GDAŃSK UNIVERSITY OF TECHNOLOGY

FACULTY OF CHEMISTRY

The author of the PhD dissertation: mgr André Fernandes

Scientific discipline: Chemical Sciences

DOCTORAL DISSERTATION

Title of PhD dissertation: Application of Advanced Oxidation Processes in the treatment of effluents from bitumen production at basic pH conditions

Title of PhD dissertation (in Polish): Zastosowanie procesów zaawansowanego utleniania w warunkach zasadowego pH do oczyszczania ścieków z produkcji asfaltów

Supervisor
signature
dr hab. inż. Grzegorz Boczkaj, prof. PG

Gdańsk, 2020

STATEMENT

The author of the PhD dissertation: André Fernandes

I, the undersigned, agree/~~do not agree~~* that my PhD dissertation entitled:
Application of Advanced Oxidation Processes in the treatment of effluents from bitumen production at basic pH conditions

may be used for scientific or didactic purposes.[1]

Gdańsk, 10 of July of 2020
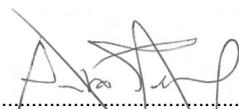
....
signature of the PhD student

Aware of criminal liability for violations of the Act of 4th February 1994 on Copyright and Related Rights (Journal of Laws 2006, No. 90, item 631) and disciplinary actions set out in the Law on Higher Education (Journal of Laws 2012, item 572 with later amendments),[2] as well as civil liability, I declare, that the submitted PhD dissertation is my own work.

I declare, that the submitted PhD dissertation is my own work performed under and in cooperation with the supervision of dr hab. inż. Grzegorz Boczkaj, prof. PG

This submitted PhD dissertation has never before been the basis of an official procedure associated with the awarding of a PhD degree.

All the information contained in the above thesis which is derived from written and electronic sources is documented in a list of relevant literature in accordance with art. 34 of the Copyright and Related Rights Act.

I confirm that this PhD dissertation is identical to the attached electronic version.

Gdańsk, 10 of July of 2020

....
signature of the PhD student

I, the undersigned, agree/~~do not agree~~* to include an electronic version of the above PhD dissertation in the open, institutional, digital repository of Gdańsk University of Technology, Pomeranian Digital Library, and for it to be submitted to the processes of verification and protection against misappropriation of authorship.

Gdańsk, 10 of July of 2020
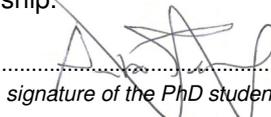
....
signature of the PhD student

*) delete where appropriate.

---

[1] Decree of Rector of Gdansk University of Technology No. 34/2009 of 9th November 2009, TUG archive instruction addendum No. 8.

[2] Act of 27th July 2005, Law on Higher Education: Chapter 7, Criminal responsibility of PhD students, Article 226.

ACKNOWLEDGEMENTS

To prof. Grzegorz Boczkaj,

For his guidance, support, knowledge sharing, translator, understanding and patience throughout these 4 years. It was a very important person in this journey.

To Friends in Poland,

For the warm welcome, positive energy, encouragement and support. With them, Gdansk was like home along these years, making these journey a lot easier.

À Familia e amigos,

Agradeco profundamente aos meus pais, irmão, cunhada, sobrinhos pelo apoio constante, não me deixarem desistir, por aturarem o meu mau humor e ser anti-social, mesmo nos períodos mais dificeis.. em que existiam outras prioridades...

Um abraço especial aos amigos de Setúbal, de Biológica e Erasmus tugas por, me encoragar que o mais dificil já estava feito, entenderem a importância deste passo e entender o meu "isolamento do mundo" e ser "anti-social"

To Grupa Lotos S.A., Lotos Asfalt Sp. z o,

For the possibility of using the effluents from bitumen production to conduct the research

Contents

Abbreviation table

Abbreviation	Terminology
$	American Dollars
AOPs	Advanced Oxidation Processes
BOD_5	Biological Oxygen Demand after 5 days
BTEX	Benzene/ Toluene / Ethylbenzene / Xylene
CB	Conductive Band
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
E°	Standard oxidation potential
H_2O	Water
H_2O_2	Hydrogen Peroxide
H_2S	Hydrogen sulfide
H-AOPs	Hydroxyl radical related AOPs
$HO^\bullet$	Hydroxyl radicals
k	Thousand
O-VOCs	Oxygen Containing Volatile Organic Compounds
O_3	Ozone
O_3/H_2O_2	Peroxone
PMS	Peroxymonosulfate
PS	Persulfate
pKa	Dissociation constant
PZC	Point of zero charge
r_{ox}	Mass ratio between oxygen introduced in the oxidant source and the chemical oxygen demand of the effluent
S-AOPs	Sulfate radical related AOPs
SMP	Semiconductor particle
$SO_4^{\bullet-}$	Sulfate radicals
t-VOCs	Total Volatile Organic Compounds
TiO_2	Titanium Dioxide
UV	Ultraviolet
VB	Valence band
VOCs	Volatile Organic Compounds
VNCs	Volatile Nitrogen Compounds
VSCs	Volatile Sulfur Compounds
WW	Wastewater

Summary of the Dissertation in Polish

W pracy przedstawiono wyniki badań nad zastosowaniem niekatalitycznych, fotolitycznych i fotokatalitycznych procesów zaawansowanego utleniania (ang. *Advanced Oxidation Processes*, AOPs) bazujących na „klasycznych" utleniaczach (ozon, nadtlenek wodoru i ich połączenie tzw. proces perokson) oraz utleniaczach z grupy nadsiarczanów (nadsiarczan sodu i mononadsiarczan potasu) do oczyszczania ścieków pochodzenia rafineryjnego - z produkcji asfaltów naftowych.

Badania wykazały, że AOPs wybrane w ramach niniejszej pracy, są efektywną metodą degradacji LZO obecnych w ściekach modelowych i rzeczywistych oraz pozwalają na istotne obniżenie parametrów ChZT i BZT_5. Stwierdzono synergistyczne działanie układu fotokatalitycznego UV/TiO_2 z utleniaczami zewnętrznymi.

Optymalne i najbardziej ekonomiczne okazały się AOPs z zastosowaniem peroksonu. Badania tej pracy wykazały, że badane AOPs stanowią efektywną i obiecującą technologię do wstępnego oczyszczania ścieków z produkcji asfaltów naftowych, przed etapem końcowego oczyszczania na drodze procesów oczyszczania biologicznego. AOPs zapewniają eliminację ze ścieków większości związków tlenoorganicznych - silnie toksycznych dla osadu czynnego stosowanego do oczyszczania typowych ścieków rafineryjnych. Jednocześnie efektywnemu utlenianiu ulegają lotne związki siarkoorganiczne (LZS) charakteryzujące się silną odorowością.

Summary of the Dissertation in English

The dissertation presents studies of non-catalytic, photolytic and photocatalytic advanced oxidation processes (AOPs) (with application of ozone (O_3), hydrogen peroxide (H_2O_2) and their combination, i.e. Peroxone (O_3/H_2O_2)) and sulfate related AOPs based on sodium persulfate and potassium peroxymonosulfate for the treatment of refinery effluents from bitumen production.

The studies revealed that selected AOPs were effective in the degradation of the VOCs, in the model and real wastewater (WW) and partially reduce the COD and BOD_5. A positive synergism was observed with the simultaneous application of the ultraviolet (UV) light and the Titanium Dioxide catalyst along with the external oxidants i.e. O_3, H_2O_2 and O_3/H_2O_2.

Peroxone related AOPs were the most optimal and economical processes for treatment of the post oxidative effluents from bitumen production. The AOPs studied can be considered as effective and promising technologies used as a pre-treatment stage before a biological final treatment stage, due to the elimination of most of the oxygen containing Volatile Organic Compounds (O-VOCs), known to be toxic for microorganisms of activated sludge and compounds known to have a malodor character like Volatile Sulfur Compounds (VSCs).

1. Introduction

The industrial wastewater (WW) has been under extensive research by the science community due to their serious danger to the aquatic, air and soil environment, especially in respect to the human and animal health. The WW can contain heavy metals, oil emulsions, inorganic and organic compounds, which are difficult to remove due to their solubility in water or due to the presence of persistent and recalcitrant compounds. These compounds can include, aromatics, sulfur, nitrogen, oxygen as well as high molecular compounds [1–5]. Treatment technologies like gravitational separation, centrifugation, coagulation, flotation, adsorption, biological methods, filtration methods, thermal oxidation, among others, have been used to fulfill the legislation requirements [6,7]. Nevertheless, they generate by- products like sludge, syrups or salts that need further treatment. Therefore, one of the main goals in the twenty first century is to develop a simple, safe, economical, efficient and the most important factor, non-harmful to the environment WW treatment technologies.

A one group of technologies, that have been seen as a "green chemistry" approach, since it does not produce any secondary by-products, are the Advanced Oxidation Processes (AOPs). These type of technologies generates and uses mainly hydroxyl radicals ($HO^{\bullet}$) to oxidize the organic pollutants [8,9]. The $HO^{\bullet}$ have a high standard oxidation potential (E^{o}) (2.8 V), higher than most of the species that could be used for such a purpose i.e. sulfate radicals ($SO_4^{\bullet-}$), chlorine, permanganate, persulfate anion, hydrogen peroxide (H_2O_2) and ozone (O_3)[10]. The main characteristics of the $HO^{\bullet}$ are short-life, simply produced, powerful oxidant, having electrophilic behavior, ubiquitous in nature, highly reactive and practically non-selective [11]. It reacts with a wide variety of organic compounds classes, producing lower-molecular and simpler organic compounds, or in case of full mineralization, carbon dioxide (CO_2), water (H_2O) and inorganic salts as described by equation (1) [12].

$$Organic\ species\ +\ HO^{\bullet}\ \rightarrow\ CO_2\ +\ H_2O\ +\ inorganic\ ions \qquad (1)$$
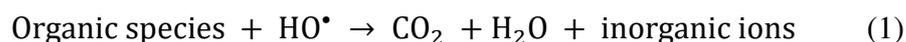
There are four reaction mechanisms of $HO^{\bullet}$, which are addition, hydrogen atom transfer, electron transfer and radical interaction [11]. The compounds containing carbon double bonds in their structure are more reactive towards $HO^{\bullet}$ attack than

saturated molecules. In addition, the reactivity towards oxidative compounds decreases with the decrease of the molecular weight and the increase of the oxidation level [10].

AOPs are useful for treating refractory pollutants resistant to other treatments such as, for example, biological technologies. A disadvantage of AOPs is related with the cost of oxidants, and electric energy when ozone (O_3) or ultraviolet (UV) are applied. For these reasons, they are considered as an alternative treatment of wastewater that cannot be biologically treated [7]. AOPs have been widely studied in a large range of WW like food [13], petroleum and refinery [14–16], textile [17], among others, mentioned in several review articles on AOPs in the recent years. Regarding the type of AOPs, they include sulfate radical related AOPs (S-AOPs) [18], ozone related AOPs [19], ultrasounds [20], catalytic related AOPs [21], among others. This literature generally did not discriminate the range of pH involved. However, some types of industrial WW are formed at basic pH conditions or for some reason have a basic pH. Its origin can be from the process conditions or when the basic pH conditions are the best solution to absorb and effectively trap acidic pollutants in the aqueous WW. Effluents like spent caustic [22], dye [23] or post-oxidative effluents from bitumen production [24] are some examples.

In the case of post oxidative and spent caustic effluents, a presence of high concentrations of sulfide ions forces further processing of the WW at basic pH conditions. A change to acidic or neutral pH will result in this case in releasing acidic compounds like hydrogen sulfide (H_2S) to the atmosphere which must be avoided. In addition, they contain a wide variety of Volatile Organic Compounds (VOCs) present in many types of industrial effluents [25–29]. The importance of wastewater treatment regarding VOCs is related with few factors. Firstly, it follows from the high biotoxicity of some groups of the VOCs, like oxygen containing VOCs (O-VOCs), to microorganisms. It makes ineffective the usage of biological methods to degrade such compounds. Secondly, open air treatment technologies (common practice at biological treatment stage) can increase the risk of VOCs emission to the atmosphere instead of their quantitative degradation. Some groups of VOCs (like volatile sulfur compounds (VSCs)) have odorous character, thus their emission from WW treatment plants will cause a lowering of the air quality in the region. Thirdly and maybe one of the most important factors, the majority of the compounds present in this work are harmful to the

6

animal and human health. Thus, the elimination of VOCs from industrial effluents could be one of the big steps contributing to a high quality of treated wastewater and possibility of reusing it, contributing to a higher sustainability. Since the effluents studied in this dissertation are the post oxidative effluents from bitumen production, pH correction before treatment will not be conducted and therefore limits the range of the AOPs studied. The AOPs technologies chosen to be studied are briefly described below.

Ozone (O_3) is a powerful oxidizing agent (E^o 2.07 V) that is able to transform the organic compounds. It is characterized by a short lifetime and low solubility in aqueous media. To overcome the low solubility, some techniques have been explored, like fixed beds of porous glass or metals, solid catalysts, stirring, line mixers, contact towers and increase of retention time by large bubble columns or diffusers [10]. Ozonation is characterized as an AOP when used in alkaline medium, in combination with UV/sun light or with addition of transition metal cations [6]. At an alkaline pH, the effect of HO^- is beneficial, where O_3 directly attacks OH^- to generate $HO^{\bullet}$ as described in Equation (2) [30].

$$O_3 + OH^- \rightarrow O_3^{\bullet-} + HO^{\bullet} \tag{2}$$

Furthermore, $HO^{\bullet}$ can react with O_3 generating much less reactive perhydroxyl radicals ($HO_2^{\bullet}$), which react with O_3 generating once more $HO^{\bullet}$ (Equations. (3) and (4)) [31].

$$O_3 + HO^{\bullet} \rightarrow O_2 + HO_2^{\bullet} \tag{3}$$

$$O_3 + HO_2^{\bullet} \rightarrow 2O_2 + HO^{\bullet} \tag{4}$$

The usage of UV light in combination with O_3 in aqueous medium can increase the formation of $HO^{\bullet}$ and its concentration as illustrated in Equations. (5) [12].

$$O_3 + H_2O + h\nu \rightarrow O_2 + 2HO^{\bullet} \tag{5}$$

Hydrogen peroxide (H_2O_2) is a weak acid with relatively high standard oxidant potential (E^o 1.77 V) which alone does not lead to the generation of hydroxyl radicals (Equations. (6) to (8)) [6].

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \tag{6}$$

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \hspace{4cm} (7)$$

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + OH^- \hspace{2cm} (8)$$
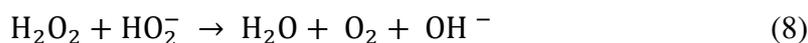
Furthermore, in the presence of an alkaline medium H_2O_2 will react with OH^- to produce perhydroxyl ions (HO_2^-) as described in Equation (9) [32].

$$H_2O_2 + OH^- \leftrightarrow HO_2^- + H_2O \hspace{3cm} (9)$$
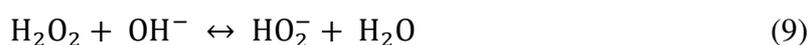
When H_2O_2 is irradiated with UV, this type of light provide enough energy to break the O-O bounds and generate $HO^\bullet$, as it is presented in Equation (10) [33].

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \hspace{4cm} (10)$$

The combination of H_2O_2 with other reagents can improve the generation of $HO^\bullet$. The combination of O_3 and H_2O_2 (O_3/H_2O_2) is named as peroxone process which combines the indirect and direct oxidation of organic compounds. The major effects in combining O_3 and H_2O_2 are the increase of oxidation efficiency by conversion of O_3 to $HO^\bullet$ and improvement of O_3 transfer from the gas to the liquid phase as demonstrated in Equation (11) [11].

$$H_2O_2 + O_3 \rightarrow HO^\bullet + HO_2^\bullet + O_2 \hspace{3cm} (11)$$
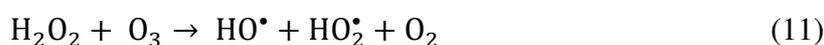
Furthermore, the combination of UV with O_3/H_2O_2, the generation of $HO^\bullet$ (Equation (12)) is enhanced and can transform H_2O_2 to $HO^\bullet$ (Equation (10)) consequently increasing the degradation rate [34].

$$O_3 + H_2O_2 + h\nu \rightarrow 3O_2 + 2HO^\bullet \hspace{3cm} (12)$$

In recent years, an increase of the interest and study of sulfate radical related AOPs (S-AOPs) was observed. The S-AOPs can be an alternative to the hydroxyl radical related AOPs (H-AOPs), generating and using sulfate radicals ($SO_4^{\bullet-}$) which possess a high standard oxidation potential (E° 2.6 V) [35]. Rastogi and co-workers concluded that the $SO_4^{\bullet-}$ have a longer half-life than $HO^\bullet$ due to the fact that $SO_4^{\bullet-}$ prefer the electron transfer reactions while $HO^\bullet$ can react by hydrogen-atom abstraction which is less dominant [36]. The term S-AOPs generally relates to a two alternative

technologies based on sodium persulfate (PS; $Na_2S_2O_8$) and potassium peroxymonosulfate (PMS; $KHSO_5$).

The persulfate anion ($S_2O_8{}^{2-}$) and peroxymonosulfate anion ($HSO_5{}^-$) are strong oxidants, with a $E^°$ of 2.01 and 1.85 V respectively, which can be activated by heat, light or by the use of a catalyst, to generate $SO_4{}^{\bullet-}$ (Equations. (13) to (18)). The sulfate radicals have high stability and longer, comparing to hydroxyl radicals, life-time and can be used in a wide range of organic contaminants [37,38].

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet-} \tag{13}$$

$$S_2O_8^{2-} + \Delta \rightarrow 2SO_4^{\bullet-} \tag{14}$$

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{\bullet-} \tag{15}$$

$$HSO_5{}^- + h\nu \rightarrow 2SO_4^{\bullet-} \tag{16}$$

$$HSO_5{}^- + \Delta \rightarrow 2SO_4^{\bullet-} \tag{17}$$

$$HSO_5{}^- + 2e^- \rightarrow 2SO_4^{\bullet-} \tag{18}$$

Sulfate radicals when present in aqueous medium or at basic pH, can be decomposed to generate $HO^\bullet$ as illustrated in Equations. (19) and (20) [39].

$$SO_4^{\bullet-} + H_2O \rightarrow HO^\bullet + HSO_4^- \tag{19}$$

$$SO_4^{\bullet-} + OH^- \rightarrow HO^\bullet + SO_4^{2-} \tag{20}$$
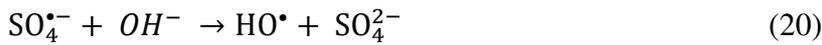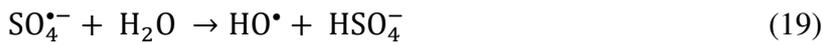
In recent years, the activation of PS by a base (NaOH) was proposed by Furman and co-workers (Equation (21)) [40].

$$2S_2O_8^{2-} + 2H_2O \xrightarrow{OH^-} 2SO_4^{2-} + SO_4^{\bullet-} + O_2^{\bullet-} + 4H^+ \tag{21}$$
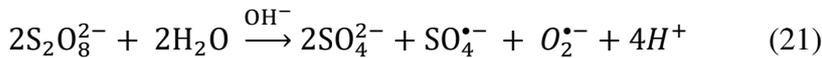
In addition, Qi and co-workers suggested a mechanism of activation of PMS by means of a base (NaOH) [41].

Another group of AOPs relates to photocatalytic processes. The photocatalytic process enables the activation of a semiconductor particle (SMP) material by means of radiation at a specific wavelength, heat or external oxidants. As showed in Equation

(22), when irradiated, adsorption of photons by SMP occurs, which acquire enough energy to conduct an electron (e^-) from its valence band (VB) to the conductive band (CB), (bandgap energy). This phenomenon leads to the formation of holes in the VB (h^+) that will act as oxidizing sites [42].

$$SMP \rightarrow SMP(e_{CB}^- + h_{VB}^+) \qquad (22)$$
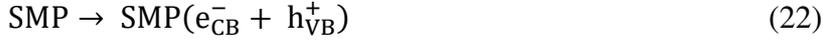
In the h_{VB}^+ sites of the catalyst surface H_2O (Equation 23)) and OH^- (Equation (24)) will act as electron donors, generating $HO^\bullet$, which can react with the organic species (reaction 1 and 2 of figure 1).

$$h_{VB}^+ + H_2O \rightarrow HO^\bullet + H^+ \qquad (23)$$

$$h_{VB}^+ + OH^- \rightarrow HO^\bullet \qquad (24)$$

If H_2O_2 is present in the medium, it plays a role of external oxidant and will act as an e^- acceptor, generating $HO^\bullet$ and OH^-, (Equation. (25)) illustrated in reaction 3, figure 1 [43]. When O_3 is present it will produce an O_3 anion (O_3^-) in the adsorption layer, which afterwards will generate $HO^\bullet$, as demonstrated in Equation (26) and exhibit in reaction 3 in figure 1 [10].

$$O_3 + e^- + H_2O \rightarrow OH^- + HO^\bullet + O_2 \qquad (25)$$

$$H_2O_2 + e_{CB}^- \rightarrow OH^\bullet + OH^- \qquad (26)$$
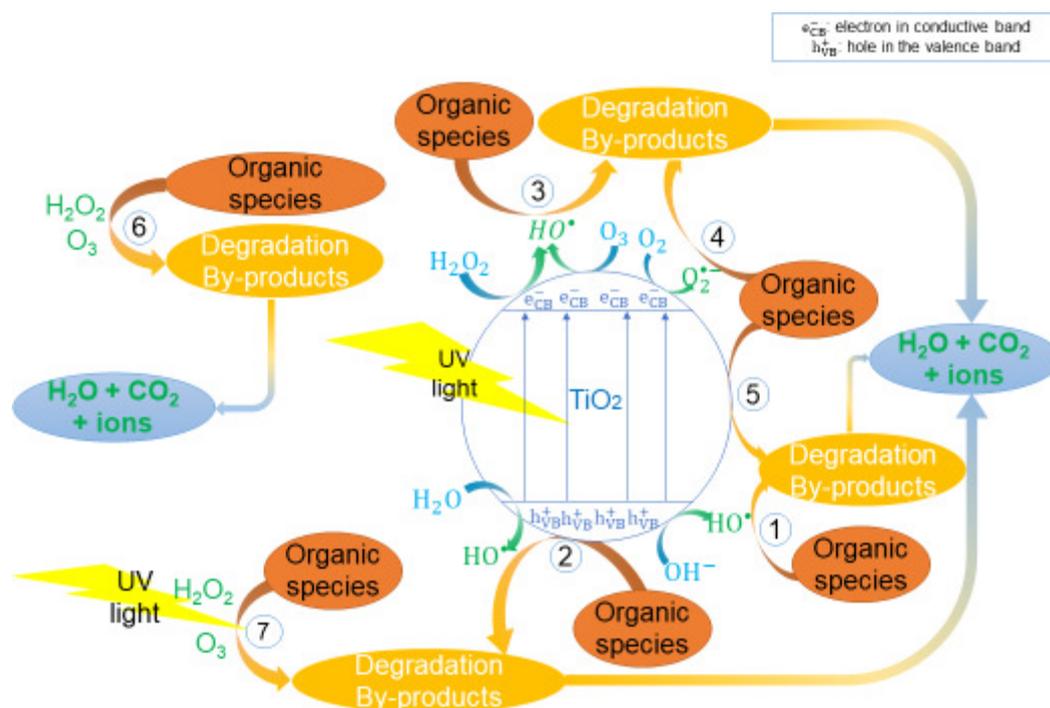
Figure 1 - Mechanism of the degradation of the organic species via different types of AOPs, non-catalytic (reaction 6), photolytic (reaction 7) and photocatalytic processes (reaction 1 to 5) [44].

The photocatalytic and catalytic processes have been applied in several types of real effluents like cellulose [43], winery [45], petrochemical [46], petroleum & refinery [47–49], post-treatment of refinery WW [50] and are considered as promising techniques in treatment of heavy polluted WW.

The technologies described above have been studied in several types of industrial effluents containing compounds that are persistent and recalcitrant to other types of technologies like biological. The AOPs and have been proving that they can effectively treat these compounds and at the same time reduce significantly the organic load. Thus, these technologies were tested in heavily polluted refinery effluents from bitumen production.

2. Plan of the research

The aim of this dissertation was to study different types of AOPs at alkaline conditions to obtain effective degradation of the organic compounds responsible for pollution load of refinery effluents from bitumen production. The processes studied were tested using a post oxidative effluents from bitumen production (Lotos Asfalt Sp. z o. o., Grupa LOTOS S.A.) and simulated caustic WW, with carefully selected VOCs commonly present in refinery effluents. The parameters of the WW quality analyzed were Chemical Oxygen Demand (COD), Biological Oxygen Demand after 5 days (BOD$_5$), sulfide ions and content of several VOCs. Important process parameters like, mass ratio between oxygen introduced in the oxidant source and the chemical oxygen demand of the effluent (r_{ox}), temperature, catalyst concentration were studied. The calculations to determine the oxidant amount needed for the r_{ox} established are explained in details in the published paper [51]. In addition, economical evaluation was performed for all processes studied to understand the feasibility of the technologies to implement them in a real case scenario. The main stages of this dissertation are briefly described below.

- An extensive review of the state of the art of the AOPs exclusively at an alkaline pH and the main operational parameters studied.
- Comparison of the degradation efficiency between the classic AOPs oxidants (O_3, H_2O_2 and O_3/H_2O_2) in the treatment of the model and real WW studied, varying parameters like temperature and r_{ox}.
- Comparison of the degradation efficiency between the sulfate related AOPs oxidants ($Na_2S_2O_8$ and $KHSO_5$) in the treatment of the model and real WW studied, varying parameters like temperature and the r_{ox}.
- Studies on possibility of increase of degradation effectiveness of pollutants present in effluents from bitumen production by photolytic and photocatalytic AOPs using UV and Titanium Dioxide (TiO_2) as a catalyst.

3. Literature review.

3.1 Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review (Publication/Attachment No. 1)

The scope of this review was to report the state of the art of AOPs at basic pH, analyze the effectiveness of each AOP at alkaline pH, determine the type of effluents and compounds that can be degraded with high efficiency, perform an economical evaluation and attempt to determine the more promising AOP to treat alkaline WW. The studied AOPs, due to the mechanism of reactions and chemical character of the used oxidants, do not produce any harmful by-products of themselves i.e. H_2O_2 decompose to water, and O_3 to oxygen. The by-products formed during oxidation are only products of oxidation of pollutants molecules. The exception is the sulfate radical related AOPs which form sulfates. A chlorination process was not studied due to its impractical nature in respect to industrial applications – they can produce harmful by-products as well as can form HCl and other corrosive species. Since this literature review was focused on the AOPs effective in strongly basic pH, the number of effective methods was limited. Thus, Fenton processes, electrochemical oxidation and ultrasounds were not reviewed and mentioned.

Most important conclusions from the reviewed literature studies on ''typical'' oxidants used in AOPs revealed that ozone based processes are the most effective. This is supported by the ozone chemistry, which clearly shows that basic conditions in this case should be preferred. Published studies revealed that H_2O_2 is not effective in basic conditions and this direction or part of studies should be preferably substituted by more promising processes such as S-AOPs.

S-AOPs are an interesting alternative to widely known AOPs based on hydroxyl radicals. The obtained effectiveness of degradation reported in review papers revealed better results for S-AOPs, but unfortunately the oxidant-pollutant ratio is generally much higher. Thus, further research should focus on effective activation of S-AOPs oxidants to improve the yield of generation of hydroxyl and sulfate radical species. This will allow to lower the amounts of the oxidant and make this process more economically effective. Still, there is no effective catalysts for AOPs at basic pH. The effectiveness of the process is much lower comparing with neutral and acidic

13

conditions. In this field, the design of processes must include the phenomena of adsorption of the compounds on the catalyst surface, which can be obtained if the surface has an opposite charge to the compounds in pH used. In some part also weak sorption interactions could be used to obtain such an affinity. Better situation can be reported in terms of photocatalytic processes. Studied TiO_2 and Zinc Oxide (ZnO) catalysts allowed to increase the effectiveness of degradation comparing with sole use of oxidants. But still neutral and acidic conditions were more effective.

The reviewed papers in many cases lacks of many important data characterizing the effluents studied as well as instrumentation used. Thus, it makes difficulties to compare different processes and obtain some general rules and conclusions, which will help other researchers to focus on really important aspects. Still, the influence of many factors of the process is not clear and demands further studies. It was presented some simple rules for planning the research which together form a ''rules of thumb" or good practice, hoping to improve the quality of the papers in the field of wastewater treatment. These rules are explained in details in the attachment 1 (paragraph 4.2 - *Strategies of planning the research for new scientists in the field).*

4. Results and discussion

4.1 Study of Different Advanced Oxidation Processes for Wastewater Treatment from Petroleum Bitumen Production at Basic pH (Publication/Attachment No. 2)

The state of the art of the AOP technology unveils that when treating effluents with an extreme basic pH, the pH is generally corrected to neutral or acidic pH. In the case of spent caustic and post oxidative effluents from bitumen production, they present a relevant concentration of sulfide ions, which can generate hydrogen sulfide (H_2S) consequently emitted to the atmosphere if the pH would be corrected to neutral or acidic pH values. In addition, they contain several sulfur compounds which can be easily emitted to the atmosphere. It was also clear from the literature review that there is a lack of studies which monitor the organic compounds present in the real effluents.

Thus, the goal of the first part of the research was to study the most effective processes for the treatment of post oxidative effluents from a bitumen production plant using simple H-AOP oxidants, i.e., O_3, O_3/H_2O_2, and H_2O_2 without pH correction. The analysis and main conclusions from this part of the research are described below.

Studies performed at 40 °C revealed, that AOPs based on H_2O_2 were less effective (33% COD and 37% BOD_5 reduction) when comparing with O_3 (36% COD and 37% BOD_5 reduction) and O_3/H_2O_2 (43% COD and 36 BOD_5 reduction). Comparing the most effective processes at 25°C, also in this case, the peroxone process (O_3/H_2O_2) was the most effective, achieving 43 and 34% of COD and BOD_5 respectively. The combination of both oxidants in basic pH contributed to the increase of $HO^{\bullet}$ amount and therefore to the higher COD reduction. The results revealed that in the case of basic pH and treatment of such a specific effluent, lower temperature allowed to increase solubility of ozone in the aqueous solution, thus increasing the amount of formed $HO^{\bullet}$ and therefore obtaining higher treatment efficiency. Further studies revealed, that O_3 at r_{ox} of 0.34 at 25 °C was the optimal process due to the significant decrease of the biotoxicity (in respect to microtox test) of the treated effluents. Sulfide ions were effectively oxidized in all procedures. This enables the usage of other types of AOPs at a lower pH, like Fenton. Volatile Sulfur Compounds (VSCs) were effectively degraded in all technologies. The Volatile Nitrogen Compounds (VNCs) were more problematic to reach effective degradation from all

VOCs studied. O_3 at a r_{ox} of 0.34 at 25 °C was the most effective to degrade the overall VOCs, while the H_2O_2 was less effective oxidant. Compounds like furfural and 2- ethyl-1-hexylamine revealed to be by-products of oxidation of other compounds. This phenomenon participated in the effect of increased biotoxicity of the effluents treated by H_2O_2 processes. H_2O_2 process revealed to be the cheapest technology studied with a treatment cost (energy cost plus the chemical cost) of 8.5 thousand (k) American dollars ($) per 1 m^3 of treated effluent. In contrast, peroxone was the most expensive with a treatment cost of 72.9 k$ per 1m^3 of treated effluent. This cost simulation assumed that the effluent COD will be lowered by 50%. These results, indicate that there is a need to conduct further studies in the combination of these oxidants with other sources to increase the treatment effectiveness and therefore decrease the costs of treatment.

It was proved that detailed process control is mandatory due to the risk of by-products formation. In addition, good effectiveness in the degradation of the VOCs and the decrease in the biotoxicity in O_3 related processes were other important outcomes.

4.2 Treatment of bitumen post oxidative effluents by sulfate radicals based advanced oxidation processes (S-AOPs) under alkaline pH conditions (Publication/Attachment No. 3)

As discussed in section 3 (Literature review), S-AOPs are considered as promising technologies for WW treatment, especially at alkaline pH conditions. Due to their higher pH range of application, these technologies can be considered a good alternative to H-AOPs, especially H_2O_2. The usage of these technologies at basic pH revealed to be scarce and lacks studies for real effluents. The already published studies were conducted mainly for model WW to target specific pollutants. This is a limiting factor and without solid results on effective treatment of real effluents, S-AOPs will remain only in the scientific field, without application in real case scenario. Thus, to compare H-AOPs and S-AOPs, studies for this thesis were performed using PS and PMS to attempt effective treatment of the effluents from bitumen production.

The experiments revealed, that the optimal r_{ox} and temperature for PS processes in terms of COD and BOD_5 degradation was 0.31 at 40 °C with 27 and 31% of COD and BOD_5 reduction. Regarding the VOCs degradation, PS with a r_{ox} of 0.41 at 40 °C was the most effective process with 82%. The optimal PS process depends whether if

the goal is to maximize the COD and BOD reduction or to degrade the VOCs present in the effluents. In the case of PMS, the best process to degrade the VOCs and decrease the COD and BOD was with a r_{ox} 1.43 at 60 ℃ obtaining 43% of COD and BOD_5 reduction and 62% degradation of the total VOCs. PS was more effective for lower r_{ox} values and PMS for higher r_{ox} values. Sulfide ions were effectively oxidized using both types of technologies which consequently eliminates the risk of H_2S formation if the pH is corrected to neutral or acidic values. Furfural and acetaldehyde, revealed to be by-products of oxidation of other compounds. In addition, non-aromatic and non-cyclic oxygen containing VOCs (O-VOCs) were more persistent to degradation. Comparing with H-AOPs there were similarities in terms of furfural and non-aromatics/cyclic O-VOCs degradation profile. Nevertheless, S-AOPs revealed that can be more effective in the degradation of 2-ethyl-1-hexylamine. A rich database of a good degradation effectiveness of numerous VOC-s in real conditions was reported. These data are valuable for other research groups focused on S-AOPs. The economical evaluation revealed, that PS process, with a treatment cost of 63.3 k\$ per 1 m^3 of treat effluent. It revealed cheaper than PMS with a treatment cost of 162.3 k\$ per 1 m^3 of treated effluent. These calculations were conducted for a scenario of 50% decrease of the COD of the effluent. It was proved that the cost of PS and PMS is a limiting factor to use these S-AOPs for industrial scale applications. Regarding the investment cost, S-AOPs, with an investment cost of 29.2 k\$, are a promising alternative to ozone based AOP-s (O_3 and O_3/H_2O_2), with an investment cost of 41 and 46 k\$ respectively. Thus, these AOPs revealed to be effective as a pre-treatment method. Comparing both H-AOPs and S-AOPs, the H-AOPs oxidants revealed to be more suitable to treat such type of effluents. Furthermore, this research revealed differences in the degradation mechanisms of specific VOCs when using sulfate or hydroxyl radicals. This aspect is discussed in section 4.3.

Other relevant feature, not usually highlighted in AOPs papers, relates to the sustainability and "green" aspect of the developed technologies. In the case of comparison of oxidants used in AOPs studied, parameters like oxidants production, ease and safety of transportation and stability during storage should be included in the life cycle assessment methodology. Thus, the persulfate based technologies as well as hydrogen peroxide offer low costs and robustness of application comparing to ozone based technologies. Also the maintenance of such installation will be cheaper and more

17

environmentally friendly. In addition, PS and PMS are produced as a powder and are stable in normal conditions of storage and transportation. H_2O_2 is produced as a solution, which demands higher capacity to store and transport it but also is less stable in normal conditions of storage and transportation. In the light of this above mentioned factors of process effectiveness as well as sustainable development, the S-AOP are a promising oxidants which can play an important role in cleaner production processes. The main limiting factor which still prevents these technologies to be tested in a real case scenario is the price of the oxidants.

4.3 Pilot scale degradation study of 16 selected volatile organic compounds by hydroxyl and sulfate radical based advanced oxidation processes (Publication/Attachment No.4)

The research plan discussed so far on the treatment of post oxidative effluents from bitumen production by H-AOPs and S-AOPs revealed partial decrease of the COD, around 45%. The compounds responsible for the low overall COD reduction are saturated hydrocarbons [31,51]. Thus, the model WW was prepared to evaluate the effectiveness of conditions selected during the studies on the real effluents, for less complex cases where only defined compounds are present.

The hypothesis stated at the beginning of this research was that for real effluents the effectiveness in respect to VOCs is underestimated due to formation of volatile by-products which overlay on the results of treatment of the primary amount of VOCs present in the effluents. The model WW carefully prepared simulates as much as possible the caustic effluents from petroleum and refinery industries, which included 3 groups of VOCs, O-VOCs, VNCs and VSCs [31,51]. Few studies followed such approach of preparing a model WW containing several types of VOCs [52–54], but on this specific type of effluents no studies were found. Therefore, the processes O_3, O_3/H_2O_2, H_2O_2, PS and PMS and respective operational parameters studied in the prepared model WW were the same as for the previous studies referred in section 4.1. and 4.2.

A comparison between H and S-AOPs was performed, i.e., the behavior of hydroxyl and sulfate radicals in degradation of several VOCs was studied. The main results revealed that peroxone (O_3/H_2O_2) process with a r_{ox} of 7.5 at 40 ºC was the most

efficient and economical technology to degrade the model WW with complete degradation of all VOCs studied after 60 min of treatment. When comparing both S-AOPs technologies, PS (r_{ox} 23.1) and PMS (r_{ox} 11.6) at 60 ºC, achieved similar total VOCs degradation, around 95% after 120 min of treatment. PMS process was considered more effective than PS due to the usage of less amount of oxidant (including dose expressed as the mass of oxidant - approx. 3 times less). H_2O_2 with a r_{ox} of 32.4 at 40 ºC obtain 74% of total VOCs degradation after 181 min of treatment, while PS and PMS obtain approx. 95%, proving that S-AOPs were more effective than H_2O_2, especially at 60 ºC. Further increase of temperature was not studied due to be unfeasible to heat the effluents above 60 ºC in terms of energy costs. VSCs were degraded between 15 to 30 min of the treatment in the O_3/H_2O_2 and 60 to 120 min in O_3, PS and PMS and therefore considered the first group of VOCs to be effectively degraded. In contrast, VNCs were the most persistent compounds to degradation in all technologies studied. This could be related to the stability of the nitro group when bonded to the aromatic rings, retarding the reaction of the hydroxyl and sulfate radicals with the VNCs and therefore lowering the degradation rate [55].The Benzene, Toluene, Ethylbenzene and Xylene (BTEX) degradation time and efficiency differs in H-AOPs and S-AOPs. $HO^{\bullet}$ were able to react first with BTEX, phenol and VSCs compounds and were less effective in the degradation of 2-nitrotoluene, nitrobenzene and 4-methylbenzaldehyde). Regarding $SO_4^{\bullet-}$, reacted first with non-aromatics O-VOCs, 2-nitrophenol and VSCs and afterwards with phenol and BTEX. The degradation of all VOCs studied was slower in case of S-AOPs. This could be related with a different oxidation mechanism of $HO^{\bullet}$ and $SO_4^{\bullet-}$ ($HO^{\bullet}$ reacts mainly via addition and $SO_4^{\bullet-}$ via electron transfer). Comparing the best processes of H-AOPs and S-AOPs, it was possible to reveal several disadvantages of PMS process comparing with O_3/H_2O_2. Firstly, PMS process takes more time to reach similar degradation than O_3/H_2O_2. Secondly, VOCs like Toluene, Xylene, Nitrobenzene and 2-nitrotoluene, did not reach full degradation in PMS processes as did by O_3/H_2O_2. Thirdly, PMS is more expensive than O_3/H_2O_2, due to the higher amount of chemicals and temperature needed. Finally, the residual sulfate ions generated from the oxidant can have a negative impact on biological technologies, but this hypothesis needs to be further studied.

The study of by-products performed by chromatographic techniques, revealed that no toxic, complex and non-biodegradable by-products were identified after

treatment. The economic analysis revealed that H-AOPs are two orders of magnitude cheaper than S-AOPs, where peroxone proved to be the cheapest technology with a cost of treatment of 10 $ per $1m^3$ of the model effluent treated. When comparing both S-AOPs technologies, PMS, with a cost of treatment of 520 $ per $1m^3$, was cheaper than PS, with a cost of treatment of 1180 $ per $1m^3$. Classical H-AOPs can be described as cheap, easy and more effective technologies to implement for VOCs degradation. The results obtained in the AOPs studied are useful not only in refinery effluents, but also in other types of industrial effluents which contain these type of VOCs in their water matrix. Comparing the costs of treatment determined for model vs real effluent clearly present a drastic difference in calculated value. The effect of the aqueous matrix of the bitumen effluents is very strong. Conclusions formed on research made exclusively for model effluents are thus overestimated in terms of effectiveness of AOPs for treatment of such a type of effluents. Many studies published in the worldwide journals highlight very optimistic effects obtained for new types of processes (including the one based on S-AOPs) obtained for model, often single compound mixtures, without further confirmation of method performance at real case scenario. Research in this thesis proved the need and role of studies performed for real effluents as a crucial stage for method evaluation.

4.4 Integrated photocatalytic advanced oxidation system ($TiO_2/UV/O_3/H_2O_2$) for degradation of volatile organic compounds (Publication/Attachment No.5)

The research plan discussed so far performed for simulated refinery effluents from bitumen production revealed that the H-AOPs based on peroxone (O_3/H_2O_2) were more effective and cheaper than S-AOPs [51,56]. Thus, to attempt a higher degradation rate at a lower cost, a photolytic and photocatalytic technologies were performed using as external oxidants H-AOPs oxidants. The aim was to evaluate the performance of the photocatalytic and photolytic technologies in caustic model WW containing several VOCs to check if these technologies have a potential to be applied for highly polluted real effluents. In this part of the research, carboxylic acids were added to the model effluent, when comparing with the model effluent prepared in section 4.3, to check if the they could be degraded via advanced oxidation technologies. In addition, oxygen related VOCs are known to be toxic to the microorganisms commonly used in biological techniques, i.e., activated sludge. The oxidation of O-VOCs allows to further

treat this type of effluents by biological technologies, which are commonly used in several types of industries, providing an important contribution for further purification of the treated effluent before being discharge to the environment.

The studies performed in this part of the research aimed the evaluation of the efficiency of photolytic (UV) and photocatalytic (UV/TiO$_2$) processes based on three different classic oxidants, O$_3$, H$_2$O$_2$ and O$_3$/H$_2$O$_2$, on a model WW with variety of VOCs. The sole use of oxidants studied, revealed that O$_3$/H$_2$O$_2$ obtain the highest efficiency with 92% of total VOCs (t-VOCs) degradation and a COD reduction of 46%. The application of UV increased the degradation efficiency of H$_2$O$_2$ and O$_3$ based processes. O$_3$/UV obtained the highest efficiency of the photolytic processes, with 94% of total VOCs degradation after 100 min of treatment. The photocatalytic processes aided with the classic AOPs oxidants proved to induce a further increase in the treatment efficiency when comparing with the sole use of oxidants and photolytic processes. The TiO$_2$/UV/O$_3$/H$_2$O$_2$ process obtained the highest efficiency with 98% of total VOCs degradation after 100 min of treatment.

Detailed studies on the mechanisms of the VOCs degradation revealed interesting findings. A first interesting mechanism, that takes place during these processes, was related with the increased concentration of nitrobenzene and 2-nitrophenol can be explained by its generation from nitrate and nitrite group formed, which further react by radical pathway with the aromatic ring of benzene or phenol [57–59]. Diagram 1 exhibits the proposed mechanism.
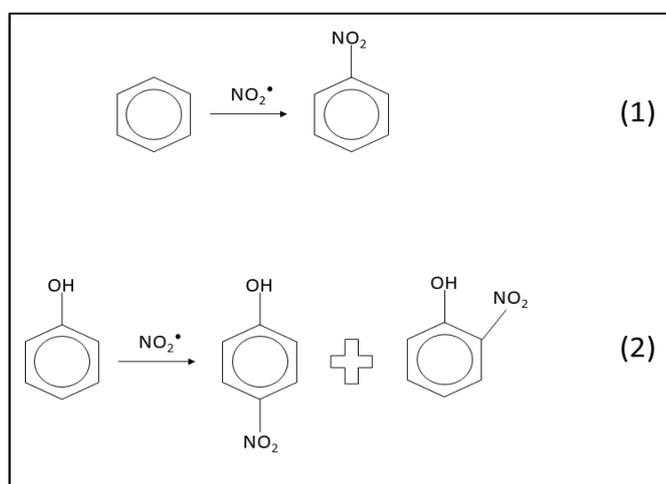
Diagram 1 – Proposed mechanism for the nitration of benzene and phenol rings to synthetize nitrobenzene (1) [57,58] and 2-nitrophenol/4-nitrophenol (2) [60].

This is possible due to nitrite ions formation from N_2 in the presence of H_2O_2. Even though this reaction occurs at a very low rate, only a small amount of nitrite is needed to trigger the reaction [60,61].

Second important mechanism affecting the by-products formation is related with the aromatic compounds degradation. It was proved that carboxylic acids can be by-products of oxidation of aromatic VOCs, by the mechanism of ring cleavage as proposed in diagram 2 [62].
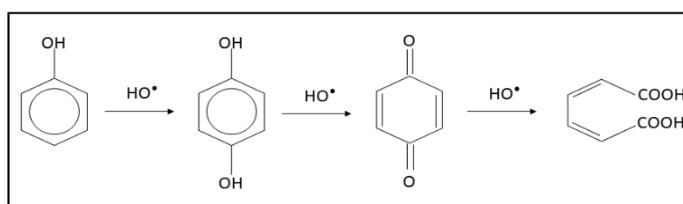
Diagram 2 – Proposed mechanism for the degradation of phenol by ring cleavage resulting in formation of carboxylic acids [62].

The third mechanism proposed that the carboxylic acids can also be degraded to shorter chain carboxylic acids aiming the full mineralization of the VOCs studied (diagram 3).

Diagram 3 – Proposed mechanism for the degradation of phenol to full mineralization. Degradation though carboxylation via HO⁺ reducing the carbon chain of the carboxylic acids to simpler acids and to CO_2 and H_2O [63–66]

This can be possible via hydroxylation and decarboxylation processes in the carbon chains, producing smaller chain acids like ketones or even aldehydes, which will step-by- step produce CO_2 and H_2O [63,64,66].

Even though $TiO_2/UV/O_3$ and $TiO_2/UV/O_3/H_2O_2$ achieved the highest t-VOCs degradation, they were not the most economical AOPs. These processes needed 100 and 60 min respectively to reach the mark of 80% of t-VOCs degradation, with a treatment cost of 25.7 and 17.4 $ per $1m^3$ treated. It was proved that a combination between UV and O_3 (UV/O_3) was the optimal AOP with a low cost of treatment – a 4 $ per 1 m^3 treated needing only 15 min of treatment to reach the milestone of 80% of t-VOCs degradation. However, to maximize the degradation of the VNCs, application of photocatalytic AOP based on TiO_2 is mandatory. In this case the cost of treatment increases to approx. 15 $ per $1m^3$ treated($TiO_2/UV/O_3$) to reach 80% of t-VOCs degradation after 60 min of treatment. The cost of treatment is lower when comparing with the sole use of the oxidant (17 $/m^3$), which proves the importance of the UV and TiO_2 in the advanced oxidation technologies. These technologies are promising at a large laboratory scale and able to be scale up to an industrial process scale in a real case scenario.

4.5 Synergistic effect of TiO_2 photocatalytic advanced oxidation processes in the treatment of refinery effluents from bitumen production (Publication/Attachment No. 6)

The photocatalytic processes can enhance the amount of $HO^{\bullet}$ produced and available, in order to react with the pollutants, present in the aqueous media. These radicals can increase the treatment efficiency and reduce the treatment cost of the target pollutant or WW when comparing with photolytic and sole use of oxidants. These statements, described in section 1, were proved in the research performed in previous section, treating a simulated refinery effluents from bitumen production [44]. To prove such statements in a real case scenario, post oxidative effluents from bitumen production were treated by photolytic and photocatalytic processes and compared with the sole use of oxidants. Section 4.1. and 4.2. revealed that the treatment of post oxidative effluents from bitumen production using classic AOPs oxidants [51] and sulfate radical based AOPs oxidants [56], achieved effective degradation of the VOCs and oxidation of the sulfide ions, a decrease in the pH to values close to neutral from the oxidation and its oxidants, along with partial COD and BOD_5 decrease.

To study the possibility of improvement of the degradation rate of the compounds present in the effluents, a photocatalytic based AOPs were studied. Thus, the aim of this part of the studies was to understand the synergy and the performance of processes based on addition of the TiO_2 and application of UV light to already studied H-AOPs. A comparison between classic AOPs oxidants (O_3, H_2O_2, O_3/H_2O_2), photolytic AOPs (O_3/UV, H_2O_2/UV, $O_3/H_2O_2/UV$) and photocatalytic AOPs ($TiO_2/UV/O_3$, $TiO_2/UV/H_2O_2$, $TiO_2/UV/O_3/H_2O_2$) was performed for treatment of the post oxidative effluents from bitumen production at their natural conditions of formation (no pH and temperature correction).

The experiments revealed that the developed technology can be implemented in two alternative scenarios – one when the goal is to maximize the degradation effectiveness and second one where the main goal is to degrade sulfide ions allowing to perform further treatment in a corrected pH values to acidic or neutral instead of the primary strongly basic pH.

A good synergism was confirmed for the approach of combining UV and TiO_2 with the oxidants studied and UV with the oxidants studied. A combined process based on ozonation performed in presence of TiO_2 and UV light obtained the highest synergism. It was proved that the matrix of the real WW studied influences negatively the degradation rate of the generality of the VOCs studied (reaction rate constant values) comparing to treatment of model effluents.

In all processes studied the sulfide ions were oxidized completely in the first 30 min of treatment, avoiding the risk of the H_2S generation and enabling the use of other types of AOPs effective at neutral or acidic pH values. The biodegradability of the treated effluents did not change significantly with values around 0.3 and 0.4 of the treated effluents, which can be considered as biodegradable. O-VOCs like 1-propanol, furfural, cyclohexanol and cyclohexanone were more problematic to be degraded via $HO^{\bullet}$ and were not degraded bellow the LOD in any process studied.

The addition of the TiO_2 decreases the operational cost of the O_3 and O_3/H_2O_2 related technologies. The optimal and most economic process was $TiO_2/UV/O_3/H_2O_2$ and is based on low consumption of oxidant (r_{ox} of 0.28) and 500 mg/L of TiO_2 with 38% of COD reduction, 84% of t-VOCs degradation and an operation cost of 126 $ per 1 m^3 of treated effluent. Obtained effectiveness, exceeds by over 30% a theoretical, based on the r_{ox}, value of COD reduction, proving the importance of the photocatalytic technology. The experiments proved that the selection of the optimal process differs from model and real effluents. The optimal processes to treat model WW, due to the less complex water matrix, were simpler AOPs (photolytic AOP), when comparing with photocatalytic processes. The high amount of salts (conductivity), turbidity, sulfide ions and presence of $HO^{\bullet}$ scavengers like carbonates and bicarbonates affected the treatment efficiency of the real effluents. This may lead to contradictory conclusions and consequently can cause a bad decision in the implementation of the technology in a real case scenario. If the goal is to degrade only the sulfide ions, the cheapest in the comparison is the H_2O_2/UV process with total cost of only 6.4 $ per 1m^3 of treated effluent, with a decrease of COD and t-VOCs by 19% and 24% respectively.

These technologies are promising as a pre-treatment stage before a second chemical treatment process at corrected pH value or biological treatment stage. Toxic compounds as well as sulfide ions were effectively degraded, thus the probability of H_2S formation

as well as emission of malodor compounds was avoided. Therefore, such technologies should be further studied at a pilot scale in a real case scenario for complete evaluation of the proposed solution. Besides the future studies on this technology at pilot scale treatment unit, the research should also include studies on implementation of available AOPs based on modified titanium dioxide with increased effectiveness in visible light, allowing successive lowering of the costs associated with energy consumption. A comparison studies between the catalyst and the energy cost of such process are still scarce and remains as an open research field. Future investigations should be focused on this aspect.

5. Dissertation summary

The aim of this dissertation was to conduct a research in different types of AOPs at alkaline conditions and reveal the optimal and economic AOP for the treatment of post oxidative effluents from bitumen production The studied technologies included non-catalytic, photolytic and photocatalytic processes using "classic" and sulfate related AOP oxidants, i.e. O_3, H_2O_2, O_3/H_2O_2, $Na_2S_2O_8$ and $KHSO_5$. The main conclusions of this dissertation are described as follows:

1) The O_3 and O_3/H_2O_2 related AOPs were more effective in treatment of the post oxidative effluents from bitumen production comparing to H_2O_2 related processes.

2) Sulfate radicals based AOPs (PS and PMS) exhibited higher treatment efficiency than H_2O_2 processes and comparable efficiency to O_3 and O_3/H_2O_2 processes. The persulfates used in these studies were activated by heat provided by the natural temperature of the effluents studied (40°C). Nevertheless, S-AOPs have higher demand of oxidant amount, which makes them not economical when applying at an industrial scale.

3) There is a need for further research in the area of the persulfate and peroxymonosulfate based AOPs in order to reduce the amount of oxidant needed to reach similar effectiveness comparing to H-AOPs and also to attempt to reduce the price of both chemicals. Current literature reports several new achievements in the field of persulfates activation but this reports relate only to simulated – one (or a few) –compounds containing effluents.

4) Sulfide ions were effectively oxidized in all types of technologies studied in the first 30 min of treatment. H_2O_2/UV was the best processes to degrade the sulfide ions with a treatment cost of 6.4 \$ per $1m^3$ of treated effluent. This can allow to reduce the pH, after oxidation of sulfide ions, to neutral or acidic conditions where the usage of other types of AOPs like Fenton is possible to reach higher purification of the treated effluents.

5) Oxygen containing VOCs (O-VOCs), including phenolic compounds, were effectively degraded in all types of AOPs studied. This is an important outcome since these compounds are toxic to microorganisms. Also the VSCs were completely degraded which ensures a good deodorization of the effluents.

On the opposite direction, VNCs were the type of VOCs that revealed to be more persistent to degradation. Nitrobenzene and 2-nitrophenol can be generated during radical reactions with compounds having aromatic ring in their structure (such as BTEXs or phenol), in the presence of nitrogen containing inorganic anions. Compounds like furfural, acetaldehyde, and 2-ethyl-1-hexylamine revealed to be by-products of oxidation formed during the treatment. Nevertheless, O_3 related AOPs were the best processes to degrade this group of compounds. In addition, it was proved that carboxylic acids are by-products formed by the mechanisms of ring opening of aromatic compounds during their oxidation by radical pathway and they can also be degraded via advanced oxidation technologies.

6) Regarding the simulated refinery effluents from bitumen production, in the sole use of the oxidants, H-AOPs were more effective and economical than S-AOPs. In addition, simpler combination of AOPs like O_3/UV revealed to be the most effective and economical processes to treat simulated refinery effluents from bitumen production, obtaining 94% of t-VOCs degradation, 43% of COD reduction with a cost of 4 $ per 1 m^3 of treated effluent.

7) A good synergy was achieved when combining UV and TiO_2 with the oxidants and UV with the oxidants in post oxidative effluents from bitumen production. The optimal and most economic process was TiO_2/UV/O_3/H_2O_2 which is based on low consumption of oxidant (r_{ox} of 0.28) and 500 mg/L of TiO_2, with 38% of COD reduction, 84% of t-VOCs degradation and an operation cost of 126 $ per 1 m^3 of treated effluent. The obtained COD reduction exceeds by over 30% the theoretical value, based on the r_{ox}, proving the importance of the photocatalytic technology.

8) When comparing both types of wastewater studied, it was clear that simpler AOPs, i.e. the combination of UV and O_3, were the optimal to degrade the simulated WW. When treating the refinery effluents from bitumen production, more complex AOPs (combination of UV, TiO_2 and peroxone) were mandatory to achieved effective treatment, which consequently increased its cost. The water matrix of the real effluents played a crucial role, due to its complexity. The presence of $HO^{\bullet}$ scavengers like carbonates and bicarbonates, high amount of salts and sulfur ions affected the amount of oxidant and

radicals available to degrade the compounds and the high turbidity affected the effectiveness of the UV and TiO_2 on the combined processes.

9) Referring to the economical point of view, classic AOPs proved to be cheaper than sulfate related AOPs. Moreover, the application of UV radiation combined with TiO_2 with the oxidants proved to reduce the cost of operation, proving the usefulness of photocatalytic and photolytic processes in treatment of such a type of industrial effluents.

10) The AOPs studied proved to reach partial COD and BOD_5 reduction, along with effective VOCs degradation. The studies revealed that the effluents contain several aliphatic and cyclic hydrocarbons, dissolved in aqueous phase, that are not effectively oxidized via AOPs. Therefore, part of the COD and BOD_5 is related with the presence of these compounds and total degradation of the COD and BOD_5 is not possible. However, presence of hydrocarbon type compounds is not an issue in respect to characteristic of refinery biological treatment plant. The type of activated sludge is effective in degradation of these type of compounds. The usefulness of developed processes related to effective removal of groups of compounds that are toxic to this type of activated sludge (oxygen containing VOCs) as well as malodorous compounds (sulfur containing VOCs as well as sulfide ions) allows to perform the biological treatment in commonly used open-reservoirs. Thus the developed processes are promising as a pre-treatment stage before the secondary/biological stage.

11) The technologies studied can be used in two different scenarios – one when the goal is to maximize the degradation effectiveness and second one where the main goal is to oxidize sulfide ions allowing to perform further treatment in a corrected pH values from the primary strongly basic pH.

12) The main important effects of these studies are a promising results that enables the possibility to further scale-up the process to a pilot scale studies in a real case scenario.

References

[1]   R. Hernandez, M. Zappi, J. Colucci, R. Jones, Comparing the performance of various advanced oxidation processes for treatment of acetone contaminated water, J. Hazard. Mater. 92 (2002) 33–50. doi:10.1016/S0304-3894(01)00371-5.

[2]   K. Ayoub, E.D. van Hullebusch, M. Cassir, A. Bermond, Application of advanced oxidation processes for TNT removal: A review, J. Hazard. Mater. 178 (2010) 10–28. doi:10.1016/j.jhazmat.2010.02.042.

[3]   S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042. doi:10.1016/S0043-1354(01)00301-3.

[4]   L.F. Liotta, M. Gruttadauria, G. Di Carlo, G. Perrini, V. Librando, Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity, J. Hazard. Mater. 162 (2009) 588–606. doi:10.1016/j.jhazmat.2008.05.115.

[5]   S. Popiel, T. Nalepa, D. Dzierzak, R. Stankiewicz, Z. Witkiewicz, Rate of dibutylsulfide decomposition by ozonation and the O3/H2O2 advanced oxidation process, J. Hazard. Mater. 164 (2009) 1364–1371. doi:10.1016/j.jhazmat.2008.09.049.

[6]   A.L.N. Mota, L.F. Albuquerque, L.T.C. Beltrame, O. Chiavone-Filho, A.M. Jr., C.A.O. Nascimento, Advanced oxidation processes and their application in the petroleum industry: a review, Brazilian J. Pet. Gas. 2 (2009) 122–142. http://www.portalabpg.org.br/bjpg.

[7]   M. Litter, Introduction to Photochemical Advanced Oxidation Processes for Water Treatment, in: P. Boule, D.W. Bahnemann, P.K.J. Robertson (Eds.), Environ. Photochem. Part II, Springer Berlin Heidelberg, 2005: pp. 325–366. doi:10.1007/b89482.

[8]   W.H. Glaze, J. Kangt, Advanced Oxidation Processes . Test of a Kinetic Model for the Oxidation of Organic Compounds with Ozone and Hydrogen Peroxide in a Semibatch Reactor, Ind. Eng. Chem. Res. 28 (1989) 1580–1587. doi:10.1021/ie00095a002.

[9]   T. Miichi, N. Hayashi, S. Ihara, S. Satoh, C. Yamabe, Generation of Radicals using Discharge inside Bubbles in Water for Water Treatment, Ozone Sci. Eng. 24 (2002) 471–477. doi:10.1080/01919510208901636.

[10] D. Shahidi, R. Roy, A. Azzouz, Advances in catalytic oxidation of organic pollutants – Prospects for thorough mineralization by natural clay catalysts, Appl. Catal. B Environ. 174–175 (2015) 277–292. doi:10.1016/j.apcatb.2015.02.042.

[11] A.S. Ameta R, Kumar A, Punjabi PB, Advanced oxidation Processes: Basics and Principles, in: F.S. Rao DG, Senthilkumar R, Anthony Byrne J (Ed.), Wastewater Treat. Adv. Process. Technol., 2013th ed., CRC Press and IWA publishing, USA, 2013: pp. 61–107. doi:10.1007/s13398-014-0173-7.2.

[12] J.M. Poyatos, M.M. Muñio, M.C. Almecija, J.C. Torres, E. Hontoria, F. Osorio, Advanced Oxidation Processes for Wastewater Treatment: State of the Art, Water. Air. Soil Pollut. 205 (2010) 187–204. doi:10.1007/s11270-009-0065-1.

[13] L.A. Ioannou, G.L. Puma, D. Fatta-Kassinos, Treatment of winery wastewater by physicochemical, biological and advanced processes: A review., J. Hazard. Mater. 286C (2014) 343–368. doi:10.1016/j.jhazmat.2014.12.043.

[14] B.H. Diya'uddeen, W.M.A.W. Daud, A.R. Abdul Aziz, Treatment technologies for petroleum refinery effluents: A review, Process Saf. Environ. Prot. 89 (2011) 95–105. doi:10.1016/j.psep.2010.11.003.

[15] A. Fakhru'l-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, J. Hazard. Mater. 170 (2009) 530–551. doi:10.1016/j.jhazmat.2009.05.044.

[16] M. Bahri, A. Mahdavi, A. Mirzaei, A. Mansouri, F. Haghighat, Integrated oxidation process and biological treatment for highly concentrated petrochemical effluents: A review, Chem. Eng. Process. - Process Intensif. 125 (2018) 183–196. doi:10.1016/j.cep.2018.02.002.

[17] A. Asghar, A.A. Abdul Raman, W.M.A. Wan Daud, Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: a review, J. Clean. Prod. 87 (2015) 826–838.

doi:10.1016/j.jclepro.2014.09.010.

[18] X. Liu, T. Zhang, Y. Zhou, L. Fang, Y. Shao, Degradation of atenolol by UV/peroxymonosulfate: Kinetics, effect of operational parameters and mechanism, Chemosphere. 93 (2013) 2717–2724. doi:10.1016/j.chemosphere.2013.08.090.

[19] T. Garoma, M.D. Gurol, O. Osibodu, L. Thotakura, Treatment of groundwater contaminated with gasoline components by an ozone/UV process., Chemosphere. 73 (2008) 825–31. doi:10.1016/j.chemosphere.2008.06.061.

[20] M. V. Bagal, P.R. Gogate, Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: A review, Ultrason. Sonochem. 21 (2014) 1–14. doi:10.1016/j.ultsonch.2013.07.009.

[21] A. Pintar, Catalytic processes for the purification of drinking water and industrial effluents, Catal. Today. 77 (2003) 451–465. doi:10.1016/S0920-5861(02)00385-1.

[22] J. Sipma, A. Svitelskaya, B. Van Der Mark, L.W. Hulshoff, G. Lettinga, C.J.N. Buisman, A.J.H. Janssen, Potentials of biological oxidation processes for the treatment of spent sulfidic caustics containing thiols, Water Res. 38 (2004) 4331–4340. doi:10.1016/j.watres.2004.08.022.

[23] N. Azbar, T. Yonar, K. Kestioglu, Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent, Chemosphere. 55 (2004) 35–43. doi:10.1016/j.chemosphere.2003.10.046.

[24] G. Boczkaj, M. Kamiński, A. Przyjazny, Process Control and Investigation of Oxidation Kinetics of Postoxidative Effluents Using Gas Chromatography with Pulsed Flame Photometric Detection (GC-PFPD), Ind Eng Chem Res. 49 (2010) 12654–12662. doi:10.1021/ie100939x.

[25] S.B. Kim, S.C. Hong, Kinetic study for photocatalytic degradation of volatile organic compounds in air using thin film TiO2 photocatalyst, Appl. Catal. B Environ. 35 (2002) 305–315. doi:10.1016/S0926-3373(01)00274-0.

[26] W. Li, Q. Niu, H. Zhang, Z. Tian, Y. Zhang, Y. Gao, Y.Y. Li, O. Nishimura, M. Yang, UASB treatment of chemical synthesis-based pharmaceutical wastewater containing rich organic sulfur compounds and sulfate and associated microbial characteristics, Chem. Eng. J. 260 (2014) 55–63. doi:10.1016/j.cej.2014.08.085.

[27] X.A. Ning, J.Y. Wang, R.J. Li, W. Bin Wen, C.M. Chen, Y.J. Wang, Z.Y. Yang, J.Y. Liu, Fate of volatile aromatic hydrocarbons in the wastewater from six textile dyeing wastewater treatment plants, Chemosphere. 136 (2015) 50–55. doi:10.1016/j.chemosphere.2015.03.086.

[28] A. Rigol, A. Latorre, S. Lacorte, D. Barceló, Determination of toxic compounds in paper-recycling process waters by gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry, J. Chromatogr. A. 963 (2002) 265–275. doi:10.1016/S0021-9673(02)00232-7.

[29] H.-H. Cheng, C.-C. Hsieh, Removal of Aromatic Volatile Organic Compounds in the Sequencing Batch Reactor of Petroleum Refinery Wastewater Treatment Plant, CLEAN - Soil, Air, Water. 41 (2013) 765–772. doi:10.1002/clen.201100112.

[30] I.A. Alaton, I.A. Balcioglu, D.W. Bahnemann, Advanced oxidation of a reactive dyebath effluent: Comparison of O3, H2O2/UV-C and TiO2/UV-A processes, Water Res. 36 (2002) 1143–1154. doi:10.1016/S0043-1354(01)00335-9.

[31] G. Boczkaj, A. Fernandes, Wastewater treatment by means of Advanced Oxidation Processes at basic pH conditions: A review, Chem. Eng. J. 320 (2017) 608–633. doi:10.1016/j.cej.2017.03.084.

[32] O. Spalek, J. Balej, I. Paseka, Kinetics of the decomposition of hydrogen peroxide in alkaline solutions, J. Chem. Soc. Faraday Trans. 78 (1982) 2349. doi:10.1039/f19827802349.

[33] P. Puspita, F. Roddick, N. Porter, Efficiency of sequential ozone and UV-based treatments for the treatment of secondary effluent, Chem. Eng. J. 268 (2015) 337–347. doi:10.1016/j.cej.2015.01.077.

[34] H. Zangeneh, a. a L. Zinatizadeh, M. Feizy, A comparative study on the

performance of different advanced oxidation processes (UV/O3/H2O2) treating linear alkyl benzene (LAB) production plant's wastewater, J. Ind. Eng. Chem. 20 (2014) 1453–1461. doi:10.1016/j.jiec.2013.07.031.

[35]   S. Khan, X. He, H.M. Khan, D. Boccelli, D.D. Dionysiou, Efficient degradation of lindane in aqueous solution by iron (II) and/or UV activated peroxymonosulfate, J. Photochem. Photobiol. A Chem. 316 (2016) 37–43. doi:10.1016/j.jphotochem.2015.10.004.

[36]   A. Rastogi, S.R. Al-Abed, D.D. Dionysiou, Sulfate radical-based ferrous–peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems, Appl. Catal. B Environ. 85 (2009) 171–179. doi:10.1016/j.apcatb.2008.07.010.

[37]   W.-D. Oh, Z. Dong, T.-T. Lim, Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: Current development, challenges and prospects, Appl. Catal. B Environ. 194 (2016) 169–201. doi:10.1016/j.apcatb.2016.04.003.

[38]   A. Long, Y. Lei, H. Zhang, Degradation of Toluene by a Selective Ferrous Ion Activated Persulfate Oxidation Process, Ind. Eng. Chem. Res. 53 (2014) 1033–1039. doi:10.1021/ie402633n.

[39]   Y. Deng, C.M. Ezyske, Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate, Water Res. 45 (2011) 6189–6194. doi:10.1016/j.watres.2011.09.015.

[40]   O.S. Furman, A.L. Teel, R.J. Watts, Mechanism of base activation of persulfate, Environ. Sci. Technol. 44 (2010) 6423–6428. doi:10.1021/es1013714.

[41]   C. Qi, X. Liu, J. Ma, C. Lin, X. Li, H. Zhang, Activation of peroxymonosulfate by base: Implications for the degradation of organic pollutants., Chemosphere. 151 (2016) 280–288. doi:10.1016/j.chemosphere.2016.02.089.

[42]   S.-Y. Lee, S.-J. Park, TiO2 photocatalyst for water treatment applications, J. Ind. Eng. Chem. 19 (2013) 1761–1769. doi:10.1016/j.jiec.2013.07.012.

[43] M. Cristina Yeber, J. Rodríguez, J. Freer, N. Durán, H. D. Mansilla, Photocatalytic degradation of cellulose bleaching effluent by supported TiO2 and ZnO, Chemosphere. 41 (2000) 1193–1197. doi:10.1016/S0045-6535(99)00551-2.

[44] A. Fernandes, M. Gągol, P. Makoś, J.A. Khan, G. Boczkaj, Integrated photocatalytic advanced oxidation system (TiO 2 /UV/O 3 /H 2 O 2)for degradation of volatile organic compounds, Sep. Purif. Technol. 224 (2019) 1–14. doi:10.1016/j.seppur.2019.05.012.

[45] O. Gimeno, F.J. Rivas, F.J. Beltrán, M. Carbajo, Photocatalytic ozonation of winery wastewaters, J. Agric. Food Chem. 55 (2007) 9944–9950. doi:10.1021/jf072167i.

[46] C. Chen, J. Yu, B.A. Yoza, Q.X. Li, G. Wang, A novel "wastes-treat-wastes" technology: role and potential of spent fluid catalytic cracking catalyst assisted ozonation of petrochemical wastewater., J. Environ. Manage. 152 (2015) 58–65. doi:10.1016/j.jenvman.2015.01.022.

[47] J. Saien, H. Nejati, Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild conditions, J. Hazard. Mater. 148 (2007) 491–495. doi:10.1016/j.jhazmat.2007.03.001.

[48] W.Z. Khan, I. Najeeb, M. Tuiyebayeva, Z. Makhtayeva, Refinery wastewater degradation with titanium dioxide, zinc oxide, and hydrogen peroxide in a photocatalytic reactor, Process Saf. Environ. Prot. 94 (2015) 479–486. doi:10.1016/j.psep.2014.10.007.

[49] P. Stepnowski, E.M. Siedlecka, P. Behrend, B. Jastorff, Enhanced photo-degradation of contaminants in petroleum refinery wastewater, Water Res. 36 (2002) 2167–2172. doi:10.1016/S0043-1354(01)00450-X.

[50] J.J. Rueda-Márquez, I. Levchuk, I. Salcedo, A. Acevedo-Merino, M.A. Manzano, Post-treatment of refinery wastewater effluent using a combination of AOPs (H2O2 photolysis and catalytic wet peroxide oxidation) for possible water reuse. Comparison of low and medium pressure lamp performance., Water Res. 91 (2016) 86–96. doi:10.1016/j.watres.2015.12.051.

[51]   G. Boczkaj, A. Fernandes, P. Makoś, Study of Different Advanced Oxidation Processes for Wastewater Treatment from Petroleum Bitumen Production at Basic pH, Ind. Eng. Chem. Res. 56 (2017) 8806–8814. doi:10.1021/acs.iecr.7b01507.

[52]   B.A. Wols, C.H.M. Hofman-Caris, D.J.H. Harmsen, E.F. Beerendonk, Degradation of 40 selected pharmaceuticals by UV/H2O2, Water Res. 47 (2013) 5876–5888. doi:10.1016/j.watres.2013.07.008.

[53]   M. Goel, H. Hongqiang, A.S. Mujumdar, M.B. Ray, Sonochemical decomposition of volatile and non-volatile organic compounds - A comparative study, Water Res. 38 (2004) 4247–4261. doi:10.1016/j.watres.2004.08.008.

[54]   Y.-S. Shen, Y. Ku, Treatment of gas-phase volatile organic compounds (VOCs) by the process, Chemosphere. 38 (1999) 1855–1866. doi:10.1016/S0045-6535(98)00400-7.

[55]   Z. Chen, X. Yu, X. Huang, S. Zhang, Prediction of reaction rate constants of hydroxyl radical with organic compounds, J. Chil. Chem. Soc. 59 (2014) 2252–2259. doi:10.4067/S0717-97072014000100003.

[56]   A. Fernandes, P. Makos, G. Boczkaj, Treatment of bitumen post oxidative effluents by sulfate radicals based advanced oxidation processes (S-AOPs) under alkaline pH conditions, J. Clean. Prod. 195 (2018) 374–384. doi:10.1016/j.jclepro.2018.05.207.

[57]   A. Fernandes, P. Makoś, J.A. Khan, G. Boczkaj, Pilot scale degradation study of 16 selected volatile organic compounds by hydroxyl and sulfate radical based advanced oxidation processes, J. Clean. Prod. 208 (2019) 54–64. doi:10.1016/j.jclepro.2018.10.081.

[58]   D. Borghesi, D. Vione, V. Maurino, C. Minero, Transformations of Benzene Photoinduced by Nitrate Salts and Iron Oxide, J. Atmos. Chem. 52 (2005) 259–281. doi:10.1007/s10874-005-5304-2.

[59]   D. Vione, V. Maurino, C. Minero, M. Lucchiari, Nitration and hydroxylation of benzene in the presence of nitrite / nitrous acid in aqueous solution,

Chemosphere. 56 (2004) 1049–1059. doi:10.1016/j.chemosphere.2004.05.027.

[60]   D. Vione, V. Maurino, C. Minero, E. Pelizzetti, Phenol photonitration upon UV irradiation of nitrite in aqueous solution I: Effects of oxygen and 2-propanol, Chemosphere. 45 (2001) 893–902. doi:10.1016/S0045-6535(01)00035-2.

[61]   A.E. Gekhman, I.P. Stolyarov, A.F. Shestakov, A.E. Shilov, I.I. Moiseev, Oxidation of molecular nitrogen with hydrogen peroxide *, Russ.Chem.Bull., Int.Ed. 52 (2003) 768–770. doi:10.1023/A:1023956100890.

[62]   S. Soltan, H. Jafari, S. Afshar, O. Zabihi, Enhancement of photocatalytic degradation of furfural and acetophenone in water media using nano-TiO2-SiO2 deposited on cementitious materials, Water Sci. Technol. 74 (2016) 1689–1697. doi:10.2166/wst.2016.343.

[63]   H. Suzuki, S. Araki, H. Yamamoto, Evaluation of advanced oxidation processes (AOP) using O3, UV, and TiO2 for the degradation of phenol in water, J. Water Process Eng. 7 (2015) 54–60. doi:10.1016/j.jwpe.2015.04.011.

[64]   V.S. Mohite, M.A. Mahadik, S.S. Kumbhar, Y.M. Hunge, J.H. Kim, A. V. Moholkar, K.Y. Rajpure, C.H. Bhosale, Photoelectrocatalytic degradation of benzoic acid using Au doped TiO2thin films, J. Photochem. Photobiol. B Biol. 142 (2015) 204–211. doi:10.1016/j.jphotobiol.2014.12.004.

[65]   B. Roig, C. Gonzalez, O. Thomas, Monitoring of phenol photodegradation by ultra v iolet spectroscopy, Spectrochim. Acta Part A. 59 (2003) 303–307. doi:10.1016/S1386-1425(02)00172-5.

[66]   M.H.M.T. Assumpção, R.F.B. De Souza, R.M. Reis, R.S. Rocha, J.R. Steter, P. Hammer, I. Gaubeur, M.L. Calegaro, M.R. V Lanza, M.C. Santos, Low tungsten content of nanostructured material supported on carbon for the degradation of phenol, Appl. Catal. B Environ. 142–143 (2013) 479–486. doi:10.1016/j.apcatb.2013.05.024.

List of Scientific achievements

Main Publications:

1. **A. Fernandes**, P. Makoś, Z. Wang, G. Boczkaj, Synergistic effect of TiO2 photocatalytic advanced oxidation processes in the treatment of refinery effluents from bitumen production, Chem. Eng. J. 391 (2020) 123488. (**IF 10.652; Q1 - Engineering, Chemical; Engineering, Environmental**)

2. **A. Fernandes**, M. Gągol, P. Makoś, J.A. Khan, G. Boczkaj, Integrated photocatalytic advanced oxidation system (TiO 2/UV/O3/H2O2) for degradation of volatile organic compounds, Sep. Purif. Technol. 224 (2019) 1–14. (**IF 5.774; Q1 - Engineering, Chemical**)

3. **A. Fernandes**, P. Makoś, J.A. Khan, G. Boczkaj, Pilot scale degradation study of 16 selected volatile organic compounds by hydroxyl and sulfate radical based advanced oxidation processes, J. Clean. Prod. 208 (2019) 54–64 (**IF 7.246; Q1 - Engineering, Environmental; Environmental Sciences**).

4. **A. Fernandes**, P. Makoś, G. Boczkaj, Treatment of bitumen post oxidative effluents by sulfate radicals based advanced oxidation processes (S-AOPs) under alkaline pH conditions. J. Clean. Prod. 195 (2018) 374–384 (**IF 6.40; Q1 - Engineering, Environmental; Environmental Sciences**)

5. G. Boczkaj, **A. Fernandes**, Wastewater treatment by means of Advanced Oxidation Processes at basic pH conditions: A review, Chem. Eng. J. 320 (2017) 608–633. (**IF 6.22; Q1- Engineering, Chemical; Engineering, Environmental**)

6. G. Boczkaj, **A. Fernandes,** P. Makoś, Study of Different Advanced Oxidation Processes for Wastewater Treatment from Petroleum Bitumen Production at Basic pH, Ind. Eng. Chem. Res. 56 (31) (2017) 56 (31), pp 8806–8814. (**IF 3.141; Q1 - Engineering, Chemical)**

Other publications

1. **A.Fernandes**, G. Boczkaj, J.Głazowska, R. Tomczak-Wandzel, M. Kamiński, Comparison of Ozonation and Evaporation as Treatment Methods of Recycled Water for Bioethanol Fermentation Process, Waste Biomass. Valor. 9 (2018). 1141-1149. (**IF 2.235; Q2 - Environmental Sciences**)

2. P. Makoś, **A. Fernandes**, G. Boczkaj, Method for the determination of carboxylic acids in industrial effluents using dispersive liquid-liquid microextraction with injection port derivatization gas chromatography-mass spectrometry, J. Chromatogr. A 1555 (2017) 10-19. (**IF 3.72; Q1 – Chemistry, Analytical**)

3. P. Makoś, **A. Fernandes**, A. Przyjazny, G. Boczkaj, Sample preparation procedure using extraction and derivatization of carboxylic acids from aqueous

samples by means of deep eutectic solvents for gas chromatographic-mass spectrometric analysis. J. Chromatogr. A 1555 (2018) 10-19. (**IF 3.86; Q1 – Chemistry, Analytical**)

4. P. Makoś, **A. Fernandes**, G. Boczkaj, Method for the simultaneous determination of monoaromatic and polycyclic aromatic hydrocarbons in industrial effluents using dispersive liquid–liquid microextraction with GC–MS. *J. Sep. Sci. 39* (2018) 2360-2367. (**IF 2.52; Q2– Chemistry, Analytical**)

5. G. Boczkaj, P. Makoś, **A. Fernandes**, A. Przyjazny, New procedure for examination of degradation of volatile organonitrogen compounds during treatment of industrial effluents. *J. Sep. Sci.*00 (2017) 1-9. (**IF 2.41; Q2– Chemistry, Analytical**)

6. G. Boczkaj, P. Makoś, **A. Fernandes**, A. Przyjazny, A new procedure for control of treatment of industrial effluents to remove volatile organosulfur compounds. *J. Sep. Sci. 39* (2016) 3946–3956. (**IF 2.56; Q2– Chemistry, Analytical**)

Book chapters:

1. G. Boczkaj, **A. Fernandes**, M. Gagol, Studies on treatment of bitumen effluents by means of Advanced Oxidation Processes (AOPs) in basic pH conditions, Frontiers International Conference on Wastewater Treatment (FICWTM), 331-336, Springer, 2017.

Conferences presentations/posters:

1. G. Boczkaj, **A. Fernandes**, M. Gagol, Studies on treatment of bitumen effluents by means of Advanced Oxidation Processes (AOPs) in basic pH conditions, Frontiers International Conference on Wastewater Treatment (FICWTM), Palermo, Italy, 21–24.05.2017.

2. **A. Fernandes**, P. Makoś, G. Boczkaj, Study and optimization of different Advanced Oxidation Processes in the treatment of petroleum bitumens wastewater at natural conditions, 1st International Conference on Sustainable Water Processing, Sitges, Hiszpania, 11-14.09.2016.

3. **A. Fernandes**, G. Boczkaj, Wastewater treatment by means of Advanced Oxidation Processes at basic pH conditions: A review, 1st International Conference on Sustainable Water Processing, Sitges, Hiszpania, 11-14.09.2016.

4. M. Momotko, N. Filipowicz, **A. Fernandes**, G. Boczkaj, H. Cieśliński, Novel phenol containing wastewater bioremediation using selected strains of psychrotolerant yeast, 1st International Conference on Sustainable Water Processing, Sitges, Hiszpania, 11-14.09.2016.

5. G. Boczkaj, N. Mazur, P. Makoś, **A. Fernandes**, Process control of volatile nitrogen-containing organic compounds (VNCs) degradation during wastewater treatment by means DLLME-GC-NPD, 22nd International Symposium on Separation Science, Toruń, 2016.

6. G. Boczkaj, P. Makoś, M. Momotko, D. Chruszczyk, **A. Fernandes**, Studies of VOC degradation using Advanced Oxidation Processes (AOP) by means of "GREEN" extraction method and GC-MS technique, 9th International Conference on Instrumental Methods of Analysis: Modern Trends and Applications, Kalamata, Grecja, 20 – 24.09.2015.
7. G. Boczkaj, P. Makoś, M. Momotko, D. Chruszczyk, **A. Fernandes**, Application of dynamic headspace and GC-MS technique for the determination of oxygenated volatile organic compounds in industrial wastewater, 9th International Conference on Instrumental Methods of Analysis: Modern Trends and Applications, Kalamata, Grecja, 20 – 24.09.2015.
8. P. Makoś, M. Momotko, D. Chruszczyk, **A. Fernandes**, G. Boczkaj, Application of gas chromatography to monitor the content of volatile organic compounds in industrial wastewater, EuroAnalysis 2015, Bordeaux, Francja, 06 – 10.09.2015.
9. P. Makoś, M. Momotko, D. Chruszczyk, **A. Fernandes**, G. Boczkaj, Application of DLLME-GC-MS and DLLME-GC-FPD for the determination of specific compounds from the group of volatile organic compounds in refinery effluents, EuroAnalysis 2015, Bordeaux, Francja, 06 – 10.09.2015.
10. P. Makoś, M. Momotko, D. Chruszczyk, **A. Fernandes**, G. Boczkaj, Determination of oxygenated volatile organic compounds in postoxidative effluents using DHS-GC-MS method, EuroAnalysis 2015, Bordeaux, Francja, 06 – 10.09.2015.
11. P. Makoś, **A. Fernandes**, G. Boczkaj, New procedure for efficiency evaluation of postoxidative wastewater treatment processes in the scope of phenols using DLLME-GC-MS, BIOTech Conference 2015, Gdańsk 26-28.08.2015.
12. P. Makoś, **A. Fernandes**, G. Boczkaj, Usefulness of dispersive liquid - liquid microextraction and gas chromatography coupled with flame photometric detector (DLLME-GC-FPD) for the determination of volatile sulphur compounds in postoxidative wastewater, BIOTech Conference 2015, Gdańsk 26-28.08.2015.
13. G. Boczkaj, P. Makoś, M. Momotko, D. Chruszczyk, **A. Fernandes**, Application of DLLME-GC-MS method in research of VOC degradation using advanced oxidation processes (AOP), 21ST International Symposium on Separation Science, Ljubljana, 30.06.-03.07.2015.

List of attachments/publications

Attachment/Publication No.1

G. Boczkaj, **A. Fernandes**, Wastewater treatment by means of Advanced Oxidation Processes at basic pH conditions: A review, Chem. Eng. J. 320 (2017) 608–633. DOI: 10.1016/j.cej.2017.03.084

Attachment /Publication No.2

G. Boczkaj, **A. Fernandes,** P. Makoś, Study of Different Advanced Oxidation Processes for Wastewater Treatment from Petroleum Bitumen Production at Basic pH, Ind. Eng. Chem. Res. 56 (31) (2017) 56 (31), pp 8806–8814. DOI: 10.1021/acs.iecr.7b01507

Attachment /Publication No.3

A. Fernandes, P. Makoś, G. Boczkaj, Treatment of bitumen post oxidative effluents by sulfate radicals based advanced oxidation processes (S-AOPs) under alkaline pH conditions. J. Clean. Prod. 195 (2018) 374–384. DOI: 10.1016/j.jclepro.2018.05.207

Attachment /Publication No.4

A. Fernandes, P. Makoś, J.A. Khan, G. Boczkaj, Pilot scale degradation study of 16 selected volatile organic compounds by hydroxyl and sulfate radical based advanced oxidation processes, J. Clean. Prod. 208 (2019) 54–64. DOI: 10.1016/j.jclepro.2018.10.081.

Attachment /Publication No.5

A. Fernandes, M. Gągol, P. Makoś, J.A. Khan, G. Boczkaj, Integrated photocatalytic advanced oxidation system (TiO 2/UV/O3/H2O2) for degradation of volatile organic compounds, Sep. Purif. Technol. 224 (2019) 1–14. DOI: 10.1016/j.seppur.2019.05.012.

Attachment /Publication No.6

A. Fernandes, P. Makoś, Z. Wang, G. Boczkaj, Synergistic effect of TiO2 photocatalytic advanced oxidation processes in the treatment of refinery effluents from bitumen production, Chem. Eng. J. 391 (2020) 123488. DOI: 10.1016/j.cej.2019.123488