UNIVERSITAT ROVIRA I VIRGILI

Application of Advanced Oxidation Processes in the Reclamation of Wastewaters from the Oil & Gas Sector

Hande Demir Duz

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Application of Advanced Oxidation Processes in the Reclamation of Wastewaters from the Oil & Gas Sector

Doctoral Thesis

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I STATE that the present study, entitled "Application of Advanced Oxidation Processes in the Reclamation of Wastewaters from the Oil & Gas Sector", presented by Hande Demir Duz for the award of the degree of Doctor, has been carried out under my supervision at the Chemical Engineering Department of this university.

Tarragona, 6th of July 2020

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SUMMARY

This thesis has been developed within two projects dealing with the reclamation of wastewater generated by the processing of oil & gas industry. The Integroil project (Horizon 2020), in which our research group (*Catheter*) at Universitat Rovira i Virgili, was one of the participants, aimed at water reuse in the oil & gas sector. Although the project included wide range of technologies to propose an integral treatment solution to the oil and gas sector, including upstream and downstream processes, the research parts that belong to Integroil project within this thesis (Chapters 3-4) deal with the treatment of downstream effluents.

For the treatment of downstream effluents, several photo-based and ozone-based advanced oxidation processes (AOPs) were assessed in detail starting from a synthetic refinery wastewater (SRW) with a complex composition. SRW was prepared with the typical organic and inorganic groups found in petroleum refinery effluents according to the literature, to simulate as much as possible the real effluents. Ultimately, this allowed obtaining more reliable information than using a one-component synthetic water. The initial results obtained with SRW allowed the treatment efficiencies to be compared with a stable effluent that has the same nature for all experiments, which would be unstable and changeable for real wastewater. Also, studying the effect of parameters such as the amounts of oxidants, pH and reaction time on SRW allowed understanding each treatment behaviour and establish the working ranges for application and further optimization in real refinery effluents. After the initial screening on SRW, the treatment performance of three different real wastewaters was investigated aiming at reaching the requirements for water reuse in the plant. The different effluents came from a petroleum refinery located in Turkey, one of which was collected after primary treatment while the other two were collected after secondary treatment. In the refineries, the treated water can be used for different purposes depending on the quality obtained after treatment. For the case refinery in this study, the total organic carbon (TOC) content needs to be below 15 mg/L and 4 mg/L for firewater and cooling water, respectively.

Among the applied photo-based treatments, although heterogeneous photo-catalysis conducted with TiO_2 and a combined process of heterogeneous photo-catalysis and photo-Fenton showed promising results for the treatment of the refinery effluents, photo-Fenton treatment revealed a superior effectiveness for application, both as a secondary and tertiary treatment, considering the improvements on TOC removal,

toxicity and biodegradability. Photo-Fenton as secondary treatment resulted as efficient as the biological treatment, presenting ca. 90% of chemical oxygen demand (COD) removal, getting final TOC values of ca. 20 mg/L. Moreover, a marked increase in the BOD_5/COD ratio from 0.38 to 0.83 was obtained, indicating an important improvement of biodegradability. That is, wastewater would be more easily treated by biological means after photo-Fenton as secondary treatment.

As a tertiary treatment, photo-Fenton process either with H_2O_2/COD=10 and $H_2O_2/Fe^{2+}=50$ or H_2O_2/COD=4 and $H_2O_2/Fe^{2+}=10$ provided a final TOC value <4 mg/L. This result reveals the possibility to reuse the effluent in the refinery plant, thus increasing the sustainability. However, besides the downstream wastewater treatment, the upstream wastewater treatment that was investigated in parallel within the Integroil project, regardless from the content of this thesis, agreed that ozone-based processes were more suitable for both upstream and downstream applications rather than photo-based treatments. Thus, ozone-based treatments were investigated as the possible solution to the refinery as tertiary treatment, to reach the final requirements for reuse and recycle purposes. Optimization studies were also conducted by experimental design. The screening tests by fractional factorial design performed on SRW revealed that the significant parameters for the treatment were ozone feed ratio, H_2O_2 amount and reaction time, while pH was found insignificant. Based on the box-Behnken, response surface methodology performed for an effluent collected after biological treatment, the significant parameters were optimized, being the ozone ratio of 0.9 g/h, H_2O_2 amount of 47 mg/L and 60 min duration. However, in case of increasing the H_2O_2 amount to 80 mg/L, the duration can be minimized to 37.5 min decreasing the energy and reagent consumption costs by a 37%, and reaching a final total organic carbon (TOC) under 4 mg/L, which is the target for reuse possibilities.

Chapters 5 and 6 are related to the treatment of oil sands process water (OSPW) currently stored in tailing ponds covering 220 km^2 of the land because of the zero-discharge policy in Alberta region, in Canada. This research is part of a second project, Resilient Reclaimed Land and Water Systems leaded by Dr. Gamal El-Din's at University of Alberta. The accumulation of OSPW in tailing ponds is becoming a serious problem due to the unknown future of its management, as well as the increasing public concern about its environmental effects including the wildlife around the tailing pond. Firstly, catalytic ozone-based and UV-based treatments with different oxidants and operating pH were compared. As catalysts, the catalytic activities of granular activated carbon-based materials previously doped with heteroatom (N or N/S) and Fe (III) were investigated, which were rarely studied for the treatment of OSPW. A catalyst selection was performed based on the fractional factorial design for catalytic ozonation of a synthetic water. Afterwards, the selected materials were investigated further for the treatment of real OSPW by initially ozone-based treatments, afterwards for photo-based treatments. Also, UV/Fenton treatment was considered as an effective method for removing the organic components present in the effluent that cause acute toxicity. Obtained results showed that the treatment efficiency by the AOPs in terms of mineralization was in the order of UV/peroxymonosulfate (PMS) < O_3 < UV/H_2O_2 < UV/Fenton, where dissolved organic carbon (DOC) removal was up to 14%, 21%, 31% and 64%, respectively. The best improvement in acute toxicity tested with *V. fischeri* was achieved by UV/Fenton, although the ozone treatments also led to great toxicity reduction. This was in agreement with the reduced concentrations of naphthenic acids, which are considered as the main contributors to the toxicity of OSPW. It was observed that transformation of the toxic compounds rather than mineralization took place for the ozone-based treatment.

Afterwards, another study of the ozone-based combined AOPs including H_2O_2 and UV-C to achieve mineralization was performed, while also aiming at reduction in toxicity arising from the organic components, including naphthenic acids present in the effluent. In this part, O_3/H_2O_2 process was tested considering the previous experiences obtained within the Integroil project. Additionally, UV-C combination to O_3-based treatments was studied for the first time to treat OSPW. Obtained results showed that considerably high DOC removals were obtained after 90 min treatment by O_3, O_3/H_2O_2, UV-C/O_3 and UV-C/O_3/H_2O_2 with a 1.8 g/h O_3 production rate, which resulted in 45%, 84%, 84% and 98%, respectively. All the treatments removed significantly the acute toxicity on *Vibrio fischeri*. Although the highest mineralization was achieved by O_3/UV/H_2O_2 treatment, O_3/H_2O_2 treatment without UV-C was found more energy-efficient to operate in terms of energy consumption. Thus, UV-C combined treatment could only be considered in case of reuse/recycle purposes in the plant that requires a high quality water.

RESUMEN

Esta tesis se enmarca dentro de dos proyectos relacionados con la recuperación (tratamiento + reutilización) de aguas residuales generadas por la industria del petróleo y gas. El proyecto Integroil (Horizon 2020), en el que participó el grupo de investigación Catheter de la Universitat Rovira i Virgili, enfocado en la reutilización del agua en el sector de petróleo y gas. El proyecto Integroil tenía como objetivo la implementación de una solución integral para el tratamiento de aguas residuales procedentes de los procesos de extracción (upstream) y de refinado del petróleo (downstream). Para ello, inicialmente se estudiaron diversas tecnologías a escala laboratorio para encontrar la mejor solución en cada una de las etapas del sistema de tratamiento. Dentro de esta tesis, los capítulos 3 y 4 son el resultado de la investigación de diferentes procesos avanzados de oxidación (AOPs) para el tratamiento de los efluentes procedentes del refinado del petróleo, es decir, aguas de refinería (downstream).

Entre los procesos avanzados de oxidación estudiados en los capítulos 3 y 4 se encuentra la ozonización (simple y combinada) y diferentes procesos fotocatalíticos. Se realizó una primera evaluación con un agua sintética compleja (SRW) compuesta de los principales grupos de compuestos orgánicos e inorgánicos presentes en efluentes de refinerías. Esto permitió, en una etapa preliminar, obtener información importante y consistente extrapolable al caso real de estudio, contrariamente a los estudios publicados, normalmente realizados con agua sintética de un solo compuesto modelo. Los resultados iniciales obtenidos con SRW permitieron comparar las eficiencias del tratamiento con un efluente estable que tiene la misma naturaleza para todos los experimentos, El estudio del efecto de parámetros tales como la cantidad y tipo de oxidante, el pH y el tiempo de reacción permitió conocer los rangos de aplicación y optimización para el tratamiento de efluentes reales.

Establecidos los parámetros más significativos con los procesos más eficaces, se investigó el tratamiento de 3 aguas residuales reales diferentes procedentes del tratamiento primario y del tratamiento secundario de una refinería de petróleo ubicada en Turquía, con el fin de alcanzar los requerimientos de reutilización en la planta. En las refinerías, el agua tratada puede usarse para diferentes propósitos, dependiendo de la calidad obtenida después del tratamiento. Para el caso de la refinería en este estudio, el objetivo es obtener un agua tratada con un contenido total

de carbono orgánico (TOC) por debajo de 15 mg/L y 4 mg/L para agua de extinción de incendios y refrigeración, respectivamente.

Entre los tratamientos basados en fotocatálisis, el proceso foto-Fenton mostró una efectividad superior tanto como tratamiento secundario como terciario, considerando las mejoras en la eliminación de TOC, toxicidad y biodegradabilidad. El proceso foto-Fenton aplicado como tratamiento secundario resultó ser más eficiente que el tratamiento biológico existente en la refinería, alcanzando valores finales de TOC de aproximadamente 20 mg/L y 88% de eliminación de DQO. El aumento en la relación DBO_5/DQO de 0.38 a 0.83 observado tras el tratamiento indica, además, que las aguas tratadas mejoran su biodegradabilidad. Si se aplica el proceso de foto-Fenton como tratamiento terciario, el TOC final disminuye a valores por debajo de 4 mg/L, valores aptos para la reutilización del efluente en la refinería, aumentando así la sostenibilidad.

A pesar de los buenos resultados obtenidos aplicando procesos fotocatalíticos, también se estudió el uso de procesos de ozonización como posible tratamiento terciario con el fin de alcanzar los requisitos para reutilización del efluente en la refinería. Los estudios de optimización se realizaron por diseño experimental. Primero se identificaron los parámetros significativos para el tratamiento (cantidad de oxidante y tiempo de tratamiento), que fueron posteriormente optimizados para un efluente tomado después del tratamiento biológico (alimentación de ozono de 0.9 g/h, concentración de H_2O_2 de 47 mg/L y 60 min de tratamiento). Sin embargo, en caso de aumentar la concentración de H_2O_2 a 80 mg/L, la duración del tratamiento se puede reducir a 37.5 min, disminuyendo los costos de consumo de energía y reactivo en un 37%, y alcanzando un TOC final por debajo de 4 mg/L, es decir, adecuado para las condiciones de reutilización.

Los siguientes capítulos de la tesis (capítulos 5 y 6) se enmarcan dentro del proyecto Resilient Reclaimed Land and Water Systems liderado por el Dr. Gamal El-Din en la Universidad de Alberta. En estos capítulos se presenta el estudio del tratamiento del agua de proceso de arenas petrolíferas (OSPW), actualmente almacenada en estanques de residuos que cubren una extensión de 220 km^2 debido a la política de descarga cero de la región de Alberta, en Canadá. La incertidumbre en la gestión de estos residuos y los efectos dañinos sobre el medioambiente han motivado la investigación en el tratamiento de estos efluentes para disminuir su toxicidad y alcanzar unos requerimientos mínimos para su posible descarga.

En este caso, se investigó la actividad catalítica de diferentes catalizadores basados en carbón activo previamente dopados con N o N/S y Fe (III), no estudiados antes para el tratamiento de OSPW. Se compararon diferentes procesos avanzados de oxidación basados en procesos de ozonización y UV, optimizando las condiciones de operación. Se hizo una primera selección de catalizadores siguiendo la metodología de diseño factorial fraccional para la ozonización catalítica de un agua sintética. Posteriormente, los materiales seleccionados se investigaron más a fondo para el tratamiento de OSPW real. Mediante el proceso UV/Fenton se obtuvo una eliminación eficaz de los componentes orgánicos causantes de toxicidad aguda presentes en el efluente.

El tratamiento UV-Fenton fue el más eficaz en la eliminación de toxicidad aguda de la OSPW, según los resultados basados en tests realizados con *V. fischeri*. Así mismo, se logró una gran reducción de la toxicidad con los tratamientos basados en ozono, resultados que fueron consistentes con la reducción de la concentración de ácidos nafténicos (considerados como el principal contribuyente de la toxicidad, como se verá más adelante) en la OSPW.

Además de la reducción de toxicidad, es importante una reducción de la concentración de compuestos orgánicos en estos efluentes, especialmente si se considera la descarga de los mismos. Los resultados obtenidos anteriormente fueron mejorados mediante la aplicación de procesos combinados O_3/H_2O_2/UV. El contenido de compuestos orgánicos disueltos (DOC) se eliminó considerablemente tras 90 min de tratamientos, llegando a eliminarse hasta un 98%. Todos los tratamientos estudiados eliminaron significativamente la toxicidad aguda de la OSPW testada en *Vibrio fischeri*, aunque la mayor mineralización se logró mediante el tratamiento con O_3/H_2O_2 irradiado con UV-C. Este método resulta prometedor para la posible reutilización del efluente tratado como agua de refrigeración, que requiere agua de alta calidad, ya que el DOC final se redujo con éxito a aproximadamente 2 mg C/L. Sin embargo, evitar el uso de UV-C resulta en un tratamiento más eficiente desde el punto de vista energético, si se normaliza el consumo de energía por porcentaje de DQO eliminado. Por tanto, la aplicación de uno u otro método está supeditado al uso final del efluente tratado.

RESUM

Aquesta tesi s'ha desenvolupat emmarcada en dos projectes relacionats amb la recuperació d'aigües residuals generades per la indústria de processament de petroli i gas. El projecte Integroil (Horizon 2020), en què el grup de recerca Catheterde la Universitat Rovira I Virgili va ser un dels participants, va tenir com a objectiu la reutilització d'aigua en el sector de petroli i gas. Tot i que el projecte va incloure una àmplia gamma de tecnologies per proposar una solució de tractament integrada a les refineries, inclosos els processos aigües amunt (extracció) i aigües avall (refinat del petroli), les parts de la investigació d'aquesta tesi que pertanyen al projecte Integroil (capítols 3-4) inclouen el tractament dels efluents *downstream* (refineries).

Per al tractament d'efluents de refineria, es van avaluar en detall diversos processos d'oxidació avançada (AOP) basats en processos fotoquímics i d'ozonització a partir d'una aigua residual sintètica de refineria (SRW) amb una composició complexa. La SRW es va preparar amb compostos representants de les famílies de grups orgànics i inorgànics típics que es troben en els efluents de les refineries de petroli, d'acord amb la literatura, per poder simular casos reals evitant possibles confusions que poden causar els estudis realitzats amb aigua sintètica d'un sol component. Els resultats inicials obtinguts amb SRW van permetre comparar les eficiències dels tractaments obtingudes amb un efluent estable que té les mateixes característiques per a tots els experiments. A més, l'estudi de l'efecte de paràmetres com ara les quantitats d'oxidants, el pH i el temps de reacció en SRW permet conèixer els rangs de treball per a següents optimitzacions que podrien fer-se amb efluents reals. Després de les proves inicials amb SRW, es van investigar els rendiments del tractament de 3 aigües residuals reals diferents, una de les quals es va recollir després del tractament primari, mentre que les altres dues es van recollir després del tractament secundari d'una refineria de petroli situada a Turquia, per tal d'assolir les condiciones per a la reutilització a la planta. A les refineries, l'aigua tractada pot usar-se per a diferents propòsits, depenent de la qualitat obtinguda després de l'tractament. Per al cas de la refineria d'aquest estudi, el seu objectiu era mantenir el contingut total de carboni orgànic (TOC) per sota de 15 mg/L i 4 mg/L per aigua d'extinció d'incendisi aigua de refrigeració, respectivament.

Entre els tractaments fotoquímics aplicats, tot i que la fotocatàlisi heterogènia amb TiO_2 i un procés combinat de fotocatàlisi heterogènia i foto-Fenton van mostrar resultats prometedors per al tractament dels efluents de la refineria, el tractament amb foto-Fenton va ser el que va mostrar una efectivitat superior, tant com a tractament secundari com a terciari, considerant les millores en l'eliminació de TOC, toxicitat i biodegradabilitat. El procés foto-Fenton com a tractament secundari va resultar més eficient que el tractament biològic, aconseguint valors finals de TOC ca. 20 mg/L i un 88% d'eliminació de DQO. A més, es va obtenir un marcat augment en la relació DBO_5/DQO de 0,38 a 0,83. Com a tractament terciari, el procés de foto-Fenton amb H_2O_2/COD=10 i H_2O_2/Fe^{2+}=50 o H_2O_2/COD=4 i H_2O_2/Fe^{2+}=10 va proporcionar un valor de TOC final inferior a 4 mg / L. Aquest resultat revela la possibilitat de reutilitzar l'efluent a la planta de refineria, augmentant així la sostenibilitat. Tanmateix, a més del tractament d'aigües residuals de refineria, el tractament d'aigües residuals amunt amb aigües produïdes (d’extracció) que es va investigar en paral·lel dins dell projecte Integroil, va concloure que els processos basats en ozó eren més adequats per a ambdues aplicacions (aigües residuals de refineria y aigües produïdes (d’extracció)) en lloc de tractaments fotoquímics. Per tant, els tractaments basats en ozó es van investigar com a possible tractament terciari per a la refineria per assolir els requisits finals per a fins de reutilització. Els estudis d'optimització també es van realitzar per disseny experimental. Les proves preliminars per disseny factorial fraccional realitzat amb l’efluent SRW van revelar que els paràmetres significatius per al tractament van ser la quantitat d'ozó alimentat, la quantitat de H_2O_2 i el temps de reacció, mentre que el pH va ser insignificant. En base als resultats obtinguts amb la metodologia de superfície de resposta de box-Behnken realitzada amb un efluent recollit després del tractament biològic, es van optimitzar els paràmetres significatius, com la producció d'ozó de 0.9 g/h, la quantitat de H_2O_2 de 47 mg/L i la durada de 60 min. No obstant això, en cas d'augmentar la quantitat de H_2O_2 a 80 mg/L, la durada del tractament es pot reduir a 37.5 min, disminuint els costos de consum d'energia i reactius en un 37%, i arribant a un valor de TOC final per sota de 4 mg/L, que és l'objectiu de les possibilitats de reutilització.

En quant al segon projecte, Resilient Reclaimed Land and Water Systems liderat pel grup de recerca del Dr. Gamal El-Din a la Universitat d'Alberta, vam participar en el tractament de l'aigua de procés de sorres petrolíferes (OSPW) actualment emmagatzemada en estanys de residus que cobreixen 220 km^2 de terra, a causa de la política de descàrrega zero a la regió d'Alberta, al Canadà (capítols 5-6). La incertesa en la gestió d'aquests residus i els efectes nocius sobre el medi ambient han motivat la investigació en el tractament d'aquests efluents per disminuir la seva toxicitat i assolir uns requeriments mínims per a la seva possible descàrrega.

En primer lloc, es van comparar els tractaments catalítics basats en ozó i UV amb diferents oxidants i pH. Com a catalitzadors, es va estudiar l'activitat catalíticade materials granulars basats en carbó activat prèviament dopats amb heteroàtoms (N o N/S) i Fe(III), poc utilitzats en estudis previs per al tractament de OSPW. Es va fer una primera selecció de catalitzadors seguint la metodologia de disseny factorial fraccional per l'ozonització catalítica d'una aigua sintètica. Posteriorment, els materials seleccionats es van investigar més a fons per al tractament d'un efluent OSPW real. Mitjançant el procés UV/Fenton, es va obtenir una eliminació eficaç dels components orgànics causants de toxicitat aguda presents en l'efluent. Els resultats obtinguts van mostrar que l'eficàcia de l'tractament per part dels AOP en termes de mineralització era de l'ordre d'UV/PMS<O_3 <UV/H_2O_2<UV/Fenton, on l'eliminació de DOC era de fins a 14%, 21%, el 31% i 64% respectivament. Els millors resultats demillora en la toxicitat aguda realitzada amb *V. fischeri* es va aconseguir amb el procés UV/Fenton, encara que els tractaments amb ozó també van conduir a una gran reducció. Això estava d'acord amb les menors concentracions d'àcids naftènics, que es consideren com el principal contribuent a la toxicitat de OSPW. Així, amb els tractaments basats en ozó va produir-se preferentment la transformació dels compostos tòxics en lloc d'una mineralització.

A més de la reducció de toxicitat, és important una reducció de la concentració de compostos orgànics en aquests efluents, especialment si es considera la descàrrega dels mateixos. Els resultats presentats anteriorment van ser millorats mitjançant l'aplicació de processos combinats O_3/H_2O_2/UV. El contingut de compostos orgànics dissolts (DOC) es va disminuir considerablement després de 90 min de tractament, arribant a eliminar fins a un 98%. Tots els tractaments estudiats van eliminar significativament la toxicitat aguda de la OSPW testada en *Vibrio fischeri*, tot i que el major grau de mineralització es va aconseguir mitjançant el tractament amb O_3/UV/H_2O_2. Aquest mètode resulta prometedor per a la possible reutilització de l'efluent tractat com a aigua de refrigeració, que requereix aigua d'alta qualitat, ja que el DOC final es va reduir amb èxit a aproximadament 2 mg C/L. No obstant això, evitar l'ús de radiació UV-C resulta en un tractament més eficient des del punt de vista energètic, si es normalitza el consum d'energia per percentatge de DQO eliminat. Per tant, l'aplicació d'un o altre mètode està supeditat a l'ús final de l'efluent tractat.

1

Structure
&
Objectives of the Thesis

1.1 Structure of the Thesis

This thesis approaches the applications of mainly photo-based and ozone-based advanced oxidation processes for the reclamation of wastewaters produced by oil & gas sector. Two real case issues arising from upstream and downstream processing of conventional and unconventional fossil fuels were handled deeply contributing the evolution of this thesis that is presented in 8 chapters.

This chapter presents the structure of the thesis by chapters with a brief overview for the reader about their content. The main and specific objectives of the thesis are also given in ***Chapter 1***.

In ***Chapter 2,*** an introduction to the water scarcity problem caused by over abstraction of the freshwater due to the high industrial demands and, the massive effluents generated by the industries including oil & gas sector is presented. The reason of the wastewater generation, some general information about typical composition of the effluents of oil & gas industry and applied traditional treatment techniques have been given to clarify the current situation that needs to be coped with. Also, classifications and fundamentals of AOPs are presented, focusing more on those AOPs applied within this thesis.

The effluents studied in this thesis can be organized in two separate sections: as petroleum refinery wastewater, which is discussed in detail in Chapters 3 and 4, and OSPW, which is discussed in detail in Chapters 5 and 6.

Regarding the first part (i.e., petroleum refinery wastewater), the treatments of a synthetically prepared effluent and real effluents collected after primary and secondary treatments from a refinery located in Turkey were examined in detail. ***In Chapter 3***, solar light assisted photo-Fenton and heterogeneous photo-catalysis are investigated to reach zero discharge concept in the refinery. Initial tests were performed on a multi-component synthetic wastewater to simulate the real cases. After optimizing the operating parameters for synthetic water, two different real effluents collected before and after biological treatment were studied so as to evaluate the applied AOPs as secondary or tertiary treatment. ***Chapter 4*** is focused on a statistical approach to optimize the ozone-based treatment, which was considered as a tertiary treatment in the refinery, so as to achieve reuse and recycle purposes in the plant. Firstly, screening tests by fractional factorial design in Minitab software were performed on the same synthetic wastewater studied in Chapter 3.

Afterwards, optimization by Box-Behnken response surface methodology was performed for the real effluents previously treated by biological treatment.

The second part of the thesis involves the application of different AOPs on OSPW collected from a tailing pond of a company located in Canada. ***In Chapter 5***, it is presented the research work performed at the University of Alberta, in Canada, involving catalytic AOPs such as ozone-based and UV-based processes using as-prepared granular activated carbon-based catalysts for OSPW treatment. Different oxidants were considered (e.g., ozone, H_2O_2 and PMS) in order to investigate their effects on the treatment efficiencies. Initially, catalytic activities of the 10 prepared catalysts were tested with a synthetic water using a fractional factorial design by which some of the catalysts were eliminated. Selected materials were tested on real OSPW comparing mentioned AOPs. ***In Chapter 6***, the synergetic effect of the O_3/H_2O_2 and UV-C irradiation to treat OSPW was investigated in detail. The combination of UV-C/O_3/H_2O_2 was studied for the first time to treat OSPW. An economic approach for each treatment was also presented.

Chapter 7 presents the general conclusions obtained by different studies discussed in the previous chapters. Main connections between the treatment of different effluents and also some future work recommendations are given.

Chapter 8 includes the list of publications and communications arisen from the studies conducted during this Ph.D.

1.2 Objectives of the Thesis

As it was shortly mentioned previously, the main objective of this thesis is the search of efficient treatments for wastewaters generated by the oil & gas sector applying photo-based and ozone-based AOPs. The current configurations of the production process units cause consumption of huge amounts of fresh water and traditional water treatment techniques that are currently used in the industries are not efficient enough to overcome this urgent problem of water scarcity. Thus, this thesis is aimed to present real case studies from oil & gas industry, for which the generated effluents were treated by different types of AOPs to both decrease the freshwater abstraction for the processing by allowing its reuse, and decrease the toxic contaminants in the effluents that have to be discharged eventually.

Specifically, for the research focused on the treatment of petroleum refinery wastewater presented in chapters 3 and 4, the applications of the AOPs to reach reusing requirements in the plant, such as cooling water and fire water, were investigated in order to decrease freshwater use in the plant, which cannot be achieved simply by the traditional water treatment techniques. Regarding the quality of the water that can be reused in the plant, final TOC less than 15 mg/L and 4 mg/L for firewater and cooling water, respectively, were targeted. Also, deciding the proper placement of AOPs in the treatment plant (either as secondary or tertiary treatment) was another aim to fill the gap related to reusing issues in the sector. In chapter 3, high mineralization using solar light instead of UV and very low amounts of reactants not to produce any sludge at the end of the treatments were aimed. In chapter 4, systematically optimization by experimental design and reduced costs for high efficiencies reach the appropriate final TOC were the principle targets.

For the research part conducted with OSPW in chapters 5 and 6, since the OSPW is stored in tailing ponds because of the zero-discharge policy, ideally obtaining a treated effluent appropriate for reusing, or at least being able to be discharged was aimed. In chapter 5, especially reducing the concentration of naphthenic acids and toxicity regardless from mineralization became important for discharging scenarios; whereas in chapter 6, mineralization was also the intention for reuse purposes.

For all effluents treated in this study, finding the optimum process conditions and amounts of reactants to propose an applicable treatment was aimed.

2

Introduction

2.1 Introduction

Water is one of the essentials to maintain the survival of ecosystem and the development of human society [1]. With the increasing human being activities, global freshwater consumption rose significantly at more than twice the rate of population growth increasing the world's water stress. Currently, more than a billion people live in water-scarce regions, experiencing lack of access to safe drinking water, and as many as 3.5 billion could experience water scarcity by 2025 with possible increasement in diseases related to unsafe water, sanitation and hygiene [2,3]. High-volume water consuming activities including industrial, agricultural and domestic sectors are also necessary for the survival of human being despite of raising the organic load in the wastewater treatment plants accelerating the water scarcity due to the unequal water demand and water supply [1,4]. Although water resources are generally managed locally, as nations are interconnected by international trades, potential production loss due to the water scarcity in water intensive sectors such as agriculture and power generation, can lead to production losses in distant economies making the local water scarcity into a worldwide concern [5].

According to Eurostat (***Figure 2.1***), from 2010 to 2017, averagely 288 billion m^3/year fresh surface and ground water was abstracted in Europe to be used for different purposes including manufacturing, agriculture and public supply. Around 10% of that converted into wastewater. The sharp increase in 2016 was caused by the water abstraction of North Macedonia, which could be an unusual situation [6].

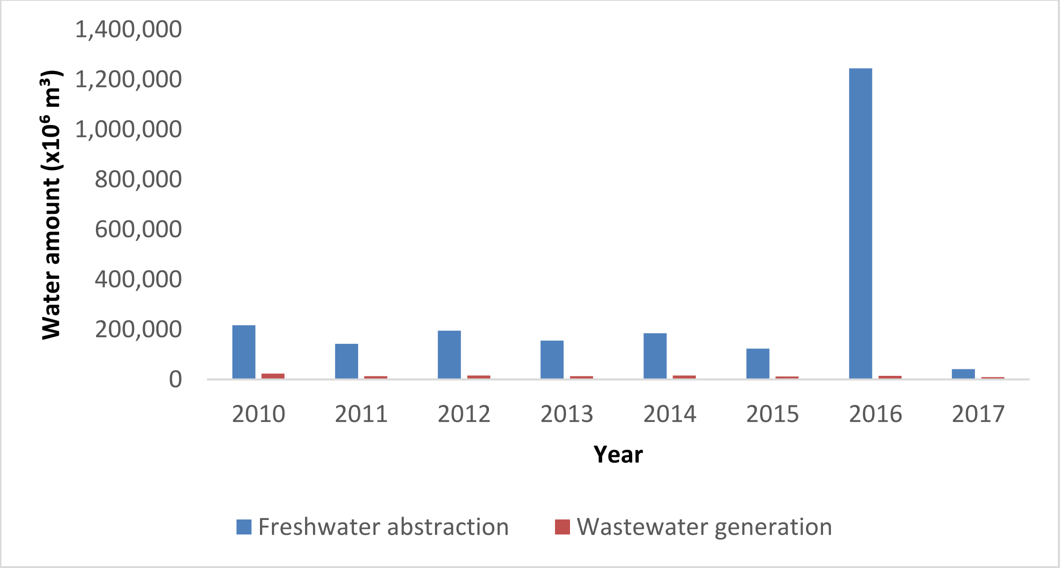

Figure 2.1 Water abstraction and wastewater generation in Europe [6].

Over abstraction of water is the main problem that causes water stress. With the climate change and increasing population, it will be more severe in the future [7]. Therefore, the reclamation of wastewater becomes crucial to decrease the possible water scarcity problems.

Industrial sector is one of the main water users and a major water polluter in Europe. Eurostat previously reported the share of industrial sectors by categories according to their water use as given in ***Table 2.1*** [8]. Refined petroleum products, chemicals & chemical products are the third major category that uses high volume of water after food and electric sectors, getting further attention in terms of environmental impacts.

2.2 Water/Wastewater Sources in Oil & Gas Sector

Increasing energy demand over the time causes a continuous consumption of fossil fuels globally. Oil & Gas industry is growing in parallel processing the fossil fuels by conventional and unconventional methods, which consist of complex stages, to produce valuable products [9,10]. Here, petroleum refineries where crude oil is processed can be considered as the conventional way of processing (downstream), whereas bitumen extraction from oil sands in order to be upgraded into synthetic crude oil can be considered as unconventional process (upstream), which is specific to Alberta region in Canada. Canada has the third largest oil reserves after Venezuela and Saudi Arabia in the form of oil sands, approximately 98% of which is deposited in the province of Alberta [10,11].

During the refining process, crude oil is distilled into fractions and then, these fractions are modified by different processes such as cracking, condensation, polymerization and alkylation. Thus, commercial products such as gasoline, naphtha, jet fuel, fuel oils, and petrochemical feedstocks are obtained [12,13]. As the nature of the processing, a considerable amount of water is consumed in process units including crude oil desalting, distillation, hydro-treating and water cooling systems [9,14].

To optimize the water use in a refinery, the water inlet and outlet analysis has to be considered (***Figure 2.2***). According to the *Petroleum refining water/wastewater use and management report* published by the International Petroleum Industry Environmental Conservation Association (IPIECA), the water inlet could be purchased potable water from a municipality or could be supplied from surface water (lake, river and sea water) and ground water.

Table 2.1 Share of manufacturing categories in the total water use in industry (%) [8].

	Food products	Textile	Paper & paper products	Refined petroleum products, chemicals & chemical products	Basic metals	Motor vehicles, trailers, semi-trailers & other transport equipment	Other manufacturing	Construction	Production & distribution of electricity (incl. cooling purposes)	Mining & quarrying
Belgium (2009)	2.2	0.1	0.9	16.6	2.2	0.0	0.7	0.0	76.5	0.8
Bulgaria (2011)	0.7	0.1	0.6	1.9	0.5	0.1	0.8	0.1	94.6	0.6
Czech Republic	1.5	0.5	4.5	10.5	3.0	0.1	1.3	0.0	75.4	3.3
Germany (2010)	1.6	0.1	1.9	10.7	2.6	0.2	1.2	0.0	78.3	3.4
Spain (2010)	3.2	0.4	2.0	5.9	2.5	0.2	0.9	0.4	84.4	0.1
Cyprus (2010)	0.2	0.0	0.0	0.0	0.0	0.0	0.2	0.0	99.4	0.1
Latvia (2007)*	10.4	9.4	0.2	4.1	16.8	0.5	4.4	1.3	52.2	0.7
Lithuania (2011)	2.9	0.5	0.6	7.7	0.0	0.0	0.9	0.0	87.3	0.2
Malta (2009)*	58.3	8.3	0.0	8.3	0.0	8.3	16.7	0.0	0.0	0.0
Netherlands (2010)	2.0	0.0	0.7	21.5	2.0	0.0	0.5	0.0	73.3	0.0
Poland (2011)	1.0	0.1	1.2	5.1	0.5	0.0	0.8	0.1	90.6	0.7
Slovenia (2011)	10.4	1.5	31.4	24.5	15.5	1.6	12.8	0.0	0.4	2.0
Sweden (2010)	0.5	0.0	7.0	4.3	2.8	0.1	0.5	0.0	84.6	0.1
Norway (2009)	3.2	0.1	16.8	46.0	14.3	0.2	11.9	3.4	0.0	4.0
Macedonia (2009)*	90.4	0.3	3.4	4.5	0.9	0.3	0.2	0.0	0.0	0.0
Serbia (2011)	0.6	0.0	0.1	0.4	1.1	0.1	0.3	0.0	97.1	0.3
Turkey (2010)	3.8	2.4	0.5	2.3	15.6	0.1	1.5	0.6	72.3	0.9

*Only public water supply.

In case of raw water, such as surface water or ground water, pre-treatment would be required depending on its compatibility with the process units since raw water contains suspended solids as well as dissolved organics and inorganics that can produce corrosion and deposition problems. Water in crude and rain are also other water sources that enter to the system [15].

Since oil & gas sector is one of the most water-consuming industries, consequently, significant amount of wastewater is generated after processing. The amount and specification of the water/wastewater used/generated in the refinery is different for each refinery and highly depends on the process configuration, specifications of the petroleum such as density, sulfur content, total acid number and the product requirements that has to be achieved [16]. The water that was not contacted with hydrocarbons or had minimal contamination, can be reused in the plant. However, even in that case, in a typical refinery, approximately 3.5–5 m^3 of wastewater is generated per 1 ton of crude oil processed [17,18]. The process water that cannot be reused before treatment is typically sent to the wastewater treatment plant that is situated at the facility. Alternatively, it can be sent to a third-party treatment facility after pre-treatment [15].

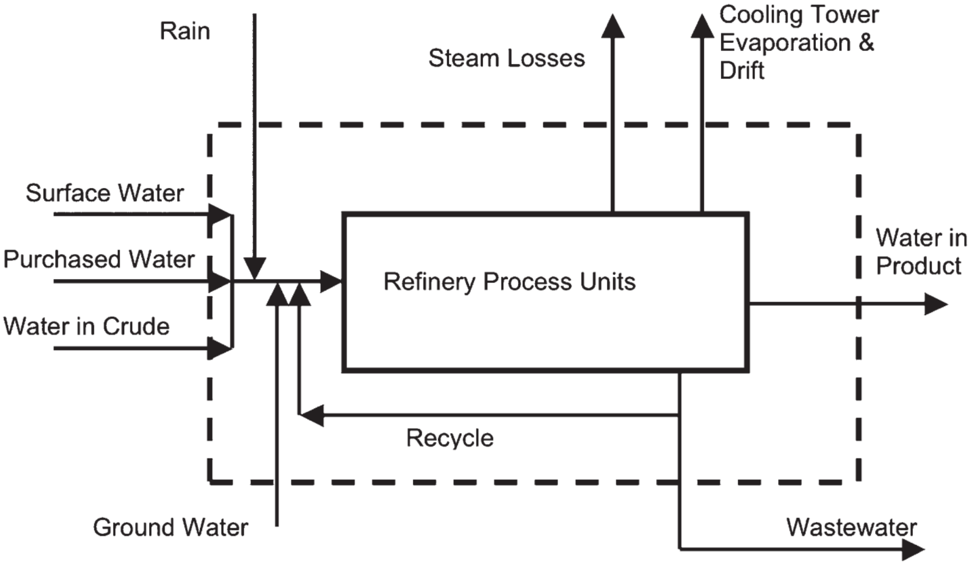

Figure 2.2 The typical water balance in a refinery [15].

In the case of upstream processing of oil sands practically being applied in Canada, other water intensive techniques are used before refining in order to extract the fossil fuels from naturally occurring geologic reservoirs, such as hydraulic fracturing for shale gas reservoirs and mining for oil sands deposits [10]. Oil sands deposits are located at varying depths beneath the ground. Only 18% of the recoverable bitumen can be accessed by surface mining of shallow oil sand deposits (i.e., up to 75 m), from where surface mined oil sands are transferred to the extraction plant in the form of slurry. The rest are situated in deeper deposits, where bitumen is extracted by in-situ processes such as steam injection into a well in order to heat and loosen the bitumen inside the oil sands. Thus, bitumen can directly be pumped to the surface [19]. After extraction, the greater part of bitumen is upgraded into more valuable synthetic crude oil with lower viscosity and sulfur content and then refined into gasoline or diesel fuels. Only a minor part of it is directly processed into fuels without previous upgrading [20].

Typical water distribution of the bitumen extraction process from surface mined oil sands is presented in ***Figure 2.3*** . Bitumen is separated from sand and clay by Clark hot water extraction method, in which surface mined oil sands are mixed with hot water [21]. This process consumes approximately 3 m^3 of fresh water per m^3 of oil produced, which is supplied from local freshwater resources such as Athabasca River [19,22]. Consequently, high volume of process water called as oil sands process water (OSPW) is formed after processing, 80% of which is reused in the extraction process. Remained 20% is stored in tailing ponds because of zero discharge policy, which will need to be treated eventually [23].

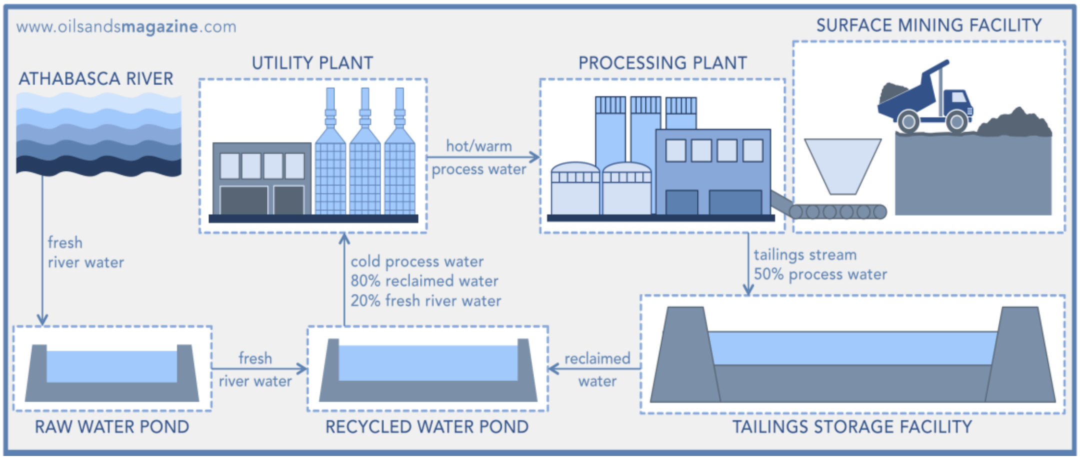

Figure 2.3 Typical water distribution for oil sands mining [24].

So far, global water scarcity in industrial sectors and the environmental concerns including oil & gas sector has been presented. Also, water and wastewater sources in oil & gas sector was discussed for better understanding of the water stress caused by processing fossil fuels. In the following sections of this chapter, it will be described the main environmental problems of the effluents generated after upstream and downstream processing of fossil fuels. Furthermore, an introduction to the environmentally friendly treatment methods called Advanced Oxidation Processes (AOPs) will be presented.

2.2.1 Petroleum refinery wastewater

In a refinery, generated wastewater is a function of the number of units and their configuration, which creates a fluctuation in the final effluent's composition [25]. Final effluent includes process associated water such as condensed steam, stripping water, spent caustic solutions, cooling/boiling tower blowdown, wash water, alkaline and acid waste neutralization water [26]. Other non-process units such as sanitary, crude tank and laboratory water also contribute to the total volume of the effluent. [25]. ***Table 2.2*** presents the main contaminants and some quantified parameters encountered in the effluents of the refinery units. Since the generated effluents are different and complex, sustainable treatment solution is a major concern to optimize the water use in production units [27,28].

Table 2.2 Typical contaminants and characterization of the effluents generated in the refinery units [26,27].

Unit	**Contaminants**	**Unit**	**Contaminants**
Crude desalting	Free oil, ammonia, sulfides and suspended solids	**Polymerization**	Sulfides, mercaptans, ammonia
Crude oil distillation	Sulfides, ammonia, phenols, oil, chloride, mercaptans	**Alkylation**	Spent caustic, oil, sulfides
Thermal cracking	H_2S, ammonia, phenols	**Isomerization**	Low level of phenols
Catalytic cracking	Oil, sulfides, phenol, cyanide, ammonia	**Reforming**	Sulfide
Hydrocracking	High in sulfides	**Hydrotreating**	Ammonia, sulfides, phenol

	Parameters					
Unit	**Oil (mg/L)**	**H_2S (mg/L)**	**NH_3 (mg/L)**	**Phenols (mg/L)**	**TOC (mg C/L)**	**TSS (mg/L)**
Distillation	50-500	50-500	50-500	<50	50-500	50-500
Hydrotreater	50-500	>500	>500		50-500	
Visbreaker	50-500	50-500	50-500	50-500	50-500	<50
Fluid Catalytic Cracker	50-500	>500	>500	50-500	50-500	<50
Hydrocracker	50-500	>500	>500		<50	

Figure 2.4 shows an example of a typical water treatment train applied in petroleum refineries [26]. Preliminarily, crude solids and substances are removed mechanically, and the resulted effluent is sent to an equalizing basin to homogenize the water quality and laminar variations before primary treatment. As the primary treatment, firstly, free oils and emulsified oils are removed by gravimetric and flotation processes, respectively. Depending on the characteristics of the effluent, either it could directly be transferred to secondary treatment or a coagulation/flocculation/sedimentation step can be applied. The effluent of the primary treatment is sent to another equalizing basin before the secondary treatment, which is usually a biological treatment followed by a separation process to remove micro-organisms before discharge or tertiary treatment [29]. At the beginning of the preliminary treatment, a segregation step based on the total dissolved solids (TDS) of the effluents may be performed in order to handle the effluents with high TDS (such as desalter effluent, tank bottom sediment and water, and spent caustic) and the low TDS (such as stripped sour water, stormwater and miscellaneous wastewater) in separate lines. Although this separation is not frequently applied in refineries, it would be wise in the regions with water scarcity [15].

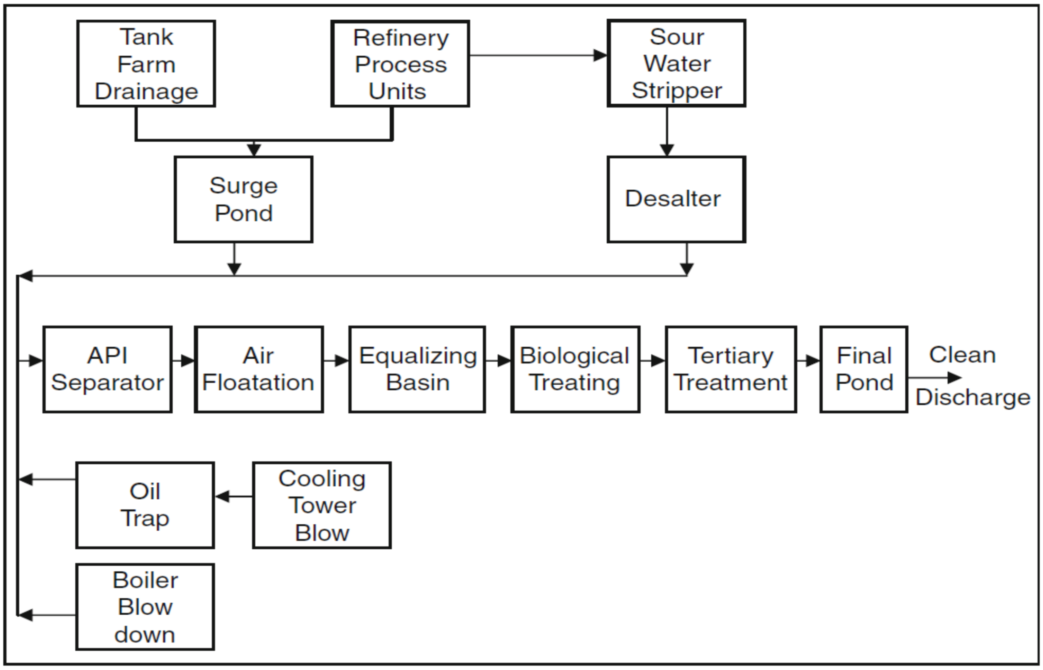

Figure 2.4 Typical wastewater treatment scheme of a refinery [26].

Although biological treatment is the most common process used in petrochemical industry, it does not always reach the proper water quality, especially in presence of recalcitrant organic components that are toxic and resistant to biological treatment. For those cases, a tertiary treatment including AOPs could be applied to achieve discharging standards or even further, allowing reusing the treated water in the facility with the aim of reducing fresh water use [30,31].

2.2.2 Oil sands process water (OSPW)

The effluent from bitumen extraction process (previously presented in ***Figure 2.3***) that consists of a slurry of sand, silt, clay, and residual bitumen is stored in tailing ponds for solid particle settlement. After the settlement, the overlaying water, OSPW, is reinjected into the extraction unit according to the existing policy since OSPW is toxic to the aquatic lifeforms [32,33]. Although reinjection allows a decrease in freshwater use, the quality of the OSPW decreases during the subsequent cycles, dropping the bitumen extraction efficiency and also causing corrosion in extraction facilities [19,33].

OSPW is an alkaline and brackish water that contains several kinds of metal cations, anions and organic compounds [19,34]. Conventional techniques including mechanical and chemical treatments, as mentioned previously in this chapter, ***section 2.2.1***, are some of the processes previously used to treat OSPW, being as economic, energy efficient and environmentally friendly as biological treatment. However, naphthenic acids found in OSPW are persistent to biodegradation, which requires advanced treatments to degrade those compounds or transform them to other non-toxic compounds [35].

Naphthenic acids (NAs) are one group of carboxylic acids present in petroleum sources due to natural formation by either insufficient catagenesis or bacterial biodegradation in the deposits. In Canada, biodegradation of mature petroleum is the reason of their existence in oil sands deposits [36]. NAs are chemically stable and non-volatile, surface active organic acids that are released to the water during bitumen extraction, especially at high pH [36–38]. NAs predominantly include alkyl substituted cycloaliphatic carboxylic acids with single or fused multiple rings. Small amount of acyclic aliphatic acids such as paraffinic or fatty acids, aromatic olefinic, hydroxy, and dibasic acids may also exist. The polarity and non volatility of NAs changes by their molecular weight, giving different physical, chemical, and toxicological properties to the individual components [39].

The aquatic toxicity of OSPW is often associated with NAs presence and their surfactant properties that help hydrophobic compounds to enter easily to the lipid bilayer of the cell membrane, causing disruption and cell death [23,39]. Thus, the proper treatment of OSPW especially focused to the abatement of NAs is essential, either to increase the quality of OSPW for recycling, which will eventually decrease the freshwater use, or to discharge OSPW safely by reducing its toxicity [23].

2.3 Advanced Oxidation Processes (AOPs)

Classically, AOPs in water treatment relies on the clean technologies that produce hydroxyl radicals (HO•) so as to attack organic contaminants and ideally yield CO_2, H_2O and some inorganic ions as final products under mild conditions, or at least, transform the contaminants into harmless products [40–42]. HO• is an unselective, strong oxidant that could be produced by many different ways [40]. In addition to HO•, in progress of time, the contribution of other radicals has often been established, by which the AOP concept is accepted in a widened sense rather than being limited by only HO• based oxidation [43]. A general classification of AOPs can be done but not limited to in ***Table 2.3*** .

This thesis is mainly focused on ozonation, peroxone and Fenton/Fenton-like processes as non-photochemical AOPs, and their combination with light irradiation as photochemical AOPs, to treat the effluents from the oil & gas sector. Heterogeneous photo-catalytic oxidation and peroxymonosulfate (PMS) treatments were other AOPs also investigated within the thesis. Therefore, these treatments are detailed in the following sections.

Table 2.3 General classification of AOPs [44].

Non-photochemical	Photochemical
Ozonation (O_3)	Photocatalytic oxidation, UV/Catalyst
Peroxone (O_3/H_2O_2)	UV/H_2O_2
Fenton/Fenton-like	UV/O_3
Wet air oxidation (WAO)	UV/O_3/H_2O_2
Electrochemical oxidation	Photo-Fenton

2.3.1 Fenton/Fenton-like/photo-Fenton processes

Fenton reaction (***Eq. 1***) is one of the well established and highly effective AOPs that produce OH• by decomposition of hydrogen peroxide (H_2O_2) by ferrous iron (Fe(II)) at acidic pH around 3. Also, other intermediates such as hydroperoxyl radicals, superoxide anions, hydroperoxide anions, and oxide radical ions may be produced [45–48]. The process is favorable because of the safe and environmentally benign handling of the reagents without requiring any complicated or pressurized apparatus [48].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \qquad \textbf{(1)}$$

Despite the advantages gained by low cost operation and easy separation of iron that made full scale applications possible of Fenton process, the restrictions caused by the high amount of sludge produced by the precipitation of iron afterwards, and the operation pH, which is the key factor to prevent from iron precipitation, directed the attentions towards Fenton-like processes including iron free applications that could be performed at higher pH values [47].

In Fenton-like reaction (***Eq. 2***), $HO_2^{\bullet}$ radical that has lower oxidation power than OH•, is produced. Therefore, in Fenton-like processes, both the less reactivity of the produced radicals and the ca. 7600 times slower rate of reaction than that of Fenton reaction typically lead to less efficient treatments. However, depending on the reaction medium containing $HO_2^{\bullet}$ radical, an organic radical and/or superoxide ion ($O_2^{\bullet-}$), a rapid regeneration of Fe^{2+} by the reduction of Fe^{3+} presented by ***Eqs. 3-5*** may take place allowing an increase in the treatment efficiency [49,50].

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

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+ \qquad \textbf{(3)}$$

$$Fe^{3+} + R \rightarrow Fe^{2+} + R^+ \qquad \textbf{(4)}$$

$$Fe^{3+} + O_2^{\cdot -} \rightarrow Fe^{2+} + O_2 \qquad \textbf{(5)}$$

Regardless the advantages or disadvantages of Fenton/Fenton-like processes mentioned above, these processes need high amount of iron species much more greater than their discharging limits, which range between 2-10 mg/L depending on the country legislations [51,52]. Thus, their use implies further management including precipitation, re-dissolution, separation and recovery after being used in Fenton/Fenton-like processes before discharging [51]. In the meantime, photo-Fenton process overcomes this shortcoming by its accelerated reversible mechanism to regenerate Fe^{2+} under UV irradiated conditions [50]. In Fenton process, since Fenton-like reaction is slower than the Fenton reaction, Fe^{3+} is accumulated in the system and the reaction cycle does not continue when Fe^{2+} is consumed totally.

However, in the presence of UV irradiation, photo-reduction of Fe^{3+} to Fe^{2+} occurs, which eventually react with H_2O_2 to generate OH• and ferric ion. As long as there is enough H_2O_2 in the system, the cycle continues, requiring much lower amounts of Fe^{2+} for the treatment which allows decreasing the reactant and their further management costs. In addition, using sun light instead of UV light would reduce operation costs further [53].

2.3.2 Heterogeneous photocatalysis

Degradation of contaminants in water by heterogeneous photocatalysis is performed by using a semiconductor such as TiO_2, ZnO, Fe_2O_3, CdS or ZnS, and UV irradiation. The absorption of photon energy equal to or greater than the semiconductor's band gap energy induces the generation of valence band hole/conduction band electron pair that interact with hydroxyl ions and oxygen so as to generate OH• and superoxide anion, respectively (***Figure 2.5***) [54–56]. Instead of the interaction between the pairs and reactants, their recombination (either radiative or non-radiative) can take place, inhibiting the oxidation reactions [56]. Therefore, for an efficient application of photocatalysis there are still many challenges including the suppression of the recombination, the possible application of visible light and the recovery of the catalyst for reuse [40,57]. In order to improve the reaction efficiency, different strategies such as the geometry of the reactor and the working conditions, slurry or immobilized catalyst use and doping with other noble metals, metal ions or anions were studied in numerous investigations [40,57,58].

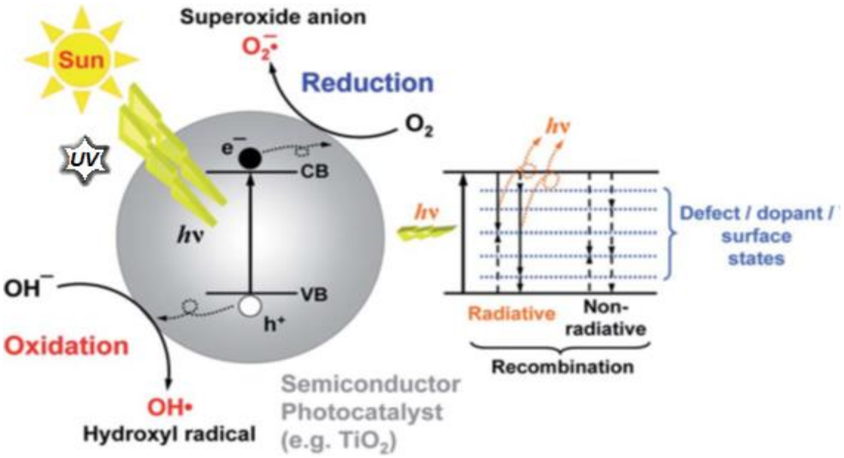

Figure 2.5 The mechanism of photocatalysis [56].

Ideally, a photocatalyst should possess high stability and adsorption ability via efficient photonic activation, as well as being abundant with low cost [40]. In this line, TiO_2 is the most preferred catalyst so far in terms of its environmentally friendly applicability in industry, with advantages such as high photochemical stability, high activity and low cost [40].

2.3.3 Ozone-based AOPs

Ozone is one of the most powerful oxidants, with a high standard reduction potential after fluorine, hydroxyl radical and atomic oxygen (***Table 2.4***). It can be produced from pre-treated air or pure oxygen by UV irradiation or electrical discharge [59]. Ozone is known for its strong disinfection abilities as well as for the removal of taste, odor, color, microcoagulation and hydrogen sulfide removal from water, which made its use attractive, especially for drinking water treatment since 1906 [60]. Ozone is an unstable and very selective molecule that reacts fast with the contaminants in water, either by direct reactions or indirect reactions via OH• radicals generated by ozone decomposition. Its decomposition is highly dependent on pH. At low pH, direct reactions generally with π bonds, amines and sulfide take place, while increasing the pH or by addition of H_2O_2, the O_3 decomposition is accelerated leading to indirect, unselective reactions by OH· besides the direct reactions [61].

Table 2.4 Standard reduction potential of some oxidants [59].

Oxidant	**Std. Reduction Potential (V)**
Fluorine(F_2)	3.03
Hydroxyl radical (HO•)	2.80
Atomic oxygen	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Potassium permanganate ($KMnO_4$)	1.67
Hypobromous acid (HbrO)	1.59
Chlorine dioxide (ClO_2)	1.50
Hypochlorous acid (HClO)	1.49
Chlorine (Cl_2)	1.36
Bromine (Br_2)	1.09

Ozone treatment of the wastewater can be performed solely or in combination with other chemical substances or energy sources, including H_2O_2 and/or UV-C as well as catalysts, in order to generate more radicals so as to improve the treatment efficiency by the synergetic effects of combined technologies. Today, the applications of ozone are not limited only to treatment of drinking water. It is also used as oxidant to remove organic pollutants and, as pre or post treatment in the water treatment facilities of industries [62]. A large scale ozonation/biofiltration system with 67,000 m^3 daily water treatment capacity for reuse aims, placed in a petroleum refinery in China is one of those examples [63].

2.3.4 Peroxymonosulfate (PMS) treatment

As mentioned previously, the advantages of Fenton processes such as easy applicability with high efficiency and low cost, directed the researches to find alternatives that may overcome the limitations, especially the operating pH. As an unconventional AOPs that do not mainly produce OH• radicals, the attentions have been directed toward PMS treatment, which is considered as a modified Fenton treatment, since it generates sulfate radicals through the reaction of a transition metal that could be Co, Cu, Fe and Mn, and an oxidant, Oxone® (potassium peroxymonosulfate) [64,65]. Among these metals, Co has been found as the most effective metal to accelerate the decomposition of Oxone®, whose self-decomposition is very slow, through ***Eq. 6*** to sulfate radicals ($SO_4^{\bullet -}$), which eventually attacks contaminants in water in a wider pH range [65].

$$Co^{2+} + HSO_5^{-} \rightarrow Co^{3+} + SO_4^{\cdot -} + OH^{-} \qquad \textbf{(6)}$$

On the other hand, some studies have been also devoted to develop metal-free catalysts such as heteroatom-doped graphene to activate Oxone®, to avoid metal leaching that could lead to another environmental problem [46].

References

[1] Z. Zeng, J. Liu, H.H.G. Savenije, A simple approach to assess water scarcity integrating water quantity and quality, Ecol. Indic. 34 (2013) 441–449. doi:10.1016/j.ecolind.2013.06.012.

[2] W.H. Organization, Health and Environment Linkages Initiative - HELI, (2020). https://www.who.int/heli/risks/water/water/en/ (accessed May 22, 2020).

[3] World Resources Institute, Water, (2020). https://www.wri.org/our-work/topics/water (accessed May 22, 2020).

[4] Y. Abdulaziz Mustafa, A. Ibrahim Alwared, M. Ebrahim, Removal of oil from wastewater by

advanced oxidation process/homogeneous process, J. Eng. 19 (2013) 686–694.

[5] S. Qu, S. Liang, M. Konar, Z. Zhu, A.S.F. Chiu, X. Jia, M. Xu, Virtual Water Scarcity Risk to the Global Trade System, Environ. Sci. Technol. 52 (2018) 673–683. doi:10.1021/acs.est.7b04309.

[6] Eurostat, Annual freshwater abstraction by source and sector, (2020). http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=env_wat_abs (accessed April 28, 2020).

[7] European Commission, Water Reuse-Environment, (2018). https://ec.europa.eu/environment/water/reuse.htm (accessed April 21, 2020).

[8] J. Forster, Archive:Water use in industry - Statistics Explained, (2014). https://ec.europa.eu/eurostat/statistics-explained/index.php/Archive:Water_use_in_industry (accessed April 20, 2020).

[9] S. Sevda, I.M. Abu-Reesh, H. Yuan, Z. He, Bioelectricity generation from treatment of petroleum refinery wastewater with simultaneous seawater desalination in microbial desalination cells, Energy Convers. Manag. (2017). doi:10.1016/j.enconman.2016.05.050.

[10] T. Brunner, J. Axsen, Oil sands, pipelines and fracking : Citizen acceptance of unconventional fossil fuel development and infrastructure in Canada, Energy Res. Soc. Sci. 67 (2020) 101511. doi:https://doi.org/10.1016/j.erss.2020.101511.

[11] C. Li, L. Fu, J. Stafford, M. Belosevic, M. Gamal El-Din, The toxicity of oil sands process-affected water (OSPW): A critical review, Sci. Total Environ. 601–602 (2017) 1785–1802. doi:10.1016/j.scitotenv.2017.06.024.

[12] ATSDR, Toxicological profile for total petroleum hydrocarbons (TPH), Atlanta, 1999. https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=424&tid=75.

[13] M. Al Zarooni, W. Elshorbagy, Characterization and assessment of Al Ruwais refinery wastewater, J. Hazard. Mater. 136 (2006) 398–405. doi:10.1016/j.jhazmat.2005.09.060.

[14] S. Parkash, Refining Processes Handbook, Elsevier, Burlington, 2003. doi:https://doi.org/10.1016/B978-0-7506-7721-9.X5000-2.

[15] Petroleum refining water/wastewater use and management Operations Best Practice Series 2010, IPIECA. (2010) 1–55. http://www.ipieca.org/resources/good-practice/petroleum-refining-water-wastewater-use-and-management/ (accessed June 6, 2017).

[16] F. Guedes, A. Szklo, P. Rochedo, F. Lantz, L. Magalar, E.M.V. Arroyo, Climate-energy-water nexus in Brazilian oil refineries, Int. J. Greenh. Gas Control. 90 (2019) 102815. doi:https://doi.org/10.1016/j.ijggc.2019.102815.

[17] F. Benyahia, M. Abdulkarim, A. Embaby, Refinery wastewater treatment : a true technological challenge, in: Seventh Annu. U.A.E. Univ. Res. Conf., 2006: pp. 1–8. doi:10.13140/RG.2.1.4642.8562.

[18] G. Hayder, M.Z. Ramli, M.A. Malek, A. Khamis, N.M. Hilmin, Prediction model development for petroleum refinery wastewater treatment, J. Water Process Eng. 4 (2014) 1–5. doi:10.1016/j.jwpe.2014.08.006.

[19] E.W. Allen, Process water treatment in Canada’s oil sands industry: I. Target pollutants and treatment objectives, J. Environ. Eng. Sci. 7 (2008) 123–138. doi:10.1139/S07-038.

[20] A.D. Charpentier, J.A. Bergerson, H.L. MacLean, Understanding the Canadian oil sands industry’s greenhouse gas emissions, Environ. Res. Lett. 4 (2009) 014005. doi:10.1088/1748-9326/4/1/014005.

[21] S. Dong, E. Kim, A. Alpatova, H. Noguchi, Y. Liu, M.G. El-din, Treatment of oil sands process-affected water by submerged ceramic membrane microfiltration system, Sep. Purif. Technol. 138 (2014) 198–209. doi:10.1016/j.seppur.2014.10.017.

[22] A.K.H. Al jibouri, J. Wu, S.R. Upreti, Heterogeneous catalytic ozonation of naphthenic acids in water, Can. J. Chem. Eng. 97 (2018) 67–73. doi:10.1002/cjce.23209.

[23] L.D. Brown, A.C. Ulrich, Oil sands naphthenic acids : A review of properties, measurement, and treatment, Chemosphere 127 (2015) 276–290. doi:http://dx.doi.org/10.1016/j.chemosphere.2015.02.003.

[24] O.S. Magazine, Water Usage, (2020). https://www.oilsandsmagazine.com/technical/environment/water-usage (accessed May 22, 2020).

[25] 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.

[26] M.A. Fahim, T.A. Alsahhaf, A.S. Elkilani, Environmental Aspects in Refining, in: Fundam. Pet. Refin., Elsevier B.V., Oxford, 2010: pp. 423–455. doi:10.1016/B978-0-444-52785-1.00019-X.

[27] M.H. El-Naas, M.A. Alhaija, S. Al-Zuhair, Evaluation of a three-step process for the treatment of petroleum refinery wastewater, J. Environ. Chem. Eng. 2 (2014) 56–62. doi:10.1016/j.jece.2013.11.024.

[28] I.N. Dias, A.C. Cerqueira, G.L. Sant’Anna Jr., M. Dezotti, Oil refinery wastewater treatment in biofilm reactor followed by sand filtration aiming water reuse, J. Water Reuse Desalin. 2 (2012) 84–91. doi:10.2166/wrd.2012.022.

[29] C.P. Bergmann, A.M. Bernardes, M.A.S. Rodrigues, J.Z. Ferreira, Electrodialysis and water reuse, Springer, Heidelberg, 2014. doi:10.1007/978-3-642-40249-4.

[30] J. Qin, M.H. Oo, G. Tao, K.A. Kekre, Feasibility study on petrochemical wastewater treatment and reuse using submerged MBR, J. Memb. Sci. 293 (2007) 161–166. doi:10.1016/j.memsci.2007.02.012.

[31] I. Oller, S. Malato, J.A. Sánchez-Pérez, Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review, Sci. Total Environ. 409 (2011) 4141–4166. doi:10.1016/j.scitotenv.2010.08.061.

[32] D.M. Grewer, R.F. Young, R.M. Whittal, P.M. Fedorak, Naphthenic acids and other acid-extractables in water samples from Alberta : What is being measured ?, Sci. Total Environ. 408 (2010) 5997–6010. doi:10.1016/j.scitotenv.2010.08.013.

[33] C. Benally, M. Li, M. Gamal El-Din, The effect of carboxyl multiwalled carbon nanotubes

content on the structure and performance of polysulfone membranes for oil sands process-affected water treatment, Sep. Purif. Technol. 199 (2018) 170–181. doi:10.1016/j.seppur.2018.01.030.

[34] C. Wang, N. Klamerth, S.A. Messele, A. Singh, M. Belosevic, M. Gamal El-Din, Comparison of UV/hydrogen peroxide, potassium ferrate(VI), and ozone in oxidizing the organic fraction of oil sands process-affected water (OSPW), Water Res. 100 (2016) 476–485. doi:10.1016/j.watres.2016.05.037.

[35] K. Loganathan, P. Chelme-Ayala, M. Gamal El-Din, Pilot-scale study on the reverse osmosis treatment of oil sands tailings pond water: Impact of pretreatment on process performance, Desalination. 360 (2015) 52–60. doi:10.1016/j.desal.2014.12.045.

[36] J.S. Clemente, P.M. Fedorak, A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids, Chemosphere 60 (2005) 585–600. doi:10.1016/j.chemosphere.2005.02.065.

[37] K. Qian, W.K. Robbins, C.A. Hughey, H.J. Cooper, R.P. Rodgers, A.G. Marshall, Resolution and Identification of Elemental Compositions for More than 3000 Crude Acids in Heavy Petroleum by Negative-Ion Microelectrospray High-Field Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Energy and Fuels. (2001) 1505–1511. doi:10.1021/ef010111z.

[38] F.M. Holowenko, M.D. Mackinnon, P.M. Fedorak, Characterization of naphthenic acids in oil sands wastewaters by gas chromatography-mass spectrometry, Water Res. 36 (2002) 2843–2855.

[39] J. V. Headley, D.W. Mcmartin, A Review of the occurrence and fate of naphthenic acids in aquatic environments, J. Environ. Sci. Heal. Part A. 39 (2004) 1989–2010. doi:10.1081/ESE-120039370.

[40] A.R. Ribeiro, O.C. Nunes, M.F.R. Pereira, A.M.T. Silva, An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU, Environ. Int. 75 (2015) 33–51. doi:10.1016/j.envint.2014.10.027.

[41] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today. 53 (1999) 51–59. doi:10.1016/S0920-5861(99)00102-9.

[42] E.M. Aieta, K.M. Reagan, J.S. Lang, L. McReynolds, J.-W. Kang, W.H. Glaze, Advanced Oxidation Processes for Treating Groundwater Contaminated With TCE and PCE: Pilot-Scale Evaluations, J. Am. Water Works Assoc. 80 (1988) 57–63.

[43] X. Xu, G. Pliego, J.A. Zazo, S. Sun, P. García-Muñoz, L. He, J.A. Casas, J.J. Rodriguez, An overview on the application of advanced oxidation processes for the removal of naphthenic acids from water, Crit. Rev. Environ. Sci. Technol. 47 (2017) 1337–1370. doi:10.1080/10643389.2017.1348113.

[44] S.K. Sharma, 3. Green Chemistry for Dyes Removal from Waste Water : Research Trends and Applications, in: Green Chem. Dye. Remov. from Waste Water Res. Trends Appl., Green Chemistry for Dyes Removal from Waste Water : Research Trends and Applications, Massachusetts, 2015: pp. 87–117.

[45] S.-H. Do, B. Batchelor, H.-K. Lee, S.-H. Kong, Hydrogen peroxide decomposition on manganese oxide (pyrolusite): Kinetics, intermediates, and mechanism, Chemosphere 75 (2009) 8–12. doi:10.1016/j.chemosphere.2008.11.075.

[46] C. Wang, J. Kang, H. Sun, H.M. Ang, M.O. Tadé, S. Wang, One-pot synthesis of N-doped graphene for metal-free advanced oxidation processes, Carbon N. Y. 102 (2016) 279–287. doi:10.1016/j.carbon.2016.02.048.

[47] D.B. Miklos, C. Remy, M. Jekel, K.G. Linden, U. Hübner, Evaluation of advanced oxidation processes for water and wastewater treatment e A critical review, Water Res. 139 (2018) 118–131. doi:https://doi.org/10.1016/j.watres.2018.03.042.

[48] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, Chemosphere 55 (2004) 1235–1243. doi:10.1016/j.chemosphere.2003.12.022.

[49] M.A. Oturan, J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2577–2641. doi:10.1080/10643389.2013.829765.

[50] A. Rubio-Clemente, E. Chica, G.A. Peñuela, Petrochemical wastewater treatment by photo-fenton process, Water. Air. Soil Pollut. 226 (2015). doi:10.1007/s11270-015-2321-x.

[51] T. Soltani, B.K. Lee, Improving heterogeneous photo-Fenton catalytic degradation of toluene under visible light irradiation through Ba-doping in BiFeO3 nanoparticles, J. Mol. Catal. A Chem. 425 (2016) 199–207. doi:10.1016/j.molcata.2016.10.009.

[52] H. Demir-Duz, O. Ayyildiz, A.S.A.S. Aktürk, M.G.M.G. Álvarez, S. Contreras, Approaching zero discharge concept in refineries by solar–assisted photo-Fenton and photo-catalysis processes, Appl. Catal. B Environ. 248 (2019) 341–348. doi:10.1016/j.apcatb.2019.02.026.

[53] A. Babuponnusami, K. Muthukumar, A review on Fenton and improvements to the Fenton process for wastewater treatment, J. Environ. Chem. Eng. 2 (2014) 557–572. doi:10.1016/j.jece.2013.10.011.

[54] M.M. Bello, A.A. Abdul Raman, Trend and current practices of palm oil mill effluent polishing: Application of advanced oxidation processes and their future perspectives, J. Environ. Manage. 198 (2017) 170–182. doi:10.1016/j.jenvman.2017.04.050.

[55] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends, Catal. Today. 147 (2009) 1–59. doi:10.1016/j.cattod.2009.06.018.

[56] A.B. Djurišić, Y.H. Leung, A.M. Ching Ng, Strategies for improving the efficiency of semiconductor metal oxide photocatalysis, Mater. Horizons. 1 (2014) 400–410. doi:10.1039/c4mh00031e.

[57] W.-Y. Choi, J. Chung, C.-H. Cho, J.-O. Kim, Fabrication and photocatalytic activity of a novel nanostructured TiO2 metal membrane, Desalination. 279 (2011) 359–366. doi:10.1016/j.desal.2011.06.038.

[58] J. Fu, M. Ji, Z. Wang, L. Jin, D. An, A new submerged membrane photocatalysis reactor (SMPR) for fulvic acid removal using a nano-structured photocatalyst, J. Hazard. Mater.

(2006). doi:10.1016/j.jhazmat.2005.09.039.

[59] M. Pera-titus, V. Garcia-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes : a general review, Appl. Catal. A Gen. 47 (2004) 219–256. doi:10.1016/j.apcatb.2003.09.010.

[60] K.I. Rakness, History and application, in: Ozone Drink. Water Treat. Process Des. Oper. Optim., American Water Works Association., Denver, 2005: pp. 1–16.

[61] U. Von Gunten, Ozonation of drinking water : Part I . Oxidation kinetics and product formation, Water Res. 37 (2003) 1443–1467.

[62] F.J. Beltran, Ozone reaction kinetics for water and wastewater systems, Lewis Publishers, Boca Raton, 2004.

[63] Suez, Advanced Wastewater Treatment for Polishing Treatment Associating Ozonation and Biofiltration, (2020). https://www.suez.com/en/our-offering/success-stories/our-references/chengdu-refinery-industrial-wastewater-treatment-and-reuse (accessed May 23, 2020).

[64] G.P. Anipsitakis, D.D. Dionysiou, Degradation of Organic Contaminants in Water with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt, Environ. Sci. Technol. 37 (2003) 4790–4797. doi:10.1021/es0263792.

[65] M.T. Yang, Z.Y. Zhang, K.Y.A. Lin, One-step fabrication of cobalt-embedded carbon nitride as a magnetic and efficient heterogeneous catalyst for activating oxone to degrade pollutants in water, Sep. Purif. Technol. 210 (2019) 1–9. doi:10.1016/j.seppur.2018.07.086.

3

Approaching Zero Discharge Concept in Refineries by Solar Assisted Photo-Fenton and Photo-catalysis Processes

Applied Catalysis B: Environmental 248 (2019) 341–348

3.1 Introduction

Petroleum refinery is one of the industrial activities, which use larger amount of water and consequently produce large amount of wastewater that contains various organic pollutants, from aromatic to aliphatic compounds [1]. Although it has a very important place in the world economy, there are too many concerns for its environmental effects [2,3]. The discharging limits determined by legislations have been decreasing, forcing the industries to develop more effective methods for the removal of these various organic recalcitrant contaminants [4].

On the other hand, depending on the refinery size and process configuration, the amount of produced wastewater is 0.4–1.6 times the amount of processed crude oil [5,6]. Recycling this water for different purposes such as process water, cooling water and fire water after treatment (depending on the quality standards) is a remarkable option to meet the water needs of the plant [7,8]. From this point of view, the treated effluent may play an important role in sustainable management of water resources through decreasing wastewater discharges, which also presents an economical advantage [9].

So far, conventional treatment techniques based on physicochemical, mechanical and biological methods have been used to remove the organic contaminants from wastewater [4]. However, these processes produce concentrated sludge, which requires further operations. Besides, they perform with limited efficiency in case of emulsified oil and small oil droplets [10]. Thus, in recent years, attentions have been directed toward advanced oxidation processes (AOPs), which generate highly reactive oxidants such as hydroxyl radicals, to transform organic compounds by means of oxidation and mineralization into harmless compounds like H_2O, CO_2 and inorganic salts [11,12].

Conventionally, treatment of refinery effluents composes of preliminary, primary and secondary treatments. In the preliminary step, crude solids and substances are removed mechanically. In the primary treatment, API (American Petroleum Institute) oil-water separators and dissolved air flotation (DAF) processes are applied in order to remove free and emulsified oils. As a secondary treatment, biological treatment is applied, which may remove up to 90% of organic materials in the effluent. Although the discharging requirements are reached after secondary treatment, reuse of this treated water can only be possible by removal of some specific compounds [9]. Apart from this, although biological treatment is considered as the most cost-effective technique, the treatment units require large area due to residence time required and the biomass after treatment must be separated by membrane filtration that requires more energy [13,14]. However, this study wants to explore AOPs as an alternative to biological treatment or as an improver to this treatment.

Among the different types of AOPs, photo-Fenton and heterogeneous photo-catalysis processes have been investigated as treatment solutions to petroleum refineries. However, they have been mainly applied to one-component synthetic wastewaters, especially with phenols, and only few of them deal with real refinery wastewaters (RRWs). For photo-Fenton processes, mostly the effects of the Fenton reagent rates, pH and temperature under UV-A/UV-C irradiation sources have been investigated. Mustafa et al. have treated synthetically prepared gas oil contaminated wastewater by photo-Fenton under UV-C irradiation for 150 min. They achieved 72% of COD removal at 30 °C and pH 3 under optimal amounts of H_2O_2 and Fe^{2+} (400 mg/L and 40 mg/L, respectively) [2]. Coelho et al. compared the efficiencies of different AOPs on petroleum refinery sour waters. They observed slightly better DOC removal by Fenton and photo-Fenton processes rather than other AOPs. They achieved 88% of DOC removal by preliminary Fenton (30 min) and photo-Fenton (60 min) with 8 g/L H_2O_2 and 0.8 g/L $FeSO_4$ [15]. Kavitha et al. also suggested a method to recover the iron used in the treatment in order to use it several times avoiding the production of sludge [16]. However, this kind of multistep recovery processes may be more costly than conventional solid waste management due to some additional processes and energy consumptions. Thus, exploring the advantages of photo-Fenton using the reagents under discharging limits could be worthier than recovery processes. Y.-H. Huang et al. studied the photo-Fenton treatment with low concentration of ferric ions for phenol-contaminated water under UV-A irradiation. A 98% of COD removal was achieved by 120-min photo-Fenton treatment with 5 mg/L Fe^{3+}, revealing that efficient organic removal can also be achieved through the use of few amount of reagents [17].

On the other hand, for heterogeneous photo-catalysis process, some researchers have focused on developing new type of catalysts active especially under visible light. Z. Ghasemi et al. immobilized the TiO_2 nanocrystals into the structure of Fe-ZSM-5 zeolite by sol-gel method and achieved 80% of COD removal from a petroleum refinery wastewater collected before DAF. The treatment took place during 240 min at pH 4 [18]. R.-C. Wang et al. also explored the phenol removal with visible-light photo-catalysis and sonolysis using $ZnFe_2O_4/TiO_2$-immobilized granular activated carbon. Despite the degradation of organics reached a maximum of 84% after 240-min treatment, the reuse of the catalyst decreased the degradation performance [19].

Degussa P25 is a well-known semiconductor, with applications in air purification, solar energy conversion, and wastewater treatment [20], where huge number of studies report its high efficiency as photo-catalyst. This may be due to the high surface area and the mixed anatase and rutile crystal structure, and due to these properties, P25 was selected in this study for reclamation of wastewater in refineries.

This study is focused on finding a feasible solution for a refinery located in Turkey to minimize the fresh water requirement by reuse and recycle of treated effluent with solar AOPs avoiding massive use of reagents, limiting energy consumption and favoring its implementation in a present plant with minor changes. For this, our approach entails the use of solar energy in either heterogeneous photo-catalysis or photo-Fenton processes (or a combination of both) as wastewater polishing treatment, using minimum catalyst amounts and reactants below the discharging limits. This limit for iron is 10 mg/L for 2-hour composite sample and 8 mg/L for 24-hour composite sample for hydrocarbon production facilities such as petroleum refineries in Turkey. Moreover, the limit for COD is 300 mg/L and 250 mg/L, and that for hydrocarbons is 15 mg/L and 10 mg/L for 2-hour and 24-hour composite sample, respectively. Composite sample is defined as a method that several samples are collected periodically in the same sample bottle before the measurement to represent all process during 2 hours or 24 hours.)

Unlike the studies focused on reduction of the catalyst amounts, this study portrays the initial optimization attempts of solar-assisted processes on a multicomponent synthetic wastewater and then the corresponded real case optimizations for the two different effluent type in the refinery to find the best AOP position to be settled. TOC and COD removal efficiencies, water compositions, BOD and toxicity analyses were performed to establish whether these AOPs are more advantageous as a secondary or tertiary treatment.

Furthermore, this study is focused on the basis of a zero-discharge approach through both reducing the amount of generated wastes, and reducing fresh water consumption through reuse of the treated water in the different refinery operations. For the reuse purposes, it is essential to maintain the TOC content below 15 mg/L and 4 mg/L for firewater and cooling water, respectively. Therefore, TOC removal results were followed closely in this study for the assessment of initial sustainability objective.

3.2 Experimental

3.2.1 Materials

Toluene (Sigma-Aldrich, 99.5%), phenol (Sigma-Aldrich, 99-100%), o-cresol (Sigma-Aldrich, 99%), nonane (Sigma-Aldrich, 99%), hexadecane (Sigma-Aldrich, 99%), naphthalene (Acros Organic, 99%) and xylene (Panreac, 98%) were used in the preparation of synthetic refinery wastewater (SRW) as the organic representatives of the real refinery wastewater (RRW). Ammonium chloride, sodium bicarbonate (Sigma-Aldrich, 99.9%) and sodium chloride (Fluka, 99.5%) were used as inorganic representatives of the RRW. Triton-x (Sigma-Aldrich, nanopowder form, 25 nm average diameter, particle size<100 micron) were used as a surfactant in order to emulsify nonane, hexadecane and naphthalene, which are almost non-soluble in water. Sulfuric acid and sodium hydroxide solutions were used to adjust pH.

H_2O_2 (Acros Organic, 35 wt%), $FeSO_4.7H_2O$ (Panreac, 99%), sodium bisulfite solution (Sigma-Aldrich, 40%) and TiO_2, Aeroxide® P25 (Acros Organics) were used in Fenton, photo-Fenton, and photo-catalysis experiments. Dichloromethane (DCM, Sigma-Aldrich, 99.5%), acetonitrile (ACN, Riedel-de Haën, 99.9%) and phosphoric acid (Sigma-Aldrich, 85%) were used for analytical procedures.

The real wastewaters before and after secondary biological treatment have been supplied from a petroleum refinery which is located in Turkey to examine the performance of the processes on real cases.

3.2.2 SRW preparation and water properties

Seven representatives of aromatic and aliphatic hydrocarbons that are frequently detected in refinery wastewater were selected as target contaminants to investigate their removal efficiency by photo-assisted AOPs. The composition of SRW was selected according to previous researches conducted with RRWs and is given in ***Table 3.1*** [6,15,21–24]. The SRW preparation procedure started by the addition of 5 mg Triton-x and the required amounts of salts and non-soluble components into 900 mL distilled water, then followed by the emulsification step with a homogenizer at 7000 rpm during 30 min. Salts were added before emulsification due to their positive effect on decreasing interfacial tension between oil and surfactant solution [25]. Afterwards, the required amounts of soluble organic components were added into the mixture under continuously stirring at 450 rpm with a magnetic stirrer. Finally, the solution was completed into 1000 mL with distilled water and stirred 30 minutes more to ensure a stable wastewater before using in the experiments.

Table 3.1 Composition of SRW.

Component	Conc (mg/L)	Component	Conc (mg/L)
Toluene	10	Naphthalene	10
Nonane	10	Hexadecane	10
Phenol	10	Ammonium Chloride	70
o-Cresol	20	Sodium Chloride	247
Xylene	10	Sodium bicarbonate	160

RRW1 was collected after primary treatment process before biological treatment and it is composed mostly of phenols and derivatives, as well as BTEX, naphthalene and derivatives and C14-C19 alkanes. On the other hand, RRW2 collected after biological treatment process contained mainly C11-C16 alkanes. The effluents were kept in the fridge at 4 ^{o}C before the experiments. A characterization (such as COD, BOD, suspended solid, the concentration of metals and trace elements) of the real wastewaters (3-month average values) was performed and compared to those of SRW in order to explain the possible performance differences (see ***Table 3.2***).

3.2.3 Treatment procedures

Solar light was simulated by a solar box equipped with an air-cooled 1500-W Xenon lamp, which allows 300-800 nm wavelengths to pass through (ATLAS, SUNTEST CPS+). Irradiance was set to 250 W/m^2.

SRW and RRW2 (300 mL) were treated only by photo-Fenton and heterogeneous photo-catalysis while RRW1 was also treated by the combination of these two methods. The mean reaction temperature during the reactions in solar box was 35 ^{o}C. All the experiments were performed by duplicate.

Furthermore, Fenton treatment was also applied to confirm the efficiency of the light activity for both SRW and RRW1-2 with the H_2O_2/COD weight ratio (w/w) of 2 and H_2O_2/Fe^{2+} weight ratio (w/w) of 10 at pH 3 and at 35 ^{o}C.

Table 3.2 Characterization of wastewaters used in the present study.

Water characteristics used in the experiments

	TOC (mg C/L)	COD (mg O_2/L)	pH	Cl^- (mg/L)	NH4 (mg/L)	HCO_3 (mg $CaCO_3$/L)
SRW	68	236	8.00	196	24	116
RRW1	130	450	8.78			
RRW2	17	40	6.72			

3 Months average characteristics of RRW

	Suspended Solid (mg/L)	Oil & Grease (mg/L)	COD (mg O_2/L)	TOC (mg C/L)	BOD	Conductivity (µS/cm)	pH
RRW1	25.6	32.1	476.8	111.3	181.2	1804.8	8.5
SD*	8	18.3	142.5	66.1	52.4	934.6	0.5
RRW2	43.3	22.6	108.2	39.3	38.5	3396.7	7,1
SD**	11.1	1.4	22.7	27.2	6.6	1694.7	0,2

	HCO_3 (mg $CaCO_3$/L)	Zn (µg/L)	Cl^- (mg/L)	NH_4 (mg/L)	Mn (µg/L)	SO_4 (mg/L)	Fe (mg/L)
RRW1	156.8	229	183.7	23.2	105.9	288.9	0.6
SD*	42.6	207.4	100.6	13.5	15.2	104	0.5
RRW2	78.3	228.3	309.2	10	164.1	408.5	0.6
SD**	30.9	134.9	289.5	6.1	74.1	41.9	0.5

SD*: Standard deviations of the analyses performed with RRW1

SD**: Standard deviations of the analyses performed with RRW2.

3.2.3.1 Photo-Fenton

Photo-Fenton experiments were carried out during 90 min at pH 3, which was found to be optimum pH for Fenton process [26–28]. The H_2O_2/COD ratio (w/w) ranged from 1 to 10 while the H_2O_2/Fe^{2+} ratio (w/w) was between 5 and 100. Before the experiments, pH of the wastewaters was adjusted around 4 to make the iron species soluble. Then, the required amount of $FeSO_4{\cdot}7H_2O$ was added. Afterwards, the reaction has been started by addition of H_2O_2 under continuous stirring and pH was adjusted to 3, immediately. Samples were collected at specific intervals during the reaction for analyses and checked with semi-quantitative H_2O_2 strips to determine its remaining concentration in the samples. In case of containing H_2O_2, sodium bisulfite has been used to quench the reaction in the samples.

For the RWW treatments the duration enlarged up to 180 min depending on the degradation rates and H_2O_2 concentrations of the intermediate samples.

3.2.3.2 Heterogeneous photo-catalysis

Heterogeneous photo-catalysis experiments have been firstly performed at free pH during 360 min with TiO_2 catalyst concentrations of 100, 250 and 500 mg/L. All experiments have been started with 30-min adsorption step under dark condition. This duration has been decided according to the results of 60-min adsorption tests of the catalyst. In addition, the pH effect between 3 and 8 has been examined with 250 mg/L catalyst.

The samples collected during the experiments were centrifuged during 10 min at 5000 rpm before the analytical procedures.

3.2.3.3 Photo-Fenton/photo-catalysis combination

RRW1 was exposed to the combination of these two processes either subsequently or at the same time in order to evaluate the performance of these systems either separately or together. In “one after the other” concept, 360-min photo-catalysis with 500 mg/L TiO_2 has been employed after 180-min photo-Fenton treatment with a H_2O_2/COD ratio (w/w) of 4 and a H_2O_2/Fe^{2+} ratio (w/w) of 100. Before adding the catalyst, pH was increased to 7. In the case of synchronous mode, firstly the pH of the water has been adjusted around 4. Afterwards, 100 mg/L TiO_2 has been added into the water in order to perform adsorption procedure before the addition of Fenton reagents. Subsequent to 30-min adsorption, Fenton reagents have been added to the reaction medium and pH has been adjusted to 3, immediately. Reactions took place during 90 min under solar light.

3.2.4 Characterization

Total organic carbon (TOC) analyses were performed with a Shimadzu TOC-L (CSN 638-91109-48) analyzer to evaluate the mineralization degree during experiments.

Chemical oxygen demand (COD) analysis was performed by colorimetric method with AQUALYTIC® Tube Tests COD Vario.

The biological oxygen demand (BOD_5) was measured using respirometric method with a Velp equipment (VELP Scientifica). Polyseed® was used as the microbial culture source.

Microtox® acute toxicity testing was performed with *Vibrio Fischeri* according to the 81.9% basic test protocol with 9 dilutions from Microtox Omni Software during 15 min using a Microtox® Model 500 Analyzer that is a laboratory-based, temperature-controlled, self-calibrating luminometer used for measuring acute toxicity. The results were expressed by EC50 value, which was defined as the effective nominal concentration of treated wastewaters by volume percent that caused reduction in the intensity of light emission by 50%.

Before the BOD_5 and toxicity analyses, the pH of the samples were adjusted into 6-8 range and filtered. For the purpose of better comparison between the treatment methods, all analyses results have been examined and compared for the 90-min-sample of the treatments.

Qualitative and quantitative analyses of the samples were performed by GC-MS and HPLC. HPLC analyses were conducted with HPLC system supplied by Shimadzu equipped with a diode array detector (DAD) using a gradient method. Water (containing 0.1% phosphoric acid): ACN was used as mobile phase. For the separation of the analytes, a Mediterranea HPLC column (C18, 2.1 × 150 mm, 3.5 µm, Teknokroma, USA) was used at a temperature of 40°C. The DAD wavelength was set at 254 nm. Before GC-MS analysis, samples were extracted by dichloromethane (DCM). For the extraction, 5 mL sample were saturated with required amount of NaCl and shook by hand. Then, 1 mL of DCM was added into the sample. After shaking by hand again, samples have been placed horizontally on a laboratory shaker that worked for 1.5 hours at 120 U/min and followed by 5 min centrifuge at 3500 rpm. Finally, the extract was analyzed by GC-MS (QP2010, SHIMADZU) equipped with ZB-5MS PLUS column and using a splitless injection mode. For the SRW, the same extraction procedure has been applied without salt as well, since the extraction of hexadecane, phenol and o-cresol was better in the presence of salt while that of other components was better in the absence of salt. The extraction percentages of hexadecane, phenol and o-cresol with salt were 85±1, 100 and 70±2, while those of toluene, xylene, nonane and naphthalene without salt were 77±1, 77±3, 24±1 and 85±3, respectively.

3.3 Results and Discussions

3.3.1 SRW (synthetic refinery wastewater)

In photo-Fenton experiments, the TOC removal ranged from 72 to 81%, the best TOC removal being achieved for a H_2O_2/COD ratio of 2 and a H_2O_2/Fe^{2+} ratio of 50. This result may be considered as the first proof of concept approach to the zero-discharge philosophy, since only less than 10 mg/L Fe^{2+} was necessary to reach more than 80% of mineralization in 90 min. ***Figure 3.1a-3.1b*** show the results with a fixed H_2O_2/COD ratio of 2 and a variable H_2O_2/Fe^{2+} ratio, and a fixed H_2O_2/Fe^{2+} ratio of 50 and varying H_2O_2/COD ratio, respectively. The importance of finding an optimum H_2O_2 and Fe^{2+} ratio has been highlighted, similarly to that found in many studies related to Fenton reactions. Thus, at a fixed H_2O_2/COD=2, an increase in the iron concentration did not enhance the efficiency of the oxidation reaction, in terms of TOC removal (***Figure 3.1a***). Furthermore, the mineralization of organic matter increased with the decreasing Fe concentration. This is often attributed to the competitive reactions of H_2O_2 with the excessive Fe^{2+} ions to form Fe^{3+}, which leads to lower degradation rates [3,29]. On the other hand, it was found that the optimal H_2O_2 concentration corresponded to a ratio H_2O_2/COD=2 with a H_2O_2/Fe^{2+} ratio of 50 (***Figure 3.1b***).

According to GC-MS results (***Figure Appx. A1***), the oxidation of BTEX, phenols and naphthalene was observed after 90 min of treatment. Whereas, some part of alkanes (nonane and hexadecane) still remained. This result was confirmed by HPLC analysis (***Figure Appx. A2***), which showed the abatement of the aromatic components and appearance of some acids and other by-products at retention times between 2-5 min. This products may be tentatively small chain organic acids such as formic acid, acetic acid, benzoic acid, maleic acid and oxalic acid [17,30,31], however they could not be defined specifically. On the other hand, although hexadecane and nonane after GC-MS analyses presented almost the totality of the components in the sample (ca. 96% in area basis), traces of xylene, o-cresol and ketones were also detected after photo-Fenton treatment.

The recalcitrant properties of the alkanes are due to the absence of electron pairs in these saturated molecules with no low energy empty π orbitals and no high energy filled n orbitals. The oxidation of the alkanes by hydroxyl radicals takes place by abstraction of a hydrogen atom to form water, presenting k_2 values between 10^6-10^8 $M^{-1}s^{-1}$, while that of aromatic components takes place by the hydroxylation or electrophilic addition with k_2 values between 10^8-10^{10} $M^{-1}s^{-1}$. Hence, oxidation of that saturated molecules need very reactive reagents or very extreme reaction conditions [32,33].

In the case of heterogeneous photo-catalysis, the best result achieved was around 80% of TOC removal after 360-min reaction at pH 8. This result was obtained with 250 mg/L of TiO_2 catalyst, and an increase of catalyst to 500 mg/L did not lead to an increase of TOC removal (81%) (***Figure 3.1c***).

The pH effect was also examined with 250 mg/L of catalyst. The results (***Figure 3.1d***) highlight the influence of the pH of the reaction medium on the degradation rates. At pH 3, the degradation decreased remarkably compared to pH 5, where a 91% of TOC removal could be achieved. Increasing pH to 8 also led to a decrease in the degradation efficiency of P25, which indicates that the overall degradation is favored at pH near to the zero charge point of TiO_2 (at pH 6.25).The composition of the waters treated in this study is complex, containing both polar and apolar compounds that can interact in different forms with the catalyst surface. Therefore, 60-min adsorption tests with SRW at pH 3, 5 and 8 using 250 mg/L TiO_2 revealed a higher adsorption at acidic pH (slightly higher at pH 5) than at basic pH. The adsorption capacities were 26%, 29% and 10% for the pH 3, 5 and 8, respectively. The protonated surface of the TiO_2 at acidic pH (pH 3 and 5) favor the adsorption of phenolic compounds and substituted aromatics. Thus, it seems reasonable that a better adsorption can lead to a better photo-catalytic performance. Oturan et al. also underlined the crucial role of the pH on the efficiency of photo-catalysis that has to be optimized primarily [28]. However, other factors such as the presence of anions in solution or the number of hydroxyl groups and defects on the catalyst surface may also play a role on the degradation performance, and their influence is still under debate. Additionally, the positive effect of UV light exposure of TiO_2 nanoparticles in acidic medium can be the other reason of this enhancement. In acidic medium, when the electrons and holes are generated, the electrons react with oxygen molecules, which produce superoxide radical anions. Instead, the holes react with water producing hydroxyl radicals. Thus, two different reactive species can decompose the organic contaminants improving the treatment efficiency [34].

GC-MS analysis (***Figure Appx. A3***) showed that, even if some oxidation by-products are produced after 90-min treatment (e.g. phenolic compounds from phenol and o-cresol, naphthalene, C9 to C16 alkanes, aldehydes, ketones and BTEX), these compounds were mostly removed after 360 min. A 91% of TOC removal was achieved after treatment, and the remained 9% is formed by C14-16 alkanes, alcohols and ketones (as identified by GC-MS) and carboxylic acids (detected by HPLC, ***Figure Appx. A4***). In addition, nonane was not detected after treatment by heterogeneous photo-catalysis in contrast to photo-Fenton treatments.

Toxicity analyses of the initial sample gave an EC50 value of 3%. After photo-catalysis treatment (90 min) with 250 mg/L TiO_2 at pH 3, 5 and 8, the EC50 values obtained were 7%, 17% and 10%, respectively. Therefore, toxicity was only slightly decreased by photo-catalysis. However, for 90-min photo-Fenton experiments, samples have been mostly found to be non-toxic, and the highest effect on bioluminescence observed was 9%, 15% and 39% for the H_2O_2/COD ratio of 2, 1 and 4, respectively. Thus, photo-Fenton process showed to be more efficient than heterogeneous photo-catalysis in decreasing the initial toxicity of the SRW after 90-min treatments. This may be due to the presence of residual toxic intermediates after 90-min photo-catalytic treatment, such as phenol and phenolic derivatives [35], which were only able to be decomposed after longer period of treatment by photo-catalysis with TiO_2.

After these promising degradation results obtained with the SRW, these processes have been applied to RRWs to make comparisons and improvements for real samples. The possible application of AOPs as either a secondary treatment or a tertiary treatment has been considered. The optimum conditions obtained with SRW has been taken as the reference for the starting points of RWW treatments.

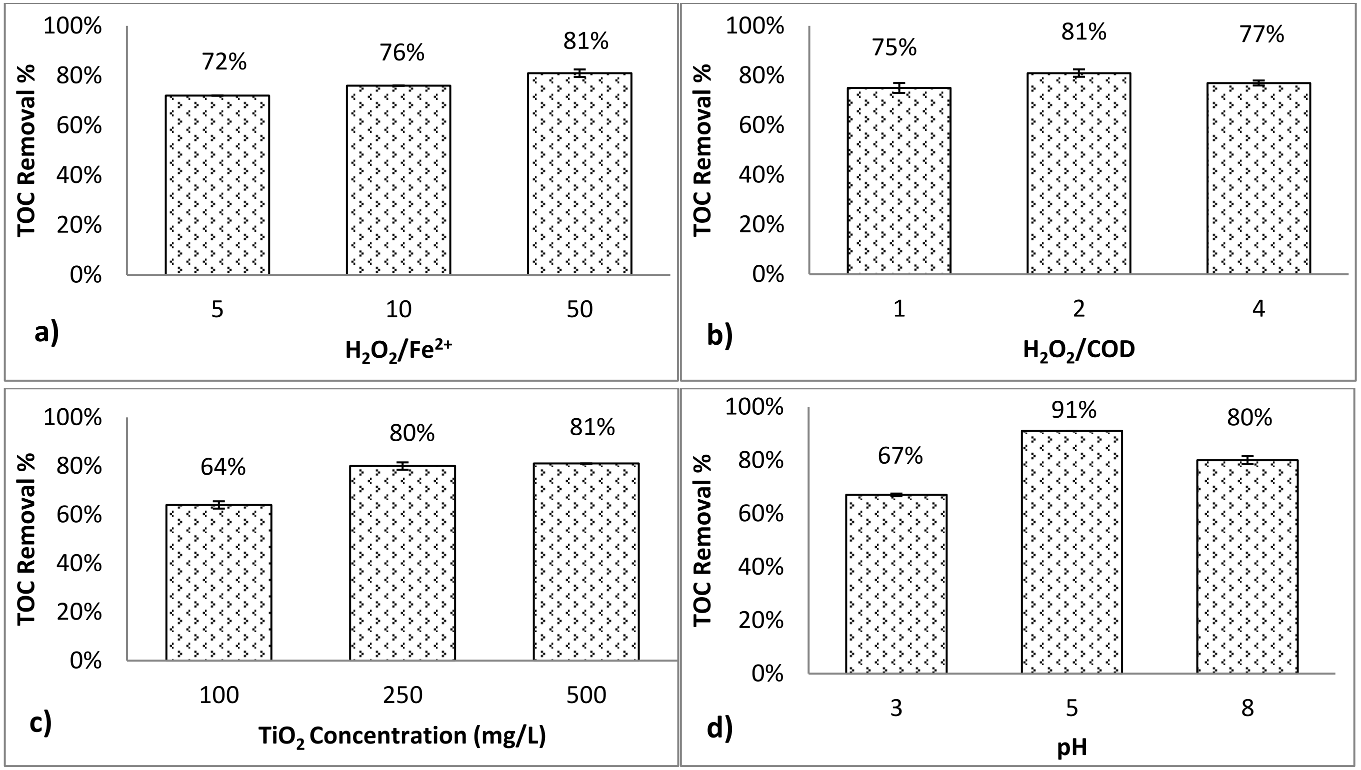

Figure 3.1 TOC removals after 90-min Photo-Fenton experiments at pH 3 a) at a constant H_2O_2/COD ratio of 2 with different amounts of Fe^{2+}, b) at a constant H_2O_2/Fe^{2+} ratio of 50 with different amounts of H_2O_2; TOC removals by photo-catalysis with TiO_2 after 360 min: c) effect of catalyst amount; d) effect of pH for treatment by 250 mg/L catalyst.

3.3.2 RRW1 (real refinery wastewater after DAF treatment)

An initial photo-Fenton test with the H_2O_2/COD ratio of 2 and the H_2O_2/Fe^{2+} ratio of 50 resulted in a 58% of TOC removal after 90-min treatment. Total consumption of H_2O_2 has been observed at the end of 90-min treatment. When a new addition of H_2O_2 was done after this time, the degradation of organics increased to 74% after 90 min more treatment. This result showed that the treatment of RWW1 needed more H_2O_2 reagent than that of SRW. This could be because of the composition of the water, which includes transition metals such as manganese (Mn) that acts as H_2O_2 scavenger [36,37].

After these initial observations, new experiments were conducted for 180 min to ensure a total H_2O_2 consumption without quenching with sodium bisulfite. As it is shown in ***Figure 3.2***, when the H_2O_2/COD ratio was kept at 4, TOC removal increased from 68% to 74% after 180 min of treatment with the increasing H_2O_2/Fe^{2+} ratio from 10 to 100. In that case the required amount of Fe^{2+} significantly decreased from 180 mg/L to 18 mg/L. Besides that, with excessive amounts of H_2O_2 as in the case of H_2O_2/COD ratio of 10 and H_2O_2/Fe^{2+} ratio of 50, where the required amount of Fe^{2+} was 90 mg/L, the degradation completed at 90 min with the result of 75% TOC removal and with 150-300 mg/L residual H_2O_2 content. After the completion of 180 min, the degradation percentage did not change even though H_2O_2 was consumed completely. Hence, it can be concluded that it is possible to remove the same amount of TOC either by 90-min photo-Fenton treatment with high amounts of reagents or by 180-min treatment with very less amounts of reagents. Aljuboury et al. also evaluated the performance of solar-photo-Fenton treatment on a real petroleum refinery effluent with initial TOC value of 220-265 and, they achieved max. 59.3% of TOC removal with 60 mg/L Fe^{2+} and 850 mg/L H_2O_2 after 127 min of reaction time, which were the optimum conditions determined by an experimental design [38].

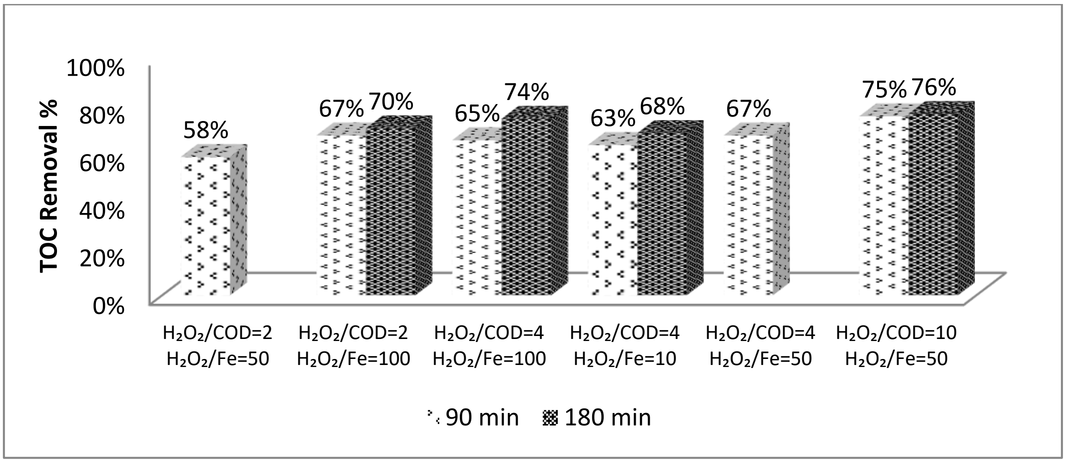

Figure 3.2 TOC removal rates in RRW1 by photo-Fenton depending on the reagent ratios and time.

For the heterogeneous photo-catalysis experiments, 26%, 27% and 30% of TOC removals have been achieved with the 100, 250 and 500 mg/L TiO_2, respectively. In comparison to SRW results, the mineralization by heterogeneous photo-catalysis was rather lower. This behavior difference may be explained by the high turbidity presented in RRW1 which blocks the light transmission [39]. On the other hand, since the maximum TOC removal achieved by photo-Fenton was 75%, a 360-min photo-catalysis experiment was performed with 500 mg/L TiO_2 subsequent to 180-min photo-Fenton with the H_2O_2/COD ratio of 4 and H_2O_2/Fe^{2+} ratio of 100. Total TOC removal after 180-min photo-Fenton/360-min photo-catalysis resulted in 90%. Although 74% of mineralization has been achieved during photo-Fenton step, photo-catalysis step mineralized the 63% of remained part, which also confirmed the turbidity effect. A decrease in the turbidity during photo-Fenton step might have increased the efficiency of the TiO_2-photo-catalysis step, which resulted in 63% rather than 30% achieved by only heterogeneous photo-catalysis. In addition, the difference between initial compositions before and after photo-Fenton may be another reason for the improvement of photo-catalysis with TiO_2.

As photo-Fenton decreased the turbidity and heterogeneous photo-catalysis resulted in an efficient method in waters with low turbidity, the possible synergetic effect of the synchronized combination of both treatments was examined to shorten the reaction time. When H_2O_2/Fe^{2+} ratio were kept at 100, 71%, 79% and 84% of TOC removal was achieved with the H_2O_2/COD ratio of 2, 4 and 10, respectively after 90 min treatment in the presence of 100 mg/L of TiO_2, which improved the degradation rate achieved by only photo-Fenton (75%). COD removal rates resulted in 85% and 88% for the H_2O_2/COD ratio of 4 and 10, respectively (H_2O_2/Fe^{2+} ratio was 100 and

TiO_2 concentration was 100 mg/L). The synergetic effect of the combined procedure has also been studied by Aljubory et al, on a real petroleum effluent with an initial TOC value of 243 mg/L. They achieved max. 62% of TOC removal with 660 mg/L TiO_2, 500 mg/L H_2O_2 and 10 mg/L Fe^{2+} [40].

Furthermore, GC-MS and HPLC results (***Figures Appx. A5-A6***), also confirmed the removal of the main products, mostly composed of phenolic components, BTEX and C11-19 alkanes, and formation of some by-products (presumable short chain organic acids) after 90-min combined treatment. In addition, small amount of C12-C16 alkanes, some alcohols and organosulfur compounds have been detected after treatment. Again, alkanes have presented resistance to these oxidation processes. Even though the molecule sizes of the alkanes got smaller by breaking the chains, they were found not to be completely degradable.

Toxicity analyses performed with RRW1 confirmed the trend observed with SRW, and photo-Fenton process showed to be more efficient in reducing the associated toxicity. After 90-minphoto-Fenton treatment with a H_2O_2/COD ratio of 2 and H_2O_2/Fe^{2+} ratio of 100, the effluent produced presented an EC50 value of 70% in contrast to the initial value of 1%. However, the effluent produced by photo-catalysis at pH 5 with 250 mg/L TiO_2 showed high toxicity, whose EC50 value was 1%. This was because of the poor oxidation efficiency of TiO_2-photo-catalysis on RRW1. In case of the combined treatment, the synergy observed with respect to the TOC removal was also noticed with regards to toxicity. In the effluent obtained after 90-min combined treatment with the H_2O_2/COD ratio of 2, and the H_2O_2/Fe ratio of 100 in the presence of 100 mg/L TiO_2, the EC50 value was increased to 82%, while that of H_2O_2/COD=4 (other parameters were kept constant) presented only highest effect of 39% on bioluminescence (maximum reduction in the intensity of light emission, which did not reach to 50%).

Therefore, photo-Fenton could be applied to the real refinery wastewater after primary treatment as an alternative to a biological process, as similar final TOC values are achieved. In the case of photo-Fenton (using only 9 mg/L Fe^{2+}) the final TOC reached up to 24 mg/L, while the TOC after biological treatment was 17 mg/L. Furthermore, the advantages would be a lower COD content of the effluent compared to the one after biological treatment and the non-toxic properties after the treatment, thanks especially to the removal of the aromatic fractions, which are much more toxic than the aliphatic compounds.

Photo-assisted processes can also be applied after the primary treatment to improve the biodegradability, in case that a subsequent biological process is applied. To monitor this property, BOD_5/COD ratios were measured after the different operating conditions tested, revealing that the photo-Fenton process with a H_2O_2/COD ratio of 2 and a H_2O_2/Fe^{2+} ratio of 50 improved greatly the BOD_5/COD ratio, reaching a value of 0.83 after 90 min of treatment, which was 0.38 initially. Generally, $BOD_5/COD \geq 0.4$ is considered as highly biodegradable [41].

3.3.3 RRW2 (real refinery wastewater after biological treatment)

With the idea of having good quality effluents to reuse in the plant, the application of AOPs as tertiary treatment was also considered. From this point of view, despite the low initial TOC concentration of RRW2 (17 mg/L), this concentration was decreased to less than 4 mg/L and 1 mg/L by photo-Fenton and heterogeneous photo-catalysis, respectively. This represents values far below the limit of discharge and makes the process especially attractive for water reuse purposes.

A 78% of mineralization was achieved after 180-min photo-Fenton treatment either with $H_2O_2/COD=10$ and $H_2O_2/Fe=50$ or $H_2O_2/COD=4$ and $H_2O_2/Fe=10$ (***Figure 3.3***), which resulted in less than 4 mg/L of TOC value. In the former case, the concentration of ferrous ion used was 8 mg/L, while the concentration in the second case was 16 mg/L.

Under dark conditions, Fenton experiments conducted with $H_2O_2/COD=2$ and $H_2O_2/Fe=10$ at pH 3 at 35 ^oC led to a 19% of TOC removal, while removal at room temperature was only 3%. Here, the positive effect of the light assisted Fenton process might be emphasized. Moreover, although the removal efficiency of the Fenton process over the photo-Fenton was a significantly lower, within the Fenton treatment, increasing temperature led to an increase in the reaction efficiency. This effect may be attributed to the higher generation of hydroxyl radicals due to the increase in the concentration of $Fe(OH)^{2+}$ by elevated temperature [42]. However, the different activation energy between the organics and the hydroxyl radicals may demonstrate different behavior, which results in efficiency or inefficiency of the temperature on the treatment system [43].

Photo-catalysis experiments conducted during 360 min with 100, 250 and 500 mg/L TiO_2 at pH free (pH 6.72) resulted in 33%, 70% and 73% of mineralization, respectively. However, here the positive effect of acidic pH has been emphasized again, which was explained previously. The same treatment with 500 mg/L at pH 5 resulted in 92% TOC removal, where the final TOC value was less than 1 mg/L and the COD value was below the detection limit.

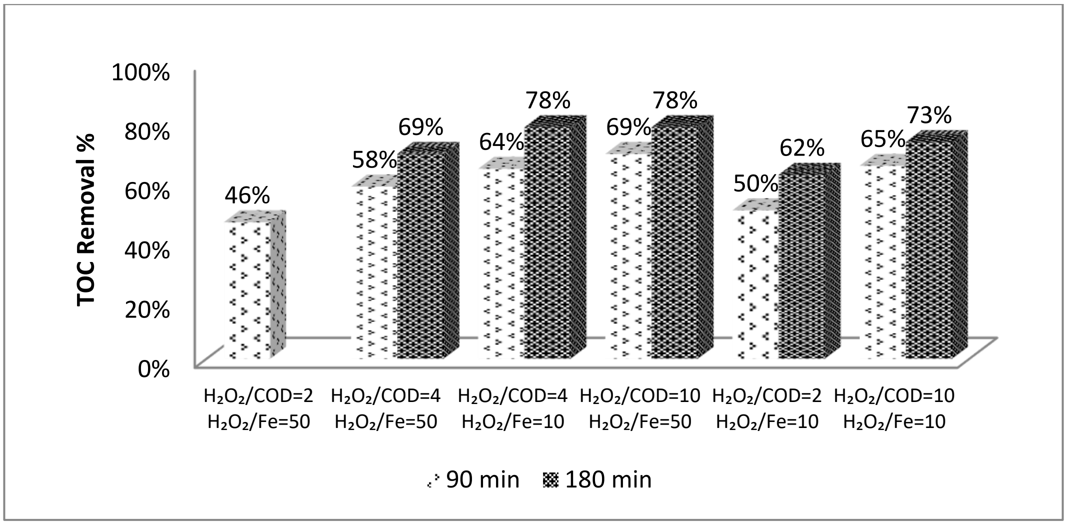

Figure 3.3 TOC removal rates in RRW2 by photo-Fenton depending on the reagent ratios and time.

According to the GC-MS analysis, the main components detected in the raw wastewater were C11-C16 alkanes. This composition is also similar to the RRW1 after treatment that is presented in this chapter, ***section* 3.3.2**. Although the concentrations of alkanes were decreased after the treatment of RRW2, some small amount of C11-C16 alkanes, such as pentadecane and hexadecane were detected.

Toxicity analyses were performed in that sample treated by TiO_2-photo-catalysis at pH 5, which was found to be the optimum pH in this study. The results showed that EC50 value was 42% for the treatment with 100 mg/L catalyst. On the other hand, for the catalysts amounts of 250 mg/L and 500 mg/L, the samples after treatment was mostly non-toxic and the maximum effect of these samples was found to be 24% and 42% for the amounts of 250 mg/L and 500 mg/L, respectively. However, initial RRW2 was already non-toxic with a maximum effect of 28%. Here, the non-toxic properties of the water were maintained while the quality of the effluent was increased for reuse purposes.

3.3.4 Impact of the tested technologies

As mentioned in ***section* 3.1**, the amount of produced wastewater is 0.4–1.6 times the amount of processed crude oil. 40-45% of this water requirement used in cooling towers and steam generation units. The other part is mostly used for other purposes such as processing units or firewater [44]. However, in a typical refinery, fresh water is used for different purposes such as process water, boiler and cooling water, firewater, tap water and utility water systems [8] .

Even though every application within the refinery presents different water requirements, for the main applications needed, it is essential to maintain the TOC content below 15 mg/L and 4 mg/L for firewater and cooling water, respectively. Besides that, pH and conductivity values, oil, total suspended solid (TSS) and chloride contents are other criterions that must be controlled for firewater, while the hardness and alkalinity are additional criterions for cooling water.

According to the obtained results of this study, AOPs as the tertiary treatment (on RRW2) may allow to obtain water of the requested quality to be reused as fire water or cooling water either after 360-min photo-catalysis with 250 mg/L and 500 mg/L TiO_2 that reduced the TOC value under 4 and 1 mg/L, respectively, or after 180-min photo-Fenton with 8 mg/L ferrous ion, which resulted in a TOC value of 3 mg/L. Here, in the case of cooling water reuse, precipitated ferrous ion has to be managed since it is higher than the requirements for cooling water, although it is lower than the discharging limits. Besides that, although AOPs as secondary treatment (on RRW1) was not sufficient to reach reuse aims by itself, it may be useful to reduce reaction time and waste production compared to biological treatment, achieving similar final TOC values and enhanced biodegradability.

3.4 Conclusions

High efficiencies of solar-light assisted photo-Fenton and photo-catalysis treatments on SRW have been revealed through this research. However, when considering real effluents with different characteristics and, economic and environmental limitations, photo-Fenton process under solar light presented the best performance either as pre-treatment or post-treatment.

In case of the photo-Fenton application as pre-treatment to a biological treatment, improved biodegradability and toxicity has been highlighted. As a matter of fact, it could be an alternative to a biological treatment with a very similar final TOC value and lower COD content compared to the effluent obtained after biological treatment.

On the other hand, considering photo-Fenton as a post-treatment after a biological treatment, especially the final TOC and COD values achieved meet the water requirements to be reused in the refinery. In case of providing other water properties such as conductivity and hardness, these effluents can be a good candidate to compensate the cooling water and firewater requirements of the refinery. However, although the final iron content is not a problem for reuse issues as firewater, it is an obstacle to handle previously in case of reusing as cooling water. In that case, detailed economic and environmental analysis should be performed to evaluate the possible problems and their solutions such as the management of 8 mg/L iron as a solid waste and the possibility of recovering this iron for reuse purposes.

Depending on the water consumption and required properties of the process units, reducing discharges significantly by reusing and recycling the effluents produced could be possible by a photo-Fenton treatment while reducing the required energy by means of the solar light.

References

[1] 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.

[2] Y. Abdulaziz Mustafa, A. Ibrahim Alwared, M. Ebrahim, Removal of oil from wastewater by advanced oxidation process / homogeneous process, J. Eng. 19 (2013) 686–694.

[3] A.L.N. Mota, L.F. Albuquerque, L.T.C. Beltrame, O. Chiavone-Filho, A. Machulek Jr., C.A.O. Nascimento, Advanced oxidation processes and their application in the petroleum industry: a review, Brazilian J. Pet. Gas. 2 (2008) 122–142. doi:10.5419/bjpg.v2i3.57.

[4] 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.

[5] C.F. Bustillo-Lecompte, M. Knight, M. Mehrvar, Assessing the performance of UV/H2O2 as a pretreatment process in TOC removal of an actual petroleum refinery wastewater and its inhibitory effects on activated sludge, Can. J. Chem. Eng. 93 (2015) 798–807. doi:10.1002/cjce.22180.

[6] M.H. El-Naas, M.A. Alhaija, S. Al-Zuhair, Evaluation of a three-step process for the treatment of petroleum refinery wastewater, J. Environ. Chem. Eng. 2 (2014) 56–62. doi:10.1016/j.jece.2013.11.024.

[7] B.M. Souza, B.S. Souza, T.M. Guimarães, T.F.S. Ribeiro, A.C. Cerqueira, G.L. Sant'Anna, M. Dezotti, Removal of recalcitrant organic matter content in wastewater by means of AOPs aiming industrial water reuse, Environ. Sci. Pollut. Res. 23 (2016) 22947–22956. doi:10.1007/s11356-016-7476-5.

[8] Petroleum refining water/wastewater use and management Operations Best Practice Series 2010, IPIECA. (2010) 1–55. http://www.ipieca.org/resources/good-practice/petroleum-refining-water-wastewater-use-and-management/ (accessed June 6, 2017).

[9] C.P. Bergmann, A.M. Bernardes, M.A.S. Rodrigues, J.Z. Ferreira, Electrodialysis and water

reuse, Springer, Heidelberg, 2014. doi:10.1007/978-3-642-40249-4.

[10] M.A. Tony, P.J. Purcell, Y. Zhao, Oil refinery wastewater treatment using physicochemical, Fenton and photo-Fenton oxidation processes, J. Environ. Sci. Heal. Part A Toxic/Hazardous Subst. Environ. Eng. 47 (2012) 435–440. doi:10.1080/10934529.2012.646136.

[11] G. Moussavi, A. Khavanin, R. Alizadeh, The investigation of catalytic ozonation and integrated catalytic ozonation/biological processes for the removal of phenol from saline wastewaters, J. Hazard. Mater. 171 (2009) 175–181. doi:10.1016/j.jhazmat.2009.05.113.

[12] B. Bianco, I. De Michelis, F. Vegliò, Fenton treatment of complex industrial wastewater: Optimization of process conditions by surface response method, J. Hazard. Mater. 186 (2011) 1733–1738. doi:10.1016/j.jhazmat.2010.12.054.

[13] S. Adham, A. Hussain, J. Minier-matar, A. Janson, R. Sharma, Membrane applications and opportunities for water management in the oil & gas industry, 440 (2018) 2–17.

[14] L. Yu, J. Chen, Z. Liang, W. Xu, L. Chen, D. Ye, Degradation of phenol using Fe3O4-GO nanocomposite as a heterogeneous photo-Fenton catalyst, Sep. Purif. Technol. 171 (2016) 80–87. doi:10.1016/j.seppur.2016.07.020.

[15] A. Coelho, A. V. Castro, M. Dezotti, G.L. Sant'Anna Jr., Treatment of petroleum refinery sourwater by advanced oxidation processes, J. Hazard. Mater. 137 (2006) 178–184. doi:10.1016/j.jhazmat.2006.01.051.

[16] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, Chemosphere 55 (2004) 1235–1243. doi:10.1016/j.chemosphere.2003.12.022.

[17] Y.H. Huang, Y.J. Huang, H.-C. Tsai, H.-T. Chen, Degradation of phenol using low concentration of ferric ions by the photo-Fenton process, J. Taiwan Inst. Chem. Eng. 41 (2010) 699–704. doi:10.1016/j.jtice.2010.01.012.

[18] Z. Ghasemi, H. Younesi, A.A. Zinatizadeh, Preparation, characterization and photocatalytic application of TiO2/Fe-ZSM-5 nanocomposite for the treatment of petroleum refinery wastewater: Optimization of process parameters by response surface methodology, Chemosphere 159 (2016) 552–564. doi:10.1016/j.chemosphere.2016.06.058.

[19] R.-C. Wang, C.-W. Yu, Phenol degradation under visible light irradiation in the continuous system of photocatalysis and sonolysis, Ultrason. Sonochem. 20 (2013) 553–564. doi:10.1016/j.ultsonch.2012.07.014.

[20] L. Aoudjit, P.M. Martins, F. Madjene, D.Y. Petrovykh, S. Lanceros-Mendez, Photocatalytic reusable membranes for the effective degradation of tartrazine with a solar photoreactor, J. Hazard. Mater. 344 (2018) 408–416. doi:10.1016/j.jhazmat.2017.10.053.

[21] M. Al Zarooni, W. Elshorbagy, Characterization and assessment of Al Ruwais refinery wastewater, J. Hazard. Mater. 136 (2006) 398–405. doi:10.1016/j.jhazmat.2005.09.060.

[22] 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.

[23] I.N. Dias, A.C. Cerqueira, G.L. Sant'Anna Jr., M. Dezotti, Oil refinery wastewater treatment in biofilm reactor followed by sand filtration aiming water reuse, J. Water Reuse Desalin. 2 (2012) 84–91. doi:10.2166/wrd.2012.022.

[24] L. Yan, H. Ma, B. Wang, W. Mao, Y. Chen, Advanced purification of petroleum refinery wastewater by catalytic vacuum distillation, J. Hazard. Mater. 178 (2010) 1120–1124. doi:10.1016/j.jhazmat.2010.01.104.

[25] S. Ferdous, M.A. Ioannidis, D.E. Henneke, Effects of temperature, pH, and ionic strength on the adsorption of nanoparticles at liquid-liquid interfaces, J. Nanoparticle Res. 14 (2012) [850]. doi:10.1007/s11051-012-0850-4.

[26] A. Babuponnusami, K. Muthukumar, A review on Fenton and improvements to the Fenton process for wastewater treatment, J. Environ. Chem. Eng. 2 (2014) 557–572. doi:10.1016/j.jece.2013.10.011.

[27] D. Huang, C. Hu, G. Zeng, M. Cheng, P. Xu, X. Gong, R. Wang, W. Xue, Combination of Fenton processes and biotreatment for wastewater treatment and soil remediation, Sci. Total Environ. 574 (2017) 1599–1610. doi:10.1016/j.scitotenv.2016.08.199.

[28] M.A. Oturan, J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2577–2641. doi:10.1080/10643389.2013.829765.

[29] A.R. Dincer, N. Karakaya, E. Gunes, Y. Gunes, Removal of COD from oil recovery industry wastewater by the advanced oxidation processes (AOP) based on H2O2, Glob. NEST J. 10 (2008) 31–38.

[30] H. Wang, Q. Guan, J. Li, T. Wang, Phenolic wastewater treatment by an electrocatalytic membrane reactor, Catal. Today. 236 (2014) 121–126. doi:10.1016/j.cattod.2014.05.003.

[31] E. V. Boikov, M. V. Vishnetskaya, A.N. Emel'yanov, I.S. Tomskii, N. V. Shcherbakov, The selective catalytic oxidation of toluene, Russ. J. Phys. Chem. A. 82 (2008) 2233–2237. doi:10.1134/S003602440813013X.

[32] V.S.R. Rajasekhar Pullabhotla, C. Southway, S.B. Jonnalagadda, Ozone initiated oxidation of hexadecane with metal loaded γ-Al2O3 catalysts, Catal. Lett. 124 (2008) 118–126. doi:10.1007/s10562-008-9434-4.

[33] E. Brillas, I. Sire, M.A. Oturan, I. Sirés, M.A. Oturan, Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton 's Reaction Chemistry, Chem. Rev. 109 (2009) 6570–6631. doi:10.1021/cr900136g.

[34] N. Daels, M. Radoicic, M. Radetic, S.W.H. Van Hulle, K. De Clerck, Functionalisation of electrospun polymer nanofibre membranes with TiO2 nanoparticles in view of dissolved organic matter photodegradation, Sep. Purif. Technol. 133 (2014) 282–290. doi:10.1016/j.seppur.2014.06.040.

[35] M. Iqbal, J. Nisar, M. Adil, M. Abbas, M. Riaz, M.A. Tahir, M. Younus, M. Shahid, Mutagenicity and cytotoxicity evaluation of photo-catalytically treated petroleum refinery wastewater using an array of bioassays, Chemosphere 168 (2017) 590–598. doi:10.1016/j.chemosphere.2016.11.021.

[36] S.-H. Do, B. Batchelor, H.-K. Lee, S.-H. Kong, Hydrogen peroxide decomposition on manganese oxide (pyrolusite): Kinetics, intermediates, and mechanism, Chemosphere 75 (2009) 8–12. doi:10.1016/j.chemosphere.2008.11.075.

[37] D. Zhao, B.L. Yi, H.M. Zhang, H.M. Yu, MnO2/SiO2-SO3H nanocomposite as hydrogen peroxide scavenger for durability improvement in proton exchange membranes, J. Memb. Sci. 346 (2010) 143–151. doi:10.1016/j.memsci.2009.09.031.

[38] D. al D.A. Aljuboury, P. Palaniandy, H. Bin Abdul Aziz, S. Feroz, Evaluation of the solar photo-Fenton process to treat the petroleum wastewater by response surface methodology (RSM), Environ. Earth Sci. 75 (2016) [333]. doi:10.1007/s12665-015-5192-y.

[39] H. Lee, S.H. Park, S.J. Kim, B.H. Kim, H.S. Yoon, J.S. Kim, S.C. Jung, The effect of combined processes for advanced oxidation of organic dye using CVD TiO2film photo-catalysts, Prog. Org. Coatings. 74 (2012) 758–763. doi:10.1016/j.porgcoat.2011.09.024.

[40] D.A.D.A. Aljuboury, P. Palaniandy, H.B.A. Aziz, S. Feroz, Treatment of petroleum wastewater using combination of solar photo-two catalyst TiO2 and photo-Fenton process, J. Environ. Chem. Eng. 3 (2015) 1117–1124. doi:10.1016/j.jece.2015.04.012.

[41] H. Zhuang, H. Han, W. Ma, B. Hou, S. Jia, Q. Zhao, Advanced treatment of biologically pretreated coal gasification wastewater by a novel heterogeneous Fenton oxidation process, J. Environ. Sci. 33 (2015) 12–20. doi:10.1016/j.jes.2014.12.015.

[42] S. Rahim Pouran, A.R. Abdul Aziz, W.M.A. Wan Daud, Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters, J. Ind. Eng. Chem. 21 (2015) 53–69. doi:10.1016/j.jiec.2014.05.005.

[43] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, J. Environ. Chem. Eng. 4 (2016) 762–787. doi:10.1016/j.jece.2015.12.016.

[44] F.R. Pombo, A. Magrini, A. Szklo, An analysis of water management in Brazilian petroleum refineries using rationalization techniques, Resour. Conserv. Recycl. 73 (2013) 172–179. doi:10.1016/j.resconrec.2013.02.004.

4

Reuse and Recycle Solutions in Refineries by Ozone-Based Advanced Oxidation Processes: A Statistical Approach

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4.1 Introduction

Water scarcity is a worldwide issue even for the countries with significant source of water [1]. For many industries, economic and environmental impact of the wastewater forms a driving force to find sustainable solutions for its management in terms of the hazard to the environment, especially to the human and animal health [2,3]. Petroleum industry is one of those industries that produce significant amount of wastewater, which is sometimes more than the amount of processed crude oil depending on the configuration of the plant and the type of crude oil [4,5].

Petroleum downstream industry composes of a series of separation and treatment steps that process thousands of barrels of crude oil per day into valuable products grouped as light, middle and heavy distillates (i.e. petroleum gas, gasoline, kerosene, fuel oil, asphalt) [6,7]. Due to the complex and large scale continuous processing, high amount of wastes of different nature are generated [7], wastewater being among the most important one. Although substantial progress has already been made over the last few years to reduce its volume, still now for every 1000 m^3/h of raw water required for refinery processes, 200-600 m^3/h of wastewater are discharged [8]. Wastewater management is, therefore, essential to decrease the amount of raw water need for the processing and the produced wastewater generated (e.g. production line including vapor condensation, process water and spent caustic in crackers, cooling tower and pump/compressor cooling) [9]. The composition of the wastewater may be different depending on the plant configuration. However, in general, it may contain biodegradable or recalcitrant organic and inorganic compounds, which are very toxic, and the treatment efficiencies must be evaluated case by case for each plant and process [10]. Integrated approaches including end-of-pipe treatment and reuse/recycle solutions considering the natural water cycle must be applied for sustainable water management [11].

Ozone-based AOPs, including single ozonation and UV/H_2O_2/O_3 combinations, are fast and effective treatments to mineralize a wide number of organic compounds, and especially unsaturated and aromatic hydrocarbons in contaminated water [5,12]. Thus, ozone-based treatments for either synthetic refinery wastewater (SRW) or real refinery wastewater (RRW) have been studied several times [5,13,14].

Coelho et al. compared different AOPs treatments including ozonation for petroleum refinery sourwater with initial dissolved organic carbon (DOC) of 300-440 mg/L. The authors compared H_2O_2, H_2O_2/UV, UV, photocatalysis, ozonation, Fenton and photo-Fenton. The most efficient treatment was photo-Fenton yielding up to 83% DOC removal. In contrast, single ozonation removed only 35% of DOC [15]. Souza et al. studied several homogeneous AOPs for industrial reuse purposes in a Brazilian refinery. The wastewater treated in this study (initial TOC = 12-19 mg C/L) was collected after biological treatment to enhance the quality of the effluent by AOPs before the reverse osmosis application. They found that around 90% of TOC removal can be achieved through UV/O_3 combination, while the single UV or O_3 treatments led to a maximum removal of 10% and 20%, respectively (depending on the UV power and O_3 concentration) [16].

The presence of H_2O_2 during the ozone treatment has been found to improve organics degradation [3] via a O_3 decomposition to produce HO• [5]. However, this fact may change by the composition of the wastewater, which varies by the stage where the water is collected (before or after the pretreatment of secondary treatment). Boczkaj et al. studied the treatment of wastewaters from petroleum bitumen by O_3 and O_3/H_2O_2 methods at basic pH, the latter being the most effective method to reduce COD (up to 43%), which make this system valid as a pretreatment method [17].

Besides finding the most efficient treatment for a case, identification and optimization of the significant operational parameters is fundamental. Experimental design may give a complete picture of the system response to the changes of the different variables with less amount of experiments, and consequently, less resources and time [18]. Depending on the purpose, the applications may vary as either screening designs (factorial designs) or optimization designs (response surface designs) [19].

This study explores the efficiency of ozone-based advanced oxidation processes (AOPs) as treatment method for reusing and recycling purposes in a refinery in Turkey. Here, it is aimed the study of the O_3/H_2O_2 system to achieve great values of mineralization in refinery wastewaters collected after secondary treatment to fulfill with the water standards for reusing and, hence, reducing the refinery water demand. With this motivation, a final TOC value lower than 4 mg C/L was established as the target to reach for water reuse in cooling towers in the plant (cooling/boiling water) or as firewater. The study composed of preliminary screening on SRW to determine the working boundaries for experimental design and optimization studies on RRW. SRW was used to ensure the stable experimental conditions reducing RRW consumption. Thus, experimental design for screening was performed on SRW only to understand the role of parameters on the removal efficiency. Based on the well-established parameter effects, experimental design for optimization was done specifically for RRW collected in two different stages of the refinery treatment system to decide the placement of AOPs that may achieve the reuse aims.

4.2 Experimental

4.2.1 Materials

Synthetic refinery wastewater (SRW) was prepared from the mixture of toluene (Sigma-Aldrich, 99.5%), xylene (Panreac, 98%), phenol (Sigma-Aldrich, 99-100%), o-cresol (Sigma-Aldrich, 99%), naphthalene (Acros Organic, 99%), nonane (Sigma-Aldrich, 99%), hexadecane (Sigma-Aldrich, 99%), ammonium chloride, sodium bicarbonate (Sigma-Aldrich, 99.9%) and sodium chloride (Fluka, 99.5%). Sulfuric acid and sodium hydroxide solutions were used to adjust pH.H_2O_2 (Acros Organic, 35wt%) was used in peroxone experiments while potassium iodide (Sigma-Aldrich, KI) was used for trapping remaining ozone. Dichloromethane (DCM, Sigma-Aldrich, 99.5%), acetonitrile (ACN, Riedel-de Haën, 99.9%) and phosphoric acid (Sigma-Aldrich, 85%) were used for analytical procedures.

The composition, characteristics and the preparation procedure of the SRW are given in chapter 3, ***section 3.2.2***.

Real refinery wastewater (RRW) was collected from a petroleum refinery located in Turkey at two different stages after biological treatment denominated as RRW2 and RRW3.

The organic composition of the effluents determined by GC-MS analyses contained mainly long chain alkanes after the traditional treatments applied in the refinery supported by the characteristic analyses results obtained during the collection month as presented in ***Table 4.1***, where SD* and SD** presents the standard deviation of the measurements. Initial characterization is also given in ***Table 4.1*** for all kinds of wastewater (synthetic or real effluents) treated in this study.

Table 4.1 Characterization of wastewaters.

Characteristics of the water treated in the experiments

	TOC (mg C/L)	COD (mg O_2/L)	pH
SRW	68	236	8
RRW2	15.3	40	8.2
RRW3	27	80	7.5

Average characteristics of RRW

	Suspended Solid (mg/L)	Oil & Grease (mg/L)	COD (mg O_2/L)	TOC (mg C/L)	pH	C5-C10 TPH (mg/L)	C10-C40 TPH (mg/L)
RRW2	43.3	22.6	108.2	39.3	7.1	11	0.05
SD*	11.1	1.4	22.7	27.2	0.2	0.67	0.02
RRW3		<10	40	13.7	6.5	12.1	0.08
SD**			20.4	6	0.3	1.16	0.01

4.2.2 Treatment procedure

Peroxone experiments were performed in a laboratory-scale semi-batch setup as illustrated in ***Figure 4.1***. Ozone was produced from pure oxygen by using Anseros ozone generator (COM-AD-02 or COM-AD-04 depending on the required O_3 amount) and fed into the reactor with a volume of 1L containing 300 mL of effluent by an inert, porous diffuser. Residual ozone concentration of the outlet gas stream was measured by Anseros ozone analyzer (GM-6000-RTI). For the treatment of SRW and RRW2, required amount of H_2O_2 was added at once just before starting the O_3 feed, while discontinuous addition of H_2O_2 was also considered for RRW3 beside the former method. For the discontinuous addition, required amount of H_2O_2 was added equally at four times each 15 min from 0 to 45 min. The first addition was done before O_3 feed.

Preliminary experiments were conducted with SRW to determine a working range of parameters initially. Two levels of O_3 concentration were considered as minimum and maximum (1.16 g/h and 4.14 g/h, respectively). The effect of H_2O_2 and O_3 dosage, time and pH were roughly examined. Experiments were conducted during 90 min. Single ozone studies were also conducted in order to examine the effect of H_2O_2presence in the reaction medium.

Detailed, statistical analysis of the independent variables was carried out by fractional factorial design as the screening test for the SRW with the boundaries determined according to the preliminary experiments. The optimization was assessed by Box-Behnken design-based response surface methodology for RRW2 according to the initial screening experiment results conducted with SRW.

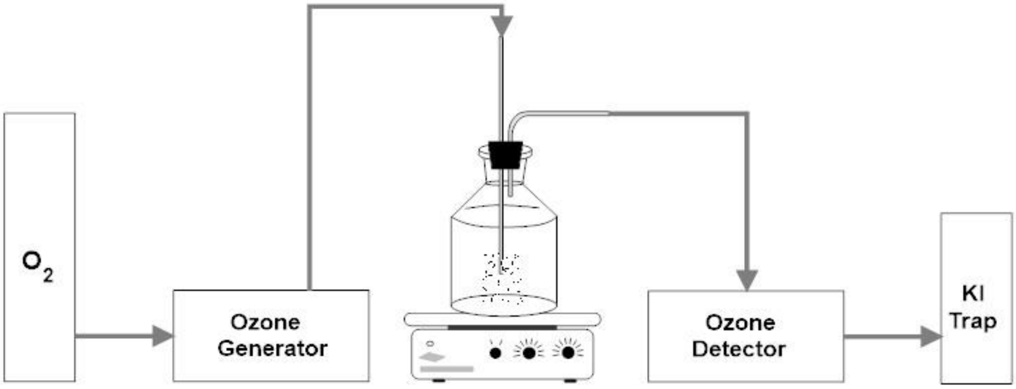


Figure 4.1 Semi-batch ozonation setup.

The treatment conditions of RRW3 were determined according to the optimization boundaries of RRW2 with the expectations of similar consumption behavior since the water specifications were similar although RRW3 contained rather higher initial TOC and COD. Thus, the suitability of the model obtained for RRW2 for other effluents was evaluated, which results highly interesting in case of changes of the wastewater characteristics depending on the processing of the plant in general.

For the experiments conducted with RRW, ozone consumption was studied in detail to enlighten the questions related to minimum required O_3 amount that should be fed into the reactor. To do so, firstly blank studies were performed by passing O_3 directly through the measurer and the produced O_3 was recorded every minute by the ozone detector. Later, during the reactions, ozone content of the reactor outlet was recorded every minute. Applied O_3 dose was calculated roughly based on the mass balance (***Eq. 1***).

$$O_3\text{ (reacted + dissolved) (g)} = O_3\text{ (inlet) (g)} - O_3\text{ (outlet) (g)} \qquad \textbf{(1)}$$

4.2.3 Analytical methods

Total organic carbon (TOC) was chosen as the response of the experimental design to estimate the mineralization degree during experiments. TOC analyses were carried out with a Shimadzu TOC-L (CSN 638-91109-48) analyzer.

Ozone consumption was monitored by Anseros ozone analyzer in order to observe the required amount of O_3 that must be fed to the reactor.

GC-MS and HPLC were used for qualitative and quantitative analyses of the samples. Before GC-MS analysis, compounds were extracted from either the raw or treated water according to the method developed and explained in chapter 3, ***section 3.2.4***.

4.2.4 Design of experiments

There are many factors affecting the impact of the treatment. Thus, design of experiments is getting crucial to know the most important variables that must be controlled during the treatment to reach a cost-effective treatment. This information can be obtained easily by means of the statistical analysis of a set of experiments in a short time with less resources than the classical experimental plan based on keeping the variables constant in turn.

Statistical analysis of the treatment responses was performed by Minitab 17 Statistical Software. Preliminary statistical assessments of the degradation efficiency depending on the chosen factors and their possible interactions were carried out by 2 level fractional factorial design for screening experiments, which is a widely used method to identify the factors having larger effects on the response [20]. Further optimization has been then performed by Box-Behnken design with only those significant factors obtained by the former design. Box-Behnken is a three-level fractional factorial design that is efficient in the number of required experiments [21]. The independent variables and their levels are presented in ***Table 4.2***. Experiments were randomized to take the unexplained variability of the response into account [22].

Table 4.2 Independent variables of the experimental design.

	Level of Value	A: H_2O_2 (mg/L)	B: O_3 (g/h)	C: Time	D: pH
Fractional Factorial	-	23.65	0.9	15	6
	+	473.8	2.7	90	11
Box-Behnken	-	4	0.9	15	*N/A*
	+	80	2.7	60	*N/A*

4.3 Results and Discussions

4.3.1 Preliminary experiments on SRW

Preliminary ozone and peroxone experiments were conducted with SRW at pH 10 since alkaline pH has been reported in several researches as favorable for ozone-based treatments [3,23,24]. According to TOC analyses, higher ozone dosage led to higher TOC removal. Thus, 57% and 63% of TOC removal was achieved by 90-min single ozonation with the O_3 concentration of 1.16 g/h and 4.14 g/h, respectively. Although ozone itself presented relatively good effectiveness on the oxidation of components, ozone/H_2O_2 process was much more effective to treat this kind of wastewater. In this case, TOC removal values ranging between 74% and 91% were observed after 90-min treatment with an O_3 concentration of 1.16 g/h and 4.14 g/h, respectively, and variable concentrations of H_2O_2 (H_2O_2/COD ratio (w/w) of 1, 2 and 5). The effect of H_2O_2 and O_3 concentrations on the treatments conducted at pH 10 during 90 min is presented in ***Figure 4.2a*** in detail. Blue symbols represent the means of first factor (H_2O_2/COD) at each level of the second factor (O_3 dose), while red symbols represent the means of each level of the second factor. Notably, the H_2O_2 addition to the system increased the TOC removal efficiency; however, an increase in the H_2O_2 dose did not produce changes in the TOC removal at all, indicating that presence of H_2O_2 is necessary to improve the oxidation rate; meanwhile its concentration appears to be insignificant for this system. Thus, further studies were made at lower H_2O_2 concentrations and variable pH with a constant O_3 concentration of 4.14 g/h, and results are presented in ***Figure 4.2b***.

As previously seen, for the treatment of SRW by the ozone/H_2O_2 process, the amount of H_2O_2 did not change the TOC removal rate significantly, especially for the high O_3 dose applications. The same behavior was found with varying the pH of the medium. These results may be assigned to the reaction of ozone with hydroxyl and hydroperoxide ions, which initiates the ozone decomposition reaction in water to yield superoxide ion that might make the amount of H_2O_2 insignificant [25]. This fact has been confirmed by very few amount of H_2O_2 addition (for H_2O_2/COD (w/w)=0.1, which used 23.6 mg/L H_2O_2), which again achieved 90% of removal by 4.14 g/h O_3 dosing while that of single ozonation reached only to 63%. Thus, detailed statistical analysis was performed in order to determine the significant factors and their interaction for peroxone treatment in a complex matrix, which may not be achieved by the method that consists of the variation of one variable while keeping the others constant [26]. As the amount of H_2O_2 was insignificant when the O_3 amount was high, the highest level of the O_3 amount was chosen between 1.16 g/h and 4.14 g/h avoiding the excessive O_3 consumption, while the minimum amount was kept lower than 1.16 g/h.

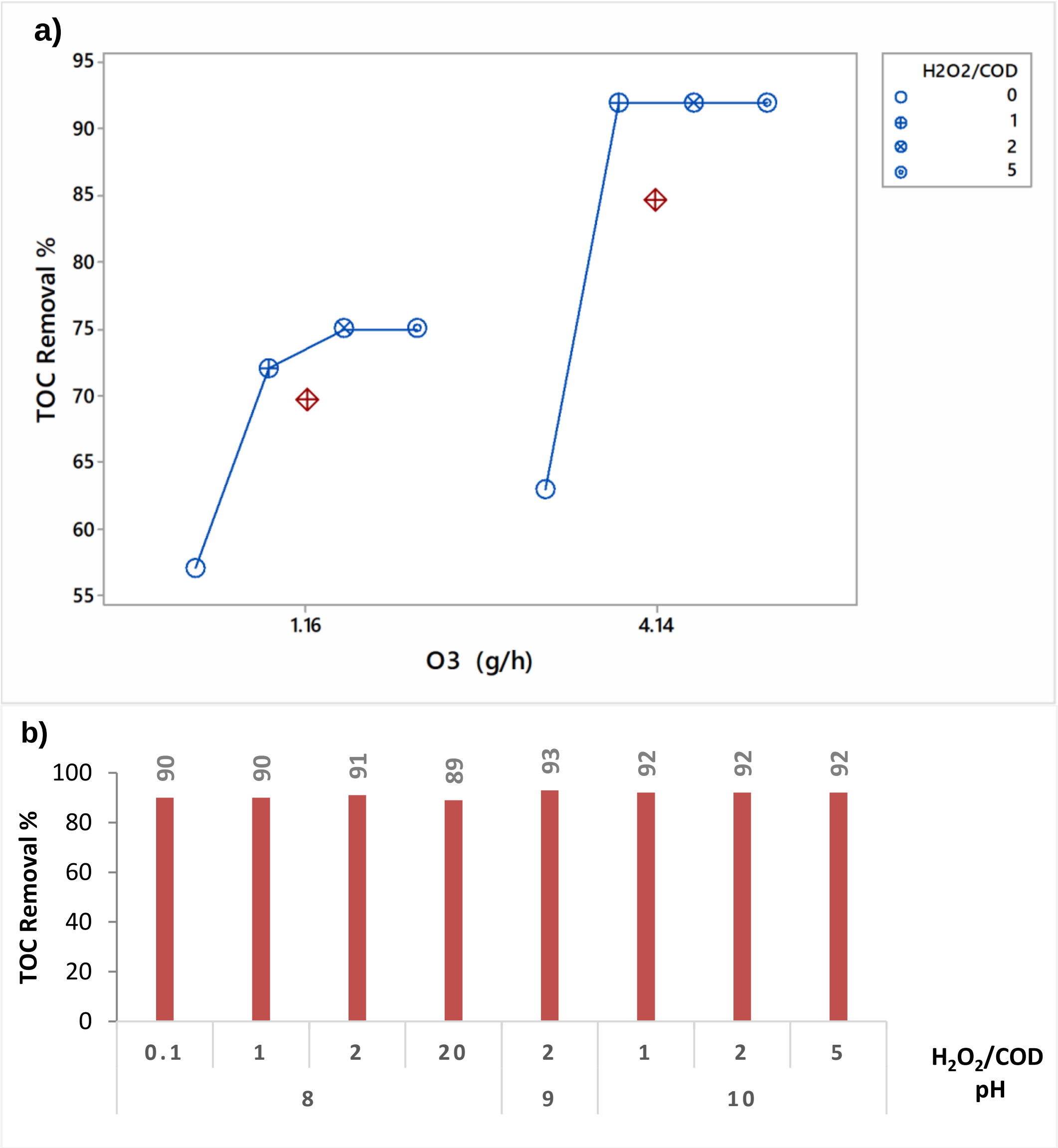


Figure 4.2 a) The effect of variable H_2O_2 and O_3 concentrations on treatment efficiency of SRW at a constant pH 10; b) The effect of variable H_2O_2 concentration and pH on treatment efficiency of SRW at a constant O_3 concentration of 4.14 g/h.

4.3.2 Experimental design

4.3.2.1 Fractional factorial design for peroxone treatment of SRW

2-level fractional factorial design of peroxone treatment has been performed with SRW in order to determine the significant parameters that should be controlled for the RRW treatments. Initially, four variables as H_2O_2 amount, O_3 amount, time and pH change have been considered to examine closely. Three replications on the center points were also performed to ensure reproducibility and reliability of the results, requiring 11 experiments (2^{4-1}+3) in total. ***Table 4.3*** presents the set of experiments and the obtained response based on TOC removals.

Table 4.3 Experimental setup and the corresponded responses by fractional factorial design for SRW.

StdOrder	A: H_2O_2 (mg/L)	B: O_3 (g/h)	C: Time	D: pH	TOC Removal
9*	248.4	1.8	52.5	8.5	84.4
6	473.1	0.9	90	6	83.1
5	23.7	0.9	90	11	72.1
1	23.7	0.9	15	6	33.7
3	23.7	2.7	15	11	48.4
2	473.1	0.9	15	11	43.9
7	23.7	2.7	90	6	89.2
8	473.1	2.7	90	11	85
11*	248.4	1.8	52.5	8.5	85.4
10*	248.4	1.8	52.5	8.5	83.6
4	473.1	2.7	15	6	47.3

*Center points

The analysis of variance (ANOVA), given in ***Table 4.4***, indicated that neither pH nor the 2-way interactions between H_2O_2 concentration and time or pH were significant for the model. However, since pH was the main variable and it had an effect in terms of 4-way interactions, only the 2 way interactions that showed P-values higher than 0.05 have been excluded from the model, which is generally preferable to simplify the system whenever possible [27].

Table 4.4 ANOVA obtained by fractional factorial design.

Analysis of Variance

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	6	4359.94	726.66	1216.58	0.000
Linear	4	3251.46	812.86	1360.92	0.000
A	1	31.60	31.60	52.91	0.002
B	1	172.05	172.05	288.05	0.000
C	1	3045.90	3045.90	5099.52	0.000
D	1	1.90	1.90	3.18	0.149
2-Way Interactions	1	87.78	87.78	146.97	0.000
A*B	1	87.78	87.78	146.97	0.000
4-Way Interactions	1	1020.70	1020.70	1708.88	0.000
A*B*C*D	1	1020.70	1020.70	1708.88	0.000
Error	4	2.39	0.60		
Lack-of-Fit	2	0.76	0.38	0.47	0.681
Pure Error	2	1.63	0.81		
Total	10	4362.33			

Thus, the simplified model (with the ***eq. 2***) presented a regression coefficient (R^2) of 99.95% and adjusted R^2 of 99.86%. P value of the lack-of-fit was also 0.681 (>0.05), which indicated that model and the data were well fitted and the variations around the model were negligible [28]. On the other hand, 4-way interaction term was totally confounded with the center point term and its P value exhibits a significant curvature in the model.

$$\text{TOC Removal} = 84.467 + 1.988\,A + 4.637\,B + 19.512\,C - 0.488\,D - 3.312\,A*B - 21.629\,A*B*C*D \qquad \textbf{(2)}$$

Residual plots presented in ***Figure 4.3*** showed normal distribution of the residuals that scattered randomly around zero.

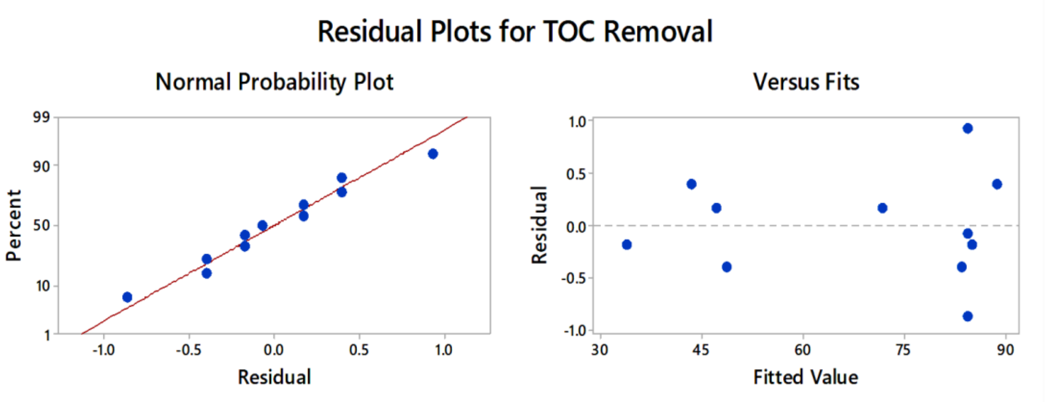


Figure 4.3 Residual plot by fractional factorial design for SRW.

4.3.2.2 Response surface methodology by Box-Behnken design for RRW2

Petroleum refinery effluents contain large variety of compounds from inorganic to organic that are poorly biodegradable [29,30]. Due to the complex nature of the effluents, organic fractions are represented by bulk parameters such as TOC, COD and BOD, which are easier parameters to observe, rather than detailed analytical methods [9].

In this study, TOC was chosen as the key parameter because of its simple and fast measurement. Besides, TOC is one of the common parameters that must be measured to determine the water quality before discharging or recycling through the processes. Although the target values are changeable depending on the plant, in our case, it was determined a final TOC value lower than 4 mg C/L to take the place of fresh water need of cooling/boiling tower after treatment.

According to the initial assessment of variables and their interactions by 2-level fractional factorial design, Box-Behnken design was performed for RRW2 with three variables as H_2O_2 (mg/L), O_3 (g/h) and time. pH has been excluded to simplify the process since it was mainly found insignificant for the treatment. Experiments were conducted at its natural pH=8.2 according to the set of experiments proposed by the software, which are given in ***Table 4.5***. ANOVA data of the design (***Table 4.6***) presents insignificant effects of 2-way interactions. However, although their P-value was higher than 0.05, in terms of the negative effect on S and R^2, they were kept in the model. Model contained two squared effects (A*A and C*C) with P-value< 0.05 which showed the presence of curvature in the response surface.

Table 4.5 Experimental setup and the corresponding responses by Box-Behnken design.

Run	StdOrder	A: H_2O_2 (mg/L)	B: O_3 (g/h)	C: Time	TOC Removal%	Predicted Removal	Final TOC
1	4	80	2.7	37.5	71.08	76.17	4.43
2	1	4	0.9	37.5	24.1	29.23	11.62
3	5	4	1.8	15	23.64	16.72	11.69
4	3	4	2.7	37.5	37.62	38.42	9.55
5	9	42	0.9	15	37.16	41.70	9.62
6	6	80	1.8	15	52.57	54.47	7.26
7	15*	42	1.8	37.5	66.37	68.25	5.15
8	13*	42	1.8	37.5	68.92	68.25	4.76
9	12	42	2.7	60	74.75	72.05	3.86
10	7	4	1.8	60	36.88	37.87	9.66
11	11	42	0.9	60	71.19	72.54	4.41
12	14*	42	1.8	37.5	73.12	68.25	4.11
13	8	80	1.8	60	75.26	75.62	3.79
14	10	42	2.7	15	60.09	60.58	6.11
15	2	80	0.9	37.5	74.33	66.98	3.93

Table 4.6 ANOVA obtained for RRW2 by Box-Behnken design with predicted optimum conditions and the responses by the model.

Analysis of Variance

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	7	5085.53	726.5	34.61	0
Linear	3	3914.11	1304.7	62.15	0
A	1	2850.13	2850.13	135.78	0
B	1	168.91	168.91	8.05	0.025
C	1	895.07	895.07	42.64	0
Square	2	1007.32	503.66	23.99	0.001
A*A	1	897.63	897.63	42.76	0
C*C	1	158.42	158.42	7.55	0.029
2-Way Interaction	2	164.11	82.05	3.91	0.072
A*B	1	70.31	70.31	3.35	0.11
B*C	1	93.8	93.8	4.47	0.072
Error	7	146.94	20.99		
Lack-of-Fit	5	123.71	24.74	2.13	0.35
Pure Error	2	23.23	11.62		
Total	14	5232.47			

Levels			**Response Values**				
C_{H2O2} (mg/L)	***C_{O3} (g/h)***	***Time (min)***	***TOC Removal %***		***Final TOC (mg C/L)***	***Desirability value***	***TOC Removal observed SD%***
			Observed	***Predicted***			
70	0.9	60	77.08	81.16	3.51	1	0.58
47	0.9	60	77.68	75.26	3.3	1	0.2

$$\text{TOC Removal} = -42.0 + 1.622\,A + 19.22\,B + 1.868\,C - 0.01077\,A{*}A - 0.01290\,C{*}C - 0.1226\,A{*}B - 0.239\,B{*}C \quad \textbf{(3)}$$

Residual plots given in ***Figure 4.4*** show normal distribution of the residuals that scattered randomly around zero. Contour plots present the effect of H_2O_2 amount (A), O_3 amount (B) and time (C) on the response. When time was set at its middle value, the amounts of H_2O_2 and O_3 exhibited an opposite balance to reach the same TOC removal. That is, in case of increase in O_3 concentration, H_2O_2 dosing may be decreased and vice versa. On the other hand, when the O_3 amount was set at 1.8 g/h, optimum removal can be achieved with H_2O_2 amount between 40-80 mg/L by a 30-60 min treatment. ***Figure 4.5*** indicates how predicted values fitted with the responses achieved.

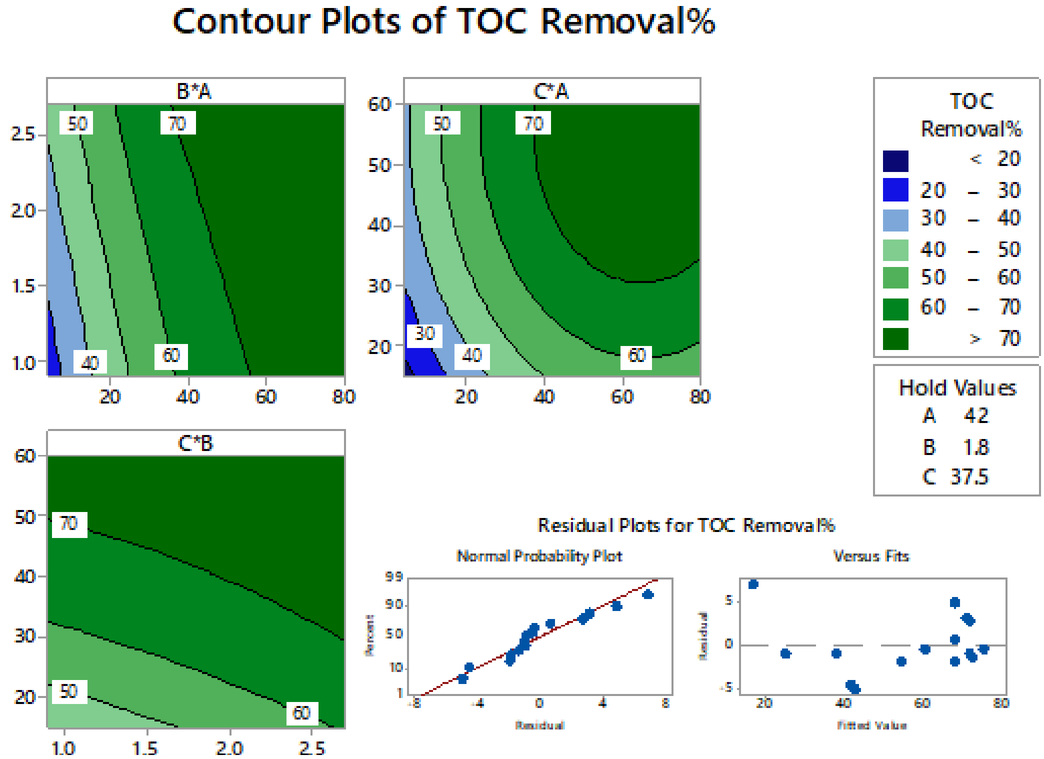


Figure 4.4 Residual and contour plots obtained by Box-Behnken design for RRW2, where A = the amount of H_2O_2 (mg/L), B= the amount of O_3 feed (g/h), C = time (min).

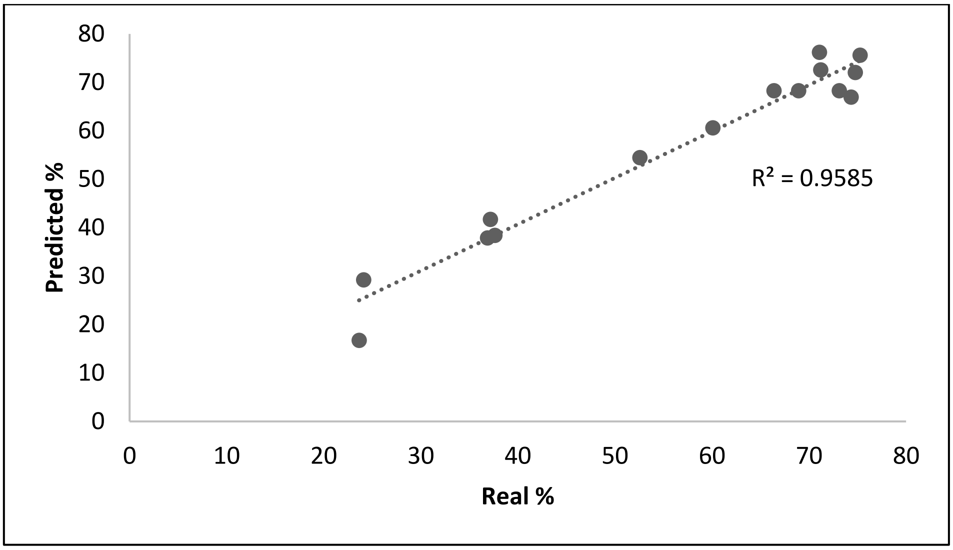


Figure 4.5 Experimental responses versus predicted responses by Box-Behnken design applied for RRW2.

According to ***Table 4.6***, the quadratic model obtained by the Box-Behnken design (***eq. 3***) with a Model F-value of 34.61 was considered significant. The lack of fit of 2.13 indicates that there is a good fit of the model relative to pure error. This is seen, in addition, with the regression coefficient (R^2) of 97.19%, adjusted R^2 of 94.38% and predicted R^2 of 82.43% that presents the adequate match of the model and the response. Therefore, the model was used to determine the optimized parameters for the current process. ***Table 4.6*** also presents the optimum conditions predicted by the model with the desirability of 1 and their responses either the observed or the predicted ones which had low standard deviation (SD) as expected.

4.3.3 Treatment assessment by TOC

Considering the feasibility of the ozone-based treatment for the treatment of RRW2, the boundaries that were determined for the response surface methodology were kept reasonable in terms of the costs of the operation and the resources.

According to the optimized parameters presented in ***Table 4.6***, it is possible to reach the final TOC requirements with the H_2O_2 amount down to 47 mg/L when the treatment lasts 60 min keeping the O_3 feed rate at 0.9 g/h. However, considering the cost of O_3 production, it can be more realistic to apply the parameters given in Run 15 in ***Table 4.5***, which could reduce the operation time down to 37.5 min rather than 60 min while increasing the H_2O_2 amount to 80 mg/L. Thus, some of the energy requirement for the O_3 formation from O_2 and for other operations could be saved by increasing the consumption of the reagent. A comparison between these two cases was performed in terms of energy and reagent consumptions (***Table 4.7***). The calculation of electrical energy per order (EEO) for O_3 treatment was reported before by Jiménez et al. by the ***eq. 4***, where the P is rated power, V is the volume of effluent treated, t is the treatment duration and TOC_i and TOC_f is initial and final TOC values [24].

$$EEO\ (\frac{kWh}{m^3}) = \frac{P(kW)*t(h)*1000}{V(L)*\log(\frac{TOC_i}{TOC_f})} \qquad \textbf{(4)}$$

The rated power (P) was calculated as 0.19 kW including 0.002 kW of stirring, 0.008 kW for ozone measurer with O_3 destruction catalyst and 0.009 kW for ozone generator, which was calculated by for the constant O_3 production of 0.9 kg/h that was used for the optimum conditions obtained by the model (ozone generator consumed around 10 kW/Kg O_3 according to the supplier). As the reagents, 38,57 m^3/h of oxygen (with a unit price of 3 Eur/m^3 [31]) gas for O_3 generation and H_2O_2 with a unit price of 346 Eur/m^3 were consumed. Thus, 37% of total cost could be saved by changing parameters. Also, since the operation and reagent costs of the large-scale operations are lower than those of laboratory scale operations, the saving can be higher for scaled-up operations.

In accordance with the treatment conditions and response of RWW2, RRW3 was treated within the parameter boundaries that were considered for RRW2 to compare the treatment impact depending on the changing characteristics. The initial treatment of RRW3 conducted with the optimized parameters of RRW2 (***Table 4.6***) resulted in an average TOC removal of 67%, by which final TOC reached ca. 9 mg C/L. Thus, although the boundaries for H_2O_2 and O_3 were kept at the same range, treatment time was enlarged up to 90 min rather than 60 min to check whether the target final TOC can be reached.

Table 4.7 Energy consumption comparison of different operation parameters.

	Treatment Conditions					Costs per unit		
	C_{H2O2} (g/m^3)	Required 35% H_2O_2 (L/m^3)	O_3 (kg)	Time (h)	EEO (kWh/m^3)	O_2 (Eur/m3)	35% H_2O_2 Eur/m^3	Cost of energy (Eur/kWh)
Case 1	47	0.07	0.9	1	95.1	3	346	0.148
Case 2	80	0.12	0.56	0.625	67.1			

Calculated cost per treatment								
Case 1				Case 2				
35% H_2O_2 Eur/m^3	Energy (Eur/m^3)	O_2 (Eur/m^3)	Total (Eur/m^3)	35% H_2O_2 Eur/m^3	Energy (Eur/m^3)	O_2 (Eur/m^3)	Total (Eur/m^3)	Cost save
0.025	14	116	130	0.042	10	72	82	37%

Figure 4.6 presents the effect of H_2O_2 addition to the system. For all cases, most of the total organic carbon was removed in 30 min in the presence of H_2O_2. However, in the absence of H_2O_2 (***Figure 4.6a***), TOC removal reached up to 56% with an O_3 dosing of 2.7 g/h after 90 min treatment, while the treatment efficiency of 1.8 g O_3/h was already 54%. Ozone depletion (calculated by residual O_3 measured during both experiments) was higher at the highest feed rate, indicating that even if ozone dissolved in RRW3 can be increased, reacted ozone does not increase, which showed the unnecessity of excessive amount of O_3 feed for the treatment. In the presence of H_2O_2, even with small addition of H_2O_2 (***Figure 4.6b***), TOC removal efficiency was slightly increased in 30 min (10% more than the treatment without H_2O_2). When the H_2O_2/COD ratio (w/w) was increased to 1.05 (***Figure 4.6c***), 30-min treatment efficiency reached around 60% regardless to the O_3 feed amount, while that of the H_2O_2/COD ratio (w/w) 2 (***Figure 4.6d***) varied between 55% to 75% depending on the O_3 feed ratio. This behavior could be explained by the changes in radicals that competed to attack the organic contaminants faster than the other while changing the intermediate product. Thus, the reaction pathway may change depending on the by-products occurred during the treatment. Bourgin et al. explained the similar behavior of the selectivity of direct reaction of ozone and the O_3/H_2O_2 treatment due to the hydroxyl radicals on the abatement of some micropollutants from water [32].

In the best of the cases giving the maximum removal, the final TOC reached for RRW3 was 5.15 mg C/L. This value was obtained by using the highest amounts of reagents after 90-min treatment, which were H_2O_2/COD ratio (w/w) of 2 and 2.7 g O_3/h. On the other hand, the target TOC (4 mg C/L) could only be reached by discontinuous addition of H_2O_2 rather than its initial addition at once. When the required amount of H_2O_2 (160 mg/L for the H_2O_2/COD ratio (w/w) of 2) was added at 4 times (40 mg/L for each addition in every 15 min), final TOC of 3.32 mg C/L was reached after 90-min treatment. This suggests that, in those cases where the $H_2O_2$is added at once for RRW3 treatment, there is an excessive H_2O_2 present in the solution which likely acts as a scavenger, thus consuming the HO· generated. Although the O_3 depletion (measured as the difference between feed rate and residual rate) is higher at higher concentrations of H_2O_2 (because of the interactions between them), the rate may vary due to the scavenging effect of excessive H_2O_2 (and hydroxyl ion) in reacting with hydroxyl radical, which negatively affects the organics degradation/mineralization.

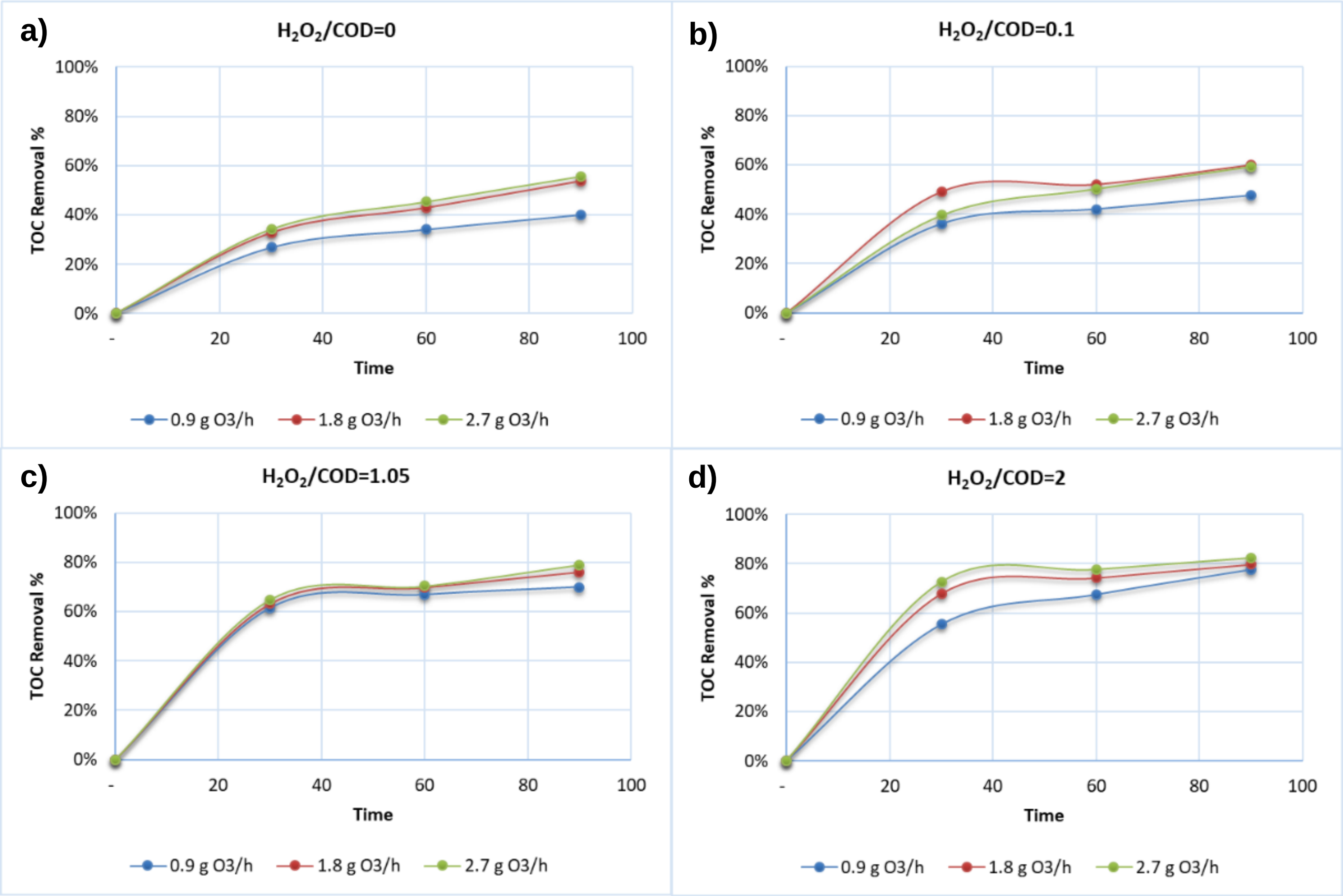


Figure 4.6 RRW3 Treatment efficiencies of ozone-based studies depending on the varied H_2O_2/COD ratios (w/w) between 0-2.

Then, the compositional difference between RRW2 and RRW3 affects to the treatment efficiencies or required amounts of reagents. In this case, RRW3 present higher amount of recalcitrant products (likely saturated alkanes) than RRW2 having an inhibiting effect on the ozonation treatment. Thus, fluctuations in the water properties and components that can occur either during the production or in the different points of each plant pretreatment may affect to the ozonation efficiency to achieve the water requirements to reuse.

4.3.4 Oxidant consumption

The contour plots present a relationship between H_2O_2 and O_3 (***Figure 4.4***), which motivates further attention to oxidant consumption behavior during the treatments. Thus, initially, ozone consumption (calculated from residual monitored during the reactions) has been considered as a significant indicator to find the optimized amount of oxidant to be fed into the system. ***Figure 4.7*** shows the importance of the initial O_3 feed rate recorded during the experiments conducted with RRW2. The time factors have been selected according to the case of reaching to 0.9 g feed (Feed(g) = O_3 dose (g/h)*t (h)). Thus, O_3 dosing was performed during 60 min, 30 min and 20 min for 0.9 g/h, 1.8 g/h and 2.7 g/h O_3 feed, respectively. According to the obtained results, when the feed rate was kept at 0.9 g/h, increasing H_2O_2 amount did not change the O_3consumption rate, which reached only up to 9% of the feed amount. However, when the feed rate increased to 1.8 g/h and 2.7 g/h, consumed amount of O_3 increased to 25% when the O_3feed reached to 0.9 g. Besides, increasing the feed rate from 1.8 g/h to 2.7 g/h did not change either the O_3 consumption or the TOC removal significantly, which presented the high amount of O_3feed to be redundant. Khuntia et al., reported the similar consumption increase with increasing O_3 dose [33].

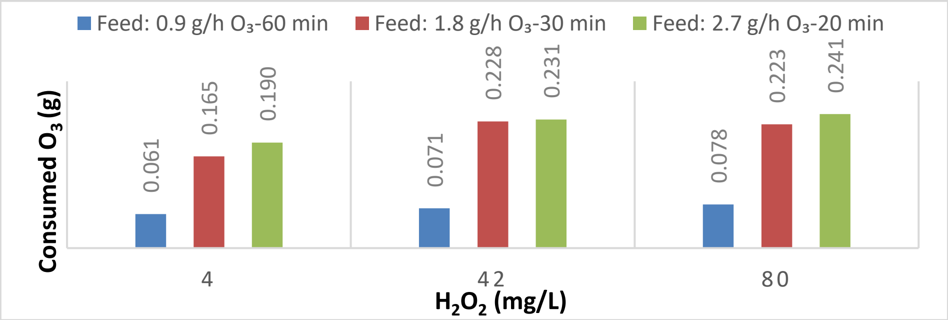


Figure 4.7 Ozone consumption (reacted + dissolved) at the time that reached to the same O_3 feed amount of 0.9 g by different feed rate.

Figure 4.8 exhibits the significance of the optimum oxidant feed for the maximum TOC removal for the experiments conducted with RRW2 during 37.5 min. The number of run represents the conditions of the experiments given in ***Table 4.5*** previously. The green data present the ratio of consumed O_3 amount calculated based on the ***eq. 1*** to remove TOC (mole/mole), while the purple data present the ratio between consumed O_3 and consumed H_2O_2 (mole/mole). The consumed amount of H_2O_2 was determined by the semi-quantitative strips that gives a range of concentration in mg/L. In case of any detected H_2O_2 amount in the samples, calculations were made based on the lower scale of the range assuming the higher amount of reagent consumption. Notably, when an insufficient amount of H_2O_2 was added to the reactor (i.e. 4 mg/L) as in the case of Run 2 and 4, most of the O_3 seems not to react with the organic matter, reaching a low %TOC removal and, therefore, being ineffective treatment conditions. On the other hand, when higher amount of H_2O_2 (i.e. 80 mg/L) was fed as in the cases of Run 1 and Run 15, the oxidants resulted more efficient in removing the carbon content. In these cases, both the O_3 cons/TOC and O_3 cons/H_2O_2 cons ratios decrease compared to the former cases. Indeed, conditions used in Run 15 were markedly more efficient in terms of effective consumption of oxidants reaching the higher TOC removal while reducing the unreacted oxidant amount. This result totally agrees with the optimized conditions found previously through box-Behnken response surface methodology to achieve lower costs maintaining high TOC removal, as presented in this chapter, ***section 4.3.3***.

In case of the treatment of RWW3, similar consumption behavior was obtained. When the treatment ends in 30 min (***Figure 4.9a***), the most effective reagent consumption was achieved with 160 mg/L of H_2O_2 and 0.9 g/h O_3 (E7) reaching 55% of TOC removal. The increase in O_3 dose resulted in higher TOC removal; however, this also cause an increase in O_3 wastage. On the other hand, increasing the reaction time to 90 min (***Figure 4.9c***) led to higher TOC removals still preserving the effective consumption of the reagents. Nevertheless, again the optimum conditions can be determined according to the cost analysis for each case.

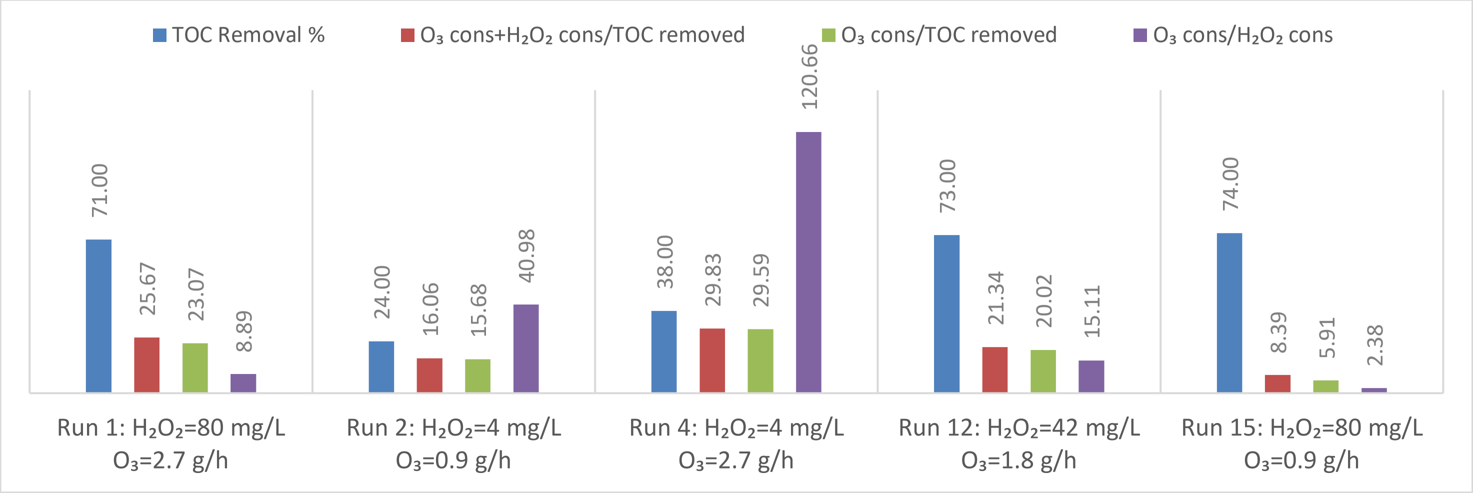


Figure 4.8 The oxidant consumption ratios (mole/mole) compared to TOC removal % for RRW2 treatment during 37.5 min.

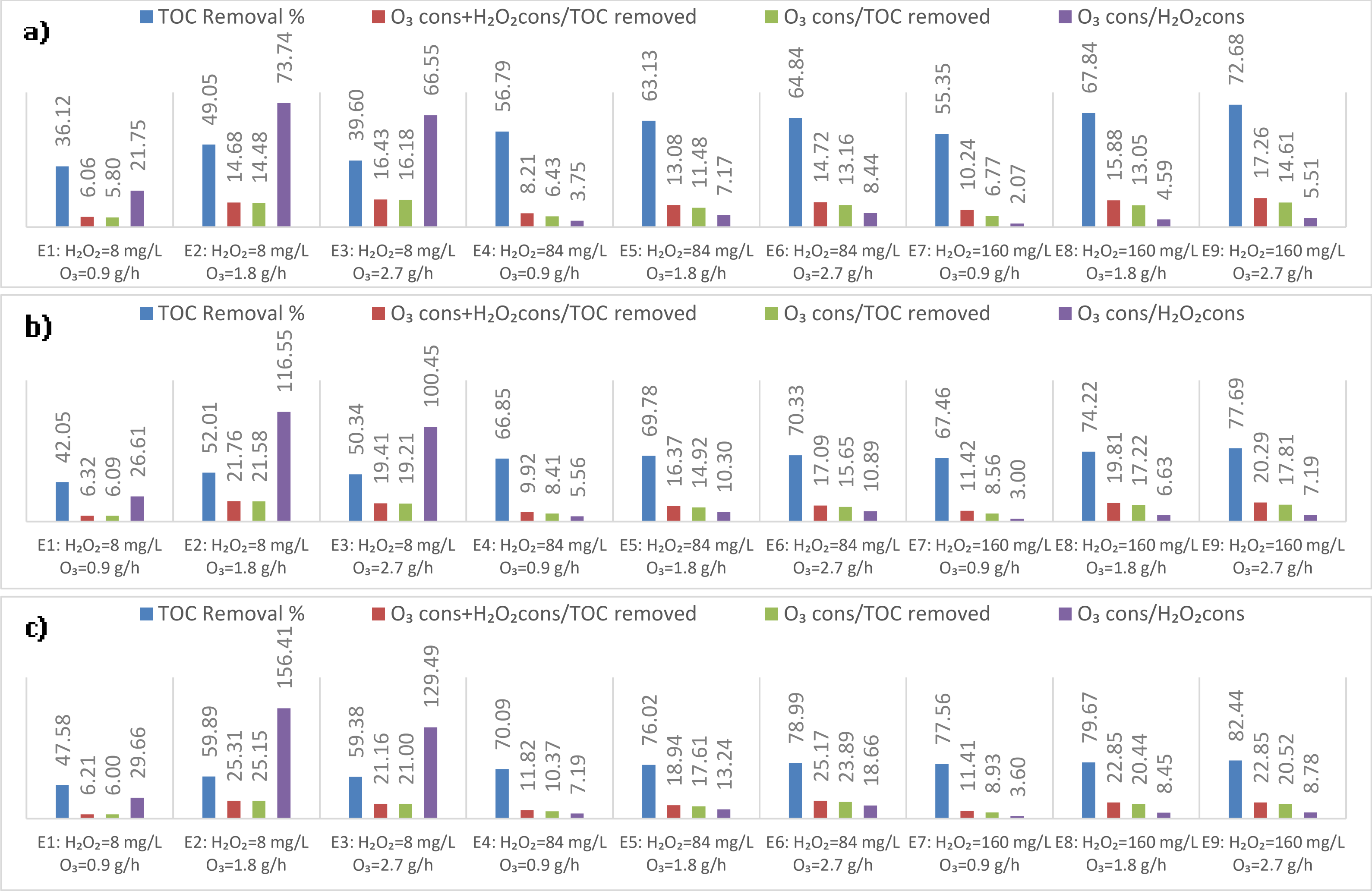


Figure 4.9 The oxidant consumption ratios (mole/mole) compared to TOC Removal % for RRW3 treatment a) 30 min, b) 60 min, c) 90 min.

4.4 Conclusions

The selection of optimal conditions for effective degradation of two wastewater effluents from a refinery in Turkey collected after biological treatment was studied using fractional factorial design; whereas, the optimization of the significant parameters was performed by Box-Behnken response surface methodology.

According to the screening results obtained by the fractional factorial design, it was found that both the reagents concentration used for the treatment and the time were very significant for the treatment efficiency, while pH was found insignificant in terms of its effect on TOC removal. The optimized parameters by Box-Behnken design indicated that it is possible to reach the TOC requirements for reuse purposes by adjusting the amount of H_2O_2 and reaction time at low feed O_3 rates. Thus, optimization allows reducing operational costs maintaining the process effectiveness to reach the stablished target. The ratio between consumed O_3 and H_2O_2 played a crucial role for an optimum treatment either in terms of efficiency or for the operation costs. However, the effect of initial characteristics of the effluents must be taken into account to determine the appropriate oxidant feed.

According to local water specifications for reclamation, peroxone treatment appears as a promising technique for water polishing allowing water recycling in refineries. The final characteristics of the treated water make it suitable to be reused in the plant's cooling towers or stored for fire extinction or cleaning purposes, which are the major water consumption sources of a refinery. This allows decreasing substantially the raw water consumption and generates a positive impact at different levels: social, economic and environmental.

An important point concerns to the fluctuation in the characteristics of the effluent, which was found rather significant in the treatment efficiency and the operational conditions that should be adjusted. This is especially important for real applications in situ, since the water variability in the refinery is highly expected with time and season. However, we have shown here that this problem may be overcome by means of detailed statistical approaches, which may be extrapolated to a refinery scenario through the development of a decision support system.

References

[1] I.N. Dias, A.C. Cerqueira, G.L. Sant'Anna Jr., M. Dezotti, Oil refinery wastewater treatment in biofilm reactor followed by sand filtration aiming water reuse, J. Water Reuse Desalin. 2

(2012) 84–91. doi:10.2166/wrd.2012.022.

[2] C.J. Escudero, O. Iglesias, S. Dominguez, M.J. Rivero, I. Ortiz, Performance of electrochemical oxidation and photocatalysis in terms of kinetics and energy consumption. New insights into the p-cresol degradation, J. Environ. Manage. 195 (2017) 117–124. doi:10.1016/j.jenvman.2016.04.049.

[3] 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.

[4] M.H. El-Naas, M.A. Alhaija, S. Al-Zuhair, Evaluation of a three-step process for the treatment of petroleum refinery wastewater, J. Environ. Chem. Eng. 2 (2014) 56–62. doi:10.1016/j.jece.2013.11.024.

[5] A.L.N. Mota, L.F. Albuquerque, L.T.C. Beltrame, O. Chiavone-Filho, A. Machulek Jr., C.A.O. Nascimento, Advanced oxidation processes and their application in the petroleum industry: a review, Brazilian J. Pet. Gas. 2 (2008) 122–142. doi:10.5419/bjpg.v2i3.57.

[6] M. Al Zarooni, W. Elshorbagy, Characterization and assessment of Al Ruwais refinery wastewater, J. Hazard. Mater. 136 (2006) 398–405. doi:10.1016/j.jhazmat.2005.09.060.

[7] S. Srikanth, M. Kumar, S.K. Puri, Bio-electrochemical system (BES) as an innovative approach for sustainable waste management in petroleum industry, Bioresour. Technol. 265 (2018) 506–518. doi:https://doi.org/10.1016/j.biortech.2018.02.059.

[8] IFP Energies nouvelles, Water in fuel production, Panaroma 2011. (2010) 1–10. https://www.researchgate.net/publication/276292861_Water_in_fuel_production_Oil_production_and_refining (accessed September 28, 2019).

[9] S. Jafarinejad, S.C. Jiang, Current technologies and future directions for treating petroleum re fi neries and petrochemical plants (PRPP) wastewaters, J. Environ. Chem. Eng. 7 (2019) 103326. doi:https://doi.org/10.1016/j.jece.2019.103326.

[10] C.F. Bustillo-Lecompte, M. Knight, M. Mehrvar, Assessing the performance of UV/H2O2 as a pretreatment process in TOC removal of an actual petroleum refinery wastewater and its inhibitory effects on activated sludge, Can. J. Chem. Eng. 93 (2015) 798–807. doi:10.1002/cjce.22180.

[11] X. Jia, Z. Li, R.R. Tan, D.C.Y. Foo, T. Majozi, F. Wang, Interdisciplinary contributions to sustainable water management for industrial parks, Resour. Conserv. Recycl. 149 (2019) 646–648. doi:https://doi.org/10.1016/j.resconrec.2019.06.034.

[12] S.S.H. Ziabari, S.M. Khezri, R.R. Kalantary, Ozonation optimization and modeling for treating diesel-contaminated water, Mar. Pollut. Bull. 104 (2016) 240–245. doi:10.1016/j.marpolbul.2016.01.017.

[13] V.S.R. Rajasekhar Pullabhotla, C. Southway, S.B. Jonnalagadda, Ozone initiated oxidation of hexadecane with metal loaded $^{\gamma}$-Al2O3 catalysts, Catal. Lett. 124 (2008) 118–126. doi:10.1007/s10562-008-9434-4.

[14] C. Chen, H. Chen, X. Guo, S. Guo, G. Yan, Advanced ozone treatment of heavy oil refining wastewater by activated carbon supported iron oxide, J. Ind. Eng. Chem. 20 (2014) 2782–2791. doi:10.1016/j.jiec.2013.11.007.

[15] A. Coelho, A. V. Castro, M. Dezotti, G.L. Sant'Anna Jr., Treatment of petroleum refinery sourwater by advanced oxidation processes, J. Hazard. Mater. 137 (2006) 178–184. doi:10.1016/j.jhazmat.2006.01.051.

[16] B.M. Souza, B.S. Souza, T.M. Guimarães, T.F.S. Ribeiro, A.C. Cerqueira, G.L. Sant'Anna, M. Dezotti, Removal of recalcitrant organic matter content in wastewater by means of AOPs aiming industrial water reuse, Environ. Sci. Pollut. Res. 23 (2016) 22947–22956. doi:10.1007/s11356-016-7476-5.

[17] G. Boczkaj, A. Fernandes, P. Makos, Study of different advanced oxidation processes for wastewater treatment 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.

[18] S.T. Narenderan, S.N. Meyyanathan, V.V.S.R. Karri, Experimental design in pesticide extraction methods : A review, Food Chem. 289 (2019) 384–395. doi:10.1016/j.foodchem.2019.03.045.

[19] P.K. Sahu, N.R. Ramisetti, T. Cecchi, S. Swain, C.S. Patro, J. Panda, An overview of experimental designs in HPLC method development and validation, J. Pharm. Biomed. Anal. 147 (2018) 590–611. doi:10.1016/j.jpba.2017.05.006.

[20] D.C. Montgomery, Design and analysis of experiments, Eighth, John Wiley & Sons, Inc., Hoboken, 2017. https://lccn.loc.gov/2017002355.

[21] M. Jamshidnezhad, Experimental design in petroleum reservoir engineering, in: Exp. Des. Pet. Reserv. Stud., Gulf Professional Publishing, Waltham, 2015.

[22] J. Rodríguez-Chueca, C. Amor, J.R. Fernandes, P.B. Tavares, M.S. Lucas, J.A. Peres, Treatment of crystallized-fruit wastewater by UV-A LED photo-Fenton and coagulation-flocculation, Chemosphere 145 (2016) 351–359. doi:10.1016/j.chemosphere.2015.11.092.

[23] A.R. Ribeiro, O.C. Nunes, M.F.R. Pereira, A.M.T. Silva, An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU, Environ. Int. 75 (2015) 33–51. doi:10.1016/j.envint.2014.10.027.

[24] S. Jiménez, M. Andreozzi, M.M. Micó, M.G. Álvarez, S. Contreras, Produced water treatment by advanced oxidation processes, Sci. Total Environ. 666 (2019) 12–21. doi:10.1016/j.scitotenv.2019.02.128.

[25] F.J. Beltran, Ozone reaction kinetics for water and wastewater systems, Lewis Publishers, Boca Raton, 2004.

[26] A. Deligiorgis, N.P. Xekoukoulotakis, E. Diamadopoulos, D. Mantzavinos, Electrochemical oxidation of table olive processing wastewater over boron-doped diamond electrodes: Treatment optimization by factorial design, Water Res. 42 (2008) 1229–1237.

doi:10.1016/j.watres.2007.09.014.

[27] G. Hayder, M.Z. Ramli, M.A. Malek, A. Khamis, N.M. Hilmin, Prediction model development for petroleum refinery wastewater treatment, J. Water Process Eng. 4 (2014) 1–5. doi:10.1016/j.jwpe.2014.08.006.

[28] S. Shafiei, A. Ebadi, A.D. Kiadehi, A. Aghaeinejad-Meybodi, A. Khataee, Degradation of Fluoxetine using catalytic ozonation in aqueous media in the presence of nano-γ-alumina catalyst: Experimental, modeling and optimization study, Sep. Purif. Technol. 211 (2018) 551–563. doi:10.1016/j.seppur.2018.10.020.

[29] 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.

[30] R. de Abreu Domingos, F.V. da Fonseca, Evaluation of adsorbent and ion exchange resins for removal of organic matter from petroleum refinery wastewaters aiming to increase water reuse, J. Environ. Manage. 214 (2018) 362–369. doi:10.1016/j.jenvman.2018.03.022.

[31] Boconline, Boconline, (2019). https://www.boconline.co.uk/shop/en/uk/gas-a-z/oxygen/oxygen-cylinder (accessed October 3, 2019).

[32] M. Bourgin, E. Borowska, J. Helbing, J. Hollender, H. Kaiser, C. Kienle, C.S. Mcardell, E. Simon, U. Von Gunten, Effect of operational and water quality parameters on conventional ozonation and the advanced oxidation process O3/H2O2 : Kinetics of micropollutant abatement, transformation product and bromate formation in a surface water, Water Res. 122 (2017) 234–245. doi:http://dx.doi.org/10.1016/j.watres.2017.05.018.

[33] S. Khuntia, M. Kumar Sinha, B. Saini, An approach to minimize the ozone loss in a series reactor: A case of peroxone process, J. Environ. Chem. Eng. 6 (2018) 6916–6922. doi:10.1016/j.jece.2018.10.069.

5

Comparison of Catalytic Ozone, UV/H_2O_2, UV/PMS and UV/Fenton in Degrading the Naphthenic Acids in Oil Sands Process Water

5.1 Introduction

Northern Alberta has the third largest oil reserves in the world after Venezuela and Saudi Arabia in the form of oil sands, which cover more than 140.000 km^2 of surface area [1]. Oil sands are a mixture of sand, clay and water that contain an extra heavy crude oil variant known as bitumen. Bitumen is extracted by warm water and upgraded into synthetic crude oil [2,3]. The extraction process is the most water demanding part of the production requiring water approximately 2-5 times of processed crude oil [4,5]. Consequently, an alkaline and relatively brackish water called oil sands process water (OSPW) is generated and stored in tailing ponds for its reuse such as in the bitumen extraction process, process cooling and material hydro-transport due to the zero discharge policy [5,6]. OSPW contains a variety of metal cations, anions, organic matters and suspended particles. Naphthenic acids (NAs) are the main compounds of the organic fraction, which are naturally generated in crude oils and oil sands bitumen [7,8]. Particularly in Canada, NAs are of concern because of their high concentrations in tailing ponds and also their detrimental effects, especially to the aquatic environment [8].

Advanced oxidation processes (AOPs) are considered clean technologies for the treatment of contaminated waters that apply produced hydroxyl radicals (HO•), which will attack the organic contaminants. The efficiency of AOPs is based on the generation of these highly reactive radicals that are unselective oxidizing species (E^0=2.80 V) [9].

Ozone-based technologies are one of those AOPs which can degrade organic contaminants by both direct and indirect reactions under mild conditions by means of strong oxidation potential of ozone (O_3) and hydroxyl radicals, respectively [10,11]. π-bonds containing hydrocarbons such as aromatics can be oxidized by direct reactions in few minutes while indirect reactions can take place in case of the ozone-resistant components that cannot be degraded by direct reactions [12]. Previous studies showed the advantage of ozone-based processes on NAs molecules with higher molecular weights and numbers of rings and are more bio-recalcitrant. Thus, bio-recalcitrant NAs can be transformed into biodegradable compounds, so that the ozonation process can be followed by the biological treatment to remove the remaining contaminants [13]. However, by now, the operation costs of ozone-based processes compared to traditional treatment techniques restrict their full-scale operations especially when high ozone concentrations are needed. Therefore, there is a gap to decrease the operation costs in terms of the amount of the reactants and the operation time, while increasing the degradation efficiency.

Other promising techniques to treat OSPW could be photocatalytic AOPs. In the presence of UV irradiation and H_2O_2 as an oxidant, photons produced by UV light generate hydroxyl radicals ($^\bullet OH$) by means of homolytic cleavage of H_2O_2. $^\bullet OH$ is a strong oxidant with a redox potential of 2.6 - 2.9 V at acidic pH and 1.8 -1.9 V at basic pH [7]. As an alternative to H_2O_2, Oxone®, which is known as potassium peroxymonosulfate (PMS), has been stated as a common oxidizing agent in many studies [14,15]. Its environmentally friendly properties, stability and commercial availability increase the interest of its use as an oxidant instead of H_2O_2. PMS provides HSO_5^- anions susceptible of being activated to a strong oxidant, $SO_4^{\bullet-}$, by either transferring one electron from a metal such as Fe^{2+}, Co^{2+} and Ag^+ or by direct photolysis under proper reaction conditions [16].

AOPs are widely used as pre-treatment or post-treatment for the treatment of industrial effluents. However, recently heterogeneous catalytic AOPs were considered as powerful treatment methods increasing the efficiencies of classical AOPs and decreasing their drawbacks. Activated carbon (AC) is commonly used especially for the adsorption treatment of OSPW. However, there are very few studies that dealt with the AC catalyzed ozonation process [13]. Similarly, only few studies tried to examine the treatment efficiency of Fe-based catalysts on petroleum related components/wastewater and none of them dealt with oil sands related wastewater. Although iron species can be used themselves as catalyst, different kinds of materials such as AC, Al_2O_3 and SiO_2 have been used as support in order to prevent from clustering, especially for the magnetic particles [17–19]. Shahamat et al removed 70% of chemical oxygen demand (COD) from phenol contaminated water by 60-min magnetic carbon (Fe_3O_4/AC) catalyzed ozonation at neutral pH [20]. Mehdi et al. obtained 50% of COD removal from high saline petrochemical wastewater by catalytic ozonation with a magnetic catalyst (powdered AC/Fe_3O_4) at pH 5, while that of pH 7 was 48% [19].

Thus, this study presents the performances of granular activated carbon (GAC)-based catalysts to treat OSPW by catalytic AOPs in order to enhance the treatment efficiencies and reduce toxicity to reach discharging or even reusing limits. GAC-based materials were chosen as support due to their high surface area and excellent adsorption abilities. Iron (III) was selected as metal dopant to obtain magnetic particles while preventing from clustering of the magnetic particles by means of GAC as a support material [19]. Also, possible advantages of Fe doped materials in

Fenton-like treatment and PMS activation was of interest. Thus, photo-based AOPs with the same catalysts were investigated in detail to compare different AOPs. UV-based treatments were also compared with homogeneous photo-catalysis (photo-Fenton) using the same nominal amount of Fe doped in GAC-based catalysts.

5.2 Materials and Methods

5.2.1 OSPW and reagents

Raw OSPW was collected from an oil sands tailings pond in northern Alberta and stored at 4 °C until being used. Before the treatments, OSPW was filtered using a 0.45µm nylon membrane in order to remove suspended solids that could increase the consumption of reagents and decrease the light transmittance in those cases where the light-based treatments are applied. The general specifications of the OSPW after filtration are given in ***Table 5.1***.

Table 5.1 General specifications of the OSPW.

DOC (mg C/L)	COD (mg O_2/L)	O_2-NAs Conc. (mg/L)	pH
86	245	26.4	8.45

Initial ozone treatments were performed on a synthetic water to compare the catalyst performances on the same conditions for all treatment parameters. 1-adamantane carboxylic acid (ACA, >98%, TCI) was chosen as the model compound. ACA is a diamond-structured compound commonly found in OSPW [21]. It is reported as one of the most recalcitrant compounds found in OSPW which cannot be degraded simply by biological treatment [22]. The 200 mg/L stock solution of ACA was buffered by 20 mmol sodium bicarbonate ($NaHCO_3$) and pH was adjusted to 9 to mimic the pH and alkalinity of OSPW. For the applied experiments, corresponding dilutions were done to reach initial ACA concentration of 50 mg/L. This final concentration was aimed to mimic the typical NAs concentration in OSPW, which generally ranges 40-70 mg/L and could reach up to 130 mg/L [22].

For the catalyst preparation, GAC was purchased from Calgon Carbon Corporation (Pittsburgh, PA, USA) and was modified for further use. Nitric acid (68-70%) was purchased from Fischer Scientific. Urea and melamine (99%, Sigma-Aldrich) were used as the nitrogen (N) doping sources while thiourea (99%, Alfa Aesar) was used for nitrogen/sulphur (N/S) doping. Fe (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, 99%, Sigma-Aldrich) was used as the Fe (III) precursor for the catalyst modification step.

$FeSO_4.7H_2O$ (99%, Sigma-Aldrich) was used as Fenton reagent. H_2O_2 (30%, Fisher) and potassium peroxymonosulfate (PMS, 99%, Alfa Aesar) were used as the oxidizing agents in different treatments.

5.2.2 Catalyst preparation procedure

Prior to use, GAC was sieved to a particle size between 0.6-1.4 mm, then washed by Milli-Q water and dried at 110 °C to be used as the starting material labelled as GAC0. The modification procedure of GAC was composed of several steps according to previous studies [23,24]. In brief, GAC was washed by 6M nitric acid solution via Soxhlet system for 3 h to remove the accumulated impurities such as N, P, K, Ca, Al, Si and Fe from the surface of the material [25]. Also, it may increase the surface area as well as improving the surface chemistry by hydrophilic functional group introduction [26]. The obtained material was washed by Milli-Q water several times until neutral pH to remove excessive acid, then filtered and dried in an oven at 110 °C (labeled as GAC1). Afterwards, N (by urea or melamine) or N/S (by thiourea) functional groups were introduced into GAC1. To do so, 2 g of GAC1 was added into 1 M of either 100 mL urea or thiourea solution and shaken at 200 rpm by New Brunswick™ Innova® 2100 platform shaker (Eppendorf Inc., USA) for 24 h at room temperature followed by filtration and drying at 110 °C. The obtained materials were calcined at 450 °C under N_2 atmosphere and denominated as GAC-U and GAC-TU depending on the doping source, urea and thiourea, respectively. For the material prepared with melamine (GAC-M), the method previously reported by Messele et al. was followed [23]. Briefly, 2 g of GAC1 was added into 1 M of melamine suspension in 80% ethanol (100 ml) and stirred at 70°C for 5 h. Afterwards, the mixture was boiled to evaporate the solvent. Obtained slurry was dried at 110 °C and later calcined at 450 °C under N_2 atmosphere. As the last step, the obtained materials were impregnated with 5% Fe (III) with the aim of obtaining magnetic properties after calcination at 600 °C under N_2 atmosphere. For the impregnation, required amount of $Fe(NO_3)_3.9H_2O$ was dissolved in 15 mL of Milli-Q water. Then, 2 g of the selected material was added into the solution to be ultrasonicated for 1 h at 60 °C [20]. Obtained materials were labeled as GAC0-Fe, GAC1-Fe, GAC-UFe, GAC-MFe and GAC-TUFe. ***Table 5.2*** summarizes the nomenclature of the catalysts with their main preparation features.

Table 5.2 Nomenclature and descriptions of original and modified catalysts.

Material	Name	Pre-treatment of GAC support	Heteroatom doping	1st Cal.	Nominal Fe (III) doping (wt%)	2nd Cal.
1	GAC0	Milli-Q water	-	-	-	-
2	GAC1	6M HNO_3	-	-	-	-
3	GAC-U	6M HNO_3	N doping by Urea	450ºC	-	-
4	GAC-M	6M HNO_3	N doping by Melamine	450ºC	-	-
5	GAC-TU	6M HNO_3	N/S doping by Thiourea	450ºC	-	-
6	GAC0-Fe	Milli-Q water	-	-	5%	600ºC
7	GAC1-Fe	6M HNO_3	-	-	5%	600ºC
8	GAC-UFe	6M HNO_3	N doping by Urea	450ºC	5%	600ºC
9	GAC-MFe	6M HNO_3	N doping by Melamine	450ºC	5%	600ºC
10	GAC-TUFe	6M HNO_3	N/S doping by Thiourea	450ºC	5%	600ºC

5.2.3 Preliminary selection of catalysts on ACA removal by catalytic ozonation

Statistical approach in experimental studies plays an important role in planning and performing the experiments, analysing and interpreting the results efficiently and economically in terms of the experimental costs and time consumption [27]. In this part of the study, this approach has been used to select the most efficient catalysts for the ACA removal based on its quantification by liquid chromatography–mass spectrometry (LC-MS) analysis. The set of experiments for 2-level fractional factorial were designed by Minitab 17 software considering the effects of the catalyst amount, O_3 dose, pH and time. Fractional factorial design is a very useful tool to screen the effects of the variable on the response [28]. ***Table 5.3*** presents the boundaries of the design and the experimental plan that was performed for the treatment of synthetic water. For each catalyst, 11 experiments were conducted including 3 repetitions at the center points of each variable. The low and high levels of the parameters were decided considering the possible working range of each for the treatment of OSPW based on the previous experience of the authors [29,30]. In the case of O_3 dose, the high level was limited at 25 mg/L since the maximum O_3 concentration in the stock solution that could be reached with the current system was 42 mg/L.

Table 5.3 Experimental conditions and experimental plan.

	Levels	
Independent Variables	**Low**	**High**
A: Amount of Catalyst (mg/L)	100	1000
B: O_3 dose (mg/L)	5	25
C: pH	3	9
D: Reaction time (min)	15	90

Run	StdOrder	A	B	C	D
1*	11	550	15	6	52.5
2	3	100	25	3	90
3	4	1000	25	3	15
4*	10	550	15	6	52.5
5	8	1000	25	9	90
6	5	100	5	9	90
7	6	1000	5	9	15
8	1	100	5	3	15
9*	9	550	15	6	52.5
10	2	1000	5	3	90
11	7	100	25	9	15

*Center points

5.2.4 Ozone treatment procedure

Ozone treatments were conducted in 30 ml batch reactors with an ozone dose ranged from 10 to 25 mg/L. O_3 gas was produced by an O_3 generator (PCI-Wedeco, Water Technology, Herford, Germany) from pure O_2. Required ozone was supplied from an O_3 stock solution that was prepared by bubbling the ozone gas through a fine-pore diffuser into Milli-Q water, which was placed in an ice-bath to decrease the O_3 decomposition rate by time. The concentration of O_3 stock solution was monitored by a spectrophotometer at 260 nm, which was also confirmed by indigo method. At the time that the concentration reached the desired level, a dilution was made with the O_3 containing stock solution to supply the required ozone dose for treatment. For the catalytic ozone treatments, required catalyst amount that ranged between 0.1 g/L and 1 g/L was added to the reactors before O_3 addition. The reactors were kept closed without headspace during the treatment. The operation pH was varied from 3 to 9 for the treatment of ACA while it was kept at its natural value (pH 8.45) for OSPW treatment. Ultrasonication was used instead of mixing, which was also recommended for enhancing the reaction efficiency while reducing the reagent and time requirements by means of increased mass transfer [31]. Adsorption tests and single ozonation tests were performed as control experiments.

5.2.5 UV-based treatment procedures

UV-based treatments were studied only for OSPW in order to compare the treatment efficiencies of UV-based processes to those of ozonation. Experiments were carried out with a quasi-collimated beam UV apparatus equipped with a 1 kW medium pressure mercury lamp (Model PSI-I-120, Calgon Carbon Corporation, PA, USA). The treatments were performed in a glass beaker with a volume of 60 ml for 90 min. The irradiance was measured as 4.5 mW/cm^2 by a calibrated UV detector (Model SED 240, International Light, MA, USA) connected to a radiometer (Model IL 1400 A, International Light, USA). The effect of different oxidants was investigated with the presence of 0.1 g/L catalyst at different pH (3 and natural pH of OSPW). Treatment efficiencies of the H_2O_2-applied heterogeneous oxidation processes were compared to those of homogeneous process, which was UV/Fenton in this study.

90-min UV/Fenton experiments were conducted at pH 3, which was reported as the optimum pH in many studies [32,33]. The amount of Fe^{2+} was kept at 5 mg/L avoiding an excessive use of reagent and not to form any sludge to be managed further. The ratio of H_2O_2/COD (w/w) was varied between 1 and 5. Remained H_2O_2

detected by semi-quantitative H_2O_2 strips was quenched by sodium bisulphite solution after the treatment.

Catalytic UV/oxidant experiments were carried out during 90 min with two sorts of oxidants (e.g., H_2O_2 and PMS) to compare the activation efficiency of different oxidants for this type of effluent and catalysts. The weight ratio of oxidant/COD was kept at 2.5. The catalyst amount used in the experiments was 0.1 g/L. The working pH was kept as the initial pH of the effluent for both two oxidants. Additionally, pH 3 treatment was studied for H_2O_2 to be considered as Fenton-like treatment comparing with the classical photo-Fenton experiments. All the samples have been quenched by sodium bisulphite after the treatments conducted with PMS. In the case of H_2O_2, only the samples containing H_2O_2 after treatment were quenched. The remained H_2O_2 in the samples was determined using semi-quantitative H_2O_2 strips.

5.2.6 Analytical methods

5.2.6.1 Characterization of catalysts

X-ray diffraction (XRD) analysis using a Rigaku XRD Ultima IV diffractometer with Cu Kα source radiation with an angular 2θ-diffraction range between 10° and 80° was employed to determine the crystal structure and crystallinity of the catalyst.

N_2 physisorption was performed at -196 ^{o}C using a surface area analyzer (Autosorb-1MP Quanthachrome, USA) in order to obtain textural properties of the catalysts. Specific surface areas were calculated according to BET method. Microporosity was assessed by the t-plot method.

Fourier transform infrared (FT-IR) attenuated total reflectance (ATR) analysis was carried out using a Jasco FT-IR 6700 Spectrometer to determine the functional groups on the catalysts. Germanium crystal was employed in ATR. All spectra were recorded from 4000 to 450 cm^{-1} at a scan rate of 2 mm/s.

The morphology of the catalysts was examined by an environmental scanning electron microscopy (ESEM). Energy dispersive X-Ray (EDX) was performed on the samples in ESEM using a FEI Quanta 600 microscope equipped with energy dispersive X-ray microanalysis from Oxford Instruments operating at high vacuum with an accelerating voltage of 20 kV.

5.2.6.2 Evaluation of treatments

The fluorescent organic compounds in raw/treated OSPW were analysed using Fluorescence Spectrophotometer (Varian Cary Eclipse, Ontario, Canada). Synchronous fluorescence spectroscopy (SFS) analysis is a semi-quantitative analysis that gives the ring structure information of the effluent as the group of one-ring, two-rings and so on [34]. The analysis method was previously reported by Abdalrhman et al., for analysing fluorescent aromatic species. The excitation wave lengths ranged from 200 to 600 nm while emission wavelengths ranged from 218 to 618 nm. Scanning speed was set to 600 nm/min and the photomultiplier (PMT) voltage was set at 800 mV [35].

Dissolved organic carbon (DOC) of the samples was measured by a total organic carbon analyzer (Shimadzu TOC-V CHS/CSN).

Classical NAs concentrations of raw/treated OSPW was determined by ultra-performance liquid chromatography coupled with a time-of-flight mass spectrometer (UPLC-TOF-MS) using a UPLC Phenyl BEH column (Waters, MA, USA) in high resolution mode. The injection solution was prepared with 500 µL of the sample, 100 µL of internal standard (4.0 mg/L of myristic acid-1-^{13}C in methanol), and 400 µL methanol reaching a final sample volume of 1 mL as reported before [36]. The removal efficiency results were presented based on the carbon number of the compounds and the double bond equivalence (DBE) number which refers to the hydrogen deficiency ($DBE= -z/2$) [37].

The concentration change of model compound, ACA, was monitored by liquid chromatography coupled with a mass spectrometer (LC-MS, Waters Acquity, USA). The column used for NAs analysis was a C18 (1.7 µm, 50 mm × 2.1 mm) and column temperature was set at 40°C. The analyses were carried out with a mobile phase of 4 mM ammonium acetate with 0.1% acetic acid and 100% acetonitrile. Flow rate and injection volume were 0.4 mL/min and 2 µL, respectively.

Microtox® acute toxicity of the treated/untreated OSPW on *V. fischeri* bacteria was investigated using 81.9% screening test standard protocol using Microtox® 500 Analyzer. The inhibition effect of the samples on *V. fischeri* was measured after 5 min and 15 min cultivation based on the change in the luminescence intensity. Suitable osmotic pressure of the samples was ensured before cultivation. Phenol standard (100 mg/L) was used to check the sensitivity of the *V. fischeri* before the analyses [35].

5.3 Results and Discussions

5.3.1 Initial catalyst selection and effects of selected parameters

The initial selection of the catalysts was made based on the removal efficiency of the model compound (ACA) obtained by the set of experiments indicated in ***Table 5.3***, which consists of 11 runs for each catalyst. ***Figure 5.1a*** and ***Figure 5.1b*** present the responses over the runs for the catalysts without and with Fe, respectively. It was found that GAC0 (i.e., without Fe) was highly effective by itself in the ACA removal and better than most of the other catalysts prepared without Fe. Several researches reported previously catalytic activity of activated carbon in the ozonation process through enhanced decomposition of dissolved ozone on the carbon surface into OH and O-radicals [38–40]. This result was also supported by the DOC removal levels presented in ***Figure 5.1c*** and ***Figure 5.1d***. Lower removal efficiencies obtained by DOC than LC-MS indicated the transformation of ACA component into other by-products rather than total mineralization. Additionally, the adsorption tests conducted with 1000 mg/L catalysts for 90 min (***Figure 5.2***) showed that ACA was highly adsorbed by the catalysts at acidic pH (pH 3) while its adsorption was quite low at pH 9, except by GAC0, which adsorbed 36% of ACA after 90 min conduction time.

Metal supported carbon could enhance the catalyst efficiency through the creation of new surface active centers; however, in general, the catalysts doped with Fe exhibited less efficiency than the ones without Fe loading. In both cases either being doped by Fe or not, the catalysts N-doped by melamine exhibited in general the lowest ACA removal efficiency. Thus, only GAC0 (as initial catalyst), GAC-U, GAC-TU, GAC-UFe and GAC-TUFe were selected to be studied further.

The main effect plots obtained by the software for each catalyst (given in ***Appx. B***) show that an increase in the amount of catalyst, ozone dose and time led to an increase in removal efficiency for all catalysts. However, change in pH influenced negatively on the efficiency of catalysts doped with Fe. This could be due to different form of Fe deposited on the material at acidic and alkaline pH. For the catalysts without Fe, increasing pH increased the removal efficiency having positive effect except from GAC-U and GAC-TU.

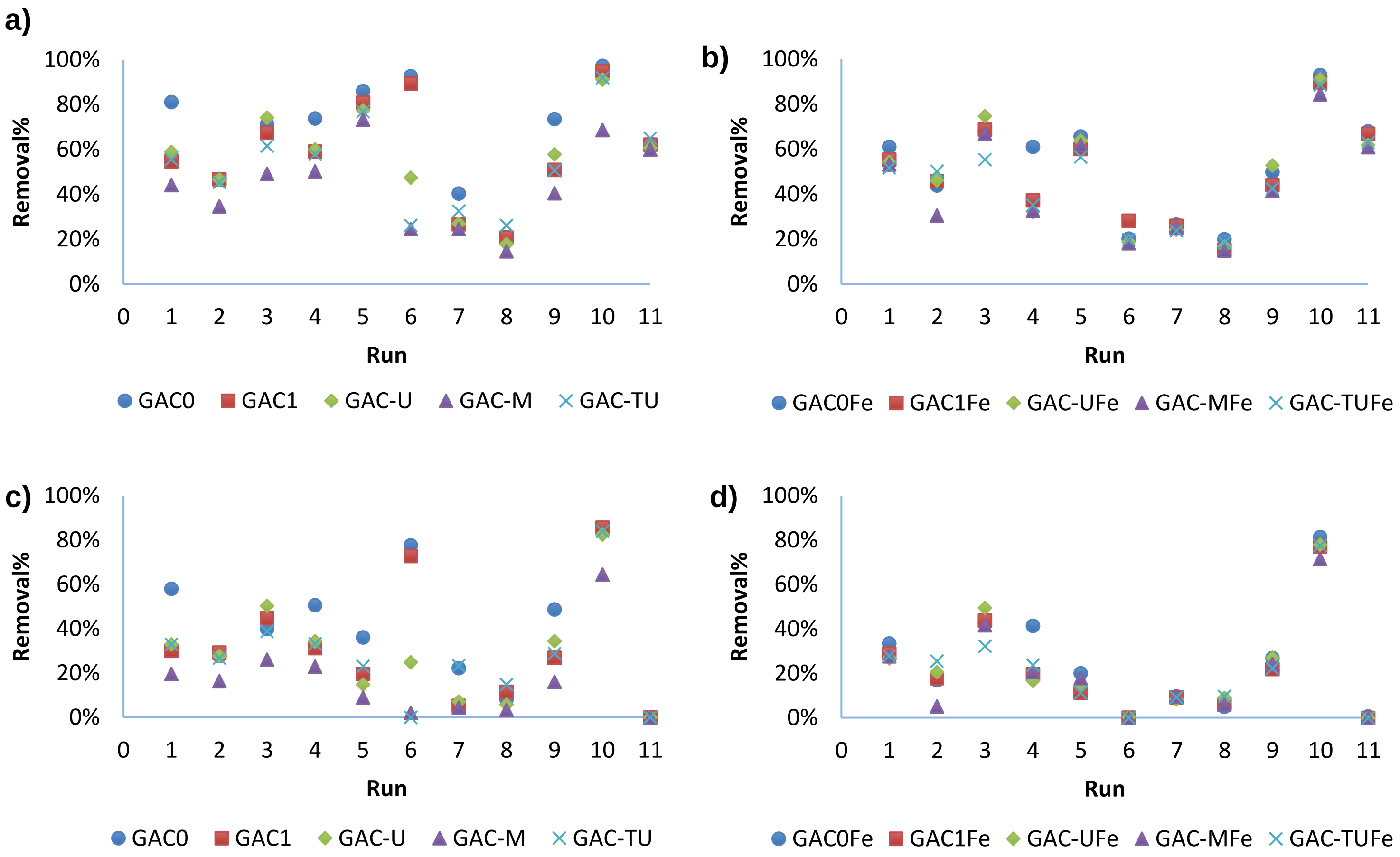


Figure 5.1 Removal efficiencies of different catalysts in experimental runs obtained by LC-MS: a) catalysts without Fe, b) catalysts with Fe; obtained by DOC: c) catalysts without Fe, d) catalysts with Fe.

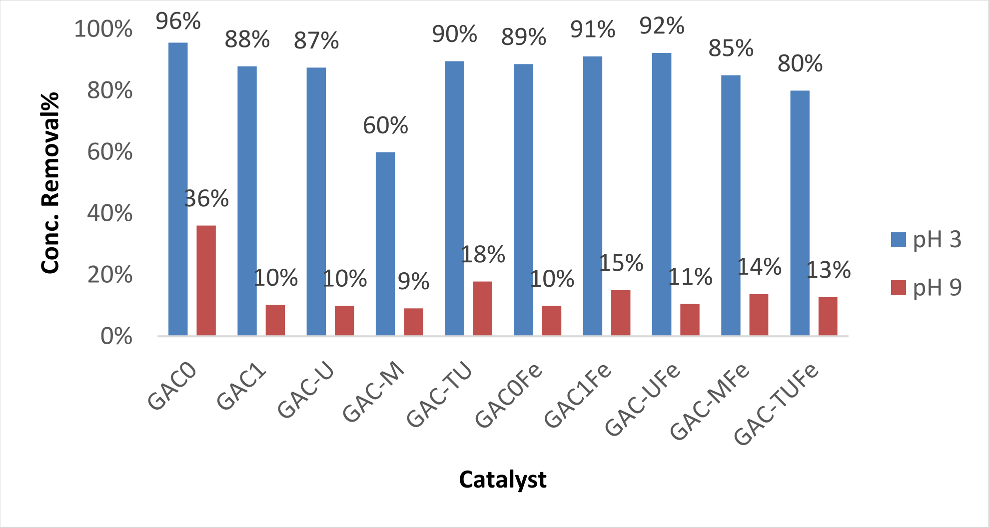


Figure 5.2 90-min adsorption of ACA by 1 g/L catalysts at varied pH.

5.3.2 Characterization of the selected catalysts

Textural properties obtained by N_2 physisorption (***Table 5.4***) revealed that GAC0 was highly microporous with 954 m^2/g of BET surface area and total pore volume of 0.57 cm^3/g. Nitrogen doping by urea (GAC-U) and later Fe impregnation (GAC-UFe) did not cause any change on the surface area, while N/S doping by thiourea (GAC-TU) resulted in a decrease of surface area at expenses of microporosity, likely due to the blockages in the pore structure caused by N/S penetration to the pores [24]. Later Fe doping on GAC-TU caused an increase on surface area of GAC-TUFe, similarly to that observed in the study of M.-X. Liu et al, where authors reported a N/S doped magnetic catalyst [41].

Table 5.4 Textural properties of the catalysts analyzed by N_2 adsorption.

	GAC0	GAC-U	GAC-TU	GAC-UFe	GAC-TUFe
S (BET) (m^2/g)	954	951	811	953	901
S (micro) (m^2/g)	842	827	695	806	775
S (meso) (m^2/g)	112	124	116	147	126
V (total) (cm^3/g)	0.57	0.58	0.51	0.59	0.56
V (micro) (cm^3/g)	0.38	0.38	0.32	0.37	0.35
V (meso) (cm^3/g)	0.19	0.20	0.19	0.22	0.20

The XRD patterns of all the catalysts (***Figure 5.3)*** presented broad diffraction peaks in the 24° and 44° two theta range which correspond to the (002) and (101) diffraction peaks of carbon materials with low graphitization [24,42]. Only GAC-UFe displayed the diffraction peaks of Fe_3O_4 at 2θ 30.2º, 35.5º, 54º, 57.3º and 62.7º, which correspond to (022), (131), (242), (151) and (044) planes, respectively (JCPDS file no. 96-100-1033). Diffraction peak corresponding to (040) plane was not observed due to overlapping with amorphous carbon diffraction lines. The pattern of GAC-TUFe was similar to those of initial materials, although (131) plane with very low intensity of Fe_3O_4 could be identified. Given that both materials contain similar amount of Fe (as will be discussed later), the differences between both Fe-supported samples can be explained by a better Fe dispersion on the GAC-TUFe catalyst surface [24].

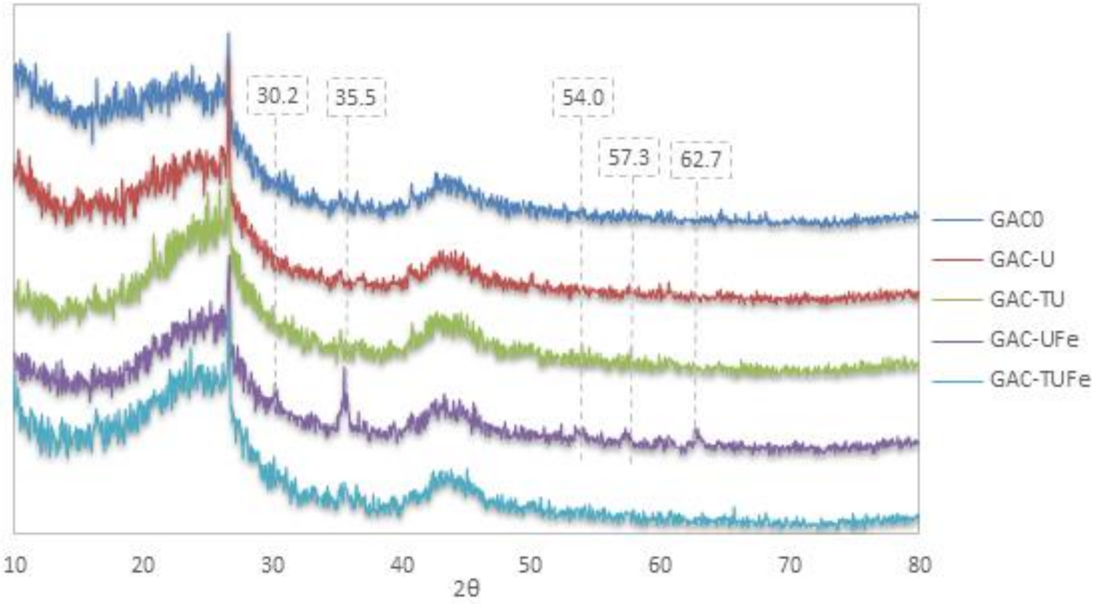


Figure 5.3 XRD patterns for GAC based catalysts.

The functional groups of the catalysts were investigated by FTIR (***Figure 5.4***). The IR bands at 1586 cm^{-1} correspond to C=C/C=N functional groups [43]. The bands at 1080 cm^{-1} and 1040 cm^{-1} are assigned to the asymmetric stretching C-O vibration of the ether and C-O groups linked to aromatic carbons, respectively [44]. These bands are both more intense in all the catalysts except mere GAC0, indicating higher concentration of oxygen atoms than GAC0 in modified catalysts, as also found by EDX analyses [45]. At 1720 cm^{-1}, the absorption band detected for GAC-UFe was assigned to the C=O stretching [45].

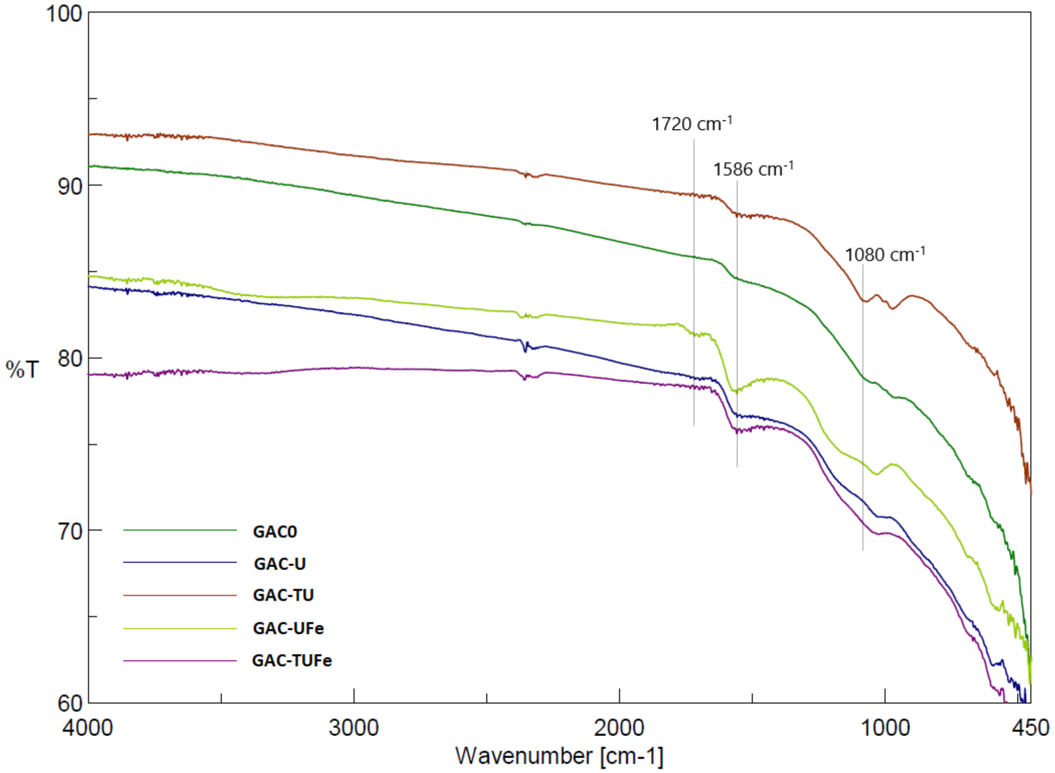
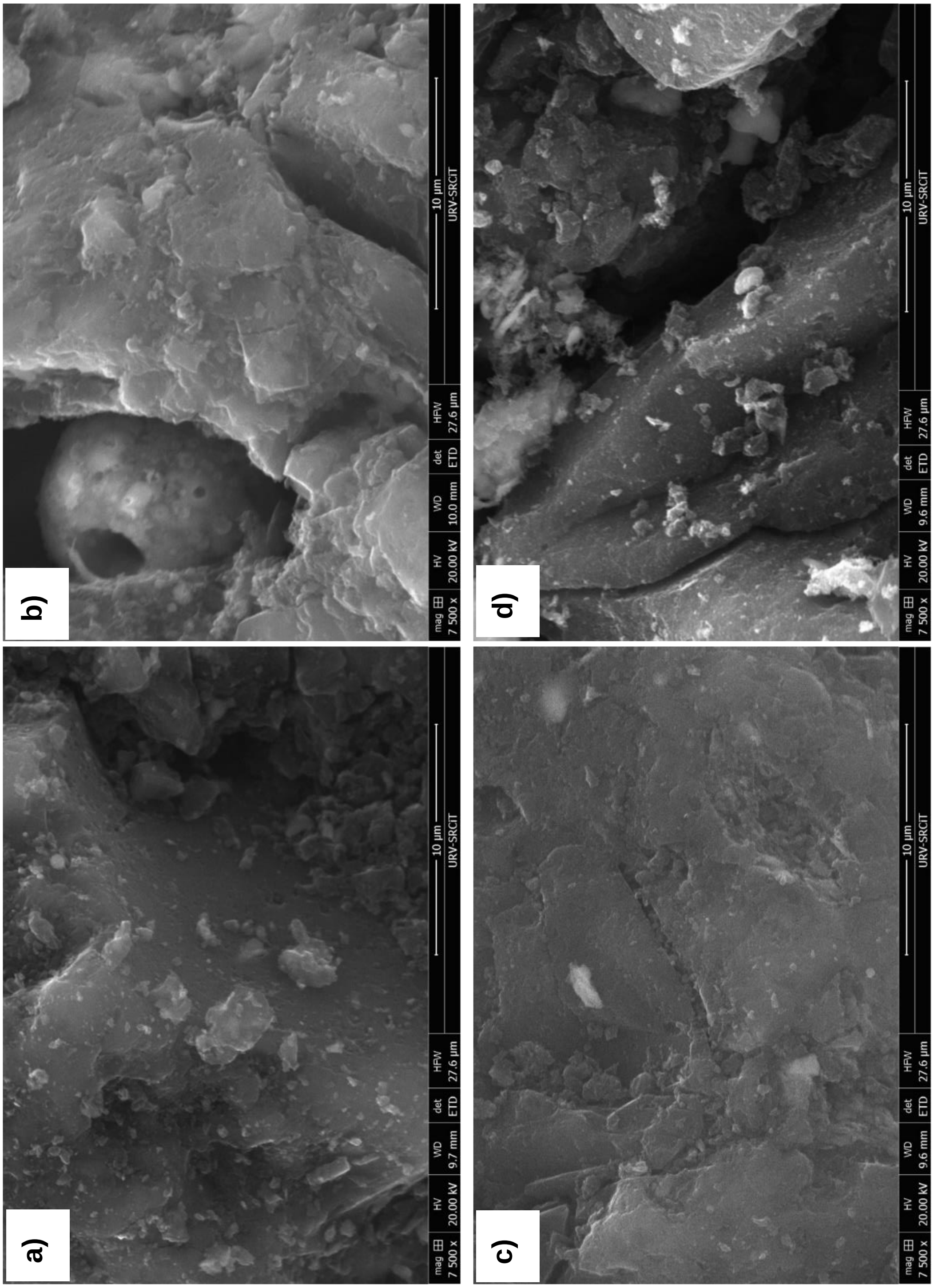


Figure 5.4 FTIR spectra of the catalysts.

Environmental scanning electron microscopy technique (ESEM) was used to investigate the surface physical morphology of the materials (***Figure 5.5a-5.5e*** and EDX elemental micro-analyses are given in ***Table 5.5***). At a first glance, no great differences were found among the different materials. ***Figures 5.5a, 5.5c*** show that GAC0 and GAC-TU have a relatively smother surface if compared with GAC-U and Fe-modified carbon materials (***Figures 5.5b, 5.5d, 5.5e***), which present more caverns on the surface. This fact is also in agreement with the BET surface area results, which decreased significantly in GAC-TU, being similar for the rest of materials. Additionally, the introduction of hydrophilic functional groups by nitric acid wash can be observed by the increased O atoms in the modified catalysts (***Table 5.5***). Besides, sulphur was found in GAC-TU and GAC-TUFe samples (***Table 5.5***). Around a 7 wt% and 9 wt% of Fe was detected on the surface of GAC-UFe (***Figure 5.5d***) and GAC-TUFe (***Figure 5.5e***), respectively, which were well spread on the GAC support as found by EDX analysis ***(Figure Appx. B1)***.


a)
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URV-SRCiT
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WD 10.0 mm
det ETD
HFW 27.6 µm
10 µm
URV-SRCiT
c)
mag ⊞ 7 500 x
HV 20.00 kV
WD 9.6 mm
det ETD
HFW 27.6 µm
10 µm
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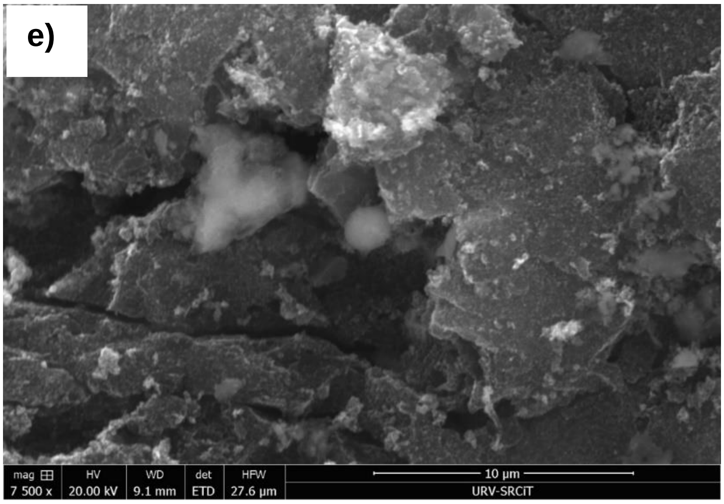


***Figure* 5.5** *Morphology of the catalysts a) GAC0, b) GAC-U, c) GAC-TU, d) GAC-UFe, e) GAC-TUFe.*

***Table* 5.5** *EDX elemental micro-analyses.*

	GAC0		**GAC-U**		**GAC-TU**		**GAC-UFe**		**GAC-TUFe**	
Element	**Wt%**	**At%**	**Wt%**	**At%**	**Wt%**	**At%**	**Wt%**	**At%**	**Wt%**	**At%**
C	84.62	89.92	83.41	88.52	84.39	90.71	72.79	82.9	65.3	77.69
O	9.77	7.79	12.05	9.6	6.88	5.55	15.28	13.06	18.21	16.27
Al	1.26	0.6	1.16	0.55	1.38	0.66	1.61	0.82	2.3	1.22
Si	2.01	0.92	1.98	0.9	2.11	0.97	2.24	1.09	2.8	1.42
S	1.4	0.56	0.69	0.27	5.24	2.11	0.83	0.35	2.56	1.14
Fe	0.94	0.22	0.71	0.16			7.25	1.78	8.83	2.26

5.3.3 Degradation efficiency of OSPW by SFS and DOC

5.3.3.1 Ozone-based treatments

SFS is known to be a powerful tool for simultaneous analysis of multi-component medium without any pre-treatment of samples. It is a simple, selective and sensitive analysis that can detect single-ring and fused-ring aromatics in OSPW, rapidly [7,46]. Compounds with a low energy π→π* transition or n→π* transition are required to be detected via fluorescing under UV irradiation [7]. For ozone-based treatments, as given in ***Figure 5.6***, initial composition labelled as OSPW-D (D=diluted) exhibited three peaks at 270 nm, 300 nm and 330 nm, which corresponded to one aromatic ring, two fused aromatic rings and three fused aromatic rings, respectively.

Adsorption tests conducted with 0.5 g of catalyst (***Figure 5.6a***) revealed that all the catalysts, except for GAC-UFe, presented similar adsorption behaviour, which were effective on adsorbing two and three fused rings aromatic components completely. The lower adsorption of two and three fused ring aromatics by GAC-UFe may be because of the changes on the surface properties of the materials upon modifications, such as surface charge that may change the adsorption efficiency of different components existing in OSPW.

Single O_3 treatment (25 mg/L O_3) without catalyst (***Figure 5.6b***), was effective to remove the aromatic rings completely, as expected, since ozone can react with aromatic components directly and rapidly. To observe the effect of the presence of catalyst on the treatment, O_3 concentration was decreased to 10 mg/L (***Figure 5.6c-5.6d***). Single ozonation in this case did not lead to complete removal of aromatic rings, but when using a catalyst, the removal was significantly enhanced, especially for one ring aromatics. This, on the one hand, suggests the generation of more highly oxidative species, which, together with components adsorption on the catalyst surface favour the organics oxidation. On the other hand, the presence of the catalyst allows decreasing the O_3 concentration needed for the treatment.

Although the efficiency of catalysts before and after surface modification was similar, a slight enhancement on the removal of fluorescent organic compounds was observed with the modified catalysts compared to GAC0. Besides, decreasing the catalyst amount to 0.1 g/L resulted in a decrease in the removal of aromatic components.

The results obtained by SFS analysis were in agreement with the DOC removal occurred by ozone-based treatments (***Figure 5.7***). DOC removal increased when using a catalyst; whereas, no DOC removal was obtained by single ozonation either with 10 mg/L or 25 mg/L O_3 dose, which would be explained by transformation of components rather than mineralization. In the case of 0.5 g/L catalyst use, highest DOC removal took place by adsorption (without O_3 feed), which was averagely 28%. In the presence of O_3, DOC removal was decreased to 16% and 10% in average for the O_3 dose of 10 mg/L and 25 mg/L, respectively. This adverse effect between adsorption and O_3 addition could be because of the formation of smaller molecules by O_3, decreasing their adsorption comparing to bigger size molecules initially present in OSPW [36]. In the case of low catalyst amount with 10 mg/L O_3, DOC removal could not be achieved.

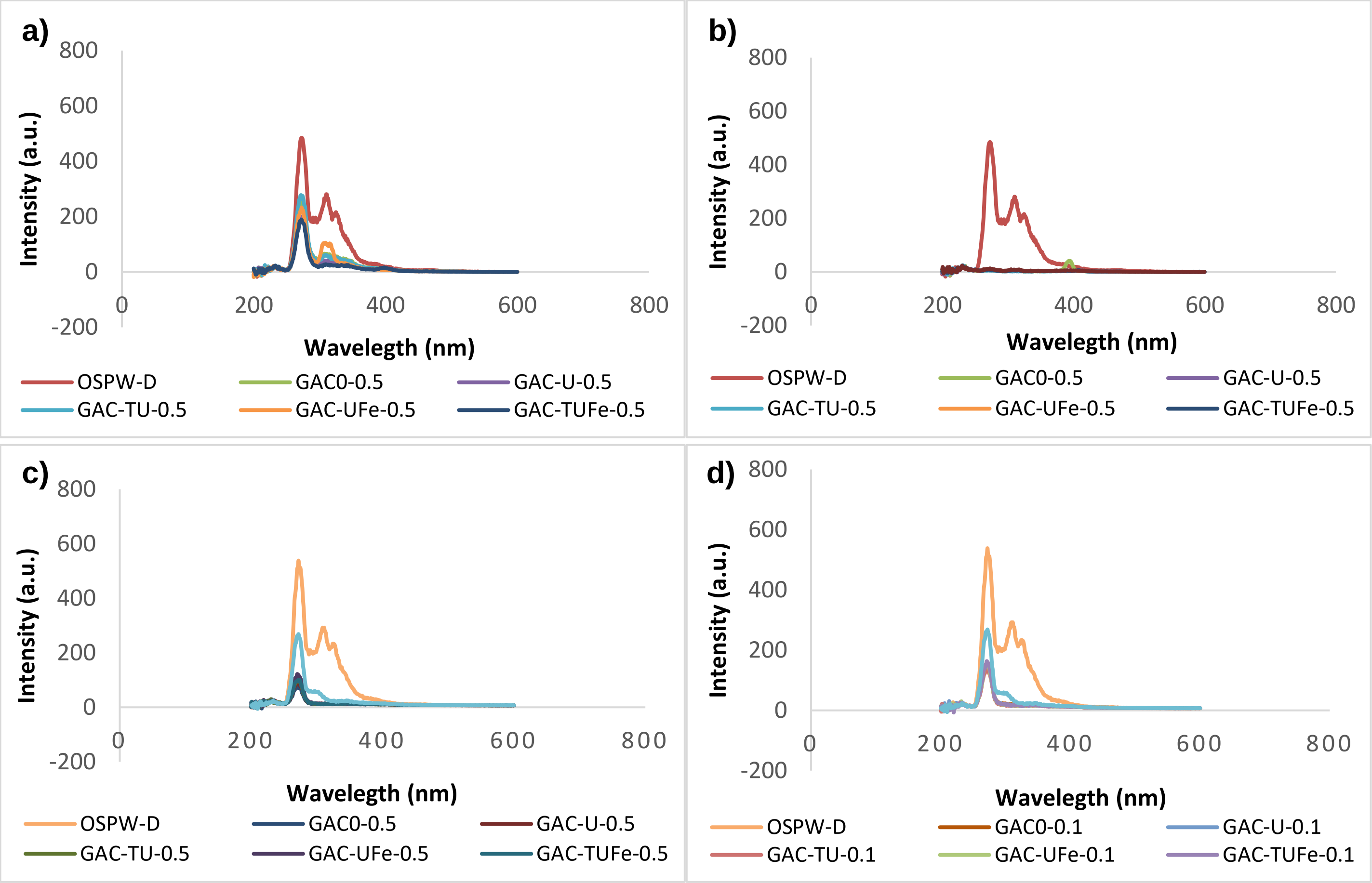


Figure 5.6 SFS analysis for 90 min of ozone-based treatment conducted at its natural pH with and without the use of catalyst: a) only adsorption with 0.5 g/L catalysts, b) ozonation with 25 mg/L O_3 and 0.5 g/L catalyst, c) ozonation with 10 mg/L O_3 and 0.5 g/L catalyst, d) ozonation with 10 mg/L O_3 and 0.1 g/L catalyst.

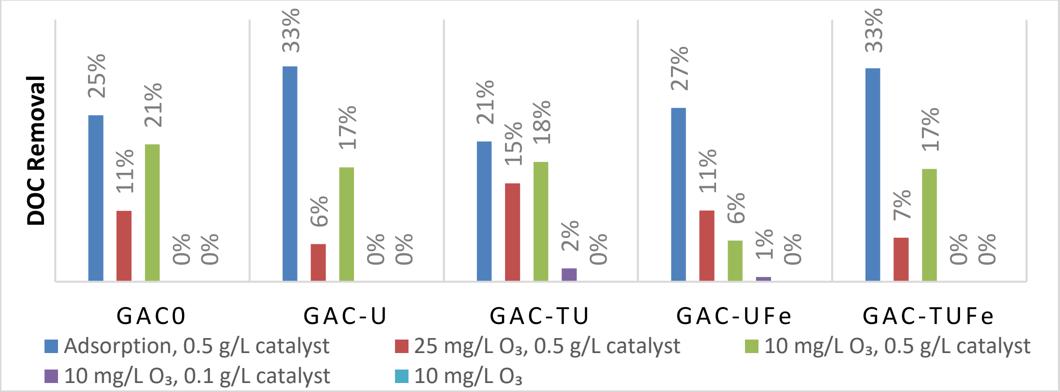


Figure 5.7 DOC removal occurred by ozone-based treatments.

5.3.3.2 UV-based treatments

UV-based homogeneous and heterogeneous photo-catalysis treatments with H_2O_2 and PMS were also studied to treat OSPW being inspired of promising results obtained for the treatment of a petroleum refinery effluent by photo-Fenton with very low Fe^{2+} amount reported recently [30]. It is well known that among AOPs, Fenton process is preferred more frequently because of their relatively simple and economic applicability. However, its drawbacks such as limited pH range and large sludge production are always of concern [47]. Photo-Fenton treatment was considered as a solution to avoid any sludge production using lower amounts of Fe species than discharging limits [30,48]. Even so, the limitation caused by the pH range is still a drawback that could be achieved by Fenton-like processes using other kinds of catalysts that may be active at higher pH. Thus, first intention for the application of UV-based treatments in this study was to examine the effectiveness of photo-Fenton process at pH 3 with 5 mg/L Fe^{2+} and optimize the applied oxidant amount for the treatment of OSPW. Then, second aim was to investigate the activity of produced catalysts with the same oxidant amount (H_2O_2 or PMS) of optimized photo-Fenton treatment and varied pH (pH 3 and pH 8.45, which is the natural pH of OSPW) The amount of catalyst used in the experiments was chosen as 0.1 g/L for two reasons: i) the nominal Fe amount doped on the GAC support was 5 mg/L for the Fe doped catalysts, which was also the same Fe^{2+} amount used for homogeneous treatment. Thus, heterogeneous and homogeneous photo-based treatments could be compared for the same scale of Fe content. ii) using this amount also enable to compare the UV-based treatments and O_3-based treatment for the same scale of catalyst amount.

According to SFS analyses of UV-based treatment, ***Figure 5.8*** revealed that only adjusting the pH into 3 decreased the aromatics concentration of OSPW significantly. A decrease in intensity by 75% for the first peak was observed, corresponding to single ring aromatics. The behaviour was similar for two fused and three fused ring peaks. This could be due to the poor solubility of NAs in acidic or neutral pH [4], which was also observed visually with color change from light yellow to darker yellow with newly formed suspended solids. However, in terms of DOC, the decrease in the initial carbon concentration due to the pH adjustment was 23%. Thus, DOC removal efficiencies at varied pH were calculated accordingly by taking into consideration the initial DOC change by pH.

UV/Fenton treatment at pH 3 was firstly investigated with 5 mg/L Fe^{2+}, and varied H_2O_2/COD ratios from 1 to 5. ***Figure 5.9a*** presents the DOC removal efficiencies versus the different H_2O_2/COD ratios (w/w). The optimum ratio found was H_2O_2/COD=2.5 based on DOC removal (63% compared to 51% or 26% for H_2O_2/COD=2 and 1, respectively) reaching a final DOC value of 24 mg/L. The use of higher oxidant amount did not lead to an increase of DOC removal. Besides, SFS analysis given in ***Figure 5.8a*** confirmed the effectiveness of photo-Fenton treatment on removing fluorescent compounds. Low dose of H_2O_2 led to a decrease in the removal of those compounds with fused rings ≥2. Ultimately, oxidant/COD=2.5 ratio (w/w) was chosen for further treatments performed with the produced catalysts.

Using any of the prepared catalysts (0.1 g/L) under the same conditions (i.e, pH 3 and oxidant/COD=2.5) resulted in lower activity than UV-Fenton treatment according to DOC analysis. This may be due to the light absorptive property of GAC based materials presenting low photocatalytic activity, which might have decreased the reaction efficiency compared to homogeneous UV/Fenton treatment, although some studies presented the synergetic effect of carbon materials in degradation of contaminants in water by photocatalysis [49,50]. Also, it was expected that the efficiencies of homogeneous catalysis would be higher than heterogeneous catalysis due to better contact with the target compounds and faster reaction rates. Averagely 29% and 14% DOC removals were achieved by heterogeneously catalyzed UV/H_2O_2 process at pH 8.45 and pH 3, respectively, presenting similar removal efficiencies by all the catalysts (***Figure 5.9b-5.9c***). However, here it should be considered that adjusting the pH to 3 already removes 23% of the DOC. The efficiency of only the photocatalysis treatment is 14% for pH 3. Considering the total removal, the final DOC reached at pH 8.45 and pH 3 is almost the same, which should be overthought to decide the best operating pH. Additionally, the treatments conducted with PMS revealed much lower DOC removal efficiency than the other treatments with H_2O_2

reaching averagely 10% for all catalysts (***Figure 5.9d***). Thus, the treatments with PMS were not examined further by the other analytical techniques.

Blank experiments including only UV, only oxidant and UV/oxidant were also performed at pH 3 and 8.45. When single UV treatment either at pH 3 or pH 8.45 was applied, although the fluorescent compounds decreased significantly, their complete removal did not take place. After 90-min UV exposure, although a visible color change from light yellow to darker was observed, there was no DOC change. Therefore, the decrease in the fluorescent compound concentration and the color change could be due to the transformation of the compounds by UV irradiation. When an oxidant was added in the presence of UV irradiation, the SFS peaks decreased almost totally; whereas, DOC removal by UV/H_2O_2 was 29% and 11% for pH 8.45 and pH 3, respectively. The DOC removal of the UV/PMS at pH 8.45 was only 7%. The effect of the catalyst type could not be assessed by SFS analysis.

5.3.4 Quantification of NAs

Detailed analyses of NAs in raw and treated effluents play an important role to evaluate the success of the treatment. NAs are considered as the main components of OSPW that contributes to acute and chronic toxicity of various aquatic organisms [3]. Therefore, detailed examination of NAs during the treatments could clarify the changes in toxicity as well as the treatment efficiency.

NAs are a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids with a general chemical formula $C_nH_{2n+z}O_x$, where n, z and x indicate the number of carbon atoms, the hydrogen deficiency arising from double bonds and/or rings and the number of oxygen atoms, respectively [7]. $C_nH_{2n+z}O_2$ classical formula represents the NAs that are in high concentrations initially, while $C_nH_{2n+z}O_x$ x>2 NAs are formed after oxidation [51]. Due to the wide range of NAs present in OSPW, their detection can be accomplished relating with the n and z numbers as a general profile instead of individual identification [8]. Semi-quantification of detected NAs is made with internal standard calibration where the signal of NAs are compared to the signal of the internal standard, myristic acid-1-^{13}C [6]. Initial classical NAs concentration of raw OSPW used in this study was 26.4 mg/L according to UPLC-TOF-MS quantification, which was in the similar ranges reported before [52].

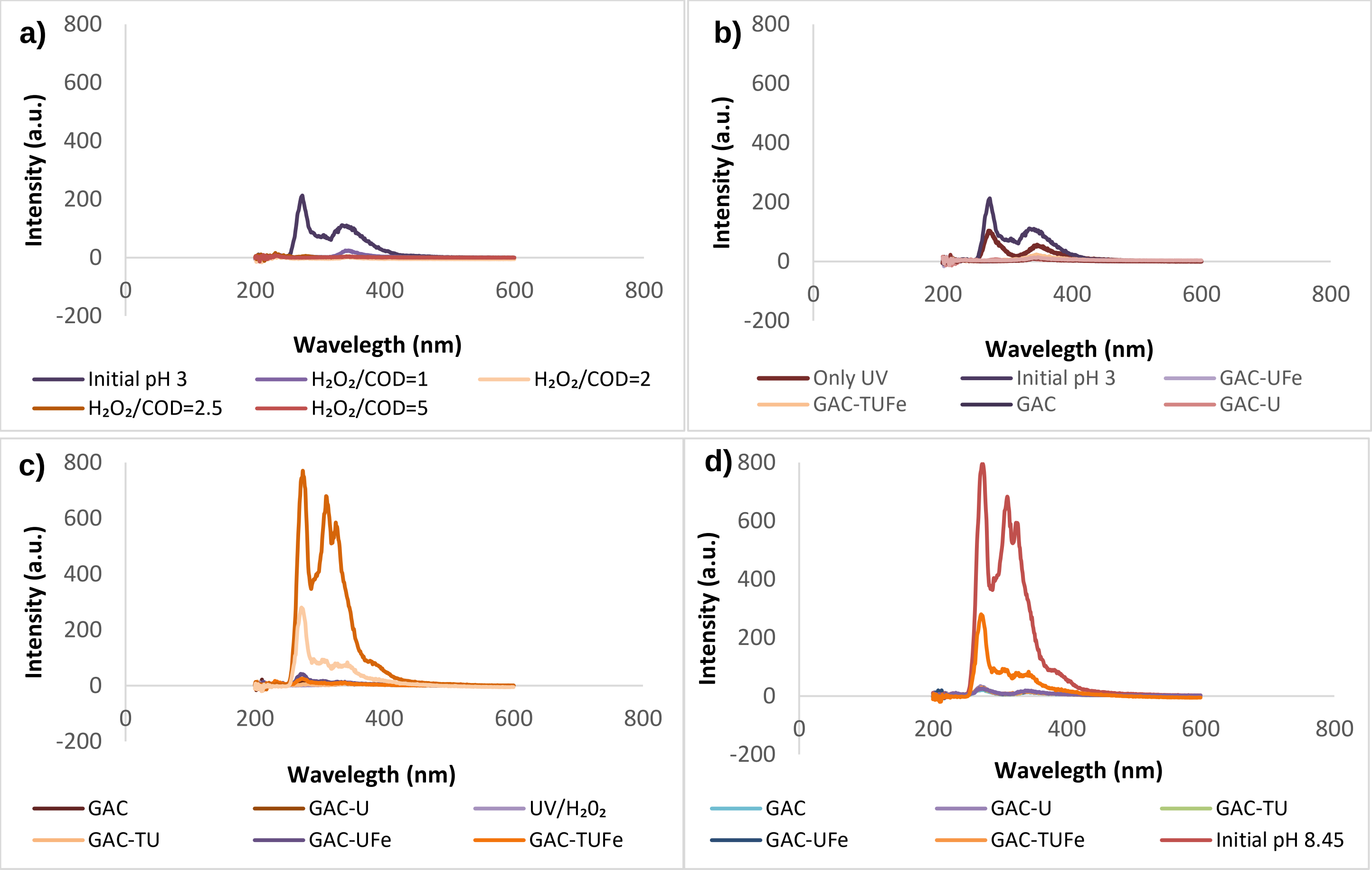


Figure 5.8 SFS analysis for UV-based treatment with and without the use of catalyst: a) UV/Fenton with 5 mg/L Fe and variable H_2O_2/COD from 1 to 5 at pH 3, b) UV/H_2O_2/Catalyst (0.1 g/L cat. and H_2O_2/COD=2.5) at pH 3, c) UV/H_2O_2/Catalyst (0.1 g/L cat. and H_2O_2/COD=2.5) at pH 8.45, d) UV/PMS/Catalyst (0.1 g/L cat. and PMS/COD=2.5) at pH 8.45.

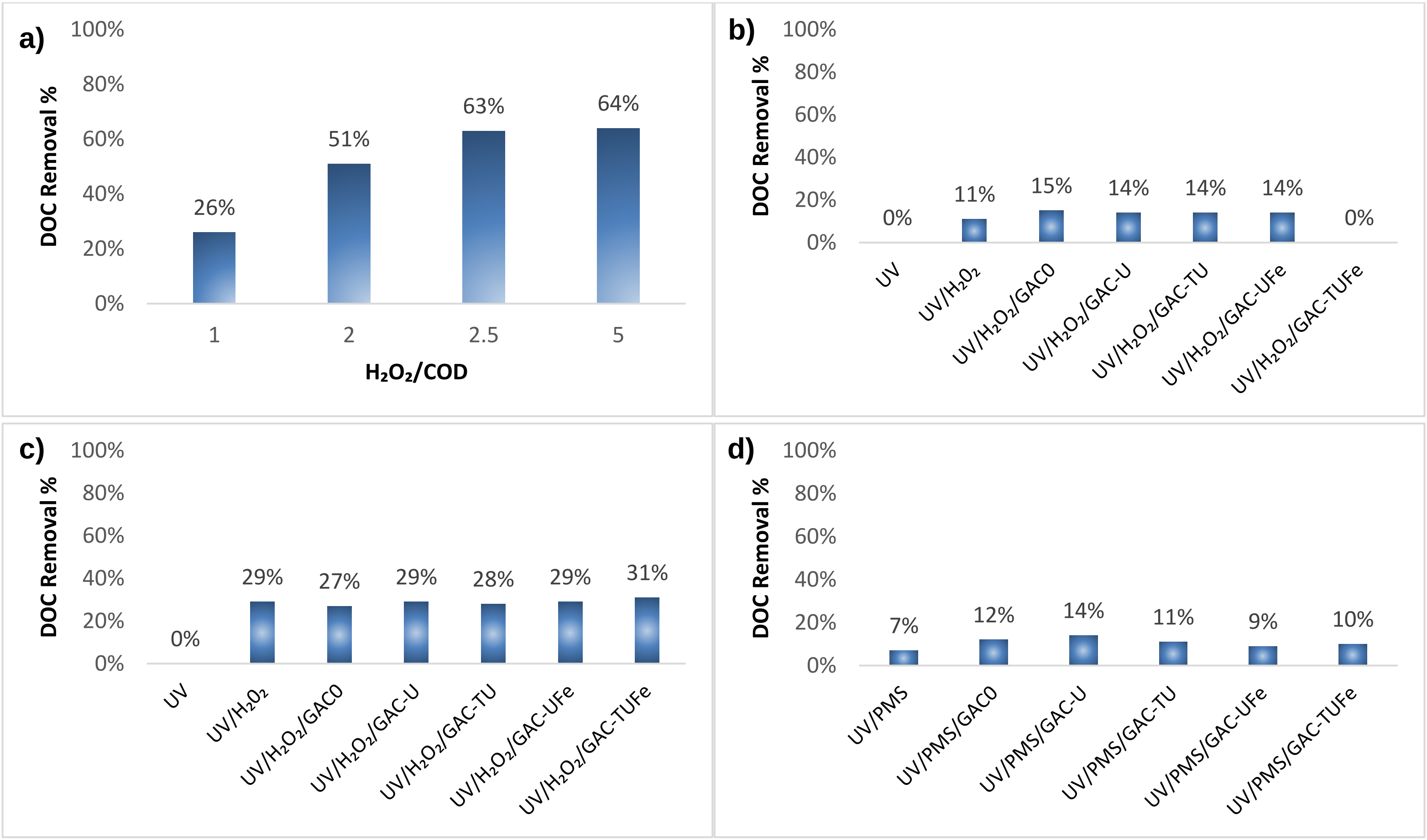


Figure 5.9 DOC removal by 90 min of a) photo-Fenton conducted with 5 mg/L Fe^{2+} and variable H_2O_2/COD ratios at pH 3, b) UV/H_2O_2/catalyst (0.1 g/L cat. and H_2O_2/COD=2.5) at pH 3, c) UV/H_2O_2/catalyst (0.1 g/L cat. and H_2O_2/COD=2.5) at pH 8.45, d) UV/PMS/catalyst (0.1 g/L cat. and PMS/COD=2.5) at pH 8.45.

5.3.4.1 Ozone-based treatments

Quantification of NAs in raw and O_3 treated (with/without catalyst) samples collected at the end of treatment (i.e., 90 min) were performed to compare the effect of O_3 dose and catalyst amount on the removal efficiency of NAs in OSPW. The adsorption capacity of the produced materials in terms of NAs concentration removal was also discussed.

O_2-NAs removal percentage based on the carbon number and DBE number of the present compounds after 90-min O_3 treatment with 25 mg/L O_3 and 0.5 g/L of catalysts are shown in ***Figure 5.10a-5.10b***. At least 92% of C14-C18 compounds were removed either by catalytic or single ozonation, while complete removal of C19-C21 was achieved in all the cases. The removal efficiency of those components with lower carbon number is difficult to establish accurately due to the formation of low carbon components as by-products from the oxidation of the higher number carbon components. Both the oxidation/removal and production of low carbon components occur at the same time. However, the impact of the catalytic processes rather than single ozonation is significant. Thus, it was observed an increased removal efficiency for the C9-C15 compounds when a catalyst was used, which could be due to the enhanced adsorption presented by the materials. Although the set of catalysts presented similar performance, the highest performance was achieved by GAC-TU for the removal of C11-C13 compounds. Notably, GAC0 presented significant removal capacity for C9-C10 compounds suggesting more economic catalytic application avoiding catalyst modification costs. The increase in the C9 concentration presented in ***Figure 5.10a*** accounts for the formation of small molecules from bigger molecules by bond breaking. This could also be seen from the removal of DBE number in ***Figure 5.10*c** which demonstrated almost total removal of π bonds producing saturated molecules (DBE=0). The 90 min of adsorption tests performed with 0.5 g/L catalysts (***Figure 5.10c-5.10d***) revealed that the higher the carbon number and DBE value of the compounds, the higher the removal% by adsorption occurred. Nevertheless, the total NAs concentration after adsorption ranged between 9.7-15.6 mg/L, while that of ozone applied treatments ranged between 1.0-2.3 mg/L indicating need of O_3 use to enhance the efficiency of the treatment. Additionally, GAC-TU catalyst combined with O_3 presented slightly higher efficiencies compared to the rest of catalysts tested. This could be because of the S atom embedded in the material that causes better activation of ozone although its adsorption ratio was lower than the other catalysts [53]. However, it should be noted that the adsorption capacity of the materials could be different in the presence/absence of oxidant, which may change the porosity and surface chemistry of the material [54].

The effect of decreasing the O_3 dose (10 mg/L) is presented in ***Figure 5.11a-5.11b***. The removal efficiency of the compounds regarding to their carbon number and DBE value was decreased significantly as compared with those of higher O_3 dose treatments (***Figure 5.10a-5.10b***). At this O_3 dose (10 mg/L), the catalytic treatments resulted in higher removal of the compounds with high carbon number than single ozonation, which is in agreement with the SFS results given in ***Figure 5.6c-5.6d***. However, the increase in C8-C10 compounds and lower removal efficiency of DBE confirmed the partial oxidation of π bonds, as also seen by SFS analysis. Thus, O_3 was found to be the main responsible of the oxidation, and it needs to be dosed sufficiently for a possible complete mineralization. Additionally, the use of lower amounts of catalysts (***Figure 5.11c-5.11d***) resulted in decreasing the NAs removal efficiency. Considering the total removal of NAs summarized in ***Table Appx. B1***, proper treatment method and the most economic treatment conditions can be decided depending on the objective of the treatment of OSPW, which was obtaining a treated effluent appropriate for discharging in this chapter. When the O_3 feeding dose was 25 mg/L, high removal of NAs up to 96% was achieved by catalytic applications. However, single ozonation also removed 92% of NAs at this O_3 concentration. Thus, only ozonation rather than catalytic treatment could be an option to reduce the cost of catalyst production, its recovery and regeneration after treatment. As the second option, O_3 dose could be reduced down to 10 mg/L. However, in this case, a catalytic treatment must be applied to reach high NAs removal efficiencies (up to 92%) since the NAs removal efficiency of single ozonation with 10 mg/L O_3 was only 63%.

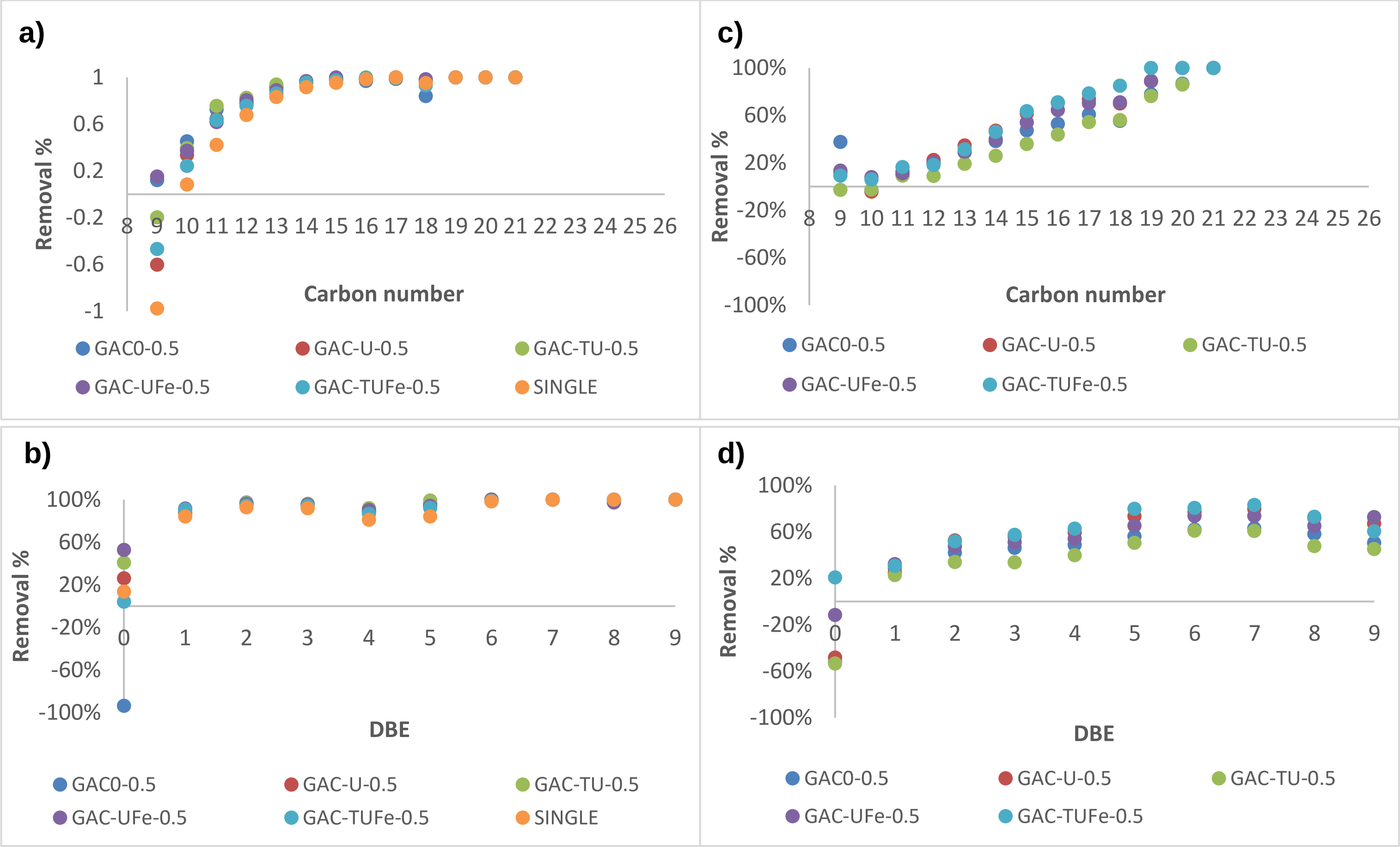


Figure 5.10 Removal of O_2-NAs by 90- min catalytic O_3 treatment with 25 mg/L O_3 and 0.5 g/L catalyst with respect to a) carbon number and b) DBE number. Removal of O_2-NAs by 90-min adsorption with respect to c) carbon number and d) DBE number.

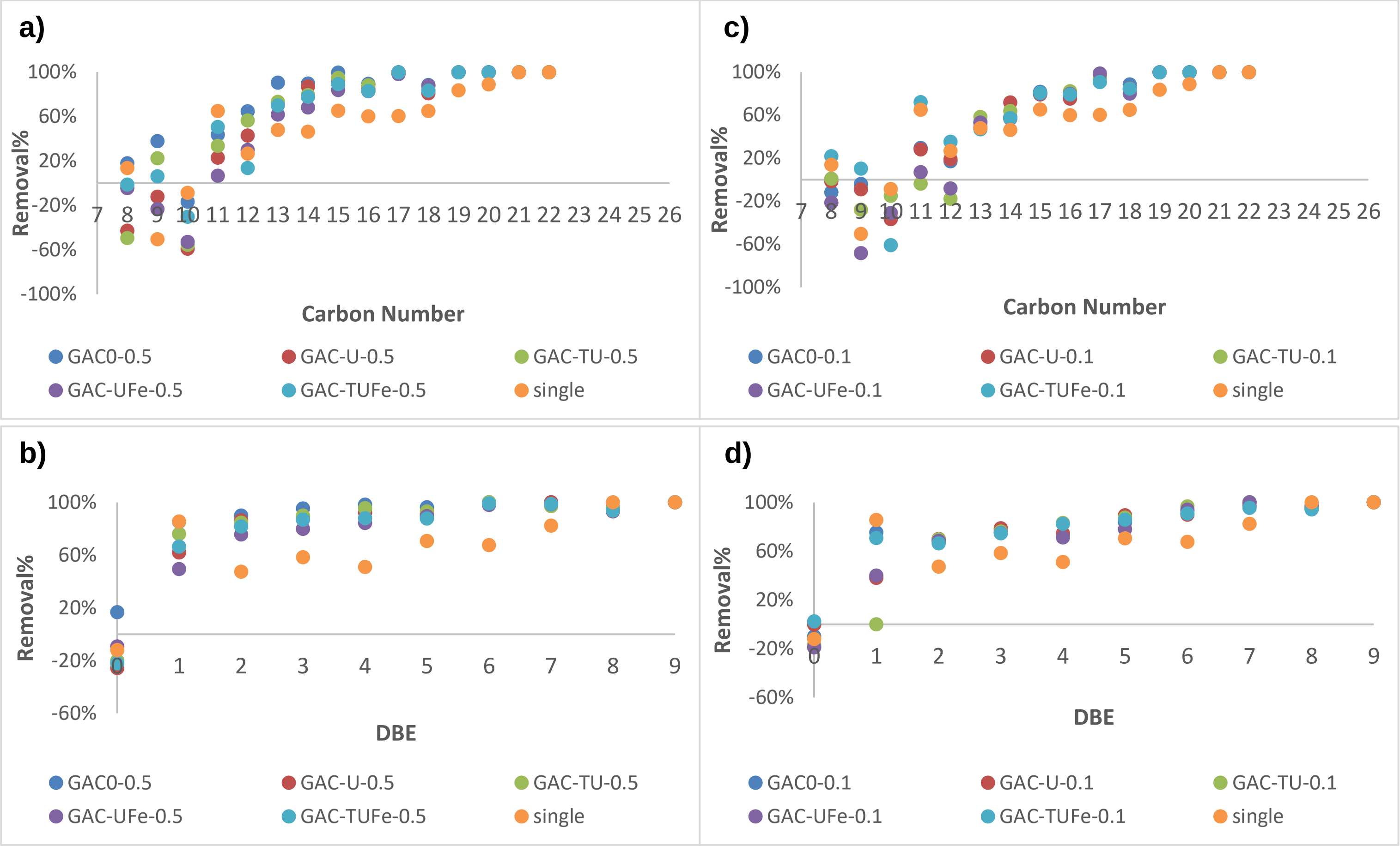


Figure 5.11 Removal of O_2-NAs by 90-min catalytic O_3 treatment with 10 mg/L O_3 and 0.5 g/L catalyst with respect to a) carbon number and b) DBE number. Removal of O_2-NAs by 90-min catalytic O_3 treatment with 10 mg/L O_3 and 0.1 g/L catalyst with respect to c) carbon number and d) DBE number.

5.3.4.2 UV-based treatments

The NAs concentration change after treatment by UV/Fenton was first examined since the degradation efficiencies with regards to SFS and DOC analyses were quite promising by this treatment although the acidic operation pH was still a challenge. Later, NAs after other UV-based treatments applied using H_2O_2 were compared with those of UV/Fenton. Since the degradation efficiencies by PMS discussed in section 3.3 were not promising enough, those samples were not included to study further.

The quantified O_2-NAs in raw OSPW drastically decreased from 26 mg/L to 1.7 mg/L after pH adjustment to 3 although the DOC removal was only 23%. This concentration difference could be because of the presented form of NAs at different pH values. At natural form of OSPW (pH≈8.5), NAs are present as a mixture of ions and neutral molecules depending on their pK_a values and they are mostly in neutral form at acidic pH [55]. Thus, the concentration removal of the samples treated at pH 3 are presented in ***Figure 5.12*** calculated accordingly.

Among the UV-based processes performed at pH 3, photo-Fenton treatments exhibited the best NAs removal efficiency resulting in up to 99% of O_2-NAs removal depending on the applied H_2O_2 dose. The most efficient O_2-NAs removal was obtained with the H_2O_2/COD ratio of 2. Higher dose of H_2O_2 resulted in lower removal of O_2-NAs, contrarily to that observed with DOC removal, which resulted better at higher H_2O_2 dose. This suggests the production of new O_2-NAs rather than total mineralization to CO_2 and H_2O_2 at the lower H_2O_2/COD ratios. The blank experiments conducted with only UV light removed just 36% of O_2-NAs, which could be the transformation of O_2-NAs to another compound since the DOC did not change after UV exposure.

In the case of the catalytic UV-based treatments performed at pH 8.45, UV/H_2O_2 treatment either with or without catalyst led to 98% of O_2-NAs removal. Hereby, any positive effect of catalysts on removal efficiency was not observed either by UPLC-TOF-MS or SFS and DOC for the treatments at pH 8.45. The current removals were so as to UV/H_2O_2.

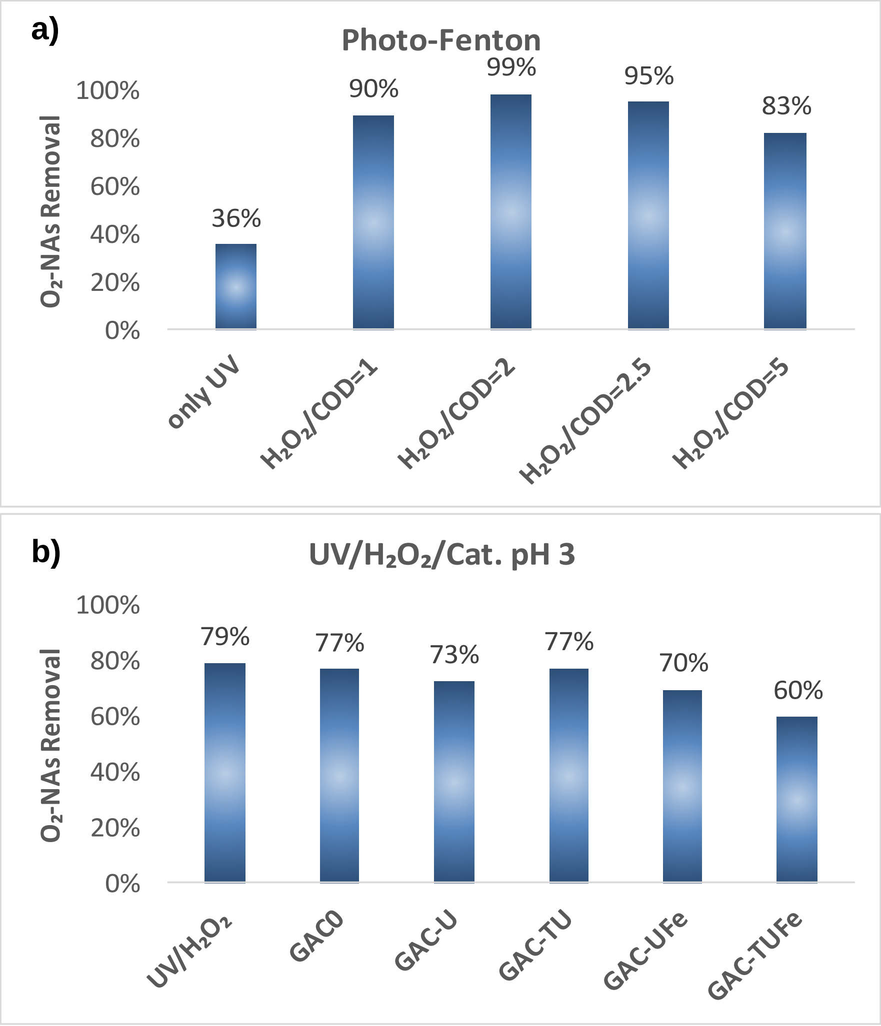


Figure 5.12 Removal of O_2-NAs by 90-min treatments at pH 3 a) Photo-Fenton with 5 mg/L Fe^{2+} and variable H_2O_2 dose b) UV/H_2O_2/Catalysts (0.1 g/L) with H_2O_2/COD=2.5 dose.

5.3.5 Toxicity

It is often reported that the presence of NAs in OSPW is the main reason of its acute toxicity, although their toxic effect could vary depending on the NAs structure (alicyclic or aromatic) and their molecular weight [56]. Based on the preliminary toxicity tests performed by Microtox using *V. fischeri*, the toxicity of the samples after adsorption decreased significantly, suggesting that the compounds with bigger molecule size including ring structures may be responsible for the acute toxicity, as they were adsorbed by the catalysts according to both SFS analysis and NAs quantification by UPLC-TOF-MS. The same behaviour was observed in those O_3-based treated samples. This can also demonstrate that complete mineralization is not necessary to reduce toxicity of the effluent, considering the low DOC removals achieved by adsorption and applied O_3-based treatments. However, the highest toxicity reduction rates were observed for the photo-Fenton treatments. Nevertheless, these results need further confirmation, therefore details are not provided.

5.4 Conclusions

This study compared different catalytic AOPs for the reclamation of OSPW using granular activated carbon-based materials. A compilation of the results is presented in ***Tables Appx. B1-Appx. B2***. From the point of prepared catalysts, the selected materials for the experiments done with real OSPW were found more suitable for the ozone-based treatments in general considering mineralization, NAs removal and mild operation parameters including natural pH and room temperature. However, a cost and sustainability study for the production of the catalysts should be considered, since there was no significant difference between the efficiencies of the treatments conducted with the modified and non-modified GAC, although it was enhanced slightly by modified catalysts.

Concerning the mineralization, which may allow the discharge or reuse of the effluent after treatment, UV/Fenton process was found the best method to achieve higher removal ratios reaching up to 64% with a very low Fe^{2+} concentration, that may be appropriate to discharge after treatment without further sludge removal or reuse it in the plant either for general purposes or for the process units. Also, 99% of NAs was removed, which could reduce the corrosion of the process units caused by NAs, in case of it is reused in the plant. However, the main drawback of this treatment method would be the operating pH, which must be around 3 that would increase the cost of the material used for the treatment units and also the reagent used for regulating the pH around 7 after treatment.

References

[1] C. Li, L. Fu, J. Stafford, M. Belosevic, M. Gamal El-Din, The toxicity of oil sands process-affected water (OSPW): A critical review, Sci. Total Environ. 601–602 (2017) 1785–1802. doi:10.1016/j.scitotenv.2017.06.024.

[2] T. Leshuk, T. Wong, S. Linley, K.M. Peru, J. V. Headley, F. Gu, Solar photocatalytic degradation of naphthenic acids in oil sands process-affected water, Chemosphere 144 (2016) 1854–1861. doi:10.1016/j.chemosphere.2015.10.073.

[3] C. Benally, M. Li, M. Gamal El-Din, The effect of carboxyl multiwalled carbon nanotubes content on the structure and performance of polysulfone membranes for oil sands process-

affected water treatment, Sep. Purif. Technol. 199 (2018) 170–181. doi:10.1016/j.seppur.2018.01.030.

[4] X. Xu, G. Pliego, J.A. Zazo, S. Sun, P. García-Muñoz, L. He, J.A. Casas, J.J. Rodriguez, An overview on the application of advanced oxidation processes for the removal of naphthenic acids from water, Crit. Rev. Environ. Sci. Technol. 47 (2017) 1337–1370. doi:10.1080/10643389.2017.1348113.

[5] E.W. Allen, Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives, J. Environ. Eng. Sci. 7 (2008) 123–138. doi:10.1139/S07-038.

[6] R. Huang, Y. Chen, M.N.A. Meshref, P. Chelme-Ayala, S. Dong, M.D. Ibrahim, C. Wang, N. Klamerth, S.A. Hughes, J. V. Headley, K.M. Peru, C. Brown, A. Mahaffey, M. Gamal El-Din, Characterization and determination of naphthenic acids species in oil sands process-affected water and groundwater from oil sands development area of Alberta, Canada, Water Res. 128 (2018) 129–137. doi:10.1016/j.scitotenv.2018.07.111.

[7] C. Wang, N. Klamerth, S.A. Messele, A. Singh, M. Belosevic, M. Gamal El-Din, Comparison of UV/hydrogen peroxide, potassium ferrate(VI), and ozone in oxidizing the organic fraction of oil sands process-affected water (OSPW), Water Res. 100 (2016) 476–485. doi:10.1016/j.watres.2016.05.037.

[8] J.S. Clemente, P.M. Fedorak, A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids, Chemosphere 60 (2005) 585–600. doi:10.1016/j.chemosphere.2005.02.065.

[9] A.R. Ribeiro, O.C. Nunes, M.F.R. Pereira, A.M.T. Silva, An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU, Environ. Int. 75 (2015) 33–51. doi:10.1016/j.envint.2014.10.027.

[10] V.S.R. Rajasekhar Pullabhotla, C. Southway, S.B. Jonnalagadda, Ozone initiated oxidation of hexadecane with metal loaded $^{\gamma}$-Al2O3 catalysts, Catal. Lett. 124 (2008) 118–126. doi:10.1007/s10562-008-9434-4.

[11] J. Wang, Z. Bai, Fe-based catalysts for heterogeneous catalytic ozonation of emerging contaminants in water and wastewater, Chem. Eng. J. 312 (2017) 79–98. doi:10.1016/j.cej.2016.11.118.

[12] F.J. Beltran, Ozone reaction kinetics for water and wastewater systems, Lewis Publishers, Boca Raton, 2004.

[13] A.K.H. Al jibouri, J. Wu, S.R. Upreti, Heterogeneous catalytic ozonation of naphthenic acids in water, Can. J. Chem. Eng. 97 (2018) 67–73. doi:10.1002/cjce.23209.

[14] K.Y.A. Lin, Z.Y. Zhang, Metal-free activation of Oxone using one-step prepared sulfur-doped carbon nitride under visible light irradiation, Sep. Purif. Technol. 173 (2017) 72–79. doi:10.1016/j.seppur.2016.09.008.

[15] K.Y.A. Lin, Y.C. Chen, Accelerated decomposition of Oxone using graphene-like carbon nitride with visible light irradiation for enhanced decolorization in water, J. Taiwan Inst. Chem. Eng. 60 (2016) 423–429. doi:10.1016/j.jtice.2015.10.046.

[16] H.L. So, W. Chu, Y.H. Wang, Naphthalene degradation by Fe 2+ /Oxone/UV – Applying an unconventional kinetics model and studying the reaction mechanism, Chemosphere 218 (2019) 110–118. doi:10.1016/j.chemosphere.2018.11.091.

[17] H. Park, J. Kim, H. Jung, J. Seo, H. Choi, Iron oxide nanoparticle-impregnated alumina for

catalytic ozonation of para-chlorobenzoic acid in aqueous solution, Water Air Soil Pollut. 225 (2014) 1975. doi:10.1007/s11270-014-1975-0.

[18] J. Bing, C. Hu, Y. Nie, M. Yang, J. Qu, Mechanism of catalytic ozonation in Fe2O3/Al2O3@SBA-15 aqueous suspension for destruction of ibuprofen, Environ. Sci. Technol. 49 (2015) 1690–1697. doi:10.1021/es503729h.

[19] M. Ahmadi, B. Kakavandi, N. Jaafarzadeh, A.A. Babaei, Catalytic ozonation of high saline petrochemical wastewater using PAC @ FeIIFe2IIIO4 ; Optimization, mechanisms and biodegradability studies, Sep. Purif. Technol. 177 (2017) 293–303. doi:10.1016/j.seppur.2017.01.008.

[20] S. Nasseri, A. Mahvi, Y. Shahamat, A. Esrafili, M. Farzadkia, M. Gholami, Magnetic heterogeneous catalytic ozonation: a new removal method for phenol in industrial wastewater, J. Environ. Heal. Sci. Eng. 12 (2014) 50. doi:10.1186/2052-336x-12-50.

[21] A. Dissanayake, A.G. Scarlett, A.N. Jha, Diamondoid naphthenic acids cause in vivo genetic damage in gills and haemocytes of marine mussels, Env. Sci Pollut Res. 23 (2016) 7060–7066. doi:10.1007/s11356-016-6268-2.

[22] S.S. Tiwari, O.T. Iorhemen, J.H. Tay, Aerobic granular sludge and naphthenic acids treatment by varying initial concentrations and supplemental carbon concentrations, J. Hazard. Mater. 362 (2019) 348–357. doi:https://doi.org/10.1016/j.jhazmat.2018.09.043.

[23] S.A. Messele, O.S.G.P. Soares, J.J.M. Órfão, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, J. Font, Zero-valent iron supported on nitrogen-containing activated carbon for catalytic wet peroxide oxidation of phenol, Appl. Catal. B Environ. 154–155 (2014) 329–338.

[24] H. Qin, R. Xiao, J. Chen, Catalytic wet peroxide oxidation of benzoic acid over Fe/AC catalysts: Effect of nitrogen and sulfur co-doped activated carbon, Sci. Total Environ. 626 (2018) 1414–1420. doi:10.1016/j.scitotenv.2018.01.206.

[25] E. Bouleghlimat, P.R. Davies, R.J. Davies, R. Howarth, J. Kulhavy, D.J. Morgan, The effect of acid treatment on the surface chemistry and topography of graphite, Carbon N. Y. 61 (2013) 124–133. doi:10.1016/j.carbon.2013.04.076.

[26] A. Allwar, R. Hartati, I. Fatimah, Effect of nitric acid treatment on activated carbon derived from oil palm shell, AIP Conf. Proc. 1823 (2017). doi:10.1063/1.4978202.

[27] J. Anthony, Design of Experiments for Engineers and Scientists, Elsevier Ltd, Oxford, 2003. doi:https://doi.org/10.1016/B978-0-7506-4709-0.X5000-5.

[28] D.C. Montgomery, Design and analysis of experiments, Eighth, John Wiley & Sons, Inc., Hoboken, 2017. https://lccn.loc.gov/2017002355.

[29] H. Demir-Duz, A.S. Aktürk, O. Ayyildiz, M.G. Alvarez, S. Contreras, Reuse and recycle solutions in refineries by ozone-based advanced oxidation processes : A statistical approach, J. Environ. Manage. 263 (2020) 110346. doi:https://doi.org/10.1016/j.jenvman.2020.110346.

[30] H. Demir-Duz, O. Ayyildiz, A.S.A.S. Aktürk, M.G.M.G. Álvarez, S. Contreras, Approaching zero discharge concept in refineries by solar–assisted photo-Fenton and photo-catalysis processes, Appl. Catal. B Environ. 248 (2019) 341–348. doi:10.1016/j.apcatb.2019.02.026.

[31] S.M. Joshi, P.R. Gogate, Treatment of landfill leachate using different configurations of ultrasonic reactors combined with advanced oxidation processes, Sep. Purif. Technol. 211 (2019) 10–18. doi:10.1016/j.seppur.2018.09.060.

[32] A. Rubio-Clemente, E. Chica, G.A. Peñuela, Petrochemical wastewater treatment by photo-fenton process, Water. Air. Soil Pollut. 226 (2015). doi:10.1007/s11270-015-2321-x.

[33] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, J. Environ. Chem. Eng. 4 (2016) 762–787. doi:10.1016/j.jece.2015.12.016.

[34] P. Pourrezaei, A. Alpatova, K. Khosravi, P. Drzewicz, Y. Chen, P. Chelme-Ayala, M. Gamal El-Din, Removal of organic compounds and trace metals from oil sands process-affected water using zero valent iron enhanced by petroleum coke, J. Environ. Manage. 139 (2014) 50–58. doi:10.1016/j.jenvman.2014.03.001.

[35] A.S. Abdalrhman, Y. Zhang, M. Gamal El-Din, Electro-oxidation by graphite anode for naphthenic acids degradation, biodegradability enhancement and toxicity reduction, Sci. Total Environ. 671 (2019) 270–279. doi:10.1016/j.scitotenv.2019.03.262.

[36] R. Qin, D. Lillico, Z. Tong, R. Huang, M. Belosevic, J. Stafford, M.G. El-din, Separation of oil sands process water organics and inorganics and examination of their acute toxicity using standard in-vitro bioassays, Sci. Total Environ. 695 (2019) 133532.

[37] Z. Fang, R. Huang, P. Chelme-Ayala, Q. Shi, C. Xu, M. Gamal El-Din, Comparison of UV/Persulfate and UV/H2O2 for the removal of naphthenic acids and acute toxicity towards Vibrio fischeri from petroleum production process water, Sci. Total Environ. 694 (2019) 1–10. doi:10.1016/j.scitotenv.2019.133686.

[38] M. Sanchez-Polo, U. Von Gunten, J. Rivera-Utrilla, Efficiency of activated carbon to transform ozone into OH radicals: Influence of operational parameters, Water Res. 39 (2005) 3189–3198. doi:10.1016/j.watres.2005.05.026.

[39] J. Riviera-Utrilla, M. Sanchez-Polo, Ozonation of 1,3,6-naphthalenetrisulphonic acid catalysed by activated carbon in aqueous phase, Appl. Catal. B Environ. 39 (2002) 319–329.

[40] C.A. Guzman-Perez, J. Soltan, J. Robertson, Kinetics of catalytic ozonation of atrazine in the presence of activated carbon, Sep. Purif. Technol. 79 (2011) 8–14. doi:10.1016/j.seppur.2011.02.035.

[41] M. Liu, X. Deng, D. Zhu, H. Duan, W. Xiong, Magnetically separated and N, S co-doped mesoporous carbon microspheres for the removal of mercury ions, 27 (2016) 795–800.

[42] W. Da Oh, S.K. Lua, Z. Dong, T.T. Lim, Performance of magnetic activated carbon composite as peroxymonosulfate activator and regenerable adsorbent via sulfate radical-mediated oxidation processes, J. Hazard. Mater. 284 (2015) 1–9. doi:10.1016/j.jhazmat.2014.10.042.

[43] R. Atchudan, T.N.J.I. Edison, S. Perumal, P. Thirukumaran, R. Vinodh, Y.R. Lee, Green synthesis of nitrogen-doped carbon nanograss for supercapacitors, J. Taiwan Inst. Chem. Eng. 102 (2019) 475–486. doi:10.1016/j.jtice.2019.06.020.

[44] O. Guo-Li, G. Jian-Feng, H. Tuo-Ping, A. Fu-Qiang, W. Yu, W. Yan-Jun, Z. Dong, Synthesis of an activated carbon based urea formaldehyde resin and its adsorption and recognition performance towards Fe(III), RSC Adv. 5 (2015) 71878–71882. doi:10.1039/c5ra11795j.

[45] M. Pedrosa, L.M. Pastrana-Martínez, M.F.R. Pereira, J.L. Faria, J.L. Figueiredo, A.M.T. Silva, N/S-doped graphene derivatives and TiO2 for catalytic ozonation and photocatalysis of water pollutants, Chem. Eng. J. 348 (2018) 888–897. doi:10.1016/j.cej.2018.04.214.

[46] G. Hua, J. Broderick, K.T. Semple, K. Killham, I. Singleton, Rapid quantification of polycyclic aromatic hydrocarbons in hydroxypropyl- b -cyclodextrin (HPCD) soil extracts by synchronous fluorescence spectroscopy (SFS), 148 (2007) 176–181. doi:10.1016/j.envpol.2006.10.040.

[47] Y. Pan, M. Zhou, X. Li, L. Xu, Z. Tang, M. Liu, Novel Fenton-like process (pre-magnetized Fe0/H2O2) for efficient degradation of organic pollutants, Sep. Purif. Technol. (2016). doi:10.1016/j.seppur.2016.06.011.

[48] Y. Abdulaziz Mustafa, A. Ibrahim Alwared, M. Ebrahim, Removal of oil from wastewater by advanced oxidation process/homogeneous process, J. Eng. 19 (2013) 686–694.

[49] E.M. Saggioro, A.S. Oliveira, T. Pavesi, J.C. Moreira, Effect of Activated Carbon and Titanium Dioxide on the Remediation of an Indigoid Dye in Model Waters, Rev. Chim. 65 (2014) 237–241.

[50] I.V. Gala, j. j. López-Penalver, M. Sánchez-Polo, J. Rivera-Utrilla, Activated carbon as photocatalyst of reactions in aqueous phase, Appl. Catal. B Environ. 142–143 (2013) 694–704. doi:10.1016/j.apcatb.2013.06.003.

[51] M.N.A. Meshref, N. Klamerth, M.S. Islam, K.N. McPhedran, M. Gamal El-Din, Understanding the similarities and differences between ozone and peroxone in the degradation of naphthenic acids: Comparative performance for potential treatment, Chemosphere 180 (2017) 149–159. doi:10.1016/j.chemosphere.2017.03.113.

[52] J. Xue, Y. Zhang, Y. Liu, M. Gamal El-Din, Dynamics of naphthenic acids and microbial community structures in a membrane bioreactor treating oil sands process-affected water: impacts of supplemented inorganic nitrogen and hydraulic retention time, RSC Adv. 7 (2017) 17670–17681. doi:10.1039/c7ra01836c.

[53] Y. Guo, Z. Zeng, Y. Li, Z. Huang, Y. Cui, In-situ sulfur-doped carbon as a metal-free catalyst for persulfate activated oxidation of aqueous organics, Catal. Today. 307 (2018) 12–19. doi:http://dx.doi.org/10.1016/j.cattod.2017.05.080.

[54] X. Liu, H. Yin, A. Lin, Z. Guo, Effective removal of phenol by using activated carbon supported iron prepared under microwave irradiation as a reusable heterogeneous Fenton-like catalyst, J. Environ. Chem. Eng. (2017). doi:10.1016/j.jece.2017.01.010.

[55] R. Huang, K.N. McPhedran, N. Sun, P. Chelme-Ayala, M. Gamal El-Din, Investigation of the impact of organic solvent type and solution pH on the extraction efficiency of naphthenic acids from oil sands process-affected water, Chemosphere 146 (2016) 472–477. doi:10.1016/j.chemosphere.2015.12.054.

[56] A.G. Scarlett, H.C. Reinardy, T.B. Henry, C.E. West, R.A. Frank, L.M. Hewitt, S.J. Rowland, Acute toxicity of aromatic and non-aromatic fractions of naphthenic acids extracted from oil sands process-affected water to larval zebrafish, Chemosphere 93 (2013) 415–420. doi:10.1016/j.chemosphere.2013.05.020.

6

Synergetic Effect of O_3/H_2O_2 and UV-C Light Irradiation for the Treatment of Oil Sands Process Water

6.1 Introduction

Bitumen obtained from oil sands is an unconventional fossil fuel that became important in the market due to increasing global demand for oil [1]. However, processing bitumen produces several wastes including produced waste gases or produced water that cause several environmental problems [2]. Regarding produced water, bitumen extraction from oil sands by caustic hot water forms nine cubic meters of raw tailings called oil sands process water (OSPW) per a cubic meter of produced oil [3]. OSPW consisting of water, sand, clay, unrecovered bitumen and other organics including naphthenic acids (NAs) is stored in tailing ponds because of the zero-discharge policy. Typically, a 80% of OSPW is reused in subsequent extraction processes, while the rest must be further managed [3,4]. As a part of the industry's reclamation plan, OSPW in tailings ponds needs to be treated and eventually be discharged into terrestrial and/or aquatic habitat [5]. Particularly, the major concern in OSPW treatment is the abatement of naphthenic acids (NAs) because of their high concentration (20-80 mg/L) and their acute and subchronic toxic effects on aquatic organisms compared to other organic compounds [6].

Naphthenic acids are natural components of bitumen that solubilize during the extraction process. The term of NAs includes mainly alkyl substituted cycloaliphatic carboxylic acids with lower amounts of acyclic aliphatic, aromatic olefinic, hydroxy, and dibasic acids [7]. NAs are expressed by the general formula of $C_nH_{2n+z}O_x$ where n represents the number of carbon atoms, Z is a negative even integer associated with the ring structure and double bonds existing in the component, and x stands for the number of oxygen atoms [8,9]. Due to the complex nature of NAs mixture, the analytical methods developed up to now allow solely the detection of general profile of the mixture related to their carbon content and Z number instead of the detection of the individual components [10].

The environmental management of OSPW could be done cost effectively by biological treatment to reduce the toxicity in some sort. However, in terms of accomplishing with the discharging policies, biological treatment is a very slow process with low efficiency because of the bio-recalcitrant characteristics of NAs in general [11]. Likewise, adsorption by different adsorbents including organic-rich soil, biochar and activated carbon has been reported because of its high efficiency in NAs removal. However, an extra cost is required for regeneration of the adsorbent or its disposal after use [12]. Thus, advanced oxidation processes (AOPs) are getting essential to reach a balance between cost and treatment efficiency avoiding further disposal managements after treatment.

Among AOPs, ozone has wide range of applications in various kinds of effluents from different sectors and its application is not limited to wastewater treatment but also for potable water disinfection, air cleaning, food processing and preserving and health sector due to the high reactivity of ozone [13,14]. Indeed, ozonation is currently used at a large-scale as a stage of municipal wastewater treatment facilities because of its disinfection, decolorization and deodorization power and degradation of micropollutants and organic compounds. In terms of investment and operational costs, which was stated as 0.02-0.07 Eur/m^3 of treated wastewater, it was found feasible to be operated [15]. However, the efficiency of the treatment would depend on the complexity of the wastewater. The presence of components that easily react with O_3 can be removed in few seconds to 2 min. by direct reaction of O_3. Once they are removed completely or their concentration decreases, the O_3 decomposition gets slower and, indirect reactions gain importance for the removal of recalcitrant components so as to achieve higher treatment efficiencies depending on the type of organic molecules and medium pH [16].

In case of OSPW, several studies have been focused on the potential decrease of NAs concentration in OSPW rather than aiming at mineralization, in order to reduce the toxicity of the effluent and/or increase the biodegradability by either ozone or O_3/H_2O_2 treatment. In some cases, applied ozone treatments were in batch mode, i.e., O_3 was fed into water to form a stock solution of O_3 in order to be added to batch reactor at once [8]. The studies performed by semi-batch mode, where O_3 was bubbled into a batch reactor with a constant volume of OSPW, applied very low amounts of oxidants only enough to transform contaminants into other compounds improving the toxicity. In this case, no mineralization was observed after treatment, but this was not the objective of these studies. [17,18]. In other studies, it has been reported higher toxicity after ozone treatment caused by the generated by-products [19].

Optimised amounts of oxidants are crucial to increase treatment efficiency achieving the mineralization of the by-products and consequently, the reduction in toxicity. This optimized parameters and the systems are specific to the configurations of the units [20]. Furthermore, the feeding methods including batch, semi-batch and continuous modes, and the design of the reactor are also critical for a successful treatment. Especially for the treatments where O_3 was bubbled into the effluent, the effect of the size of the O_3 bubbles has been reported [21,22]. The study of Chu et al., where the performance difference between a microbubble generator and a conventional bubble contactor was investigated, confirmed the enhancement in mass transfer improving the removed total organic carbon (TOC) per gram of ozone consumed by accelerated formation of hydroxyl radicals (OH•) when microbubble generator was used [22].

Thus, this study explores the efficient treatment of OSPW aiming at mineralization rather than transformation of contaminants by semi-batch ozone-based AOPs, where O_3 was fed into the reactor by a microporous diffuser, combined with H_2O_2 and/or ultraviolet C irradiation (UV-C) looking for increasing the concentration of available radicals to boost the effectiveness in the degradation of recalcitrant contaminants. Here and to the best of our knowledge, the combined O_3-based treatments in the presence of UV-C irradiation are studied for the first time to treat OSPW. The optimum amounts of reactants, reaction time and the effect of UV-C application have been systematically studied, and the feasibility of the applied processes, including an economic comparison is also discussed. This will allow a possible reusing and/or discharging solution to the sector, where current zero-discharge policy causes a decrease in the quality of the OSPW recycled to processing unit; and thus, an increase in the volume of the effluent stored in tailing ponds by time due to the lack of an established method to treat OSPW.

6.2 Experimental

6.2.1 Materials and methods

Raw OSPW was collected from an oil sands tailing pond in northern Alberta and stored at 4 °C until being used. Main parameters were measured periodically to confirm its stability. Only insignificant differences between the measurements have been observed. Before the treatments, OSPW was filtered using a 0.45 μm nylon membrane to remove suspended solids that could increase the consumption of reagents and decrease the light transmittance (important parameter in case of the light-based treatments). ***Table 6.1*** presents the initial characteristics of OSPW used in this study, after filtration.

Hydrogen peroxide (H_2O_2, 35 wt%, Acros Organic) was used as the oxidant in the ozone-based treatments while potassium iodide (KI, Sigma-Aldrich) were used as a trap to destroy residual O_3 after treatments. Sulfuric acid and sodium hydroxide solutions (1M) were used for pH adjustment of the samples collected for biological based analyses when needed, while sodium bisulfite ($NaHSO_3$, 40%, Panreac) was used for quenching remained H_2O_2 in the samples and stopping the reaction.

Table 6.1 Initial characteristics of raw OSPW.

DOC (mg C/L)	COD (mg O_2/L)	pH	Conductivity (mS/cm)
100	270	8.5	4.6

Ozone (O_3) based experiments were performed in a laboratory scale semi-batch system consisting of an ozone generator, a quartz reactor, a residual ozone measurer and an ozone trap. In the case of UV-C combined treatments, the reactor was surrounded by 4 UV-C low pressure lamps (15W each) that emit mostly at 254 nm. Ozone was produced from pure oxygen by an ozone generator and fed into the quartz reactor containing 300 mL of effluent by an inert, porous diffuser. The outlet gas stream of the reactor was connected to an ozone analyzer to measure residual O_3 during the treatment. In the case of tests involving H_2O_2, desired amounts of H_2O_2 were added into the effluent at once just before starting the O_3 feed. Blank experiments were also conducted to establish the effectiveness of the single processes.

Applied O_3 production rates were 0.9 g/h, 1.8 g/h and 2.7 g/h while varied doses of H_2O_2 were tested (calculated based on the weight/weight ratio of H_2O_2 to initial chemical oxygen demand (COD) and ranged between 0.1 and 5). All the treatments took place during 90 min at natural pH conditions. Samples were collected every 30 min for detailed analysis.

6.2.2 Analytical methods

Dissolved Organic Carbon (DOC) was measured by Shimadzu TOC-L (CSN 638-91109-48) analyzer. Microtox® acute toxicity of the treated/untreated OSPW on *V. fischeri* bacteria was investigated using 81.9% screening test standard protocol with a Microtox®500 Analyzer. The inhibition effect of the samples on *V. fischeri* was measured after 15 min cultivation based on the change in the luminescence intensity. The results were expressed by EC_{50} concentration, defined as the effective nominal concentration of raw/treated OSPW by volume percent that caused reduction in the intensity of light emission by 50%.

6.3 Results and Discussions

6.3.1 Dissolved organic carbon (DOC) removal

DOC analysis is a fast and easy technique to evaluate the treatment efficiencies, which gains importance especially for the treatment of real effluents with complex organic composition like OSPW. For this, the effect of combining H_2O_2 and UV-C to single O_3 treatment was assessed initially by DOC removal. The initial tests of OSPW were focused on single ozonation, conducted with O_3 production rates of 0.9 g/h, 1.8 g/h and 2.7 g/h, which removed 33%, 45% and 53% of DOC, respectively after 90 min treatment. Scott et al. previously reported approximately 25% of TOC removal after 130 min ozone treatment of OSPW, where ozone was fed to the system continuously reaching 35 mg/L of dissolved ozone in the reactor [17]. Thus, single ozonation seems not to be effective enough to mineralize the recalcitrant components present in OSPW. The introduction of promoters of the ozone decomposition to increase the concentration of OH• radicals, consequently the occurrence of indirect reactions, can favour the mineralization of those recalcitrant components present in OSPW.

Introducing H_2O_2 into the system led to a significant increase of the DOC removal efficiency (***Figure 6.1***), as expected. It is frequently reported that in the presence of H_2O_2, the conversion rate of O_3 to HO• and dissolved O_3 amount increases. Besides, the generation of HO• and HO_2• radicals from the activation of H_2O_2 by O_3 or O_3 decomposition promoted by H_2O_2 can take place [23]. Thus, 71% of DOC removal was achieved after 90 min of O_3/H_2O_2 treatment with 0.9 g/h O_3 production rate and H_2O_2/COD=2. Whereas, increasing the O_3 production rate to 1.8 g/h and 2.7 g/h O_3 (maintaining the H_2O_2/COD ratio) led to a DOC removal of 84% and 86%, respectively, indicating that higher production rates of O_3 than 1.8 g/h, in the presence of H_2O_2, do not lead to significant changes in the DOC removal. Thus, UV-C combined treatments were performed only with O_3 production rates of 0.9 g/h and 1.8 g/h.

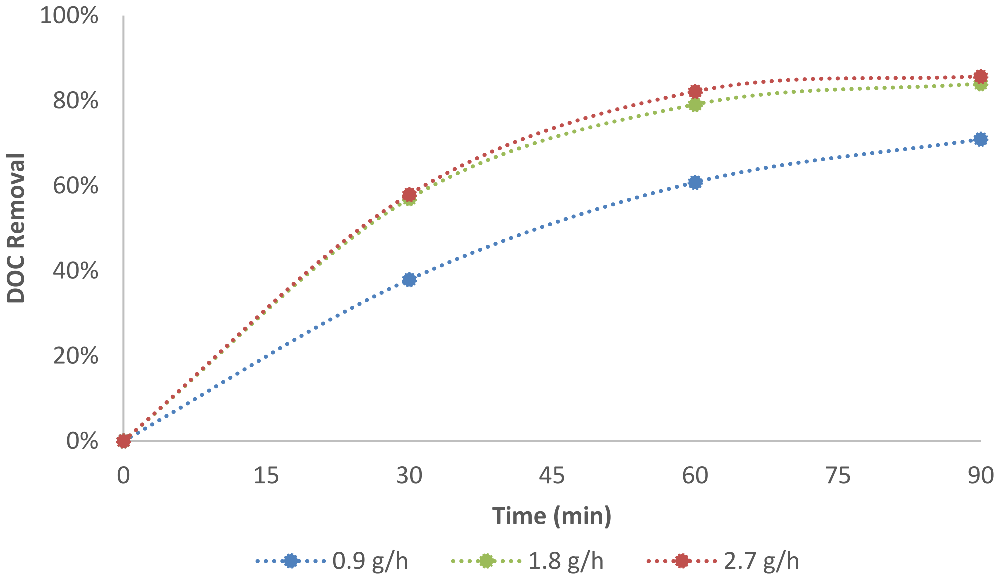


Figure 6.1 DOC removal efficiency by O_3/H_2O_2 treatment with varied production rates of O_3 and a constant H_2O_2/COD ratio of 2.

UV-C integration to O_3-based treatments (***Figure 6.2***) enhanced the treatment efficiencies in great extent, allowing a shorter treatment time. This is likely due to the synergetic effect of the combined O_3 treatment with UV-C and/or H_2O_2, which may form hydroxyl, peroxyl and superoxide radicals increasing the reaction efficiencies, according to the literature [24,25]. Besides this, in-situ production of H_2O_2 from UV-C and O_3 can also occur, as reported before in several studies, favouring DOC removal by increased amounts of radicals [26,27]. After 90 min, DOC removal reached by single ozonation with 0.9 g/h and 1.8 g/h increased from 33% and 45% to 67% and 84%, respectively, solely due to its combination with UV-C. In the case of H_2O_2 addition to UV-C/O_3 system, DOC removals after 90 min of treatment reached 87% and 98% for 0.9 g/h and 1.8 g/h O_3 production rates, respectively. Remarkably, this triple combination (i.e., H_2O_2/O_3/UV-C) conducted with 1.8 g/h of O_3 and H_2O_2/COD ratio of 2, already allowed a 65% and 92% of DOC removal in 30 min and 60 min, respectively.

Due to the improved results obtained by the use of a triple H_2O_2/O_3/UV-C combination, the effect of H_2O_2 concentration has been studied further. The DOC removal trend after the triple H_2O_2/O_3/UV-C combination (***Figure 6.3***) with H_2O_2/COD=1.05 and H_2O_2/COD=2 was very similar, reaching 83% and 87%, respectively, after 90 min of treatment. Any decrease or increase of H_2O_2 dose caused a noticeable decrease in the removal efficiency either due to a lower radicals production (in the case of the lowest dose) or due to the scavenging effect of H_2O_2 itself (in the case of the highest dose) [28].

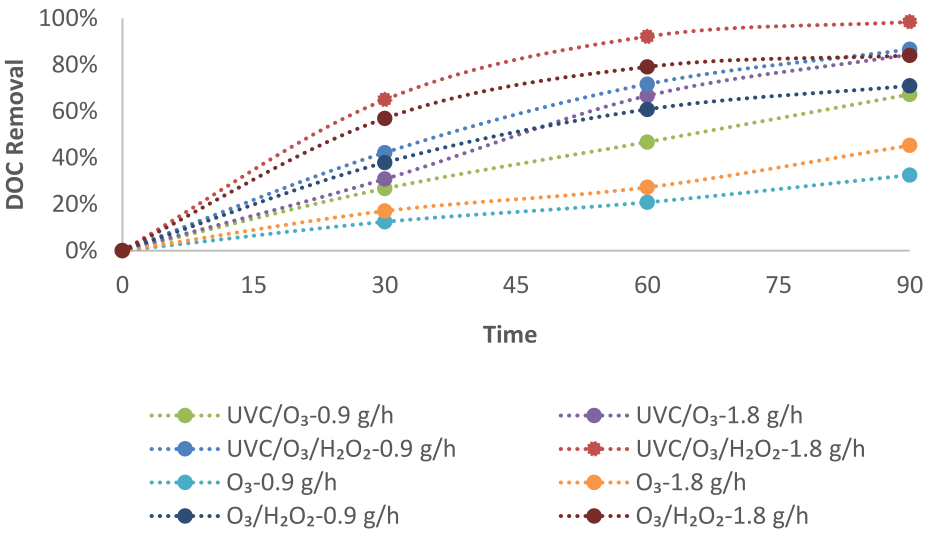


Figure 6.2. DOC removal efficiency by UV-C based treatments with varied production rates of O_3 with/without a constant H_2O_2/COD ratio of 2.

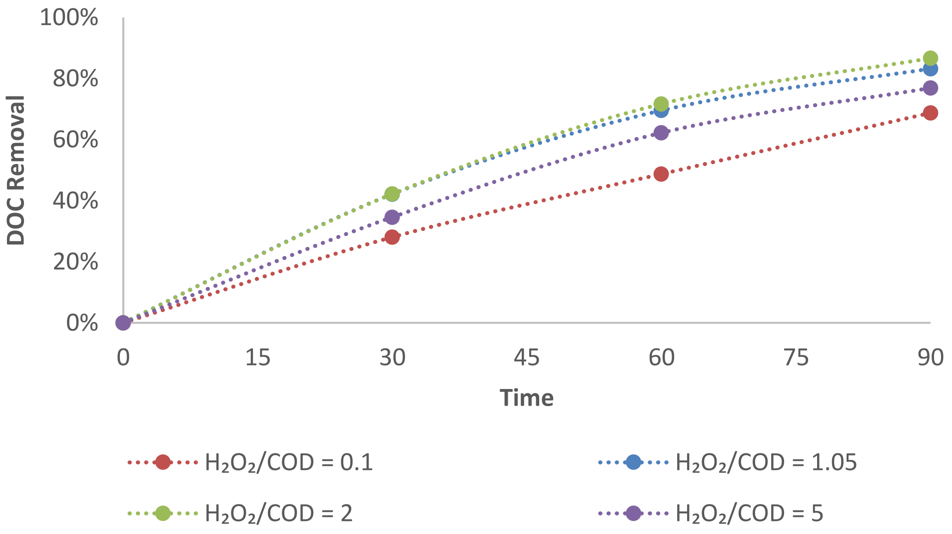


Figure 6.3 DOC removal efficiency by UV-C based treatments with varied ratios of H_2O_2/COD and a constant O_3 production rate of 0.9 g/h.

6.3.2 Toxicity evaluation

Toxicity of OSPW has been studied frequently as an indicator of effectiveness of the treatment. Raw OSPW present acute toxicity due to the presence of NAs and other organic components such as polycyclic aromatic hydrocarbons (PAHs), BTEX (benzene, toluene, ethyl benzene, and xylenes) and phenols [29]. Therefore, due to the complex nature of OSPW, toxicity is assessed for the entire OSPW composition or for its main constituents, such as NAs fractions or other organic fractions instead of individual components [29–31]. Accordingly, an effective treatment method that allows dischargement of OSPW safely by reducing its toxicity became a necessity unless treated effluent is reused in the plant.

Microtox is a rapid and relatively economic method commonly used to monitor acute toxicity of effluents like OSPW [17]. In the literature, values $EC_{50}<25\%$ are defined as very toxic, while $25\%<EC_{50}<75\%$ would be toxic and $EC_{50}>75\%$ would be considered non-toxic [32]. Inhibition test is recommended for the effluents with low levels of toxicity, for which EC50 values are not calculable [33].

Toxicity tests on *V. fischeri* performed with the samples collected after the different treatments (***Table 6.2***) revealed that 90-min single O_3 treatment with the lowest O_3 production rate (i.e., 0.9 g O_3/h) already reduced the toxicity of OSPW, presenting a EC_{50} concentration of 42%, which would still be considered toxic, compared to EC_{50} of 19% for raw OSPW. Higher O_3 production rates decreased the toxicity to suitable ranges. Thus, the maximum inhibition effects found in those samples treated after 90 min of single ozonation with O_3 production rates of 1.8 g/h and 2/7 g/h were 33% and 37%, respectively. That is, the reduction of 50% in the luminescence intensity was not reached, which demonstrates the non-toxic features of the treated OSPW. In the case of combined treatments, acute toxicity also decreased significantly in accordance with the mineralization levels obtained, as shown by DOC analysis. After 90 min of treatment with the O_3/H_2O_2 system, with H_2O_2/COD=2 under dark conditions also resulted in 43% and 26% of maximum inhibition effect for the 0.9 g/h and 1.8 g/h O_3 production rate, respectively, improving the toxicity reduction as compared to those of single ozonation After 90 min of combined treatment of UV-C/O_3/H_2O_2 the toxicity showed a maximum inhibition effect of 33% and 22% for the 0.9 g/h and 1.8 g/h O_3 production rate (with H_2O_2/COD=2), respectively, which would mean the lowest toxic properties.

Table 6.2 Toxicity tests on *V. fischeri* performed with the samples collected after the 90 min different treatments.

Process	Treatment Conditions			Toxicity Assessments	
	O_3 (g/h)	H_2O_2/COD	UV-C	EC_{50} (%)	Inhibition Effect (%)
Raw OSPW				19	99
O_3	0.9			42	62
	1.8				33
	2.7				37
O_3/H_2O_2	0.9	2			43
	1.8	2			26
UV-C/O_3	0.9		Applied		24
	1.8		Applied		41
UV-C/O_3/H_2O_2	0.9	2	Applied		33
	1.8	2	Applied		22

The positive influence of ozone-based treatments on the toxicity of OSPW has also been reported in other studies [8,11]; however, the DOC reduction reported is quite small. Therefore, not only toxicity but a general assessment of all parameters must be considered for the most appropriate treatment method for OSPW including mineralization and economy.

6.3.3 O_3 consumption analysis

Beltran, reported in detail that when ozone dissolves in water decomposes to free radicals, and indirect reactions start beside the direct reactions. This decomposition mechanism is strongly dependant on the nature of the effluent including pH or the present components [16]. In a recent study, the treatment of a petroleum refinery wastewater effluent with the same ozonation system showed a reverse balance between O_3 and the H_2O_2 concentrations, suggesting that the highest TOC removals could be reached by an optimum ratio between O_3 and H_2O_2 [28]. Thus, the consumption tendency of the oxidants for treating OSPW was tried to be clarified as an example of case studies.

The mass balance of O_3 within the system was determined by ***Eq. 1***. Here, although the dissolved O_3 concentrations of the collected samples were measured by indigo colorimetric method described by APHA [34], the residual dissolved O_3

concentrations were not taken into account due to the low detected concentrations (ranged between 3-8 mg/L) compared to those of inlet and outlet. However, it would be interesting to note that dissolved O_3 amount in samples after 90 min of treatment was as follows: UV-C/O_3/H_2O_2< UV-C/O_3< O_3< O_3/H_2O_2. Lower dissolved amount of O_3 was observed in those experiments performed in the presence of UV-C light (approx. 3.8 mg/L for UV-C/O_3/H_2O_2 and UV-C/O_3). This is indeed in agreement with the consumed O_3 amount of those treatments as showed in ***Figure 6.4b***. So that, O_3 consumptions of those systems including UV-C light (with an O_3 feed ratio of 1.8 g/h) were increased to ca. 2 g after 90 min compared to 0.5 g of O_3 consumed in the processes that do not include UV-C irradiation. The higher O_3 consumption shown by these UV-C based processes accounts for the photodecomposition of O_3 yielding H_2O_2 and subsequently hydroxyl radicals among other radicals [24]. Similarly, in addition, the O_3 consumption for O_3/H_2O_2 system (***Figure 6.4a***) was higher than that of single ozonation. This result was expected since H_2O_2 accelerates the ozone decomposition ratio that eventually leads to form hydroxyl radicals especially at alkaline pH [16].

$$O_3 \text{ consumption (reacted + dissolved) (g)} = O_3 \text{ (inlet) (g)} - O_3 \text{ (outlet) (g)} \qquad \mathbf{(1)}$$

The relationship between O_3 consumption and DOC removal (***Figure 6.5***) revealed that those treatments including the use of H_2O_2 - either with or without UV-C promoted efficient consumption of O_3 in terms of DOC removal. In the presence of H_2O_2, DOC removals of the treatments were almost two-fold, although the consumed O_3 amounts were almost the same for the treatments conducted in the absence of H_2O_2. In other words, when single ozonation is applied, O_3 consumption is mainly due to the transformation the OSPW components rather than mineralization likely due to the absence of the HO· degradation pathway. Also, the molar ratios of O_3(consumed)/DOC(removed) for the treatments conducted with 1.8 g/h O_3 production rates were calculated as 4, 6, 21 and 18 for the treatments of O_3, O_3/H_2O_2, UV-C/ O_3 and UV-C/O_3/H_2O_2, respectively, indicating that the O_3 was used more effectively in the O_3/H_2O_2 treatment considering also the DOC removal efficiency which was 45% and 84% for O_3 and O_3/H_2O_2 treatments, respectively. A previous study of another kind of petroleum refinery wastewater treatment by ozone-based processes also reported that the molar ratio of O_3(consumed)/DOC(removed) for the optimized O_3/H_2O_2 treatment was around 6 [28].

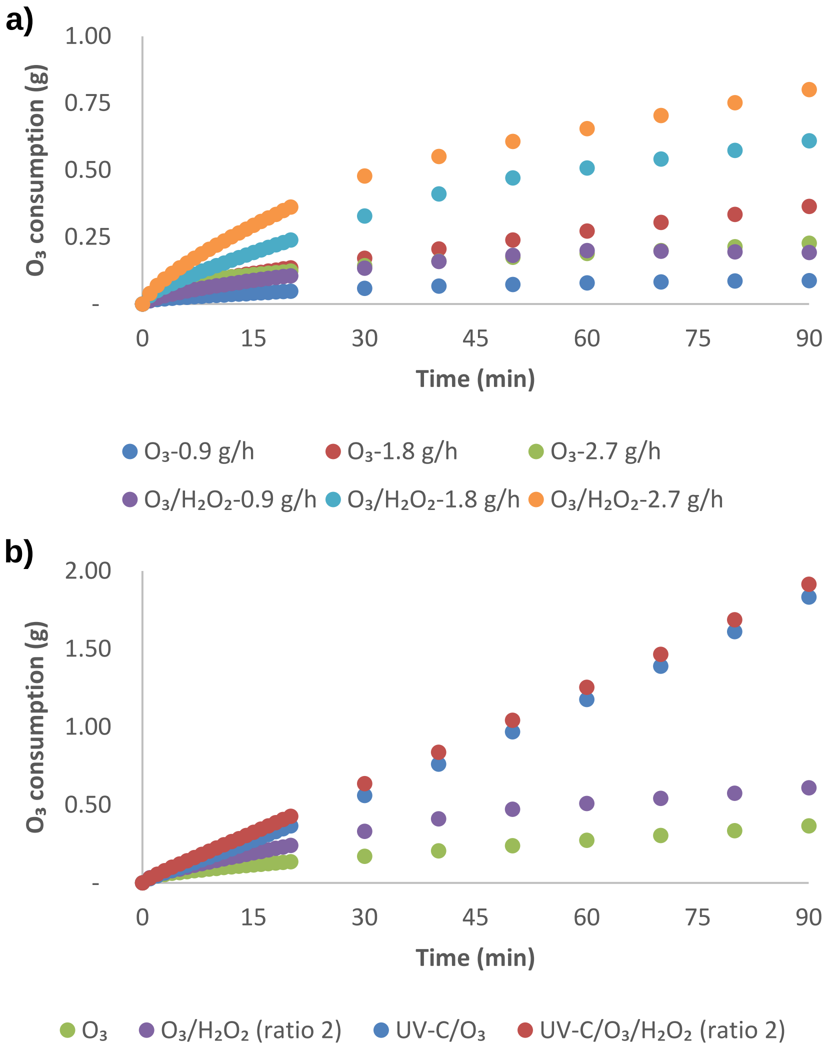


Figure 6.4 O_3 consumption during 90 min treatment by a) O_3 and O_3/H_2O_2 with $H_2O_2/COD=2$ and varied O_3 production rates b) different AOPs with O_3 production rate of 1.8 g/h.

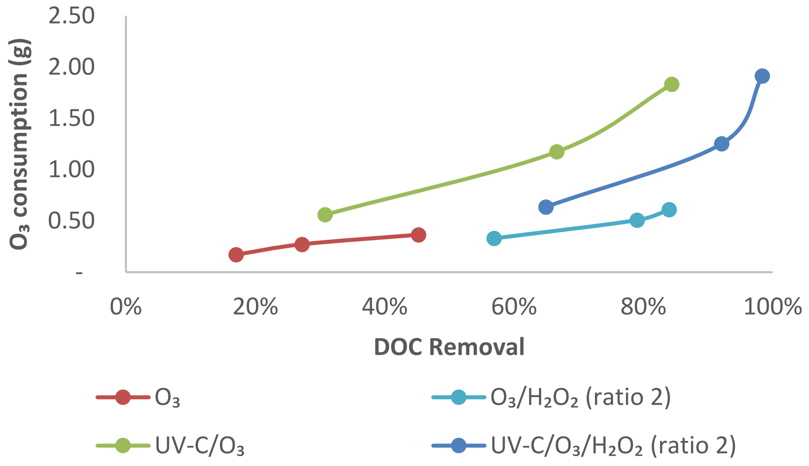


Figure 6.5 The relationship between O_3 consumption and DOC removal% for different AOPs with O_3 production rate of 1.8 g/h.

6.3.4 Operational comparison of applied treatments

The balance between operational costs and the treatment efficiencies becomes important for a feasible application of treatment processes. Although high mineralization degrees could be reached through the different combinations of UV-C, O_3 and H_2O_2, operational costs must be also considered to decide the most convenient alternative for the treatment of OSPW, also having in mind the final end of the treated effluent. The energy consumption comparison of the different treatments may help to make an approach on this question.

Energy consumption of the treatments can be assessed by the ***Eq. 2***, reported by Bolton et al., based on the electrical energy per order (EEO) on a batch system [35].

$$EEO\left(\frac{kWh}{m^3}\right) = \frac{P(kW)*t(h)*1000}{V(L)*\log\left(\frac{C_i}{C_f}\right)} \qquad \textbf{(2)}$$

where P(kW), t(h), C_i and C_f and V(L) represent rated power, reaction time, initial and final concentration, and treated volume of OSPW, respectively.

In previous studies, this equation was slightly modified using initial and final TOC instead of a target compound concentration because of the complex nature of real effluents [28,32]. In this study, calculations were made based on DOC removal expressed by the ***Eq. 3***, since the first target was reaching higher DOC removal by mineralization.

$$EEO\left(\frac{kWh}{m^3}\right) = \frac{P(kW)*t(h)*1000}{V(L)*\log\left(\frac{DOC_i}{DOC_f}\right)} \qquad \textbf{(3)}$$

EEO of the applied processes were calculated considering the energy consumption of the current laboratory-scale system. P (kW) of magnetic stirrer, O_3 measurer and UV-C lights were 0.002, 0.008 and 0.06, respectively while that of O_3 generator was calculated depending on the produced O_3 amount (10 kW/kg O_3 according to the supplier). As shown in ***Table 6.3***, it was observed that EEO corresponding to 90 min of single ozonation was pretty higher than the combined AOPs although the DOC removals were the lowest. Also, UV-C/O_3 treatment resulted in high energy demand. However, in the presence of UV-C, higher O_3 production rate resulted in lower EEO as the removal efficiency was higher at a given time. EEO values decreased to 177 kWh/m^3 and 171 kWh/m^3 for the O_3/H_2O_2 combination with O_3 production rates of 0.9 g/h and 1.8 g/h, respectively, and a H_2O_2/COD ratio of 2. This indicates a marked benefit of O_3/H_2O_2 treatment in mineralization that reached to 84% DOC removal, and economy obtained by applying 1.8 g/h of O_3 dosing in combination with H_2O_2 considering. Instead, the use of an O_3 feeding above 1.8 g/h increased the EEO significantly since DOC removal was not improved by applying higher O_3 production rate. The electrical energy need increased slightly to 243 kWh/m^3 for the treatments conducted with the UV-C/O_3/H_2O_2 system with a O_3 production rate of 1.8 g/h and H_2O_2/COD ratio of 2, if compared with the EEO of O_3/H_2O_2 treatments. However, DOC removal% obtained by UV-C/O_3/H_2O_2 was remarkably high, 98%, which expands the range of reuse purposes in the plant. In contrast, decreasing the dose of O_3 to 0.9 g/h caused a great increase in EEO, up to 452 kWh/m^3 for the same H_2O_2/COD ratio=2. Thus, it could be concluded that O_3/H_2O_2 system can offer an effective treatment with a better price, while UV-C/O_3/H_2O_2 system can provide an effluent with better quality that can increase its reuse rather than discharging.

Table 6.3 EEO comparison of different processes after 90 min treatment.

Process	**Treatment Conditions**			**P (kW) for each unit**				**EEO (kWh/m^3)**
	O_3 (g/h)	**H_2O_2/COD**	**UV-C**	**Magnetic Stirrer**	**O_3 generator**	**O_3 measurer**	**UV-C**	
O_3	0.9	-	-	0.002	0.009	0.008	-	556
	1.8	-	-	0.002	0.018	0.008	-	536
	2.7	-	-	0.002	0.027	0.008	-	568
O_3/H_2O_2	0.9	2	-	0.002	0.009	0.008	-	**177**
	1.8	2	-	0.002	0.018	0.008	-	**171**
	2.7	2	-	0.002	0.027	0.008	-	**219**
UV-C/O_3	0.9	-	Applied	0.002	0.009	0.008	0.06	827
	1.8	-	Applied	0.002	0.018	0.008	0.06	537
UV-C/O_3/H_2O_2	0.9	2	Applied	0.002	0.009	0.008	0.06	452
	1.8	2	Applied	0.002	0.018	0.008	0.06	**243**
UV-C/O_3/H_2O_2	0.9	0.1	Applied	0.002	0.009	0.008	0.06	782
	0.9	1.05	Applied	0.002	0.009	0.008	0.06	509
	0.9	5	Applied	0.002	0.009	0.008	0.06	621

It must be noted that EEO values were calculated for the laboratory scale system used in this study only to present how EEO would change by single or combined treatment methods. EEO of large-scale, optimized treatment systems, where a study of the best lamp type (if any) and O_3 production/injection systems would be performed, may be much lower than the presented values. Besides the process capacity, it is worthy to mention that EEO is highly dependent of the water features, eg. concentration of contaminants, turbidity, presence of recalcitrant components and radical scavengers. The effluent treated in this study is a real waste effluent with a very complex matrix that presents high concentrations of naphtenic acids, known by their high toxicity and resistance to mineralization. Thus, it is reasonable to expect higher energy demand than that needed in case studies where only one or few components are present in a pure water matrix.

6.4 Conclusions

This study explored an efficient and environmentally friendly treatment method that can add value to the industry’s reclamation plan for the OSPW, which currently is stored in tailing ponds until it is treated properly. For this aim, ozone based AOPs including the different combinations of O_3, H_2O_2 and UV-C were investigated in detail as a candidate to treat OSPW. In contrast to many studies, mineralization rather than transformation of the recalcitrant components was targeted so as to reclaim the effluent after treatment, which could be then reused in the bitumen extraction or upgrading units without lowering the quality of the products or causing corrosion in the process units. Additionally, the treated effluent could be discharged safely to the environment.

Optimized O_3/H_2O_2 treatment can be considered as a feasible treatment method in terms of the mineralization degree, which decreased the final DOC down to ca. 15 mg C/L and eliminated the acute toxicity completely. These features make the effluent being discharged safely, after decreasing its alkalinity, or being reused in the extraction process since its quality is improved significantly. Thus, reusing improved quality of the treated effluent in extraction process can offer a remedy to the current problems due to the decreases in extraction efficiencies over time meanwhile increasing the pollution degree of OSPW in tailing ponds.

When UV-C light was irradiated during O_3/H_2O_2 treatment, final DOC was reduced down to 2 mg C/L with the consequent removal of toxicity. This method allows the treated water being used as cooling/boiling water in the units used for bitumen upgrading. However, in this case, it is expected that the operation costs would increase slightly in the case of a large-scale application, based in our observations at lab-scale. Therefore, a global evaluation considering the costs of water processing or purchasing that is used for these systems should be performed.

The real effluent used in this study provides important information of the efficiency of the different AOPs tested in case of extrapolation to a larger scale. The efficiency showed by these treatment methods may bring the following benefits: i) the reduction of water use by decreasing the external water demand of the bitumen and heavy oils extraction plants in the search of a more resource efficient and environmental friendly processes; and ii) the opening up to the recovering and reclamation of land, decreasing the negative impact on the local fauna and possible seepage to surface water.

References

[1] E.W. Allen, Process water treatment in Canada’s oil sands industry: I. Target pollutants and treatment objectives, J. Environ. Eng. Sci. 7 (2008) 123–138. doi:10.1139/S07-038.

[2] G. Boczkaj, M. Gągol, M. Klein, A. Przyjazny, Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants, Ultrason. Sonochem. 40 (2018) 969–979. doi:10.1016/j.ultsonch.2017.08.032.

[3] L.D. Brown, A.C. Ulrich, Oil sands naphthenic acids : A review of properties, measurement, and treatment, Chemosphere 127 (2015) 276–290. doi:http://dx.doi.org/10.1016/j.chemosphere.2015.02.003.

[4] G. Mannina, Frontiers in Wastewater Treatment and Modelling, Springer, Cham, 2017. doi:10.1007/978-3-319-58421-8.

[5] R. Huang, Y. Chen, M.N.A. Meshref, P. Chelme-Ayala, S. Dong, M.D. Ibrahim, C. Wang, N. Klamerth, S.A. Hughes, J. V. Headley, K.M. Peru, C. Brown, A. Mahaffey, M. Gamal El-Din, Characterization and determination of naphthenic acids species in oil sands process-affected water and groundwater from oil sands development area of Alberta, Canada, Water Res. 128 (2018) 129–137. doi:10.1016/j.scitotenv.2018.07.111.

[6] Z. Fang, R. Huang, P. Chelme-Ayala, Q. Shi, C. Xu, M. Gamal El-Din, Comparison of UV/Persulfate and UV/H2O2 for the removal of naphthenic acids and acute toxicity towards Vibrio fischeri from petroleum production process water, Sci. Total Environ. 694 (2019) 1–10. doi:10.1016/j.scitotenv.2019.133686.

[7] J. V. Headley, D.W. Mcmartin, A Review of the occurrence and fate of naphthenic acids in aquatic environments, J. Environ. Sci. Heal. Part A. 39 (2004) 1989–2010. doi:10.1081/ESE-120039370.

[8] M.N.A. Meshref, N. Klamerth, M.S. Islam, K.N. McPhedran, M. Gamal El-Din, Understanding the similarities and differences between ozone and peroxone in the degradation of naphthenic acids: Comparative performance for potential treatment,

Chemosphere 180 (2017) 149–159. doi:10.1016/j.chemosphere.2017.03.113.

[9] T. Leshuk, T. Wong, S. Linley, K.M. Peru, J. V. Headley, F. Gu, Solar photocatalytic degradation of naphthenic acids in oil sands process-affected water, Chemosphere 144 (2016) 1854–1861. doi:10.1016/j.chemosphere.2015.10.073.

[10] J.S. Clemente, P.M. Fedorak, A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids, Chemosphere 60 (2005) 585–600. doi:10.1016/j.chemosphere.2005.02.065.

[11] A.K.H. Al jibouri, J. Wu, S.R. Upreti, Heterogeneous catalytic ozonation of naphthenic acids in water, Can. J. Chem. Eng. 97 (2018) 67–73. doi:10.1002/cjce.23209.

[12] X. Xu, G. Pliego, J.A. Zazo, S. Sun, P. García-Muñoz, L. He, J.A. Casas, J.J. Rodriguez, An overview on the application of advanced oxidation processes for the removal of naphthenic acids from water, Crit. Rev. Environ. Sci. Technol. 47 (2017) 1337–1370. doi:10.1080/10643389.2017.1348113.

[13] C. Wei, Z. Fengzhen, Y. Hu, C. Feng, Ozonation in water treatment : the generation, basic properties of ozone and its practical application, Rev. Chem. Eng. 33 (2017) 49–89. doi:10.1515/revce-2016-0008.

[14] H. Karaca, Y.S. Velioglu, Ozone Applications in Fruit and Vegetable Processing, Food Rev. Int. 23 (2007) 91–106. doi:10.1080/87559120600998221.

[15] A. Ried, J. Mielcke, A. Wieland, The Potential Use of Ozone in Municipal Wastewater, Ozone Sci. Eng. 31 (2009) 415–421. doi:10.1080/01919510903199111.

[16] F.J. Beltran, Ozone reaction kinetics for water and wastewater systems, Lewis Publishers, Boca Raton, 2004.

[17] A.C. Scott, W. Zubot, M.D. MacKinnon, D.W. Smith, P.M. Fedorak, Ozonation of oil sands process water removes naphthenic acids and toxicity, Chemosphere 71 (2008) 156–160. doi:10.1016/j.chemosphere.2007.10.051.

[18] C. Wang, N. Klamerth, S.A. Messele, A. Singh, M. Belosevic, M. Gamal El-Din, Comparison of UV/hydrogen peroxide, potassium ferrate(VI), and ozone in oxidizing the organic fraction of oil sands process-affected water (OSPW), Water Res. 100 (2016) 476–485. doi:10.1016/j.watres.2016.05.037.

[19] J.C. Anderson, S.B. Wiseman, N. Wang, A. Moustafa, L. Perez-Estrada, M.G. El-din, J.W. Martin, K. Liber, J.P. Giesy, Effectiveness of Ozonation Treatment in Eliminating Toxicity of Oil Sands Process-Affected Water to Chironomus dilutus, Environ. Sci. Technol. 46 (2012) 486–493. doi:dx.doi.org/10.1021/es202415g |.

[20] M.H. El-Naas, M.A. Alhaija, S. Al-Zuhair, Evaluation of an activated carbon packed bed for the adsorption of phenols from petroleum refinery wastewater, Environ. Sci. Pollut. Res. (2017). doi:10.1007/s11356-017-8469-8.

[21] Z. Xia, L. Hu, Treatment of Organics Contaminated Wastewater by Ozone Micro-Nano-Bubbles, Water. 11 (2019) 55. doi:10.3390/w11010055.

[22] L. Chu, X. Xing, A. Yu, Y. Zhou, X. Sun, Enhanced ozonation of simulated dyestuff wastewater by microbubbles, Chemosphere 68 (2007) 1854–1860.

doi:10.1016/j.chemosphere.2007.03.014.

[23] G. Boczkaj, A. Fernandes, P. Makos, Study of different advanced oxidation processes for wastewater treatment 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.

[24] M.S. Lucas, J.A. Peres, G. Li Puma, Treatment of winery wastewater by ozone-based advanced oxidation processes (O3, O3/UV and O3/UV/H2O2) in a pilot-scale bubble column reactor and process economics, Sep. Purif. Technol. 72 (2010) 235–241. doi:10.1016/j.seppur.2010.01.016.

[25] B.W. Liu, M.S. Chou, C.M. Kao, B.J. Huang, Evaluation of Selected Operational Parameters for the Decolorization of Dye- Finishing Wastewater Using UV/Ozone, Ozone Sci. Eng. 26 (2004) 239–245. doi:10.1080/01919510490455557.

[26] J.Y.U. Kim, G.G. Bessegato, B.C. de Souza, J.J. da Silva, M.V.B. Zanoni, Efficient treatment of swimming pool water by photoelectrocatalytic ozonation: Inactivation of Candida parapsilosis and mineralization of Benzophenone-3 and urea, Chem. Eng. J. 378 (2019) 1–10. doi:10.1016/j.cej.2019.122094.

[27] S.T. Summerfelt, Ozonation and UV irradiation - An introduction and examples of current applications, Aquac. Eng. 28 (2003) 21–36. doi:10.1016/S0144-8609(02)00069-9.

[28] H. Demir-Duz, A.S. Aktürk, O. Ayyildiz, M.G. Alvarez, S. Contreras, Reuse and recycle solutions in refineries by ozone-based advanced oxidation processes : A statistical approach, J. Environ. Manage. 263 (2020) 110346. doi:https://doi.org/10.1016/j.jenvman.2020.110346.

[29] C. Li, L. Fu, J. Stafford, M. Belosevic, M. Gamal El-Din, The toxicity of oil sands process-affected water (OSPW): A critical review, Sci. Total Environ. 601–602 (2017) 1785–1802. doi:10.1016/j.scitotenv.2017.06.024.

[30] E. Garcia-Garcia, J.Q. Ge, A. Oladiran, B. Montgomery, M.G. El-Din, L.C. Perez-Estrada, J.L. Stafford, J.W. Martin, M. Belosevic, Ozone treatment ameliorates oil sands process water toxicity to the mammalian immune system, Water Res. 45 (2011) 5849–5857. doi:10.1016/j.watres.2011.08.032.

[31] E. Garcia-Garcia, J. Pun, L.A. Perez-Estrada, M.G. El Din, D.W. Smith, J.W. Martin, M. Belosevic, Commercial naphthenic acids and the organic fraction of oil sands process water downregulate pro-inflammatory gene expression and macrophage antimicrobial responses, Toxicol. Lett. 203 (2011) 62–73. doi:10.1016/j.toxlet.2011.03.005.

[32] S. Jiménez, M. Andreozzi, M.M. Micó, M.G. Álvarez, S. Contreras, Produced water treatment by advanced oxidation processes, Sci. Total Environ. 666 (2019) 12–21. doi:10.1016/j.scitotenv.2019.02.128.

[33] How to use the Microtox ® Acute Toxicity Test to perform an In-House Toxicity Reduction Evaluation (TRE), (2006). http://foros.santafe-conicet.gob.ar/fotorreactores/archivos.php?action=downloadfile&filename=Mtx-TRE20Guide.pdf&directory=Procedimientos de uso de los equipos/Microtox (accessed January 24, 2020).

[34] APHA Method 4500-O3: Standard Methods for the Examination of Water and Wastewater,

1992.

[35] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems, J. Adv. Oxid. Technol. 1 (1996) 13–17. doi:10.1351/pac200173040627.

CHAPTER 6: Synergetic Effect of O_3/H_2O_2 and UV-C Light Irradiation for the Treatment of Oil Sands Process Water

7

Main Conclusions & Future Works

This thesis aimed to contribute to the reclamation of wastewaters from the oil & gas industry that generates high amount of effluents, increasing the water stress worldwide. Different types of advanced oxidation processes were applied to upstream and downstream effluents collected from two petroleum related industries: a petroleum refinery located in Turkey and oil sand processing plant located in Canada. The efficiencies of photo-based and ozone-based treatments for the effluents compared and discussed in detail taking into account the objectives stated in Chapter 1.

The applied treatments for the petroleum refinery effluents included in Chapter 3 and Chapter 4 revealed that:

- ✓ Initial photo-based and ozone-based experiments conducted with a complex simulated synthetic refinery wastewater, containing a mixture of BTEX, PAHs and alkenes in a saline matrix, guided the treatment of real effluents in terms of identifying the initial parameters such as the amount of reactants and the reaction conditions on a stable medium, considering the known composition of the synthetic effluent. Detailed study of the real effluents showed that both higher amount of reactants and reaction time were necessary, comparing to synthetic refinery wastewater, due to more complex composition of the real effluents.
- ✓ Photo-Fenton was the most effective photo-based treatment for the treatment of RRW1 effluent (i.e., collected before biological treatment). Although photo-Fenton was performed by adding very low amount of Fe to the medium, this method was not appropriate when looking at the reuse of the treated effluents, considering the final TOC reached after treatment (ca. 20 mg/L). Even so, photo-Fenton can be used instead of biological treatment, which can prevent from the huge amount of sludge formation, since the amount of iron that will precipitate at the end of the treatment is quite low. In this sense, also, faster treatment than biological treatment would be possible. Heterogeneous photo-catalysis was found to be ineffective to treat RRW1 despite the high effectiveness showed in the treatment of SRW and RRW2. This demonstrates the high impact of turbidity on heterogeneous photo-catalysis. Contrarily to that found with RRW1 water, either photo-Fenton or heterogeneous photo-catalysis with TiO_2 made it possible to reuse treated RRW2 (i.e., collected after biological treatment) as cooling water or firewater. However, in both cases, the recovery of the catalysts (8 mg/L for

photo-Fenton, 500 mg/L for photo-catalysis with TiO_2) must be considered after the treatment.

- ✓ The application of O_3/H_2O_2 as a tertiary treatment was found to be the best option considering all effluents produced in the refinery, as well as no sludge production. The importance of the parameters optimization by experimental design has been demonstrated to reduce the operation costs while achieving high treatment efficiency that allow water reuse in the plant. It should be considered that the optimization has to be performed on a case-by-case analysis, since different properties of the effluents may effect the treatment efficiencies, and as a result, the optimized parameters.

The applied treatments for the oil sands process water included in Chapter 5 and Chapter 6 revealed that:

- ✓ Statistical approaches can be used for screening the effect of parameters on a response, which was the concentration removal in this thesis. This approach allowed selecting the best catalysts and knowing the significant parameters quickly and reliably. In Chapter 5, fractional factorial design was studied for different catalysts to observe the effects of O_3 dose, catalyst amount, pH and reaction time on the ACA concentration removal. An increase in the O_3 dose, catalyst amount and reaction time, increased the removal efficiency while the effect of the pH was varied depending on the catalyst (in some cases negatively).
- ✓ Considering both O_3 treatment and photo-based treatments applied in Chapter 5, GAC based materials were more effective when ozone or H_2O_2 were used as oxidant rather than PMS in terms of the final concentration of NAs and mineralization degree.
- ✓ The comparison between batch ozonation, UV/H_2O_2, UV/PMS and UV/Fenton suggested that UV/Fenton applied at pH 3 with 5 mg/L Fe^{2+} was more effective to obtain high mineralization rather than transformation of components, which would allow the discharge of the effluent after treatment or increasing its reuse opportunity in the plant.
- ✓ When the interests are directed toward mineralization by ozone-based treatments, which was not possible to reach by batch mode with low amount of O_3 dose, O_3/H_2O_2 treatment applied in semi-batch mode was found to be the most effective treatment of OSPW considering the mineralization degree reached after 90 min treatment and economic comparisons. In addition to O_3/H_2O_2 process, the use of UV-C with O_3/H_2O_2 can allow to obtain a good

quality of effluent to reuse it in the plant for several purposes, since the final DOC was ca. 2 mg/L after treatment.

In general, considering all the applied treatments within this thesis, O_3/H_2O_2 treatment was found as the best process to be used in oil & gas sector since it resulted suitable for both upstream and downstream process effluents, according also to previous studies of the research group performed on produced water. Through this treatment it was obtained a high mineralization degree at mild conditions (natural temperature and pH as well as atmospheric pressure), which results in high quality water after treatment. The treatment system can be optimized to reduce residual ozone that escapes in gas phase without reacting in liquid phase. Thus, the cost of the treatment system can be reduced significantly.

However, in some cases, photo-based treatments could be more interesting considering the possibilities of using sun as the energy source. In that case, photo-Fenton system can be a suitable candidate to treat the effluents from oil & gas sector with lower cost, according to the results obtained at lab scale treatment that was performed in a solar light simulator. Some more improvements to reduce the cost, such as increasing the operation pH, could be studied, since this treatment at pH 3 reached high efficiencies for both effluents with very low amount of catalyst, which decreased down to 5 mg/L in this thesis. The discharging limit for Fe is ranged between 2-10 mg/L depending on the policies of different countries.

8

Publications

&

Communications

8.1 Published Articles

Demir-Duz, H., Ayyildiz. O., Akturk, A. S., Álvarez, M. G., Contreras, S. (2020). Reuse and recycle solutions in refineries by ozone-based advanced oxidation processes: A statistical approach. Journal of Environmental Management Vol. 263, pp.110346 (https://doi.org/10.1016/j.jenvman.2020.110346).

Demir-Duz, H., Ayyildiz. O., Akturk, A. S., Álvarez, M. G., Contreras, S. (2019). Approaching zero discharge concept in refineries by solar–assisted photo-Fenton and photo-catalysis processes. Applied Catalysis B: Environmental, Vol 248, pp. 341-348 (https://doi.org/10.1016/j.apcatb.2019.02.026).

8.2 Articles to Be Submitted

Demir-Duz, H., Messele, S. A., Álvarez, M. G., Contreras, S., El-Din, M. G. (2020). Comparison of Catalytic Ozone, UV/H_2O_2, UV/PMS and UV/Fenton in Degrading the Naphthenic Acid Fraction in Oil Sands Process Water.

Demir-Duz, H., Pérez-Estrada, L., Messele, S. A., Álvarez, M. G., El-Din, M. G., Contreras, S. (2020). Synergetic Effect of O_3/H_2O_2 and UV-C Light Irradiation for the Treatment of Oil Sands Process Water.

8.3 Oral Communications

Demir-Duz, H., Messele, S. A., Álvarez, M. G., Contreras, S., El-Din, M. G (October, 2019). Comparison of UV/Fenton, UV/H_2O_2, UV/Oxone and Ozone in degrading the naphthenic acids in oil sands process water. Oral presentation at IOA24 Ozone World Congress & Exhibition, Nice, France.

Demir-Duz, H., Ayyildiz. O., Akturk, A. S., Álvarez, M. G., Contreras, S. (June, 2019), Reuse and recycle solutions in refineries by Ozone/H_2O_2: A real case study by Box-Behnken experimental design. Oral presentation at 6th European Conference on Environmental Applications of AOPs, Portoroz, Slovenia.

Demir-Duz, H. (May, 2019), Application of advanced oxidation processes in the reclamation of wastewaters from the oil & gas sector. Oral presentation at 16th Doctoral Day, URV, Tarragona, Spain.

Demir-Duz, H., Messele, S. A., Álvarez, M. G., Contreras, S., El-Din, M. G. (May, 2019) Catalytic ozone-based treatment of oil sands process water by heteroatom doped Fe/GAC. Oral presentation at CAWQ-11th Western Canadian Symposium on Water Quality Research, Edmonton, Canada.

Demir-Duz, H., Álvarez, M. G., Contreras, S. (June, 2018) Petroleum refinery wastewater treatment by photo-Fenton and photo-catalysis under solar light irradiation. Oral presentation at 10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA10), Almeria, Spain

8.4 Poster Presentation

Demir-Duz, H., Messele, S. A., Álvarez, M. G., Contreras, S., El-Din, M. G. (May, 2019) Granular activated carbon-based catalysts for treatment of oil sands process water by advanced oxidation processes. Poster presentation at University of Alberta Energy week, FES Colloquium, Edmonton, Canada.

Demir-Duz, H., Álvarez, M. G., Contreras, S. (June, 2018) Petroleum refinery wastewater treatment by photo-Fenton and photo-catalysis under solar light irradiation. Poster presentation at 10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA10), Almeria, Spain.

Demir-Duz, H., Álvarez, M. G., Contreras, S. (May, 2018), Refinery wastewater treatment solutions by advanced oxidation processes. Poster presentation at 15th Doctoral Day, URV, Tarragona, Spain

Demir-Duz, H., Álvarez, M. G., Contreras, S. (July, 2017), Application of Fenton-based processes in the reclamation of refinery wastewater, Poster presentations at 2nd Summer School on Environmental Applications of Advanced Oxidation Processes, Porto, Portugal

Demir-Duz, H., Álvarez, M. G., Contreras, S. (May, 2017), Application of advanced oxidation processes in the reclamation of wastewaters from the oil & gas sector. Poster presentation at 14th Doctoral Day, URV, Tarragona, Spain

APPENDICES

Appendix A: Additional Figures and Tables from Chapter 3

Table Appx. A1 Summary of experimental conditions tested, and main results obtained with the SRW.

Synthetic Refinery Wastewater				
Photo-Fenton increasing Fe^{2+} with constant H_2O_2			**TiO_2-photo-catalysis increasing catalyst amount**	
H_2O_2/COD	**H_2O_2/Fe^{2+}**	**TOC Removal % at 90 min**	**TiO_2 (mg/L)**	**TOC Removal % at 360 min**
2	5	72	100	64
2	10	76	250	80
2	50	81	500	81
Photo-Fenton increasing H_2O_2 with constant Fe^{2+}			**pH effect on TiO_2-photo-catalysis with 250 mg/L catalyst**	
H_2O_2/COD	**H_2O_2/Fe^{2+}**	**TOC Removal % at 90 min**	**pH**	**TOC Removal % at 360 min**
1	50	75	3	67
2	50	81	5	91
4	50	77	8	80

Table Appx. A2 Summary of experimental conditions tested, and main results obtained with the RRW1.

Photo-Fenton			
H_2O_2/COD	**H_2O_2/Fe^{2+}**	**TOC removal at 90 min (%)**	**TOC removal at 180 min (%)**
2	50	58	-
2	100	67	70
4	100	65	74
4	10	63	68
4	50	67	-
10	50	75	76
TiO_2-photo catalysis (pH free)			
Catalyst amount (mg/L)		**TOC removal at 90 min (%)**	**TOC removal at 360 min (%)**
100		24	26
250		26	27
500		24	30
Combination of photo-Fenton/photo-catalysis			
"One after the other" mode			
1. Step: photo-Fenton (180 min)			**TOC removal (%)**
H_2O_2/COD=4; H_2O_2/Fe^{2+}=100			74
2. Step: photo-catalysis (360 min)			
500 mg/L TiO_2			63
Total treatment (540 min)			**90**
"Synchronous" mode			
1. Step: Combination (90 min)			**TOC removal (%)**
100 mg/L TiO_2; H_2O_2/Fe^{2+}=100; H_2O_2/COD=2			71
100 mg/L TiO_2; H_2O_2/Fe^{2+}=100; H_2O_2/COD=4			79
100 mg/L TiO_2; H_2O_2/Fe^{2+}=100; H_2O_2/COD=10			84

Table Appx. A3 Summary of experimental conditions tested, and main results obtained with the RRW2.

Photo-Fenton			
H_2O_2/COD	**H_2O_2/Fe^{2+}**	**TOC removal at 90 min (%)**	**TOC removal at 180 min (%)**
2	50	46	-
4	50	58	69
4	10	64	78
10	50	69	78
2	10	50	62
10	10	65	73

TiO2-photo catalysis (pH free)		
Catalyst amount (mg/L)	**TOC removal at 90 min (%)**	**TOC removal at 360 min (%)**
100	0.1	33
250	20	70
500	27	73

TiO2-photo catalysis (pH 5)		
Catalyst amount (mg/L)	**TOC removal at 90 min (%)**	**TOC removal at 360 min (%)**
500	56	92

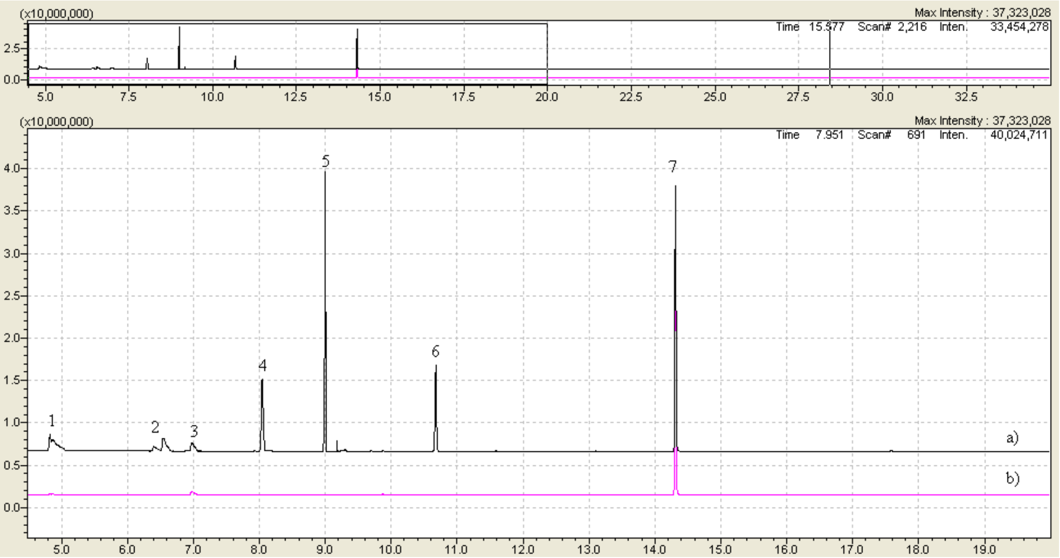


Figure Appx. A1 GC-MS chromatogram after photo-Fenton test with the H_2O_2/COD ratio of 2 and the H_2O_2/Fe^{2+} ratio of 50. a) Initial SRW; b) after 1.5h: 1) toluene; 2) xylene; 3) nonane; 4) phenol; 5) o-cresol; 6) naphthalene; 7) hexadecane.

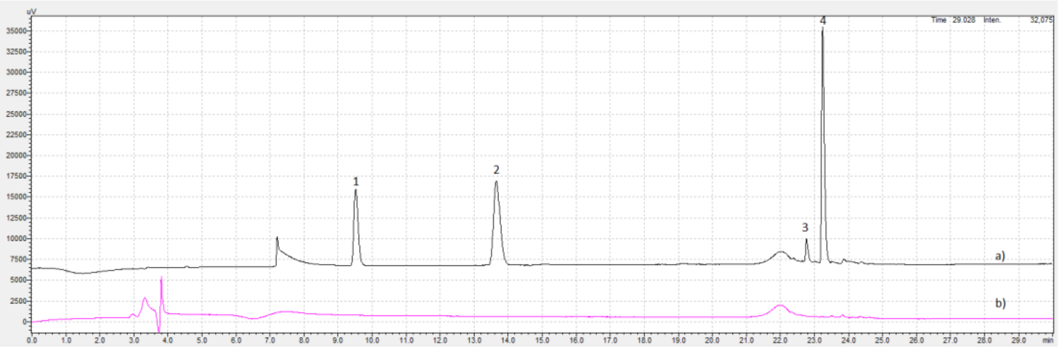


Figure Appx. A2 HPLC chromatogram after photo-Fenton with the H_2O_2/COD ratio of 2 and the H_2O_2/Fe^{2+} ratio of 50. a) Initial SRW; b) after 1.5h: 1) phenol; 2) o-cresol; 3) toluene; 4) naphthalene.

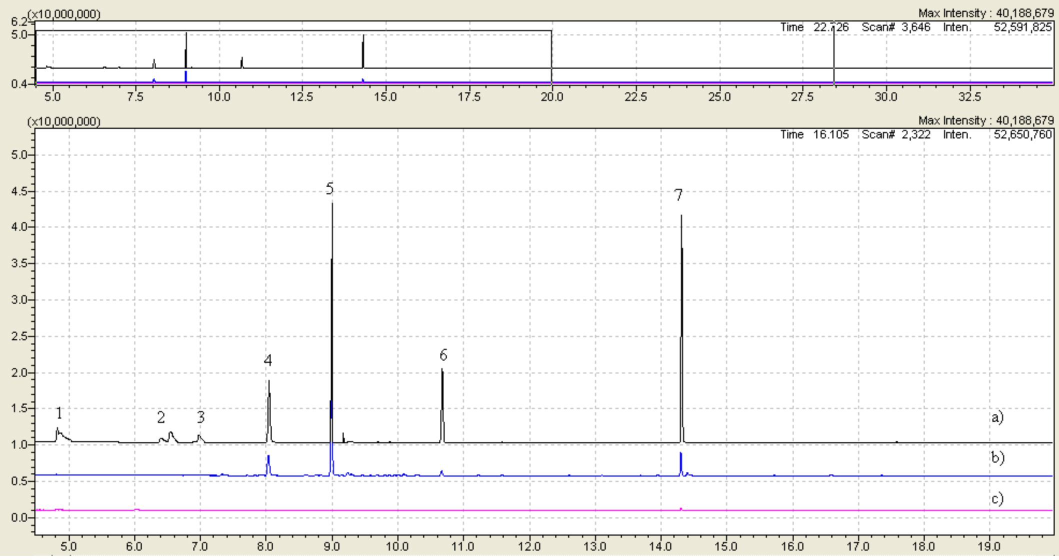


Figure Appx. A3 GC-MS chromatogram after photo-catalysis with 250 ppm catalyst a) Initial SRW; b) after 1.5h; c) after 6h: 1) toluene; 2) xylene; 3) nonane; 4) phenol; 5) o-cresol; 6) naphthalene; 7) hexadecane.

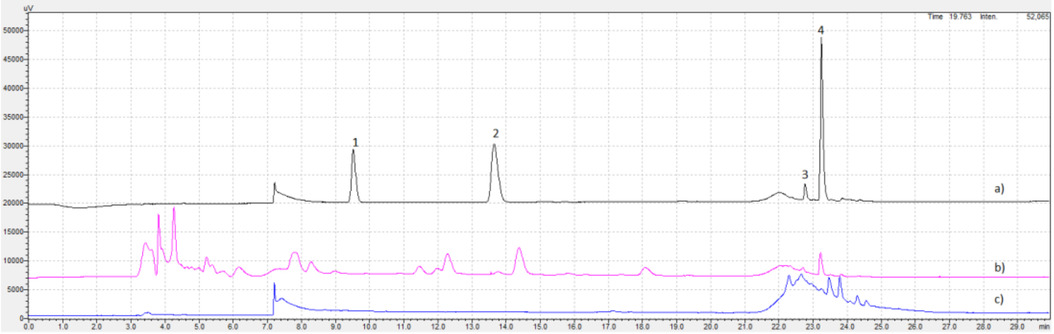


Figure Appx. A4 HPLC chromatogram after photo-catalysis with 250 ppm catalyst a) Initial SRW; b) after 1.5 h: c) after 6 h: 1) phenol; 2) o-cresol; 3) toluene; 4) naphthalene.

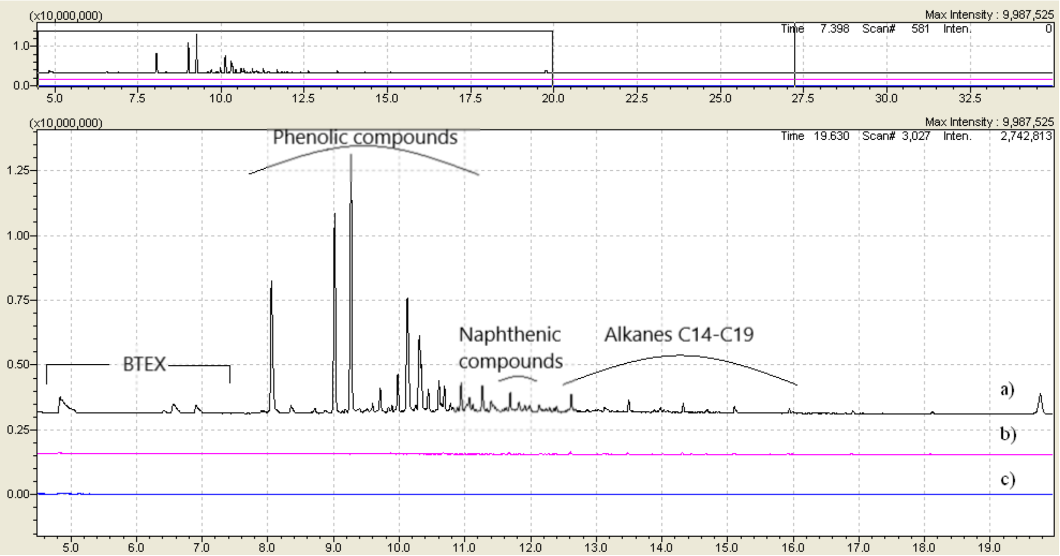


Figure Appx. A5 GC-MS chromatogram of a)Initial RRW and after 1.5h synchronous photo-Fenton/photo catalysis treatment b)H_2O_2/COD=4, H_2O_2/Fe=100, TiO_2=100ppm, pH=3; c) H_2O_2/COD=10, H2O2/Fe=100, TiO_2=100ppm, pH=3.

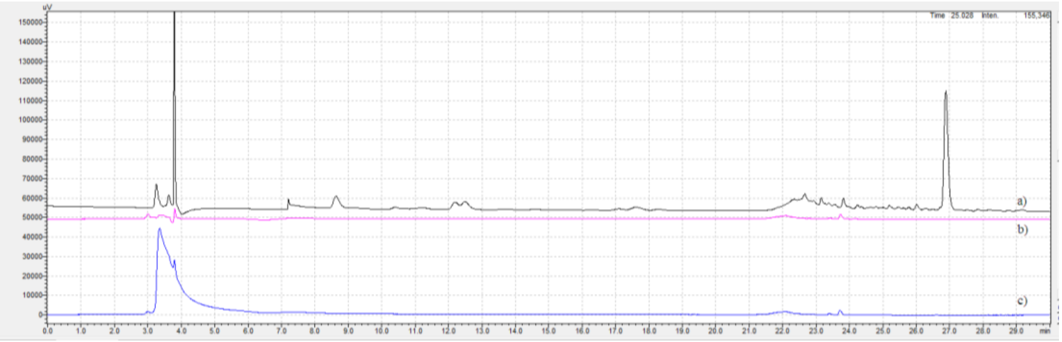
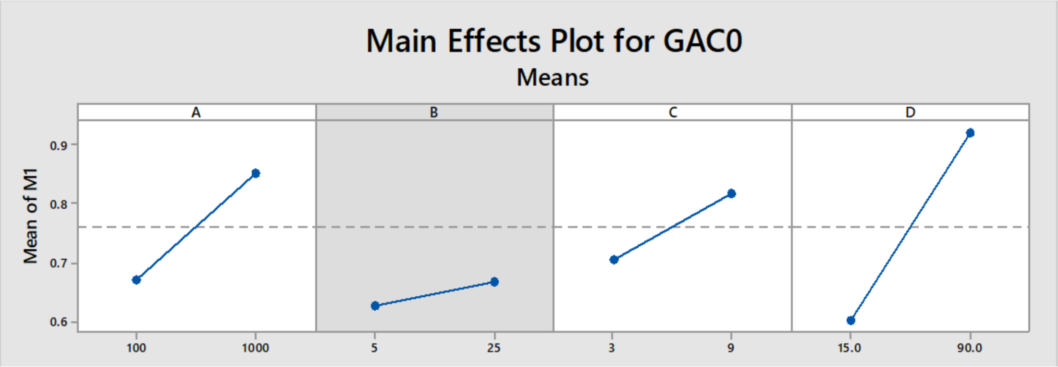
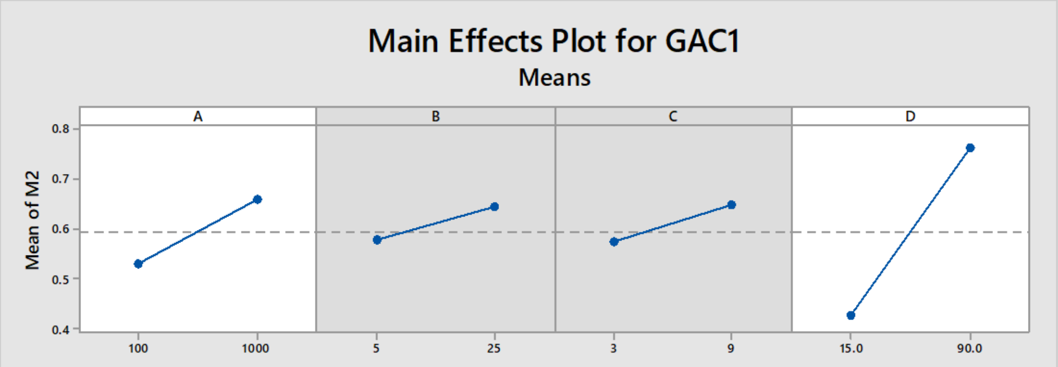


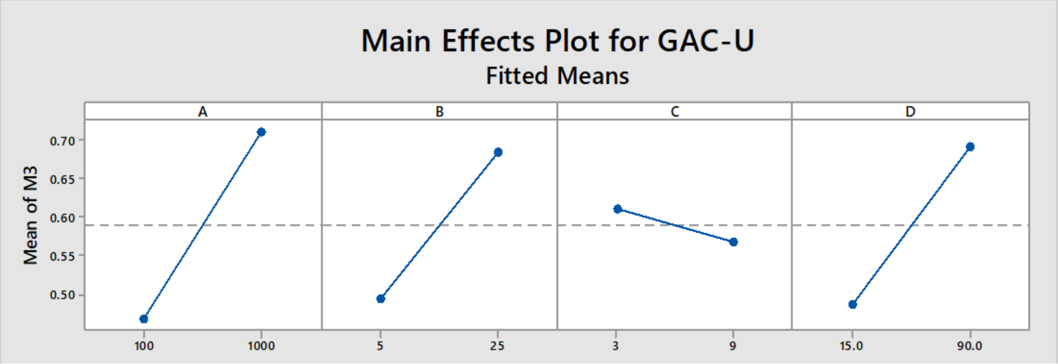
Figure Appx. A6 HPLC chromatogram of a) initial RRW and after 1.5h synchronous photo-Fenton/photo catalysis treatment b)H_2O_2/COD=4, H_2O_2/Fe=100, TiO_2=100ppm, pH=3; c) H_2O_2/COD=10, H_2O_2/Fe=100, TiO_2=100ppm, pH=3

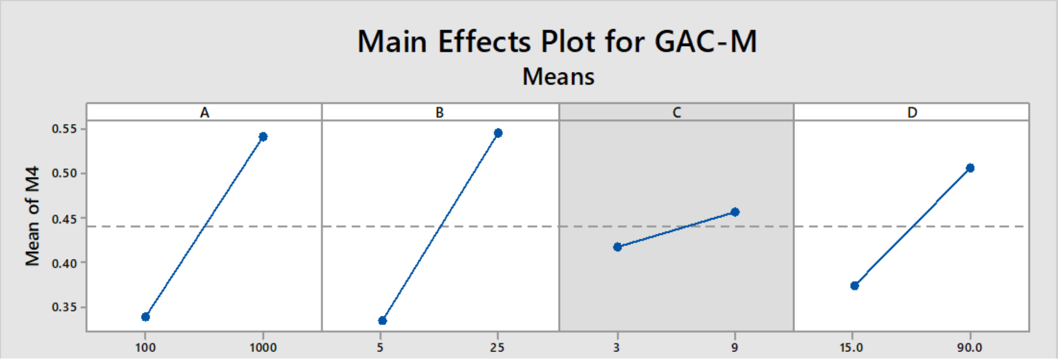
Appendix B: Additional Figures and Tables from Chapter 5

Main Effects of the parameters on the catalytic ozone treatment of effluent prepared with ACA:








Main Effects Plot for GAC-M
Means
Mean of M4
0.55
0.50
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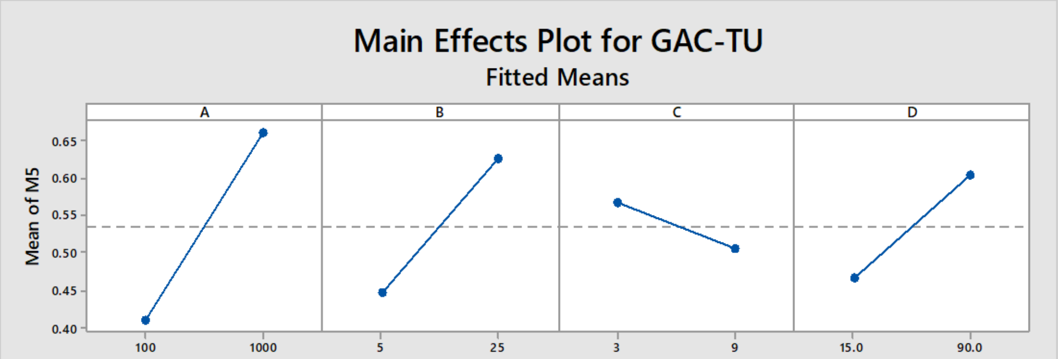
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Fitted Means
Mean of M5
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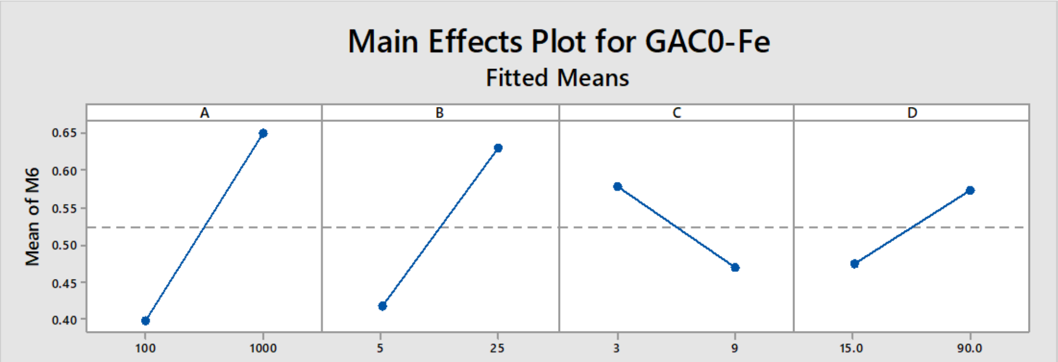
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Fitted Means
Mean of M6
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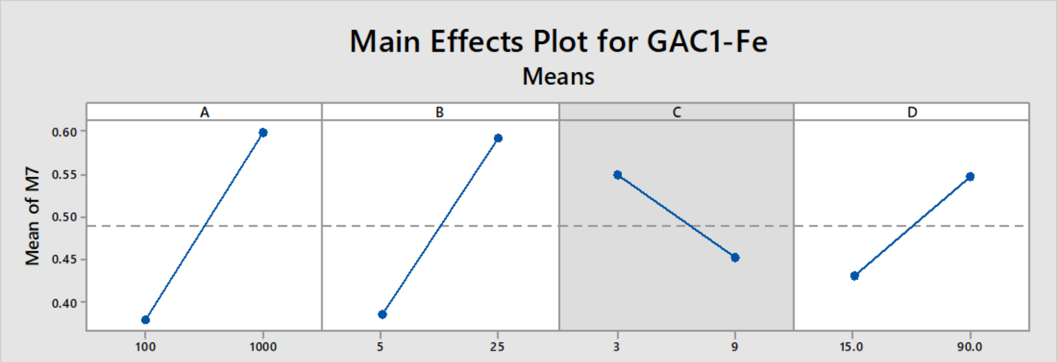
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Mean of M7
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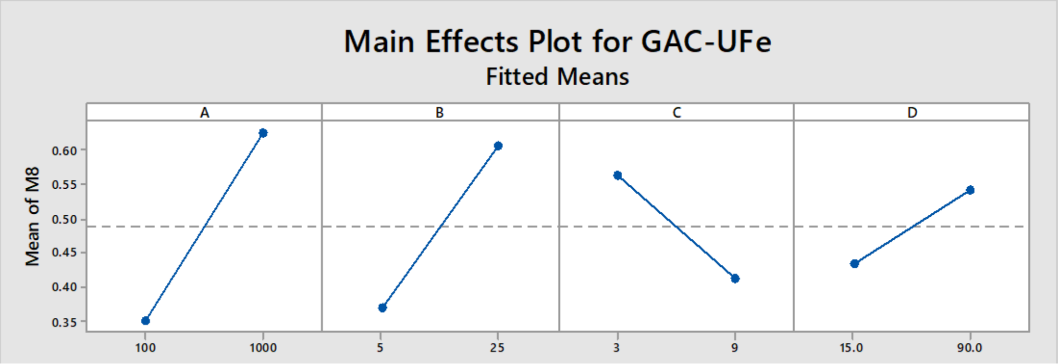
Main Effects Plot for GAC-UFe
Fitted Means
Mean of M8
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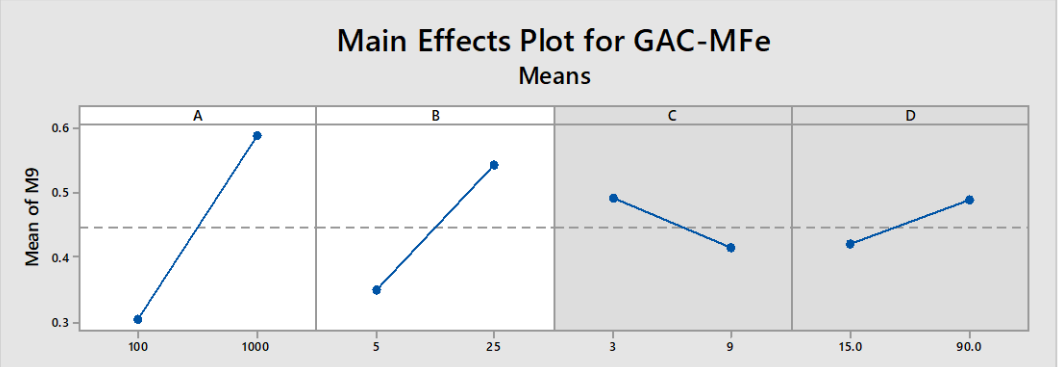
Main Effects Plot for GAC-MFe
Means
Mean of M9
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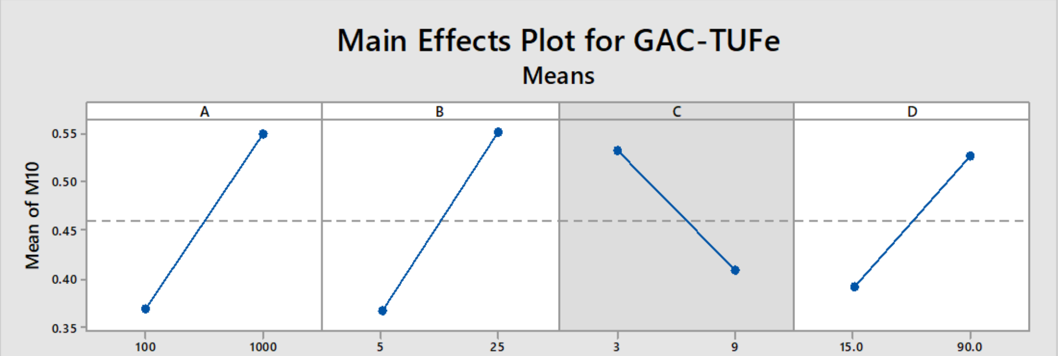
Main Effects Plot for GAC-TUFe
Means
Mean of M10
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9
15.0
90.0

Table Appx. B1 Summary of ozone-based treatments.

Treatment	Catalyst	Catalyst Amount (g/L)	O_3 amount (mg/L)	DOC	NAs
Adsorption	GAC0	0.5	-	25%	49%
	GAC-U	0.5	-	33%	60%
	GAC-TU	0.5	-	21%	41%
	GAC-UFe	0.5	-	27%	56%
	GAC-TUFe	0.5	-	33%	63%
Ozonation	GAC0	0.5	25	11%	93%
	GAC-U	0.5	25	6%	95%
	GAC-TU	0.5	25	15%	96%
	GAC-UFe	0.5	25	11%	95%
	GAC-TUFe	0.5	25	7%	93%
	Single	-	25	0%	91%
	GAC0	0.5	10	21%	92%
	GAC-U	0.5	10	17%	85%
	GAC-TU	0.5	10	18%	86%
	GAC-UFe	0.5	10	6%	81%
	GAC-TUFe	0.5	10	17%	84%
	GAC0	0.1	10	0%	78%
	GAC-U	0.1	10	0%	79%
	GAC-TU	0.1	10	2%	79%
	GAC-UFe	0.1	10	1%	77%
	GAC-TUFe	0.1	10	0%	78%
	Single	-	10	0%	63%

Table Appx. B2 Summary of photo-based treatments.

Treatment	Catalyst	Catalyst Amount (g/L)	Oxidant	Oxidant/ COD (w/w)	pH	DOC	NAs
photo-Fenton	Fe^{2+}	0.005	H_2O_2	1	3	26%	90%
		0.005	H_2O_2	2	3	51%	99%
		0.005	H_2O_2	2.5	3	63%	95%
		0.005	H_2O_2	5	3	64%	82%
Fenton-like	GAC0	0.1	H_2O_2	2.5	3	15%	77%
	GAC-U	0.1	H_2O_2	2.5	3	14%	73%
	GAC-TU	0.1	H_2O_2	2.5	3	14%	77%
	GAC-UFe	0.1	H_2O_2	2.5	3	14%	70%
	GAC-TUFe	0.1	H_2O_2	2.5	3	0%	60%
	GAC0	0.1	H_2O_2	2.5	8.45	27%	98%
	GAC-U	0.1	H_2O_2	2.5	8.45	29%	99%
	GAC-TU	0.1	H_2O_2	2.5	8.45	28%	98%
	GAC-UFe	0.1	H_2O_2	2.5	8.45	29%	99%
	GAC-TUFe	0.1	H_2O_2	2.5	8.45	31%	98%
PMS	GAC0	0.1	PMS	2.5	8.45	12%	N/A
	GAC-U	0.1	PMS	2.5	8.45	14%	N/A
	GAC-TU	0.1	PMS	2.5	8.45	11%	N/A
	GAC-UFe	0.1	PMS	2.5	8.45	9%	N/A
	GAC-TUFe	0.1	PMS	2.5	8.45	10%	N/A

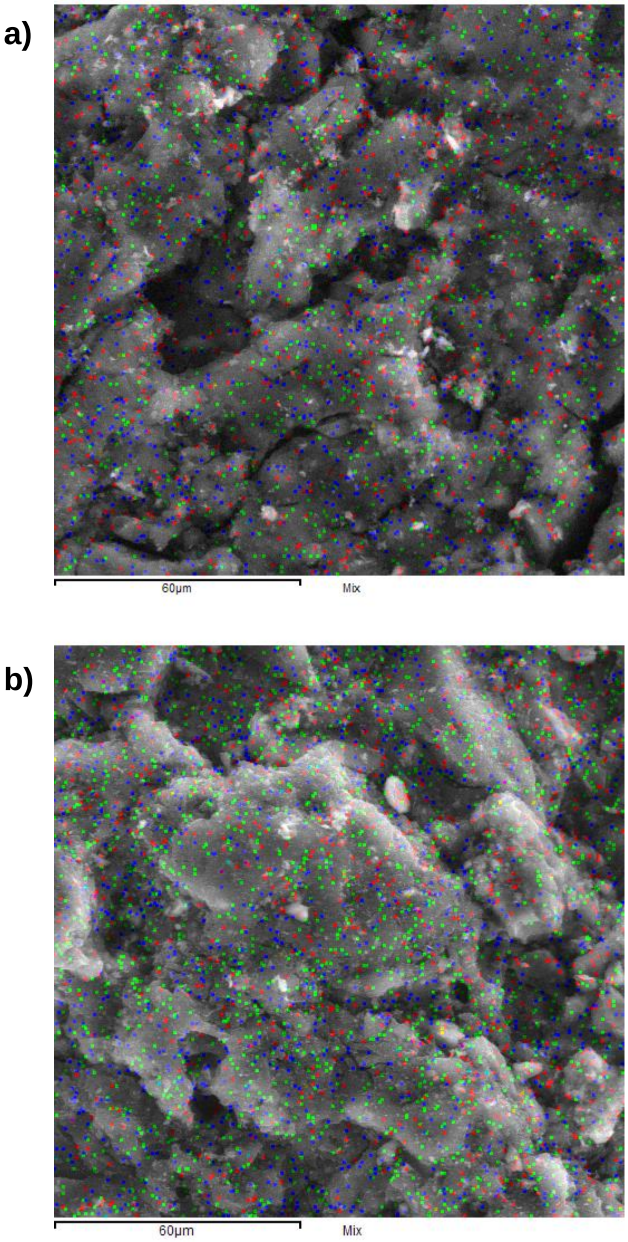

Figure Appx. B1 SEM-EDX mapping images and elemental distribution (O-red, S-green, Fe-blue) of Fe-based catalysts a)GAC-UFe, b)GAC-TUFe.