Enhanced electrokinetic process for industrial wastewater treatment containing a high concentration of Total Kjeldahl Nitrogen (TKN)

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Abstract

Enhanced electrokinetic process for treatment of industrial wastewater containing a high amount of Total Kjeldahl Nitrogen (TKN)

Nadezda Zhukovskaya

The primary objective of this research was to search for an effective method of industrial wastewater treatment containing a high amount of Total Kjeldahl Nitrogen (TKN). Photographic process wastewater is one of them. Traditional approaches, e.g. biological, filtration, carbon absorption are often ineffective in the degradation of persistent organic nitrogen. Thus, this study included four phases of investigation for an effective simultaneous removal of organic nitrogen and ammonia. In Phase I the electrochemical oxidation was performed under different operating conditions to determine the ability of this process to mineralize organic nitrogen and to determine operating ranges for the further investigation. In Phase II conventional electro-Fenton oxidation was implemented. The most successful results were obtained in Phase III, when enhanced electro-Fenton oxidation (EEFO) by additional of an oxidation agent was applied. The best removal efficiency of TKN, ammonia and organic nitrogen reached 92.4 %, 95.2 % and 81.4 % respectively. Also, it was demonstrated that enhanced electro-Fenton process with pretreatment from the ammonia can remove TKN and organic nitrogen by 95.8% and 97.2% respectively in a shorter residence time of 24 hours. In Phase IV the system was tested with a series of electrodes implemented in parallel. The results showed that the removal of organic nitrogen in a single cell and in series was similar. The developed process demonstrated an acceptable level of TKN removal while an insignificantly low amount of chemicals was added. The developed enhanced electro-Fenton oxidation method can be applied to other industrial wastewaters with a similar composition of pollutants.

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I am grateful to dedicate this work to my dear parents

and my beloved husband Nicolas

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AC: Activated carbon

A_{eff}: Effective surface area of electrode (m^2)

AOP: Advanced oxidation process

API: Active pharmaceutical ingredient

BDD: Boron doped diamond

BOD: Biological oxygen demand (mg/l)

$C_{electrode}$: Electrode consumption (kg/m^3 treated wastewater)

COD: Chemical oxygen demand (mg/l)

CON: Colloidal organic nitrogen

Conductivity (mS/cm)

DO: Dissolved oxygen (mg/l)

DON: Dissolved organic nitrogen

EAOP: Electrochemical advanced oxidation process

EF: Electro-Fenton

EK: Electrokinetic(s)

F: Faraday's number (26.81 A·h/mol)

Fe^{+2}: Ferrous ion

Fe^{+3}: Ferric ion

FF: Fered-Fenton

J: Current density (A/ m^2)

HMW: High molecular weight

HRT: Hydraulic retention time (h)

H_2O: Water

I: Current (Amps)

LMW: Low molecular weight

M: Molecular weight of the electrode material (g/mol)

MBR: Membrane bioreactor

MOx: Anode surface

$OH^{\cdot}$: Hydroxyl radical

ON: Organic nitrogen

ORP: Oxidation-reduction potential (mV)

PON: Particulate organic nitrogen

PPCP: Pharmaceutical personal care product

RH: Organic compound

t: Operating time (seconds)

T: Temperature (˚C)

TDS: Total dissolved solids (mg/l)

TKN: Total Kjeldahl Nitrogen (mg/l)

TN: Total nitrogen (mg/l)

TOC: Total organic carbon (mg/l)

TSS: Total suspended solids (mg/l)

V: Volume of water treated (m^3)

z: Valence number of electrons transferred by the anode

Chapter 1: Introduction and research objectives

1.1 Problem statement

Increase in industrial development over the last decade has adversely impacted the environment, especially water resources. Currently in Canada, over 150 billion liters of untreated and undertreated wastewater is discharged into receiving water bodies each year (Canada, 2013). These effluents contain various kinds of pollutants, which affect not only environment but also public health. One of the biggest concerns is the content of nitrogen in wastewater given that it stimulates the growth of algae and thereby decreases the concentration of dissolved oxygen, which is essential for living organism (Dongke, 2012). The nitrogen discharged from the wastewater plant may be in the form of inorganic compounds such as ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) and in the form of organic compounds, including proteins, amides, amino acids, urea and humic substances.

Similarly to other countries and provinces, Quebec is also concerned about the quality of its waters. In order to preserve water resources and public health, the government puts forth stricter regulations. Thus, Quebec municipalities, including the city of Montreal, apply more restrictive regulations with respect to wastewater containing nitrogen discharged into the collective sewage system. Therefore, the industry is seeking a new cost-effective solution for managing its wastewaters.

Traditional approaches and technical solutions in the field of water treatment are often ineffective for the treatment and disposal of wastewater containing toxic, nonbiodegradable and difficult to oxidize organic nitrogen (ON) pollutants (Zhelovitskaya et al., 2010). For example, the common physicochemical treatment, including activated carbon absorption and membrane filtration, can transfer pollutants from one phase into another, however, cannot remove it from wastewater (Ozcan, 2010). Disinfection using ozone or hypochlorite as oxidants is a well-known method, but is not efficient for the removal of persistent organics from industrial wastewaters. Moreover, it can result in the production of by-products which are even more toxic than their parent forms (Malik and Saha, 2003). One of the most efficient and popular method is the biological process. For this specific wastewater however, this process cannot be used due to the wastewater's characteristics, namely a high conductivity of 62 mS/cm. At a conductivity that is greater than 20 mS/cm, microorganisms cannot survive. A promising treatment for removal of persistent organics is technology based on the use of strong oxidants-advanced oxidation processes (AOPs) (Sun et al., 2007; Papadopoulas et al., 2007; Jain and Shrivastava 2008; Quici, 2007). These processes include chemical, photochemical or electrochemical processes (Huang 2001; Rajkumar and Palanivelu, 2004). All these processes are based on the production of the principal active species, e.g. hydroxyl radical, which is one of the strongest oxidizing agents (Lin and Lo, 1997). These radicals mineralize organic pollutants to CO_2, H_2O, NO_2 and/or oxidize them to simpler organic forms.

One of the AOP methods is the Fenton oxidation process, based on the production of Fenton’s reagents, including hydrogen peroxide and ferrous ion. However, this method also has disadvantages, including a high ferric hydroxide sludge production, use of a large amount of oxidant and a slow regeneration of the ferrous ions, which are one of the main components of the Fenton reaction (Boye et al., 2002). In contrast, electrochemical advanced oxidation processes (EAOPs) can avoid these types of disadvantages, and have additional advantages such as a lower operational cost and a higher mineralization degree (Ozcan, 2010). EAOPs consist of two processes: anodic oxidation and electro-Fenton oxidation. In anodic oxidation, mineralization happens due to a reaction with the hydroxyl radical produced on the electrode surface, via the reduction reaction of water. While in the electro-Fenton process, the organic compounds are degraded by the action of Fenton’s reagent together with anodic oxidation. However, the success of this process also depends on the nature of the wastewater. A number of studies with synthetic wastewater were done using electro-Fenton oxidation, but, studies of the electro-Fenton process applied to real wastewater have been limited. Therefore, the concepts of electrochemical oxidation and Fenton oxidation, with some modification, were applied to the wastewater in the current study in order to assess removal efficiency of organic nitrogen defined as TKN (Total Kjeldahl Nitrogen).

Research objectives

The main objective of this research was to investigate methods for removal of TKN (Total Kjeldahl Nitrogen), which comprises in industrial wastewater (represented by the photographic processing effluents) persistent organic nitrogen (ON) and ammonia with the concentrations higher than 2000 mg/l and 10000 mg/l respectively. Specific objectives included determination of operating conditions for designed reactors and investigation an impact of the designed parameters on effluent quality.

1.2 Organization of the thesis

The thesis consists of 5 chapters. Chapter 1 includes introduction, where the statement of the problem and research objectives are discussed. Chapter 2 presents the review of the existing relevant literature on the topic in order to demonstrate the fundamentals of the main processes, their advantages/disadvantages and to show the necessity of a new research approach. Chapter 3 presents a detailed description of the methodology, including the strategy of the experimental work, experimental set-up and analyses. Chapter 4 presents results obtained from the laboratory experiments and their discussion. Finally, Chapter 5 gives conclusion and explores research contributions and recommendations for future work.

Chapter 2 : Literature review

Industrial wastewater often contains the high concentration of TKN, mostly consisting of persistent organic nitrogen. In this study such wastewater is represented by effluents from the photo-producing industry. Then, a review the photographic industry process is presented in Section 2.1. This will facilitate the recognition of components used in the industrial process, their transformation and the outcomes. Then, an assumption of the composition of the final wastewater containing stable organic nitrogen (e.g. amides) and its properties is discussed in the Section 2.2. Furthermore, the transformation of nitrogen in wastewater under various treatment conditions (Section 2.3), as well as its influence on the receiving water bodies and the environment (Section 2.4 - 2.5) is discussed. The final part of this chapter (Section 2.6) provides an overview of possible treatment methods of the nitrogen-containing compounds, as well as their advantages and disadvantages.

2.1 Overview of the photographic process and wastewater composition

2.1.1 Description of the process

Photographic processing is the development or printing of paper prints, slides, negatives, enlargements, movie film, and other sensitized materials. This process includes several main steps: exposure, development, fixing, bleaching and stabilizing processes.

In the first step, photographic material is covered with a photographic emulsion, consisting of gelatin with light-sensitive silver halides. After that it is exposed to the light where formation of “a latent image” takes place. This image is almost invisible due to a minimal quantity of silver. In order to enhance the visibility of the image, a developer is used (Wang and Tselung, 2004). The developer chemically converts the exposed silver halide grains to the metallic silver.

The developer may also consist of other chemicals in order to accelerate the process (Wang and Tselung, 2004). After the conversion of the latent image into a metallic silver image, a small part of the emulsion still contains undeveloped silver halide, which has to be removed by a fixer. Typically this consists of thiosulfates $S_2O_3^{-2}$, which dissolve unused halide from the emulsion, forming a stable soluble complex $Ag(S_2O_3)_2^{-3}$ (Wang and Tselung, 2004). All of the metallic silver formed during the development is converted to silver halide by an oxidizing agent known as a “bleaching agent”. This process allows the silver to be removed from the emulsion into the fixer. The bleaching agent is chosen to oxidize the silver metal, converting it back to the silver halide without destroying the gelatin or dye. The most commonly used bleaches are iron EDTA (amide) and iron PDTA (amine).

Before the final step, residual chemicals and undesired by-products are removed by rinsing with water to avoid reactions between them, which may decline the life of the final product. The final step consists of treating of the emulsion with a stabilizer, which protects the image from aging and light fading (Wang and Tselung, 2004).

2.1.2 Photographic process wastewater characteristics

Photographic processes are very diverse. For instance, they include photofinishing laboratories, x-rays at medical and dental facilities, professional photography operations, motion picture laboratories, processing systems for scientific uses, microfilm processors and graphic arts operations, amongst others (Wang and Tselung, 2004). Due to this diversity in photographic processes and processing operations, the effluent compositions are also varying. Typical wastewater from the film industry includes: 1) film and paper wash water 2) solution make-up water and 3) area and equipment wash water, which contains heavy metals (silver), toxic organics such as hydroquinone, metol, phenidone (Bensalah et al., 2013) and high concentration of nitrogen-containing organics. None of these can be discharged into the environment without treatment.

Table 2.1 presents the typical effluent characteristics of 3 different processes including plumblingless color, conventional color, and black and white (Wang and Tselung, 2004).

Table 2.1 Characteristics of the effluents from 3 types of film industry

Process	BOD_5, mg/l	COD, mg/l	TDS, mg/l	TSS, mg/l	NH_3- N, mg/l	TKN, mg/l	SO_4^{-2}, mg/l	Iron, mg/l
Plumb-lingless color	5000-14000	30000-36000	60000-90000	10-50	6000-10000	8000-13000	3000-4000	1400-2000
Conven-tional color	200-3000	400-5000	300-3000	5-50	20-300	30-350	50-250	10-100
Black and white	300-5000	200-20000	1500-30000	5-50	350-4300	400-4500	100-300	< 0.5

It can thus be observed that these three processes have different values of physiochemical properties. Therefore, due to the varying compositions and concentrations of components, there is no one universal method of treatment of photographic processing wastewater.

2.2 Overview of amides

An amide is a class of organic compounds containing a nitrogen atom attached to an acyl group and is present in almost all wastewater generated by the photographic industry. Amides have attracted a lot of attention, due to the presence of the amide bond which is the key chemical connection in many natural important polymers such as peptides and proteins (Lehninger et al., 1993).

Amides are considered a derivative of carboxylic acids and can also be prepared from amines, anhydrides, esters, and nitriles. Amides, depending on the degree of carbon substitution on nitrogen, are divided into 3 groups: primary, secondary and tertiary (Figure 2.1).

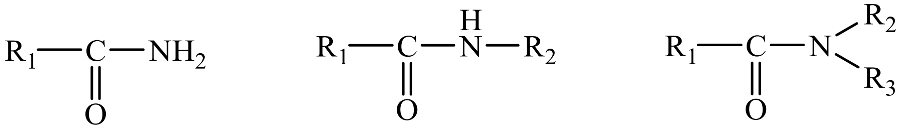

primary secondary tertiary

Figure 2.1 Types of amides

Amides may also be classified as aliphatic, aromatic (i.e. anilides or benzamides) or cyclic (lactams), depending on the nature of the nitrogen substituent and overall structure.

Due to the amides' configuration, they are considered to be a stable compound. This can be inferred from the rotational barrier around the C-N bond (Sunners et al., 1966; Drakenberg, 1972). In the traditional model of amides, resonance is a key concept (Figure 2.2). Resonance structure places the double bond between the C and the N, which leads to a planar structure, preventing the rotation around the C-N bond (Anslyn and Dougherty, 2004).

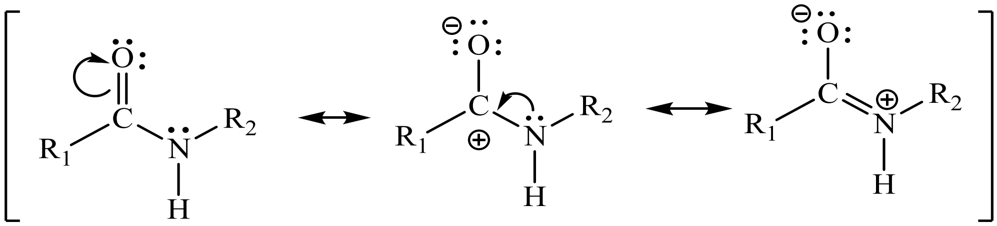


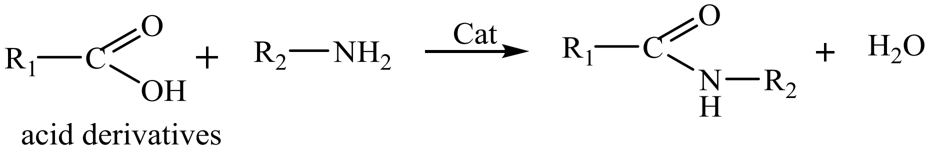
Figure 2.2 Resonance structure of the amide (Anslyn and Dougherty, 2004)

In addition, the resonance structure shows that the amide bond is stable towards the reaction with nucleophiles (Radzicka and Wolfenden, 1996). Also, the energetic factor of this structure plays an important role, because it provides a degree of stability and rigidity to the amide linkage (Mujika et al., 2006).

2.2.1 Synthesis of amides

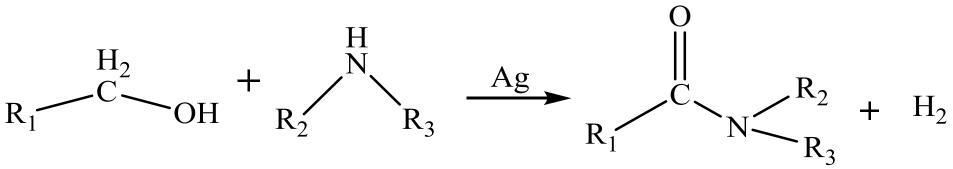
Amides have been widely used in various industrial sectors. They also play a key role for medicinal chemists. Studies have shown that the amide group appears in 25% of drugs (Ghose et al., 1999). Hence, there are numerous methods of formation of amides; most of them undergo several steps and do not have commercial application. This section will only present the synthesis of amides that could occur in photographic process conditions. These conditions include high temperature, different pH, as well as the presence of metals (Ag, Fe) and organic compounds such as acetic acid, formaldehyde, methanol and substituted amines.

The first synthesis is where amide derivatives can be synthesized very easily by the Reaction 1.1 of substituted acid group (-COOH) with different substituted amines (Kushwaha, 2011).



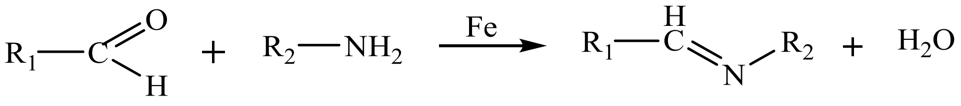
1.1

Another important method of amide synthesis is Reaction 1.2 in which amines are directly acylated by equimolar amounts of alcohols in the presence of silver to produce amides (Cheng and Hong, 2010).



1.2

An elegant alternative method is the oxidative amidation of aldehyde with amines, which is generally catalyzed by metals such as Cu, Rh, Ru Ni, Ag, Fe (Cadoni et al., 2012). Reaction 1.3 presents this synthesis.

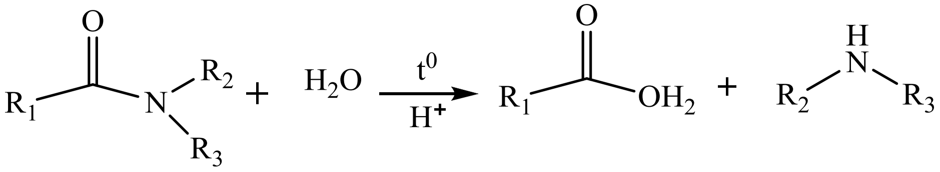


1.3

Considering conditions and chemicals present in photographic process (Section 2.1.1), it can be assumed that the formation of amides is possible in this wastewater.

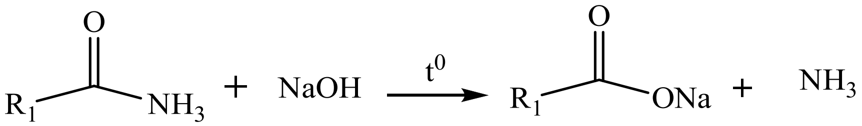
2.2.2 Chemical properties of amides

Designing a treatment method for wastewater containing amides requires defining the potential reactions which can occur under certain conditions. An overview of some of the major general reactions in which amides participate as reactants are shown below. One of the most important reactions is hydrolysis. In general, amides are stable toward hydrolysis for two reasons: 1) stabilization of the carbonyl group by the e-donating properties of the N atom (resonance structure) and 2) $-NH_2$ is a poor leaving group. Therefore, to hydrolyze amides, harsh conditions, such as the application of a strong acid or base and heating have to be presented. There are two types of hydrolysis: acid and basic. Reaction 1.4 presents acid hydrolysis.



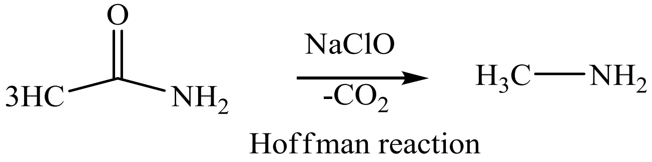
1.4

Basic hydrolysis is presented by Reaction 1.5.



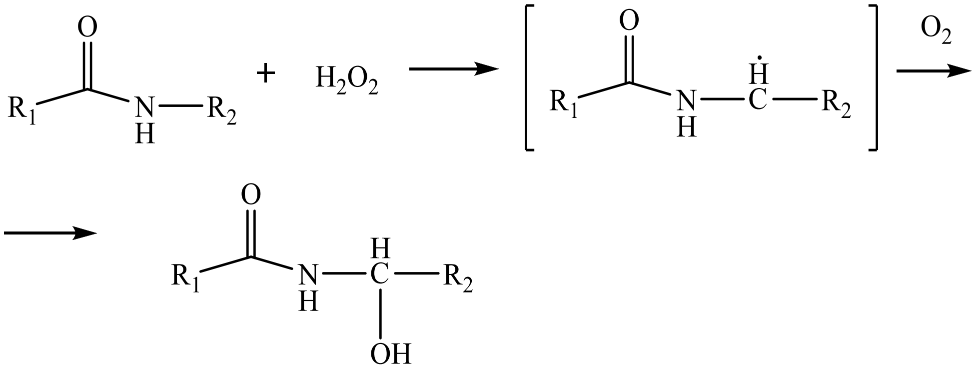
1.5

The condition for these reactions depends on the structure of the amide molecule. For example, primary linear amides can be hydrolyzed at 100 ^0C in 10 N HCl for 5 hours, while tertiary and secondary linear amides require more drastic conditions (Daughlon, 1988). Another reaction involving amides is splitting by Hoffman (Reaction 1.6), where the salt of hypochlorous acid breaks downs the amides at 50-80 C^0 to amines:



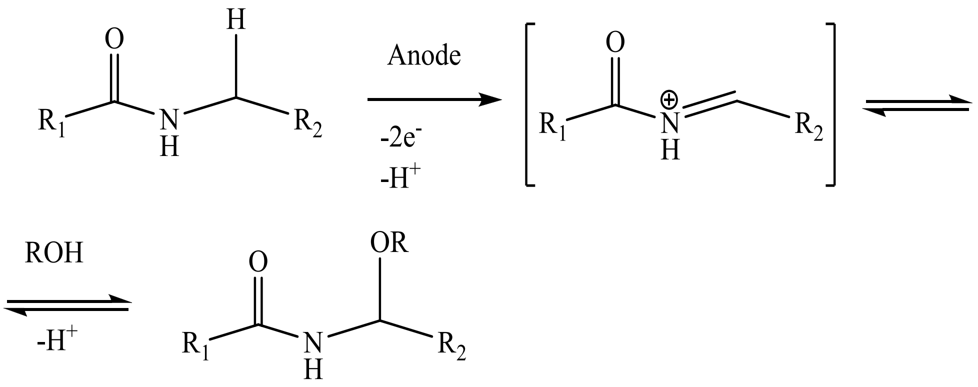
1.6

An important reaction in the chemistry of amides is oxidation with peroxyl radicals, where oxidation occurs through the formation of the α–amidoalkyl radical (Reaction 1.7), which is stabilized by carbonyl group influence (Denisov and Afanas'ev, 2005).



1.7

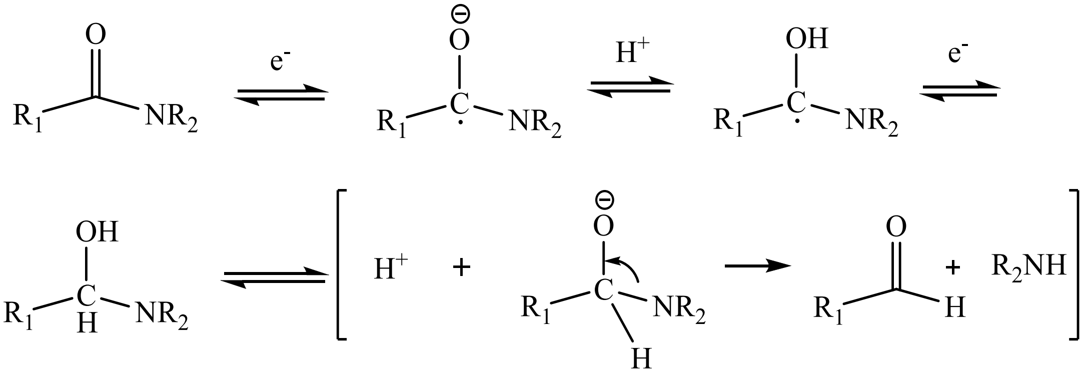
In this overview electrochemical oxidation is also important. Anodic oxidation of the amides results in the formation of only one major product (Reaction 1.8). Usually, this occurs in the presence of alcohols, acetic acid or formic acid.



1.8

This pathway describes the direct anodic oxidation of the amides to intermediated N-acylium ions via removal of one electron from the nitrogen loan pair followed by deprotonation in α-position of the N atom and further one electron oxidation (Lund and Hammerich, 2001). However, it is important to note that this pathway happens in the monosystem, where the presence of other ions is excluded.

In case of aliphatic amides (primary, secondary, tertiary) in the absence of proton donors, the reduction on the cathode takes place with the formation of aldehydes and amines (Reaction 1.9).



1.9

It is important to note that all of the above mentioned synthesizes are laboratory methods. Behavior of amides in wastewater in the presence of different ions can differentiate differ from those described above.

2.3 Nitrogen transformation in the wastewater treatment plant

The nitrogen element can be found in organic and inorganic forms in wastewater. Examples of organic compounds containing nitrogen include urea, peptides, amines and amides. Inorganic compounds containing nitrogen include ammonium ions, nitrite ions and nitrate ions. Due to its structure, nitrogen can undergo the oxidation/reduction process. Nitrification is the biological oxidation of ammonia nitrogen, while denitrification is the biological reduction of nitrates. Nitrification is a two-stage process occurring in the presence of oxygen. Ammonia-oxidizing bacteria convert ammonia to nitrites, and then nitrite-oxidizing bacteria complete the oxidation of nitrites to nitrates. Denitrification is the reduction of nitrate to nitrogen gas by facultative heterotrophic bacteria in the absence of oxygen (Gerardi, 2002). After primary treatment, the effluent consists of nitrate ions, ammonia and organic compounds in dissolved and particulate forms. After biological treatment (nitrification/denitrification) the effluent contains a low level of nitrate ions, however most of the nitrogen is in soluble organic forms (Pehlivanoglu-Mantas and Sedlak, 2008).

2.4 Organic nitrogen in final effluent

The diversity of organic compounds in wastewater primarily depends on industrial discharges. A large amount of nitrogen-containing organics originate from pharmaceutical and photographic processes, manufacturing of dyes as well as dairy industries. Examples of such substances include aniline, chelating agents, corrosion inhibitors (Gerardi, 2002) proteins, amino acids and urea (Berman and Bronk, 2003).

Among particulate organic nitrogen (PON), colloidal organic nitrogen (CON) and dissolved organic nitrogen (DON), the removal of PON does not present a challenge, since the majority is eliminated by the primary and secondary clarifier. The DON's and CON's behavior, however, remains unclear (Sattayatewa et al., 2010). With development of new technologies, the fraction of CON and DON in some plants becomes more and more significant. Thus, studies show that CON can be 60% of the effluent total nitrogen in some plants and DON can range from 52% to 95% after secondary treatment (Pagilla et al., 2008). The group of dissolved organic nitrogen is represented as a large refractory group and a labile group. One of the best examples of such recalcitrant substances is EDTA, which is used in the textile and, pulp and paper industries, as well as in photographic processes, medicines and cosmetics. It is unclear whether persistent organics are biologically active or not, after being discharged into a receiving water body. Another group of nitrogen-organics are highly labile compounds (urine, amino acids) (Dongke, 2012). Difficulty of investigating treatment methods can be attributed to the limited information about the effluent containing nitrogen organic. According to previous studies, it was found that over 70% of the DON is not identifiable through the available methods (Bronk et al., 2007). It has only recently come to light that unidentified DON is a hydrophilic molecule with low-molecular weight which is capable of passing through an ultrafilter (Pehlivanoglu-Mantas and Sedlak, 2008).

Thus, it can be concluded that the lack of information about the properties of the stable DON leads to a lack of knowledge on their environmental impact. Concerns over wastewater discharge containing these compounds and their impact on the environment motivate research on new methods of water treatment.

2.5 The impact of nitrogen-containing organics on the receiving water body

Depending on the size of the molecule, DON can be classified as either low molecular weight (LMW) or high molecular weight (HMW) compounds. LMW components constitute 20% of all DON, which are the most important source of nitrogen for microorganisms and some plants. The DON's bulk consists of uncharacterized, complex, HMW compounds, which can be more or less bioavailable.

More recently, researchers have studied factors which affect the bioavailability of effluent organic nitrogen, as well as the conditions under which the release of labile nitrogen from dissolved organic matter takes place (Bronk et al., 2010). For example, it was discovered that light is one of these factors, influencing the release of labile nitrogen (Bronk et al., 2010; Urgun-Demitras et al., 2008; Pehlivanoglu and Sedlak, 2004). Also, it was shown a possibility of photochemical production of bioavailable nitrogen from the recalcitrant dissolved organic matrix (Vahatalo and Jarvinen, 2007).

Another important factor which has to be considered alongside light is the microbial community in the effluent, as well as in the receiving water bodies (Marshall et al., 2005). Different species of microorganisms have different influence on the bioavailability of DON due to their various transport and enzyme systems (Dongke, 2012). Researchers have demonstrated how changes in the molecular structure of DON are dependent on the growth of bacteria and algae (Marshall et al., 2005). Specifically, it was shown that the composition of organic nitrogen changes with the evolution of the bacterial community (Hopkinson et al., 1998; Wiegner et al., 2006). It is also believed that bacterial activity facilitates the capture of organic nitrogen, thus making stable DON become bioavailable for algae (Berg and Jorgensen, 2006). These investigations thus lead to the conclusion that soluble organic nitrogen can contribute to the eutrophication of the water bodies (Bronk et al., 2010).

In addition, it is important to consider the toxic effects of some soluble organics on living organisms. It is known that most of the pharmaceutical compounds, such as antibiotics, beta-blockers, lipid regulators, antidepressants (Ternes at al., 2006) and personal care products (PPCPs) are soluble nitrogen-containing organics. The presence of these compounds in the environment has received a lot of attention in recent years due to their adverse impact on public health and the environment (Shishir Kumar et al., 2011). PPCPs have been considered an emerging environmental contaminant (Daughton and Ternes, 1999) due to their various toxic effects, including chronic toxicity (Zhoua et al., 2009). PPCPs are designed to target specific species and are considered to be biologically active compounds, which are not always biodegradable once they are released into the environment (Garcia-Galan et al., 2011).

Consequently, PPCPs can be dangerous for different non-target organisms leading to the altering of the ecosystem dynamics (Boxall et al., 2002; Daughton and Ruhoy, 2009). For instance, it was found that ciprofloxacin has an influence on the growth and structure of the algae in streams and rivers (Wilson et al., 2003). Due to the fast development and competitive nature of the pharmaceutical industry, many pharmaceutical compounds have not yet been studied extensively. However, it has been demonstrated that the combination of certain chemicals could be more toxic to fish and humans than the individual compounds alone (i.e. due to a synergistic effect) (Flaherty and Dodson, 2005).

Specifically, amide is one of this stable organic nitrogen. It is the most common stable organic, which is widely used in the pharmaceutical, pulp and paper, photographic and printing processes, and plastic producing industries.

2.6 Treatment of industrial wastewater

As it was previously mentioned, a lot of organic nitrogen is used in different areas of industry. These industries employ a wide array of wastewater treatments, because their wastewaters vary in composition, quantity, season, raw materials and processes used. The following chapters will provide an overview of wastewater treatment methods that can be applied to dissolved organic nitrogen removal, with a focus on physicochemical and biological methods, as well as advanced oxidation processes (AOPs).

2.6.1 Physicochemical treatment

Physicochemical treatment includes membrane separation, coagulation-flocculation, flotation processes, activated carbon, and chlorination. Coagulation and flotation treatments are not very popular methods for the removal of nitrogen organics, given that they do not produce a desired effect, due to the solubility and stability of these compounds. However, the extant literature has reported several cases in which this method was utilized, but, still with limited application. To that end, enhanced coagulation can only remove 35% of dissolved organic nitrogen in drinking water (Lee and Westerhoff, 2006). The coagulation-flotation method has been used in the treatment of drinking water; however it is in conjunction with filtration or activated carbon absorption (Ternes et al., 2002; Stackelberg et al., 2004). Yet, even with a tertiary treatment, only 70% removal of dissolved organic nitrogen could be achieved (Parkin and McCarty, 1981). Researchers have also demonstrated the limited application of this method on wastewater treatment. Specifically, they studied the behavior of several organic compounds in the physical-treatment method, including amides, and they concluded that only highly lipophilic compounds with significant sorption affinity can be removed at an approximate level of 70%, while hydrophilic compounds can be removed at a level of less than 25% (Carballa et al., 2005). It can thus be concluded that the methods described above have a limited application on the removal of DON compounds.

With regard to the membrane process, microfiltration and ultrafiltration have shown low removal efficiency from DON, due to the larger pore size as compared to micropollutants (Bellona and Drewes, 2007). Unlike microfiltration and ultrafiltration, reverse osmosis (RO) and nanofiltration have shown a very high efficiency in the removal of DON. These processes are able remove a high amount of different pharmaceutical compounds, such as antibiotics, hormones and personal care products (Watkinson et al., 2007). However, using this type of treatment leads to the creation of another problem — disposal of sludge, which contains concentrated organic substances.

A very well-known process is activated carbon (AC), which is mostly used as a tertiary treatment after conventional treatments. However, it has also been investigated for its ability to remove organic compounds. It was discovered that AC makes it possible to achieve 90% removal of estrogens; however, dissolved organic compounds and surfactants can block pores within the AC structure (Zhang and Zhou, 2005). Another problem with AC is the disposal and regeneration of carbon, containing organic nitrogen.

2.6.2 Biological treatment

Biological treatment is considered to be the most popular and economical method for treatment of different types of wastewaters. However, this method was demonstrated to have limitations, as well as being insufficient for many potentially hazardous substances (Clara et al., 2005; Joss et al., 2005). It is known that many pharmaceutical industries use the biological treatment (Raj and Anjaneyulu, 2005). Biological treatment includes aerobic and anaerobic processes. The most important factor to consider in treatment selection is wastewater characteristics, given that there are recalcitrant substances (solvents, active pharmaceutical ingredients (APIs), raw materials) which affect the efficiency of the biological treatment (Oz et al., 2004).

It has been demonstrated that the most appealing process is conventional activated sludge (AS) due to its low cost and limited operational requirements. AS can achieve high efficiency in the removal of organics (Afzal et al., 2007), but there are many factors which affect the efficiency of this process, including HRT, temperature, dissolved oxygen (DO), pH, and organic load, as well as the presence of toxic or stable compounds (LaPara et al., 2001). A number of studies were conducted using sequence batch reactors (SBRs) and membrane bioreactors (MBRs). It has been demonstrated, that, in some cases, it is possible to reach COD removal of 88% with the use of SBRs (Ileri et al., 2003). Another similar study showed lower COD removal of 63-69% (Aguado et al., 2008). MBR is also a popular method, with the potential of replacing conventional activated sludge, given that it requires less space for operating and can handle bulk organics. MBR has demonstrated high COD and BOD removal in a pharmaceutical company in Taiwan, at a removal level of approximately 95% of COD and 99% of BOD (Chang et al., 2008). However, this method cannot remove all APIs, due to the small size of organic molecules (Radjenovic et al., 2007). In order to solve this problem, the modification or combining of various pre- and post-treatment methods can be used. Researchers have obtained 98% removal of COD in the aerobic sequential batch reactor using Fenton pretreatment, where they reached 48% removal of organic content (Tekin et al., 2006). Researchers have also used ozonation as a pretreatment before the activated sludge reactor combination in a series. They demonstrated removal efficiency of approximately 90% (Alaton et al., 2004). Furthermore, hybrid treatment technology has also been investigated, in which the activated sludge process is followed by ozonation and a membrane bioreactor (MBR). Aerobic treatment reduces almost all organics and ozonation oxidize bulk organics, achieving a level of 90% removal efficiency (Helmig et al., 2005).

The anaerobic process also has gained much attention, due to its ability to deal with high concentration wastewater, low sludge yield and economical byproduct (methane) recovery. Thus, it has been shown that up-flow anaerobic batch reactor (USAR) is very efficient in removal of pharmaceutical compounds from wastewater (Chelliapan et al., 2006). It demonstrated 65% removal of COD and 80-94% removal of BOD even at a high loading rate (Sreekanth et al., 2009). Another study that the combination of 2 processes, specifically catalytic wet air oxidation and anaerobic biological oxidation, can achieve COD removal of approximately 94% (Kang et al., 2011). However, the anaerobic process is not always an effective method in the removal of recalcitrant and no-biodegradable substances.

From the above discussion, it can be seen that aerobic and anaerobic processes alone do not give always satisfying results. Moreover, these processes cannot cope with dissolved organic nitrogen such as carbamezapine, diclofenac and sulfomethexazole (Deegan et al., 2011). However, the implementation of additional pretreatment processes can solve this problem, despite that combining these methods drastically increases costs. Although this hybrid system demonstrates good results, there are some limitations to its use. For example, the biological process cannot be applied to wastewater containing toxic conditions or compounds that affect microorganisms, such as high conductivity, as well as presence of certain metal ions.

Biological treatment has also been implemented within the photographic processing industry. Some studies have demonstrated the potential of the activated sludge in the treatment of this wastewater. Thus, it was reported that approximately 68% removal of COD was achieved by a fill-and-draw activated sludge system (Pavlostathis and Sridhar, 1992; Pavlostathis and Jungee, 1994; Pavlostathis and Maeng, 1997). Another experimental study showed that reaching an acceptable level of BOD with the anaerobic-aerobic biofilm reactor is possible (Hirate et al., 1997). A two-phase fixed bed reactor packed with sponge cubic media displayed a removal level as high as 80% of BOD, however it required one year to acclimatize the microorganisms (Hirata et al., 1997). Very promising results have been shown when rotating biological contactors have been applied (Lytle, 1984). They achieved removal efficiency of BOD at a level of almost 95% with retention time of 16 hours (Lytle , 1984).

The evolution of the photographic process industry brought about many changes in the chemical composition of wastewater. There are substances that are not amenable to biological treatment, and are toxic to microorganisms. Therefore, biological treatment cannot be applied to all types of wastewater. Recently, advanced treatment processes, including filtration and advanced oxidation have shown varying degrees of efficiency for the treatment of wastewater containing nitrogen organics (Andreozzi et al, 2005; Helmig et al., 2007); however, there is no conventional method for TKN removal.

2.6.3 Advanced treatment processes

The biological and physicochemical methods described here, despite their advantages, have shown a number of disadvantages, such as the inability to treat stable organic nitrogen compounds. The advanced oxidation processes (AOP) have displayed a higher removal efficiency rate. AOP includes processes such as electro-oxidation, Fenton oxidation, photo-Fenton process, wet air oxidation, ultrasound irradiation and microwave treatment (Gadipelly et al., 2014). Depending on the composition of the wastewater and effluent requirements, AOP can be employed either alone or jointly with other processes.

AOPs are based on the formation of free radicals, which lead to mineralization of organic compounds into carbon dioxide, water, nitrogen gas and other minerals, or their conversion into less harmful compounds (Ikehata et al., 2006). This process requires chemical oxidants, such as hydrogen peroxide, ozone, transition metals and metal oxides, as well as an energy source, like UV- radiation, an electric or gamma current, or ultrasound (Ikehate et al., 2006). AOPs are a very promising method for the pretreatment of different types of industrial wastewaters, before or after a secondary treatment is applied (Oller et al., 2007). The advantage of AOPs is not only their ability to cope with stable organics, but also their potential at handling fluctuating flow rates and high concentrations of organics (Ikehata et al., 2006).

2.6.3-1 Ozonation

Ozonation is a well- known treatment for disinfection and sterilization, but it also can be applied as a tertiary or pretreatment method for oxidation of organic compounds. Ozone is a strong oxidant, which can act directly or indirectly. Direct oxidation (not an advanced oxidation in this case) can occur when ozone selectively attacks certain functional groups, such as nitrogen, phosphorus, oxygen and compounds with double bonds or aromatic rings (Ikehata et al., 2006), given that it reacts only with nucleophilic compounds (Stockinger et al., 1995). Indirect oxidation occurs when ozone decomposes in water, forming a hydroxyl radical, which is a stronger oxidizer, than ozone itself. The mechanism is presented in the Reactions 1.10 – 1.15 (Andreozzi et al., 1999):

$$O_3 + OH^- \rightarrow O_2 + OH^-_2 \qquad 1.10$$

$$O_3 + OH^-_2 \rightarrow HO_2^{\bullet} + O^{\bullet -}_3 \tag*{1.11}$$

$$HO_2 \leftrightarrow H^+ + O_2^{\bullet -} \tag*{1.12}$$

$$O_2^{\bullet -} + O_3 \rightarrow O_2 + O^{\bullet -}_3 \tag*{1.13}$$

$$O^{\bullet -}_3 + H^+ \rightarrow HO_3 \tag*{1.14}$$

$$HO_3 \rightarrow HO^{\bullet} + O_2 \tag*{1.15}$$

Ozonation has been widely studied in the removal of antibiotics from wastewater (Andreozzi et al., 2005; Balcioglu and Otker, 2003; Arslan-Alaton and Dogruel, 2004; Dantes et al., 2008), displaying relatively high removal efficiency of COD (over 50%), but low mineralization of organic compounds (~ 20%), even during a long treatment period. Although studies using synthetic wastewaters have been conducted, there is little or no literature on the ozonation treatment of real pharmaceutical effluents (Cokgor et al., 2004), due to the fact that ozonation has a number of disadvantages. Firstly, production of ozone is costly; it was shown that ozonation treatment increases energy demand by 40-50% compared with conventional treatments (Larsen et al., 2004). Secondly, not all molecular structures can be treated using this method. The results from various studies have shown that compounds with an amide structure are resistant to ozone (Nakada et al., 2007). Thirdly, the mass transfer of the ozone molecule from the gas to liquid phase is a limiting step, which reduces removal efficiency and increases the cost of treatment (Homem and Santos, 2011). Furthermore, ozonation depends on many factors, such as pH, temperature, presence of organic matter, suspended solids and chlorine, as well as carbonate ions (Gunten, 2003). Finally, there still exists a concern about the toxicity of the effluent after treatment. Some research demonstrates that molecules produced from oxidation are less inhibitory than target compounds (Lange et al., 2006), while other research suggests that there is no change in the toxicity level (Dantas et al., 2008). Still, other studies have shown that the transformed compounds were even more harmful than the parent ones (Li et al., 2008). Due to all these drawbacks, it can be concluded that the application of ozonation does not seem to be adequate for contaminated wastewaters.

2.6.3-2 Photolysis

Photolysis is the process whereby the decomposition of compounds takes place through light absorption. There are two types of processes in photolysis: direct and indirect. In the direct process, organic compounds absorb UV light and undergo self-decomposition (Boreen et al., 2004), while in indirect photolysis the photo-degradation happens by photosensitizers, which generate active oxygenated radicals, subsequently degrading the organic compounds (Legrini et al., 1993). These photosensitizers are produced by photolysis from humic and inorganic substances presented in wastewater, or, through the addition of hydrogen peroxide or ozone (Homem and Santos, 2011). Several studies were conducted in order to investigate removal efficiency of various antibiotics from wastewater and most of these studies displayed low removal efficiency of organics (Shemer et al., 2006; Arslan-Alaton and Dogruel, 2004), with the exception of light-sensitive antibiotics where they were able to achieve over 80% removal. However, the produced compounds were more harmful than the initial ones (Shaojun et al., 2008). Low concentrations of humic acid have been demonstrated to enhance the process, while high concentrations have been shown to inhibit it, given that humic acids behave as irradiation filters (Shaojun et al., 2008).

It can therefore be concluded that photolysis is an ineffective method in the treatment of wastewater, given that it can only be applied to photo-sensitive compounds (Kummerer, 2009) and low COD loadings.

In order to improve the process, a semiconductor photocatalysis was applied to accelerate the photochemical transformation by the action of a catalyst (TiO_2). This process requires three components: a catalytic photo-sensitive surface (titanium dioxide), a source of light and a suitable oxidizer (Baran et al., 2006; Reyes et al., 2006; Klauson et al., 2010). This process is based on the activation of a semiconductor by artificial light or sunlight. Recent studies on the removal of antibiotics displayed 98% removal levels by using a combination of UV/TiO_2 (Addamo et al., 2005). Furthermore, high mineralization rate of sulfonamides was achieved using photolysis (Calza et al., 2004; Baran et al., 2006). Another important factor is that produced by-products are less toxic and more biodegradable than parent compounds (Addamo et al., 2005; Reyes et al., 2006).

Despite the numerous advantages of this process, such as the availability of titanium oxide at a relatively modest price, and the fact that it is inert to nature, as well as its photostability (Legrini, 1993), and high removal efficiency, there are also disadvantages. For instance, there are difficulties in its implementation at a commercial scale due to the troublesome process of radiation penetration in a solution containing suspended solids, as well as difficulties with removal of the catalyst, which can be time consuming and costly (Britto and Rangel, 2008).

2.6.3-3 Fenton oxidation

Fenton oxidation is another very popular advanced oxidation process, which has been widely studied. Fenton has discovered the possibility to use a mixture of H_2O_2/Fe^{+2} for degradation of tartaric acid (Harber and Weiss, 1932). However, its first practical useful application was implemented to decompose H_2O_2 catalyzed by Fe^{+2} following the Reaction 1.16 (Harber and Weiss, 1932):

$$Fe^{+2} + H_2O_2 + H^+ \rightarrow Fe^{+3} + H_2O + OH^{\bullet} \qquad 1.16$$

As soon as the hydroxyl radical is formed (Reaction 1.16), it attacks the organic compounds (Reaction 1.17), contained in the waste matrix (Buxton et al., 1988).

$$RH + OH^{\bullet} \rightarrow R^{\bullet} + H_2O \qquad 1.17$$

The efficiency of Fenton oxidation depends on many factors, including temperature, pH and the ratio H_2O_2/ Fe^{+2}. For example, it was found that catalytic activity of Fe^{+2} depends on pH levels (Gallard et al., 1999). Many investigations concluded that at a pH of 2.8 it is possible to reach a maximum concentration of Fe^{+2}, while at a pH of > 5, ions Fe(III) prevail. These ions produce $Fe(OH)_3$ residue, which decomposes H_2O_2 into O_2 and H_2O and decreases the concentration of the catalyst (Gallared et al., 1999).

There a number of advantages in this process like the inexpensive Fenton’s reagent, no energy input, ease of operation and maintenance, as well as no mass transfer limitation due to its homogeneous catalytic nature. At the same time, however, there are a number of disadvantages, which include expensive treatment of sludge and a limited pH range (pH 2-3), as well as the fact that not all organics are susceptible to this type of oxidation (Nidheesh and Gandhimathi, 2012).

To improve Fenton oxidation the use of a combined system was proposed, such as photo-Fenton and electro-Fenton oxidation (discussed below).

2.6.3-4 Photo-Fenton oxidation

Photo-Fenton oxidation was first mentioned in the early 1950s, when it was discovered that electron transfer initiated by UV results in the formation of $OH^{\bullet}$ (Bates and Uri, 1953). The photo-Fenton process is well-known due to its ability oxidize refractory compounds; while with the addition of UV the classic Fenton reaction increases (Ruppert et al., 1993).

In acidic conditions in an aqueous solution, ferric ions (Fe^{+3}) exist in the form of aqueous complexes, such as $[Fe(H_2O)_6]^{+3}$, which are hydrolyzed to hydroxylates species following Reaction 1.18 (Jones, 1999):

$$Fe^{+3} + H_2O \rightarrow Fe(OH)^{+2} + H^{+} \qquad 1.18$$

After that, ferrous ions (Fe^{+2}) are regenerated by photoreduction of ferric ions (Fe^{+3}) following Reaction 1.19 (Faust and Hoigne, 1990). Formed ferrous ions further react with H_2O_2, producing hydroxyl radicals (Fenton reaction 1.16).

$$Fe(OH)^{+2} + h\nu \rightarrow Fe^{+2} + OH^{\bullet} \qquad 1.19$$

Previous research has demonstrated the applicability of photo-Fenton oxidation in the removal of 4-chlorophenol (Bauer and Fallman, 1997), nitrobenzene (Zepp et al., 1997), herbicides (Sun and Pignatello, 1993), pesticides (Martin et al., 2009) and different polymers, including polyacrylamide (Giroto et al., 2008).

2.6.4 Electrochemical processes

The electrochemical advance oxidation process became a very popular method of treatment. This process, like all AOPs, is based on the generation of an oxidizer - hydroxyl radical ($OH^{\bullet}$), which can be heterogeneously produced by direct discharge water on the anode via an electrochemical process, or indirectly homogeneously generated via Fenton's reagent.

2.6.4-1 Anodic oxidation

Anodic oxidation is a heterogeneous oxidation occurring at the anode in several steps: transport of the pollutants to the electrode, adsorption of the molecule onto the surface, direct electro-oxidation, desorption of products and transport of oxidized products to the bulk, while homogeneous oxidation occurs by oxidants produced at the anode from oxidation of the water or ions in the water. Indirect oxidation can be reversible and irreversible, whereby the oxidizer reagent can be generated by a cathodic or anodic process. The selection of the process depends not only on the nature and the structure of the electrode, but also on experimental conditions and wastewater composition (Panizza and Cerisola, 2009). It was thus found that some anodes provide partial and selective oxidation, while others are able to achieve full mineralization of organic compounds.

Over the years, electrochemical processes have displayed very good results in the removal of certain organic compounds (Hammami et al., 2008; Dirany et al., 2010; Panniza and Cerisola, 2009; Guohua, 2004). For instance, the electrochemical treatment of pharmaceutical components, such as diclofenac, carbamezapine, and ibuprofen has resulted in their complete degradation. Applying an adequate current density, boron doped diamond (BDD) anode and a flow rate lead to a successful TOC removal of 100% (Dominguez et al., 2012). Other studies, in which a BDD electrochemical treatment was applied, demonstrated 97% TOC removal during the degradation of paracetamol and diclofenac (Brillas et al., 2005; Brillas et al., 2010).

In order to understand the anodic oxidation process, Comninellis at al. (1994) proposed a mechanism for electrochemical oxidation of organics, which is dependent on the nature of the electrodes.

The first step of the process is the discharge of water molecules to form an absorbed hydroxyl radical (Reaction 1.20):

$$MO_x + H_2O \rightarrow MO_x(OH^\bullet) + H^+ + e^- \qquad 1.20$$

The following steps vary, depending on the oxygen evolution overpotential. Electrodes with low oxygen evolution overpotential, such as carbon, Pt, IrO_2 and RuO_2 have an "active" behavior. The absorbed hydroxyl radical may interact with the anode, producing a higher oxide (Reaction 1.21):

$$MO_x(\,OH^{\bullet}) \rightarrow MO_{x+1} \; + \; H^+ \; + \; e^- \qquad 1.21$$

In turn, the higher oxide can act as mediator, oxidizing the organic compounds by Reaction 1.22:

$$MO_{x+1} + \; R \rightarrow MO_x + RO \qquad 1.22$$

In case of "non-active" electrodes with high oxygen evolution overpotential (SnO_2, PbO_2, BDD), the formation of a higher oxide does not occur, instead the mineralization of the organic compounds takes place (Reaction 1.23):

$$MO_x(\,OH^{\bullet}) \; + \; R \rightarrow MO_x + CO_2 + H_2O + \; H^+ \; + \; e^- \qquad 1.23$$

However, in practice, it will be a mixed behavior, because both reactions participate in oxidation (Comninellis, 1994).

The most widely used electrode is platinum due to it high conductivity and chemical stability. This electrode was studied for the removal of different organic compounds, such as substituted phenols (Comninellis and Pulgarin, 1991; Feng and Li, 2003), synthetic dyes (Panizza and Cerisola, 2007) and herbicides (Brillas et al., 2003), where it was found that these compounds oxidized on the anode with stable intermediate by-products (Comninellis and Pulgarin, 1991).

Another well-known electrode is carbon electrode, which is appealing mostly due to its low cost and large surface area. However, it has one of the biggest drawbacks – high corrosion when using a high current density (Panizza and Cerisola, 2009). Unlike the Pt anode, the carbon electrode has displayed complete removal of chloro-substituted phenols, using a relatively low current density (Polcaro and Palmos, 1997; Polcaro et al., 2000). Other studies have shown that oxidation using a carbon electrode can remove dye and color by almost 95%, but cannot reach full removal of the COD and TOC, at removal levels of approximately 35% and 30% respectively, due to the formation by-products (Fan et al., 2008). Furthermore, removal efficiency depends on the type of carbon electrode, which can be represented in the form of carbon felt, carbon pellet, black slurry, glassy carbon, activated carbon fibers (ACF), carbon plates and graphite particles (Panizza and Cerisola, 2009). For example, electro-oxidation using ACF can efficiently remove the color (98%) and COD (76.5%) from the synthetic wastewater due to a larger specific surface area (Yi et al., 2008).

Another inexpensive and promising electrode with good conductivity and chemical stability is lead dioxide, which is widely used in industry. Lead dioxide electrodes have a high oxygen evolution overpotential, which allows the hydrogen radical production. Hence, it is expected that PbO_2 is efficient in the removal of organics. The use of lead dioxide electrodes has been demonstrated to lead to a full mineralization of phenols and their intermediates (Tahar and Svall, 1998), as well as the removal of over 97% of COD in Mecopcop herbicides (Panizza et al., 2008). Comparative studies of the lead dioxide electrode concluded that (with the exception of the boron doped diamond electrode) PbO_2 displays the best performance in the removal of almost all pollutants (Panizza and Cerisola, 2009). It can be speculated that hydrogen radicals are more strongly absorbed on the surface of the lead dioxide electrode and consequently are less reactive, while BDD has weak adsorption properties due to its inert surface (Gherardini et al., 2001). Research on the influence of the electrode material on the removal of Methylene Red by anodic oxidation demonstrated that electrodes with so called "active" behavior can permit only partial oxidation, while PbO_2 and BDD can achieve full mineralization of organic compounds (Panizza and Cerisola, 2007). Similar results were obtained in the anodic oxidation of the pesticide Methamidophos (Martinez-Huitle et al., 2008). Despite all of these advantages however, there is one disadvantage — the release of toxic lead ions by the lead dioxide electrode, mostly in the basic solution.

Unlike the lead dioxide electrode, BDD does not have such drawbacks. On the contrary, BDD is widely studied and has become very popular due to its advantages, such as high removal efficiency of organic pollutants, corrosion stability in an aggressive media, and an inert surface with low adsorption properties. So far, many investigations have demonstrated near 100% removal of a large number of organic compounds from real wastewaters (Panizza and Cerisola, 2009). Despite the numerous advantages of BDD, however, its high cost and the difficulty of finding suitable films for the thin diamond layer deposition limit the industrial application of this electrode.

It can therefore be concluded that that there is not enough information regarding the removal of dissolved organic nitrogen from real industrial wastewaters. Most investigations to date have focused on the mineralization of specific organic molecules, while very few focused on the removal of specific molecules from the wastewater matrixes.

2.6.4-2 Electrochemical advanced oxidation processes (EAOPs)

EAOP is an electrochemical treatment directed to the degradation of organic compounds using Fenton's reagent, which can be partially or completely generated from electrode reactions. Depending on how Fenton's reagent is generated, EAOPs are divided into several groups: direct cathodic generation of hydroxyl radical, which includes electro-Fenton oxidation and combined electro-Fenton oxidation (photoelectron-Fenton, solarphotoelectro-Fenton, sonoelectro-Fenton) and indirect cathodic generation of hydroxyl radical, including Fered-Fenton, Anodic Fenton oxidation, electrochemical peroxidation and combined Fenton processes (Figure 2.3).

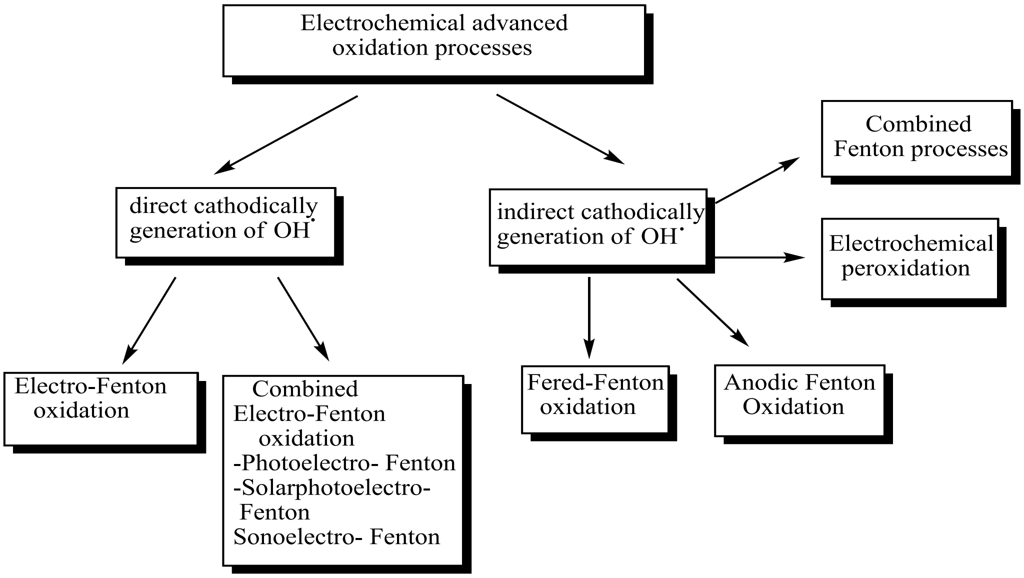


Figure 2.3 Classification of the EAOPs (adapted from the Brillas et al., 2009)

2.6.4-3 Electro-Fenton oxidation

Electro – Fenton (EF) oxidation is a very promising process due to its high mineralization degree of persistent organics. Comparing with the classic Fenton oxidation, EF process has a lower operation cost, since there is no need to use a large amount of chemicals and there is less production of sludge. In this process, organic compounds can be destroyed by two processes that can run concurrently, if there is an anode with high oxygen evolution overpotential: Fenton's reaction, and anodic oxidation. In order to understand EF oxidation, it is necessary to consider the mechanism of this process. Fenton's reagent is produced by the electrochemical reduction of oxygen (pure O_2 or bubbled air) in acidic media (Reaction 1.24) and Fe^{+3} to Fe^{+2} on the cathode (Reaction 1.25) (Qiang, 2002).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad 1.24$$

$$Fe(OH)^{+2} + e^{-} \rightarrow Fe^{+2} + OH^{-} \qquad 1.25$$

Further formation of the hydroxyl radical by the Fenton reaction 1.16 is feasible owing Reactions 1.24 and 1.25. There are also a number of adverse reactions which can take place: oxidation of hydrogen peroxide on the anode (Reaction 1.26), oxidation of the regenerated Fe^{+2} to Fe^{+3} (Reaction 1.27), as well as a number of reactions of iron ions with different radicals, which can be produced during electrochemical processes (Reactions 1.28-1.30) (Sires et al., 2007).

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^{+} + e^{-} \qquad 1.26$$

$$Fe^{+2} \rightarrow Fe^{+3} + e^{-} \qquad 1.27$$

$$Fe^{3+} + H_2O_2^{\bullet} \rightarrow Fe^{2+} + H^{+} + HO_2^{\bullet} \qquad 1.28$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^{+} + O_2 \qquad 1.29$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \qquad 1.30$$

All these unwanted reactions, as well as a presence of other ions, which also react on the electrodes, influence the mineralization of the organic compounds.

A number of studies were conducted since the discovery of this process, where researchers proposed a different configuration of the reactors, including divided and undivided cells and different operation conditions, as well as having tested different types of electrodes (Brillas et al., 2009). Table 2.2 shows recent studies on different types of experimental reactors for the EF process.

Table 2.2 Selected Electro-Fenton reactors (Brillas et al., 2009)

Reactors	Description	Removal efficiency,%	References
Bubble reactor (for decolorization of dyes)	Glass cylindrical batch reactor, with 2 bar electrodes (steel or graphite), distance between them of 240.4 mm; constant potential difference (15 V)	46% TOC reduction with residence time 21 h.	(Rosale et al. 2009)
Filter press reactor (removal of resin effluent)	Batch recirculation reactor with varied current densities for various flow rates, RuO2 coated Titanium expanded mesh anodes and stainless cathodes, 3.75 A/dm^2 current density	80% TOC removal with residence time 8 h.	(Prabhakaram et al., 2009)
Divided double-electrode electrochemical cell (leather tanning w/w)	Electrochemical batch reactor equipped with two iron electrodes 6 cm away from each other, electrical power 15.0 W	COD was reduced by 60–70% within 10 min	(Kurt et al., 2007)
Undivided three electrode electrochemical cell (removal of methyl red from aqueous solution)	Undivided system with graphite-polytetrafluoroethylene (PTFE) cathode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode with distance between the working electrode and counter electrode 3 cm, cathodic potential of −0.55 V versus SCE.	Methyl red of initial concentration of 100 mg/L could be removed 80% in 20 min.	(Zhou et al., 2007)
Double compartment cell (degradation of Rhodamine B.)	Modified divided electrolytic system with anode and cathode (Pt flakes) in compartment 1, and only cathode in compartment 2.Saltbridge was used to connect the compartments, EC= 100 mA	Full degradation after 30 min	(Yuan et al., 2011)

Another key point of this EF process is the selection of a suitable electrode as the EF system efficiency depends on the cathode (working electrode), while the production and stability of the hydroxyl radical depends on the material of the anode. Over the years, different types of cathodes were proposed, such as graphite felt, carbon felt, carbon-polytetrafluoroethylene (PTFE), Pt flakes, carbon sponge, stainless steel, BDD plate and titanium (Ti) (Nidheesh and Gandhimathi, 2012). The most commonly used anodes in the EF process are Pt (mesh, plate, flakes, sheet, gauze, grid and foil), BDD, titanium rod coated with IrO_2/RuO_2 or with IrO_2/SnO_2, carbon felt, iron and stainless steel (Nidheesh and Gandhimathi, 2012).

Despite the fact that the EF process has a number of advantages, such as relatively high efficiency in removal of toxic and persistent organics, on-site production of the H_2O_2, constant regeneration of ferrous ions and less sludge production, various combined systems based on EF system were proposed in order to enhance the efficiency of the process (Brillas et al., 2009). These combined systems include: photoelectron-Fenton, solar photoelectro-Fenton, sonoelectro-Fenton, Fered-Fenton, electrochemical peroxidation and anodic Fenton treatment (Brillas et al., 2009). The Fered-Fenton (FF) oxidation process, with continuous injection of hydrogen peroxide during the treatment, will be further discussed given that it is directly related to the current study. This process is a relatively new treatment, compared with the classic Fenton process (Gnann et al., 1993). This process needs an external continuous addition of the hydrogen peroxide and ferrous catalyst. The process is highly dependent on the concentration of the catalyst and current density, which have to be optimized for each system and wastewater.

Good results, using this method was showed by Chou et al. (1999) in the removal of a high-strength hexamine-containing wastewater. In this research, the influence of pH, cathodic material and current density on the mineralization rate of hexamine was studied. With residence time of 5 hours, COD removal efficiency of 94% was reached (Chou et al., 1999). A different study demonstrated a lower removal efficiency of the benzene sulfonic acid (BSA) solution (64% of TOC) after 480 minutes of treatment (Ting et al., 2007). In these experiments, a double or single-cathode configuration of the reactor was tested. It was concluded that a double-cathodes configuration is more efficient, due to faster generation of the ferrous ions (Ting et al., 2007). It can thus be concluded that the efficiency of the FF process depends not only on concentrations of the ferrous ion, but also on the nature of the organic compound. Figure 2.4 presents the possible oxidation pathway of the pharmaceutical compound (paracetomol), which belongs to the amide group.

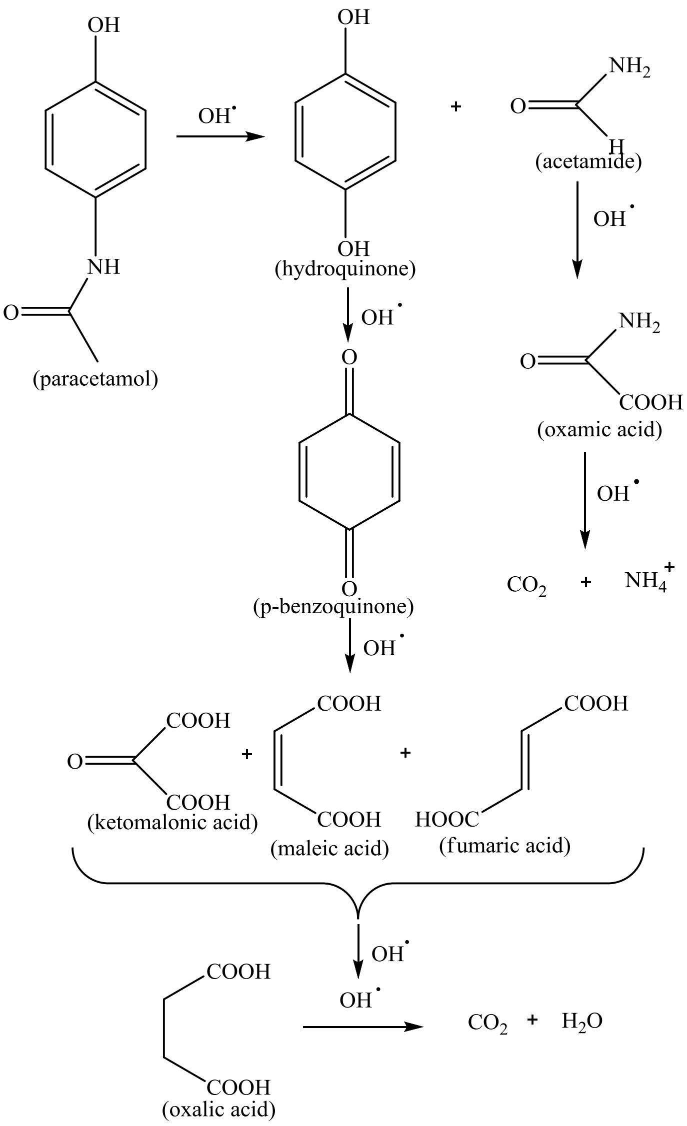


Figure 2.4 Oxidation pathway of paracetomol by EOAPs (adapted from Sires et al., 2006)

Most studies were done with synthetic wastewater, in which known organic compounds were removed, while studies on the removal of contaminants using real wastewater have been limited (Table 2.3). However- to my knowledge, no studies exist focusing on the removal of organic nitrogen using FF method. In this research, the main goal was to remove TKN, including organic nitrogen from the film-producing wastewater matrix.

Table 2.3 Treatment of real industrial wastewater by EAOPs based on Fenton's reaction (adapted from Brillas et al., 2009)

Source	Pollutant	Anode	Cathode	Current	Conditions and results
Olive oil mill wastewater (Khoufi et al., 2006)	Polyphenolic compounds	Iron plate	Iron plate	7.5 A/dm^2	Combined EF process, distance between electrodes 1.5 cm, 65 % removal with residence time 4 h.
Leather tanning industrial w/w (Kurt et al., 2007)	COD Sulphides	Iron	Iron	1.5 A	Batch reactor, distance 6 cm, 60-70 % COD removal within 10 min and 99.5 % removal of sulphides within 15 min
W/w containing dye (Chin-Ta et al., 2008)	Color	Pt/Ti	3-dimension graphite	68 A/m^2	Divided flow- by cell, 70.8 % removal of color, residence time 150 min.
Petrochemical w/w (Tinga et al., 2007)	Organic acid, poly-vinylalcohol (PVA) hexamethylene Tetramine (HEXA)	Stainless steel	Stainless steel	6 V	Batch scale EF process, 85% COD removal with residence time 180 min.
W/w from flame retardant industry (Montanaro et al., 2008)	Phosphorus retardants	Pt gas diffusion	Carbon Vulcan (GDE)	100 A/m^2	Combined EF process, 100 % oxidation

					after 1320 min.
Industrial w/w (Panizza et al., 2001)	Naphtalene-anthraquinine sulphonic acids	Pt	Graphite felt	1.8 V	Undivided cell with heat exchanger magnetic stirrer,87% COD removal, 89% color fading
PVC-stabilizer w/w (Huang et al., 2001)	Acetate	Ti/RuO_2-IrO_2	Steel	65-200 mA/cm^2	Undivided cell, FF oxidation, 89% COD removal with residence time 6 h.

It can thus be concluded, that just some works were devoted to the removal of pollutants from industrial wastewater through the EF process and that furthermore, there is no universal advanced oxidation treatment for the removal of organic compounds. It can be observed that operation conditions vary according to wastewater characteristics, which must be identified for each type of wastewater. Moreover, there is little to no literature on the treatment of wastewater containing organic nitrogen from the photographic process industry through this method. Therefore, the importance of the present study is crucial in discovering operation conditions for the FF oxidation of photographic process wastewater.

Chapter 3 : Methodology

Chapter 3 describes the research strategy of the current study (Section 3.1), provides a general description of the experimental work (Section 3.2) and analytical procedures (Section 3.3).

3.1 Research strategy

In order to achieve the objectives defined in Chapter 1, a series of bench scale laboratory experiments were performed. The approach for performing preliminary experiments includes selecting the methods, constructing the experimental set-up, defining operating parameters of the system were based on the literature review, while each subsequent experiment was based on obtained results of the precedent experimental series. The main objective of this study was to find the appropriate treatment of industrial wastewater with respect to TKN removal by applying Enhanced Electro-Fenton process. Simultaneously, this study aims to revel the following information: a) influence of the different types of oxidation methods on the removal of TKN; b) impact of the configuration of a reactor; c) the influence of the anode material on oxidation processes; d) the influence of the pH, applied voltage and ration Fe^{+2}/H_2O_2 on the efficiency of the enhanced Electro-Fenton process; e) the impact of the presence of ammonia ions on the removal of organic nitrogen. Figure 3.1 shows a schematic diagram of the research strategy developed and followed throughout this study. The current study was divided into four phases. In Phase I, consisting of 3 stages, the electrochemical phenomena was studied alone, in order to determine the impact of operational conditions and to establish whether electrical anodic oxidation has the ability to cope with the removal of TKN and organic nitrogen. Since the results from Phase I showed not sufficient treatment and according to the characteristics of wastewater, namely a high conductivity and a high concentration of iron ions, it was decided to perform electro-Fenton (EF) oxidation (Phase II).

In the Phase II, EF oxidation was studied using different air flow rate in the chosen conditions from the Phase I. Results obtained from Phase II led to further adjustment of the electro-Fenton oxidation. Therefore, in Phase III, enhancement of EF oxidation was performed by external application of hydrogen peroxide (continuously or by single feed) in different conditions. Phase III consists of 4 stages, in which different experimental conditions and their influence were studied, including applied voltage, the consumption rate of hydrogen peroxide and its feeding mode, the presence of ion exchange membranes, the mixing of the system, and, finally, the presence of ammonia ions in wastewater. A detailed description of the experimental work in Phase III is presented in Section 3.2. Based on results obtained in Phase III, the best experimental conditions were selected for performance and design of the multiple cell system (Phase IV).

Removal efficiency (%) was calculated using the following equation:

$$Removal\ rate\ \% = \frac{initial\ concentration - final\ concentration}{initial\ concentration}$$

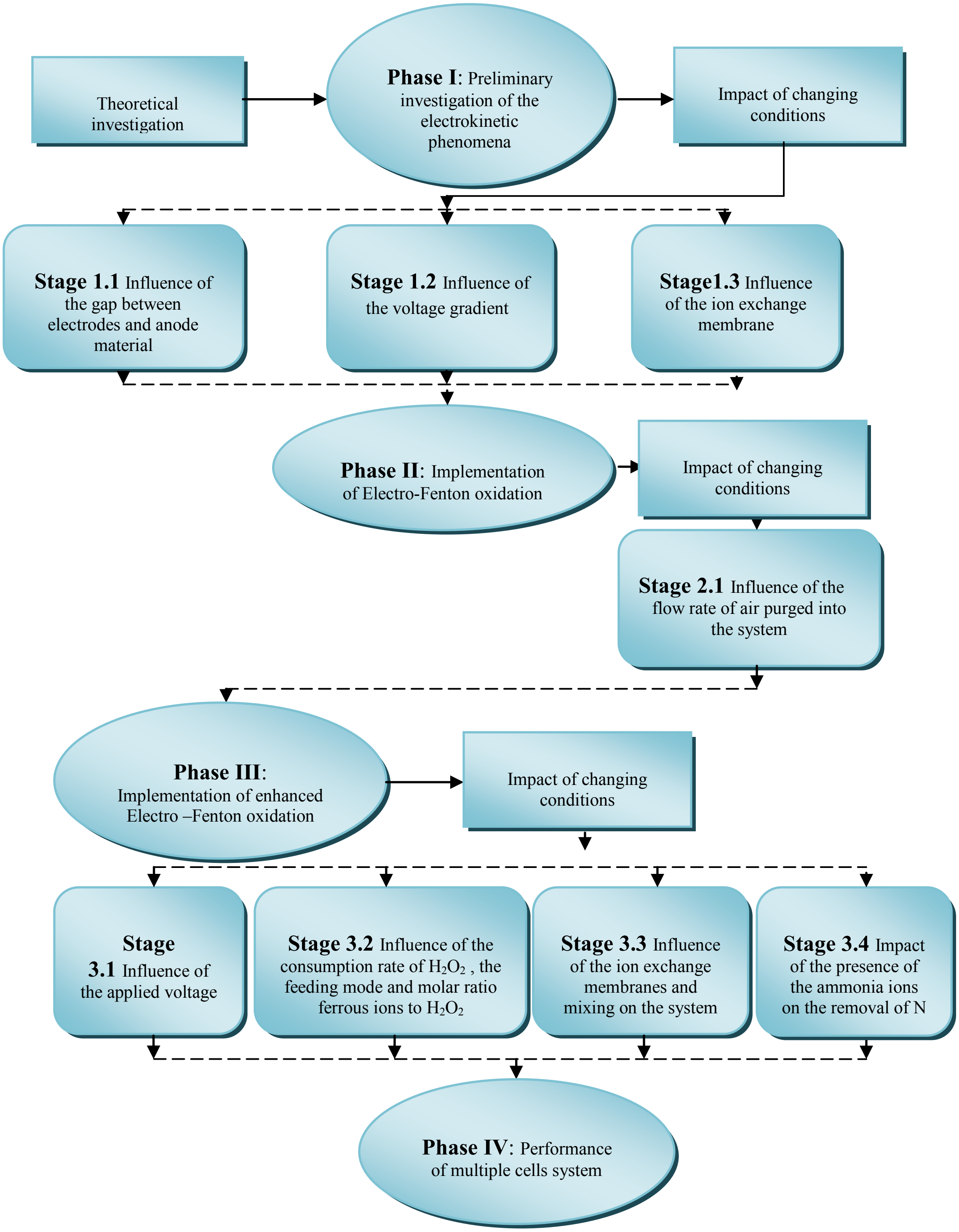


Figure 3.1 Methodology approach for the experimental work

3.2 Experimental set-up

In order to achieve all the objectives stated above, a number of experimental runs were performed. All experiments were performed at room temperature in a rectangular batch reactor.

3.2.1 Experimental set-up for Phase I

A series of different combinations of electrokinetic cells were run with raw wastewater to study the response of this wastewater to electrokinetic phenomena. The scheme of the experimental set-up used in Phase I (Stage 1.1 and Stage 1.2) is presented in Figure 3.2 a.

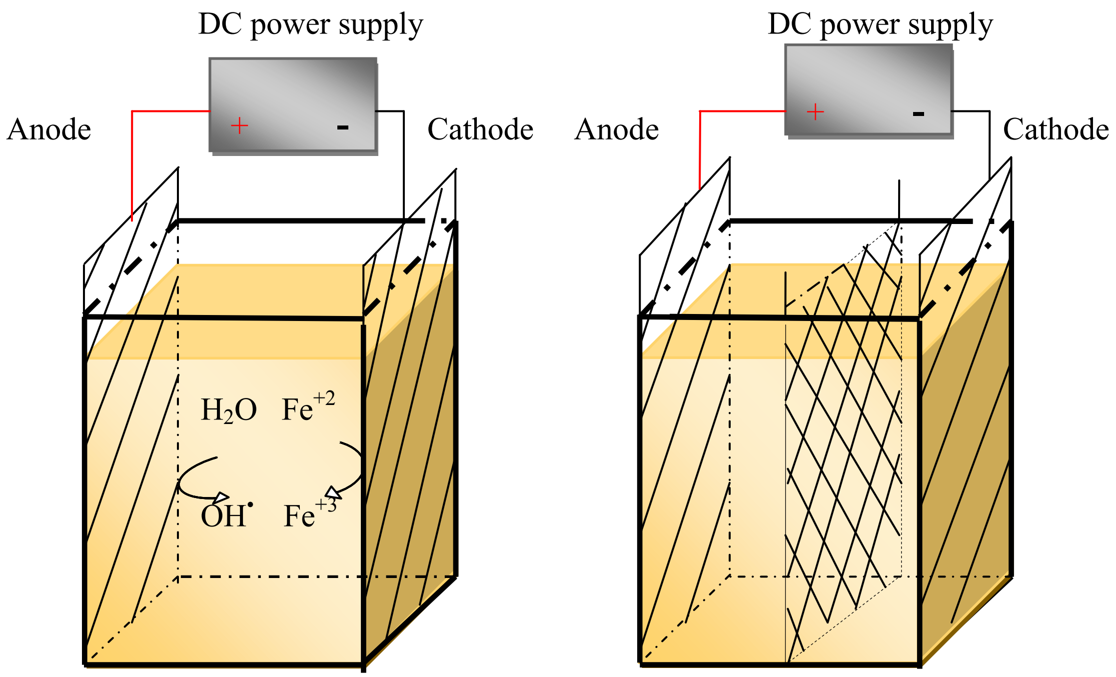


Figure 3.2 Schematic representation of set-up in Phase I: a) electrochemical oxidation without membrane, b) electrochemical oxidation with membrane

Experiments were performed in 3 different plastic rectangular reactors with the same volume (300 ml). In all experiments the current passed through the solution were measured by a multimeter built in DC power supply Abra AB-5300-1 (Elektorowicz and Hatim, 1999). To study an impact of the distance between electrodes (Stage 1.1), a series of 12 tests were performed with different anode materials, including mesh aluminum, mesh platinum and plate carbon with thickness 0.5 cm, while cathode material (stainless steel) stays the same. Table 3.1 presents the experimental conditions for the Stage 1.1.

Table 3.1 Experimental conditions in the Phase I (Stage 1.1)

Number of the experiment	Anode material	Distance between electrodes, cm	Current density, A/cm^2	Specific surface area, cm^2	Operation time, h
1	aluminum	4	0.014	14.5	72
2	aluminum	5	0.01	14.5	
3	aluminum	10	0.007	14.5	
4	carbon	2	0.026	45	
5	carbon	4	0.016	45	
6	carbon	5	0.013	45	
7	carbon	10	0.0013	45	
8	carbon	10	0.007	45	
9	platinum	2	0.175	2	
10	platinum	4	0.2	2	
11	platinum	5	0.3	2	
12	platinum	10	0.15	2	

To study an influence of the voltage gradient (Stage 1.2) 7 series of experiments were performed at the fixed voltage 2 V in case of aluminum anode and 4, 5 and 5.5 V in case of carbon and platinum anodes. The current density varied according to different specific surface areas of the anode. Reaction time was chosen to be 72 hours. Experimental conditions of Stage 1.2 are presented in the Table 3.2.

Table 3.2 Experimental conditions in the Phase I (Stage 1.2)

Number of the experiment	Anode material	Voltage gradient, V/cm	Applied voltage, V	Specific surface area, cm^2	Operation time, h
13	aluminum	0.4	2	14.5	72
14	carbon	0.8	4	45	
15	carbon	1	5	45	
16	carbon	1.1	5.5	45	
17	platinum	0.8	4	2	
18	platinum	1	5	2	
19	platinum	1.1	5.5	2	

In order to understand the influence of the configuration of the system on the process (Stage 1.3), a number of experiments were conducted in presence of various ion exchange materials (cationic and anionic polymer membrane, resins, fibrous membrane), and without the membrane (Figure 3.2 b). Characteristics of the ion exchange materials are presented in the Table 3.3.

Based on previous research (Elektorowicz and Hatim, 1999) these materials were placed 3 cm away from the cathode. Membranes were preconditioned by emersion in a 5% NaCl solution at 40^{o}C for 24 hours to allow for membrane hydration and expansion. In case of using resins as membrane materials, support construction was made. Membranes were not sealed.

Table 3.3 Characteristics of the ion exchange materials

Category	Characteristics					
type of material	polymeric cationic	polymeric anionic	fiber phosphonic	fiber sulphonic	fiber carboxylic	resins cat.
structure	gelpolysterene cross linked with divinil-benzene	gelpolysterene cross linked with divinil-benzene	polypropi-lene with copolymer of styrene and divinil-benzene	polypropi-lene with copolymer of styrene and divinil-benzene	polypropilene with copolymer of styrene and divinil-benzene	macroporous styrene divinil-benzene
functional group	sulphonic acid	quaternary ammonium	phosphonic acid	sulphonic acid	carboxylic acid	iminodiacatic acid
thickness,mm	0.45±0.025	0.45±0.025	3	3	3	Size 0.5-0.65
exchange capacity, meq/g	1.6±0,1	1.3±0.1	3	3	3	≥1.35
pH working range	1-10	1-10	0-14	0-14	5-13	1.5-14

Table 3.4 presents the conditions applied to the experimental runs in Phase I (Stage 1.3), where different type of membranes were studied. Aluminum, carbon and platinum materials were used as anode and stainless steel as cathode. Aluminum anode was placed at the distance of 10 cm with applied voltage of 2 V while carbon and platinum anodes were placed on the distance of 5 cm with applied voltage of 4 V. Four types of membrane were implemented, including cationic polymeric, anionic polymeric, cationic resins and cationic phosphonic fiber membranes.

Table 3.4 Experimental conditions in the Phase I (Stage 1.3)

Number of the experiment	Anode material	Membrane material	Distance between electrodes, cm	Applied voltage, V	Specific surface area, cm^2	Opera-tion time, h
20	aluminum	cation. polymer	10	2	14.5	72
21	aluminum	anion. polymer	10	2	14.5	
22	aluminum	cation. resins	10	2	14.5	
23	aluminum	fiber phosphonic	10	2	45	
24	carbon	cation. polymer	5	4	45	
25	carbon	anion. polymer	5	4	45	
26	carbon	cation. resins	5	4	45	
27	carbon	fiber phosphonic	5	4	45	
28	platinum	cation. polymer	5	4	2	
29	platinum	anion. polymer	5	4	2	
30	platinum	cation. resins	5	4	2	
31	platinum	fiber phosphonic	5	4	2	

3.2.2 Experimental set-up for Phase II

Figure 3.3 presents the experiment set-up scheme of Phase II. In this phase, a rectangular plastic reactor was used with a volume of 600 ml, while the working volume used for the tank was that of 300 ml. Such approach permitted to create a buffer zone for a potential foam formation during the process. Two electrodes were placed at a fixed distance of 5 cm. A stainless steel electrode was used as a cathode and mesh platinum and carbon plate were tested as anode. In spite of the same external linear dimensions of anodes, due to their different forms, they had different effective area namely 2 cm^2 and 45 cm^2 for platinum and carbon respectively. Also, the air was continuously bubbled in the aqueous solution on the cathode, with varying flow rates of air (from 15 to 125 ml/min), in order to produce hydrogen peroxide.

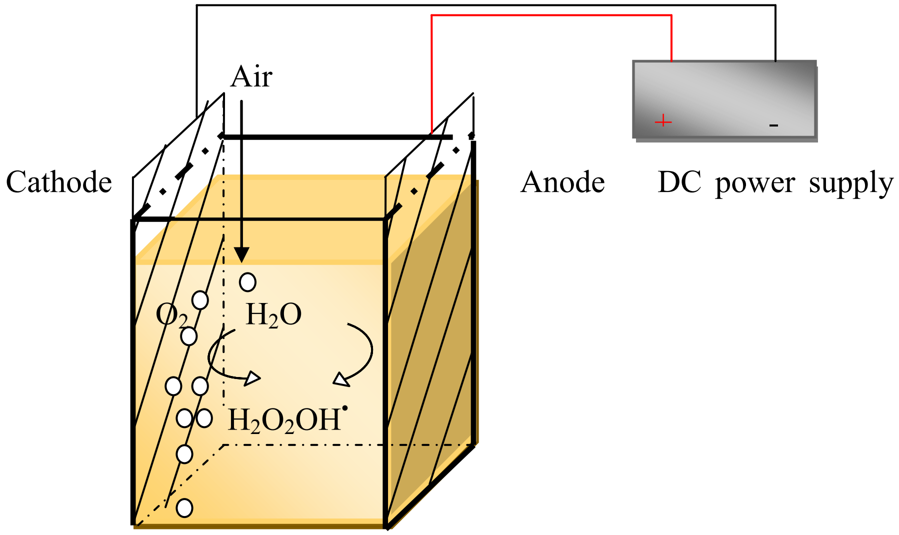


Figure 3.3 Schematic representation of experimental set-up in Phase II

In Phase II, eight experimental runs were tested in order to investigate the influence of the flow rate of air purged into the system and assess the efficiency of electro-Fenton oxidation. Table 3.5 represents the experimental conditions, where carbon and platinum anodes were placed in the distance of 5 cm with the voltage of 5.5 V with different applied air flow rates.

Table 3.5 Experimental conditions in Phase II

Number of the experiment	Anode material	Flow rate of oxygen, ml/min	Distance between electrodes, cm	Applied voltage, V	Operation time, h
32	carbon	120	5	5.5	72
33	carbon	75	5	5.5	
34	carbon	45	5	5.5	
35	carbon	20	5	5.5	
36	platinum	120	5	5.5	
37	platinum	75	5	5.5	
38	platinum	45	5	5.5	
39	platinum	20	5	5.5	

3.2.3 Experimental set-up for Phase III

The aim of Phase III was to improve electro-Fenton oxidation through the external application of a hydrogen peroxide- oxidizing agent. The study investigated an impact of dependences of different concentrations of hydrogen peroxide, mode of operation (applied voltages, mixing systems and H_2O_2/Fe^{+2} ratios) on the removal efficiency of organic nitrogen. The type of reactor of Phase III was the same as in Phase I (Figure 3.2a). Carbon electrode was selected as anode. The distance between electrodes was variable; from 3 to 10 cm. Hydrogen peroxide was provided continuously or pointy into the reactor. In the case of discrete addition hydrogen peroxide was applied at specific time intervals of 24 hours. The concentration of hydrogen peroxide was selected according to previous studies (Zhang et al., 2007) and adjusted based on the particular needs of this experiments.

In order to study the influence of mixing process on the system, two different types of mixing systems were applied: a magnetic stirrer mixing system, and a recirculation system (Figure 3.4). The recirculation system was completed using a peristaltic pump Master flex EW-07523-80. Reaction time was determined based on the residual pollutants in the solution, and was typically between 72 and 96 hours.

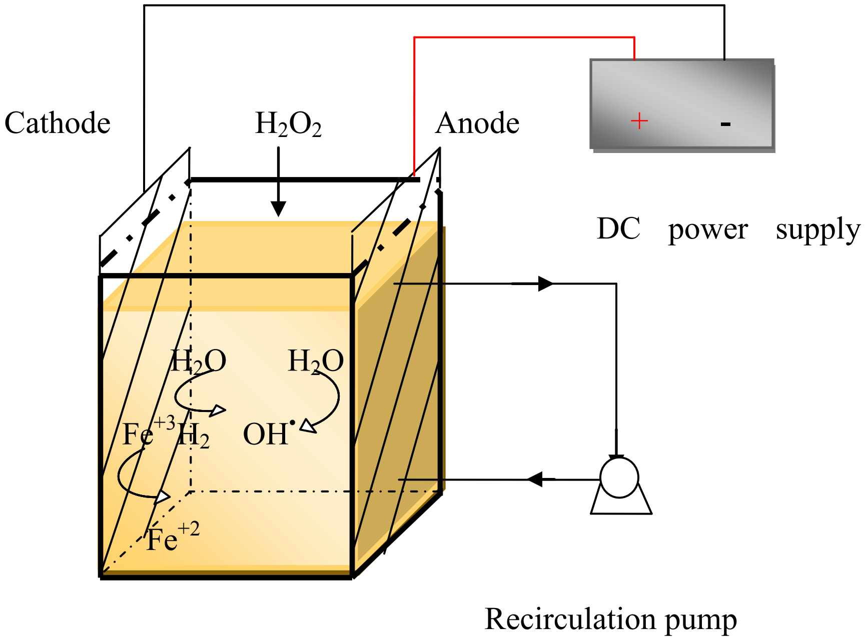


Figure 3.4 Schematic representation of experimental set-up with recirculation type of mixing

Samples were taken from the reactor each 24 hours to analyze the variation within the system. In order to find the optimum operating conditions, in terms of applied voltage, consumption rate of hydrogen peroxide, feeding mode, influence of the ion exchange membrane and mixing system on the removal efficiency of nitrogen, as well as the presence of ammonia ions in wastewater. 45 runs performed in Phase III (Table 3.6-3.12).

Experimental conditions of the Stage 3.1 present in the Table 3.6, where carbon anode was placed at the distance of 5 cm with varying applied voltages and fixed hydrogen peroxide volume of 4 ml applying in discrete feeding mode.

Table 3.6 Experimental condition in Stage 3.1 (impact of applied voltage)

Number of the experiment	Anode material	Applied voltage, V	Volume of H_2O_2, ml	Initial current, A	Operation time, h
40	carbon	3	4	0.3	72
41	carbon	3.4	4	0.6	
42	carbon	4.0	4	1	
43	carbon	5.5	4	1.25	
44	carbon	6	4	2.2	

Table 3.7 includes the experimental conditions of the Stage 3.2, where different consumption rate of hydrogen peroxide was studied with chosen voltage of 5.5 V and distance 5 cm.

Table 3.7 Experimental conditions in Stage 3.2 (impact of hydrogen peroxide)

Number of the experiment	Anode material	Volume of H_2O_2, ml	Distance between electrodes, cm	Applied voltage, V	Operation time, h
45	carbon	1	5	5.5	72
46	carbon	2	5	5.5	
47	carbon	4	5	5.5	
48	carbon	8	5	5.5	
49	carbon	12	5	5.5	
50	carbon	40	5	5.5	

Table 3.8 represents the experimental conditions of the Stage 3.2, where the influence of the different molar ratio of Fe^{+2}/H_2O_2 was investigated.

Table 3.8 Experimental conditions in Stage 3.2 (impact of Fe+2/H2O2molar ratio)

Number of the experiment	Anode material	Fe^{+2}/H_2O_2 ratio	Distance between electrodes cm	Applied voltage, V	Operation time, h
51	carbon	0.2	5	5.5	72
52	carbon	0.1	5	5.5	
53	carbon	0.05	5	5.5	
54	carbon	0.028	5	5.5	
55	carbon	0.017	5	5.5	
56	carbon	0.0058	5	5.5	

Experimental conditions in the Stage 3.2 are presented in Table 3.9, where influence of the concentration of the ferrous ions was studied on the effluent quality.

Table 3.9 Experimental conditions in Stage 3.2 (impact of the ferrous ion concentration)

Number of the experiment	Anode material	Volume of H_2O_2, ml	Additional Fe^{+2}, mmol	Initial pH	Applied voltage, V	Operation time, h
57	carbon	4	15.33	7.5	5.5	72
58	carbon	4	30.66	7.5	5.5	
59	carbon	4	30.66	3.4	5.5	

Stage 3.3 includes studying of influence of different ion exchange membranes on the removal efficiency with fixed applied voltage of 5.5 V (Table 3.10). Fiber cationic ion exchange membranes were applied on this stage.

Table 3.10 Experimental conditions in Stage 3.3 (impact of ion exchange membrane)

Number of the experiment	Anode material	Fiber membrane	Applied voltage, V	Operation time, h
61	carbon	phosphonic	5.5	72
62	carbon	carboxylic	5.5	
63	carbon	sulphonic	5.5	
64	carbon	without	5.5	

Also, Stage 3.3 investigated the influence of the mixing on the system at chosen applied voltage of 5.5 V and hydrogen peroxide volume of 4 ml (Table 3.11)

Table 3.11 Experimental conditions in Stage 3.3 (influence of the mixing process)

Number of the experiment	Anode material	Volume of H_2O_2, ml	Mixing	Applied voltage, V	Operation time, h
65	carbon	4	without	5.5	72
66	carbon	4	magnet stirrer	5.5	
67	carbon	4	recirculation	5.5	

Stage 3.4 studied the influence of the pretreatment from ammonia on the removal efficiency of the organic nitrogen using ammonia stripping tower as a pretreatment method. The initial concentration of ammonia after pretreatment was 2659 mg/l.

Table 3.12 Experimental conditions in Stage 3.4 (impact of ammonia ions)

Experiment	Voltage, V	V of H_2O_2, ml	Initial ammonia concentration, mg/l	Reaction time, h
68	5.5	4	2659	72

3.2.4 Experimental set-up for Phase IV

The best operating conditions obtained in Phase III were applied to design and test the multiple cell reactor system in Phase IV. The experimental set-up (Figure 3.5) consisted of the following major units: rectangular reactor with working volume of 700 ml, three carbon anodes and three stainless steel cathodes connected to the DC power supply. Each pair of electrodes was installed at a fixed distance of 5 cm. Hydrogen peroxide was added into each inter-electrode space every 24 hours. Samples were taken from each space in order to control the system and study the influence of changing the operation condition every 24 hours.

Table 3.13 Experimental conditions for the Phase IV

Anode material	Type of reactor	Distance between electrodes, cm	Applied voltage, V	H_2O_2/Fe^{+2} ratio	Operation time, h
carbon plate	undivided (no ion exchange membrane)	5	5.5	0.05	72

Table 3.13 represents experimental conditions for Phase IV. Carbon anode and stainless steel cathode were placed on the distance of 5 cm with applied voltage of 5.5 V and hydrogen peroxide to ferrous ions molar ratio of 0.05.

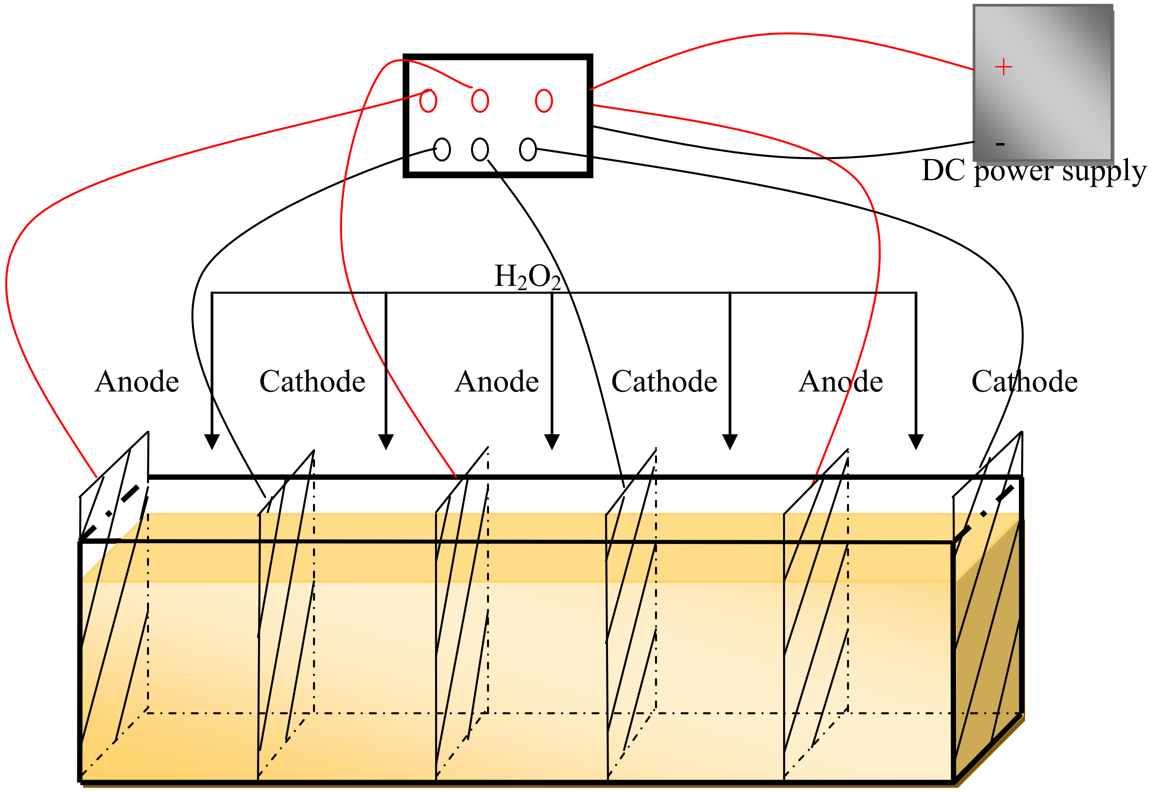


Figure 3.5 Schematic representation of experimental set-up for Phase IV

3.3 Characteristics of wastewater

Industrial wastewater produced by photographic processes was directly applied in this study. Two different samples of wastewater were used to study the influence of the concentration fluctuation on the removal efficiency of the enhanced electro-Fenton process. The main characteristics of samples are presented in Table 3.14.

Table 3.14 Characteristics of the industrial wastewater

Characteristics	Sample 1	Sample 2
Ammonia, mg/l	11800	14200
TN, mg/l	14600	18100
TKN, mg/l	13900	17800
Nitrite-nitrate, mg/l	718	310
ON, mg/l	2100	3600
pH	7.25	7.5
Conductivity, mS/cm	61.7	72
Fe^{+2}/Fe^{+3}, mg/l	2760	3000
COD, mg/l	65500	67000

3.4 Experimental analyses

The samplings for analysis were carried out every 24 hours for assessing the performance of three oxidation processes (electrochemical oxidation, electro-Fenton oxidation and enhanced electro-Fenton oxidation). The analysis performed in this research consisted of: 1) parameters measured on a daily basis such as pH, conductivity, oxidation-reduction potential (ORP), temperature, current, voltage and 2) parameters measured at the end of experiments (ammonia, TKN, TN, NO_3^-, NO_2^-,organic nitrogen). Samples were analyzed twice and a mean value was recorded. For analyzing pH, conductivity, ORP and temperature, a Hach-HQ 30 D digital meter and the corresponding probes were used. The concentration of TKN and ammonia were measured using Hach TNT vials (TNT 880 and

TNT plus 832 respectively). Values of the TN, NO_3^-/NO_2^- concentrations were included in the TKN measurements, while the concentration of organic nitrogen was found by calculating the concentrations of ammonia and TKN using the following formula:

$$\text{TKN} - \text{NH}_3\text{-N} = \text{Organic Nitrogen} \tag{3.1}$$

The electrical current was noted daily and the current density (*J)* was recalculated for each experiment by knowing the anode effective surface area (*Aeff)*:

$$J = \frac{I}{A\text{effective}}, \text{ where} \tag{3.2}$$

J – current density, (A/ m^2)

I – current, (Amps)

Aeff – effective surface area of electrode, (m^2)

In order to give approximate information about the coast of the system, the anode consumption has to be taken into account. A theoretical anode consumption rate was calculated using Faraday's Low (Kobya, 2006), while experimental consumption rate was measured by weighing the electrodes before and after the experiments.

$$\text{Faraday's Low: } Celectrode = \frac{ItM}{zFV}, \text{ where}$$

Celectrode – electrode consumption, (kg/ m^3)

I – current, (Amps)

t – operating time, (seconds)

M - molecular weight of the electrode material, (g/mol)

z - valence number of electrons transferred by the anode

F- Faraday's constant = 26.801 A·h/ mol

V- volume of treated water (m^3)

Chapter 4 : Results and discussion

4.1 Phase I

The objective of this phase was to assess the response of raw wastewater to electrokinetic phenomena in which the following variables were studied: the influence of space between electrodes, anode materials, voltage gradient and configuration of the EK cell, using ion exchange membranes. Subsequently, a series of 31 runs in various combinations of EK cells were carried out with raw wastewater to achieve the given objectives.

4.1.1 Stage 1.1 Influence of the gap between electrodes on removal efficiency

In the electrokinetic process, the distance between electrodes is one of the most important factors that affect the removal rate of pollutants and cost of the process. To study an impact of the distance between electrodes, 12 series of experiments were conducted. During the experiment, samples were taken every 24 hours.

Table 4.1 Influence of a gap between electrodes in the case of aluminum anode

Aluminum anode, specific surface area = 14.5 cm^2						
№ of experiment	Gap between electrodes, cm	Voltage, V	Current density, A/cm^2	Removal TKN, %	Removal NH_3-N, %	Removal ON, %
1	4	2	0.014	35.8	28.3	17.4
2	5	2	0.010	26.5	27.1	16.6
3	10	2	0.007	25	25.8	14.4

The results showed that achieving a removal efficiency over 50%, retention time of 72 hours is needed. Tables 4.1- 4.3 show the dependence of the process on the distance between electrodes, using different anodes. The highest removal of TKN was reached when aluminum anode was applied where the distance with of 4 cm between electrodes was preserved. However in this case, the current density was also higher, which leads to a high consumption of the anode and as a result, leads to a high production of sludge. Therefore, it was concluded that aluminum anode was not a suitable material for anode in this process.

Table 4.2 Influence of a gap between electrodes in the case of carbon anode

Carbon anode, specific surface area = 45 cm^2						
№ of experiment	Gap between electrodes, cm	Voltage, V	Current density, A/cm^2	Removal TKN, %	Removal NH_3-N, %	Removal ON, %
4	2	4	0.026	55.5	65.4	23.7
5	4	4	0.016	56.5	66.8	23.5
6	5	4	0.013	57.3	65.5	31.2
7	10	2	0.0013	33.9	40.4	13.0
8		4	0.007	35.8	45.3	13.2

When carbon electrode was applied with the gap between electrodes of 2, 4 and 5 cm the removal efficiency of TKN was 55.5%, 56.5% and 57.3% respectively while a removal efficiency of ammonia of 65.4%, 66.8% and 65.5% respectively. Then, differences in a removal of TKN and ammonia ranged around 2%. However, the removal efficiency of organic nitrogen at the 5 cm gap of 31.2% was noticeably higher than at other distances

(Table 4.2). Thus, according to the results, a distance of 5 cm was chosen for the next experiments.

Table 4.3 Influence of a gap between electrodes in the case of platinum anode

Platinum anode, specific surface area = 2 cm^2						
№ of experiment	Gap between electrodes, cm	Voltage, V	Current density, A/cm^2	Removal TKN, %	Removal NH_3-N, %	Removal ON, %
9	2	2	0.175	0.86	increased by 4%	16.6
10	4	4	0.2	6.03	2.3	17.7
11	5	4	0.3	22.8	22.5	23.9
12	10	4	0.15	0.32	increased by 4.1 %	14.8

Table 4.3 shows the effect of distance between electrodes on TKN removal in the case of platinum anode. From the results above, it can be observed that at a distance between electrodes of 5 cm, removal efficiency of all target pollutants (TKN, ammonia and organic nitrogen) were greatly higher than at a distance of 2, 4 and 10 cm.

Studies devoted to the influence of distance between electrodes on removal efficiency stated that shorter distance speeds up the anion discharge on the anode, thus improving the oxidation process (Sharma and Chopra, 2014). However, in the case of wastewater with high conductivity, a longer distance between electrodes must be selected (Crespilho and Rezende, 2004). Results from the current study confirmed the assumption made by the previous research cited above.

It can be assumed that for this type of industrial wastewater a distance of 2 cm is too short due to possible overlapping reactions on the electrodes, which might interfere with the desired reaction of mineralization. In contrast, a distance of 10 cm is too long due to higher amount of applied voltage. Thus, considering the results presented in Tables 4.1-4.3, it can be concluded that the gap of 5 cm is the best; therefore, it was selected for the next series of experiments.

4.1.2 Stage 1.2 Influence of the voltage gradient on the removal efficiency of nitrogen

The objective of this stage was to investigate the relationship between the voltage gradient and effluent quality and to study the changes of physiochemical properties, such as pH, oxidation-reduction potential (ORP) and conductivity. In Stage 1.2, a series of 7 experiments were carried out using the same types of anodes as in Stage 1.1, and a constant distance between electrodes of 5 cm, as selected in the previous stage. Different voltages values namely 2, 4, 5 and 5.5 V were applied. For aluminum anode, only one voltage gradient (0.4 V/cm) was applied due to its high dissolution. At this value of voltage gradient, the removal of TKN, ammonia and organic nitrogen were 26.5%, 27.1% and 16.6% respectively (Table 4.4).

Table 4.4 Influence of voltage gradient in case of aluminum anode

Aluminum anode, specific surface area = 14.5 cm^2				
№ of experiment	Voltage gradient, V/cm	Removal TKN, %	Removal NH_3-N, %	Removal ON, %
13	0.4	26.5	27.1	16.6

Figures 4.1 - 4.3 show the changes in pH, ORP and conductivity when applying 0.4 V/cm in the case of aluminum anode during 72 hours. All measurements were taken 3 times and the arithmetic mean was recorded.

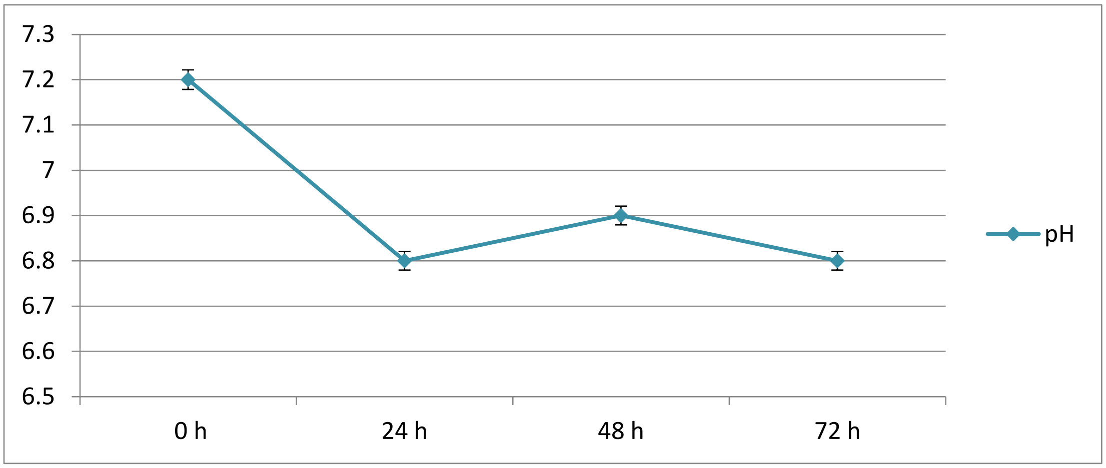


Figure 4.1 Changes of pH in the case of aluminum anode

Figure 4.1 shows insignificant changes of pH during all 72 hours of treatment, mostly due to supplying of the current which was not high. Conductivity of the wastewater during the 72 hours was decreasing (Figure 4.2).

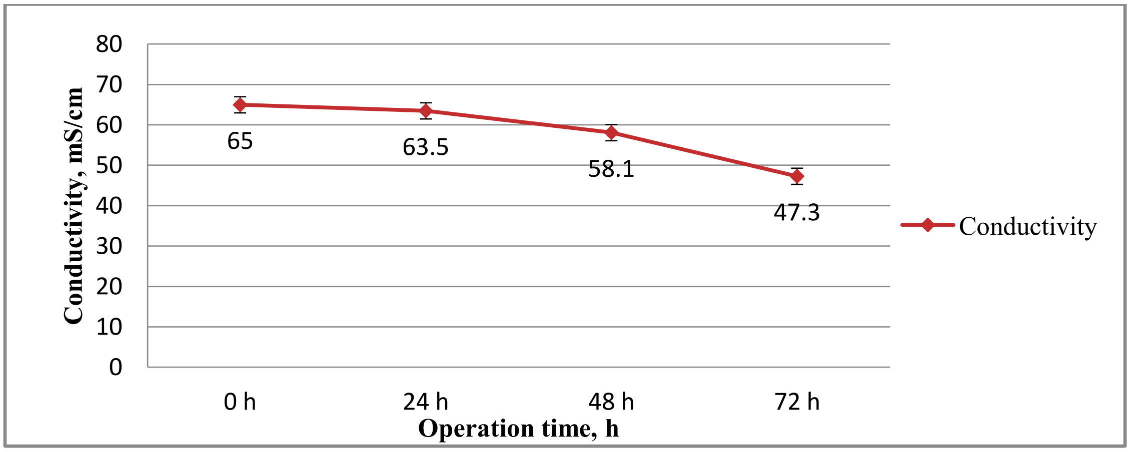


Figure 4.2 Changes of conductivity in the case of aluminum anode

This decrease is attributed to the decreasing quantities of cations and anions in the solution, which was proven by the formation of a high amount of sludge during the reaction in the reactor. Specifically, cations of aluminum resulting from the dissolution of anode bind with ions in the wastewater and form sludge.

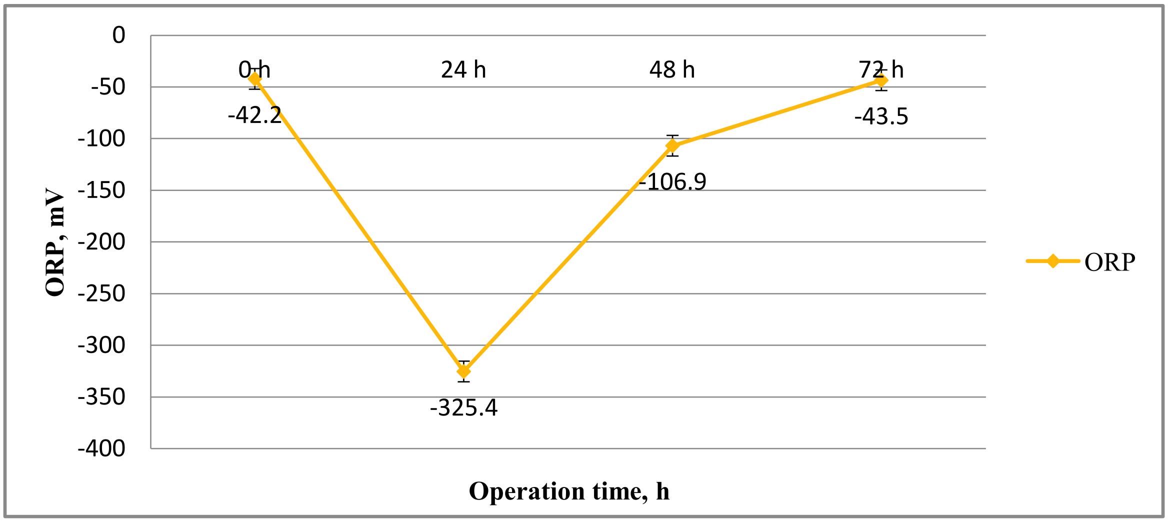


Figure 4.3 Changes of ORP in the case of aluminum anode

A drastic decrease of ORP was observed during the experiment with aluminum anode (Figure 4.3), which displays the reduction process in the first 24 hours.

Table 4.5 Changes in the concentrations of the pollutants during 72 hours in the case of aluminum anode

Time, h	TKN, mg/l	Ammonia, mg/l	ON, mg/l
0	13900	11800	2100
24	12550	10500	2050
48	11807	9803	2004
72	10216	8602	1751

Table 4.5 shows the removal of organic nitrogen was much slower than other compounds in the first 48 hours. The main process of destruction of organics happened between 48 and 72 hours during the treatment.

Figure 4.4 presents results of the experiment with duration of 72 hours at varying voltage gradients of 0.8 V/cm, 1 V/cm and 1.1 V/cm in the case of carbon anode.

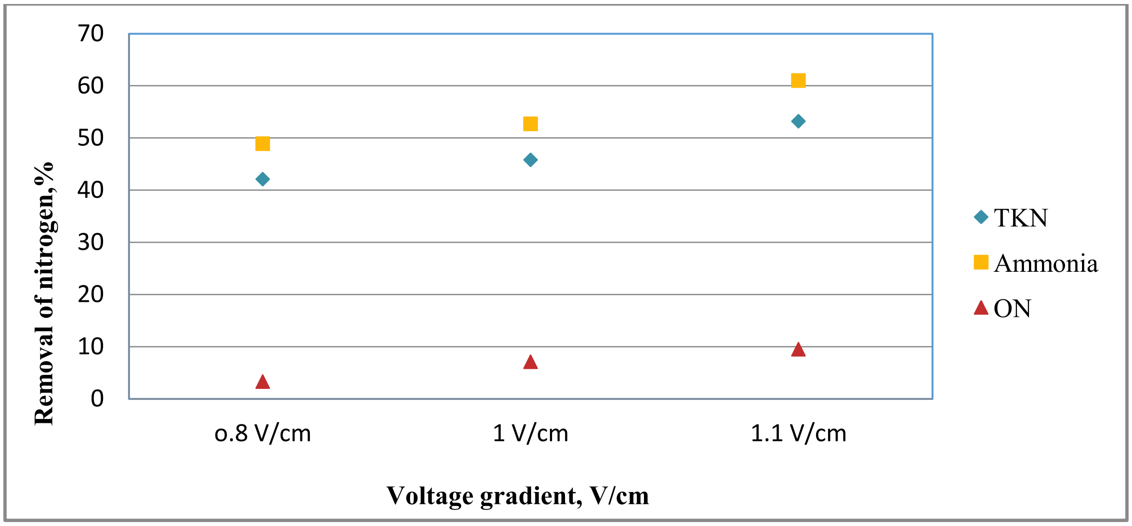


Figure 4.4 The influence of voltage gradient on the removal efficiency of nitrogen in the case of carbon anode

It could be observed, that after 72 hours of treatment, improved removal efficiency of all pollutants was achieved at a voltage gradient of 1.1 V/cm, where TKN, ammonia, organic nitrogen reached 53.2%, 61% and 9.5% respectively. It can be concluded that increasing the voltage gradient leads to a higher removal efficiency of nitrogen in wastewater.

Figures 4.5 – 4.7 show impact of voltage on pH, conductivity and ORP in a system with carbon anode.

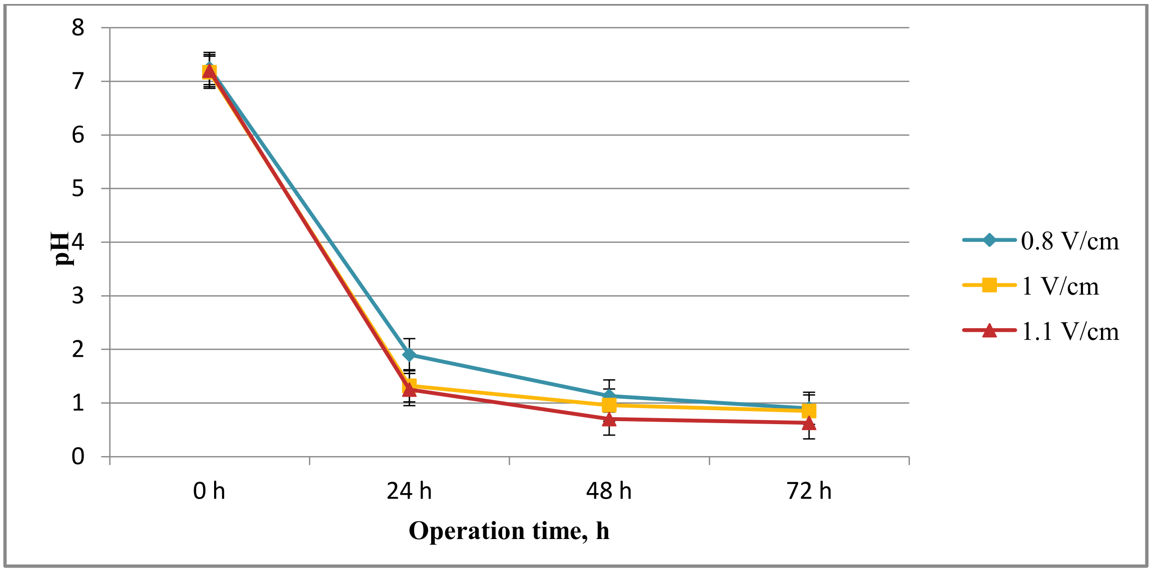


Figure 4.5 Changes of pH in the case of carbon anode

Insignificant impact of the voltage gradient on pH of wastewater was observed (Figure 4.5). Similar conclusion was made with respect to wastewater conductivity (Figure 4.6).

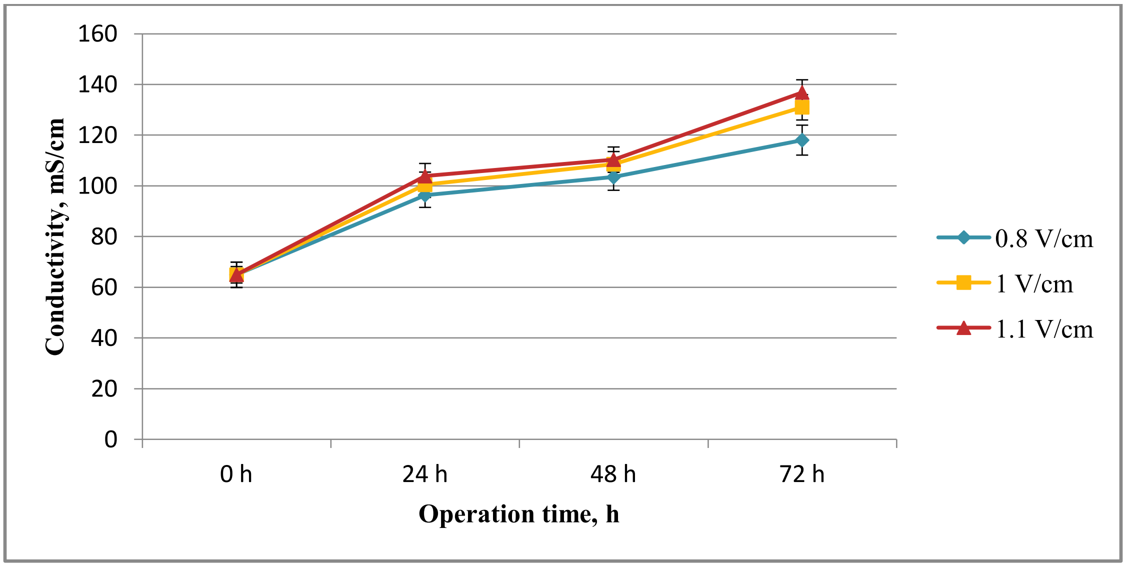


Figure 4.6 Changes of conductivity in the case of carbon anode

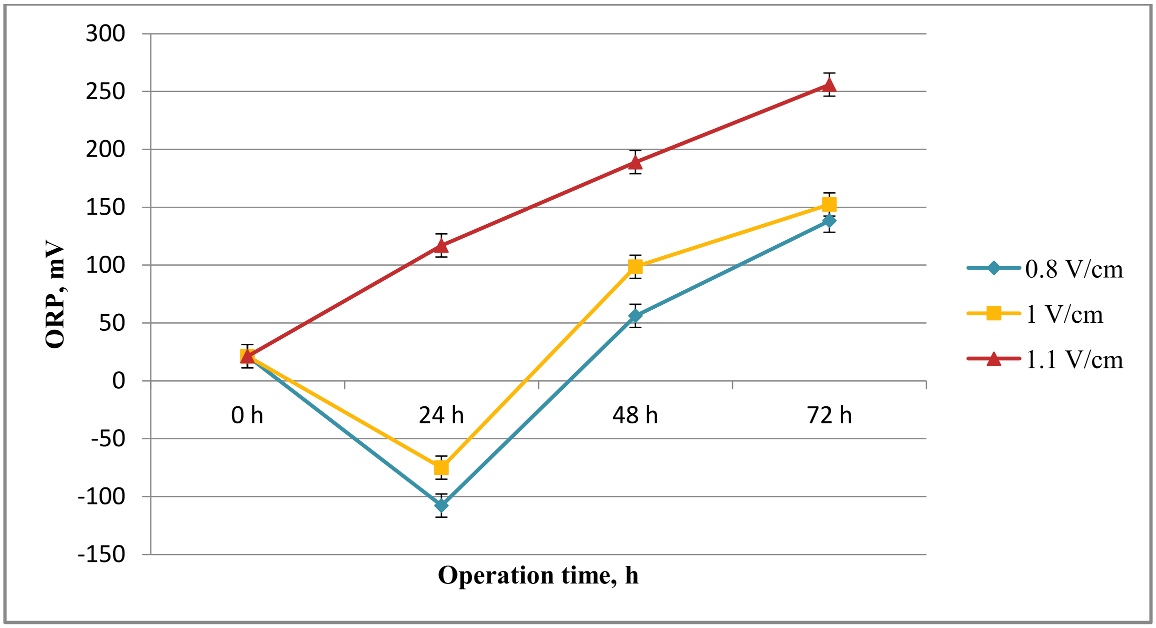


Figure 4.7 Changes of ORP in the case of carbon anode

Figure 4.7 shows that the pattern of behavior of ORP, in terms of configuration and value, is the same for both voltage gradients of 0.8 V/cm and 1 V/cm. However, at the voltage gradient of 1.1 V/cm, there is no decrease of ORP due to a faster oxidation process. This was proven by the best removal results (Figure 4.4).

Table 4.6 Influence of the voltage gradient on nitrogen removal in the case of carbon anode

Carbon anode, specific surface area = 45 cm^2				
№ of experiment	Voltage gradient, V/cm	Removal TKN, %	Removal NH_3-N, %	Removal ON, %
14	0.8	42.1	48.9	3.3
15	1	45.8	52.7	7.1
16	1.1	53.2	61	9.5

From the results above (Table 4.6), it can be concluded, that applying electrokinetic phenomena alone is not sufficient for the removal of organic nitrogen in the case of carbon anode, and that consequently, further improvements is required. Since the highest removal was obtained in the case of voltage gradient of 1.1 V/cm, therefore, the subsequent experiments were carried out at this voltage gradient.

Figure 4.8 shows the variation of removal efficiency of TKN, ammonia and organic nitrogen over varying voltage gradients, in the case of platinum anode.

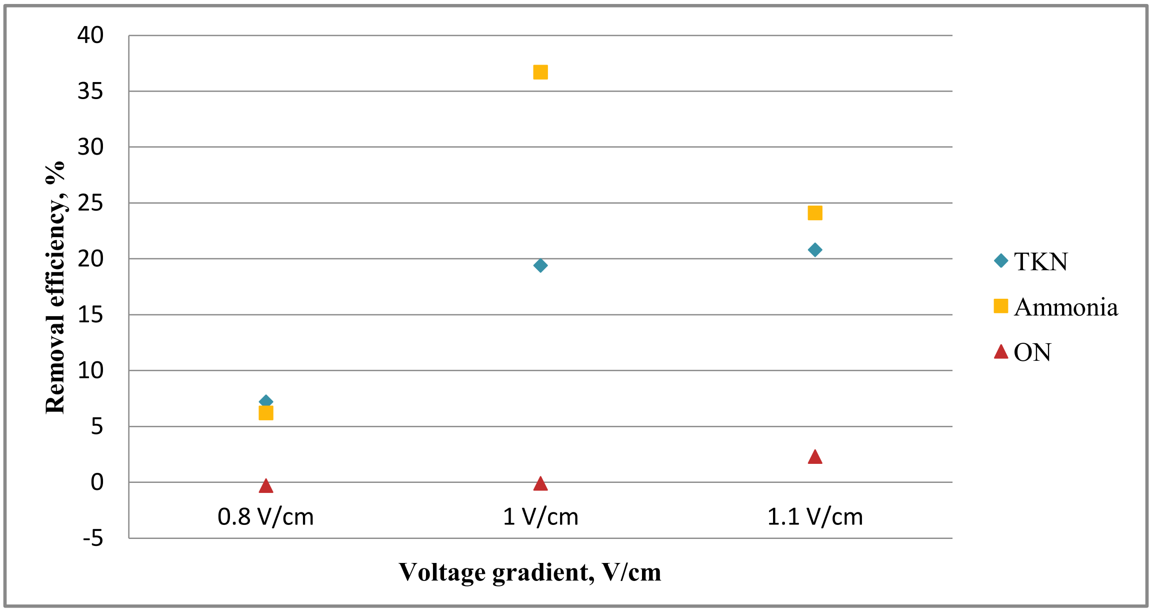


Figure 4.8 Influence of the voltage gradient on nitrogen removal in the case of platinum anode

After a 72 hour reaction time, at the highest voltage gradient of 1.1 V/cm, the removal of TKN, ammonia and organic nitrogen was 20.8%, 24.1% and 2.3% respectively. Furthermore, in the case of a low voltage gradient of 0.8 V/cm, small increase (0.3%) of organic nitrogen was observed. The production of new organic nitrogen molecules can be explained by the fact that, at a low voltage gradient, the reduction condition occurs. In this condition, a synthesis of new molecules is more likely.

Figures 4.9 – 4.11 show an influence of voltage gradient on pH, conductivity and ORP in a system with platinum anode.

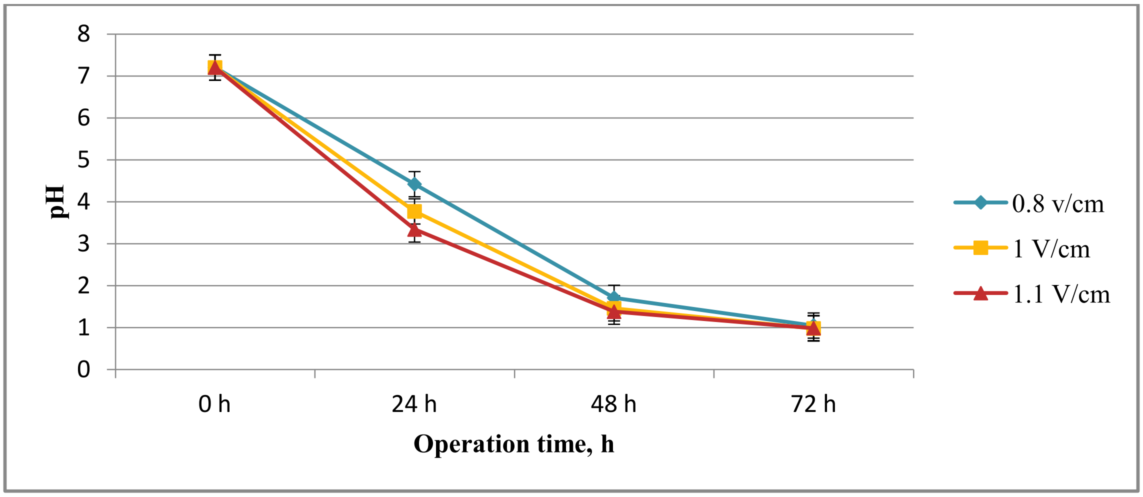


Figure 4.9 Changes of pH in the case of platinum anode

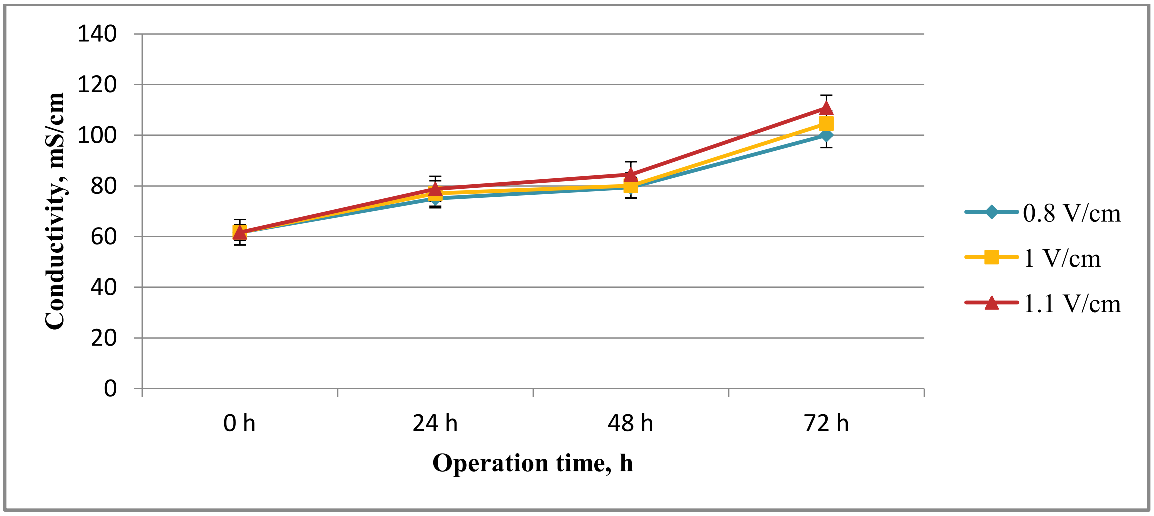


Figure 4.10 Changes of conductivity in the case of platinum anode

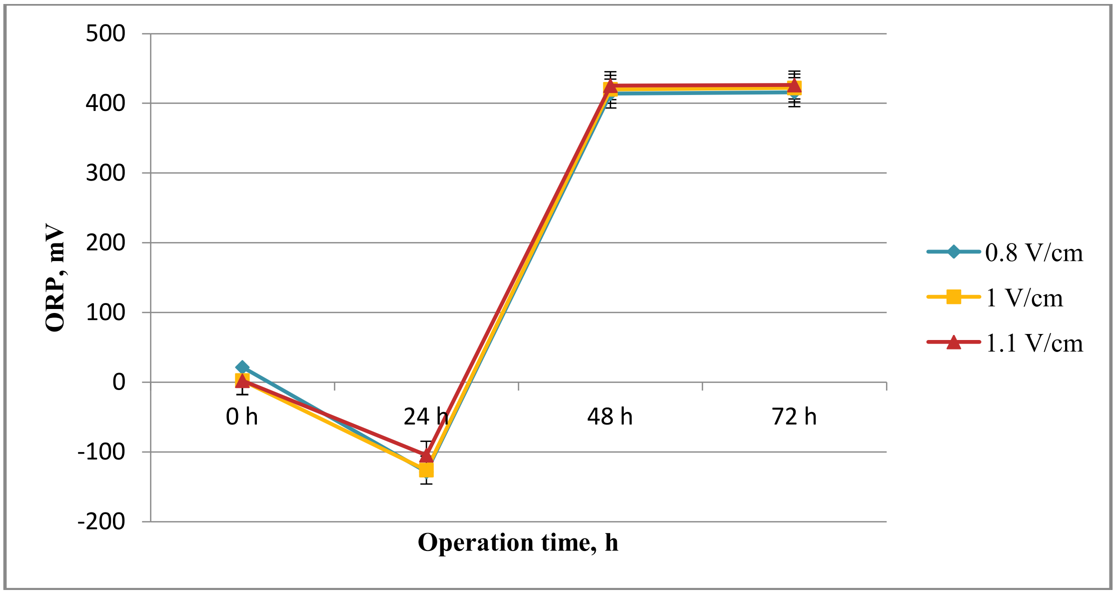


Figure 4.11 Changes of ORP in the case of platinum anode

Behavior of pH behavior is similar in presence all tested voltage gradients: 0.8 V/cm, 1 V/cm and 1.1 V/cm (Figure 4.9). Conductivity did not show dependence upon the change of the voltage gradient (Figure 4.10). Pattern of ORP's change was also similar for all voltage gradients (Figure 4.11). The patterns show a dramatic decrease of ORP during the first 48 hours, which indicates that the reduction process has occurred. However, the oxidation process took place in the period of 48 to 72 hours, in which the main degradation of organic compounds was happened. This has been proven by analyses results, which were taken every 24 hours (Table 4.7).

Results in the Table 4.7 showed that using platinum anode does not enhance the removal efficiency of nitrogen, and new improvements of the system are necessary. Therefore, ion exchange membranes were implemented and the response of this wastewater in new conditions was investigated.

Table 4.7 Influence of voltage gradient on nitrogen removal in the case of platinum anode

Platinum anode, specific surface area = 2 cm^2				
№ of experiment	Voltage gradient, V/cm	Removal TKN, %	Removal NH_3-N, %	Removal ON, %
17	0.8	7.2	6.2	+ 0.3
18	1	19.4	36.7	+0.1
19	1.1	20.8	24.1	2.3

4.1.1 Stage 1.3 Influence of the ion exchange membrane on the electrokinetic process

In Stage 1.3, twelve experiments were conducted in undivided and divided cells, with a membrane, in order to investigate an influence of the ion exchange membranes on the removal efficiency of nitrogen. Experiments were carried out with different types of membrane, including an anionic/cationic polymer ion exchange membrane, cationic exchange resins and a fiber cationic membrane. Before conducting the experiments, the pretreatment of the membrane was done. Due to the fact that the application of the membrane substantially changes the characteristics of the electrochemical process, it was decided to perform experiments with all conditions tested above, including different distances between electrodes and different voltage gradients.

Four experiments were conducted using an aluminum anode, a fixed voltage gradient at 0.2 V/cm and four types of membrane. Results are presented in Table 4.8 and Figure 4.12.

Table 4.8 Influence of the ion exchange membranes on removal efficiency in the case of an aluminum anode

Experiments	Membrane	Voltage gradient, V/cm	Removal TKN, %	Removal NH_3-N, %	Removal ON, %
20	cationic polymer	0.2	93.9	96.3	81.9
21	anionic polymer	0.2	1.05	0.4	4.7
22	cationic resins	0.2	89.2	92.8	69
23	fiber phosphonic	0.2	72.8	72.7	75.7

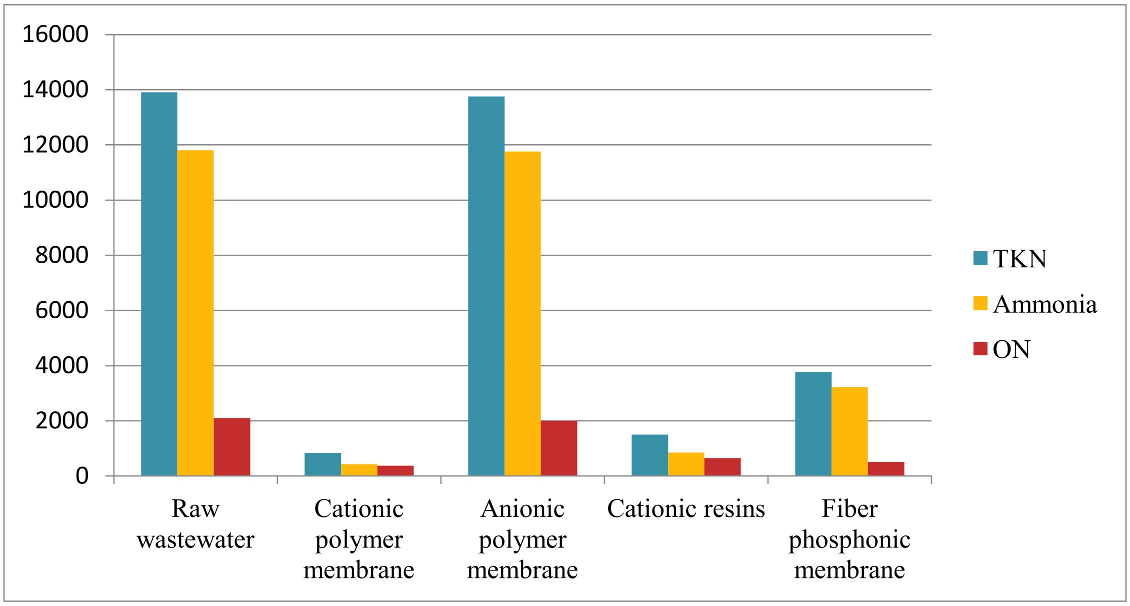


Figure 4.12 Influence of ion exchange membranes on the removal of nitrogen in the case of an aluminum anode

After 72 hours of operation, in the case of a cationic polymer membrane, removal of TKN, ammonia and organic nitrogen reached almost 94%, 96% and 82% respectively (Table 4.8). Good results were also obtained in the application of cationic resins, namely

TKN = 89.2%, ammonia = 92.8% and organic nitrogen = 69%. Lower levels of removal were achieved with a fiber cationic membrane however: TKN was at 72.8%, ammonia was at 72.7% and organic nitrogen was at 75.7%. Furthermore, an anionic polymer membrane displayed little to no removal efficiency of nitrogen from wastewater (Figure 4.12).

Despite the high removal rate using the cationic membrane, this method has significant disadvantages, because of fast electro-dissolution of the aluminum anode and a production of a large amount of sludge and foam, making process more difficult.

Additional four experiments were conducted in order to investigate the effect of the application of membranes to a system with a carbon anode at a fixed voltage gradient of 0.8 V/cm. Results presented in Table 4.9 and Figure 4.13 show different removal rate of TKN, ammonia and organic nitrogen when different membranes were applied.

Table 4.9 The influence of ion exchange membranes on the removal of nitrogen in the case of a carbon anode

Experiments	Membrane	Voltage gradient, V/cm	Removal TKN, %	Removal NH_3-N, %	Removal ON, %
24	cationic polymer	0.8	49.8	31.4	53.1
25	anionic polymer	0.8	63.6	41.4	67.6
26	cationic resins	0.8	49.2	23.8	53.8
27	fiber phosphonic	0.8	68.9	52.2	71.9
comparison	without membrane	0.8	57.3	65.5	31.2

Comparative study showed that no significant improvement in the removal of nitrogen was observed when membranes are implemented into EK cells, beside the system with cationic fiber (phosphonic) membrane (Figure 4.13). Therefore, in the system with the fiber membrane, there was an improvement in the removal of TKN by 11.6% and organic nitrogen by 40.7%. Ammonia removal, however, decreased by 13.3% when compared to the system without a membrane (Table 4.9).

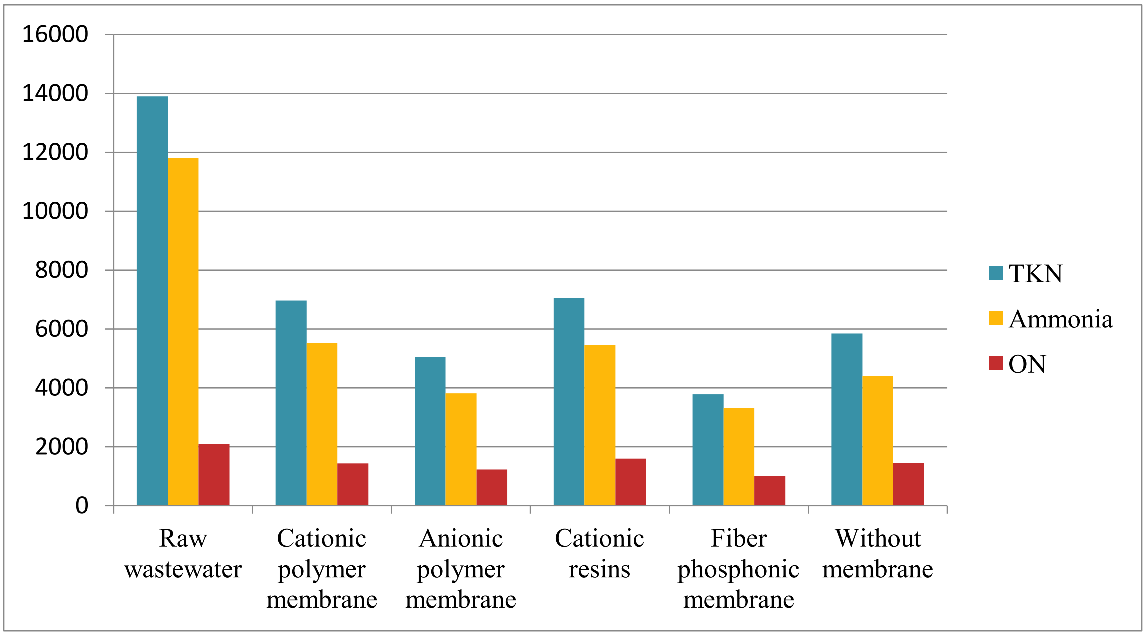


Figure 4.13 Influence of the ion exchange membrane on the removal of the nitrogen in the case of a carbon anode

The differences in the removal efficiency could be related to the structure of the membranes. It is possible that fiber membrane permits organic cations (formed due to reduction on the cathode) to pass through membrane to anode, where they are oxidized by produced hydroxyl radical.

Additional four experiments were carried out with a platinum anode, where various four types of membrane were tested at the voltage gradient of 0.8 V/cm. Results are presented in Table 4.10 and Figure 4.14.

Table 4.10 Influence of ion exchange membranes on the removal of nitrogen in the case of a platinum anode

Experiments	Membrane	Voltage gradient, V/cm	Removal TKN, %	Removal NH_3-N, %	Removal ON,%
28	cationic polymer	0.8	36.1	40.8	0.95
29	anionic polymer	0.8	6.4	+ 0.1	+6.9
30	cationic resins	0.8	35.2	40.1	5.4
31	fiber phosphonic	0.8	32.2	27.1	60.9
comparison	without membrane	0.8	22.8	22.5	23.9

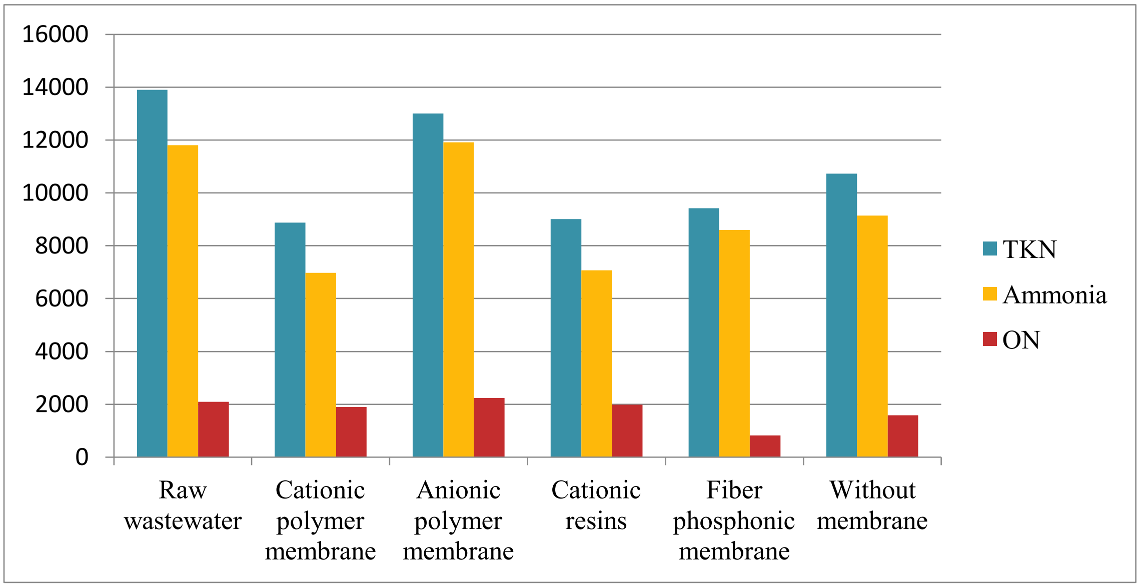


Figure 4.14 Influence of ion exchange membrane on the removal of the nitrogen in the case of a platinum anode

The results of comparative study showed that cationic polymer, cationic resins and fiber membranes all had almost the same level of TKN removal. However, a much higher removal level of organic nitrogen can be achieved using a system with a fiber membrane (60.9%), while a system without a membrane achieves only 23.9%. Cationic resins, cationic polymer and anionic polymer membranes have almost no impact on the removal of organic nitrogen. It could be due to the low permeability of these membranes for big organic molecules. Therefore, the most successful membrane in these conditions was the fiber membrane.

Based on the results obtained in Phase I, it can be concluded that electrokinetic phenomena only is not capable of significantly removing nitrogen (TKN), thus further improvements would be necessary. Overall, the results generated by Phase I permitted to determine the best parameters of the electrochemical process, such as distance between electrodes, anode material, voltage gradient and type of membrane.

4.2 Phase II

The objective of this phase was to improve the electrokinetic system by introducing air to the system in order to produce the oxidizing agent hydroxyl radical on the electrode.

4.2.1 Influence of the air flow rate purged into the system on nitrogen removal

Eight sets of experiments were conducted in order to study removal efficiency of nitrogen from wastewater by bubbling air through the solution. All experiments were conducted with a selected voltage gradient of 1.1 V/cm and a distance between electrodes of 5 cm.

Platinum and carbon anodes were chosen for phase II. Duration of each experiment was 72 hours. Results are presented in Table 4.11 and Figure 4.15.

Table 4.11 Effect of the flow rate of air purged into the system on the removal efficiency of nitrogen

Experiments	Rate of air, ml/min	Voltage gradient, V/cm	Removal TKN, %	Removal NH_3-N, %	Removal ON, %	Removal TN, %
32	120	1.2	64	74.8	3.3	62
33	75	1.2	65.1	74.5	12.1	65.6
34	45	1.2	71.6	75.3	50.5	68.6
35	20	1.2	63.7	65.4	32.2	61.1

Figure 4.15 presents the dependence of the flow rate of air bubbled through solution on the removal efficiency of nitrogen from wastewater.

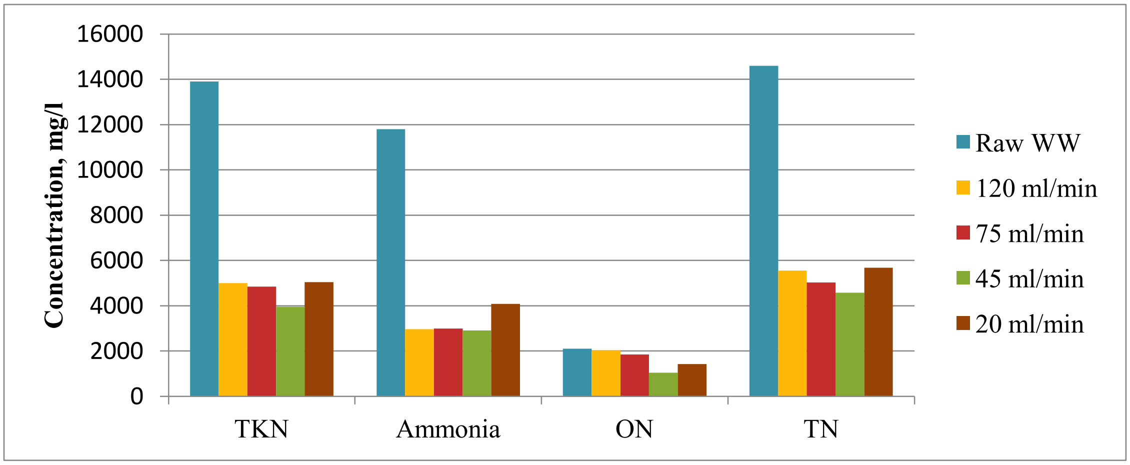


Figure 4.15 Impact of air flow rate on removal efficiency of the nitrogen in the case of carbon anode

The results indicate, that after 72 hours of operation, with flow rates of purged air of 120 ml/min, 75 ml/min, 45 ml/min and 20 ml/min, levels of TKN removal were 64%, 65.1%, 71.6% and 63.7% respectively; levels of ammonia removal were 74.8%, 74.5%, 75.3% and 64.4% respectively; and levels of organic nitrogen removal were 3.3%, 12.1%, 50.5% and 32.2%, respectively. Thus, it could be concluded that the highest rate of nitrogen removal was at the flow rate of 45 ml/min. It is possible that, at high rates of air production, the hydroxyl radical is limited due to the high velocity of air bubbles, given the little time it has to make contact with the electrode. On the other hand, a low rate of air does not offer enough of an oxygen concentration to the system in order to produce hydroxyl radicals.

Figures 4.16-4.18 demonstrate the dependence of physiochemical characteristics on flow rate changes of air purged into the system with a carbon anode.

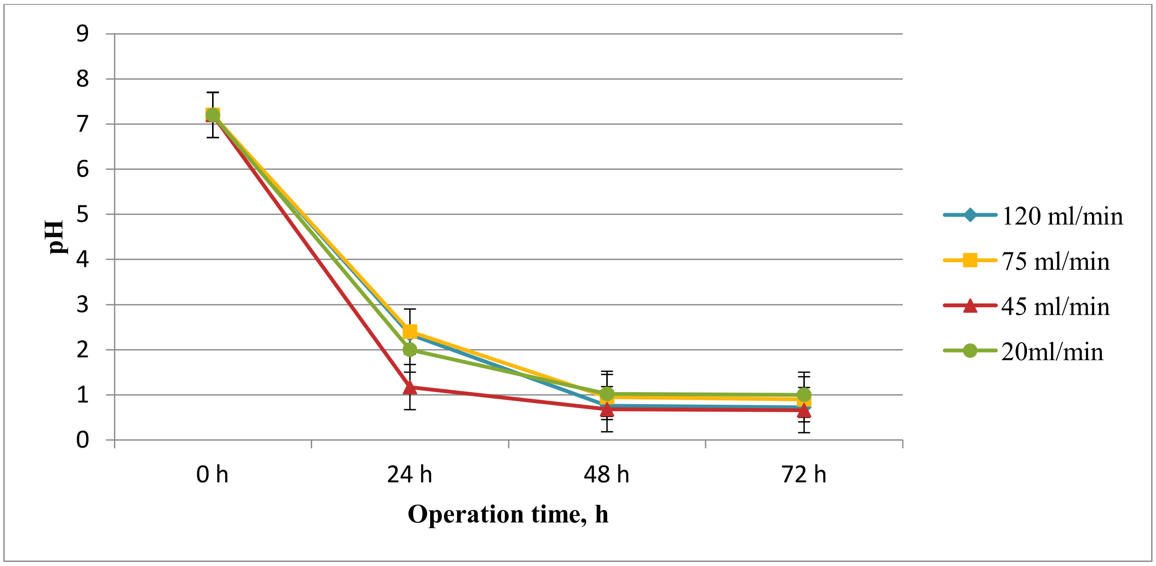


Figure 4.16 Change of pH in the case of a carbon anode

Figure 4.16 demonstrates that pH levels in the first 24 hours, at air flow rates of 120 ml/min, 75 ml/min and 20 ml/min, are almost equal, whereas a flow rate of 45 ml/min leads to a faster decrease in the pH in the first 24 hours. These results concur with those obtained in experiment 34 in Table 4.11.

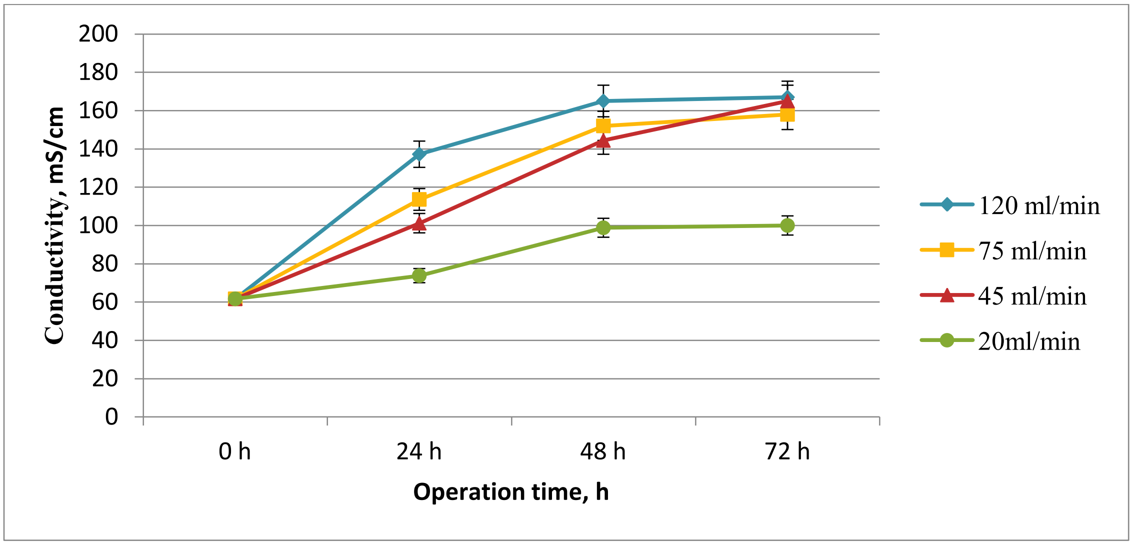


Figure 4.17 Changes of conductivity in the case of a carbon anode

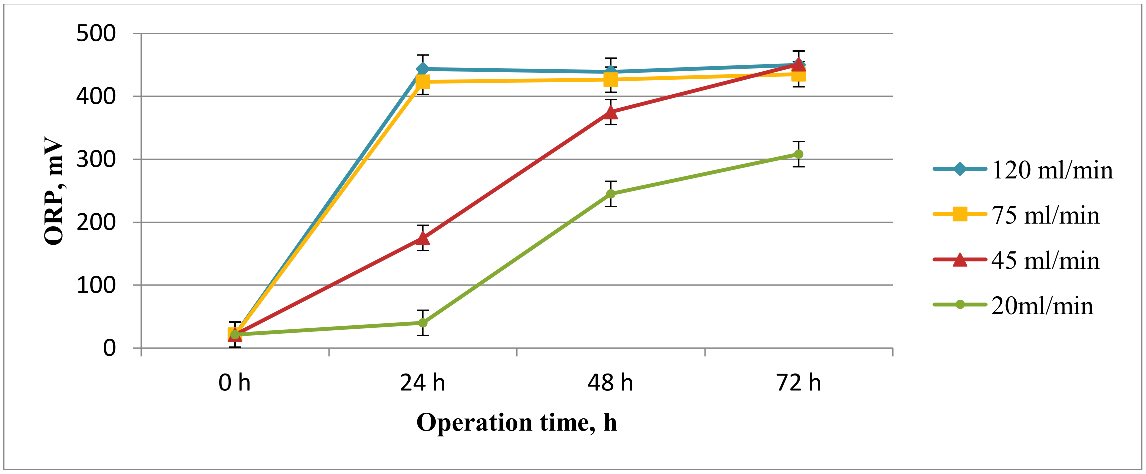


Figure 4.18 Changes of the ORP in the case of the carbon anode

At a flow rate of air of 45 ml/min, the behavior of conductivity and ORP were nearly linear (Figures 4.17, 4.18), which indicated a stability of the process. In the case of flow rates of 120 ml/min and 75 ml/min, on the other hand, high changes are observed, displaying the unstable behavior of the process.

Table 4.12 Effect of the flow rate of air on the removal efficiency of nitrogen in case of a platinum anode

Experiments	Rate of air, ml/min	Voltage gradient, V/cm	Removal TKN, %	Removal NH_3-N, %	Removal ON, %	Removal TN, %
36	120	1.2	0.3	0	1.9	2.7
37	75	1.2	9.3	7.6	19	10.3
38	45	1.2	6.5	9.3	+ 9.5	8.2
39	20	1.2	10.8	12.6	0.5	11.6

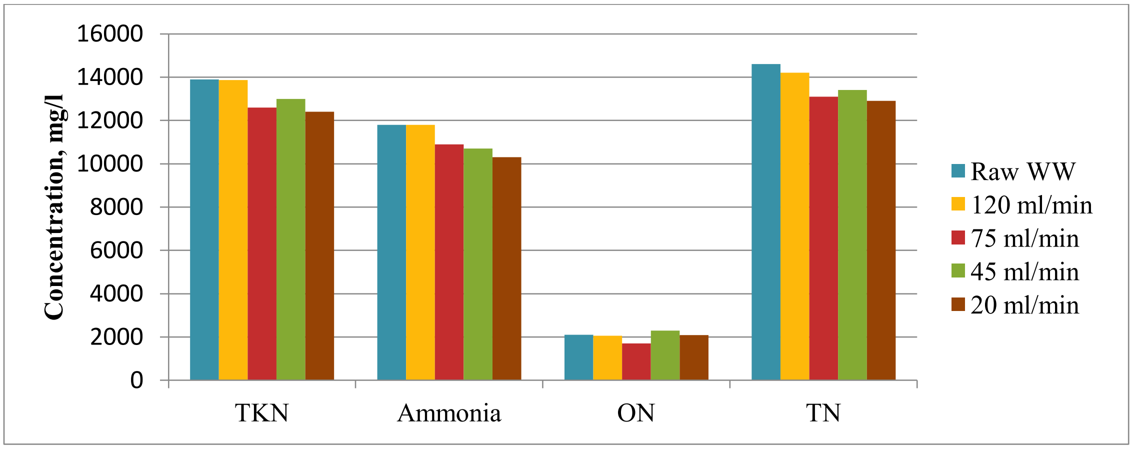


Figure 4.19 Impact of air flow rate on the removal efficiency of nitrogen in the system with a platinum anode

Another set of experiments were conducted with platinum electrodes, in which the influence of the flow rate of air on the removal of nitrogen from wastewater was investigated. Table 4.12 and Figure 4.19 display the influence of the flow rate of air on the removal efficiency of nitrogen from wastewater in the case of a platinum anode.

Results showed (Table 4.12 and Figure 4.19) that electro-Fenton oxidation in the system with a platinum anode does not offer satisfying results since the removal of nitrogen is around 10% only.

Figures 4.20-4.22 show impact of the air flow rate with a platinum anode on physiochemical characteristics of wastewater.

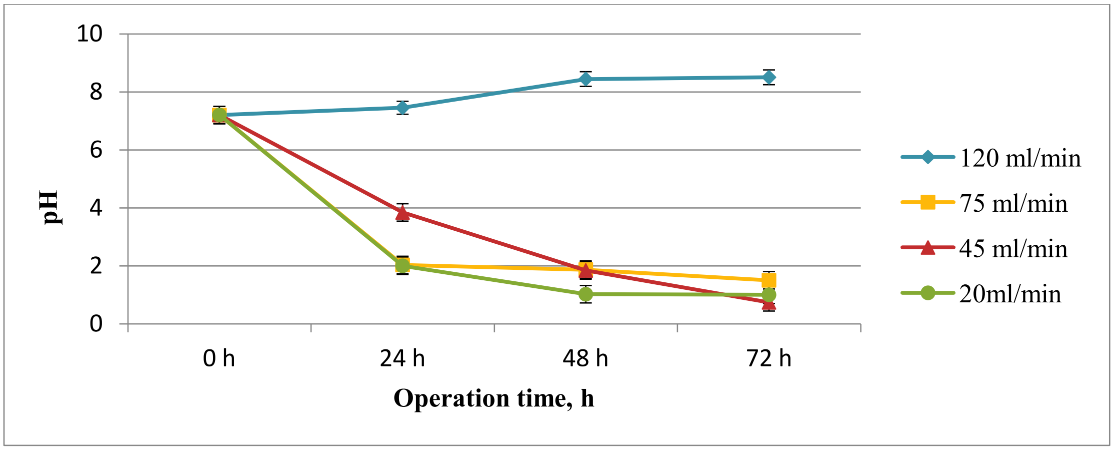


Figure 4.20 Changes of the pH in the case of a platinum anode

It can be noted that the behavior of pH in the cases of a platinum anode and carbon anode are very different. In the system with a carbon anode, behavior of pH at all flow rates is the same, while in the system with a platinum anode, pH decreases when flow rate of air is less than 75 ml/min. At flow rates of 45 and 20 ml/min, a pH of 2 was reached more quickly than at a flow rate of 75 ml/min. It is possible that at a low air flow rate, the oxygen has more time for dissolving than at higher air flow rate, and consequently, for producing more hydrogen peroxide, which is necessary for the oxidation process.

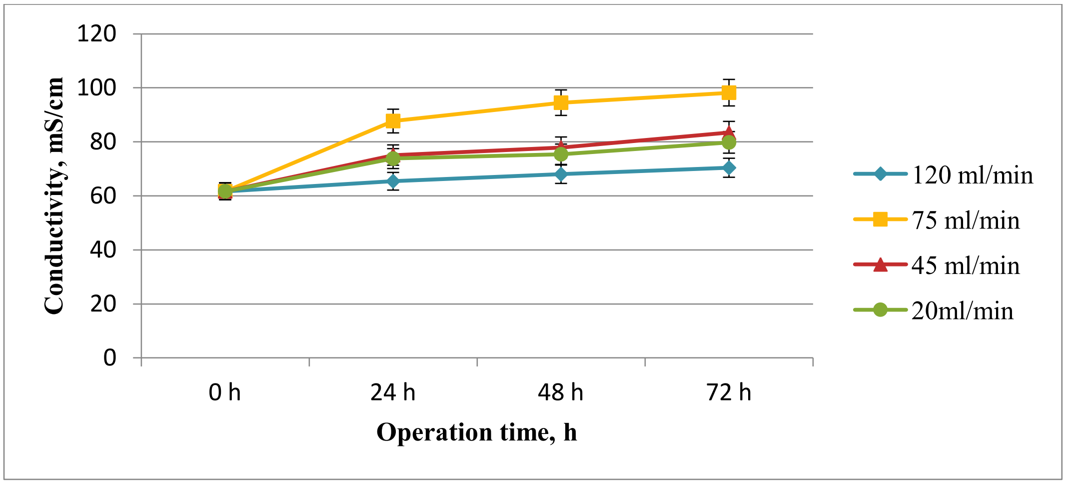


Figure 4.21 Change of conductivity in the case of a platinum anode

From Figure 4.21, it can be observed that all conductivity lines have the same pattern. During the reactions, conductivity is increasing, but at different rate.

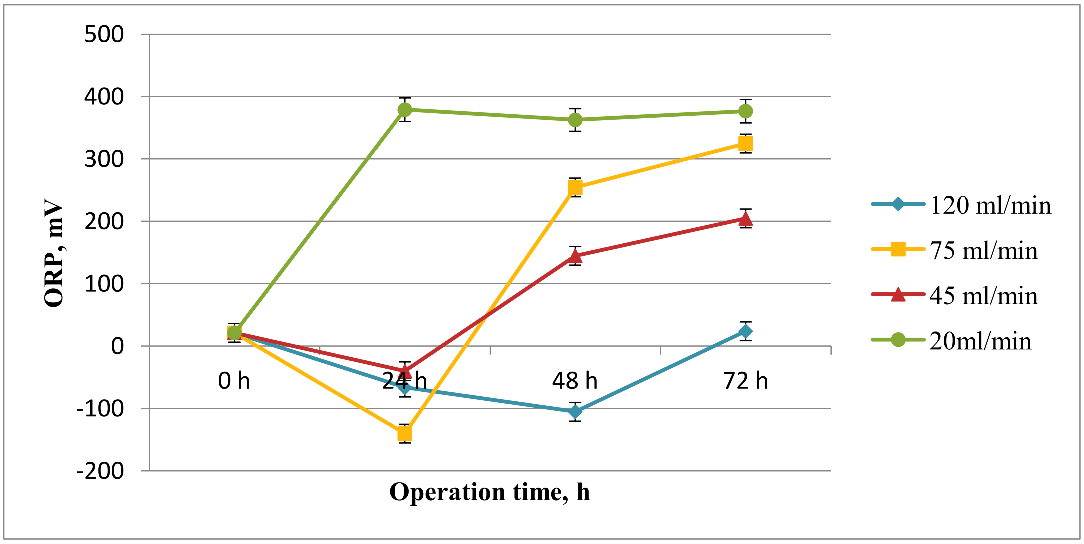


Figure 4.22 Change of the ORP in the case of a platinum anode

Figure 4.22 shows the changes of the ORP during 72 hours. At flow rates of 75 ml/ min and 45 ml/min, the reduction process takes place in the first 24 hours. At the flow rate of 120 ml/min, the reduction process is predominant, in the first 48 hours, while at the flow rate of 20 ml/min, the oxidation process is prevalent. Table 4.12 displays that the highest level of removal efficiency, in the case of a platinum anode, at a flow rate of 20 ml/min. However, the system with a platinum anode and air bubbled into the solution in order to oxidize nitrogen containing pollutants, cannot be used due to the very low level of removal efficiency at less than 10% of TKN.

Based on the results obtained in the Phase II it, can be concluded that electro-Fenton oxidation, in the systems with a carbon anode and a platinum anode, was unable to remove nitrogen at the acceptable level from wastewater.

4.3 Phase III

The objective of this phase was to improve the electrokinetic system through external application of an oxidizing agent, namely hydrogen peroxide, and to investigate the influence of the parameters on the oxidation process. These parameters include applied voltage, configuration of the cell (divided/undivided, continuous/batch), hydrogen peroxide concentration, feeding mode and H_2O_2/Fe^{+2} molar ratio. To investigate the effect of the combined electrochemical method, series of experiments were carried out. From the literature review, it is known that the anode material has a significant influence on the process due to its ability and high potential to produce strong oxidants on its surface from the electrolyte. For example, the hydroxyl radical could be produced from water oxidation on the surface of the anode: $H_2O \rightarrow OH^{\cdot} + H^{+} + e^{-}$. Furthermore, in the proposed system, hydroxyl radicals would also be generated by a reaction of hydrogen peroxide with ferrous ion (Fe^{+2}). Subsequently, these oxidants can degrade different kind of pollutants (Bensalah et al., 2013). In the current study carbon anode was selected as anode with high oxygen evolution overpotential. The distance between electrodes was preserved as 5 cm in all experiments.

4.3.1 Stage 3.1 Effect of the applied voltage on the oxidation process

Current intensity is a very important parameter in electrochemical processes. The optimization of this parameter can help to reach a higher rate of hydrogen peroxide generation, and as a result a higher degradation rate of pollutants. The experiments were conducted at a fixed voltage and changes in the electrical current were observed.

The first set of five experiments was performed with varying applied voltage and the same 4 ml amount of hydrogen peroxide was applied (Table 4.13).

Table 4.13 Effect of applied voltage on the removal efficiency of nitrogen

Experiment	Voltage, V	Initial current, A	Volume of H_2O_2 applied, ml	Removed TKN, %	Removed ammonia, %	Removed ON, %
40	3	0.3	4	24.7	16.2	58.3
41	3.4	0.6	4	72.2	71.3	75.8
42	4.0	1	4	82.6	84.2	76.1
43	5.5	1.25	4	92.4	95.2	81.4
44	6	2.2	4	75.6	81.7	51.6

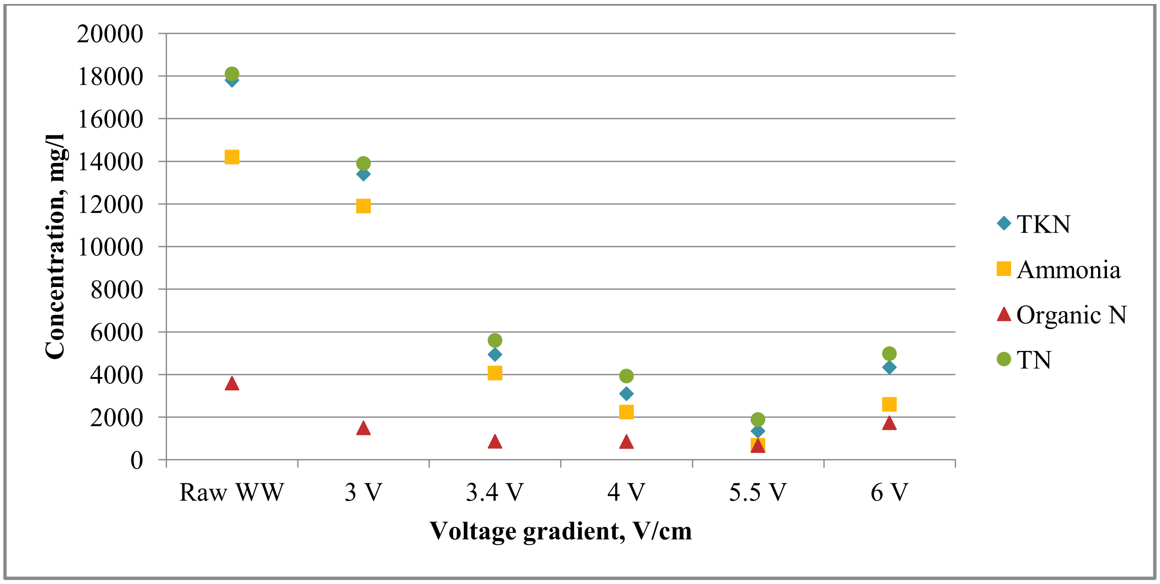


Figure 4.23 Effect of applied voltage on the removal efficiency of nitrogen

As can be seen in Table 4.13 and Figure 4.23, the removal efficiency of nitrogen increased when voltage was raised from 3 to 5.5 V, indicating an enhancement in degradation. The most effective voltage is 5.5 V, where removal efficiency of TKN, ammonia and organic nitrogen by 92.4%, 95.2% and 81.4%, respectively. Increasing the voltage led to an increase in the hydroxyl radicals' electro-generation from the oxidation of water at the anode, and sped up the electro-regeneration of ferrous ions from ferric ions ($Fe^{+3} + e^{-} \rightarrow Fe^{+2}$), which increased the efficiency of Fenton chain reactions. However, a further increase of voltage by an additional 5.5 V decreased nitrogen removal. At a high voltage, the competitive electrode reactions take place: hydrogen evolution at the cathode ($2H^{+}+2e^{-} \rightarrow H_2$) and oxygen evolution at the anode ($2H_2O \rightarrow 4H^{+}+O_2+4e^{-}$). This inhibits the main reaction of hydroxyl radical production and electro-regeneration of ferrous ions. Also, a fast accumulation of the intermediates, which are more difficult to mineralize, occurs at a high electrical current (Bensalah et al., 2013)

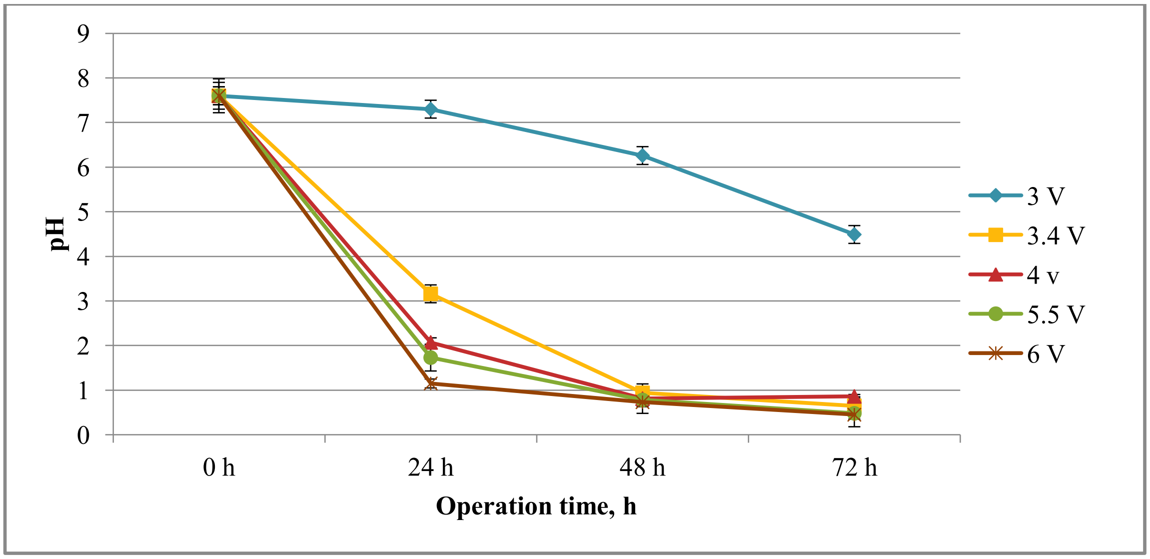


Figure 4.24 Changes in the pH at different applied voltage

From Figure 4.24, it is seen that pH, at a low voltage of 3 V, does not reach pH 4 even after 72 hours. This is demonstrated by low removal efficiency (experiment #40, Table 4.13). This outcome concurs with the literature review, in which it is stated that in the process with Fenton's reagent, pH must be less than 4. At a voltage of more than 3 V, the value of the pH, after 48 hours, is less than 1 and removal efficiency was more than 70%.

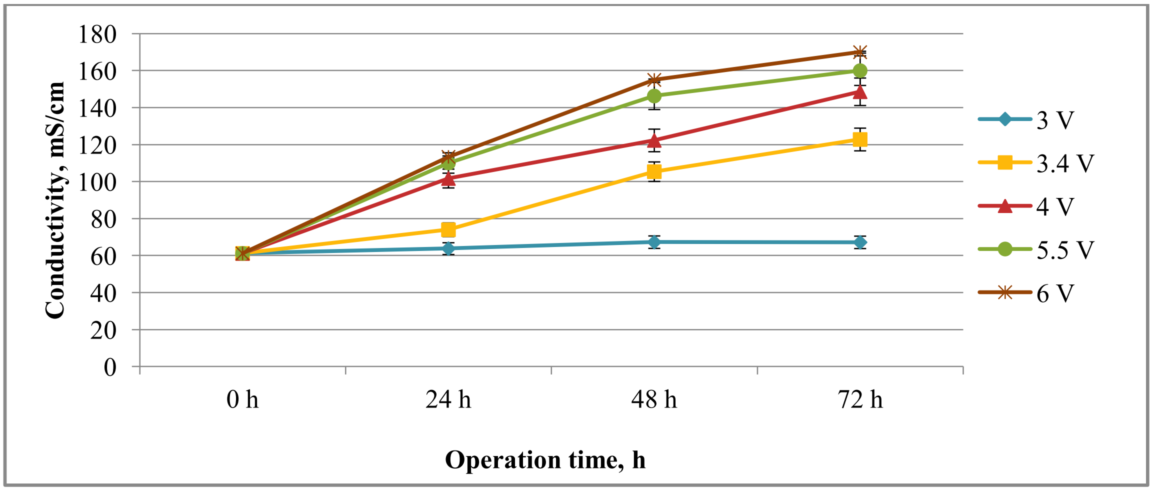


Figure 4.25 Changes in conductivity at different applied voltage

Increasing the voltage leads to an increase in conductivity (Figure 4.25). In addition, it is known that increasing the conductivity leads to the increase in degradation of organic molecules (Bensalah et al., 2013).

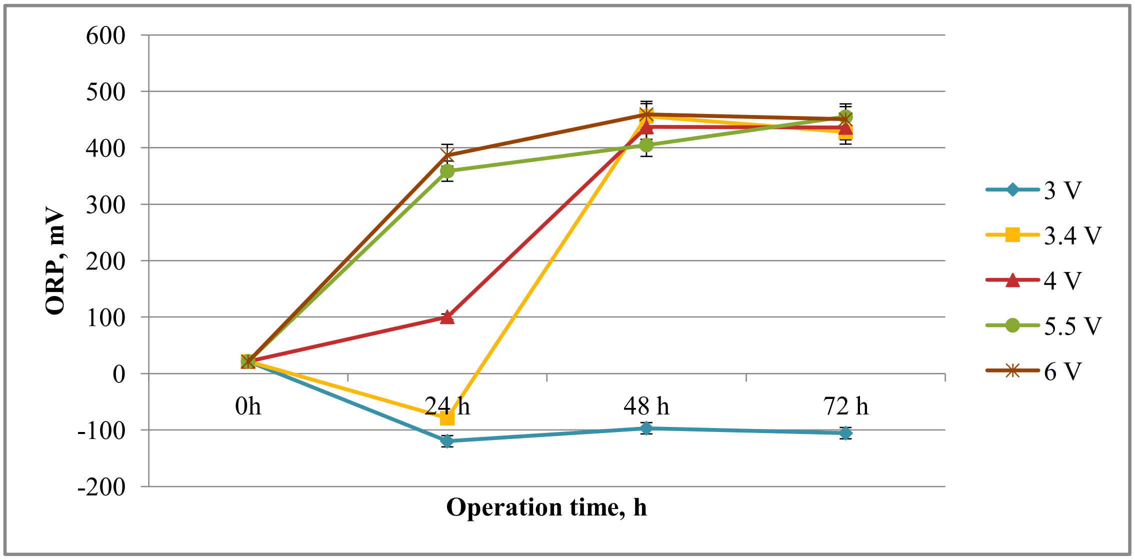


Figure 4.26 Changes of ORP at different applied voltage

At the voltage of 3 V, a reduction process took place and the removal efficiency of TKN is approximately 20% (Figure 4.26). At a voltage of 3.4 V, the reduction process took place during first 24 hours, while during subsequent 48 hours turned to oxidation process. At a voltage of 4 V, the oxidation process predominated at the beginning; while in cases of 5.5 V and 6 V, the oxidation process is fully predominate.

In this stage, it is important to observe the role of anode consumption, because it plays an important role in determining the overall cost of the process. The theoretical electrode consumption rate was calculated by Faraday’s law and compared with experimental consumption rate (Figure 4.27).

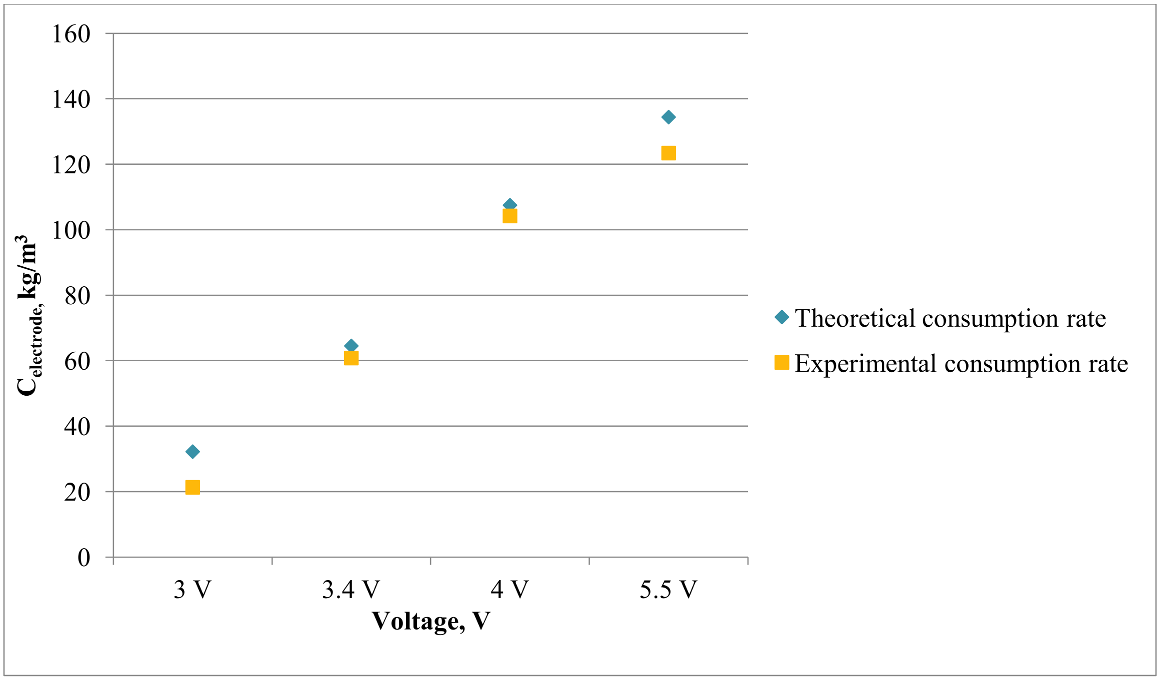


Figure 4.27 Consumption rate of carbon anode at different applied voltage

The results demonstrated a gradual increase in the consumption rate of the carbon anode as the voltage gradient reached 5.5 V in both theoretical and experimental cases.

4.3.2 Stage 3.2 Effect of the hydrogen peroxide consumption rate and H_2O_2/Fe^{+2} molar ratio

Concentration of hydrogen peroxide plays an important role in electrochemical processes. Therefore, six experiments were performed in order to obtain a desired concentration of hydrogen peroxide. Hydrogen peroxide wt. 30% was used for these experiments. A reaction time of 72 hours and a voltage of 5.5V were selected for a degradation of organic nitrogen. Results are presented in Table 4.14 and Figure 4.28.

Table 4.14 Effect of the consumption rate of hydrogen peroxide on nitrogen removal

Experiment	Volume of H_2O_2 applied, ml	Removed TKN, %	Removed ammonia, %	Removed ON, %
45	1	83	94.2	78.8
46	2	92	94.9	80.5
47	4	92.4	95.2	81.4
48	8	91.8	98	67.5
49	12	85.5	98.4	66.8
50	40	91.7	98.8	63.8

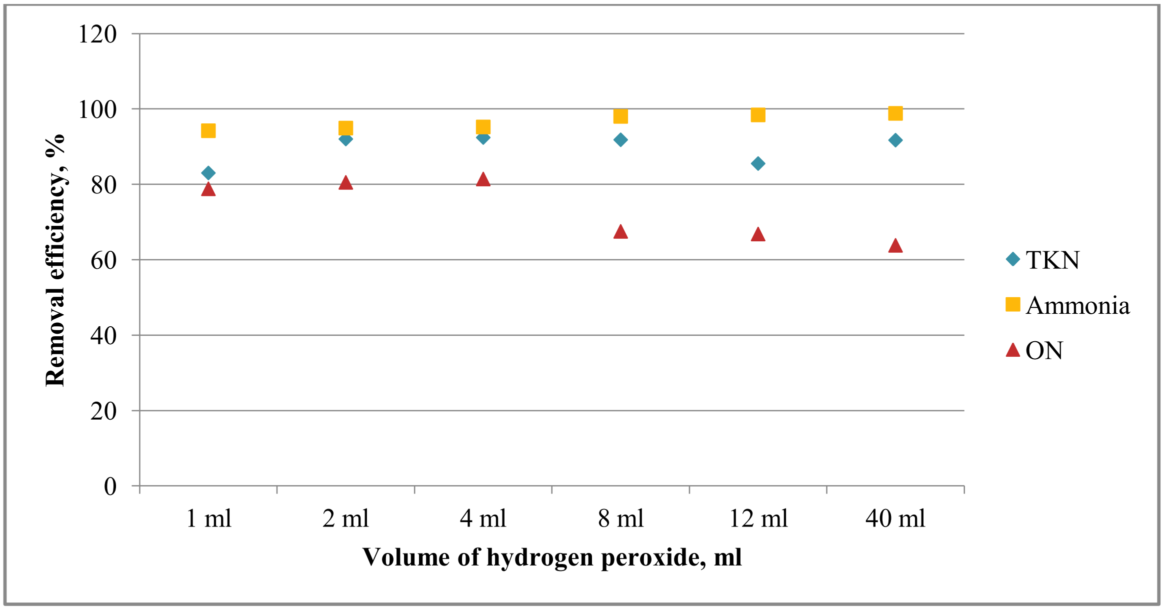


Figure 4.28 Effect of the consumption rate of hydrogen peroxide on the removal efficiency of nitrogen from wastewater

The tendency demonstrate that the highest removal efficiency (80.5% and 81.4%) of organic nitrogen can be achieved at consumption rates of 2 and 4 ml of hydrogen peroxide for 300 ml of wastewater, respectively (Table 4.14 and Figure 4.28). At a low dosage, low efficiency is attributed to a limited concentration of the hydrogen radical. At a high dosage of H_2O_2 a decrease in removal efficiency occurs due to the hydroxyl radical scavenging effect of H_2O_2 ($OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O$ and $HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2$) and the recombination of the hydroxyl radical ($2OH^{\cdot} \rightarrow H_2O$).

Another important and noteworthy parameter is the ferrous ion to hydrogen peroxide molar ratio. Analyses of initial wastewater showed the presence of iron ions. It is assumed that iron ions were in the form of Fe^{+2} at a pH of less than 4. It has been proven that the efficiency of the treatment depends on the molar ratio of Fe^{+2}/H_2O_2. Thus, when ferrous ions in the initial wastewater are present, it is necessary to add hydrogen peroxide for an effective removal rate. Table 4.15 and Figure 4.29 display the dependence of removal efficiency on the Fe^{+2}/H_2O_2 molar ratio.

Table 4.15 Effect of the Fe^{+2}/H_2O_2molar ratio on nitrogen removal

Experiment	Fe^{+2}/H_2O_2 ratio	Removed TKN, %	Removed ammonia, %	Removed ON, %
51	0.2	83	94.2	78.8
52	0.1	92	94.9	80.5
53	0.05	92.4	95.2	81.4
54	0.028	91.8	98	67.5
55	0.017	85.5	98.4	66.8
56	0.0058	91.7	98.8	63.8

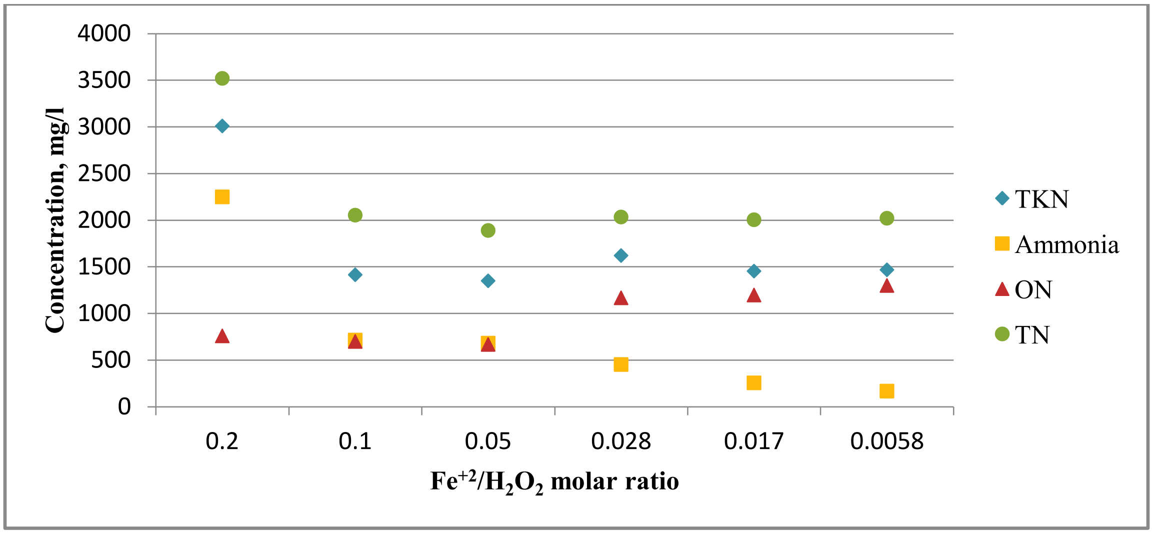


Figure 4.29 Impact of Fe^{+2}/H_2O_2 molar ratio on the removal efficiency of nitrogen

The best Fe^{+2}/H_2O_2 ratio showed to be 0.05 (Table 4.15). Generally, the efficiency of this oxidation process increases with the increase of the ferrous ion concentration. However, ferrous ions in the electrolyte solution, when present in excess, can inhibit the oxidation reaction by consuming the hydroxyl radicals.

Table 4.16 Impact of the ferrous ions concentration on the removal efficiency of nitrogen from wastewater

Experiment	Volume of H_2O_2, ml	Additional Fe^{+2}, mmol	Initial pH	Removed TKN, %	Removed ammonia, %	Removed ON,%
57	4	15.33	7.5	92.4	95.2	81.4
58	4	30.66	7.5	93	96.2	78.6
59	4	30.66	3.4	88	89.2	75

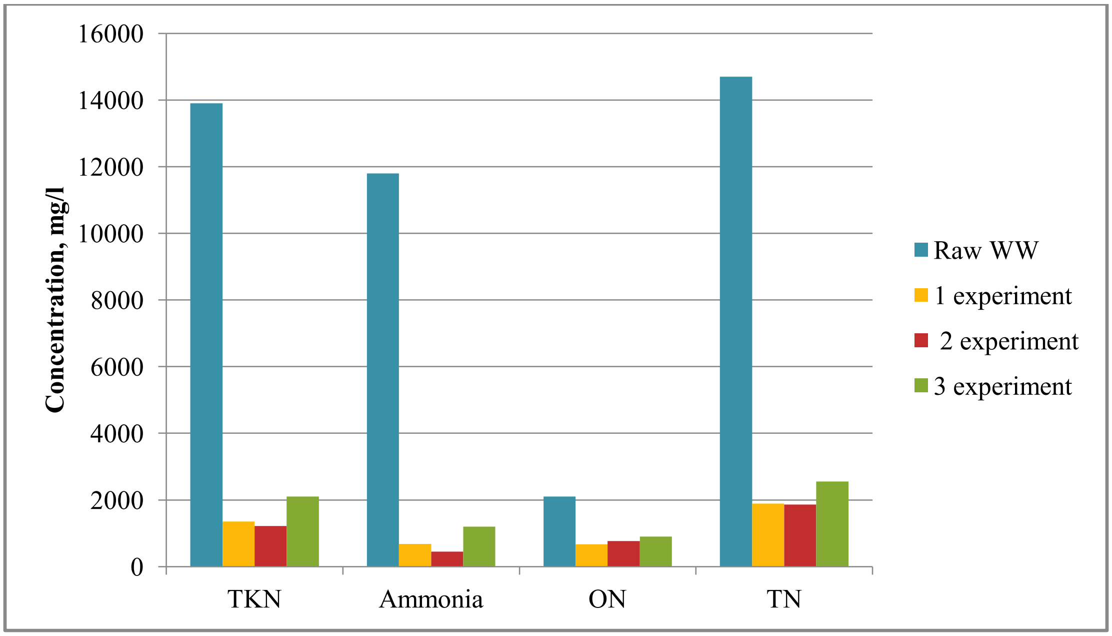


Figure 4.30 Impact of the removal efficiency of the nitrogen on the concentration of the ferrous ions

In order to see the influence of the Fe^{+2} ions, three experiments were conducted. For this experiment, the optimal consumption rate of hydrogen peroxide was chosen to be 4 ml, based on the previous experiments.

Table 4.16 and Figure 4.30, showed that, by adding ferrous ions, the removal efficiency of TKN increased from 92.4% to 93% and ammonia from 95.2% to 96.2% in the case of the initial pH of 7.5. However, the removal efficiency of organic compounds decreased from 81.4% to 78.6% due to the possible inhibition of the oxidation reaction of organics. Therefore, the improvements made to the parameters are insignificant in comparison with the outlay of the chemical reagents, which can affect the final economical cost of the process. Thus, it was determined that a more effective removal rate can be achieved with the natural content of ferrous ions in the initial wastewater, with the addition of hydrogen peroxide at a consumption rate of 4 ml.

A subsequent experiment was performed in which a significant amount of hydrogen peroxide was continuously added to the system, over a course of 6 hours, in order to potentially uncover the possibility of decreasing the retention time of the reaction. The consumption rate of hydrogen peroxide was increased by 25 times in comparison with the selected consumption rate of 4ml in the previous experiment. In this experiment, ferrous sulfate salt was added in order to keep the chosen molar ratio of Fe^{+2} to H_2O_2 equal to 0,005.

Table 4.17 Results of the experiment with the concentration of H_2O_2=100 ml per 300 ml of wastewater during 6 h

№ of experiment	Volume H_2O_2, ml	Reaction time, h	Feeding mode	Fe^{+2}/H_2O_2 molar ratio	Removed TKN, %	Removed ammonia, %	Removed ON, %
60	100	6	continuous	0.005	40.1	36.4	55

This experiment (Table 4.17) demonstrated that, after 6 hours, it was already possible to reach a level of organic nitrogen of 55%. However, along with the potential benefits of reaction time reduction, this method has a number of disadvantages, including a very high consumption of hydrogen peroxide, high amounts of sludge and foam production, as well as a total increase of discharged water.

At this stage, the feeding mode of hydrogen peroxide was also investigated. Several experiments were performed using single steps and a continuous feeding mode. Figure

4.31 compares the two feeding modes: continuous mode and discrete mode. With the continuous mode, 4 ml of hydrogen peroxide was added over the course of several hours, while with the single step mode, 4 ml of hydrogen peroxide was added at once. It could be observed that feeding mode plays a minor role in the removal of both TKN and ammonia, with a difference of 1% of TKN and 0.8% of ammonia removal. However, feeding mode is an important factor in the removal efficiency of organic nitrogen. Thus, in single step feeding, hydrogen peroxide removal efficiency is 81.4%, and in the continuous mode is 74.1%, it is 7.3% higher removal efficiency of organic nitrogen in single step feeding. When H_2O_2 was added too slowly, the concentration of hydrogen peroxide would be very low during the entire feeding time. This would result in a very high molar ratio of ferrous ions to hydrogen peroxide, and the produced hydroxyl radicals would be scavenged by the excess ferrous ions via the reaction $Fe^{+2} + OH^{\cdot} \rightarrow Fe^{+3} + OH^{-}$.

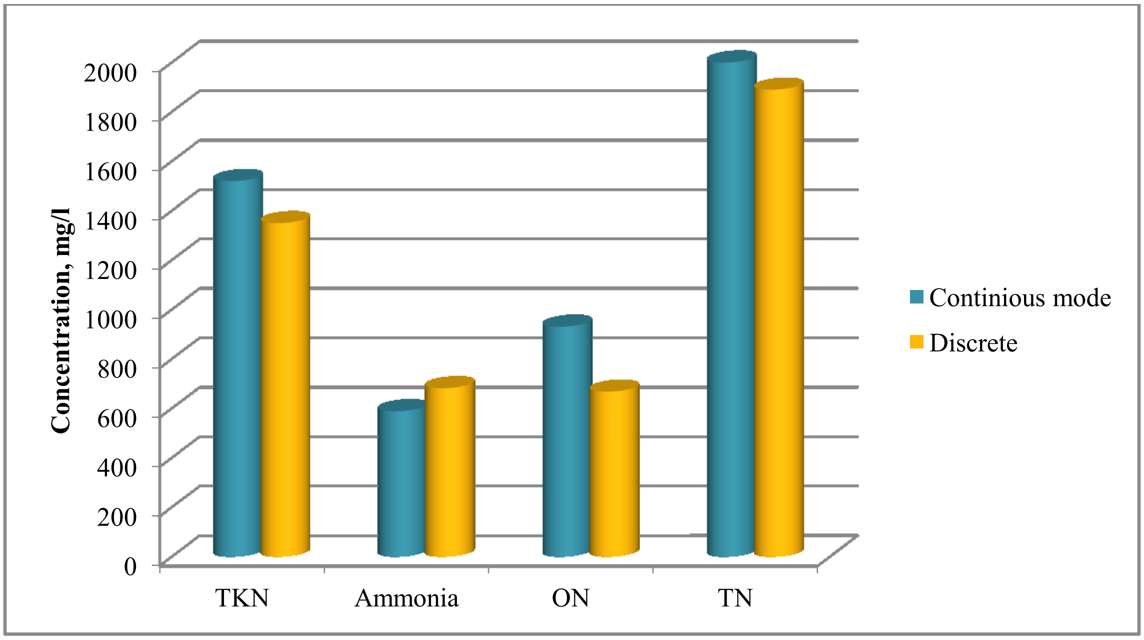


Figure 4.31 Comparison the feeding mode of hydrogen peroxide: continuous mode and discrete mode

Based on results, a significant improvement of the system was demonstrated through the addition of hydrogen peroxide. It was determined that the most effective treatment occurs at a consumption rate of hydrogen peroxide of 4 ml, with a discrete feeding mode. It was also determined that, the addition of ferrous ions does not improve the treatment.

4.3.3 Stage 3.3 Influence of the ion exchange membrane on the oxidation process and the influence of the mixing on the system

The objective of this stage was to investigate the effect of the presence of the ion exchange membrane on the system. From the previous experiments in Phase I, it was concluded that the fiber membrane better copes with the removal of organic compounds. Therefore, for this phase, experiments were conducted with different types of fiber membranes in the system with a carbon anode. The best voltage of 5.5 V and a consumption rate of 4 ml of hydrogen peroxide were selected. Results are presented in Table 4.18 and Figure 4.32.

Table 4.18 Influence of the presence of the ion exchange membranes on the removal efficiency of nitrogen

Experiment	Fiber membrane	Removed TKN, %	Removed ammonia, %	Removed ON, %
61	phosphonic	72.1	65.6	82.5
62	carboxylic	52.7	31.5	79.4
63	sulphonic	51.6	48.9	62.2
64	without	92.4	95.2	81.4

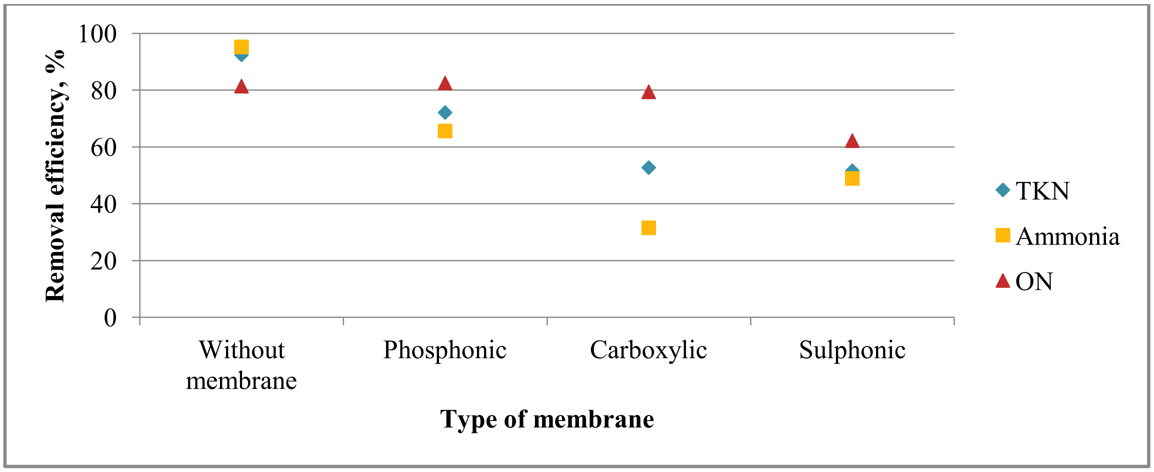


Figure 4.32 Influence of the presence of ion exchange membranes on the removal of nitrogen

From the results presented above it can be concluded that the tested membrane in this stage does not have the ability to improve the system by removing nitrogen from wastewater at an acceptable level.

In order to investigate the influence of mixing on the system, three experiments were performed. Three systems were compared, including a system with magnetic stirrer mixing, a recirculation system and a system where no mixing occurred. Results are presented in the Table 4.19 and Figure 4.33.

Table 4.19 Influence of mixing on the system

Experiments	Voltage, V	H_2O_2volume,ml	Mixing	Removed TKN,%	Removed ammonia, %	Removed ON,%
65	5.5	4	without	92.4	95.2	81.4
66	5.5	4	magnet stirrer	75.7	74.1	61.7
67	5.5	4	recirculation	88	88.7	76.7

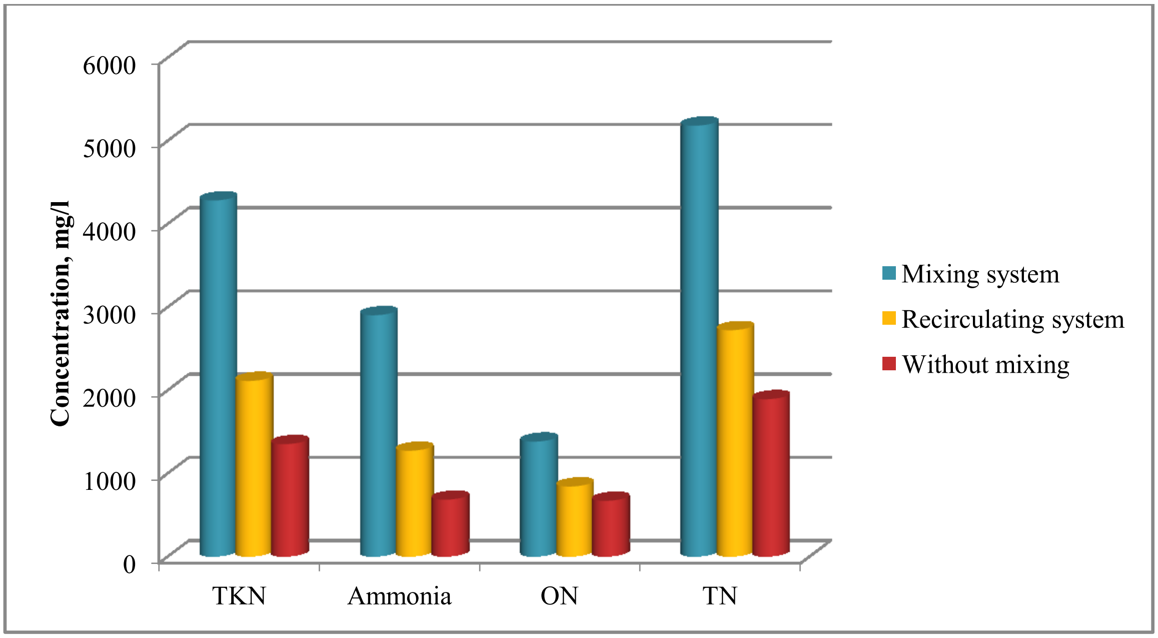


Figure 4.33 Comparison of the concentrations post-treatment in the systems with and without mixing

It could be noted that the recirculation system is better than the system with a magnetic stirrer, but the system without mixing is the most successful. Particles that form during sludge production may possibly interact with reactions on the electrodes (Figure 4.33).

Based on results from this stage, it can be concluded that the use of an ion exchange membrane, as well as mixing, do not provide a noticeable improvement to the treatment, and in some cases even worsen it.

4.3.4 Stage 3.4 Influence of the presence of ammonia ions on the removal of organic compounds

The objective of this stage was to investigate the efficiency of the process in the presence and absence of ammonia ions. When the concentration of ammonia is 5.6 times higher than the concentration of organic compounds, it is assumed that this negatively affects the removal of organic compounds. It is possibly due to the fact that a significant part of the oxidizing agent is spent on the oxidation of ammonia to gases, which can be observed during the reactions. Therefore, in this stage, it was necessary to find a method of ammonia treatment. Air stripping of ammonia was thus selected. To this end, an ammonia stripping tower was designed and subsequently used. After the ammonia-stripping, concentration of ammonia ions reached 2650 mg/l from 11800 mg/l, i.e. 81.3% less than in the initial concentration of wastewater. Following the removal of ammonia, the water was subjected to the electrochemical treatment with the best parameters selected from the previous stages: a voltage of 5.5 V, a distance between electrodes of 5 cm, an anode-carbon material, a system without mixing, and a consumption rate of hydrogen peroxide of 4 ml. Results are presented in Table 4.20 and Figure 4.34.

Table 4.20 Results of the experiment with wastewater with reduced amount of ammonia (2659 mg/l)

Experi-ment	Voltage, V	V of H_2O_2,ml	Mixing	TKN removal, %	Ammonia removal, %	ON removal ,%	TN removal, mg/l
68	5.5	4	without	95.8	92.6	97.2	95.3

Table 4.20 and Figure 4.34, show the removal efficiency of TKN, ammonia, organic nitrogen, TN by 95.8 %, 92.6 %, 97.2 % and 95.3 %, respectively after 72 hours of treatment. When comparing the results of with and without pretreatment methods, it could be observed that the removal efficiency increases from 81.4 % to 97.2 %.

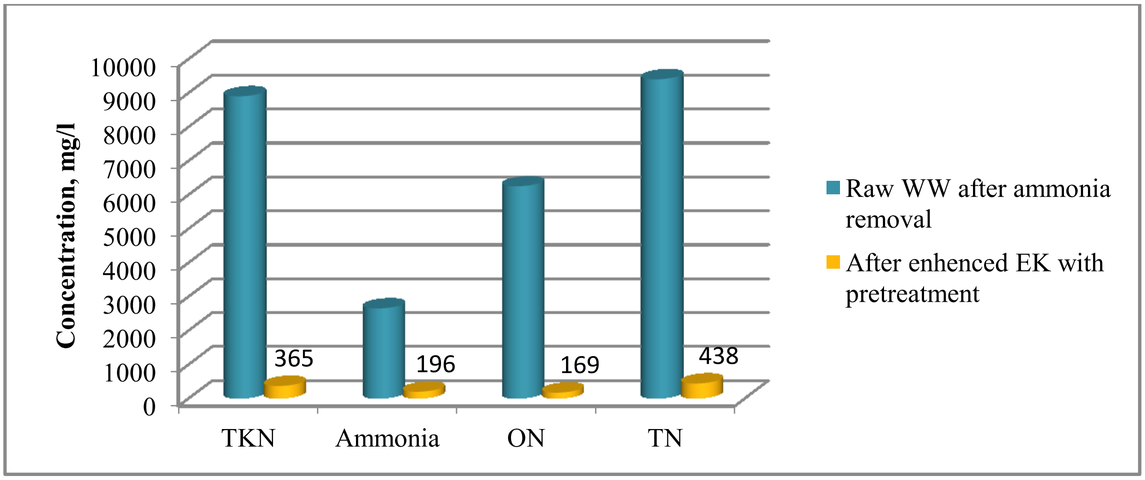


Figure 4.34 Comparison of the method with and without pretreatment from ammonia ions

This proves the previously stated theory that organic compounds compete for the oxidizing agent with high amounts of ammonia ions in the solution. Thus in order to increase the ON removal rate, a pretreatment focusing the ammonia removal is beneficial. Furthermore, such pretreatment can reduce retention time of the enhanced electrokinetic process. Figures 4.35-4.37 show and compare the impact of pH, conductivity and ORP, with pretreatment and without the pretreatment from ammonia.

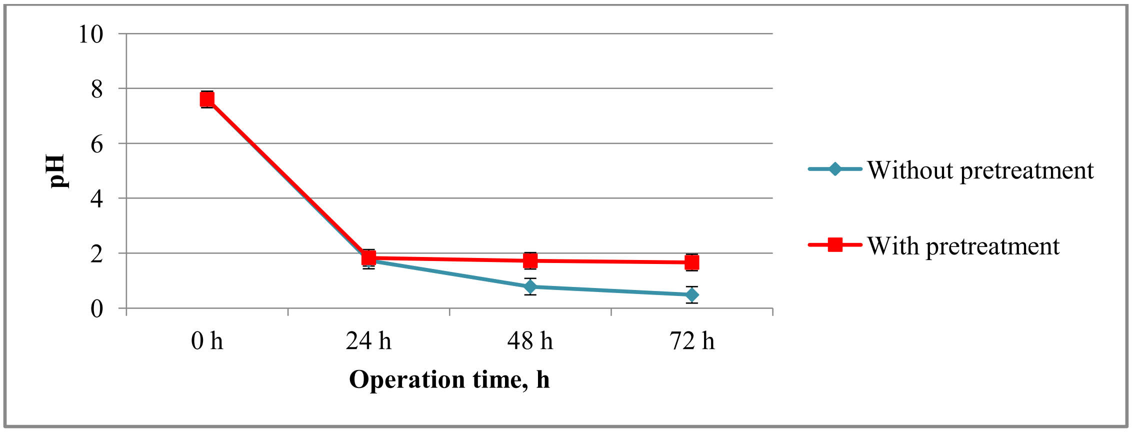


Figure 4.35 Comparison of pH in the systems with pretreatment from ammonia and without pretreatment

The value pH decreased for both cases in the first 24 hours, but after 24 hours in the system with pretreatment formed ammonia and pH was stabilized (Figure 4.35). Changes in pH were not noticeable.

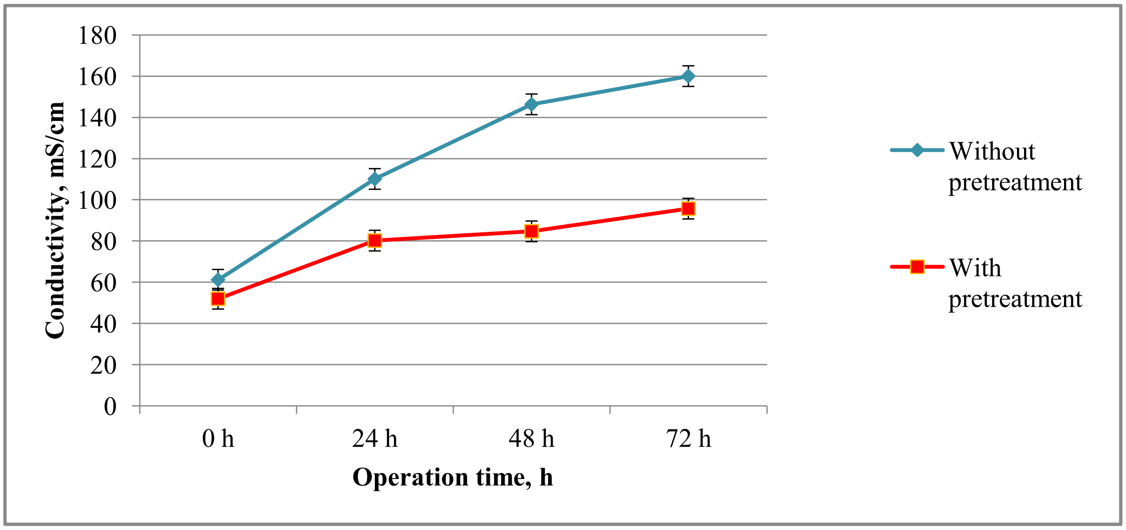


Figure 4.36 Comparison of conductivity in the systems with and without pretreatment from ammonia

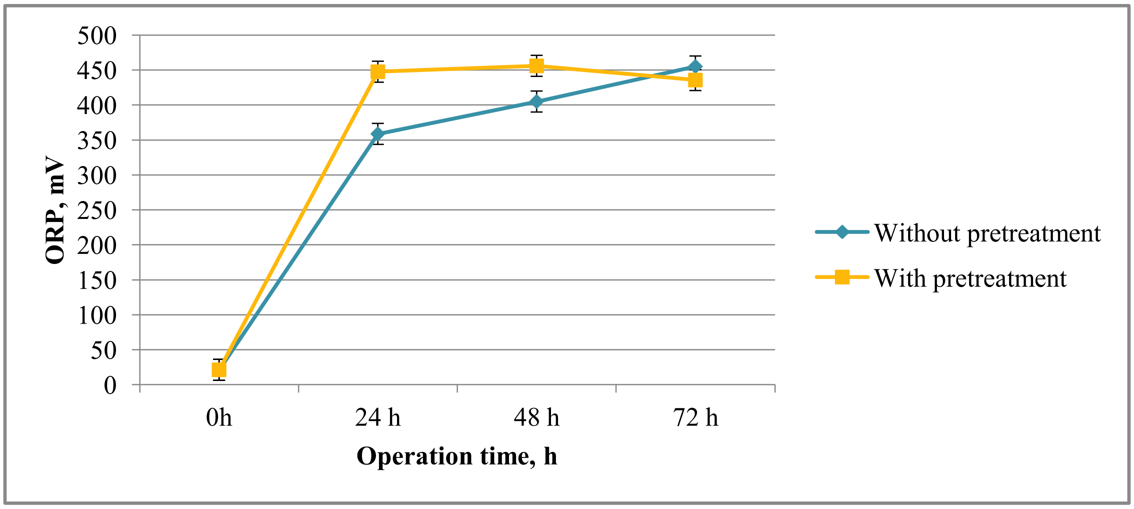


Figure 4.37 Comparison of ORP in the systems with and without pretreatment from ammonia

Figure 4.36 shows that the changes in conductivity are different for both cases. In the case of the pretreatment system, the increase of conductivity is slower, as compared to the system without a pretreatment. Also, it is important to note, that initial conductivity is different due to removal of ammonia ions in the system with the pretreatment.

It is noticed that the ORP in the system with the pretreatment reached a higher ORP value (Figure 4.37), and consequently reaches the oxidation state faster. Therefore, mineralization of organic compounds was also higher, which is confirmed by the results showed in Table 4.20.

Then, it could be concluded that removal of organic pollutants at an acceptable level is possible with a pretreatment from ammonia ions. Improvements of the pretreatment system from ammonia ions at a level of nearly 0 mg/l can lead to a more effective treatment rate of organic pollutants. The implication of an ammonia air stripping tower, however, is an increase in the costs of the system. Upon completion of Phase III, it is important to note that one disadvantage of this process is the destruction of the carbon anode. The average consumption rate (assessed based on tests in 300 ml-reactors) is 0.04 kg/l.

Phase III permitted to conclude, that the best results of nitrogen removal from the wastewater of concern, were obtained in an undivided batch reactor with carbon anode and stainless steel cathode located at the distance of 5 cm, while a discrete H_2O_2 feeding mode was applied. Table 4.21 represent the best results in the Phase III. The experiment was performed twice and the mean value of results was registered with an experiment error of 3%.

Table 4.21 Results for enhanced electro-Fenton oxidation process applied directly to industrial wastewater without pretreatment and with pretreatment

Wastewater	TKN, mg/l	Ammonia, mg/l	ON, mg/l	TN, mg/l	NO_3^- NO_2^-, mg/l	COD, mg/l
Initial	13900	11800	2100	14600	718	65500
Final without pretreatment	1350	682	668	1890	535	2500
Final with pre-treatment	365	196	169	438	73	2110

It can be assumed that high removal efficiency of stable nitrogen organics, such as amides could be achieved due to its two types of oxidation reactions. First oxidation reaction occurs due to hydroxyl radical and undergoes the pathway where formation of carbon dioxide and ammonia ions take place (Figure 4.38a). Second type of reaction occurs due to electrochemical reduction of the amide, where production of cation amide leads to a weakening the persistent amide's bonds, and further, to its rupture as it is demonstrated in Figure 4.38b.

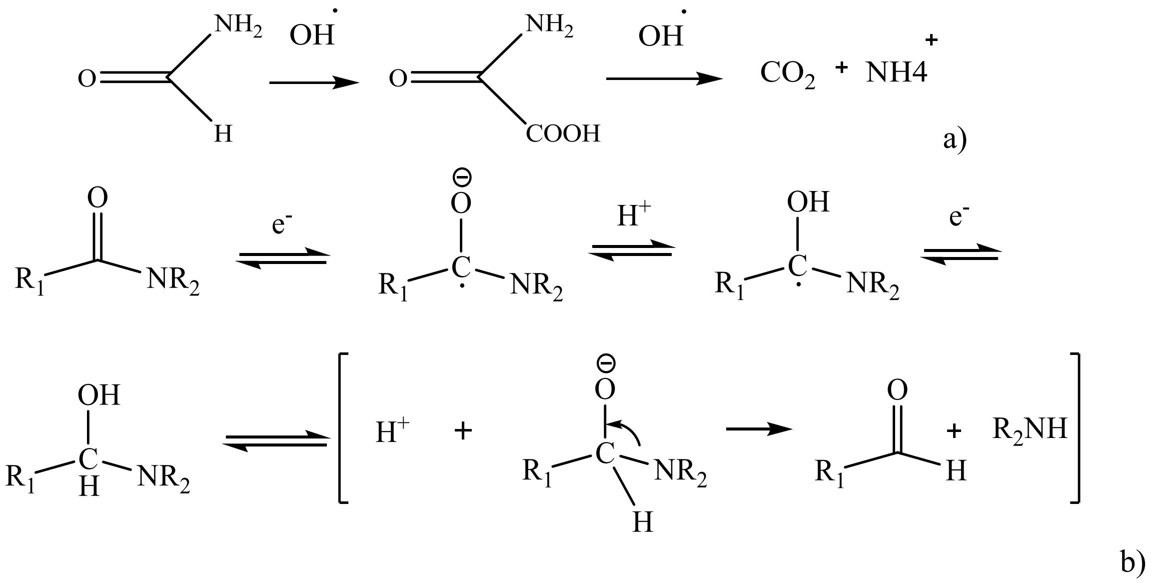


Figure 4.38 Oxidation reactions of amides: a) oxidation by hydroxyl radical, b) electrochemical reduction of amides

4.4 Phase IV

The main objective of this phase was to design and test a system in which a series of electrodes were implemented. Several experiments were performed with carbon anodes, at a distance between electrodes of 5 cm, while the best conditions from Phase III were applied (i.e. voltage of 5.5 V and H_2O_2/Fe^{+2} molar ratio of 0.05). This Phase permitted to investigate; i) influence of the multiple electrodes system on the removal efficiency of nitrogen from wastewater, ii) changes in pH, iii) variation in conductivity and iv) ORP fluctuation. Figures 4.39 - 4.41 display the behavior of the pH, conductivity and ORP for both systems: one cell with a pair of electrodes (Figure 3.2 a) and the second with a multiple pairs of electrodes (multiple cells) (Figure 3.5).

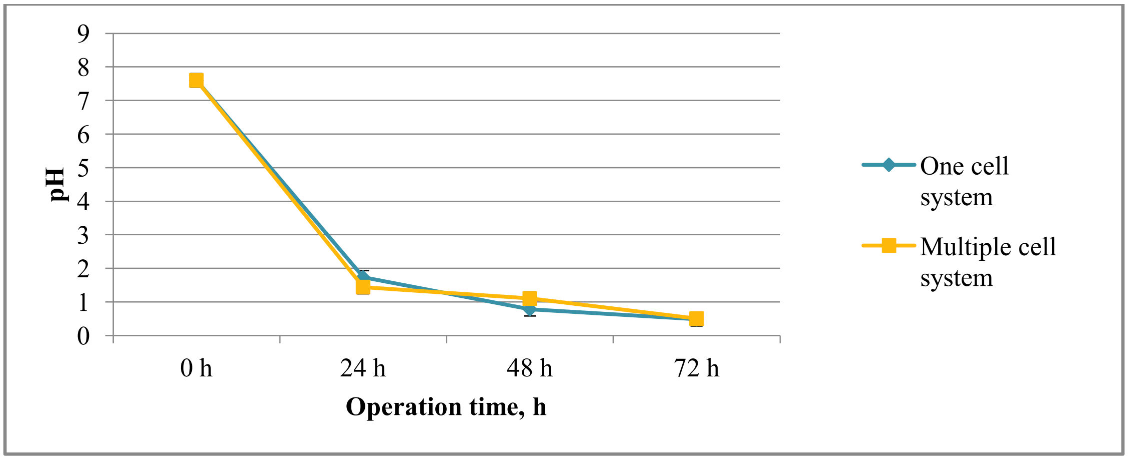


Figure 4.39 Comparison of the behavior of pH in the system with one and multiple cells

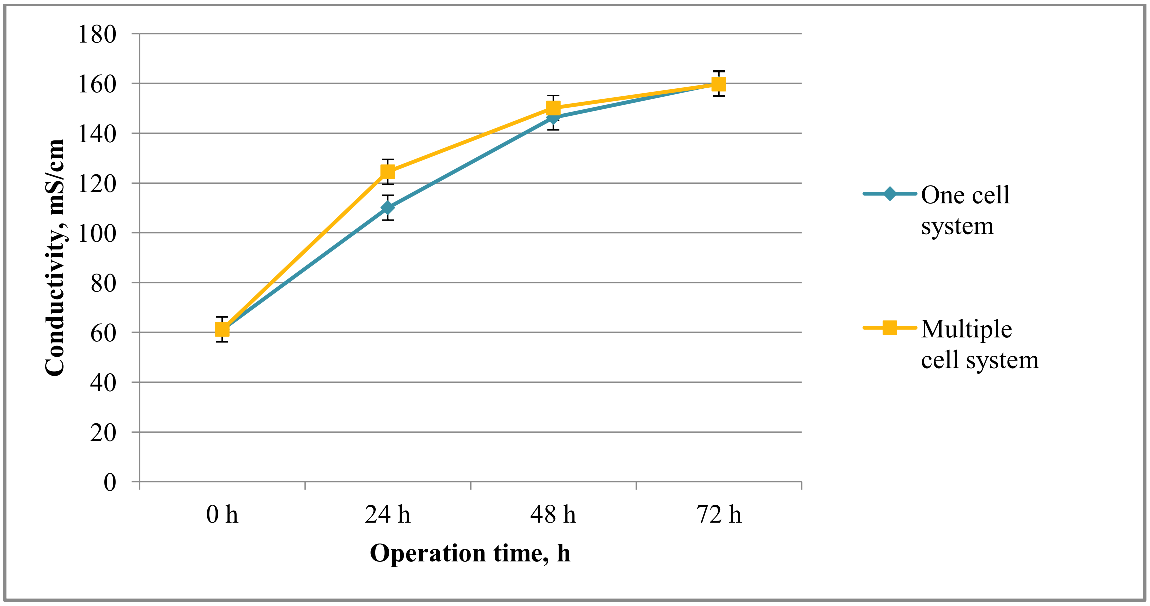


Figure 4.40 Comparison of the behavior of conductivity in the system with one and multiple cells

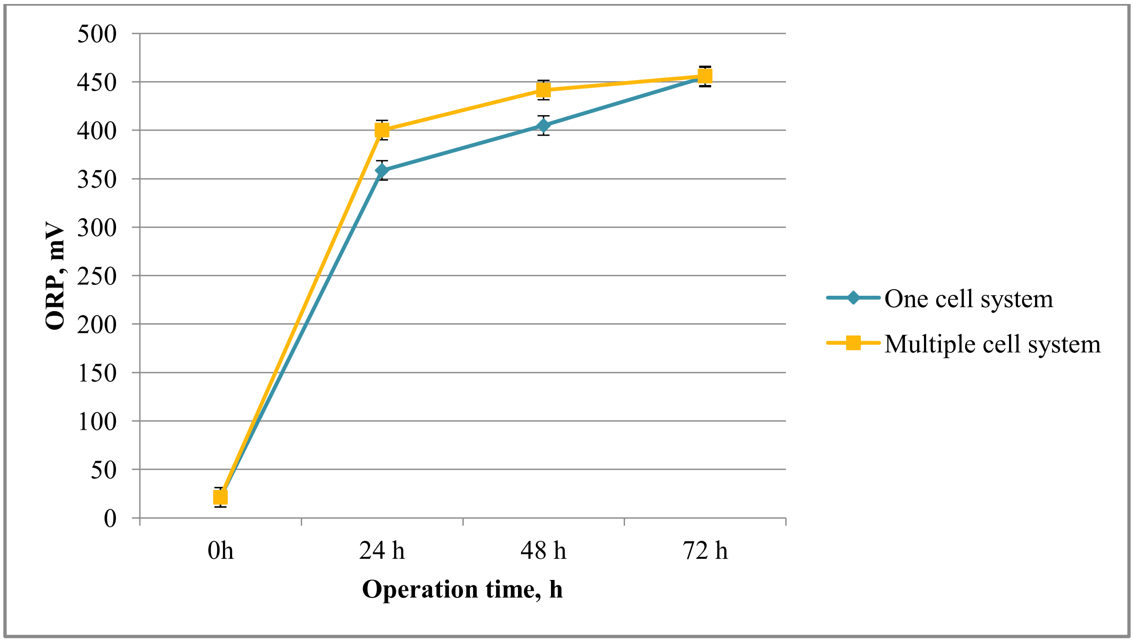


Figure 4.41 Comparison of the behavior of ORP in the system with one cell and in the system with multiple cells

The behavior of pH, conductivity and ORP has the same tendency, which proves that the multiple cells system works the same way as one cell system. However, the ORP increase quicker in one cell than in multiple cell system, therefore, the removal efficiency of nitrogen in one cell system is higher in comparison with multiple cells system.

Table 4.22 Average removal efficiency of the multiple system with parallel electrodes

System	TKN removal,%	Ammonia removal, %	ON removal,%
one cell	92.4	95.2	81.4
multiple cells	80.6	80.8	79.7

To determine the mutual influence of the electrodes on the removal efficiency of nitrogen from wastewater, the samples were taken from each space between the anode and cathode. The results are presented as an average removal efficiency of both systems in Table 4.22.

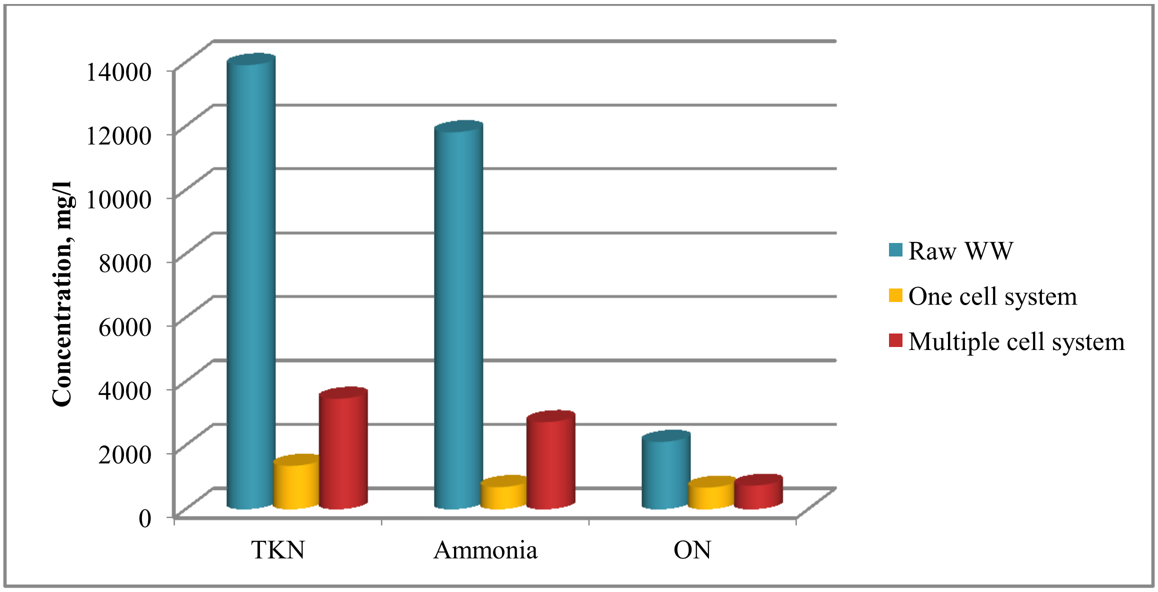


Figure 4.42 Comparison of removal efficiencies in the one and multiple cells system

From Table 4.22 and Figure 4.42, it can be observed that the average removal efficiency of TKN and ammonia in the system with a series of electrodes is lower by 12% and 15% than in the system with one pair of electrodes, respectively. This is probably due to the mutual influence of the electrodes and small fluctuations of the current in each cell; because experiment was proceed with fixed voltage. However, the removal efficiency of organic nitrogen is approximately the same in both systems, thus, the mutual influence of the electrodes and fluctuations of the current do not affect the mineralization of organic nitrogen. Nonetheless, the multiple cells system demonstrates potential in nitrogen removal from the given wastewater. Further investigations of the mutual influence of the electrodes are needed.

Chapter 5: Conclusion and future work

Chapter 5 summarizes the general conclusions from the obtained results. In addition, it discusses future developments and recommendations for the enhanced electro-Fenton oxidation.

5.1 Conclusion

The primary objective of this research was to search for an effective treatment method of industrial wastewater. The electrochemical oxidation was chosen for this research as potential treatment from the TKN, including organic nitrogen. The conclusions are presented in relation to four investigated phases:

Phase I

Based on the overall performance of electrochemical oxidation, it can be concluded that this process itself, did not give satisfactory results in the removal of organic nitrogen. However, results showed that the best gap between electrodes for such industrial wastewater was 5 cm, and the best voltage gradient for carbon anode and stainless steel cathode was 1.1 V/cm. Furthermore, a minimum retention time in reactor was found to be 72 hours.

Ion exchange materials implemented to electrochemical oxidation cell did not give satisfactory results. Combination of ion exchange membrane with an aluminum anode has a high potential in terms of mineralization of organic compounds. However, this combination has been excluded for further applications due to the fast oxidation of the aluminum anode and the production of a large amount of sludge and foam.

Phase II

The application of a conventional electro-Fenton oxidation process did not achieve the acceptable level of TKN, ammonia and organic nitrogen removal. The best flow rate of air purged into the system was found to be 45 ml/min, in which the maximum removal efficiency of TKN and organic nitrogen achieved 71.6% and 50.5% respectively, in the presence of carbon anode.

Phase III

Electro-Fenton oxidation enhanced by an external additional of hydrogen peroxide and carbon electrode showed the most successful system for removal of nitrogen from wastewater. The best removal efficiency of TKN, ammonia, and organic nitrogen reached 92.4 %, 95.2 % and 81.4 % respectively. The developed process for industrial wastewater applied the enhanced Electro-Fenton method without addition of iron since iron ions, present as a pollutant in the wastewater, were electro-transformed to Fe $^{2+}$ (adequately to Fenton process).

Enhanced electro-Fenton oxidation permitted to avoid a high amount of sludge production due to lack of the ferrous ions addition (commonly required by Fenton method).

An optimal consumption rate of hydrogen peroxide, its feeding mode and Fe^{+2}/H_2O_2 molar ratio were determined to be 0.05, while the applied voltage was 5.5 V.

Air stripping pre-treatment with respect to ammonia shortened the treatment residence time for 24 hours and improved removal of organic nitrogen by 34%.

It was concluded that the developed method of the enhanced electro-Fenton oxidation could be applied to a number of wastewater containing the high concentration of TKN even when organic nitrogen consists of persistent compounds. However, some operation conditions might require of adjustments in new cases.

Phase VI

The comparative study of one and multiple enhanced electro-Fenton reactors showed similar behavior of the observed parameters in both systems. The removal of organic nitrogen over similar residence time was also similar. However, the removal of ammonia and then TKN was observed to be lower by 15% and 12% respectively. Then, the multiple cells system showed to be a potential solution for nitrogen removal from a given wastewater.

5.2 Contributions

This study permitted to development the industrial wastewater treatment using enhanced electro-Fenton method without addition of iron taking in consideration presence of iron as a pollutant. Subsequently, the developed system also produced less sludge. These two factors showed possibility of more efficient less costly management of industrial wastewater.

This study also provided comparative studies of behavior of various types of electrodes applied to real industrial wastewater containing the high concentrations of persistent organic nitrogen. Subsequently, basic operation conditions for the TKN removal from real industrial wastewater were determined.

Furthermore, first time, an enhanced electro-Fenton system with pretreatment (ammonia air-stripping) was proven to be efficient since it achieved the removal of TKN and organic nitrogen by almost 96% and more that 97% respectively.

5.3 Future work

Further modifications to operational conditions and the reactor setup can be investigated to reduce the retention time of the treatment process. Furthermore, an examination of methods to protect the anode from corrosion while preserving its useful properties is suggested. In addition, studying more economical and affordable methods of ammonia removal as a pretreatment can lead to a successful application of the process in a full scale. Then, an optimization of the process at the larger scale would be required.

References

Addamo M Augugliaro V, Paola A, García-López E. (2005). Removal of drugs in aqueous systems by photoassisted degradation.*Journal of Appled Electrochemestry*, 35 (7-8), 765-774

Afzal M Iqbal S, Rauf S, Khalid Z. (2007). Characteristics of phenol biodegradation in saline solutions by monocultures of Pseudomonas aeruginosa and Pseudomonas pseudomallei. *Journal of Hazardous Materials*, 149, 60-66

Aguado D Montoya T, Borras L, Seco A, Ferrer J. (2008). Using SOM and PCA for analysing and interpreting data from a P-removal SBR. *Engineering Applications of Artificial Intelligence,* 21(6), 919-930

Alaton I Dogruel S, Baykal E, Gerone G. (2004). Combined chemical and biological oxidation of penicillin formulation effluent. *Journal of Environmental Management*, 73, 155-163

Andreozzi R Canterino M, Marotta R, Paxeus N. (2005). Antibiotic removal from wastewaters: The ozonation of amoxicillin. *Journal of Hazardous Materials*, 122(3), 243-250

Andreozzi R, Caprio V, Insola A, Marotta R. (1999). Advanced oxidation processes (AOP) for water purification and recovery.*Catalysis Today,*53, 51-59

Anslyn P, Dougherty D. Modern Physical Organic Chemistry. (2004), *University Science Books*, Sausalito, California

Arslan-Alaton I, Dogruel S. (2004). Pre-treatment of penicillin formulation effluent by advanced oxidation processes. *Journal of Hazardous Materials*, B 112, 105-113

Balcioglu I, Ötker M. (2003). Treatment of pharmaceutical wastewater containing antibiotics by O3 and O3/H2O2 processes. *Chemosphere*, 50, 85-95

Baran W, Sochacka J, Wardas W. (2006). Toxicity and biodegradability of sulfonamides and products of their photocatalytic degradation in aqueous solutions. *Chemosphere*, 65, 1295-1299

Bates H, Uri N. (1953). Oxidation of Aromatic Compounds in Aqueous Solution by Free Radicals Produced by Photo-excited Electron Transfer in Iron Complexes. *Journal of American Chemical Society*, 75(11), 2754-2759

Bauer R, Fallmann H. (1997). The photo-Fenton oxidation – a cheap and efficient wastewater teatment method. *Researsh on Chemical Intermediates*, 23, 341-354

Bellona C, Drewes J. (2007). Viability of a low-pressure nanofliter in treating recycled water for water reuse applications: a pilot-scale study. *Water Research*, 41(17), 3948-3958

Bensalah N, Bedoui A, Chellam S, Abdel-Wahab A. (2013). Electro-Fenton Treatment of Photographic Processing Wastewater. *Clean – Soil, Air, Water*, 41 (7), 635–644)

Berg G, Jørgensen N. (2006). Purine and pyrimidine metabolism by estuarine bacteria.*Aquatic Microbial Ecology*, 42 (3), 215-226

Berman T, Bronk D. (2003). Dissolved organic nitrogen: a dynamic participant in aquatic ecosystems. *Aquatic Microbial Ecology*, 31 (3), 279-305

Boreen A, Arnold W, McNeill K. (2004). Photochemical fate of sulfa drugs in the aquatic environment: sulfa drugs containing five-membered heterocyclic groups. *Environmental Science Technology*, 38, 3933-3940

Boxall A, Blackwell P, Cavallo R, Kay P, Tolls J. (2002). The sorption and transport of a sulphonamide antibiotic in soil systems. *Toxicology Letters*, 131 (1–2), 19–28

Boye B, Diang M, Brillas E. (2002). Degradation of herbicide 4-chlorophenoxyacetic acid by advanced electrochemical oxidation methods. *Environmental Science Technology*, 36, 3030–3036

Brillas E, Banos M, Garrido J. (2003). Mineralization of herbicide 3,6-dichloro-2-methoxybenzoic acid in aqueous medium by anodic oxidation, electro-Fenton and photoelectro-Fenton. *Electrochimica Acta*, 48 (12), 1697-1705

Brillas E, Garcia-Segura S, Skoumal M, Arias C. (2010). Electrochemical incineration of diclofenac in neutral aqueous medium by anodic oxidation using Pt and boron-doped diamond anodes. *Chemosphere*, 79, 605−612

Brillas E, Sires I, Arias C, Cabot P, Centellas F, Rodriguez R, Garrido J. (2005). Mineralization of paracetamol in aqueousmedium by anodic oxidation with a boron-doped diamond electrode. *Chemosphere*, 58, 399−406

Brillas E, Sires I, Oturan M. (2009). Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry. *Chemical Reveiws*, 109, 6570–6631

Britto J, Rangel M. (2008). Processos avançados de oxidação de compostos fenólicos em efluentes industriais.*Química Nova,*31, 114-122

Bronk D, Roberts Q, Sanderson M,Canuel E,Hatcher P, Mesfioui R. (2010). Effluent Organic Nitrogen (EON): Bioavailability and Photochemical and Salinity-Mediated Release. *Environmental Science &Technology*, 44(15), 5830-5835

Bronk D, See J, Bradley P, Killberg L. (2007). DON as a source of bioavailable nitrogen for phytoplankton.*Biogeosciences*, 4(3), 283-296

Buxton G, Greenstock C, Helman W, Ross W. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution. *Journal of Physical and Chemical Reference Data*, 17, 513-886

Cadoni R, Porcheddu A, Giacomelli G, De Luca L. (2012). One-Pot Synthesis of Amides from Aldehydes and Amines via C-H Bond Activation. *Organic Letters*, 14, 19

Calza P, Medana C, Pazzi M, Baiocchi C, Pelizzetti E. (2004). Photocatalytic transformations of sulphonamides on titanium dioxide. *Applied Catalysis B*, 53, 63-69

Government of Canada [Online] // Environmental Canada. *Wastewater*. (2013), 18-12. - http://www.ec.gc.ca/eu-ww/default.asp?lang=En&n=BC799641-1.

Carballa M, Omil F, Lema J. (2005). Removal of cosmetic ingredients and pharmaceuticals in sewage primary treatment. *Water Research*, 39, 4790–4796

Chang C, Chang J, Vigneswaran S, Kandasamy J. (2008). Pharmaceutical wastewater treatment by membrane bioreactor process- a case study in southern Taiwan. *Desalination*, 234 (1-3), 386-392

Chelliapan S, Wilby T, Sallis P. (2006). Performance of an up-flow anaerobic stage reactor (UASR) in the treatment of pharmaceutical wastewater containing macrolide antibiotics. *Water Research*, 40, 507−516

Cheng C, Hong S. (2010). Oxidative amide synthesis directly from alcohols with amines. *Organic and Biomolecular Chemistry*, 9, 20-26

Chih-Ta W, Jen-Lu H, Wei-Lung C, Yi-Ming K. (2008). Removal of color from real dyeing wastewater by Electro-Fenton technology using a three-dimensional graphite cathode. *Journal of Hazardous Materials*, 152, 601–606

Chou S, Huang Y, Lee S, Huang G, Huang C. (1999). Treatment of high strengh hexaminecontaining wastewater by electro-Fenton oxidation. Water Research, 33(3), 751-759

Clara M, Strenn B, Gans O, Martinez E,Kreuzinger N, Kroiss H. (2005). Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water Reserch*, 39(19), 4797-4807

Cokgor E, Alaton I, Karahan O, Dogruel S, Orhon D. (2004). Biological treatability of raw and ozonated penicillin formulation effluent. *Journal of Hazardous Materials*, 116 (1-2), 159-166

Comninellis C. (1994). Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment. *Electrochimica Acta*, 39(11-12), 1857–1862

Comninellis C, Pulgarin C. (1991). Anodic oxidation of phenol for waste water treatment. *Journal of Applied Electrochemistry*, 21(8), 703-708

Crespilho F, Rezende M. (2004). Electrochemistry: principles and applications. *Quimica Nova*, 27, 387-394

Dantas R, Contreras S, Sans C, Esplugas S. (2008). Sulfamethoxazole abatement by means of ozonation. *Journal of Hazardous Materials* , 150, 790-794

Dasgupta S, Hammond W, Goddard W. (1996). Crystal Structures and Properties of Nylon Polymers from Theory. *Journal of American Chemical Society*, 118, 12291–12301

Daughlon C. Acrylamidel-Polyacrylamide: Overview of Chemistry, *The California Public Health Foundation*, 1988.

Daughton C, Ruhoy I. (2009). Environmental footprint of pharmaceuticals: the significance of factors beyond direct excretion to sewers. *Environmental Toxicology and Chemistry*, 28(12), 2495–521

Daughton C, Ternes T. (1999). Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environmental Health Perspective*, 107, 907-938

Deegan A, Shaik B, Nolan K, Urell K, Tobin J. (2011). Treatment options for wastewater effluents from pharmaceutical companies. *International Journal of Environmental Science and Technology*, 8, 649−666

Denisov E, Afanas'ev I. (2005). Oxidation and Antioxidants in Organic Chemistry and Biology, *CRC Press*, Danvers

Dirany A, Sires I, Oturan N, Oturan M. (2010). Electrochemical abatement of the antibiotic sulfamethoxazole from water. *Chemosphere*, 81, 594-602

Doll T, Frimmel F. (2005). Cross-flow microfiltration with periodical back-washing for photocatalytic degradation of pharmaceutical and diagnostic residues–evaluation of the long-term stability of the photocatalytic activity of TiO2. *Water Research* , 39(5), 847-854

Domínguez J, González T, Palo P. (2012). Electrochemical Degradation of a Real Pharmaceutical Effluent. *Water, Air, Soil Pollution*, 223, 2685−2694

Dongke Y. (2012). Evaluation of effluent organic nitrogen and its impacts on receiving water bodies, *Master Thesis*.

Drakenberg T. (1972). The barrier to internal rotation in amides. VI. Acetamide. solvent dependent entropy of activation. *Tetrahedron Letters*, 13 (18), 1743-1746

Elektorowicz M, Ibeid S, Oleszkiewicz J. (2011). Simultaneous superior removal of carbon (C), phosphorus (P) and nitrogen (N) in a novel single electro-bioreactor. *Patent*, Canada

Elektorowicz M, Hatim G. (1999). Up-scaling electrokinetic processes. *2nd Symposium on Elektrokinetics*, Copenhagen, Denmark

Fan L, Zhou Y, Yang W, Chen G, Yang F. (2008). Electrochemical Degradation of Aqueous. Solution of Amaranth Azo Dye on ACF Under Potentiostatic Model. *Dyes Pigments*, 76, 440–446

Faust B, Hoigne J. (1990). Photolysis of Fe(III) - hydroxy complexes as sources of OH radicals in clouds, fog and rain. *Atmospheric Environmental*, 24 A, 79-89

Feng Y Li X. (2003). Electro-catalytic oxidation of phenol on several metal-oxide electrodes in aqueous solution. *Water Research*, 37, 2399-2407

Flaherty C, Dodson S. (2005). Effects of pharmaceuticals on Daphnia survival, growth, and reproduction. *Chemosphere*, 61, 200–207

Francis C, Sundberg R. (2001). Advansed organic chemistry: Structure and mechanisms, 4th edition - New York

Gadipelly C, Pérez-González A, Yadav G, Ortiz I. (2014). Pharmaceutical Industry Wastewater: Review of the Technologies for Water Treatment and Reuse. *Industrial and Engineering Chemical Research*, 53, 11571−11592

Gallard H, De Laat J, Legube B. (1999). Spectrophotometric study of the formation of iron(III)-hydroperoxy complexes in homogeneous aqueous solutions. *Water Research*, 33, 2929-2936

Gerardi M. (2002). Nitrification and denitrification in the activated sludge, *John Wiley and Sons Inc*

Gherardini L, Michaud P, Panizza M, Comninellis C, Vatistas N. (2001). Electrochemical oxidation of 4-chlorophenol for wastewater treatment - Definition of normalized current efficiency (phi) . *Journal of Electrochemical Society*, 148(6), D78-D82

Ghose A, Viswanadhan V, Wendoloski J. (1999). A knowledge-based approach in designing combinatorial or medicinal chemistry libraries for drug discovery. 1. A qualitative and quantitative characterization of known drug databases. *Journal of Combinatorial Chemistry*, 1, 55-68

Giroto J, Teixeira A, Nascimento C, Guardani R. (2008). Photo-Fenton removal of water soluble polymers. *Chemical Engineering and Processing* , 47, 2361-2369

Gnann M, Gregor C, Schelle S. (1993). Chemical oxidative process for purifying highly contaminated wastewater. *Patent*, Germany

Gunten U. (2003). Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Research*, 37, 1443-1467

Guohua C. (2004). Electrochemical technologies in wastewater treatment, *Separation and Purification Technology*. 38, 11-41

Haber F, Weiss J. (1932). Über die Katalyse des Hydroperoxides. *Naturwissenschaften*, 51, 948−950

Hammami S, Bellakhal N, Oturan N, Oturan M, Dachraoui M. (2008). Degradation of Acid Orange 7 by electrochemically generated (*)OH radicals in acidic aqueous medium using a boron-doped diamond or platinum anode: a mechanistic study. *Chemosphere*, 73, 678-684

Harbison K, Belly R. (1982). The biodegradation of hydroquinone. Environmental Toxicology and Chemistry, 1, 9-15

Helmig E, Fettig J, Cordone L, Schoenberg T, Demarco M, Suri P. (2005). API removal from pharmaceutical manufacturing wastewater-Results of process development, pilottesting and scale-up. *Annual Technical Exhibition and Conference,* 78th, 207-226

Helmig E, Fettig J, Cordone L. (2007). API Removal from Pharmaceutical Manufacturing Wastewater – *Results of Process Development, Pilot-Testing, and Scale-Up WEF Session*, Rhode Island

Henisch H. (1977). History of photography, Early photography in Eastern Europe, 1(1)

Hirata A, Lee H, Tsuneda S, Takai T. (1997). Treatment of photographic processing wastewater using anaerobic-aerobic biofilm reactor. *Water Science and Technology*, 36(12), 91-99

Homem V, Santos L. (2011). Degradation and removal methods of antibiotics from aqueous matrices - A review, *Journal of Environmental Management*, 92, 2304-2347

Hopkinson C, Buffam I, Hobbie J, Vallino J, Perdue M, Eversmeyer B. (1998). Terrestrial inputs of organic matter to coastal ecosystems: An intercomparison of chemical characteristics and bioavailability. *Biogeochemistry*, 43(3), 211-234

Huang Y, Chen C, Huang G, Chou S. (2001). Comparison of a novel electro-Fenton method with Fenton's reagent in treating a highly contaminated wastewater. *Water Science Technology*, 43(2), 17-24

Huang Y-H. (2001). Comparative study of oxidation of dye-Reactive Black B by different advanced oxidation processes: Fenton, electro-Fenton and photo-Fenton, *Journal of Hazardous Materials*, 83(2), 61-70

Hung C. (1995). Fate of thiocyanate in biological treatment process, *MS Thesis*, Atlanta, Georgia Institute of Technology

Hung C, Pavlostathis S. (1997). Aerobic biodegradation of thiocyanate. *Water Research*, 31, 2761-2770

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

Ileri R, Sengil I, Kulac S, Damar Y. (2003). Treatment of mixed pharmaceutical industry and domestic wastewater by sequencing batch reactor. Journal of Environmental Science and Health, 38(10), 2101-2111

Inamuddin l, Luqman M. (2012). Ion Exchange Technology I. Theory and Materials, *Springer,* NewYork

Jain R, Shrivastava M. (2008). Photocatalytic removal of hazardous dye cyanosine from industrial waste using titanium dioxide. *Journal of Hazardous Materials*, 152(1), 216-220

Jesús García-Galán M, Silvia Díaz-Cruz M, Damià Barceló. (2011). Occurrence of sulfonamide residues along the Ebro river basin Removal in wastewater treatment plants and environmental impact assessment. *Environment International*, 37, 462–473

Jones C. (1999). Applications of Hydrogen Peroxide and Derivatives, *The Royal Society of Chemistry*

Joss A, Keller E, Alder A, Göbel A, McArdell C, Ternes T, Siegrist H. (2005). Removal of pharmaceuticals and fragrances in biological wastewater treatment, *Water Research*, 39(14), 3139-3152

Kang J, Zhan W, Li D, Wang X ,Song J, Liu D. (2011). Integrated catalytic wet air oxidation and biological treatment of wastewater from vitamin B6 production. *Physics and Chemistry of the Earth*, 36, 455−458

Khoufi S, Aloui F, Sayadi S. (2006). Treatment of olive oil mill wastewater by combined process electro-Fenton reaction and anaerobic digestion. *Water Research*, 40, 2007–2016

Klauson D, Babkina J, Stepanova K, Krichevskaya M, Preis S. (2010). Aqueous photocatalytic oxidation of amoxicillin. Catalysis Today, 151, 39-45

Kodak. (1982) Disposal and treatment of photographic processing solutions- in support of clean water, *Information for a cleaner environment*

Kümmerer K. (2009). Antibiotics in the aquatic environment e a review e Part I. *Chemosphere*, 75, 417-434

Kümmerer K. (2008). Pharmaceuticals in the Environment: Sources Fate, Effects and Risks 3rd *Springer*, Berlin

Kurt U, Apaydin O, Talha Gonullu M. (2007). Reduction of COD in wastewater from an organized tannery industrial region by electro-Fenton process. Journal of Hazardous Materials, 143, 33–40

Kurt U, Apaydin O, Talha Gonullu M. (2007). Reduction of COD in wastewater from an organized tannery industrial region by Electro-Fenton process. *Journal of Hazardous Materials*, 143, 33–40

Kushwaha N, Saini R, Kushwaha S. (2011). Synthesis of some Amide derivatives, International Journal of Chemical Technological Research, 3(1), 203-209)

Lange F, Cornelissen S, Kubac D, Sein M, von Sonntag J, Hannich C, Golloch A, Heipieper H, Möder M, von Sonntag C. (2006). Degradation of macrolide antibiotics by ozone: a mechanistic case study with clarithromycin. *Chemosphere* , 65, 17-23

LaPara T, Nakatsu C, Pantea L, Alleman J. (2001). Aerobic biological treatment of a pharmaceutical wastewater: Effect of temperature on cod removal and bacterial community development. *Water Research*, 35(18), 4417- 4425

Larsen T, Lienert J, Joss A, Siegrist H. (2004). How to avoid pharmaceuticals in the aquatic environment. *Journal of Biotechnology*, 113 (1-3), 295-304

Lee W, Westerhoff P. (2006). Dissolved organic nitrogen removal during water treatment by aluminum sulfate and cationic polymer coagulation. *Water Research*, 40(20), 3767-3774

Legrini O, Oliveros E, Braun A. (1993). Photochemical Processes for Water-Treatment. *Chemical Reviews*, 93(2), 671- 698

Lehninger A, Nelson D, Cox M. (1993). Principles of Biochemistry , *Worth*, New York

Li K Yediler A, Yang M, Schulte-Hostede S, Wong M. (2008) Ozonation of oxytetracycline and toxicological assessment of its oxidation by-products, *Chemosphere*, 72, 473-478

Lin S Lo C. (1997). Fenton process for treatment of desizing wastewater. *Water Research*, 31, 2050-2056

Lund H, Hammerich O. (2001). Organic electrochemistry, Fourth Edition, New York

Lytle P. (1984). Treatment of photofinishing effluents using rotating biological contactors(RBC's). *Journal Imaging Technology*, 10, 221-226

Malik P, Saha S. (2003). Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. *Separation and Purification Technology*, 31(3), 241-250

Marshall H, Burchardt L, Lacouture R. (2005). A review of phytoplankton composition within Chesapeake Bay and its tidal estuaries. *Journal of Plankton Research*, 27 (11), 1083

Martín M Pérez J, López J, Oller I, Rodríguez S. (2009). Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation. *Water Research* , 43, 653-660

Martínez-Huitle C, De Battisti A, Ferro S, Reyna S, Cerro-López M, Quiro M. (2008). Removal of the pesticide methamidophos from aqueous solutions by electrooxidation using Pb/PbO2, Ti/SnO2, and Si/BDD electrodes. *Environmental Science and Technology*, 42, 6929–6935

Meplestor P. (1996). Modern Plastics 74, 66

Montanaro D, Petrucci E, Merli C. (2008). Anodic, cathodic and combined treatments for the electrochemical oxidation of an effluent from the flame retardant industry. *Journal of Applied Electrochemistry*, 38, 947–954

Mujika J, Matxain J, Eriksson L, Lopez X. (2006). Resonance Structures of the Amide Bond: The Advantages of Planarity. *Chemistry - A European Journal*, 12, 27

Nakada N, Shinohara H, Murata A, Kiri K, Managakia S, Sato N, Takada H. (2007). Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. *Water Research*, 41, 4373−4382

Nidheesh P, Gandhimathi R. (2012). Trends in electro-Fenton process for water and wastewater treatment: An overview. *Desalination*, 299, 1-15

Oller I, Malato S, Sánchez-Pérez J, Maldonado M, Gernjak W, Pérez-Estrada L, Muñoz J, Ramos C, Pulgarín C. (2007). Pre-industrial-scale Combined Solar Photo-Fenton and Immobilised Biomass Activated-Sludge Biotreatment. Industrial and Engineering Chemistry Research, 46(23), 7467-7475

Ouellette R. (1994). Chemistry: An Introduction to General, Organic and Biological Chemistry *Prentice Hall*

Oz N Ince O, Ince B. (2004). Effect of wastewater composition on methanogenic activity in an anaerobic reactor. Journal of Environmental Science and Health, 39 (11-12), 2029-2042

Ozcan A. (2010). Degradation of hazardous organic compounds by using electro-fenton technology, *Doctoral Thesis*

Pagilla K, Urgun-Demirtas M, Czerwionka K, Makinia J. (2008). Nitrogen Speciation in Wastewater Treatment Plant Influents and Effluents—The US and Polish Case Studies, *Water Science Technolog*y, 57, 1511-1517

Panizza M, Cerisola G. (2009). Direct And Mediated Anodic Oxidation of Organic Pollutants *Chemical Reviews*, 109, 6541-6569

Panizza M, Cerisola G. (2007). Electrocatalytic materials for the electrochemical oxidation of synthetic dyes. *Applied Catalysis B:Environmental*, 75(1-2), 95-101

Panizza M, Cerisola G. (2001) Removal of organic pollutants from industrial wastewater by electrogenerated Fenton's reagent. *Water Research*, 35(16), 3987–3992

Panizza M, Sirés I, Cerisola G. (2008). Anodic oxidation of mecoprop herbicide at lead dioxide *Journal of Applied Electrochemistry*, 38(7), 923-929

Papadopoulos A, Fatta D, Loizidou M. (2007). Development and optimization of dark Fenton oxidation for the treatment of textile wastewaters with high organic load. *Journal of Hazardous Materials*, 146(3), 558-563

Parkin G, McCarty P. (1981). A comparison of the characteristics of soluble organic nitrogen in untreated and activated sludge treated wastewaters. *Water Research*, 15, 139-145

Pavlostathis S, Jungee S. (1994). Biological Treatment of photoprocessing wastewaters. *Water Science and Technology*, 29, 89-98

Pavlostathis S, Maeng S. (1997). Aerobic biodegradation of a silver-bearing. *Environmental Toxicology and Chemistry*, 17(4), 617-624

Pavlostathis S, Sridhar K. (1992). Treatment of photoprocessing effluents by the activated sludge process. Journal of Imaging Science and Technology, 36(4), 405-411

Pehlivanoglu E, Sedlak D. (2004). Bioavailability of wastewater-derived organic nitrogen to the alga Selenastrum capricornutum.*Water Research*, 38 (14-15), 3189-3196

Pehlivanoglu-Mantas E, and Sedlak D. (2008). Measurement of dissolved organic nitrogen forms in wastewater effluents: Concentrations, size distribution and NDMA formation potential. *Water Research*, 42(14), 3890-3898

Polcaro A, Palmas S, Renoldi F, Mascia M. (2000) Three-dimensional electrodes for the electrochemical combustion of organic pollutants. *Electrochimica Acta*, 46, 389–394

Polcaro A, Palmas S. (1997). Electrochemical oxidation of chlorophenols. Industrial and Engineering Chemestry Research, 36, 1791–1798

Prabhakaran D, Kannadasan T, Ahmed Basha C. (2009). Treatability of resin effluents by electrochemical oxidation using batch recirculation reactor. International Journal of Environmental Science Technology, 6(3), 491-498

Qiang Z. (2002). Removal of selected hazardous organic compounds by electro-Fenton oxidation process. *PhD Thesis*, Proquest Information and Learning Company

Quici N. (2007). Photocatalytic degradation of citric acid under different conditions: TiO2 heterogeneous photocatalysis against homogeneous photolytic processes promoted by Fe(III) and H_2O_2 . *Applied Catalysis B: Environmental*, 71 (3-4), 117-124

Radjenovic J, Petrovic M, et Barcelo D. (2007). Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. Analytical and Bioanalytical Chemistry, 387(4), 1365–1377

Radzicka A, Wolfenden R. (1996). Rates of Uncatalyzed Peptide Bond Hydrolysis in Neutral Solution and the Transition State Affinities of Proteases. Journal of American Chemistry Society, 118, 6105-6109

Raj D, Anjaneyulu Y. (2005). Evaluation of biokinetic parameters for pharmaceutical wastewaters using aerobic oxidation integrated with chemical treatment. *Process Biochemistry*, 40, 165-175

Rajkumar D, Palanivelu K. (2004). Electrochemical treatment of industrial wastewater, *Journal of Hazardous Materials*, 113(1-3), 123-129

Reyes C Férnandez J, Freer J, Mondaca M, Zaror C, Malato S, Mansilla H. (2006). Degradation and inactivation of tetracycline by TiO2 photocatalyst. *Journal of Photochemistry and Photobiology* , A184, 141-146

Rosales E M. Pazos M, Longo M, Sanromán M. (2009). Electro-Fenton decoloration of dyes in a continuous reactor: A promising technology in colored wastewater treatment. *Chemical Engineering Journal*, 155 (1-2), 62–67

Rothschild W Allen A. (1958). Studies in the radiolysis of ferrous sulphate solutions III. Air free solution at higher pH. *Radiation Research*, 8, 101-110

Ruppert G, Bauer R, Heisler G. (1993). The photo-Fenton reaction - an effective photochemical wastewater treatment process. Journal of Photochemistry and Photobiology, A 73, 75-78

Sattayatewa C, Pagilla K, Sharp R, Pitt P. (2010). Fate of Organic Nitrogen in Four Biological Nutrient Removal Wastewater Treatment Plants. *Water Environment Research*, 82 (12), 2306-2315

Shaojun J, Shourong Z, Daqiang Y, Lianhong W, Liangyan C. (2008). Aqueous oxytetracycline degradation and the toxicity change of degradation compounds in photoirradiation process. Journal of Enviromental. Science, 20, 806-813

Sharma A, Chopra A. (2014). Influence of operating conditions on the electrolytic treatment for the removal of color, TSS, hardness and alkalinity using Al-Al electrode combination. *Journal of Applied and Natural Science* , 6(1), 279-285

Shemer H Kunukc, Y, Linden K. (2006). Degradation of the pharmaceutical metronidazole via UV, Fenton and photo-Fenton processes. *Chemosphere*, 63, 269-276

Shishir Kumar Bahera Hyeong Woo Kim, Jeong-Eun Oh, Hung-Suck Park. (2011). Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. *Science of the Total Environment*, 409, 4351–4360

Sirés I, Brillas E. (2012). Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review. *Environmental International*, 40, 212−229

Sirés I, Centellas F, Garrido J, Rodríguez R, Arias C, Cabot P,Brillas E.(2007). Mineralization of clofibric acid by electrochemical advanced oxidation processes using a boron-doped diamond anode and Fe2+ and UVA light as catalysts. *Applied Catalysis B: Environment*, 72, 373-381

Sires I, Garrido J, Rodriguez R, Cabot P, Centellas F, Arias C, Brillas E. (2006). Electrochemical Degradation of Paracetamol from Water by Catalytic Action of Fe2+, Cu2+, and UVA Light on Electrogenerated Hydrogen Peroxide. *Journal of Electrochemical Society*, 153(1), D1-D9

Sreekanth D, Sivaramakrishna D, Himabindu V, Anjaneyulu T. (2009). Thermophilic treatment of bulk drug pharmaceutical industrial wastewaters by using hybrid up flow anaerobic sludge blanket reactor. *Bioresource Technology*, 100, 2534−2539

Stackelberg P, Furlong E, Meyer M, Zaugg S,Henderson A, Reissman D. (2004). Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking water treatment plant. *Science of the Total Environment*, 329, 99-113

Stockinger H, Heinzle E, Kut O. (1995). Removal of chloro and nitro aromatic wastewater pollutants by ozonation and biotreatment. *Environmental Science and Technology*, 29, 2016-2022

Sun J, Sun S, Fan M, Guo H, Qiao L, Sun R. (2007). A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process. *Journal of Hazardous Materials*, 148(1-2), 172-177

Sun Y, Pignatello J. (1993). Photochemical reactions involved in the total mineralization of 2,4-D by Fe3+/H2O2/UV. *Environment Science and Technology*, 27, 304-310

Sunners B, Piette L, Schneider W. (1966). Proton magnetic resonance measurements of formamide. *Canadian Journal of Chemistry*, 38, 681-688

Tahar N, Savall A. (1998). Mechanistic aspects of phenol electrochemical degradation by oxidation on a Ta/PbO2 anode. *Electrochemical Society*, 145, 3427–3434

Tekin H, Bilkay O, Ataberk S, Balta T, Ceribasi I, Sanin F, Dilek F, Yetis U. (2006) Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. *Journal of Hazardous Materials*, 136, 258−265

Terhaa C, Ewell W, Dziuba S, Fassett D. (1972). Toxicity of photographic processing chemicals to fish. *Photo Science and Engineering*, 16(5), 370-377

Ternes A, et al. (2006). Detailed report,related to the overall project duration. *Poseidon*, 1.1.2001–30.6.2004.

Ternes T, Meisenheimer M, McDowell D, Sacher F,Brauch H, Haiste-Gulde B, Preuss G, Wilme U,Zulei-Seibert N. (2002). Removal of pharmaceuticals during drinking water treatment. *Environmental Science and Technology*, 36, 3855–3863

Ting W, Huang Y, Lu M. (2007). A double cathode reactor design of wastewater treatment by electro-chemical method. *ROC patent*: 316259

Tinga W, Huanga Y, Lu M. (2007). Catalytic treatment of petrochemical wastewater by electroassisted fenton technologies. *Reaction Kinetics and Catalysis Letters,* 92(1), 41−48

Urgun-Demirtas M, Sattayatewa C, Pagilla K. (2008). Bioavailability of dissolved organic nitrogen in treated effluents. *Water Environment Research*, 80(5), 397-406

Vähätalo A, Järvinen M. (2007). Photochemically produced bioavailable nitrogen from biologically recalcitrant dissolved organic matter stimulates production of a nitrogen limited microbial food web in the Baltic Sea. *Limnology and Oceanography*, 132-143

Wang L, Tselung Y. (2004). Handbook of industrial and hazardous wastes treatment, New York

Watkinson A, Murby E, Costanzo S. (2007). Removal of antibiotics in conventional and advanced wastewater treatment: Implications for environmental discharge and wastewater recycling. *Water Research*, 41(18), 4164-4176

Wiegner T, Seitzinger S, Glibert P, Bronk D. (2006). Bioavailability of dissolved organic nitrogen and carbon from nine rivers in the eastern United States. *Aquatic Microbial Ecology*, 43(3), 277-287

Wilson B, Smith V, deNoyelles F, Larive C. (2003). Effects of three pharmaceutical and personal care products on natural freshwater algal assemblages. *Environmental Science and Technology*, 37, 1713–1719

Yi F, Chen S, Yuan C. (2008). Effect of activated carbon fiber anode structure and ... degradation of dye wastewater. *Journal of Hazardous Materials*, 157, 79–87

Yuan S, Fan Y, Zhang Y, Tong M, Liao P. (2011). Pd-Catalytic in situ generation of H2O2 from H2 and O2 produced by water electrolysis for the efficient electro-Fenton degradation of Rhodamine B. *Environmental Science and Technology*, 45(19), 8514–8520

Zepp R, Faust B, Hoigné J. (1992). Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron (II) with hydrogen peroxide: the photo-Fenton reaction. *Environmental Science and Technology*, 26, 313-319

Zhang H, Fei C, Zhang D, Tang F. (2007). Degradation of 4-nitrophenol in aqueous medium by electro-Fenton method. *Journal of Hazardous Materials*, 145, 227-232

Zhang Y, Zhou J. (2005). Removal of estrone and 17-estradiol from water by adsorption. *Water Research*, 39(16), 3991–4003

Zhelovitskaya A, Yermolayeva E, Dresvyannikov A. (2010). Oxidation of organic compounds by hydroxide radical generated in the solution of the chemical and electrochemical methods. *Electrochemical Pprocesses,* 211-229

Zhou M, Yu Q, Lei L, Barton G. (2007). Electro-Fenton method for the removal of methyl red in an efficient electrochemical system. *Separation and Purification Technology*, 57(2), 380–387

Zhoua J, Zhanga Z, Banks E, Grovera D, Jiang J. (2009). Pharmaceutical residues in wastewater treatment works effluents and their impact on receiving river water. *Journal of Hazardous Materials*, 166, 655–661