

Selective denitrification by peroxidation of 4-nitrophenol using Janus-structured amphiphilic carbon nanotubes

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Thesis report submitted to
Escola Superior de Tecnologia e Gestão
Instituto Politécnico de Bragança
Master Degree in
Chemical Engineering

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ABSTRACT

Industrial pollution has grown a lot in recent times, mostly formed by oily compounds, affecting not only the environmental but also human health. As the concern increases, so does the search for effective treatment, a few years the use of different nanostructure porous carbon materials are being used in catalysis. Therefore, in this work carbon nanotubes (CNTs) were tested as catalysts in the selective denitrification of oily wastewater containing 4-nitrophenol (4-NP) by catalytic wet peroxide oxidation (CWPO). The CNTs were prepared by chemical vapor deposition, feeding sequentially ethylene (E) and/or acetonitrile (A) during different times until 20 min, resulting in samples E20, E15A5, E10A10, E5A15, E1A19 and A20, the number denoting the time feeding of each precursor and the order of appearance of the letter indicating the order of each precursor. The synthesized CNTs were tested in the CWPO of 4-NP in aqueous solutions and in simulated oily wastewater (2,2,4-trimethylpentane and water) at 80 °C, initial pH = 3.5, $C_{4-NP} = 1$ g/L, $C_{H_2O_2} = 3.56$ g/L, and $C_{catalyst} = 2.5$ g/L. The catalysts A20, E1A19 and E5A15 promoted a faster decomposition of H₂O₂ and a lower degradation of 4-NP in the aqueous system, whereas the catalysts E20, E15A5 and E10A10 (more hydrophobic character than previous ones) displayed the opposite trend, since E20 was able to remove 99% of the pollutant and A20 only 69% after 8 h of reaction. E15A5 and E10A10 catalysts were able to remove 100% of 4-NP after 24 h of reaction.

In biphasic L-L media all catalysts presented a great conversion of 4-NP after 24 h of reaction. E15A5, E10A10 and E1A19 catalyst allow to completely remove 4-NP and E5A15, A20 and E20 led to obtain a removal of 99%, 99% and 98%, respectively. Besides that, the aromaticity was also measured for comparison of materials. The lower concentration of aromatic intermediates was obtained E15A5 and E10A10 (126.34, 249.10 mg/L, respectively), and lower pH (2.42, 2.38, respectively), which supports the formation of carboxylic acids. The highest removals conversions obtained with E15A5 and E10A10 is ascribed to the capacity to stabilize Pickering emulsions by E15A5 and E10A10. The amphiphilic characteristic of this material ensures a closer contact between the liquid phases, allowing higher mass transfer.

Keywords: Catalytic wet peroxide oxidation, 4-nitrophenol, Carbon nanomaterials, Janus-structure, Pickering emulsion.

RESUMO

A poluição industrial cresceu muito nos últimos tempos, em sua maioria essa poluição é formada por compostos oleosos, afetando não apenas o ambiente, mas também a saúde humana. À medida que a preocupação aumenta também aumenta a busca por tratamentos eficientes. Há alguns anos o uso de diferentes matérias de carbono poroso nano estruturados estão sendo utilizados na catálise. Portanto, neste trabalho os nanotubos de carbono foram testados como catalisadores na oxidação seletiva de 4-nitrofenol (4-NP) presente em águas residuais oleosas por oxidação catalítica com peróxido de hidrogênio. Os nanotubos de carbono foram preparados por deposição química em fase vapor, alimentando sequencialmente etileno (E) e/ou acetonitrila (A) durante diferentes tempos até 20 min cada um, resultando nas amostras E20, E15A5, E10A10, E5A15, E1A19 e A20, o número denotando o tempo de alimentação de cada precursor e a ordem de aparecimento da letra indicando a ordem de cada precursor. Os nanotubos de carbono sintetizados foram testados no CWPO do 4-NP em soluções aquosas e em águas residuais oleosas simuladas (2,2,4-trimetilpentano e água) a 80 °C, pH inicial 3,5, $C_{4-NP} = 1$ g/L, $C_{H_2O_2} = 3,56$ g/L, e $C_{Catalisador} = 2,5$ g/L. Os catalisadores A20, E1A19 e E5A15 promoveram uma decomposição mais rápida de H_2O_2 e uma menor degradação de 4-NP no sistema aquoso, enquanto os catalisadores E20, E15A5 e E10A10 (com um caráter mais hidrofóbico que os anteriores) apresentaram tendência oposta, uma vez que, E20 foi capaz de remover 99% do poluente e A20 apenas 69% após 8 h de reação. Os dois catalisadores capazes de remover 100% de 4-NP após 24 h de reação foram E15A5 e E10A10.

Em meio L-L bifásico todos os catalisadores apresentaram uma alta conversão de 4-NP após 24 h de reação, E15A5, E10A10 e E1A19 com 100%, E5A15 e A20 com 99% e E20 com 98%. Além disso, a aromaticidade também foi medida para comparação de materiais. Os catalisadores que apresentaram concentração mais baixa dos intermediários aromáticos foram E15A5 e E10A10 (126,34, 249,10 mg/L, respectivamente), e o pH mais baixo também (2,42, 2,38, respectivamente), isso apoia a ideia da formação de ácidos carboxílicos. Esta tendência de melhores resultados pode ser atribuída à formação de emulsões Pickering pelos materiais E15A5 e E10A10. A característica anfifílica desses materiais garantem um contato mais próximo entre as fases líquidas, permitindo maior transferência de massa.

Palavras chave: Oxidação catalítica com peróxido de hidrogénio, 4-nitrofenol, nanomateriais de carbono, estrutura Janus, emulsão Pickering.

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INDEX OF ACRONYMS

4-NP	4-nitrophenol
A-PAM	Anion Polyacrylamide
AOP	Advanced Oxidation Process
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CNT	Carbon Nanotubes
CPC	Hexadecylpyridinium Chloride
CVD	Chemical Vapor Deposition
CWPO	Catalytic Wet Peroxide Oxidation
DAF	Dissolved Air Flotation
MAF	Microbubble Air Flotation
MF	Microfiltration
NF	Nanofiltration
NP	Nitrophenol
NSO	Nitrogen Sulfur Oxygen
PAC	Poly Aluminium Chloride
PFS	Poly-Ferric Sulfate
PVD	Physical Vapor Deposition
PZSS	Poly-Zinc Silicate
RO	Reverse Osmosis
S-IV	Sudan IV
SDGs	Sustainable Development Goals
TG	Thermogravimetric
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
UF	Ultrafiltration

INTRODUCTION

1 Introduction

Advanced industrial development has led over the years to the growth of oily wastewater pollution, creating the challenge for the oil industries of the treatment and disposal of the water and the reduction of impact in the environment ¹. Waters are classified as contaminated when presenting a mixture of water and bio-refractory organic compounds that changes the characteristics of the water and makes it unsuitable for the environment ². In oily wastewaters, the oily fraction can be separated and re-incorporated into the process, to use as a fuel, lubricant or other organic material ². The recovered water can also be reused in other factory processes, but in many cases the cost of water treatment for reuse is higher than its treatment for disposal ³.

Oily compounds may be presented in wastewaters in the form of free, dispersed, emulsified and/or dissolved oils and the treatment of these waters can be done by physical, biological and chemical processes. Free and dispersed oils can be separated by physical procedures such as gravitational and centrifugation, as the droplets are found to have diameters between 50 to 150 μm (dispersed oils) and larger than 150 μm (free oil). On the other hand, dissolved oils are difficult to remove and require a more elaborate filtration process, like membrane filtration ⁴⁻⁷.

Due to the complexity of oil mixtures, the treatment of oily wastewaters usually requires multi-stage processes. After more conventional treatments, the oily sludge phase should be treated or send to a separation process for its reuse, since it still contains organic components, mainly lipophilic substances, that need to be removed from the oily phase. Some treatments considered include biological treatments, pyrolysis, combustion and advanced oxidation ^{8,9}, which require high temperature or oxidizing reagents capable to transform harmful into non-harmful substances for the environment.

The lipophilic substances present in the oily sludge are a mixture of organic components, divided in 4 groups known as aliphatic, aromatics, nitrogen-sulfur-oxygen (NSO) containing compounds and asphaltenes ^{10,11}.

The content of nitrogen present in oily sludges is high and the uncontrolled use of fossil fuels nowadays has increased the emission of nitrogen compounds (NO_x), which are harmful to human health and contributing for acid rain, forcing environmental politics to be stricter worldwide in order to decrease air pollution ¹². Therefore, it is essential to search for technologies that help to reduce the content of N in the oily products of the petroleum industries, since this control is one of the keys points for the successful

management of a sustainable environment ². This work aims the removal of 4-nitrophenol, as nitrogen-containing lipophilic model substances in advanced oxidation process with Janus-structured carbon nanotubes as catalyst.

STATE OF THE ART

2 State of the art

2.1 Water pollution

World population was approximately 7.7 billion in 2019, and the United Nations estimates that the world population will reach almost 10.9 billion in 2100¹³, this estimate anticipating higher growth of industrial activities that reflects in environmental problems.

In 2015, the General Assembly of the United Nations discussed global sustainable development and created an action plan for people, planet and prosperity called Agenda 2030, focusing 17 Sustainable Development Goals (SDGs) that include the three dimensions: social, economic, and environmental. ‘Clean water and sanitation’ and ‘Life below water’ are the two goals concerning about water quality in the planet. Its aims are the improvement of water quality and water-use efficiency and to protect and ensure the sustainable use of oceans¹⁴.

The Political Guidelines focus on six major ambitions for Europe that include all 17 SDGs, as each commissioner is responsible for ensuring that the policies under their supervision are satisfied¹⁵.

In a monitoring report on the progress towards the SDGs in EU, published in May 2020, it was showed an improvement of wastewater treatment that led to less organic pollution in European rivers. The data, expressed as biochemical oxygen demand (BOD), the demand of oxygen needed for the microbial digestion of organic pollution, revealed that the BOD content decreases from values of 15 mg/L (very polluted) to 2 mg/L (clean) in 2017 on European rivers¹⁴.

Oily water affects the environment, drinking water sources and aquatic underground resources. These polluting oils create an impermeable film on the water surface that avoid the penetration of light and oxygen into it, which affects the nature of fauna and flora present there¹⁶. Some of the contaminants are light and heavy hydrocarbons, oils and many other toxic organic components^{1,17}.

The Diary of the Republic of Portugal republished new directives on the scope of water quality and the priority substances in the field of water policy. By the Decree - law 218/2015, it was stablished environmental quality standards to control the pollution and the maximum concentration of some substances in water, translated from the Directive 2013/39/EU. As recognition, by the European Community, that water is a heritage that must be protected, the Directive 2000/60/EC published a water framework directive that

defines a strategy to defend water bodies ^{18,19}. The Decree - law 236/98 establishes limit values for wastewater parameters. pH must be in the range of 6.0 to 9.0, chemical oxygen demand (COD) values lower than 150 mg/L O₂ and the limit concentration of phenolic compounds of 0.5 mg/L as the monthly average emission in the discharge of wastewaters ²⁰.

2.2 Separation of oily wastewater

2.2.1 Removal of lipophilic substances

Lipophilic substances can dissolve and interact with lipid substances, oils and fats. The lipophilicity of each component is defined by log P, where P is a solvent-water partition coefficient, which will influence whether the component is more lipophilic or more hydrophilic ²¹. The lipophilic substances present in the oily sludge, may be aliphatic, aromatics, nitrogen-sulfur-oxygen (NSO) containing compounds and asphaltenes ^{10,11}. Compounds such as alkanes, cycloalkanes, benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, phenols and various polycyclic aromatic hydrocarbons are also presented in the oil phase of oily sludges ^{22,23}. Asphaltenes and resins are in higher concentration than NSO compounds, where nitrogen is found in oily sludges at concentration values around 3%, sulfur molecules around 0.3-10% and oxygen at values lower than 4.8% ^{23,24}.

Aromatic substances are found mainly in oily phases due to their high lipophilicity, but their lipophilic character is greatly affected by functional groups and their disposition. As example, the lipophilicity of nitrophenols (NPs), expressed by the partition coefficient (P) and measured by logP, shows that 2-nitrophenol (2-NP) is more lipophilic when compared to 3-nitrophenol (3-NP) and 4-nitrophenol (4-NP)²¹. As reported by Abraham et al the different lipophilicity of NPs in water – ciclohexane 1.51, -1.44, -1.86 as values of 2-NP, 3-NP and 4-NP respectively²¹. These compounds are toxic and deserve special care in treatment and disposal, as they set a high risk to human health ^{2,21}.

Generally, NPs are found in wastewaters from the industrial manufacture of plastics, synthetic dyes, pesticides, explosives and drugs. Since they are highly toxic to all forms of living organisms, nitrophenols are included in the "Priority list of pollutants", issued by the U.S Environmental Protection Agency. Additionally, NPs have dangerous

properties that affect and inhibit the biological functions of the human body, being its maximum allowed concentration in water being set to 20 ppb ^{2,25}.

2.2.2 Separation of oily phase

Sources of oily wastewaters are very wide and, in most cases, they are produced in oil processing industries, such as petrochemical and metallurgical industries, together with maritime transport¹. The treatment of these waters can be done by physical, chemical and biological processes. Some processes, such as flotation, coagulation, adsorption and membrane separation, when not combined with other methods, are limited only to the separation of the oil-water mixture phases without another type of more advanced treatment.

2.2.2.1 Flotation

Flotation is a physical process that considers bubbling air inside the polluted water, causing the oil particles dispersed in water to adhere to the bubbles and to decrease the density of these oils, in such a way that the resultant aggregate rises and forms a layer of foam on the surface of water that is easy to remove ¹⁷.

The efficiency of the flotation mechanism is directly linked to the bubble-particle assembly, so the size of the bubble inside water is essential. Zheng et al. concluded that Microbubble Air Flotation (MAF) achieves better efficiency when compared with traditional Dissolved Air Flotation (DAF), since the smaller bubble size will lead to longer stagnation time and lower bubble rising speed. In the treatment of oily wastewaters from restaurants, with optimum parameters of 0.35 MPa, reflux ratio of 25% and reaction time of 15 min, the removal efficiency of MAF was 98% of oil, 82.8% of COD and 97.5% of turbidity, achieving better results than the DAF process ²⁶.

One way to improve the process of Dissolved Air Flotation is to consider a pre-treatment, as used in a study made with synthetic industrial effluent with oil concentration of 100 mg/L, aluminum sulfate was used to destabilize the oil droplets prior to flotation, that achieved 90% of oil removal ²⁷. Hami et al, reported in another study on dissolved air flotation investigated the performance of the treatment with addition of powdered activated carbon. The results were promising, 150 mg/L of carbon content leading to a rise in the COD and BOD removals, from 72 to 92.5% and 76 to 94%, respectively ²⁸.

2.2.2.2 Adsorption

Adsorption is a process where a material, liquid or gas, known as adsorbate, is accumulated at the surface of a solid material (adsorbent). There are two types of adsorption, physical and chemical. When the adsorbate and the adsorbent are attracted only by physical forces, generally van der Waals, the process refers to a physical adsorption (physisorption) and can be reversible. On the other hand, if adsorbate-adsorbent forms chemical bonds, the process is called chemisorption and its separation is more difficult. In wastewaters, the oily phase or non-biodegradable pollutants are the adsorbates that will adhere to the porous media of the adsorbents. The main adsorbent agents used in adsorption processes are activated carbons, organoclays, biosorbents, copolymers, zeolites and resins ^{22,29-31}.

Duraisamy et al. studied the applications and efficiencies of adsorbents, such as zeolites, that removes BTEX components, the combination of organoclays with activated carbons to remove completely petroleum hydrocarbons and copolymers that can remove up to 85% of oil from biphasic mixtures ³.

In Australia, barley straw chemically treated using cationic surfactant hexadecylpyridinium chloride monohydrate (CPC) was used as biosorbent to remove emulsified mineral oil from aqueous solution. The adsorption process was carried out in batch and the results showed a maximum removal (90%) of 518.6 mg/g at 25°C and neutral pH (6-8) ³⁰.

2.2.2.3 Coagulation-flocculation

Coagulation can be considered a two-stage process that uses first coagulating agents to destabilize the charges of suspended particles, to allow after the occurrence of the flocculation of the destabilized particles, that no longer repel each other, forming larger clusters ³². The oil in the wastewater requires a type of coagulant for each case, depending on the nature of the oil, representing this an additional difficulty in the separation process ³³.

Coagulation was investigated with ceramic membranes during treatment of an oily wastewater. Four different coagulant agents were used ((ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$),

ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) and aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$). Coagulant agents improved membrane filtration by changing the droplets of the oil. At the best conditions (50 ppm of ferrous sulphate) the removal of TOC increased from 93.8 to 97.1%³⁴.

Two of the most used coagulants in wastewater treatments are poly-aluminum chloride (PAC) and poly-ferric sulfate (PFS). However, the main problem of these organic corrosive coagulants is the large amount of formed hazardous metal containing sludge³³. An investigation made in Huazhong University of Science and Technology, to treat heavy oil wastewater, used a new type of coagulant agent, poly-zinc silicate (PZSS), due to its non-toxicity, and anion polyacrylamide (A-PAM). The comparison of PAC and PFS methodology with PZSS and A-PAM showed a better result of the new coagulant agents. Under optimum conditions, the oil removal was 99% and the suspended solid value was less than 5 mg/L³⁵.

2.2.2.4 Membrane techniques

Membranes acts as barriers, preventing the passage of unwanted substances from the oily wastewaters. Membrane processes are classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), the main difference between them being the selectivity of the membrane (pore size). In general, the MF membrane has the largest pore size, after UF, NF and finally the RO membrane with the smallest pore and, consequently, with the highest permeation resistance²².

A study made in Chine used an inorganic ceramic microfiltration membrane to treat oily wastewater, due to its known great stability at high temperatures and pressures, it has defouling properties. In this work, the NaA/ α - Al_2O_3 zeolite was examined for microfiltration. Two membranes with different pore sizes were compared, NaA1 (pore size = 1.2 μm) and NaA2 (pore size = 0.4 μm) in water emulsion containing 100 mg/L of oil, with pressure of 50 kPa and water flux in the membrane at 85 $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. NaA1 revealed the best efficiency, with 99% of oil rejection and the water containing less than 1 ml/L of oil³⁶.

Hua et al. published a crossflow microfiltration process was performed with oily wastewater using a ceramic membrane (α - Al_2O_3) with pore size of 50 nm. Under all

experimental conditions tested, the TOC removal efficiency was higher than 92.4%. The steady flux at high salt concentration (0.05 mol/L) was lower than at low salt concentration (0.001 mol/L). And at pH 5.8 the steady flux was higher than at pH 3.8³⁷. An ultrafiltration tubular membrane was modified by inorganic nano-sized alumina particles and used in the treatment of wastewater from an oil field. These alumina particles improved the membrane antifouling performance, and its recovery was 100% when using surfactant solution (pH 10). The COD and TOC removals were up to 90 and 98%, respectively. The oil content and the suspended content were both below 1 mg/L³⁸.

2.2.2.5 Comparison among the methods

Table 1 summarizes publications considering conventional methods for removal of oily phases from wastewaters, in order to compare the efficiency of oil removal with the traditional methods. In most of the cases, to achieve better results in the removal of oil, two different processes were combined.

Table 1. Comparison of the efficiency of conventional methods for removal of oily phases from wastewaters

Method	Efficiency	Ref
Microbubble Air Flotation	Oil removal = 98.0% COD = 82.8% Turbidity = 97.5%	Zheng et al. 2015 26
Dissolved Air Flotation with aluminum sulfate	Oil removal = 90%	Al-Shamrani et al. 2002 27
Dissolved Air Flotation with activated carbon	COD = 92.5% BOD = 94%	Hami et al. 2007 28
Adsorption with biosorbents	Oil removal = 94.3%	Ibrahim et al. 2012 30
Coagulation using ferrous sulphate with membrane filtration	TOC = 97.1%	Abbasi et al. 2012 34

Coagulation with PZSS and A-PAM	Suspended Oil removal = 99% Suspended Solid = 5mg/L	Zeng et al. 2007 35
NaA zeolite microfiltration membranes	Oil rejection = 99% Water containing less than 1 mg/L oil	Cui et al. 2008 36
Microfiltration with ceramic membrane (α-Al₂O₃)	TOC = 92.4%	Hua et al. 2007 37
Tubular ultrafiltration (UF) membrane with inorganic nano-sized alumina	COD = 90% TOC = 98% Oil and suspended content were bellow 1mg/L	Li et al. 2006 38

2.2.3 Treatment of oil and removal of lipophilic substances

The traditional separation processes mentioned above are limited to the physical separation between the oily and water phases, which cannot be disposed if hazardous substances are present in them, because it can affect the environmental, some examples are pollute drinking water and groundwater resources, endangering human health and atmospheric pollution. For this reason, it is necessary to combine other techniques, such as biological treatments, bioremediation, pyrolysis, combustion and advanced oxidation processes^{1,8}.

The process of pyrolysis consists in the treatment of the wastewater at high temperatures, in an atmosphere absent of oxygen (or with low presence), whereas the process of combustion requires an oxidizing agent, usually oxygen, to promote complete oxidation chemical reactions. Both heat treatments present some obstacles, such as the excessive energy necessary to achieve the required high temperatures and air pollution, since both processes emit several harmful, such as ammonia (NH₃), hydrogen cyanide (HCN), isocyanic acid (HNCO), nitric oxide (NO), nitrogen dioxide (NO₂), carbon disulfide (CS₂), sulfur dioxide (SO₂), methanethiol (CH₃SH), hydrochloric acid (HCl) and chlorine gas (Cl₂). Few studies have investigated the transfer of N, S and Cl elements from the oily phase to a free gas³⁹.

Chen et al. carried out a comparison between pyrolysis and combustion as treatments of three different types of oily sludge obtained from the Bohai offshore oilfield (ZHY), oily sludge from the Tahe oilfield (TH) and from the Yumen oilfield (YM). The comparison was made by thermogravimetric (TG) analysis at temperatures from 50 to 1000 °C, considering a constant heating rate of 10 °C/min. A flow rate of 50 mL/min of N₂ was used during pyrolysis and simulated air (N₂:O₂ = 4:1) in the combustion runs. The results showed that the atmosphere enriched with oxygen facilitated the decomposition of organic molecules in combustion, at 200–500°C. However, the weight loss obtained by pyrolysis increased at higher temperatures (> 700-800°C). In addition, pyrolysis also had less quantitative emissions of polluting gases than in the combustion process ³⁹.

On the other hand, biological treatments use live microorganisms as agents in the degradation of toxic substances. One option is bioremediation, a natural process performed by some living organisms (bacteria, fungus) which uses contaminants in its metabolism as a source of carbon and energy ^{10,40,41}.

A bioremediation process is specific to each type of polluted site. There is no species in nature that can degrade all existing components, so in each treatment it is necessary to choose the specific organisms to treat the targeted pollutants. Therefore this process depends on the type of mixture of oil and organic substances, such as hydrocarbons, for the best performance of the degradation process ^{10,11}.

Some processes, such as adsorption, are suitable to the removal of specific compounds (pollutants or impurities) found in the oil phase without changing any properties of the organic phase in order to reuse it. Substances with greater affinity for the adsorbent will be retained on its porous surface. A study carried out by Diaz de Tuesta found some parameters that interfere with the efficiency of adsorption with activated carbon, more specifically: absence of water, particle size of the carbon material and the chemical and thermal modifications made in the activated carbon, initial concentration of pollutant, water/oil volume ratio, nature of the organic phase and if has a presence of an emulsifier. In the study, the lipophilic substance of interest for removing from the oily mixture was Sudan IV (S-IV). Activated carbons were modified to observe the best conditions and treatments of the carbons on their efficiency in removing S-IV. The key characteristic for the best performance of the process was the lipophilicity of the adsorbent that interacts directly with the lipophilicity of the S-IV adsorbate ⁴².

2.2.4 Advanced oxidation processes

Advanced oxidation processes (AOPs) generates hydroxyl radicals (HO[•]), very reactive species for the oxidation of a wide range of organic matter. Most of these methods operates at ambient temperature and atmospheric pressure. The oxidizing agents can be hydrogen peroxide, ozone or/and oxygen depending on the AOP, such as Fenton, ozonation, photocatalysis, electrooxidation or catalytic wet peroxide oxidation (CWPO). The HO[•] radicals react with organic compounds producing simpler organic compounds, or carbon dioxide (CO₂), water (H₂O) and inorganic salts (containing chlorine, nitrogen, or sulfur, if present) in case of full mineralization as described in Eq 1^{9,43,44}.



The Fenton process is one of the most used and studied AOPs. Its mechanism involves the participation of ferrous ions (Fe²⁺) as catalyst and hydrogen peroxide (H₂O₂) as the oxidant⁴⁵. In this system the reaction occurs first with ferrous ions (Fe²⁺) decomposing H₂O₂ to produce, the Fe³⁺ formed previously reacts with hydrogen peroxide producing hydroperoxyl radicals and regenerating the catalyst (Eq 3). On its turn, the hydroperoxyl radicals can also react with ferric ion, also contributing to the regeneration of the catalyst (Eq 4)^{46,47}.



The process that uses H₂O₂ is known as non-toxic, once hydrogen peroxide self-decomposes into H₂O and O₂ (Eq 5). The drawback of the Fenton process is the large volume of iron sludge produced, since the iron ions are continuously lost in the process^{45,48}.



Some works dealing with Fenton oxidation focused on the removal of 4-NPs are summarized in Table 2. The removal of the 4-NP was higher than 66.4% and a TOC abatement from 49.2 to 82.1% was achieved. The optimal pH in the methods was found between 3 and 3.7 and the highest temperature of 28 °C was used⁴⁹⁻⁵².

Table 2. Overview of work done in recent years in the area of Fenton oxidation to remove NPs

N°	Process	Pollutant	Conditions	Removal	Ref
1	Fenton in a bubble column reactor	4-NP	[4-NP] = 500 mg/L [H ₂ O ₂] = 1.6 g/L [Fe ²⁺] = 80 mg/L pH = 3 T = 22-24 °C t = 120 min reaction Q air = 1 mL/min	Complete removal of 4-NP TOC removal = 49.2%	Rodrigues et al. 2017 ⁴⁹
2	Electro-Fenton with anodized graphite felts	4-NP	[4-NP] = 50 mg/L Electro – generation of H ₂ O ₂ Fe ³⁺ = 0.4 mM pH = 3 E = -0.75 V O ₂ flow rate = 0.4 L/min CF - 10*	Complete removal of 4-NP TOC removal = 78.3%	Zhou et al. 2013 ⁵⁰
3	Electro-Fenton with graphite cathode modified	4-NP	[4-NP] = 50 mg/L [H ₂ O ₂] = 175.8 mg/L 0.2 mM Fe ³⁺ E = -0.65 V pH = 3 t = 20 min O ₂ flow rate = 0.4 L/min CF - B**	Degradation of 4-NP = 78.7% TOC removal = 51.4%.	Zhou et al. 2014 ⁵¹
4	Sono-Fenton oxidation	4-NP	[4-NP] = 0.5% (w/v) H ₂ O ₂ = [5 g/L] Fe powder = 1 g/l pH = 3.7 T = 28 ± 2° C t = 90 min	Degradation of 4-NP = 66.4%	Pradhan et al. 2010 ⁵²

(*) graphite felt anode chemically modified.

(**) graphite felt cathode chemically modified.

AOPs can be conducted considering homogeneous catalysts, as in the case of the Fenton process, or heterogeneous catalysts, depending on the nature of the catalyst⁴⁶. The advantage on the use of heterogeneous catalysts is the facility of separation and regeneration of the catalyst^{46,53}.

2.3 Catalytic wet peroxide oxidation

Catalytic wet peroxide oxidation (CWPO) is a promising AOP due to its demonstrated efficiency under mild operations conditions (0.1 – 0.2 MPa and 20 – 130 °C) ⁵⁴. The CWPO process is based on the use of H₂O₂ as oxidant and a suitable heterogeneous catalyst to promote the decomposition of hydrogen peroxide into hydroxyl radicals (HO•) that will degrade the organic pollutants.

In table 3 are summarized three studies regarding CWPO to show the feasibility of the process in the treatment of real wastewaters, such as those from textile, petrochemical, olive mill, pharmaceutical, winery and cosmetic industries or urban wastewater ⁵⁵.

Table 3. Catalytic wet peroxide oxidation (CWPO) of industrial wastewaters.

Nº	Catalyst	Type of wastewater	Conditions	Results	Ref
1	Activated carbon, carbon black and graphite	Winery Wastewater COD = 3.5 - 35 g/L TOC = 11 g/L	T = 80 – 125 °C pH = 2.2 – 7, H ₂ O ₂ doses 0–1.6 stoichiometric amount related to COD. 5 g/L of graphite	Complete degradation of polyphenols, 80% COD and TOC removals.	Domínguez et al. 2014 ⁵⁶
2	MOF* containing copper Cu ₃ (BTC) ₂ (H ₂ O) ₃	Olive mill wastewater (COD 57.7 g/L)	Catalyst = 0.97 g/L H ₂ O ₂ = 113.2 mg/L T _{max} = 32.85 °C	About 96% of polyphenols present in the wastewater was removed after CWPO. Biodegradability of the wastewater significantly increased after treatment.	De Rosa et al. 2005 ⁵⁷

3	Refinery	T = 20 °C	LP lamp: removal	Rueda-
	Granular activated carbon (GAC)	wastewater effluent	GAC (141.1 g/L) Initial concentrations of H ₂ O ₂ during CWPO were 1) 160 mg/L and 2) 96 mg/L.	phenolic compounds, TOC and COD 100%, 52.3% and 84.3%, respectively MP lamp: Complete elimination of phenolic compounds, 47.6% of TOC and 91% of COD

* metal-organic framework.

The first wastewater shown in table 3 is from a wine industry. In this study it was compared different oxidation processes, being concluded that CWPO has the most promising results, with complete degradation of polyphenols and 80% of COD and TOC removal. The optimum conditions found were pH 3.8, temperature of 125 °C, 4 h of reaction, pressure of 0.7 MPa and 5 g/L of graphite, which was the most active catalyst, probably due to the Fe content (0.4 wt. %) in its composition. The leaching of Fe was also tested, but it was found negligible ⁵⁶.

De Rosa et al. dealt with the olive oil mill wastewater used a metal-organic framework (MOF) as catalyst. The material contained Cu and it was prepared with benzene-1,3,5-tricarboxylic acid. The reaction runs were carried out at room temperature and atmospheric pressure, with 0.97 g/L of catalyst and 113.2 mg/L of hydrogen peroxide. The pH has stabilized at 3.4 after 27 h of oxidation. The content of polyphenols at the end of treatment decreased 96% and biodegradable COD was up to 84% ⁵⁷.

The third wastewater shown in Table 3 is from a refinery, which was subjected to a multi-barrier treatment, consisting of filtration, hydrogen peroxide photolysis and catalytic wet peroxide oxidation (CWPO). The filtration decreased the turbidity and the suspended solids by 92 and 80%, respectively. Photolysis was separated in medium (MP) and low pressure (LP) lamps. With LP lamp it was obtained 100% removal of phenolic compounds, 52.3% of TOC and 84.3% of COD. With MP it was obtained 100% removal of phenolic compounds, 47.6% of TOC and 91% of COD. By photolysis the

hydrophilicity of the effluent increased, helping the oxidation of the remaining organic compounds during CWPO process. With CWPO, TOC and COD removals of 94.7 and 92.2% were obtained using LP lamp and 89.6 and 95% with MP lamp, respectively. The catalyst used in the CWPO was granular activated carbon (GAC) ⁵⁸.

Another comparison of CWPO processes may be done with those works focused on the oxidation of 4-nitrophenol, their efficiency and conditions. Table 4 summarizes three studies with promising results, under mild conditions, with three different materials used for the removal of the pollutant.

The first work presented in Table 4, used as catalyst carbon nanotubes synthesized by chemical vapor deposition (CVD) on Fe/ γ -Al₂O₃ catalysts (20 wt. % Fe), considering ethylene and acetonitrile as carbon and carbon/nitrogen sources respectively. The resultant materials were named as E20, E10A20 and A30, depending on the use of ethylene (E), acetonitrile (A) and time considered in the feed of each precursor. Each sample was after submitted to two treatments, one thermal and one chemical, the samples of the thermal treatment named as E20HT, E10A20HT and A20HT (HT for heat-treatment). The samples after chemical treatment (with nitric acid) named as E20N, E10A20N and A20N. The conditions of the process were initial concentration of 4-NP of 5 g/L, atmospheric pressure, T = 50 °C, pH 3, catalyst concentration of 2.5 g/l and the stoichiometric amount of hydrogen peroxide needed for the complete mineralization of 4-NP. The best results, with complete removal of 4-nitrophenol, were achieved with E30HT and E10A20HT after 8 hours of operation ⁵⁹.

Ribeiro et al. considered the use of reduced graphene oxides as catalysts, rGOG, rGOH and rGOV, obtained with three different reducing compounds, namely glucose (G), hydrazine (H) and vitamin C (V), respectively. The conditions were concentration of the pollutant 5 g/L, atmospheric pressure, T = 323 K, pH = 3, concentration of the catalyst = 2.5 g/L and concentration of H₂O₂ = 17.8 g/L. Under these conditions, the most efficient catalyst was rGOV, with 65% of 4-NP removal and TOC = 23% after 24 h. To test the stability of the catalysts, three CWPO runs were consecutively conducted and the most stable material found was rGOH, with a slightly decrease in the removal of 4-NP, 980 mg/g (49%) to 841 mg/g (42%) at the end of the third run ⁶⁰.

Lignin is an organic polymer with high carbon content, because of that, this material was studied in the preparation of activated carbons to observe the efficiency in the CWPO of 4-nitrophenol. Four materials were prepared under four temperatures (150,

200, 300, 350 °C). After 24 hours, under relatively mild conditions, T = 50 °C, pH 3, atmospheric pressure, $C_{\text{cat}} = 2.5 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 17.8 \text{ g/L}$ and 5 g/L of 4-NP, the removal of the pollutant was 70%. With the increase of temperature to 80 °C the nitrophenol was completely removed within 48 hours, with a consumption of hydrogen peroxide of 70% and a mineralization of 61%⁶¹.

Table 4. Catalytic wet peroxide oxidation (CWPO) of 4–nitrophenol

N°	Catalyst	Pollutant	Conditions	Results	Ref
1	Carbon nanotubes Fe/ γ -Al ₂ O ₃	4-NP	Model Solution of [4-NP] = 5 g/L T=50 °C, pH=3, [cat] = 2.5 g/L, atmospheric pressure, t = 8 h	Catalysts: (E30HT and E10A20HT) Total removal of 4- NP	Martin- Martinez et al. 2020 ⁵⁹
2	Graphene oxide materials	4-NP	Model Solution of [4-NP] = 5 g/L, T = 323 K, pH = 3, [cat] = 2.5 g/L, atmospheric pressure, [H ₂ O ₂] ₀ = 17.8 g/L, t = 24 h	Removal 4-NP = 65% TOC = 23%	Ribeiro et al. 2015 ⁶⁰
3	Activated carbons from lignin materials	4-NP	Model Solution of [4-NP] = 5 g/L, T = 80 °C, pH = 3, [cat] = 2.5 g/L ,atmospheric pressure, [H ₂ O ₂] ₀ = 17.8 g/L, t = 48 h	Complete removal of 4-NP H ₂ O ₂ consumption = 70% Mineralization = 61%	Martin- Martinez et al. 2017 ⁶¹

In general, heterogeneous catalysts used in CWPO are classified as supported and non-supported catalysts (Figure 1). Supported catalysts allow active species, as iron, to increase its surface area. Some materials that can be applied as supports are alumina, silica, activated carbons and clays. However, the presence of iron species in heterogeneous catalysts present a major disadvantage, the possibility of iron leaching from the catalyst^{54,55}.

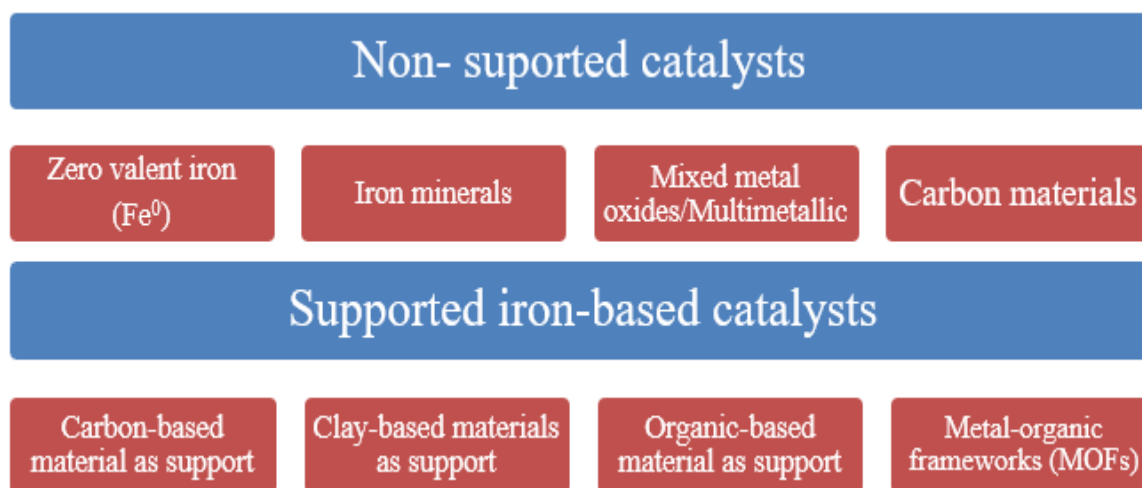


Figure 1. Classification of typical catalysts used for CWPO (adapted from ⁵⁵).

The metal leaching is one of the major problems that appears in CWPO, so recently, metal-free materials are being studied and found to be very promising alternatives to iron supported catalysts. Studied metal-free catalysts includes carbon black, activated carbons, glycerol-based carbon materials, carbon xerogels and carbon nanotubes (CNTs). The possibility to synthesize metal-free catalysts for CWPO reflects an improvement in comparison with the Fenton process, since the synthesized materials won't result in the leaching of iron and the formation of iron sludge ^{2,54,55}.

2.4 Amphiphilic carbon nanotubes

CNTs are tubular forms of carbon-based materials with an inner diameter within the range of the nanometer order, known as versatile catalytic supports or catalysts due to their high mechanical resistance, high thermal stability and large surface area ^{54,62}. The most used techniques for the growth of CNTs are arc discharge, laser ablation and chemical vapor deposition (CVD). These methods use energy to create carbon atoms from carbon sources, generating CNTs. The arc discharge method was the first application to produce CNTs at temperatures higher than 1700 °C, resulting in CNTs with fewer structure defects when compared with CNTs produced from other methods. Laser ablation uses laser beam to vaporize graphite containing catalyst materials (usually Ni or Co) at 1200 °C and an inert atmosphere. Chemical vapor deposition uses relative low temperatures (500 – 1000 °C) and the size of the CNTs varies according to the size of the catalyst particles. The process uses carbon in the gas phase and an energy source such as

resistively heated coil. Usually methane, carbon monoxide or acetylene are carbon sources used in this process ⁶³⁻⁶⁵.

In CVD processes, the carbon sources used are mostly hydrocarbons, such as methane, ethane, ethylene, acetylene, xylene, isobutane or ethanol. The preferable catalysts are transition metals like Fe, Co, Ni, and sometimes Au and Pd. Some parameter as pressure, catalyst concentration and catalyst particle size influences in the synthesis of CNTs ^{63,65,66}. Pd catalysts with particle sizes of 4.4, 1.4, 1.3 and 1.2 nm led to diameter of produced CNTs of 12, 16, 18 and 18 nm and surface area of 258, 257, 196 and 194 m²/g for Pd/E30, Pd/E10A20, Pd/A20E10 and Pd/A30 respectively ⁶⁶. As the catalyst particle size decreases, the produced CNTs surface area also decreases, and the diameter increases.

Amphiphilic CNTs or Janus-structured CNTs may be prepared using two different carbon precursors fed sequentially, as in previous works done in the research group where this dissertation will be carried out ^{54,66}. In this work, Janus-structured CNTs were synthesized using Fe/ γ -Al₂O₃ (20 wt.% Fe) as catalyst. The Fe-containing catalyst was pre-reduced *in situ* with hydrogen at 650 °C during 30 min. The hybrid nanotubes were grown by CVD in a fluidized bed reactor using ethylene and acetonitrile at 35 °C as carbon and nitrogen/carbon sources respectively, during the following periods: (1) C₂H₄ for 30 min (E30); (2) C₂H₃N for 20 min, followed by C₂H₄ for 20 min (A20E20); (3) C₂H₄ for 10 min, followed by C₂H₃N for 20 min (E10A20); (4) C₂H₃N for 20 min, followed by C₂H₄ for 10 min (A20E10); and (5) C₂H₃N for 30 min (A30). As can be observed by Transmission Electron Microscopy (TEM), in Fig. 2, the different growth in the CNTs and the amphiphilic with double structure, undoped and N-doped, resembling to Janus particles ².

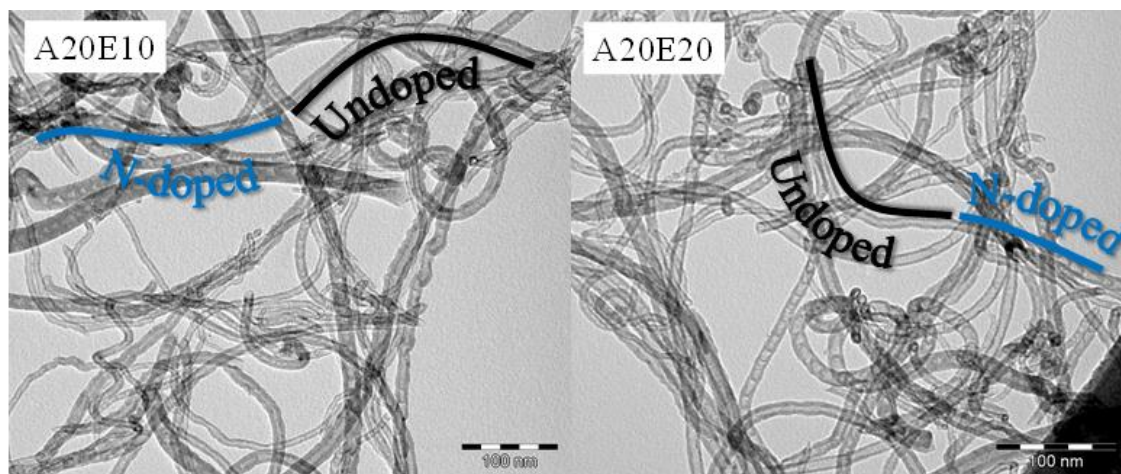


Figure 2. Janus-CNTs prepared from two sources sequent fed: ethylene and acetonitrile.

Janus particles are amphiphilic materials able to interact with aqueous and oily phase at the same time, the solid material act as emulsifier, promoting an increase in the interface between immiscible liquid phases and stabilizing the emulsions, known as Pickering emulsions. Being easy to break the emulsion and to recover the two phases, Pickering emulsion is ideal to use at water/oil biphasic systems as treatment of oily wastewater contaminated with lipophilic pollutants^{67,68}.

The catalyst with this property is important because it enable the reaction at the liquid-liquid interface, ensuring a greater mass transfer of the pollutant between phases. Therefore, the CWPO with hydroxyl radicals oxidizing the lipophilic pollutants present in the oily sludge promotes more hydrophilic products, which with the Janus Particles will enhance their transfer to the water phase, cleaning the oil phase².

MATERIALS AND METHODS

3 Materials and Methods

3.1 Reactants

- ✓ 4-Nitrophenol (98%). Acros Organics. Formula: $C_6H_5NO_3$
- ✓ Hydrogen peroxide (30% w/v). Fisher Chemical; Formula: H_2O_2
- ✓ Titanium (IV) oxysulfate (15 wt.% in dilute sulfuric acid, H_2SO_4 99.99%). Aldrich; Formula: $TiOSO_4$
- ✓ Sulfuric acid (98%). Labkem; Formula: H_2SO_4
- ✓ Sodium sulphite anhydrous (98%). Panreac; Formula: Na_2SO_3
- ✓ 2,2,4-Trimethylpentan. VWR Chemicals; Formula: C_8H_{18}
- ✓ Acetonitrile. VWR Chemicals; C_2H_3N
- ✓ Orthophosphoric Acid. Fisher Chemical; H_3PO_4
- ✓ Distilled water
- ✓ Ultrapure Water

3.2 Synthesis description of the CNTs

The CNTs used in this work were synthesized in partnership with Chemistry Laboratory from University of Toulouse by CVD process in a fluidized-bed reactor using ethylene (carbon source) and acetonitrile (nitrogen/carbon sources), as described elsewhere^{2,54,66}. The CVD synthesis was conducted by employing $AlCoFeO_4$, as catalyst. Six samples were produced by feeding sequentially the fluidized bed reactor with ethylene (E) and/or acetonitrile (A) during the following periods: (1) C_2H_4 for 20 min; (2) C_2H_4 for 15 min followed by C_2H_3N for 5 min (3) C_2H_4 for 10 min followed by C_2H_3N for 10 min; (4) C_2H_4 for 5 min followed by C_2H_3N for 15 min; (5) C_2H_4 for 1 min followed by C_2H_3N for 19 min (6) C_2H_3N for 20 min; resulting in E20, E15A5, E10A10, E5A15, E1A19, A20 samples, respectively as shown in Table 5. Eventually, the synthesized CNTs were purified under reflux at 140 °C in an aqueous solution of H_2SO_4 (50 vol. %) for 3 h, to facilitate the total dissolution of the alumina and exposed Fe particles.

Table 5. CNTs samples and its respectively precursors time (min).

CNT	E20	E15A5	E10A10	E5A15	E1A19	A20
Ethylene time (min)	20	15	10	5	1	0
Acetonitrile time (min)	0	5	10	15	19	20

3.3 Characterization Techniques

3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier Transform Infrared Spectroscopy (FTIR) spectra of the 6 CNT samples were recorded on a Perkin Elmer FT-IR spectrophotometer UATR Two infrared spectrophotometer, with a resolution of 4 cm^{-1} . The range of wavenumber used in the analysis was from 450 to 4000 cm^{-1} . All the measurements were done at room temperature using CNT with non-additional treatments (in solid state).

3.3.2 Transmission electron microscopy (TEM)

The transmission electron microscopy (TEM) images were obtained using a JEOL 1011 operating at 100 kV.

3.3.3 Surface and pore analyzer

The textural properties of the materials were determined from N_2 adsorption-desorption isotherms at $-196\text{ }^\circ\text{C}$, obtained in a Quantachrome NOVATOUGH XL4, following the same procedure as elsewhere⁶⁹. Briefly, the degasification of the catalysts was conducted at $120\text{ }^\circ\text{C}$ during 16 h and then BET, Langmuir specific surface area (S_{BET} , $S_{Langmuir}$) were determined using BET and Langmuir methods. The external surface area (S_{ext}) and the micropore volume (V_{mic}) were obtained by the t -method (thickness was calculated by employing ASTM standard D-6556-01). The microporous surface area (S_{mic}) was determined as the subtraction of S_{ext} from S_{BET} . The total pore volume (V_{Total}) was determined at $p/p^0 = 0.98$. Calculations of those methods were all done by using TouchWinTM software v1.21.

IUPAC document of 1985 grouped adsorption isotherms and hysteresis loops in different types. The old classification was refined, due to new characteristic types of isotherms that have been identified.⁷⁰ The new updated classification by IUPAC of isotherms and hysteresis loop are represented in Figure 3 and Figure 4, respectively.

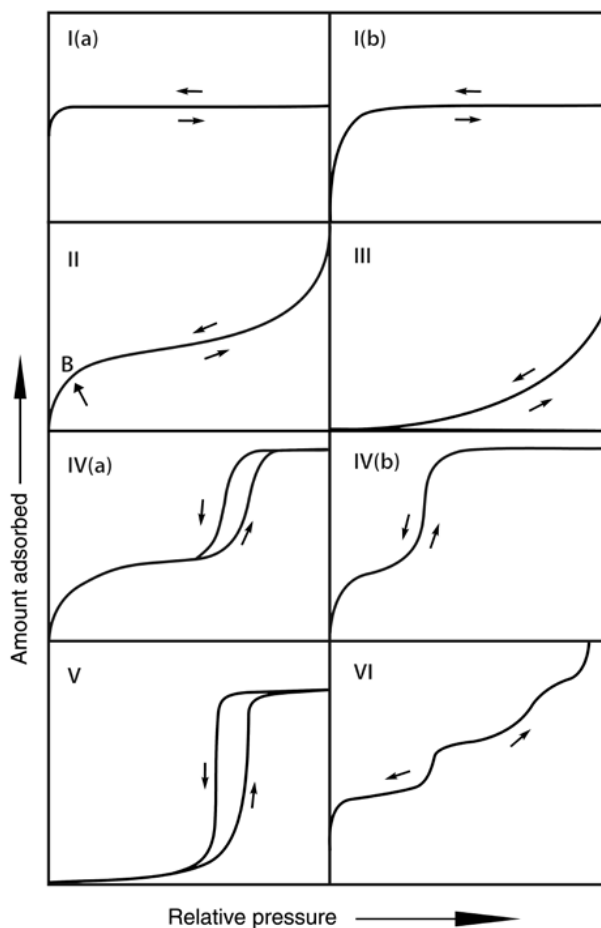


Figure 3. Classification of physisorption isotherms.⁷⁰

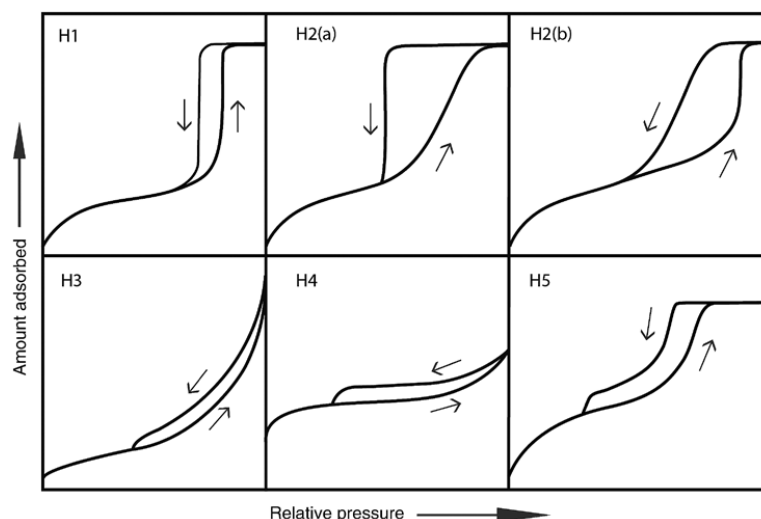


Figure 4. Classification of hysteresis loops. ⁷⁰

3.4 CWPO of 4 – Nitrophenol

3.4.1 CWPO of 4-NP in aqueous solution

The oxidation reactions were carried out in a 250 mL round flask reactor well-stirred (600 rpm), attached to a condenser, and a temperature measurement thermocouple. The reactor was loaded with 50 mL of 1 g/L 4-NP aqueous solution and heated by immersion in an oil bath monitored by a temperature controller until 80 °C. The solution was previously acidified to reach pH 3.5 through an H₂SO₄ solution (0.5 M). A calculated volume of hydrogen peroxide (30% w/v) was injected into the system, to reach a H₂O₂ concentration of 3.56 g/L, which is the stoichiometry concentration needed for mineralization (complete oxidation of organic matter)⁷¹. After its complete mixing, a catalyst concentration of 2.5 g/L was added to the solution, that moment being considered as $t_0 = 0$ min. Samples of 1 mL were periodically withdrawn following selected times: 5, 15, 30, 60, 120, 240, 360, 480, and 1440 min and placed in Eppendorf for H₂O₂, 4-NP concentration, and TOC analysis. In order to separate de catalyst from de liquid aliquot, each sample was centrifugated. After 1400 min of reaction the remaining catalyst was separated by filtration, washed with distilled water, and dried overnight in an air oven at 60 °C, while the liquid media was stored in a refrigerator for further analysis. Figure 5 shows the CWPO system used in the described experiments.

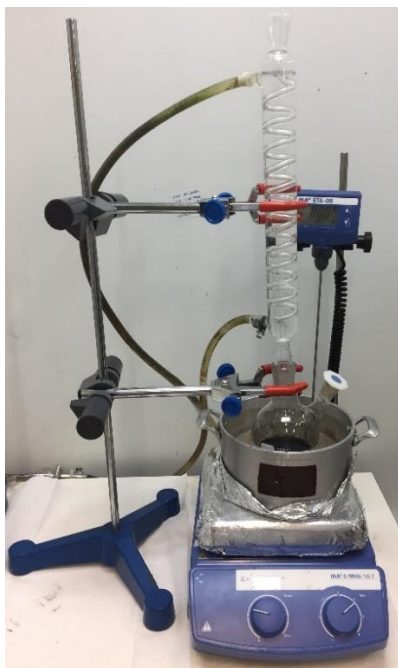


Figure 5. Set-up installation used in CWPO experiments.

3.4.2 CWPO of 4-NP in biphasic medium

The biphasic oxidations conditions were similar to aqueous CWPO 80 °C, initial pH in aqueous phase of 3.5, 2.5 g of catalyst per liter of oil and water, $C_{4\text{-NP aqueous},0} = 1$ g/L and stoichiometric amount of H_2O_2 needed for total 4-NP mineralization. 4-NP was added in water, and then the organic phase (Isooctane) was included, the mixture was stored for a week so that the equilibrium was reached until the theoretical concentration in the aqueous phase was 1 g/L (O/W = 1:9 (v/v)). The initial concentration in the two phases was left to freely change according to the partition coefficient of 4-NP between both phases ($\log P = -2.09$ in a alkane-water mixture⁷²). As reported by Abraham et al. the partition coefficient into various alkanes is very nearly equivalent, independent of the alkane used⁷². The concentration calculated from oily phase was 10 ppm (as the total concentration of the medium is nearly 1 g/L and the total volume is still 50 mL the concentration of hydrogen peroxide used will be the same as aqueous CWPO). In which run, during 10 min, the reactions were sonicated to

stabilize the emulsion (minimum time reported for the stabilization of emulsions²), the samples were periodically withdrawn following selected times: 5, 30, 60, 120, 240, 480, and 1440 min. The catalyst was separated by filtration, and the liquid media was stored for further analysis

3.5 Emulsion formation

The ability of the catalyst to form emulsion was tested in flasks of 9 mL loaded with 4.5 mL, 0.5 mL of distilled water and isooctane respectively (O/W = 1:9 (v/v) and 12.5 mg of which catalyst). During 10 min the medium was sonicated and then immediately taken to the optical microscope for observation and images with Microscope Nikon Eclipse 50i coupled with a Nikon digital sight DS-SM camera.

3.6 Analytical methods

3.6.1 H₂O₂ determination

The determination of H₂O₂ concentration of CWPO runs were carried out by collecting 0.2 mL of sample stored in an eppendorf and diluted with distilled water in a 20 mL volumetric flask, containing 1 mL of H₂SO₄ (0.5 M) and 0.1 mL of TiOSO₄. The samples were analyzed by UV-VIS spectrophotometry (T70 spectrometer, PG Instruments, Ltd.) at the wavelength of 405 nm to determine its absorbance.

A calibration curve was previously made in the concentration range from 1 to 3600 mg/L represented in Figure 6, the value of R² found was 0.999, which shows a good adjust for the linear regression.

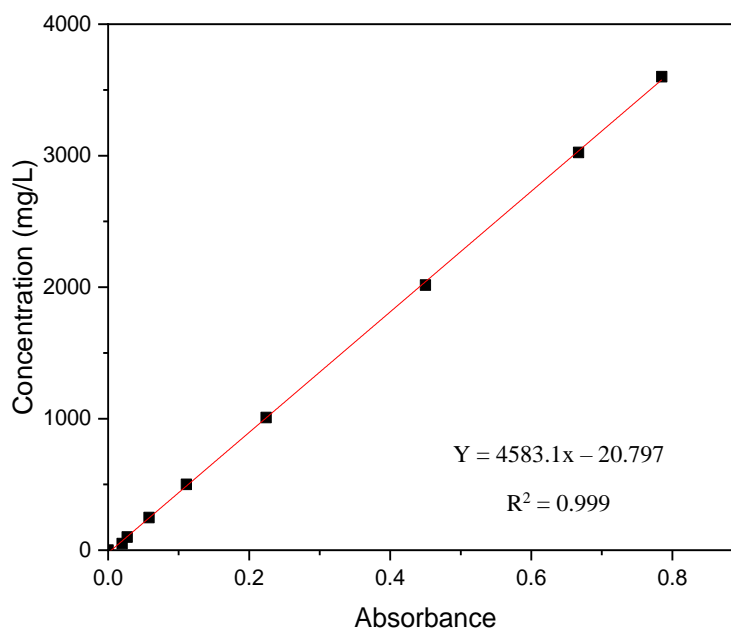


Figure 6. Calibration curve for H₂O₂ concentration.

3.6.2 4-nitrophenol in aqueous phase and its oxidized intermediates

The equipment used for HPLC analysis was a Jasco system equipped with a UV-VIS detector (UV-2075 Plus), a quaternary gradient pump (PU-2089 Plus) for solvent delivery (0.300 mL/min) and a NUCLEOSIL 5 μ m C18-100Å column (150 mm x 2.1 mm). The wavelength used to measure the peaked absorbance of the compounds was 277 nm. The mobile phases were a mixture of ultrapure water with phosphoric acid (A) and acetonitrile (B), with A:B ratio = 90:10. With this methodology, it was possible to analyze the model pollutant (4-NP) and its possible oxidized intermediates, such as hydroquinone, 1,4-benzoquinone, 4-nitrocatechol and catechol.^{60,73}

3.6.3 Total organic carbon

The analysis of the Total Organic Carbon (TOC) from liquid aliquots was performed by using a SHIMADZU TOC-L equipment, with 0.4 mL of the samples diluted made up to 20 mL in a volumetric flask.

3.6.4 4-NP concentration in organic phase

To analyze the concentration of 4-NP in the oily phase of CWPO L-L biphasic system (isooctane/water), aliquots of 0.10 mL of samples stored at the eppendorfs were placed in a flask with 0.6 mL of isooctane. The samples were analyzed by UV-VIS spectrophotometry (T70 spectrometer, PG Instruments, Ltd.) at the wavelength of 284 nm to determine its absorbance.

A calibration curve of 4-NP in isooctane was previously made in the concentration range from 0.5 to 5 mg/L as represented in Figure 7. The value of R^2 was 0.994, which shows a good adjust.

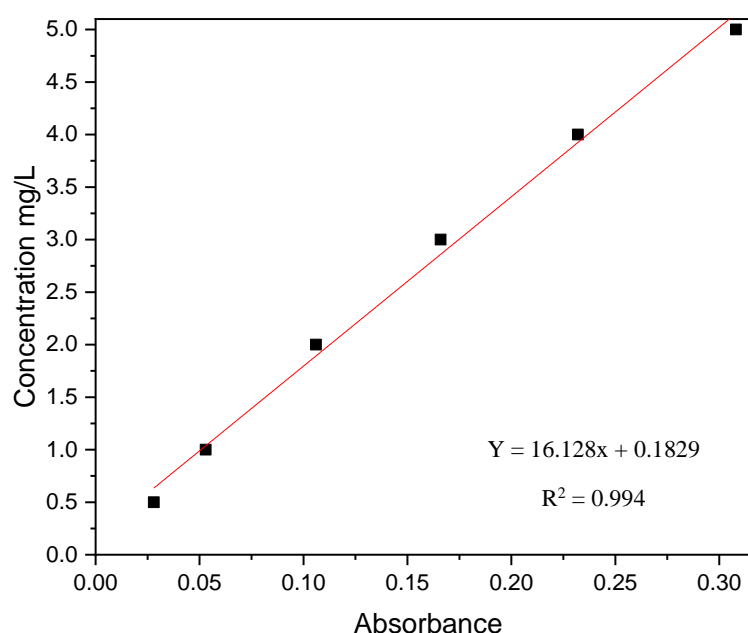


Figure 7. Calibration curve of 4-NP in isooctane.

3.6.5 Aromaticity

To measure the amount of aromatics present in the reaction and to observe if there was a formation of aromatics intermediates, it was necessary to obtain a calibration curve. The standard aromatic used was 4-NP, as a form of comparison, with the aromaticity is only for the pollutant or if will be observed formation of other aromatics. This monitoring is not qualitative, but quantitative. The curve concentration was in the range from 1 to 80 mg/L represented in Figure 8. The figure shows a good adjust with 8 points and R^2 value was 0.999. The quantification of aromaticity

concentration of the aqueous CWPO was performed by collecting 1 mL sample from the solution present in the reactor only from the 24 h eppendorf and diluted with a buffer solution with pH 7 in a 20 mL volumetric flask, while in biphasic CWPO the aromaticity concentration was carried out with all seven samples withdrawn from the medium. It was collected 0.1 mL from the eppendorfs and diluted with a buffer solution in a 5 mL volumetric flask. All samples were analyzed by UV-VIS spectrophotometry (T70 spectrometer, PG Instruments, Ltd.) at the wavelength of 254 nm to determine its absorbance.

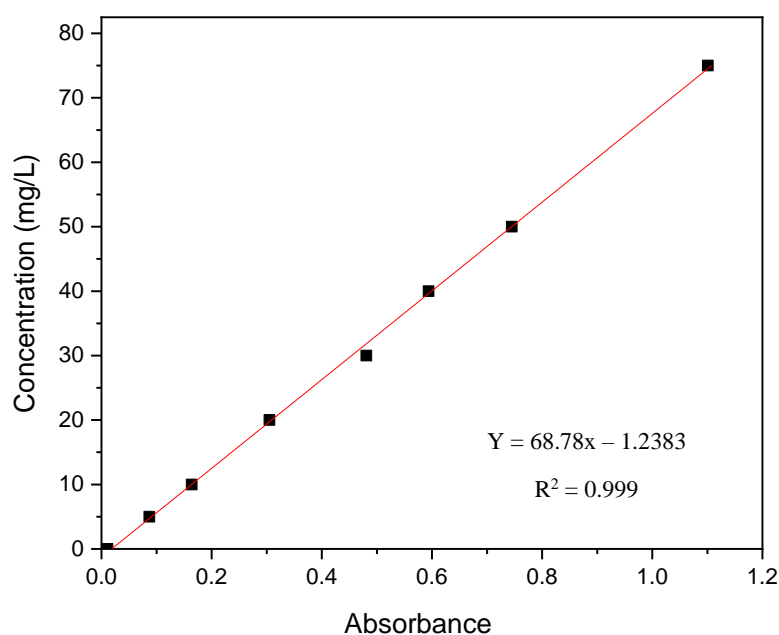


Figure 8. Calibration curve of aromaticity.

RESULTS AND DISCUSSION

4 Results and Discussion

4.1 Characterization Techniques

The catalytic materials were tested by Fourier Transformed Infra-Red spectroscopy (FT-IR), Transmission Electron Microscopy (TEM) and adsorption isotherms of N₂ at 77 K.

4.1.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 9 shows the FT-IR spectra of the six different CNTs recorded between 450 and 4000 cm⁻¹.

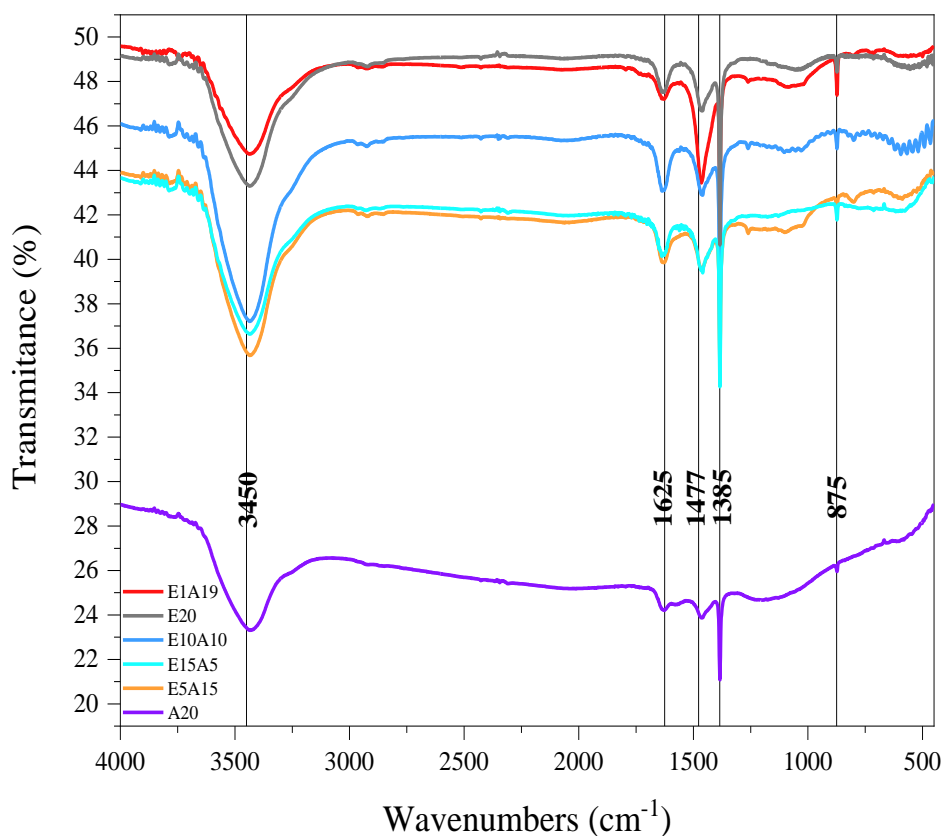


Figure 9. FT-IR spectra of the CNTs.

In the FT-IR spectra, it can be observed the same bands for all the materials with a difference between their intensity. The band appearing at 3405 cm⁻¹ is due to intermolecular hydroxyl groups (OH:OH)⁷⁴, while that appearing at 1625 cm⁻¹ represents a carbonyl with H bonded (CNT-COOH)^{75,76}. At 1477 cm⁻¹ the band represents CH₂ bending⁷⁷, and the band at 1385 cm⁻¹ represents C-H in-plane

bending⁷⁸. The very weak peak at around 875 cm⁻¹ observed for all samples excluding A20, can be assigned to isolated aromatic C-H out-of-plane bending vibrations⁷⁹.

4.1.2 Transmission electron microscopy (TEM)

Figure 10 shows the microphotographs obtained by TEM analysis of the synthesized CNTs.

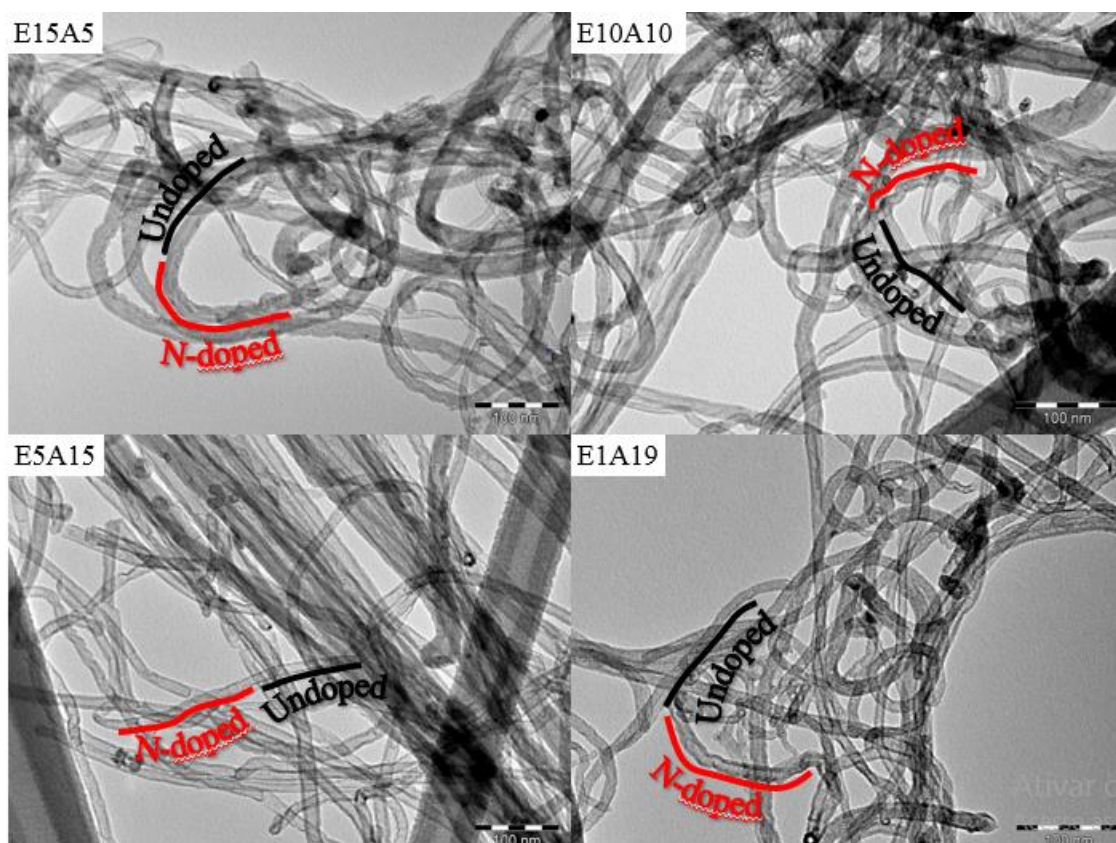


Figure 10. TEM images of the synthesized CNTs.

TEM images of the samples E20 and A20 were not taken, since it was considered that the structures of these materials were identical to E30 and A30 reported by Diaz de Tuesta et al.². As the TEM images show in the report, E20 sample (undoped) is characterized by a very regular wall and small external diameter, while sample A20 (N-doped) show a bamboo-like structure and a larger diameter.

In the samples synthesized using both precursors, ethylene and acetonitrile, (E15A5, E10A10, E5A15, E1A19) both structures can be observed, the regular one

(undoped) represented by a black line, and the bamboo-like structure (N-doped) indicated by a red line, confirming the synthesis of Janus-structured materials.

In Table 6 are represented the minimum and maximum external and internal diameters of the catalysts. The results show minimum external diameters between 10.00 and 14.21 nm that probably is from the undoped part, in agreement with the E30 sample that possess the $d_{\text{ext min}} = 10 \text{ nm}$.² The maximum external diameter values of 21.80 to 27.45 nm must represent N-doped sections, that, as reported elsewhere, are due to the “bamboo-like” structure that presents larger diameters.^{2,54}

Table 6. Minimum external diameter ($d_{\text{ext min}}$), maximum external diameter ($d_{\text{ext max}}$), minimum internal diameter ($d_{\text{int min}}$) and maximum internal diameter ($d_{\text{int max}}$) of the catalysts able to form pickering emulsion.

	$d_{\text{ext min}}$ (nm)	$d_{\text{ext max}}$ (nm)	$d_{\text{int min}}$ (nm)	$d_{\text{int max}}$ (nm)
E15A5	10.00	21.80	3.50	12.73
E10A10	9.86	24.91	5.57	13.26
E5A15	14.21	27.45	7.85	11.89
E1A19	10.72	26.67	5.89	13.20

4.1.3 Surface and pore analyzer

The porosity of the materials was assessed using N_2 adsorption-desorption isotherms at 77 K, represented in **Erro! Fonte de referência não encontrada.**

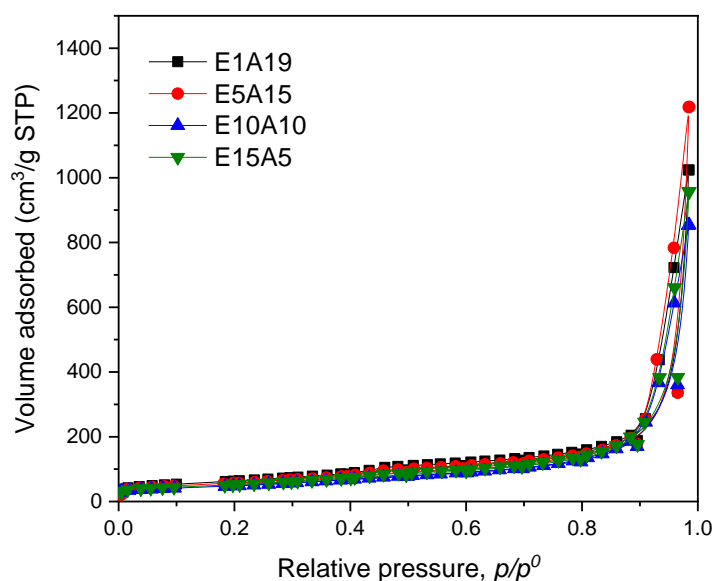


Figure 11. Adsorption isotherms of N₂ at 77 K of Janus amphiphilic CNTs.

As can be observed, all the materials show a low adsorbed N₂ volume at low relative pressure (p/p^0). On the other hand, at higher relative pressures, a hysteresis loop between the adsorption and the desorption branches is observed. Comparing the physisorption isotherms of the CNTs in Figure 11 with the IUPAC classification⁷⁰, it is possible to conclude that in this work the isotherms fits in Type II. This classification is attributed to nonporous or macroporous adsorbents. Regarding the hysteresis loop it can be classified as H3. These two classifications together are typically found for macroporous materials. And this type of isotherm is caused by the aggregation of the CNTs. All the studied materials show identical adsorption-desorption profiles.

Analyzing the isotherms by the t -plot method, the external specific surface area, S_{BET} and $S_{lagmuir}$, were determined and reported in Table 7, the values are very similar, and it can be confirmed that the materials are not microporous. Additionally, the microporous surface area and the micropore volume determined by the t -plot method was found to be zero ($S_{mic} = V_{mic} = 0$). The BET surface areas of all samples vary between 187 and 230 m²/g.

Table 7. Textural properties of the synthesized CNTs.

	$S_{BET} = S_{ext} \text{ (m}^2\text{/g)}$	$S_{Langmuir} \text{ (m}^2\text{/g)}$
E15A5	190	201
E10A10	187	195
E5A15	211	222
E1A19	230	245

These results are in agreement with other studies^{2,54} with Janus structures (E30, E10A20, A20E20, A20E10 and A30), which also have shown that the materials are not microporous ($S_{mic} = V_{mic} = 0$), and that the BET surface values ($245 < S_{BET} < 285 \text{ m}^2\text{/g}$) are higher but closer to those found in this work. Martin Martinez et al. reported the use of CNTs for the CWPO of 4-NP with materials E30, E10A20, E3A27, A30 and also revealed values nearly those in Table 7. The materials reached values of S_{BET} in the interval of 196 to 275 $\text{m}^2\text{/g}$ ⁵⁴.

4.2 Experimental Reactions

All the CNTs were used as a catalyst in the CWPO of 4-NP in aqueous solution and in biphasic system. In order to evaluate the efficiency of each CNT, the concentration of 4-NP, H₂O₂ and TOC (only in the aqueous medium) were followed upon reaction time. Emulsion and adsorption tests were performed with all the samples, in order to evaluate if the Pickering emulsions are formed and if the removal of the pollutant by adsorption is significant when compared with the removal obtained by oxidation with hydrogen peroxide.

4.2.1 Pickering emulsions with CNTs

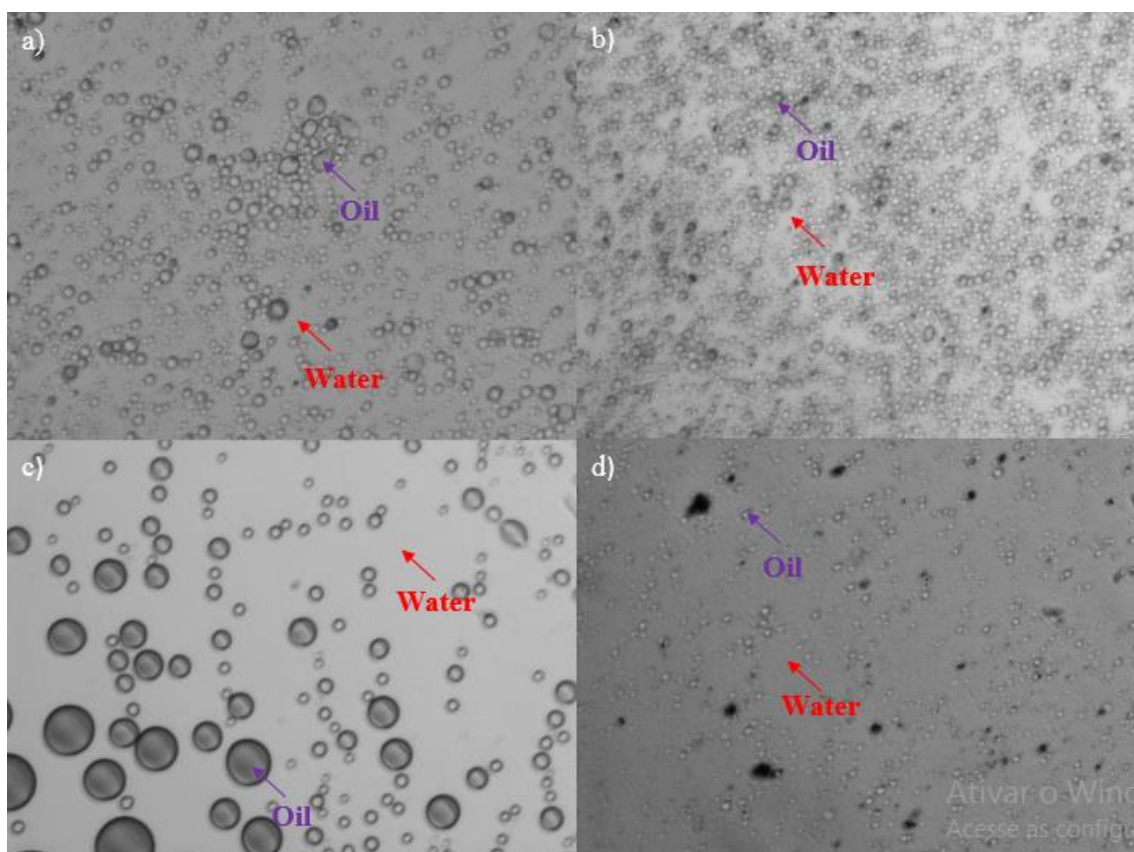


Figure 12. Optical Microscope Images of the isooctane in water Pickering emulsions stabilized by a) E20, b) E15A5, c) E10A10 and d) E5A15 CNTs at O/W = 1:9 (v/v) and $C_{CNT} = 2.5$ g/L.

The ability of the CNTs to act as Pickering emulsifiers was tested in the stabilization of a water-isooctane biphasic mixture (O/W = 0.5:4.5 mL/mL and 12.5 mg of CNT). The emulsion stabilization was achieved under sonication during 15 min (E20, E15A5 and E10A10), 60 min (E5A15) and 120 min (E1A19, A20) and then immediately taken to optical microscopes. The images captured with a 40X objective lens are represented in Figure 12.

The CNTs which form perfectly stable Pickering emulsions for isooctane/water mixture are E20, E15A5, E10A10 and E5A15, and are presented in Figure 12, while no emulsion was formed in the presence of E1A19 and A20, even after 120 min of sonication (not shown in Figure 12). Accordingly, it can be assumed that as higher is the N-content (hydrophilic) part in the CNTs, higher is the difficulty to form Pickering emulsions. It is concluded that the higher N-content more difficult was to stabilize the Pickering

emulsions, since E1A19 and A20 did not formed emulsions, even after a longer time under sonication.

4.2.2 CWPO of 4-NP in aqueous medium

The CNTs prepared were evaluated in the CWPO of 4-NP in aqueous solution. Figure 13 shows the normalized concentration of H₂O₂ and 4-NP as a function of time of reaction (N.C. = Non catalytic).

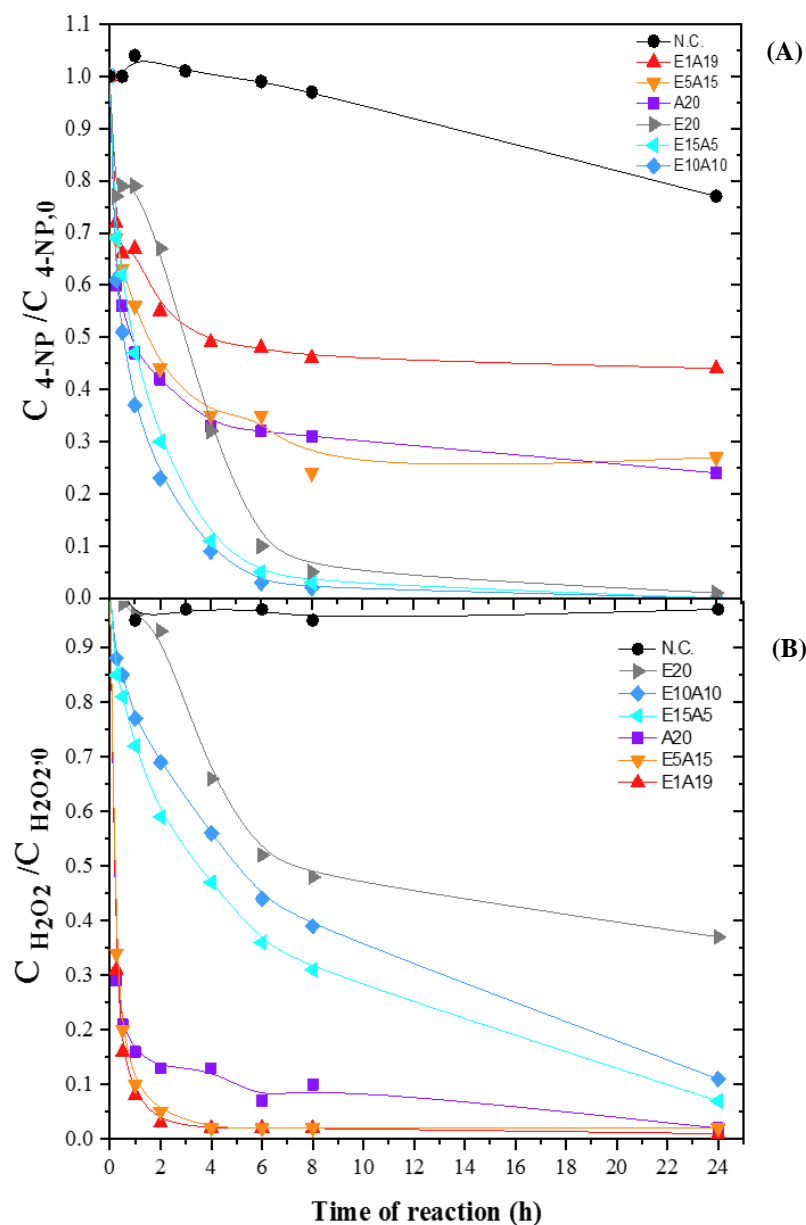


Figure 13. Normalized concentration of (A) 4-NP and of (B) H₂O₂ along time of reaction, under the operational conditions: $C_{4-NP,0} = 1$ g/L, $C_{H_2O_2,0} = 3.56$ g/L, $C_{cat} = 2.5$ g/L, $pH_0 = 3.5$ and $T = 80$ °C.

As can be observed, all tested CNTs are efficient catalysts, since the conversions of 4-NP and H₂O₂ ($23\% < X_{4-NP} < 100\%$ and $3\% < X_{H_2O_2} < 99\%$) are higher than those obtained in the non-catalytic run (4-NP and hydrogen peroxide conversions of 23% and 3%, respectively).

The highest conversions of 4-NP (Figure 13A) in the CWPO of 4-NP were obtained with catalysts E20, E15A5 and E10A10, with values up to 90% after 6 h

of reaction. Both Janus structured CNTs present 100% conversion of the pollutant after 24 h of reaction. H_2O_2 concentration profiles of these materials present a slowly decrease when compared with A20, E1A19 and E5A15.

Analyzing the concentration of H_2O_2 in Figure 13B, it is interesting to observe that the three CNTs with higher N-content show the faster decomposition of H_2O_2 , up to 80% after 1 h of reaction. In addition, the same materials (A20, E1A19 and E5A15) present lower conversion of 4-NP (Figure 13A), 76, 56 and 73%, respectively, after 24 h of reaction. This result means that a higher N-content, corresponding to materials with higher hydrophilic character, leads to higher conversions of H_2O_2 and lower removals of 4-NP.

Similar results were observed in the literature regarding the influence of N-content present in the CNTs, and the consequence in the pollutant and H_2O_2 conversions. In previous works, with the same 4-NP as pollutant, the catalysts were also synthesized using ethylene and acetonitrile, and it was also reported an inverse trend between 4-NP removal and hydrogen peroxide consumption for CNTs respect to the different N-contents⁵⁴. Another work using 2-NP as model pollutant for the CWPO also achieved higher hydrogen peroxide conversion and lower removal of the pollutant with the highest hydrophilic materials².

The fast decomposition of H_2O_2 leading to a lower conversion of the pollutant can be explained by secondary reactions, in this situation the hydrogen peroxide present lower efficiency in the formation of hydroxyl radicals (HO^\bullet), decreasing the rate of oxidation.

The analysis of TOC was performed with all materials, the samples were taken from the reaction media. The results are represented in Figure 14.

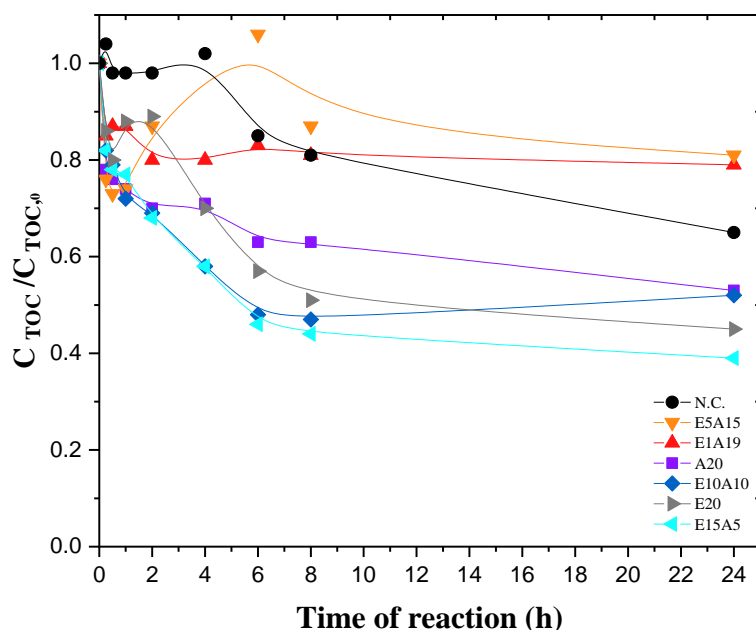


Figure 14. Normalized concentration of TOC along time under the operational conditions: $C_{4-NP,0} = 1$ g/L, $C_{H_2O_2,0} = 3.56$ g/L, $C_{cat} = 2.5$ g/L, $pH_0 = 3.5$ and $T = 80$ °C.

The graphic shows an appreciable conversion of TOC. N.C. data was a little strange with 35% of conversion, but it was expected, since in Figure 13A, the non-catalytic run had a little conversion of 4-NP after 24h.

From the catalysts, the better ones were E15A5 (61%), E20 (55%), E10A10 (48%), followed by A20 (47%), E1A19 (21%) and E5A15 (19%). Results that are also in agreement with

Figure 13A, since the catalysts that presented better conversions of the pollutant also reached higher mineralization results.

It can be concluded that CNTs with higher N-content and a lower lipophilicity had a rapid conversion of H_2O_2 because of its interactions that led to a lower degradation of the pollutant and mineralization. While the other catalysts, E20, E15A5, E10A10 showed a controllable consumption of hydrogen peroxide along the 24 hours carrying to an almost 100% of 4-NP oxidation for all the materials, and also better results of total organic carbon conversions.

Figure 15 depicts the liquids recovered after all the CWPO runs performed.

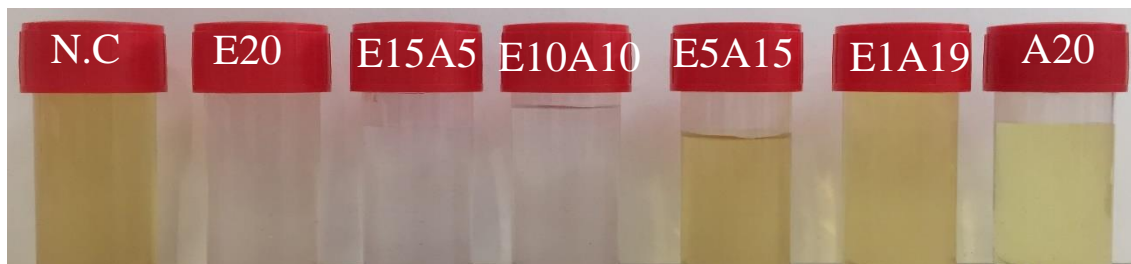


Figure 15. Reaction medium recovered after the CWPO runs in aqueous phase, upon removal of the catalysts N.C; E20; E15A5; E10A10; E5A15; E1A19; and A20.

As can be observed in Figure 15, there is a change of color in some of the treated solutions obtained at the end of the CWPO runs. Specifically, E20, E15A5 and E10A10 are capable of removing the color, since with these three materials removals up to 99% of the pollutant were obtained. As known, 4-NP has a yellow coloration in water, the color from the initial solution was very similar to N.C (a) medium recovered flask.

The others three liquids obtained with E5A15, E1A19 and A20 presents a slightly difference in the color when compared with the liquid obtained after the non-catalytic run, due to the slight removal of 4-NP, as represented in Figure 13A.

The concentration of the aromatic intermediate compounds upon reaction time observed in the CWPO runs with each catalyst is represented in Figure 16.

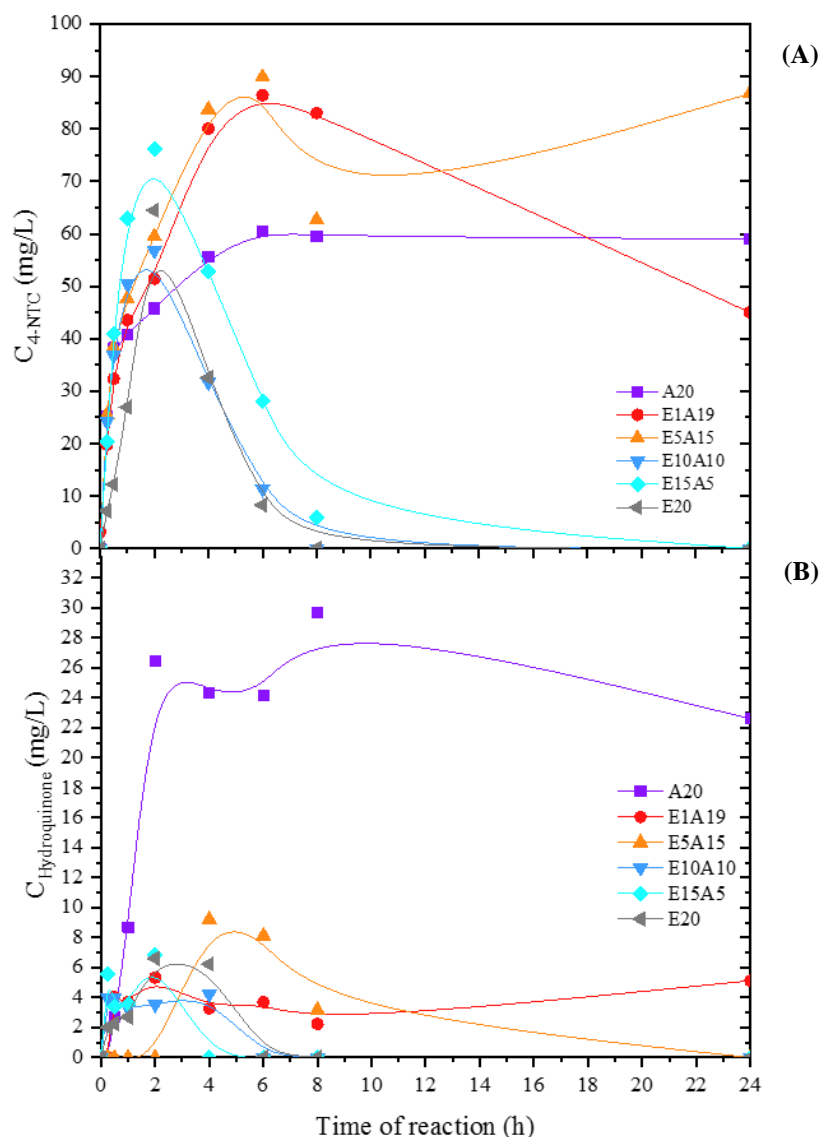


Figure 16. Concentration evolution of the reaction byproducts resulting from the CWPO of 4-NP, (A) 4-nitrocatechol and (B) hydroquinone. Operating conditions:

$$C_{4\text{-NP},0} = 1 \text{ g/L}, C_{\text{H}_2\text{O}_2,0} = 3.56 \text{ g/L}, C_{\text{cat}} = 2.5 \text{ g/L}, \text{pH}_0 = 3.5 \text{ and } T = 80 \text{ }^\circ\text{C}.$$

In the sequential degradation of the CWPO run in aqueous solution, it was noticed the formation of intermediates, such as 4-nitrocatechol (4-NTC) and hydroquinone. In Figure 16A is represented the concentration evolution of 4-NTC, whose concentration increases with all catalysts until 2 h of reaction. After that, the concentration of 4-NTC decreases achieving zero after 24 h of reaction with E20, E15A5 and E10A10, whereas the intermediate is still present at the aqueous medium at the same time with the others three catalysts: A20 (59.0 mg/L), E1A19 (45.0 mg/L) and E5A15 (86.7 mg/L).

The concentration of hydroquinone upon reaction time is shown in Figure 16B. The values of concentration are lower when compared with the values of 4-NTC. The concentration of hydroquinone with the three catalysts E20, E15A5 and E10A10 follows the same behavior as found for 4-NTC, the concentration increasing until 2 h of reaction and right after decreasing until the intermediate is totally degraded after 6 h of reaction. The catalyst A20 led to the highest concentration of hydroquinone (22.6 mg/L) still present in the reaction medium after 24 h of reaction. E5A15 and E1A19 led to obtain low concentrations of hydroquinone, while E1A19 finished the reaction after 24 h of reaction with 5.13 mg/L still present in the medium. With E5A15 a zero concentration of the intermediate was obtained.

Furthermore, the pH was measured after 24 h of CWPO, reaching values of 2.42, 2.34, 2.31, 2.65, 2.42 and 2.60 with E20, E15A5, E10A10, E5A15, E1A19 and A20, respectively. This was ascribed to the formation of carboxylic acid compounds (not identified) during the CWPO of 4-NP, as observed in other works. Some of the generated acids reported were oxalic, malic, acetic, formic, nitric, malonic and maleic.^{54,73} The materials with highest performance (E15A5 and E10A10) lead to the lowest pH (2.34 and 2.31, respectively) observed after 24 h, meaning that a high degree of oxidation was reached.

There are some previous works reported in the literature that analyze the removal of 4-NP by CWPO in aqueous solution with CNTs and other materials such as graphene-based and carbon black.^{54,60,73} All those works considered initial concentration of 4-NP of 5 g/L and operation conditions of pH = 3, T = 50 °C, C_{cat} = 2.5 g/L and the stoichiometric amount of H₂O₂ needed for the complete mineralization of 4-NP., which enables close comparisons with the results obtained in this work, even though these reports use different concentration and temperature. In the reported CWPO results performed with CNTs higher conversion of pollutant was also reached with the hydrophobic catalyst (E30 = 100%) while with the most hydrophilic (A30) only 9% of 4-NP was removed, and the decomposition of H₂O₂ very fast.⁵⁴ Graphene-based materials, at the same conditions reported for the CNTs, reached the highest 4-NP removal of 65% with rGOV (reduced graphene oxide with vitamin C).⁶⁰ And the work done with carbon black presented 95.9, 65.5 and 40.4% removals of the pollutant after 24 h of reaction time

with P-DCB, B-DCB and N-DCB, respectively materials (P-, B- and N- meaning P, B and N doped carbon blacks, respectively).⁷³

In Figure 17 is represented the concentration analyzed by UV-VIS of 4-NP and of aromatic intermediate compounds, to detect if the aromatics are formed from 4-NP or if they are formed from others intermediates that were detected or not.

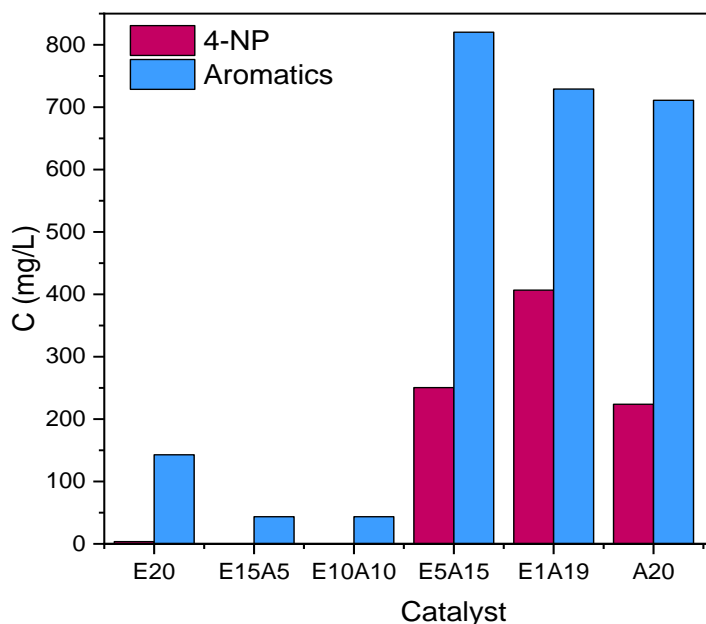


Figure 17. Concentration of 4-NP and aromatics after 24 h of reaction in CWPO runs performed in aqueous solution. Operating conditions: $C_{4-NP,0} = 1$ g/L, $C_{H_2O_2,0} = 3.56$ g/L, $C_{cat} = 2.5$ g/L, $pH_0 = 3.5$ and $T = 80$ °C.

The aromatics were measured in the aqueous system only in the final recovered medium, and the graph compare the concentrations of 4-NP and of aromatics after 24 h of reaction. It is possible to observe that for E20, E15A5 and E10A10 4-NP concentration is very low or even zero, and there is still presence of aromatics in the final medium that were not detected by HPLC (142.9, 43.59 and 43.59 mg/L, respectively). These aromatics at the end of reaction are not ascribed to the intermediates identified in Figure 16, since for all these three CNTs 4-NTC and hydroquinone presented a concentration of 0 mg/L at the end of reaction.

For E5A15, E1A19 and A20, there still presence of 4-NP in the system at the end of reaction, as also shown in

Figure 13B, but the concentration of aromatics is much higher than that of 4-NP, meaning that medium aromatic intermediates exist in the reaction medium, as already discussed in Figure 16. Concentration evolution of the reaction byproducts resulting from the CWPO of 4-NP, (A) 4-nitrocatechol and (B) hydroquinone. Operating conditions: $C_{4-NP,0} = 1$ g/L, $C_{H_2O_2,0} = 3.56$ g/L, $C_{cat} = 2.5$ g/L, $pH_0 = 3.5$ and $T = 80$ °C.. Although, the concentration of aromatics also presents a contribution from undetected intermediates (E5A15 = 482.98 mg/L, E1A19 = 215.23 mg/L and A20 = 405.83 mg/L) without the contribution of 4-NP, 4-NTC and hydroquinone.

4.2.3 Adsorption

In order to compare the removal achieved by adsorption and by CWPO, adsorption tests were performed at the same operating conditions than used in the CWPO run in aqueous medium, but in the absence of H_2O_2 ($C_{4-NP,0} = 1$ g/L, $C_{cat} = 2.5$ g/L, $pH_0 = 3.5$ and $T = 80$ °C). The results obtained for removal of 4-NP after 24 h in the adsorption tests, compared with the removals obtained in the aqueous CWPO process after 24 h, is exhibited in

Figure 18.

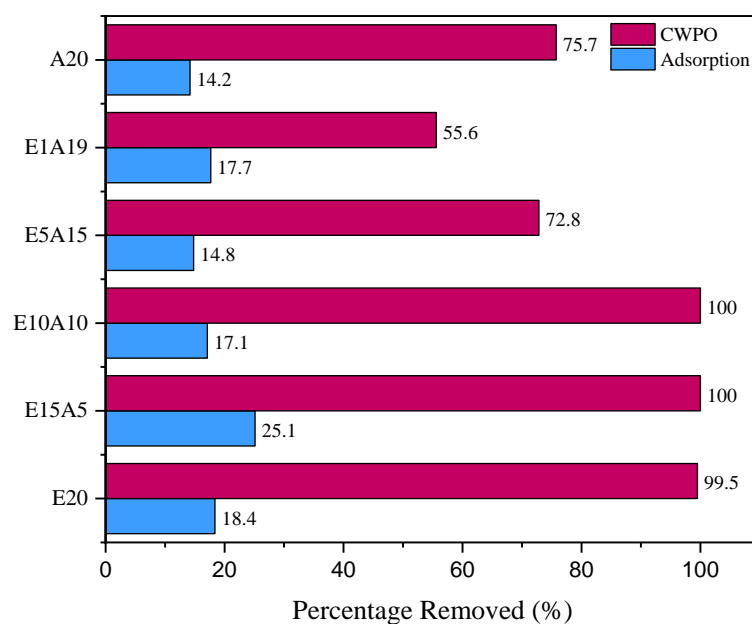


Figure 18. Comparison between the removals of 4-NP by CWPO in aqueous solution and adsorption after 24 h under the operating conditions: $C_{4-NP,0} = 1$ g/L, $C_{cat} = 2.5$ g/L, $pH_0 = 3.5$, $T = 80$ °C and $C_{H_2O_2,0} = 3.56$ g/L (CWPO runs).

The results for adsorption of 4-NP using the synthesized CNTs show that the pollutant is adsorbed on the CNTs, reaching removals from 14.2 until 25.1% after 24 h of contact time. On the other hand, removals of 4-NP higher than 55.6% are achieved by CWPO after 24 h of reaction.

Therefore, it is possible to discard the possibility of the 4-NP be being mostly adsorbed by the materials and not oxidized by CWPO, also confirmed with the decrease of the final pH's and the formation of intermediates for all synthesized CNT's.

4.2.4 Catalytic Wet Peroxide Oxidation (CWPO) in biphasic medium

The same CNTs tested in the CWPO of 4-NP in aqueous medium were evaluated in the CWPO of 4-NP in biphasic system (water/isooctane). Figure 19 shows the concentration of H_2O_2 and of 4-NP as a function of time of reaction.

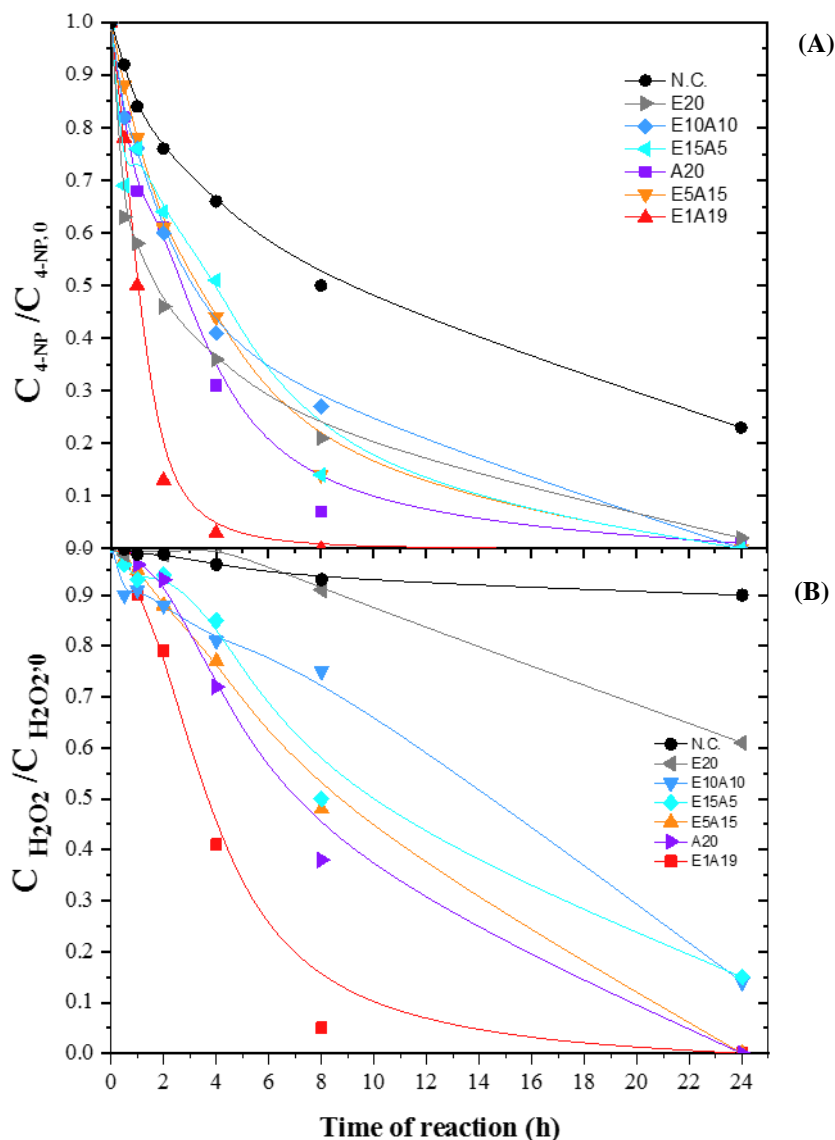


Figure 19. Normalized concentration of (A) 4-NP and of (B) H_2O_2 along time of reaction, under the operational conditions: $C_{4-NP, aqueous,0} = 1$ g/L, O/W = 5:45 (v/v), $C_{H_2O_2,0} = 3.56$ g/L, $C_{cat} = 2.5$ g/L, $pH_0 = 3.5$ and $T = 80$ °C.

A mixture of water and isooctane (O/W: 1:9 v/v) was chosen to model oily wastewater. The conversion of the pollutant 4-NP is presented in Figure 19A. It can be observed that the only synthesized materials that did not promote 100% conversion of the pollutant after 24 h of reaction is E20 (98%), E5A15 (99%) and A20 (99%). E1A19 shows the highest catalytic activity, with a 97% removal of 4-NP being achieved after 4 h of reaction, likely due to the faster consumption rate of H_2O_2 in comparison with the other materials. It is interesting to observe that the presence of two phases (oil and water)

delayed the hydrogen peroxide consumption and changed the behavior of the CWPO runs, the fast consumption of hydrogen peroxide led to a faster pollutant removal.

A hypothesis is that the catalysts are present in both phases forming the emulsions, leading to a lower contact with the aqueous phase when compared with the previously aqueous CWPO, which is located the hydrogen peroxide.

The consumption of H_2O_2 (Figure 19B) with the more hydrophilic materials (A20, E5A15 and E1A19) was faster than with the others (E15A5, E10A10 and E20). Total consumption of hydrogen peroxide was observed after 24 h of reaction with all hydrophilic materials, while with the more hydrophobic materials a longer time was needed to decrease the curve. As lower is the hydrophilicity of the material, lower is the consumption of hydrogen peroxide observed: E20, E15A5 and E10A10 allowed conversions of 39, 85 and 86%, respectively, after 24 h of reaction. In the non-catalytic run only 10% of total conversion of H_2O_2 was obtained.

The analysis of TOC for biphasic CWPO was performed with all materials and the results are represented in Figure 20.

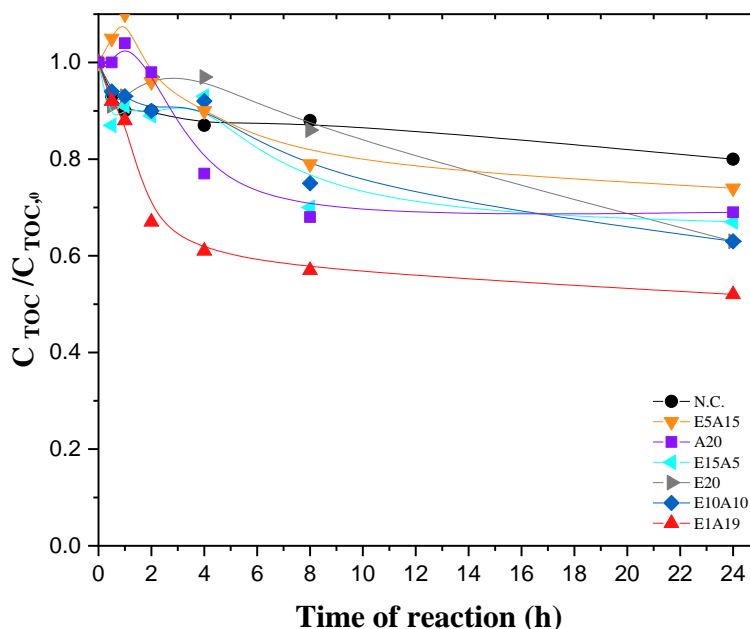


Figure 20. Normalized concentration of TOC along time of reaction, under the operational conditions: $C_{4-NP, \text{aqueous}, 0} = 1 \text{ g/L}$, $O/W = 5:45 \text{ (v/v)}$, $C_{H_2O_2, 0} = 3.56 \text{ g/L}$, $C_{\text{cat}} = 2.5 \text{ g/L}$, $\text{pH}_0 = 3.5$ and $T = 80 \text{ }^\circ\text{C}$.

The result for TOC runs presented values of conversion from 20% until 48%, the lowest conversion from non-catalytic run, and the highest from E1A19 catalyst. As seen in Figure 19 all materials were similar and up to 98% of 4-NP removal. It seems that the presence of an oily phase decreased the rapid consumption of hydrogen peroxide, and lead to a greater pollutant removal for all the materials. This provided a controllable reaction and similar results from the CNTs for H₂O₂ consumption, 4-NP removal and mineralization. After E1A19 with a highest total organic carbon conversion E10A10 and E20 presented 37% of mineralization, followed by E15A5 (33%), A20 (31%) and E5A15 (26%).

In Figure 21 is represented the effluents recovered at the end of the biphasic CWPO experiments. As observed, the change of the color in the system is evident in the non-catalytic reaction compared to the others. The strong yellow color disappeared, but the effluents still present a yellow aspect. In the picture the most translucent samples are E15A5, E10A10 and E1A19.



Figure 21. Reaction medium recovered after at the end of the biphasic CWPO runs, upon removal of the catalysts N.C; E20; E15A5; E10A10; E5A15; E1A19; A20, respectively.

The only intermediate detected by HPLC during the biphasic CWPO runs in the medium of reaction was 4-nitrocatechol (4-NTC). The concentration of this oxidized intermediate compound along reaction time is depicted in Figure 22.

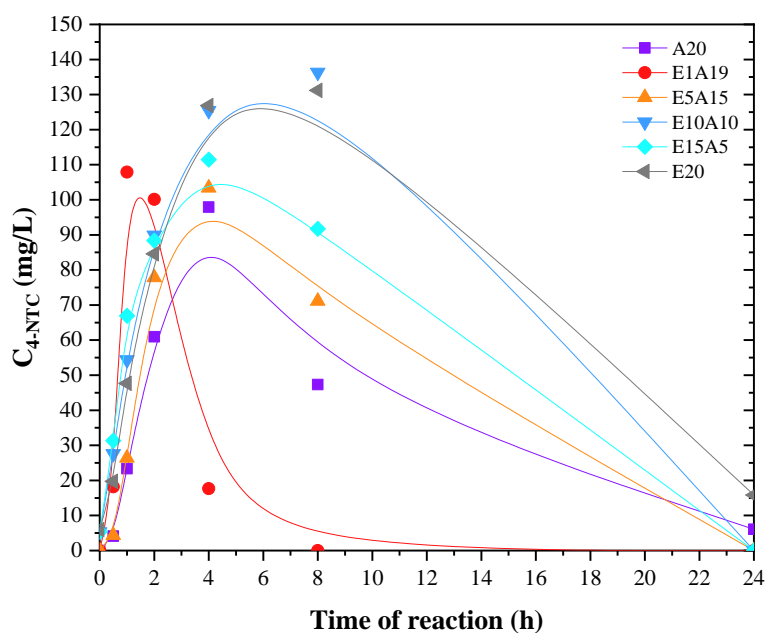


Figure 22. 4-NTC concentration (mg/L) in biphasic medium along time under the operational conditions: $C_{4-NP, aqueous,0} = 1$ g/L, O/W = 5:45 (v/v), $C_{H_2O_2,0} = 3.56$ g/L, $C_{cat} = 2.5$ g/L, pH₀ 3.5 and T = 80 °C.

4-NTC was detected in the medium of reaction of the biphasic CWPO with all CNTs. E1A19 led to the fastest formation and consumption. With E20 and E10A10 the highest concentration of 4-NTC were obtained (131.19 and 136.36 mg/L, respectively) after 8 h of reaction. Furthermore, all Janus structured CNTs (E15A5, E10A10, E15A5 and E1A19) allow to obtain a complete removal of 4-NTC after 24 h of reaction, while A20 and E20 are not able to degrade 4-NTC in 24 h, a concentration of 6,07 and 15.83 mg/L, respectively, being obtained at this time of reaction.

The pH value of the aqueous phase recovered from the biphasic CWPO experiments was observed to decrease during the reaction runs, reaching values of 2.57, 2.42, 2.38, 2.45, 2.57 and 2.44 with E20, E15A5, E10A10, E5A15, E1A19 and A20, respectively. This decrease is likely due to the formation of carboxylic acid groups as intermediates compounds during the biphasic CWPO of 4-NP runs.

In Figure 23 is shown the concentration of the aromatics along 24 h of reaction.

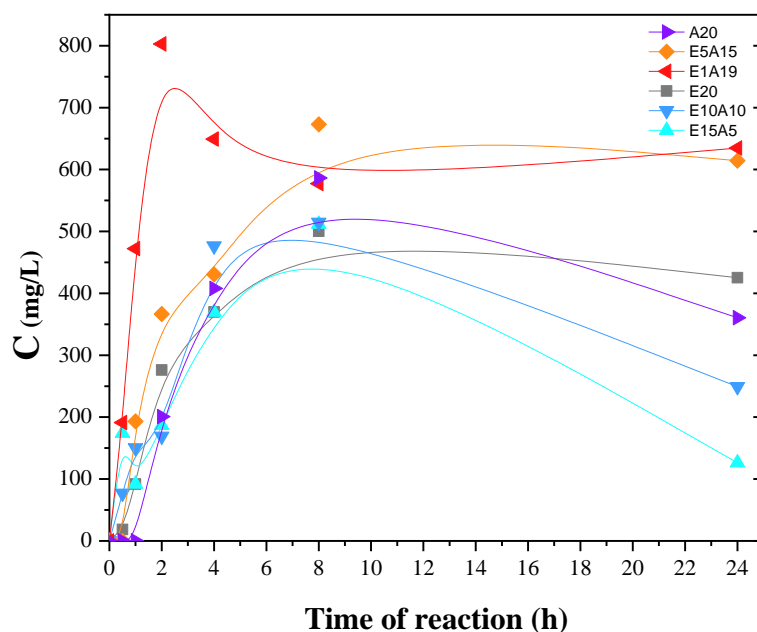


Figure 23. Concentration of aromatics along time in biphasic CWPO runs. Operational conditions: $C_{4-NP, aqueous,0} = 1$ g/L, O/W = 5:45 (v/v), $C_{H_2O_2,0} = 3.56$ g/L, $C_{cat} = 2.5$ g/L, pH₀ 3.5 and T = 80 °C.

The biphasic CWPO was performed with all aliquots taken from the flask and the aromaticity was calculated along 24 h. The results above are concentration of aromatics without the concentration of 4-NP, so the results are only of aromatic intermediates formed in the reaction medium, this includes 4-NTC.

As it can be observed, all CNTs lead to an increase in the concentration of aromatics, complementing Figure 22 regarding the formation of 4-NTC in the biphasic CWPO runs. It can thus be stated that, in addition to 4-NTC, there is other aromatic intermediates not detected by HPLC, and even after 24 h their concentration is still significant reaching values of 425.27, 126.34, 249.10, 614.28, 634.70 and 360.48 mg/L with E20, E15A5, E10A10, E5A15, E1A19 and A20, respectively.

CONCLUSION AND FUTURE RESEARCH

5 Conclusions

Advance treatment of wastewater containing 4-nitrophenol is viable by CWPO with the carbon nanotubes catalyst prepared with two precursors ethylene and acetonitrile forming structures undoped and n-doped, respectively, known as Janus particles. The CWPO runs in aqueous solutions done with more hydrophilic catalysts leads to less than 80% of pollutant removal within 24 h of reaction, because of the faster consumption of H_2O_2 within 2 h that almost reach 100% of conversion. The other CNTs more hydrophobic presented controllable consumption of hydrogen peroxide that influenced a better oxidation of 4-NP, reaching 100% of pollutant removal for E15A5 and E10A10 and 99% for E20, studied at the same operation conditions of $T = 80\text{ }^\circ\text{C}$, $C_{\text{H}_2\text{O}_2,0} = 3.56\text{ g/L}$, $C_{\text{cat}} = 2.5\text{ g/L}$, pH 3.5 and $C_{4\text{-NP}} = 1\text{ g/L}$.

On the other way, with the presence of two phases isooctane (oil) and water as the biphasic medium of CWPO, the results were different. The presence of an oily phase decreased the fast consumption of H_2O_2 for hydrophilic CNTs and all the materials presented similar curves and conversions. The catalyst with the lowest catalytic activity was E20, since it led to obtain only 39% of H_2O_2 conversion, while the other catalysts allow to obtain conversion values higher than 80% of hydrogen peroxide. Regarding the conversion of pollutant, all catalysts show a high catalytic activity, removals of 4-NP of 100% for E15A5, E10A10 and E1A19, 99% for E5A15 and A20 and 98% for E20 were obtained after 24 h of reaction.

The two materials that reached the lower values of pH and aromaticity were E15A5 and E10A10, and because of that it is possible to conclude that these two catalysts presented a higher formation of carboxylic acids. In addition, adsorption runs showed a maximum contribution in the removal of the pollutant 4-NP between 14 and 26%, evidencing that the removal of the pollutant by CWPO is mainly due to the oxidation, instead of adsorption.

To conclude, Janus structures E15A5 and E10A10 presented better performance in aqueous and biphasic CWPO. In biphasic oxidation that was ascribed to the fact that these materials were able to form Pickering emulsions.

6 Future Research

The carbon nanotubes were synthesized with two precursors, ethylene and/or acetonitrile to be used as catalysts in two different CWPOs, first only in aqueous phase and the second one with two phases (oil and water). In this context, all prepared CNTs present catalytic activity in both CWPOs aqueous and biphasic of 4-NP. It would be interesting for future works evaluate other volume fractions of oil and water, and if this condition affects the performance of the materials, for example a higher volume of oil in mixture with water. In addition, another research would be focus on the use of real oily wastewater to evaluate the performance of the Janus structure materials in the selective oxidation of pollutants with nitrogen.

REFERENCES

REFERENCES

1. Yu, L., Han, M. & He, F. A review of treating oily wastewater. *Arab. J. Chem.* **10**, S1913–S1922 (2017) . doi:10.1016/j.arabjc.2013.07.020.
2. Diaz de Tuesta, J. L. *et al.* Janus amphiphilic carbon nanotubes as Pickering interfacial catalysts for the treatment of oily wastewater by selective oxidation with hydrogen peroxide. *Catal. Today* **356**, 205–215 (2020) . doi:10.1016/j.cattod.2019.07.012.
3. T., R., Heydari, A. & Henni, A. State of the Art Treatment of Produced Water. in *Water Treatment* 199–222 (InTech, 2013). . doi:10.5772/53478.
4. Rosa, J. J. da & Rubio, J. TRATAMENTO DE EFLUENTES OLEOSOS POR FLOCULAÇÃO PNEUMÁTICA EM LINHA E SEPARAÇÃO POR FLOTAÇÃO - PROCESSO FF. *Doutorado UFRGS* (Universidade Federal do Rio Grande do Sul, 2002).
5. Silva, P. K. L. da, Neto, A. A. D. & Melo, J. L. de S. REMOÇÃO DE ÓLEO DA ÁGUA DE PRODUÇÃO POR FLOTAÇÃO EM COLUNA UTILIZANDO TENSOATIVOS DE ORIGEM VEGETAL. *Mestrado UFRN* (Universidade Federal do Rio Grande do Norte, 2008).
6. Gobbi, L. C. A. & Porto, P. S. da S. TRATAMENTO DE ÁGUA OLEOSA POR ELETROFLOCULAÇÃO. *Mestrado UFES* (Universidade Federal do Espírito Santo, 2013).
7. Stephenson, M. T. A Survey of Produced Water Studies. in *Produced Water. Technological/Environmental Issues and Solutions*. 1–11 (: J.P. Ray and F.R. Engelhardt, Eds., 1992). . doi:10.1007/978-1-4615-2902-6_1.
8. da Silva, L. J., Alves, F. C. & de França, F. P. A review of the technological solutions for the treatment of oily sludges from petroleum refineries. *Waste Manag. Res. J. a Sustain. Circ. Econ.* **30**, 1016–1030 (2012) . doi:10.1177/0734242X12448517.
9. Khatri, J., Nidheesh, P. V., Anantha Singh, T. S. & Suresh Kumar, M. Advanced oxidation processes based on zero-valent aluminium for treating textile wastewater. *Chem. Eng. J.* **348**, 67–73 (2018) . doi:10.1016/j.cej.2018.04.074.

10. Mrayyan, B. & Battikhi, M. N. Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge. *J. Hazard. Mater.* **120**, 127–134 (2005) . doi:10.1016/j.jhazmat.2004.12.033.
11. Reddy, M. V., Devi, M. P., Chandrasekhar, K., Goud, R. K. & Mohan, S. V. Aerobic remediation of petroleum sludge through soil supplementation: Microbial community analysis. *J. Hazard. Mater.* **197**, 80–87 (2011) . doi:10.1016/j.jhazmat.2011.09.061.
12. Oliveira, A. A. S. *et al.* Biphasic oxidation reactions promoted by amphiphilic catalysts based on red mud residue. *Appl. Catal. B Environ.* **144**, 144–151 (2014) . doi:10.1016/j.apcatb.2013.07.015.
13. United Nations; Department of Economic and Social Affairs. *World population prospects 2019: Highlights. United Nations* <http://www.ncbi.nlm.nih.gov/pubmed/12283219> (2019).
14. Bley, S. J. *et al.* *Assessing Sustainable Development in the European Union: Monitoring report on progress towards the SDGs in an EU context. eurostat Statistical books 2020 edition* (Luxembourg: Publications Office of the European Union, 2020). . doi:10.2785/555257.
15. von der Leyen, U. *A Union that strives for more: My agenda for Europe.* (2019).
16. Santo, C. M. E. *A INDÚSTRIA DE REFINAÇÃO DE PETRÓLEO Características e Tratamento das Águas Residuais. Laboratory of Separation and Reaction Engineering - LSRE. Universidade do Porto.*
17. Hui, L., Yan, W., Juan, W. & Zhongming, L. A Review: Recent Advances in Oily Wastewater Treatment. *Recent Innov. Chem. Eng. (Formerly Recent Patents Chem. Eng.* **7**, 17–24 (2015) . doi:10.2174/2211334707666140415222545.
18. The European Parliament and the Council of the European Union. *Directives of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official Journal of the European Union* vol. 2013 (2013).
19. The European Parliament and the Council of the European Union. *DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23*

- October 2000 establishing a framework for Community action in the field of water policy. Official Journal of the European Communities* vol. 168 (2000).
20. Ministério do Ambiente. *Decreto Lei nº 236/98. Diário da Republica - I Série -A* vol. 176 (1998).
 21. Abraham, M. H., Du, C. M. & Platts, J. A. Lipophilicity of the Nitrophenols. *J. Org. Chem.* **65**, 7114–7118 (2000) . doi:10.1021/jo000840w.
 22. Igunnu, E. T. & Chen, G. Z. Produced water treatment technologies. *Int. J. Low-Carbon Technol.* **9**, 157–177 (2014) . doi:10.1093/ijlct/cts049.
 23. Padaki, M. *et al.* Membrane technology enhancement in oil–water separation. A review. *Desalination* **357**, 197–207 (2015) . doi:10.1016/j.desal.2014.11.023.
 24. Kriipsalu, M., Marques, M. & Maastik, A. Characterization of oily sludge from a wastewater treatment plant flocculation-flotation unit in a petroleum refinery and its treatment implications. *J. Mater. Cycles Waste Manag.* **10**, 79–86 (2008) . doi:10.1007/s10163-007-0188-7.
 25. Agency for Toxic Substances and Disease Registry U.S. Public Health Service. *Toxicological Profile For Nitrophenols: 2-NITROPHENOL, 4-NITROPHENOL.* (1992).
 26. Zheng, T. *et al.* Separation of Pollutants from Oil-Containing Restaurant Wastewater by Novel Microbubble Air Flotation and Traditional Dissolved Air Flotation. *Sep. Sci. Technol.* **50**, 2568–2577 (2015) . doi:10.1080/01496395.2015.1062396.
 27. Al-Shamrani, A. ., James, A. & Xiao, H. Separation of oil from water by dissolved air flotation. *Colloids Surfaces A Physicochem. Eng. Asp.* **209**, 15–26 (2002) . doi:10.1016/S0927-7757(02)00208-X.
 28. Hami, M. L., Al-Hashimi, M. A. & Al-Doori, M. M. Effect of activated carbon on BOD and COD removal in a dissolved air flotation unit treating refinery wastewater. *Desalination* **216**, 116–122 (2007) . doi:10.1016/j.desal.2007.01.003.
 29. Fakhru'l-Razi, A. *et al.* Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.* **170**, 530–551 (2009) .

doi:10.1016/j.jhazmat.2009.05.044.

30. Ibrahim, S., Ang, H.-M. & Wang, S. Adsorptive separation of emulsified oil in wastewater using biosorbents. *Asia-Pacific J. Chem. Eng.* **7**, S216–S221 (2012) . doi:10.1002/apj.506.
31. Gupta, V. K. & Suhas. Application of low-cost adsorbents for dye removal – A review. *J. Environ. Manage.* **90**, 2313–2342 (2009) . doi:10.1016/j.jenvman.2008.11.017.
32. Ikhsan, S. N. W., Yusof, N. ;, Aziz, F. & Misdan, N. A REVIEW OF OILFIELD WASTEWATER TREATMENT USING MEMBRANE FILTRATION OVER CONVENTIONAL TECHNOLOGY. *Malaysian J. Anal. Sci.* **21**, 643–658 (2017) . doi:10.17576/mjas-2017-2103-14.
33. Shi, Y., Fan, M., Brown, R. C., Sung, S. & Van Leeuwen, J. Comparison of corrosivity of polymeric sulfate ferric and ferric chloride as coagulants in water treatment. *Chem. Eng. Process. Process Intensif.* **43**, 955–964 (2004) . doi:10.1016/j.cep.2003.09.001.
34. Abbasi, M., Sebzari, M. R. & Mohammadi, T. Effect of Metallic Coagulant Agents on Oily Wastewater Treatment Performance using Mullite Ceramic MF Membranes. *Sep. Sci. Technol.* **47**, 2290–2298 (2012) . doi:10.1080/01496395.2012.665974.
35. Zeng, Y., Yang, C., Zhang, J. & Pu, W. Feasibility investigation of oily wastewater treatment by combination of zinc and PAM in coagulation/flocculation. *J. Hazard. Mater.* **147**, 991–996 (2007) . doi:10.1016/j.jhazmat.2007.01.129.
36. Cui, J., Zhang, X., Liu, H., Liu, S. & Yeung, K. L. Preparation and application of zeolite/ceramic microfiltration membranes for treatment of oil contaminated water. *J. Memb. Sci.* **325**, 420–426 (2008) . doi:10.1016/j.memsci.2008.08.015.
37. Hua, F. L. *et al.* Performance study of ceramic microfiltration membrane for oily wastewater treatment. *Chem. Eng. J.* **128**, 169–175 (2007) . doi:10.1016/j.cej.2006.10.017.
38. Li, Y. S., Yan, L., Xiang, C. B. & Hong, L. J. Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes. *Desalination*

- 196**, 76–83 (2006) . doi:10.1016/j.desal.2005.11.021.
39. Chen, G. *et al.* Nitrogen, sulfur, chlorine containing pollutants releasing characteristics during pyrolysis and combustion of oily sludge. *Fuel* **273**, 1–14 (2020) . doi:10.1016/j.fuel.2020.117772.
 40. Jasmine, J. & Mukherji, S. Characterization of oily sludge from a refinery and biodegradability assessment using various hydrocarbon degrading strains and reconstituted consortia. *J. Environ. Manage.* **149**, 118–125 (2015) . doi:10.1016/j.jenvman.2014.10.007.
 41. Hu, G., Li, J. & Zeng, G. Recent development in the treatment of oily sludge from petroleum industry: A review. *J. Hazard. Mater.* **261**, 470–490 (2013) . doi:10.1016/j.jhazmat.2013.07.069.
 42. Diaz de Tuesta, J. L., Silva, A. M. T., Faria, J. L. & Gomes, H. T. Removal of Sudan IV from a simulated biphasic oily wastewater by using lipophilic carbon adsorbents. *Chem. Eng. J.* **347**, 963–971 (2018) . doi:10.1016/j.cej.2018.04.105.
 43. Boczkaj, G., Fernandes, A. & Makoś, P. Study of Different Advanced Oxidation Processes for Wastewater Treatment from Petroleum Bitumen Production at Basic pH. *Ind. Eng. Chem. Res.* **56**, 8806–8814 (2017) . doi:10.1021/acs.iecr.7b01507.
 44. Pinho, M. T., Gomes, H. T., Ribeiro, R. S., Faria, J. L. & Silva, A. M. T. Carbon nanotubes as catalysts for catalytic wet peroxide oxidation of highly concentrated phenol solutions: towards process intensification. *Appl. Catal. B Environ.* **165**, 706–714 (2015) . doi:10.1016/j.apcatb.2014.10.057.
 45. Babuponnusami, A. & Muthukumar, K. A review on Fenton and improvements to the Fenton process for wastewater treatment. *J. Environ. Chem. Eng.* **2**, 557–572 (2014) . doi:10.1016/j.jece.2013.10.011.
 46. Ribeiro, A. R., Nunes, O. C., Pereira, M. F. R. & Silva, A. M. T. 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**, 33–51 (2015) . doi:10.1016/j.envint.2014.10.027.
 47. Bethi, B., Sonawane, S. H., Bhanvase, B. A. & Gumfekar, S. P. Nanomaterials-based advanced oxidation processes for wastewater treatment: A review. *Chem.*

- Eng. Process. - Process Intensif.* **109**, 178–189 (2016) .
doi:10.1016/j.cep.2016.08.016.
48. Wang, N., Zheng, T., Zhang, G. & Wang, P. A review on Fenton-like processes for organic wastewater treatment. *J. Environ. Chem. Eng.* **4**, 762–787 (2016) .
doi:10.1016/j.jece.2015.12.016.
 49. Rodrigues, C. S. D., Borges, R. A. C., Lima, V. N. & Madeira, L. M. p-Nitrophenol degradation by Fenton's oxidation in a bubble column reactor. *J. Environ. Manage.* **206**, 774–785 (2018) . doi:10.1016/j.jenvman.2017.11.032.
 50. Zhou, L. *et al.* Electro-Fenton degradation of p-nitrophenol using the anodized graphite felts. *Chem. Eng. J.* **233**, 185–192 (2013) . doi:10.1016/j.cej.2013.08.044.
 51. Zhou, L., Zhou, M., Hu, Z., Bi, Z. & Serrano, K. G. Chemically modified graphite felt as an efficient cathode in electro-Fenton for p-nitrophenol degradation. *Electrochim. Acta* **140**, 376–383 (2014) . doi:10.1016/j.electacta.2014.04.090.
 52. Pradhan, A. A. & Gogate, P. R. Degradation of p-nitrophenol using acoustic cavitation and Fenton chemistry. *J. Hazard. Mater.* **173**, 517–522 (2010) .
doi:10.1016/j.jhazmat.2009.08.115.
 53. Soon, A. N. & Hameed, B. H. Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process. *Desalination* **269**, 1–16 (2011) . doi:10.1016/j.desal.2010.11.002.
 54. Martin-Martinez, M. *et al.* Role of Nitrogen Doping on the Performance of Carbon Nanotube Catalysts: A Catalytic Wet Peroxide Oxidation Application. *ChemCatChem* **8**, 2068–2078 (2016) . doi:10.1002/cctc.201600123.
 55. Rueda Márquez, J., Levchuk, I. & Sillanpää, M. Application of Catalytic Wet Peroxide Oxidation for Industrial and Urban Wastewater Treatment: A Review. *Catalysts* **8**, 673 (2018) . doi:10.3390/catal8120673.
 56. Domínguez, C. M., Quintanilla, A., Casas, J. A. & Rodríguez, J. J. Treatment of real winery wastewater by wet oxidation at mild temperature. *Sep. Purif. Technol.* **129**, 121–128 (2014) . doi:10.1016/j.seppur.2014.04.003.
 57. De Rosa, S. *et al.* Chemical Pretreatment of Olive Oil Mill Wastewater Using a

- Metal-Organic Framework Catalyst. *J. Agric. Food Chem.* **53**, 8306–8309 (2005) . doi:10.1021/jf0512609.
58. Rueda-Márquez, J. J., Levchuk, I., Salcedo, I., Acevedo-Merino, A. & Manzano, M. A. Post-treatment of refinery wastewater effluent using a combination of AOPs (H₂O₂ photolysis and catalytic wet peroxide oxidation) for possible water reuse. Comparison of low and medium pressure lamp performance. *Water Res.* **91**, 86–96 (2016) . doi:10.1016/j.watres.2015.12.051.
59. Martin-Martinez, M. *et al.* Carbon nanotubes as catalysts for wet peroxide oxidation: The effect of surface chemistry. *Catal. Today* **357**, 332–340 (2020) . doi:10.1016/j.cattod.2019.03.014.
60. Ribeiro, R. S. *et al.* Graphene-based materials for the catalytic wet peroxide oxidation of highly concentrated 4-nitrophenol solutions. *Catal. Today* **249**, 204–212 (2015) . doi:10.1016/j.cattod.2014.10.004.
61. Martin-Martinez, M. *et al.* Lignin-based activated carbons as metal-free catalysts for the oxidative degradation of 4-nitrophenol in aqueous solution. *Appl. Catal. B Environ.* **219**, 372–378 (2017) . doi:10.1016/j.apcatb.2017.07.065.
62. Lorençon, E., Ferreira, D. C., Resende, R. R. & Krambrock, K. Amphiphilic gold nanoparticles supported on carbon nanotubes: Catalysts for the oxidation of lipophilic compounds by wet peroxide in biphasic systems. *Appl. Catal. A Gen.* **505**, 566–574 (2015) . doi:10.1016/j.apcata.2015.05.016.
63. Purohit, R., Purohit, K., Rana, S., Rana, R. S. & Patel, V. Carbon Nanotubes and Their Growth Methods. *Procedia Mater. Sci.* **6**, 716–728 (2014) . doi:10.1016/j.mspro.2014.07.088.
64. Hiremath, N. & Bhat, G. High-performance carbon nanofibers and nanotubes. in *Structure and Properties of High-Performance Fibers* 79–109 (Elsevier, 2017). . doi:10.1016/B978-0-08-100550-7.00004-8.
65. Prasek, J. *et al.* Methods for carbon nanotubes synthesis—review. *J. Mater. Chem.* **21**, 15872–15884 (2011) . doi:10.1039/c1jm12254a.
66. Purceno, A. D. *et al.* Magnetic amphiphilic hybrid carbon nanotubes containing N-doped and undoped sections: powerful tensioactive nanostructures. *Nanoscale* **7**,

- 294–300 (2015) . doi:10.1039/C4NR04005H.
67. Oliveira, A. A. da S. & Moura, F. C. C. Compósitos Anfifílicos Magnéticos contendo ferro e carbono: Síntese , Caracterização e Aplicações. (Universidade Federal de Minas Gerais, 2014).
 68. Perro, A., Reculosa, S., Ravaine, S., Bourgeat-Lami, E. & Duguet, E. Design and synthesis of Janus micro- and nanoparticles. *J. Mater. Chem.* **15**, 3745–3760 (2005) . doi:10.1039/b505099e.
 69. Karimi, M. *et al.* CO₂ Capture in Chemically and Thermally Modified Activated Carbons Using Breakthrough Measurements: Experimental and Modeling Study. *Ind. Eng. Chem. Res.* **57**, 11154–11166 (2018) . doi:10.1021/acs.iecr.8b00953.
 70. Thommes, M. *et al.* Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **87**, 1051–1069 (2015) . doi:10.1515/pac-2014-1117.
 71. Masso, C. M., Gomes, H. T., Pietrobelli, J. M. T. & Tuesta, J. L. D. De. Valorization of compost in the production of carbon-based materials for the treatment of contaminated wastewater. *Mestrado IPB* (Instituto Politécnico de Bragança, 2018).
 72. Abraham, M. H. ., Chadha, H. S. ., Whiting, G. S. . & Mitchell, R. C. Hydrogen Bonding. 32. An Analysis of Water-Octanol and Water-Alkane Partitioning and the $\Delta \log P$ Parameter of Seiler. *J. Pharm. Sci.* **83**, 1085–1100 (1994) . doi:10.1002/jps.2600830806.
 73. Diaz de Tuesta, J. L. *et al.* The pH effect on the kinetics of 4-nitrophenol removal by CWPO with doped carbon black catalysts. *Catal. Today* **356**, 216–225 (2020) . doi:10.1016/j.cattod.2019.08.033.
 74. Mansor, N. B. A., Tessonier, J. P., Rinaldi, A., Reiche, S. & Kutty, M. G. Chemically modified multi-walled carbon nanotubes (MWCNTs) with anchored acidic groups. *Sains Malaysiana* **41**, 603–609 (2012).
 75. Yudianti, R. Analysis of Functional Group Sited on Multi-Wall Carbon Nanotube Surface. *Open Mater. Sci. J.* **5**, 242–247 (2011) . doi:10.2174/1874088X01105010242.

76. Baykal, A. *et al.* Acid Functionalized Multiwall Carbon Nanotube/Magnetite (MWCNT)-COOH/Fe₃O₄ Hybrid: Synthesis, Characterization and Conductivity Evaluation. *J. Inorg. Organomet. Polym. Mater.* **23**, 726–735 (2013) . doi:10.1007/s10904-013-9839-4.
77. Okolo, C., Rafique, R., Iqbal, S. S., Saharudin, M. S. & Inam, F. Carbon Nanotube Reinforced High Density Polyethylene Materials for Offshore Sheathing Applications. *Molecules* **25**, 2960 (2020) . doi:10.3390/molecules25132960.
78. Liao, L. & Pan, C. Enhanced Electrochemical Capacitance of Nitrogen-Doped Carbon Nanotubes Synthesized from Amine Flames. *Soft Nanosci. Lett.* **1**, 16–23 (2011) . doi:10.4236/snsl.2011.11004.
79. Teng, L. & Tang, T. IR study on surface chemical properties of catalytic grown carbon nanotubes and nanofibers. *J. Zhejiang Univ. A* **9**, 720–726 (2008) . doi:10.1631/jzus.A071503.