58	47
7	120	8.59 ± 0.27%	8/10	10.54	5.89	13.18	52
H2O2	0.05	ml					
Stock	7.8	ml					
Water	242.15	ml					
TiO2	0.125	g					

Table A. 11: Results of experiment conducted on 31.10.2017

31.10 Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**pH**	**TC*DR**	**conversion**
Water		1.80 ± 9.35%					
1	0	15.51 ± 3.45%	8/10	20.64	6.33	25.80	0

2	5	12.87 ± 4.44%	8/10	16.79	3.13	20.99	19
3	15	9.57 ± 0.73%	8/10	11.97	3.26	14.97	42
4	30	7.68 ± 3.41%	8/10	9.22	3.26	11.52	55
5	45	6.72 ± 0.43%	8/10	7.81	3.27	9.77	62
6	60	4.86 ± 23.70%	8/10	6.08	3.3	6.08	75
7	90	3.56 ± 1.18%	8/10	4.45	3.57	4.45	84
8	120	3.36± 4.12%	8/10	4.20	2.93	4.20	84
H2O2	0.05	ml					
Stock	7.8	ml					
Water	242.15	ml					
TiO2	0	g					
Fe (III)	0.0025	g					

Table A. 12: Results of experiment conducted on 3.11.2017

3.11 Sample	**Time (min)**	**TOC (mg/l)**	**Dilution ratio**	**Correction**	**pH**	**TC*DR**	**conversion**
Water		4.24 ± 47.19%					
1	0	16.89 ± 2.53%	8/10	22.66	7.03	28.32	0
2	5	16.91 ± 1.47%	8/10	22.69	3.46	28.36	0
3	15	14.61 ± 0.89%	8/10	19.33	3.93	24.16	15
4	30	10.20 ± 41.88%	8/10	12.89	4.15	16.12	43
5	45	12.56 ± 2.41%	8/10	16.34	4.3	20.42	28
6	60	10.94 ± 1.98%	8/10	13.97	4.49	17.47	38
7	90	7.59 ± 22.24%	8/10	9.08	4.54	11.36	60
8	120	3.54 ± 0.34%	8/10	4.43	4.83	4.43	84
H2O2	0.05	ml					
Stock	7.8	ml					
Water	242.15	ml					
TiO2	0.125	g					
Fe (III)	0.0025	g					

Table A. 13: Results of experiment conducted on 16.11.2017

16.11 Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**conversion**	**[C6H6O]o (ppm)**	**Phen. Conversion**
Water		1.47 ± 17.99%						
1	0	17.87 ± 0.95%	24.09	6.56	30.11	0	8.866	0
2	30	15.89 ± 1.63%	21.20	3.58	26.50	12	4.358	51
3	60	14.67 ± 3.80%	19.42	3.65	24.27	19	1.345	85
4	90	12.60 ± 1.55%	16.40	3.72	20.49	32	0.47	95
5	120	10.40 ± 0.96%	13.19	3.96	16.48	45	0.491	94
H2O2	0	ml						
Stock	6.5	ml						
Water	243.5	ml						
TiO2	0.125	g						
Phenol	0.0014	g						

Table A. 14. Results of experiment conducted on 8.11.2017

8.11 Sample	Time (min)	TOC (mg/l)	Correction	pH	TC*DR	Conversion	[C6H6O]o (ppm)	Phen. Conversion
Water		1.21 ± 2.02%						
1	0	18.41 ± 1.15%	24.88	8.05	31.09	0	27.437	0
2	30	16.84 ± 0.02%	22.58	4.7	28.23	9	9.381	66
3	60	14.50 ± 0.02%	19.17	4.77	23.96	23	3.47	87
4	90	12.70 ± 0.62%	16.54	4.87	20.68	34	1.148	96
5	120	10.30 ± 1.15%	13.04	5	16.30	48	0.439	98
H2O2	0	ml						
Stock	5.1	ml						
Water	244.9	ml						
TiO2	0.125	g						
Phenol	0.0025	g						

Table A. 15: Results of experiment conducted on 17.11.2017

17.11 Sample	Time (min)	TOC (mg/l)	Correction	pH	TC*DR	conversion	[C6H6O]o (ppm)	Phen. Conversion
Water		2.71±75.45%						
1	0	17.99±0.51%	24.13	6.81	30.16	0	21.992	0
2	15	16.64±0.46%	22.29	3.59	27.86	8	6.951	68
3	30	13.98±0.63%	18.41	3.24	23.01	24	1.674	92
4	45	11.95±0.89%	15.45	3.28	19.31	36	0.51	98
5	60	10.20±1.18%	12.89	3.48	16.12	47	0.187	99
6	90	7.52±0.79%	8.98	3.68	11.23	63	0	100
7	120	4.77±1.79%	5.96	4.08	5.96	80	0	100
H2O2	0.05	ml						
Stock	5.1	ml						
Water	244.85	ml						
TiO2	0.125	g						
Phenol	0.0025	g						

Table A. 16: Results of experiment conducted on 18.11.2017

18.11 Sample	Time (min)	TOC (mg/l)	Correction	pH	TC*DR	Conversion	[C6H5ClO]o (ppm)	CP Conversion
Water		1.56 ± 15.02%						
1	0	18.06 ±0.15%	24.36	7.81	30.46	0	13.473	0
2	30	15.04 ± 0.02%	19.96	3.6	24.95	18	2.893	79
3	60	12.43 ± 2.85%	16.15	3.24	20.18	34	1.814	87
4	90	8.30 ± 1.86%	10.12	3.57	12.65	58	0	100
5	120	4.59 ± 0.34%	5.74	3.8	5.74	81	0	100
H2O2	0	ml						
Stock	5.8	ml						
Water	239.5	ml						
TiO2	0.125	g						
CP	0.002	ml						

Table A. 17: Results of experiment conducted on 20.11.2017

20.11a Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**New conversion**	**[C6H5ClO]o (ppm)**	**CP. Conversion**
Water		1.90 ± 2.68%						
1	0	18.63 ± 1.05%	25.20	7.34	31.50	0	5.24	0
2	30	17.05 ± 0.19%	22.89	3.66	28.61	9	0.235	96
3	60	14.50 ± 0.23%	19.17	3.53	23.96	24	0	100
4	90	11.15 ± 1.01%	14.28	3.33	17.85	43	0	100
5	120	8.19 ± 1.51%	9.96	3.59	12.45	60	0	100

H2O2	0	ml
Stock	6.8	ml
Water	240.8	ml
TiO2	0.125	g
CP	0.001	ml

20.11b Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**conversion**	**[C6H6O]o (ppm)**	**CP Conversion**
Water		2.71±75.45%						
1	0	17.33 ± 0.05%	23.30	6.05	29.12	0	11.843	0
2	15	15.11 ± 0.78%	20.06	3.67	25.07	14	2.308	81
3	30	12.03 ± 0.27%	15.56	3.05	19.46	33	0	100
4	45	10.28 ± 1.67%	13.01	3.01	16.26	44	0	100
5	60	9.59 ± 0.46%	12.00	3.18	15.00	48	0	100
6	90	7.15 ± 0.70%	8.44	3.41	10.55	64	0	100
7	120	4.73 ± 1.41%	5.91	3.51	5.91	80	0	100

H2O2	0.05	ml
Stock	5.8	ml
Water	239.3	ml
TiO2	0.125	g
CP	0.002	ml

Table A. 18: Results of experiment conducted on 21.11.2017

21.11 a Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**conversion**	**[C6H5ClO]o (ppm)**	**DCP Conversion**
Water		1.61 ± 19.40%						
1	0	18.63 ± 1.46%	25.20	6.76	31.50	0	5.614	0
2	30	16.22 ± 0.12%	21.68	4.3	27.10	14	1.646	71
3	60	14.97 ± 0.70%	19.85	4.15	24.82	21	0.676	88
4	90	13.05 ± 0.19%	17.05	3.97	21.32	32	0.559	90
5	120	11.81 ± 0.63%	15.24	4.13	19.05	40	0.504	91

Solution	250	ml
H2O2	0	ml
Stock	7	ml
Water	182.25	ml
TiO2	0.125	g
Dichlor (20ppm)	60.75	ml

21.11 b Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**conversion**	**[C6H5ClO]o (ppm)**	**DCP Conversion**
Water		1.60 ± 10.34%						
1	0	18.11 ± 0.71%	24.44	5.56	30.55	0	9.805	0
2	30	15.24 ± 0.47%	20.25	2.77	25.31	17	1.594	84
3	60	13.10 ± 0.20%	17.13	2.66	21.41	30	0.932	90
4	90	11.57 ± 0.93%	14.89	2.72	18.62	39	0.702	93
5	120	8.25 ± 1.74%	10.05	2.67	12.56	59	0.465	95

H2O2	0	ml
Stock	6.5	ml
Water	121.5	ml
TiO2	0.125	g
Dichlor (20ppm)	121.5	ml

Table A. 19: Results of experiment conducted on 22.11.2017

22.11 Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**Conversion**	**[C6H6O]o (ppm)**	**DCP Conversion**
1	0	18.93 ± 1.16%	25.63	4.66	32.04	0	10.071	0
2	15	15.68 ± 0.75%	20.89	2.55	26.11	19	1.448	86
3	30	12.74 ± 0.71%	16.60	2.29	20.75	35	0.71	93
4	45	11.01 ± 0.44%	14.08	2.56	17.59	45	0.737	93
5	60	9.25 ± 0.23%	11.51	2.65	14.38	55	0.624	94
6	90	4.76 ± 1.04%	5.95	2.97	5.95	81	0	100
7	120	3.10 ± 0.77%	3.88	3.7	3.88	88	0	100

H2O2	0.05	ml
Stock	6.5	ml
Water	121.5	ml
TiO2	0.125	g
dichlor (20ppm)	121.5	ml

Table A. 20: Results of experiment conducted on 23.11.2017

23.11 Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**Conversion**	**[C6H5ClO]o (ppm)**	**TCP Conversio**
Water		2.02 ± 14,42%						
1	0	19.72±1.13%	26.79	6	33.48	0	5.085	0
2	30	17.69 ± 0.27%	23.82	3.36	29.78	11	1.577	69
3	60	15.93±0.26%	21.26	3.27	26.57	21	0	100
4	90	14.99±0.11%	19.88	3.1	24.85	26	0	100
5	120	13.17±0.54%	17.23	3.27	21.53	36	0	100

H2O2	0	ml
Stock	7.2	ml
Water	236.8	ml
TiO2	0.125	g
TCP(250ppm)	6	ml

Table A. 21: Results of experiment conducted on 24.11.2017

24.11a Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**Conversion**	**[C6H5ClO]o (ppm)**	**TCP Conversion**
Water		1.83 ± 5.36%						
1	0	17.80 ± 1.18%	23.98	6.07	29.98	0	9.361	0
2	30	15.27 ± 0.28%	20.29	3.2	25.37	15	1.6	83
3	60	14.76 ± 0.09%	19.55	3.07	24.44	18	1.46	84
4	90	12.03 ± 0.11%	15.56	3.12	19.46	35	0	100
5	120	10.58 ± 0.83	13.45	3.16	16.81	44	0	100

Solution	250	ml
H2O2	0	ml
Stock	6.5	ml
Water	233.76	ml
TiO2	0.125	g
Tri (250ppm)	9.74	ml

24.11b Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**Conversion**	**[C6H6O]o (ppm)**	**TCP Conversion**
Water								
1	0	18.36 ± 0.56%	24.80	4.45	31.00	0	17.916	0
2	15	15.04 ± 0.39%	19.96	2.6	24.95	20	1.542	91
3	30	11.99 ± 0.24%	15.51	2.36	19.38	37	0	100
4	45	10.20 ± 0.15%	12.89	2.61	16.12	48	0	100
5	60	9.39 ± 0.76%	11.71	3.03	14.64	53	0	100
6	90	6.23 ± 1.71%	7.10	3.2	8.87	71	0	100
7	120	4.17 ± 1.95%	5.21	3.42	5.21	83	0	100

H2O2	0.05	ml
Stock	6.5	ml
Water	233.76	ml
TiO2	0.125	g
TCP(250ppm)	9.74	ml

Table A. 22: Results of experiment conducted on 25.11.2017

25.11 Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**conversion**	**[C6H5ClO]o (ppm)**	**NP. Conversion**
Water		1.58 ± 0.91%						
1	0	19.71 ± 0.97%	26.77	6.91	33.47	0	6.576	0
2	30	16.97 ± 0.58%	22.77	3.31	28.47	15	0.939	86
3	60	14.44 ± 0.31%	19.08	3.35	23.85	29	0.804	88
4	90	12.32 ± 0.54%	15.99	3.4	19.98	40	0.779	88
5	120	9.69 ± 0.43%	12.15	3.49	15.19	55	0	100

H2O2	0	ml
Stock	6.87	ml
Water	230.93	ml
TiO2	0.125	g

Nitrophenol (100ppm)	12.2	ml

Table A. 23: Results of experiment conducted on 27.11.2017

27.11a Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**conversion**	**[C6H5ClO]o (ppm)**	**NP Conversion**
Water		1.68±4.03%						
1	0	18.84±-0.94%	25.50	6.85	34.73	0	10.088	0
2	30	15.64±0.20%	20.83	3.31	27.91	20	3.937	61
3	60	14.17±0.16%	18.69	3.26	24.78	29	1.102	89
4	90	13.41±0.11%	17.58	3.41	23.16	33	0.774	92
5	120	12.40±1.24%	16.10	3.57	21.01	39	0	100

H2O2	0	ml
Stock	6	ml
Water	220	ml
TiO2	0.125	g
Nitrophenol (100ppm)	10	ppm

27.11b Sample	**Time (min)**	**TOC (mg/l)**	**Correction**	**pH**	**TC*DR**	**Conversion**	**[C6H5ClO]o (ppm)**	**NP Conversion**
Water		1.73 ± 1.51%						
1	0	17.75 ± 0.82%	23.91	6.57	29.89	0	10.914	0
2	15	16.15 ± 0.07%	21.58	3.16	26.97	10	3.26	70
3	30	12.58 ± 0.65%	16.37	2.94	20.46	32	1.379	87
4	45	11.11 ± 1.12%	14.22	3.12	17.78	41	0.931	91
5	60	9.77 ± 1.52%	12.27	3.39	15.33	49	0.821	92
6	90	6.76 ± 1.04%	7.87	3.61	9.84	67	0.774	93
7	120	3.80 ± 1.22%	4.75	3.94	4.75	84	0	100

H2O2	0.05	ml
Stock	6	ml
Water	220	ml
TiO2	0.125	g
Nitrophenol (100ppm)	10	ppm