Universidade de Aveiro Departamento de Ambiente e Ordenamento
Ano 2019

Mohammadreza Kamali

Tratamento de águas residuais industriais com nanomateriais sintetizados para um ambiente sustentável

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Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Ciências e Engenharia do Ambiente, realizada sob a orientação científica da Doutora Maria Isabel Capela, Professora Associada do Departamento de Ambiente e Ordenamento da Universidade de Aveiro, e co-orientação da Doutora Maria Elisabete Jorge Vieira da Costa, Professora Auxiliar do Departamento de Engenharia de Materiais e Cerâmica da Universidade de Aveiro

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palavras-chave

Efluentes industriais, Tecnologias de tratamento, nanomateriais projetados, Sustentabilidade

resumo

A qualidade dos efluentes finais de atividades industriais tem sido, ao longo de várias décadas, objeto de esforços significativos para melhorar o desempenho dos seus métodos de tratamento, seja por via físico-química, biológica ou uma combinação destes. Entre as tecnologias emergentes, o recurso a nanomateriais sintetizados (ENMs) tem sido alvo de especial atenção nos últimos anos. A presente tese teve como objetivo realizar estudos experimentais, levantamentos de informação e revisões críticas, a fim de sintetizar nanomateriais sustentáveis para o tratamento de poluentes recalcitrantes existentes em efluentes industriais. Paralelamente, a sustentabilidade de outros métodos biológicos e físico-químicos foi avaliada criticamente, tendo-se sugerido os métodos de tratamento mais sustentáveis para serem adotados pelas indústrias. Foi demonstrado nesta tese que o recurso à abordagem de Tagguchi pode auxiliar consideravelmente no controlo das propriedades de partículas nanométricas à base de ferro, sintetizadas por um processo de redução em fase líquida. O estudo deste sistema revelou que tanto a razão (agente redutor/ Fe^{3+}) como a concentração de Fe3+ são os parâmetros que determinam características críticas dos precipitados, incluindo a sua composição de fases cristalinas, grau de cristalinidade e área superficial específica. As nanopartículas de ferro de valência zero com propriedades melhoradas, sintetizadas pela utilização de irradiação por ultrasons, foram testadas com sucesso para degradar corantes orgânicos (azul de metileno como corante modelo) que são compostos dominantes nas águas residuais de algumas indústrias, designadamente de fábricas de têxteis. A recuperação dos nanomateriais após a sua aplicação em tratamentos de efluentes também é um dos aspectos mais importantes a ter em consideração na seleção e síntese de nanomateriais sustentáveis para aplicações ambientais. Um novo nanocompósito de ZnO/Fe_3O_4 sobre Bentonite, produzido neste trabalho, revelou uma capacidade aceitável para decomposição fotocatalítica do 2,4 diclorofenol, além da capacidade de ser recuperado após utilização. Testaram-se também nanocompósitos magnéticos na degradação de AOXs de efluentes da indústria do papel e celulose que evidenciaram um desempenho aceitável nessas aplicações. Definiu-se também nesta tese um contexto para a avaliação da sustentabilidade das melhores tecnologias disponíveis para lidar com efluentes industriais, tendo-se revelado a eficiência dos métodos de tratamento biológico para lidar com efluentes industriais, embora com alguma limitação para lidar com efluentes industriais fenólicos. Com um processo de aclimatação preciso, conseguiu-se uma eficiência muito elevada para a biodegradação do fenol, com alto grau de resistência ao choque da concentração inicial de fenol, utilizando-se o processo de lamas ativadas. Mediante uma revisão crítica da literatura, e como perspectivas de futuro a extrair do presente trabalho, aponta-se a possibilidade de integrar nanomateriais sintetizados e tratamento biológico nas tecnologias de membrana, para superar as barreiras actualmente existentes ao rápido desenvolvimento das tecnologias de membrana para o tratamento industrial efluentes.

palavras-chave Industrial effluents, Treatment technologies, Engineered nanomaterials, Sustainability

resumo

Quality of the final discharged effluents from industrial activities has been the subject of significant efforts over several decades to improve the performance of the methods applied for their treatment, either by physico-chemical, biological, or a combination of these processes. Among the emerging technologies, the application of various types of engineered nanomaterials (ENMs) has gained a particular attention in recent years. The present thesis aimed to carry out either experimental studies, surveys and critical reviews in order to synthesize the most sustainable nanomaterials for the treatment of recalcitrant pollutants from the content of industrial effluents. In parallel, the sustainability of other biological and physicochemical methods has been critically assessed and the most sustainable treatment methods have been suggested to be adopted by the industries. It was demonstrated in this thesis that the application of Tagguchi approach can considerably aid to control the properties of iron-based nanoscale particles synthesized by a liquid-phase reduction process. Working with this system revealed that both the (reductant/Fe^{3+}) ratio, (R), and the Fe^{3+}concentration, [Fe_3^+], are the parameters that determine critical characteristics including particle crystalline phase composition, crystallinity and surface area although R has been revealed as the most important one. Nano zero valent iron particles with enhanced properties, synthesized by utilization of ultrasonic irradiation, was successfully tested to degrade organic dyes (methylene blue, as a case study) which are dominant in the wastewater from some industries such as textile factories. Recovery of the nanomaterials after being applied for the treatment purposes is also among the most important parameters for the selection and synthesis of the most sustainable nanomaterials for environmental applications. A novel ZnO/Fe_3O_4 on Bentonite nanocomposite prepared in this thesis showed acceptable photocatalytic decomposition of 2,4 dichlorophenol besides the ability to be recovered after being used. Magnetic nanocomposites were also tested for the degradation of AOXs from pulp and paper mill effluents and showed acceptable performance in such applications. A framework was also developed in this thesis for the sustainability assessment of the best available technologies to deal with industrial effluents, showing the efficiency of biological treatment methods to deal with industrial effluents although having some limitation to deal with phenolic industrial effluents. With a precise acclimatization process, very high efficiency for the biodegradation of phenol with a high degree of resistance to the shock of initial phenol concentration was achieved using activated sludge process. The results of a critical review, as the future outlook of this thesis, indicated the possibility of integration of engineered nanomaterials and also biological treatment with the membrane technologies in order to overcome the existing barriers for the rapid development of membrane technologies for the treatment of industrial effluents.

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Chapter 1: General Introduction

Quality of the final discharged effluents from industrial activities has been the subject of significant efforts over several decades to improve the performance of the methods applied for their treatment, either by physico-chemical, biological, or a combination of these processes. On the other hand, industries around the world are currently struggling with the economic profitability [1]. In this situation, stringent environmental regulations have also forced industries, especially those releasing recalcitrant compounds in their effluents, to adopt efficient treatment technologies. Hence, it is vital to consider both the importance of technical and economic factors when selecting the most appropriate treatment technologies [2]. In addition, long-term sustainability considerations enforce industries to include environmental and health [3] as well as social criteria in the decision-making process for the selection of the best treatment strategies [4]. Integration of all these aspects to select the most appropriate techniques for the treatment of recalcitrant compounds in industrial effluents is a complex task which needs framework to identify the most suitable technology among a set of existing technologies.

Among the emerging technologies, the application of various types of engineered nanomaterials (ENMs) actually available has gained a particular attention in recent years. In this regard, a number of metallic and non-metallic compounds has been synthesized and used to deal with various environmental contaminates. Although this technology has shown an incredible potential for water and wastewater treatments, various aspects of its sustainability remain to be discussed. Wider application of this technology also necessitates boosting its efficiency especially to deal with recalcitrant pollutants. Engineered nanomaterials should have advanced properties such as high specific surface area and high crystallinity to perform well in harsh conditions of real industrial effluents environment. In this regard, application of green and efficient technologies for the synthesis of advanced types of engineered nanomaterials is highly welcome.

Other physico-chemical and biological treatment methods have been also developed in recent years in order to satisfy the need for clean water resources. While the research is focused on the development of new technologies (such as oxidation with engineered nanomaterials), industries must be assisted to adopt the best available and sustainable technologies to deal with their produced effluents. However, selection of the most appropriate technologies for the treatment of highly polluted industrial effluents to satisfy stringent environmental standards while considering various technical, environmental, economic and social aspects is a very complicated task [5].

In order to address the mentioned field of interest in the development of industrial wastewater treatment technologies, the present thesis has been organized as the following chapters:

Chapter 1 presents a general introduction to the thesis.

Chapter 2 aimed to presents an overview on the current state of the developments associated with the treatment of P&P mill effluents in order to study the potentials for improvements in the treatment of industrial effluents, especially using engineered nanomaterials.

Chapter 3 was organized to assess the performance of engineered nanomaterials for the treatment of industrial effluents and to deal with recalcitrant pollutants according to sustainability criteria using a decision-making process to ensure that long term benefits are achieved with nano-treatment technologies. In this study, the importance of sustainability criteria for the treatment of industrial effluents was determined and criteria were categorised in technical, economic, environmental and social branches while the current status of the nanotechnology regarding the criteria was critically discussed. This chapter also aimed to select the most sustainable types of nanomaterials for real applications and to guide future studies in this field. In this regard, Iron-based nanomaterials have been proposed according to the sustainable criteria studied in this section. in addition, the available technologies to be adopted by the industries to deal with produced effluents containing recalcitrant pollutants were ranked using a fuzzy-delphi methodology. The opportunities for the improvement of various methods have also been discussed according to the results achieved.

Chapter 4 aimed to address ultrasonic irradiation (UI) or sonochemistry as a powerful tool for the synthesis of a number of nanostructures. Then, the potential of UI as an environmentally friendly method was applied to develop nanomaterials which could end up in finer powder particles with better crystallinity. Taguchi experimental design has been also applied in these section in order to minimize the number of experiments leading to optimized nanomaterials with high performance for environmental clean-up purposes.

Chapter 5 was designed to test the efficiency of the nanomaterials synthesized in the present thesis, considering sustainable development criteria, to deal with recalcitrant pollutants such as AOXs and chlorophenols in industrial effluents. The importance of the treatment conditions (such as pH, temperature, additives, etc.) has been also discussed in this chapter. A case study on the biodegradation of phenol with promoted efficiency in a sequencing batch reactor (SBR) after a precise acclimatization procedure has been also presented and the effects of parameters such as initial temperature, initial phenol concentration, and acclimatization on the phenol biodegradation were studied during the experiments.

The following abreviations have been used through this thesis.

Nomenclature			
AC	Activated Carbon	NSSC	Neutral Sulfite Semi-Chemical
AD	Anaerobic Digestion	nZVI	Nano Zero Valent Iron
AHP	Analytical Hierarchy Process	OC	Operating Costs
A-MBR	Algal Membrane Bioreactor	OI	Odor Impact
AnDMBRs	Anaerobic Dynamic Membrane Bioreactors	OLR	Organic Loading Rate
AO	Anodic Oxidation	PA	Public Acceptance
AFs	Anaerobic Filters	PAC	Polymeric Aluminum Chloride
AOPs	Advanced Oxidative Processes	PAM	Polyacrylamide
AOX	Adsorbable Organic Halogens	PBR	Photobioreactor
AS	Activated Sludge	PC	photocatalysis
ABR	Anaerobic Baffled Reactor	PCP	Pentachlorophenol
BDDs	Boron-Doped Diamond electrodes	PFASC	Polymeric Ferric Aluminum Sulfate Chloride
BECMRs	Bioelectrochemical Membrane Reactors	POME	Palm Oil Mill Effluent
BET	Brunauer, Emmett, Teller	PMR	Photocatalytic Membrane Reactor
BI	Biodegradability Index	P&P	Pulp and Paper
BJH	Barrett, Joyner, Halenda	PPI	Pulp and Paper Industry
BMP	Biochemical Methane Potential	PPMW	Pulp and Paper Mill Wastewater
BOD	Biochemical Oxygen Demand	PPMS	Pulp and Paper Mill Sludge
CBA	Choosing-by-Advantages	PPS	Pulp and Paper Sludge
CMC	Carboxymethyl Cellulose	PRB	Potential to Recover By-Products

CNTs	Carbon Nanotubes	PSA	Poly-Silicic Acid
CE	CO$_2$ Emission	PS	Process Stability
COD	Chemical Oxygen Demand	PVA	Polyvinyl Alcohol
CPP	Chemical Pulping Process	PVDF	Polyvinylidene Fluoride
CP	Combination Possibility	RCF	Recovered Fiber
CSAC	Coconut Shell Based Activated Carbon	RCS	Release of Chemical Substances
CTMP	Chemothermomechanical Pulping	RFP	Recycled Fiber Pulp
CWAO	Catalytic Wet Air Oxidation	RO	Reverse Osmosis
CWPO	Catalytic Wet Peroxide Oxidation	ROS	Reactive Oxygen Species
DC	DC power	SAnMBR	Submerged Anaerobic Membrane Bioreactors
DCS	Dissolved and Colloidal Substances	SBR	Sequencing Batch Reactor
DCP	Dichlorophenol	SCOD	Soluble Chemical Oxygen Demand
DOE	Design of Experiments	SCP	Semi-Chemical Pulping
DSA	Dimensionally Stable Anodes	SGBR	Static Granular Bed Reactor
DTA	Differential Thermal	SRT	Solids Retention Time
EAOPs	Electrochemical Advanced Oxidation Processes	SGBR	Static Granular Bed Reactor
ECF	Elemental Chlorine Free	S/N	Signal-to-Noise Ratio
EFB	Empty Fruit Bunch	Ms	Saturation Magnetization
EI	Ease of Implementation	SSA	Specific Surface Area
EAOP	Electrochemical Advanced Oxidation Process	SS	Suspended Solids
ENMs	Engineered Nanomaterials	SSBR	Specific Substrate Biodegradation Rate
ENPs	Engineered Nanoparticles	SVI	Sludge Volume Index
FBRs	Fluidized Bed Reactors	SW	Softwood
FDM	Fuzzy-Delphi Method	SWG	Solid Wastes Generation
FTOC	Filtered Total Organic Carbon	SWCNT	Single-walled Carbon Nanotubes
FWHM	Full-width at Half Maximum Intensity	TCF	Total Chlorine Free
GAC	Granular Activated Carbon	TCOD	Total Chemical Oxygen Demand
GAC-SBBR	Granular Activated Carbon Sequencing Batch Biofilm Reactor	TDS	Total dissolved Solids
GHGs	Greenhouse Ggases	TE	Treatment Efficiency
GR	Green Rust	TEM	Transmission Electron Microscopy
HRT	Hydraulic Retention Time	TG	Thermo-gravimetric
H&S	Health and Safety	TOC	Total Organic Carbon
HSR	Health and Safety Risks	TOPSIS	Technique for Order of Preference by Similarity to Ideal Solution
HW	Hardwood	TS	Total Solids
II	Initial Investments	TSS	Total suspended Solids
KP	Kraft Pulp	TMP	Thermomechanical Pulping
LMB	Leuco Methylene Blue	UASB	Upflow Anaerobic Sludge Blanket
LTAD	Low Temperature Anaerobic Digestion	UAF	Upflow Anaerobic Filter
MCDM	Multi Criteria Decision Making	UAPBR	Upflow Anaerobic Packed Bed Reactor
MBPR	Membrane Photobioreactor	UASB	Upflow Anaerobic Sludge Blanket
MSBR	Maximum Substrate Biodegradation Rate	UHV	Ultra High Vacuum
MB	Methylene Blue	UF	Ultrafiltration
MBR	Membrane Bioreactor	UI	Ultrasonic Irradiation
MBT	Multi-Barrier Treatment	UV	Ultraviolet
MC	Maintenance Cost	UVI	Ultraviolet Irradiation
MFCs	Microbial Fuel Cells	VFAs	Volatile Fatty Acids
M-H	Magnetic Hysteresis	VI	Visual Impact
MP	Mechanical Pulping	VSM	Vibrating Sample Magnetometer
MLSS	Mixed Liquor Suspended Solids	VOCs	Volatile Organic Compounds
MTBE	Methyl-Tert-Butyl Ether	WO	Wet Oxidation
nHAp	Nanohydroxyapatite	WRP	Water Reuse Potential
NF	Nanofiltration	XRD	X-ray Diffraction
NI	Noise Impact	ZPC	Zero Charge Point

Chapter 2: Treatment of Industrial Effluents - Literature Review

- Kamali, M., Gameiro, T., Costa, M. E. V., & Capela, I. (2016). Anaerobic digestion of pulp and paper mill wastes - An overview of the developments and improvement opportunities. *Chemical Engineering Journal*, *298*, 162–182, (IF_5=6.73). https://doi.org/10.1016/j.cej.2016.03.119
- Mohammadreza Kamali, Seyedeh Azadeh Alavi Borazjani, Zahra Khodaparast, Mohammadreza Khalaj, Akram Jahanshahi, Elizabete Costa, Maria Isabel Capela, Additive and Additive-Free Treatment Technologies for Pulp and Paper Mill Effluents: Advances, Challenges and Opportunities, Accepted with revision requested for publication in Water Resources and Industry (IF=7.6).

2.1 Additive and Additive-Free Treatment Technologies for Pulp and Paper Mill Effluents: Advances, Challenges and Opportunities

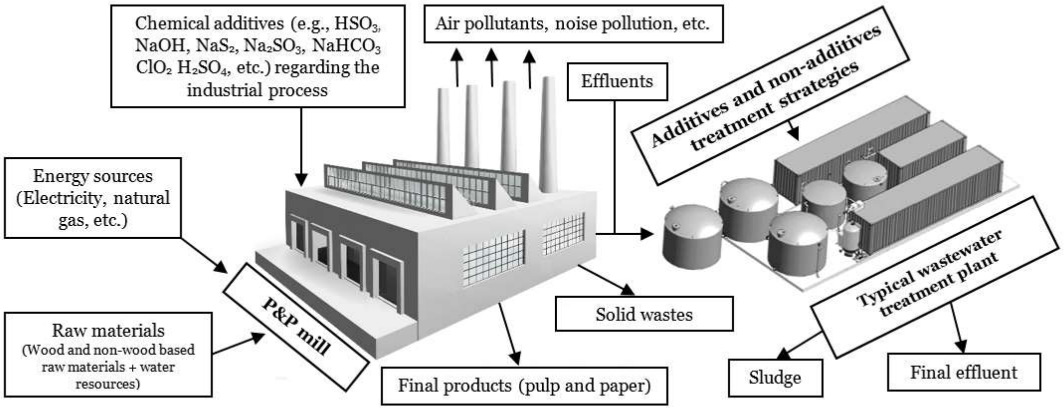


Fig. 2. 1. Graphical Abstract.

2.1.1 Abstract

In the present manuscript, novel effluent treatment processes for pulp and paper mill effluents are divided into two categories: a) those involving the use of chemical additives and b) those which are free of such chemicals. It is especially of high importance for pulp and paper industry to adopt the most cost-effective treatment methods and for the environmental communities to be sure that adoption of an efficient treatment method will not create secondary environmental adverse impacts. Hence, this paper critically reviews the recent studies on the treatment of pulp and paper mill effluents while providing suggestions for further studies on the application of various physic-chemical and biological methods for the treatment of such complex effluents containing a number of recalcitrant pollutants.

Keywords: Pulp and paper industry, industrial effluents, chemical additives, non-additive treatment processes.

2.1.2 Introduction

It is well known that the effluents from pulp and paper mills (PPMs) are highly polluted byvarious types of recalcitrant organic pollutants such as adsorbable organic halides (AOXs), as well as inorganic chemicals normally added during the process of producing pulp and/or paper [5–7]. However, the amount of pollutants loaded to the final effluents is highly dependent on various parameters such as the type and the stage of the manufacturing process and the type of the raw materials used for the production of pulp and/or paper [8]. Due to this fact, there is a need for treatment methods which are efficient enough, while being both cost-effective and environmentally friendly. It is also of high importance to emphasize that the effluents treatment technology to be adopted by the industry must have the ability to be easily transferred from lab-scale installations to full-scale applications. This is one of the most important issues that must be taken into consideration because a number of methods developed so far for the removal/degradation of recalcitrant compounds were used in lab-scale experiments but with a limited number of evidences for a rapid transferring of the newly developed techniques to real-scale applications [9]. There are a number of barriers for the commercialization of the novel wastewater treatment technologies. The expertise and financial supports required (for instance in terms of the initial investments), the insufficiency of the regulations especially in the developing countries which are not able to force complying with the scientific-based environmental standards, and the treatment costs associated with the application of advanced treatment methods are among the most important barriers. Although European Commission (2015)[10] has described the best available technologies to be adopted in large scale applications by pulp and paper mill industry, there is still a need for the industry to continue the collaborations with the researchers to prove and implement new emerging technologies for higher water quality standards. This paper aims to explain the role of chemical additives in wastewater treatment, and also to address the chemical free methods, specifically for the treatment of the P&P mill effluents. The novel treatment methods which have been developed very recently, have also been critically reviewed based on their individual role and their cumulative effects when combined with biological or other physical-chemical methods.

2.1.3 Novel P&P mill wastewater treatments

As stated before, it is of high importance to evaluate each treatment method according to several criteria including their treatment efficiency, their subsequent environmental drawbacks and also the economic issues attributed to the treatment method under consideration. Accordingly, this section has been divided into three main topics involving methods with the application of chemical additives, non-additive methods and a combination of both mentioned treatment methods to deal with the effluents from pulp and paper mill industries.

2.1.3.1 Additive-based treatment methods

The addition of various chemicals (such as coagulants, oxidation agents, etc.) has been developed as a promising way to treat highly polluted and complex effluents. This section considers the recently developed methods based either on the addition of a single chemical, or those relying on the addition of multiple chemical compounds for the treatment of pulp and paper mill effluents. Considering that the sustainable development of the treatment methods are highly related to both the efficiency of the applied method and also to the probable subsequent toxic effects of the chemical additives, such features have been highlighted in this section [11].

2.1.3.1.1 Single-additive treatment methods

The addition of a single chemical to the content of the pulp and paper mill effluents is the basis of conventional treatment methods such as adsorption, flocculation and coagulation, oxidation, etc. However, recent published papers have mainly focused on the adsorption and oxidation when just a single strategy is desired for the treatment of pulp and paper mill effluents.

Adsorption has been demonstrated as an efficient method for the treatment of various types of wastewaters due to numerous advantages such as simplicity in design as well as cost-effectiveness in terms of initial investment and land requirements [12]. In order to remove both colour and organic/inorganic contaminants from pulp and paper mill wastewater, various adsorbents including activated carbon, silica, fuller's earth, coal ash, bentonite, etc. have been applied [5]. Among the existing adsorbents, it has been reported in the literature that activated carbons can offer a higher adsorption performance due to its specific characteristics such as high specific surface area, large pore volume, high-speed kinetic, and coarse texture [13,14]. However, drawbacks such as being expensive and the need for costly and time-consuming measures to remove the molecules adsorbed inside the pores [15] have stimulate the search to explore substitutes that are available, with low-cost, are reusable and ease of application[16].

Over the recent years, the performance of various adsorbents has been tested in order to remove dyes and other pollutants from PPMW. Sajab et al. [14] studied the effects of oil palm empty fruit bunch (EFB) fibers modified with cationic polyethylenimine on the removal of colour and organic pollutants from bleaching P&P effluents originated from two treatment stages: primary clarifier and biological aeration tank, named as A and B effluents, respectively. Their experimental results indicated that by increasing the adsorbent dosage, colour and biological oxygen demand (BOD) were significantly reduced in both A and B effluents. For the adsorbent dosage of 9 g/L, there was a BOD_5 reduction of approximately 32.3% and 90.4% in A and B effluents, respectively. Moreover, the maximum colour removal was reported to be 93.6% and 87.5%, respectively, although total organic carbon (TOC) was only slightly reduced. It should be also noted that in their study, an inverse relationship was observed between pH and colour and TOC removals.

As discussed by Kamali et al. (2016)[9] some effluents, especially those from *Eucalyptus sp.* pulp and paper making processes, may contain relatively high amounts of phosphorus. In this case, cost effective methods are also required to treat such effluents preventing their discharge to the environment. Among the recent studies for the removal of phosphorus from the effluents, Barbosa et al. (2013)[17] suggested the application of ashes (both fly and bottom ashes [18]), because of their high phosphorus adsorption capacity and their low cost. By addition of fly ash or bottom ash to a P&P mill wastewater (solid/liquid ratio=34.45 g/L for fly ash and 46.59 g/L for bottom ash) more than 90% of the phosphorus removal was achieved. Ecotoxicological studies using two organisms including *Vibrio fischeri* and *Artemia franciscana* also indicated that there was no acute toxic effects of the supernatant effluents resulting from treated P&P mill wastewater using this method. Although there are some reports in the literature on the application of ashes from various origins for the treatment of different effluents, as a single treatment additive [19,20], the number of published works on the treatment of effluents from P&P mills using these materials is rare. It is worthy to note that this technique can provide an opportunity to deal with highly polluted effluents such as those from P&P mills, especially those from bleaching stages.

Providing adequate nitrogen sources for the microorganisms has also been an issue for conventional wastewater treatment plants using biological processes. So, exploring proper nitrogen sources as an additive to enhance the microbial activities would be a need for most wastewater treatment practices. Blank et al. (2016)[21] applied a tertiary treatment by controlling the algal growth inside a photo-bioreactor. They indicated chitin as a good alternative source of nitrogen for the treatment of P&P mill wastewater using algae .Their results showed that algae and cyanobacteria can grow well in the presence of chitin, and they can uptake and remove the phosphorus from the effluent.

The application of wastes from treatment plants for the treatment of industrial effluents can be an attractive candidate, especially in terms of economic considerations. As an example, a batch adsorption system was developed by Khan et al. (2015)[22] in which the inactivated secondary excess sludge obtained from the treatment of P&P mill effluent was utilized as an adsorbent to remove three major phytosterols: ß-sitosterol, ß-sitostanol and campesterol during secondary PPMW treatment. In their study, increasing the concentration of inactivated secondary excess sludge from 20 to 2000 mg/L caused more than 80% reduction in liquid-phase sterol concentration during the first 2-4 h. Moreover, following the same trend, all the three mentioned plant sterols were easily adsorbed onto the inactivated sludge.

Surface area is a main characteristic for an adsorbent as it may determine its available active surface sites to adsorb the targeted pollutants. Hence, the interest of very recent studies has also been to maximize the surface area of the adsorbents. Boonpoke (2015)[13] examined the effectiveness of adsorption method using water hyacinth based-activated carbon with highsurface area (1066 m^2/g) in both batch and continuous experiments for PPMW treatment. Within the first 40 min, chemical oxygen demand (COD) and colour were removed rapidly. The highest removal efficiency for COD and colour (91.70% and 92.62%, respectively) was observed under continuous mode. Furthermore, it can be an area for further studies to develop adsorbents with very high specific surface area using some novel techniques in the preparation of these materials e.g., ultrasonic irradiation [23,24] in order to prepare adsorbents with both high surface area and high adsorption capacity [25,26].

The use of ion exchange resins for adsorbing harmful contaminants from P&P mill effluents has also became recently of interest to industries. In this regard, polystyrene spheres (PSs) have been extensively applied as a matrix substance due to its advantages such as cheapness, availability and high mechanical stability. However, the cationic or anionic groups on the surface of conventional ion exchange resins are of short-molecular chains [27]. In order to overcome this problem, Xiao et al. (2015)[28] through the application of modifications to the spheres surface with a fibrous polymer, intended to study the efficiency of cationic polystyrene spheres for the removal of anionic contaminants from paper-making white water. The process started with the acylation of PS spheres by acryloyl chloride. Then, poly methacryloxyethyl-trimethyl ammonium chloride (PMAC) was grafted onto cationic PSs spheres using surface-initiated free-radical polymerization approach. The effect of temperature and reaction time on the removal of dissolved and colloidal substances (DCS) was then investigated in the cationic PSs concentration of 10 g/L. Their results showed that the adsorption performance of cationic PSs can be improved by increasing the temperature due to raising the molecular motion in the system. Furthermore, at longer reaction times, more DCS could be adsorbed onto the surface of cationic polystyrene spheres. Finally, the obtained cationic PSs spheres indicated the high reusability feature which can be considered as a cost-effective adsorbent for reducing the DCS from the white water.

Reusability studies have also been addressed in very recent studies. Mixing adsorbent materials such as biochar, organobentonite and activated carbon with zero-valent iron (ZVI) particles was found to be a beneficial way for separating the adsorbate from the adsorbent, which resulted in the increase of the adsorbent life time [29]. In addition, it has been reported in the literature that doping adsorbents with another compound can enhance their overall efficiency. For instance, doping with some metal catalyst like nickel can enhance the dechlorination rate of pentachlorophenol (PCP) by zero-valent iron magnetic biochar composites (ZVI-MBC). The removal efficiency of Ni-ZVI-MBC for the PCP removal from the synthetic and real PPMW was evaluated by Devi & Saroha (2015)[30]. They reported that Ni-ZVI-MBC is the most efficient compound among the studied materials (97.5% in 60 min). However, the application of advanced adsorbents such as biopolymers [31] and advanced nanomaterials [31] can be recommended for further studies in order to develop effective and cost-benefit methods to deal with highly polluted and complex wastewaters from P&P industry.

There are several reports in the literature on the application of oxidation processes for the treatment of PPMW effluents [8]. However, it can be stated that the full-scale implementation of the most conventional oxidation methods is not economically feasible due to high energy and chemicals requirements for the complete degradation of recalcitrant compounds. Hence, advanced oxidation processes (AOPs) which are able to convert the recalcitrant compounds into more biodegradable substances are considered as a promising alternative within the existing techniques of the PPMW treatment [32,33]. Among the various AOPs, ozone (e.g., as O_3/UV or O_3/H_2O_2), Fenton's process (H_2O_2/Fe^{+2}), photo-Fenton reactions (UV/H_2O_2/Fe^{+2}), and UV radiation together with hydrogen peroxide (UV/H_2O_2) were found to have good performances for removing the recalcitrant contaminants from P&P mill effluents [34]. In general, according to the results obtained from the relevant studies, ozonation with a COD removal of approximately 40% has been successfully implemented at industrial scale, mainly due to the presence of these type of facilities previously allocated for pulp bleaching in some paper mills, whereas Fenton processes with a better efficiency for COD removal (approximately 65-75 %) at a laboratory scale, can be considered an opportunity for further developments in order to be used at large-scale applications [35].

Some recent studies have also been successfully applied, using nano-scale catalysts for the wet oxidation (WO) of PPMW. For example, Anushree et al. (2015a)[36] investigated the catalytic wet air oxidation (CWAO) of PPMW by NiO-CeO_2 nano-catalysts, prepared via a co-precipitation process. The results showed 62% and 75% of COD and colour removals, respectively, at the mild operational conditions of 90˚C and 1 atm. These results can be considered as a proof for the effectiveness of nanomaterials (such as $Ce_{40}Ni_{60}$ nano-catalyst) for the oxidation of non-biodegradable compounds, due to their low size, high surface area and pore size and volume. Anushree, et al. (2015b)[37] applied the synthesized mesoporous $Ce_{1-x}Fe_xO_2$ mixed oxides as heterogeneous catalysts for CWAO of paper mill wastewater. Under optimal conditions (temperature 90 ˚C, pressure 1 atm, catalyst dosage 1 g/L, pH=4, and reaction time of 2 h), $Ce_{0.4}Fe_{0.6}O_2$ mixed oxides revealed optimum COD and colour removals (74% and 82%, respectively). In addition, examining the possibility of catalyst recovery and reuse exhibited that $Ce_{0.4}Fe_{0.6}O_2$ can be applied for three times without a significant reduction in catalytic performance. Non-catalytic wet oxidation methods have also been wider applied compared to CWAO approach due to its both operational simplicity and low cost [38,39]. In a study of a non-catalytic WO process, Dudala, et al. (2014)[40] obtained COD and colour reductions of 55% and 70%, respectively, from synthetic pulping liquor. The reaction was performed for 4 h at 170˚C and 0.37 MPa of pressure. At the end of the oxidation process, the biodegradability of the wastewater was increased from 0.22 to 0.66. From these results, it may be inferred that the non-catalytic wet oxidation process can also present an acceptable efficiency to reduce contaminants from PPMW.

Combination of oxidation processes and electricity is another option to maximize the treatment efficiency of the pulp and paper mill effluents. Amongst the electrochemical advanced oxidation processes (EAOPs), anodic oxidation (AO) method has attracted a great attention over recent years for reducing toxic and recalcitrant compounds from highly polluted and complex wastewaters [41]. In this process, highly reactive hydroxyl radicals (•OH) are generated at the anode surface (M), according to Eq. (1) [42].

$$M + H_2O \rightarrow M(\bullet OH) + H^+ + e^- \qquad \text{Eq. (1)}$$

Anodic oxidation process is an environmentally friendly technique in which various materials such as platinum, graphite, doped and undoped PbO_2, boron-doped diamond electrodes (BDDs), etc. can be used as anodes [43]. In this respect, Salazar et al. (2015)[44] treated raw acid and alkaline bleaching effluents from a hardwood-based Kraft pulp mill by AO-H_2O_2 process containing an air-diffusion cathode and a DSA-RuO_2 or BDD anode at constant cell voltage (2–12 V). In their study, BDD anode showed a much better performance in the mineralization of the recalcitrant organic compounds when compared to DSA-RuO_2 anode after 9 h, enhancing TOC removal by 75% and 65% from alkaline and acid effluents, respectively. This can be explained by the higher oxidizing capability of its physisorbed $^{\bullet}OH$ and its more inert surface. Three dimensional electrode reactors are another possible solution in this regard [45–49]. Jing et al. (2015)[50] used a novel three-dimensional electrode reactor for the degradation of acidified reed pulp black liquor (Fig. 2.2). Both types of direct electrolysis based on anodic oxidation and indirect electrolysis based on microcell mechanism revealed a TOC removal percentage of approximately 35.57%. It should be concluded that the three-dimensional electrode systems can be successfully applied for the degradation of PPMW due to their high specific surface area, low energy requirement and high mass transfer when compared to the traditional two-dimensional electrode systems.

The application of polysilicate composite coagulants, as newly developed inorganic polymer coagulants based on poly-silicic acid (PSA) and metal salts, has attracted great attention in the wastewater treatment field, due to their distinctive capabilities for charge neutralization, as well as for adsorption and coagulation of colloidal particles [51]. In this regard, He et al. (2016)[52] prepared a poly-silicic-cation coagulant with different Si/(Al+Fe) molar ratios through synchronous polymerization, for the tertiary treatment of recycled paper mill wastewater. In this study, the polymeric aluminum chloride (PAC) was used as benchmark with respect due to its high-quality coagulant ability. The results clearly showed a lower cost as well as an excellent performance of the new poly-silicic-cation coagulant for the removal of COD, color and turbidity (67, 95, and 99%, respectively) from the pulp and paper mill effluents when compared with the traditional PAC treatment.

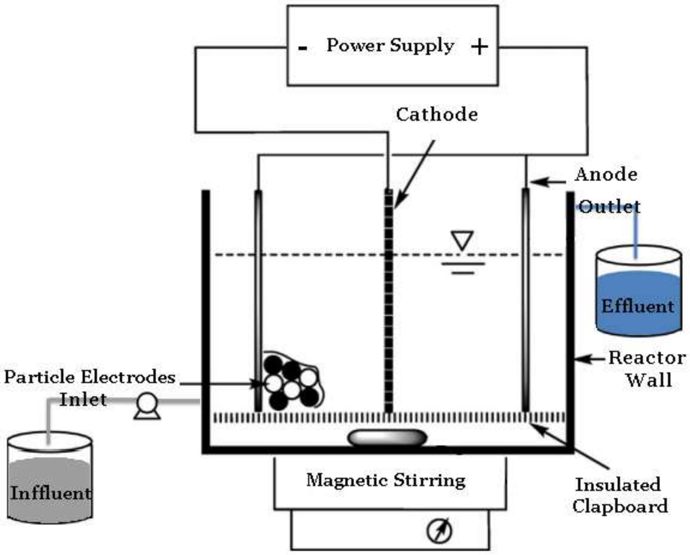


Fig. 2. 2. A schematic of a three-dimensional electrode reactor, adapted from Jing et al. (2015) [50].

2.1.3.1.1 Multiple additive treatment methods

The application of a combination of two or more single additives is another opportunity to enhance the treatment efficiency of the pulp and paper mill effluents due to the synergic effects of the individual additives on the removal of recalcitrant organic pollutants. However, the number of the combined additive methods is relatively rare in the literature for the treatment of pulp and paper mill effluents. Sticky contaminants is a prevalent problem in mills producing pulp and paper from recycled fibers which can lead to serious consequences on the paper machine, on the production downtime due to the increase in the proceedings related to the maintenance, cleaning, replacing of equipment, etc., and on the increase of the production wastes [53]. Liu et al. (2013)[54] evaluated the use of a bentonite & polyacrylamide (PAM) particle flocculation system for the treatment of recycled fiber PPMW. Under the optimal conditions (bentonite dosage: 150 mg/L, PAM dosage: 10 mg/L, pH: 6.4, temperature: 60˚C), 91.26%, 90%, 99.56%, and 95.58% of methyl-tert-butyl ether (MTBE) extract, COD, turbidity and suspended solids (SS), respectively, were removed. Additionally, the average particle size after treatment was reduced from 40.95 μm to 0.5 μm. Therefore, the bentonite adsorption and coagulation treatments were found to be efficient for recycled fiber pulp wastewater treatment, particularly due to its high capacity for the removal of large size particles and suspended colloidal substances like stickies from PPMW.

There are also recent reports on the application of industrial wastes for the treatment of industrial effluents. For instance, Yang et al.(2019) [55] prepared an inorganic polymeric ferric aluminium sulfate chloride (PFASC) composite coagulant using waste pickling liquor from steel mills together with polyacrylamide (PAM) in a tertiary treatment. They removed COD and chroma 65.3% and 71.2% respectively, under initial pH 7.5, 1 ml/L PFASC, 1.0 ppm PAM. Very recently, the application of combined additive systems using advanced oxidation processes have also gained a huge attention. For instance, Gopalakrishnan et al., (2018) [56] used solar/Fe^{2+}/TiO_2/H_2O_2 process for the treatment of pulp and paper wastewater and found a maximum COD and colour removals of 98% and 97% respectively at optimum conditions of flow rate = 75 mL/min, liquid depth = 5 cm and residence time = 75 min. AOPs using Fenton reactions have also demonstrated good performance with other physic-chemical methods. Grötzner et al., (2018) [57] achieved 95% for TOC, 61% for COD, and 76% for lignin contents removals using a sequence of coagulation-flocculation-sedimentation and AOP by Fenton process for the treatment of chemical thermal mechanical pulping effluents from a Brazilian pulp and paper industry.

As a conclusion, it seems that there is room for further studies and developments in the application of combined low-cost and high efficiency chemical additives. Meanwhile, studies on the toxic effects and the relevant environmental drawbacks and life cycle assessment of the combined additives would be essential to promote the full-scale application of such methods. Table 2.1 provides a summary of the very recent publications on the use of additives for the treatment of pulp and paper mill effluents.

Table 2. 1. A summary of the very recent additive based methods applied for the treatment of pulp and paper mill wastewater.

Method	Experimental Conditions						Parameters									Ref.
	Effluents origin	Time	pH	Additive(s)	Additive dosage (g/L)	Temperature (ºC)	COD		BOD		Color (%)		Other parameters			
							Initial (mg/L)	Removal (%)	Initial (mg/L)	Removal (%)	Initial (pt-Co)	Removal (%)	Parameter Substance	/Initial	Removal	
Adsorption	Bleaching		7.3	oil palm EFB	9		1500		240	32.3	963	93.6				[14]
			8.5	oil palm EFB	9		122		148	90.4	429	87.5				
Adsorption				Fly ash bottom ash	34.45 46.59								Phosphorous		90%	[17]
Adsorption		2-4 days		Chitin	2								Phosphorous	280 µg/L	2.6 µg/L day	[21]
Adsorption	Sterol spiked PPMW	first 2-4 h	7	PPM Secondary Sludge	2		736 ±15						Sterol: campe	850 µg/L	80%	[22]
													Sterol: ß-sitosta	2300 µg/L		
													Sterol: ß-sito	3500 µg/L		
Adsorption		40 min		WHAC^a			674	91.7			831	92.62				[13]
Adsorption	With water	Initial minutes	-	Cationic PS	10	40									53.8%	[28]
Adsorption	Synthetic and real effluents	240 min	6	Ni-ZVI-MBC	0.2	40							PCP	1.77 mg/L	100%	[30]
CWAO	After primary clarifier	150 min	4	NiO-CeO$_2$ nano-catalysts	1	90	865	62	234		2768	75				[36]
CWAO	Primary clarifier	120 min	4	Ce0.4Fe0.6O$_2$ mixed oxides	1	90	865±32.14	74	234±12.84		2768±114.46	82				[37]
Anodic Oxidation	Bleaching	9 h	10.5	BDD anode			1500±12	-	595±5		1077±3		TOC	594 mg/L	75%	[44]
													AOX	25.1mg/L		
Anodic Oxidation	Bleaching	9 h	2.5	BDD anode			1250±12	-	563±6		496±4		TOC	499 mg/L	65%	[44]
													AOX	19.2 mg/L		
Anodic Oxidation	Black Liquor	2 h	2.5	GACE^b		25	220.6487±6487	-					TOC	83.70 mg/L	35.57%	[50]
Coagulation	Aerobic PPMW		7.2	PSC^c	< 10	-	120	67				95	Turbidity	70 NTU	99%	[52]
Adsorption & Coagulation	pulping, floatation deinking	2-5 min (stirring)	6.4	Bentonite	0.15	60	3020	89.67	-	-	867.4	93.08	Turbidity	108 NTU	99.56%	[54]
													MTBE extract	236.8 mg/L	91.26%	
				PAM	0.01								particle size	40.95 µm	0.51	
													CD	1065.4 µmol/L	85.92%	
													SS	860mg/L	95.58%	

a. Water hyacinth based-activated carbon.
b. Granular Activated Carbon Electrode.
c. Poly-silicic-cation with Si/(Al+Fe).

2.1.3.2 Non-additive treatment method

This section aims to review the very recent advances in the treatment of P&P mill effluents using the methods which are independent of chemical additives application. To this end, physical, biological treatments and their combinations are included in this section.

2.1.3.2.1 Physical treatments

So far some single physical treatments such as sonochemical irradiation [58], electrical flow [59], or a combination of different physical treatments [60] have been applied for the decontamination of effluents from various origins. However, the number of literature publications on the single physical treatments of PPME is relatively rare. With the aim of reducing colour and turbidity, Shaw & Lee (2009)[61] carried out an ultrasonic treatment (at 357 kHz) of effluents from Kraft P&P mill. It was observed that the irradiation of ultrasound for 25 h resulted in the drop in the absorbance of the spectra above 250 nm for aromatic compounds. Ultrasound irradiation (20 KHz-10 MHz) can cause the cavitation involving the formation, growth, and instantaneous implosive collapse of bubbles in the liquid. This process generates local hot spots with high temperatures (up to 5000 °C) and pressures exceeding 500 atm [62] together with shock wave and micro-jet (400 km/h) [63,64]. Under these conditions, the destruction of the aromatic compounds in the content of the effluent is facilitated. The simultaneous removal of colour and COD by using physical methods has been reported by Ebrahimi et al. (2016)[65]. They developed a multi-stage ceramic membrane system consisting of a microfilter, an ultrafilter and a nanofilter to diminish COD and residual lignin from alkaline bleaching effluent of a P&P industry (Fig. 2.3). Such a combination can act as an energy-saving and environmentally friendly method for the removal of contaminants and organic matters from PPME as aimed by some other related studies [66–70]. According to the results obtained by Ebrahimi et al. (2016)[65], the sequential two-stage process using microfilter and ultrafilter resulted in a good performance in terms of COD and residual lignin removal by 45% and 73%, respectively.

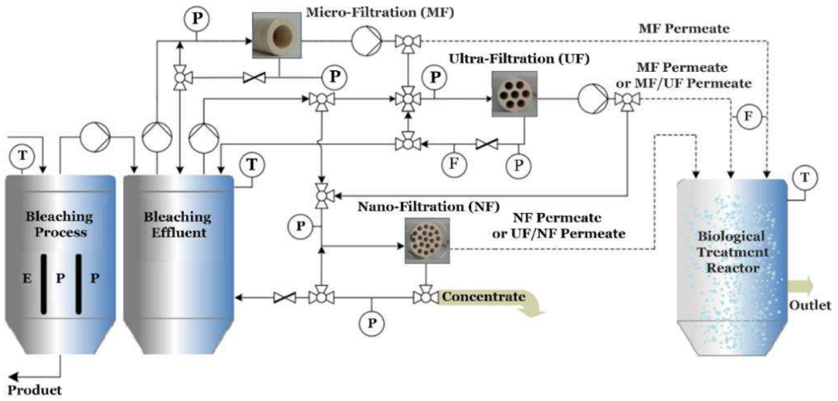


Fig. 2. 3. A schematic of a multi stage filtration process for the treatment of bleaching effluents, adapted from Ebrahimi et al. (2016)[65].

2.1.3.2.2 Biological treatment methods

Biological treatment methods, which rely on the activity of various strains of microorganisms to break down organic substances and harmful compounds, seem to be economically and environmentally superior to most physical and chemical methods applied for the treatment of different types of effluents, including PPMW. The main problem with the application of biological treatments has been the incomplete treatment of the stream, especially in the case of the presence of recalcitrant pollutants such as AOXs in bleaching effluents and lignin-derivatives in the liquor. However, some efforts have been very recently applied to reinforce the bacterial activities to remove such complex compounds. Hooda, et al, (2015)[71] employed a rod-shaped Gram-positive bacterial strain RJH-1 (isolated from sludge) for the treatment of pulp and paper mill effluents. Although during initial 24 h of experiments, no significant changes happened to COD and colour, probably due to the slow adaptation of the bacteria to wastewater conditions, after a 5 days batch experiments 69 % COD, 47 % colour and 37 % lignin removals were observed. It is worthy to note that microbial strain was also capable to reduce AOXs by 39%. Other microbial strains have been also recently extracted from other media and applied for the P&P mill effluents treatment. Tyagi et al. (2014) [72] isolated two dominant bacteria *Bacillus subtilis* and *Micrococcus luteus*, as well as one fungi *Phanerochaete crysosporium* from the soils polluted with P&P mill effluent. They applied microbial stains for the treatment of the effluents from a pulp and paper industry and achieved a lignin removal of 97% after 9 days. In this period, the consortium was also capable to remove 87.2% and 94.7% of BOD and COD, respectively. Similar removals of BOD and COD by other bacterial consortiums have also been recently observed. Significant removals of BOD, COD, and total solids (TS) of 81.25%, 53.23%, and 81.19%, respectively, were achieved by Nadaf & Ghosh (2014) [73] by utilization of a non-sporulating bacteria, namely *Rhodococcus sp*. NCIM 2891 for the degradation and detoxification of PPMW. Likewise, the concentration of heavy metals recorded from the biologically treated effluent was less compared to that of influents. Besides the bacterial consortiums, some algal communities have also shown a good performance for removing the organic material, toxic compounds, and nutrients from PPMW in a cost-effective manner [74]. For example, Usha et al. [75] reported removal efficiencies of 82%, 75%, 65% and 71.29% for BOD, COD, NO_3-N and PO_4-P, respectively, from PPMW using a mixed culture of microalgae in an outdoor open pond.

Natural-like systems such as constructed wetlands (CWs) have also recently attracted a significant interest as promising biological options to diminish the nutrients and the pollutants from wastewaters [76]. The main advantages of such systems are their cost-effectiveness and less environmental impacts as compared to conventional treatment approaches [77]. Choudhary et al. (2013) [78] studied the performance of horizontal subsurface flow (HSSF) constructed wetland planted with *Canna indica* for the removal of pollutants from PPMW. At an HRT of 5.9 days, the average percentage removals of 89.1% and 67-100% were achieved for AOX and chlorophenolics, respectively, from PPMW. Moreover, Arivoli et al. (2015)[79] evaluated the efficiency of vertical flow constructed wetlands by using three common aquatic macrophytes (i.e. *Typha angustifolia*, *Phragmites australis* and *Erianthus arundinaceus*) for the removal of heavy metals from P&P mill effluent. The results showed average removals of 74%, 80%, 60%, 70%, 71%, and 70% for iron, copper, manganese, zinc, nickel, and cadmium, respectively. Furthermore, among the three species of macrophytes used in CWs, *E. arundinaceus* showed the best performance.

Anaerobic digestion (AD) processes with different levels of performance have been also reported in the literature for the bio-treatment of P&P mill effluents. Nevertheless, among the various kinds of effluent streams generated from P&P mills, the full-scale AD has been only performed successfully for effluents from the bleached/unbleached thermo-mechanical pulp (TMP) and chemical thermo-mechanical pulp (CTMP) as well as neutral sulfite semi-chemical (NSSC) and Kraft/sulfite mill condensates [80]. It is worth noting that despite AD has numerous advantages , especially low excess solid wastes produced and energy recovery in the form of biogas, the existence of some obstacles has restricted the full-scale applications of AD in the P&P mills. These barriers are mainly related with the innate hardness in associated to the digestion of non-biodegradable compounds such as lignocellulosic material and also facing with a diversity of inhibitors (e.g., sulfur, resin acids, ammonia, heavy metals, and organochlorine compounds) as well as the necessity of adjusting specific operational conditions and the need for adopting proper reactor configuration for anaerobic degradation optimization [81]. Very recent studies have been mainly focused on overcoming these obstacles and optimizing the AD performance for complying with the stringent environmental standards and achieving economic benefits. In an effort, Steffen et al. (2016) [82] studied an anaerobic digestion experiment for evaluating the biochemical methane potential (BMP) of separating fines from industrial recycled fiber pulp (RFP). In order to obtain a better understanding, conventional chemical and mechanical pulps were used as benchmarks for methane production. While methane yields of fines from mechanical pulps and RFP were measured as 21-28 mL/g_{VS} and 127 mL/$g_{VS,}$ respectively, a highest methane yield (375 mL/g_{VS}) was attained for fines fractions from chemical pulps owing to the fact that refining chemical pulp increases the fibers' bonding surface area, thereby causing greater access of microorganisms to the fibers and increasing rate of biodegradation. On the contrary, a large amount of lignin in the fines fractions from mechanical pulps, in addition to a high content of inorganic fine particles ($CaCO_3$) and the greater hydrolysis residue regarding the separated fines from RFP might be the reasons for lower gas production. The results suggested that the fines fractions from RFP are appropriate for biogas production even though the obtained biogas yields were merely one-third as compared to the ones obtained with chemical pulp fines.

Amongst the various types of anaerobic reactors, upflow anaerobic sludge blanket (UASB) has retained a special place in the P&P industry over the past few years. Indeed the main reasons for adopting this type of reactor are related to its profitability in terms of high organic loading rate (OLR) capacity, together with the low operation expense, and the production of rich methane biogas as by-product [83,84].

When focusing on the anaerobic treatment of especial P&P mill effluents, some opportunities for further studies are still identified. For instance, very few studies have been carried out so far on the treatment of bagasse effluents from P&P industry especially by conventional AD reactors such as UASBs [85]. Furthermore, no model has been developed to predict the COD removal percentage, COD removal rate, and biogas production from the mentioned effluents. Sridhar et al. (2016)[86] studied the anaerobic digestion of bagasse effluents from P&P industry to explore the interactive effects of influent chemical oxygen demand (COD_{in}), hydraulic retention time (HRT), and temperature on the performance of a continuous UASB reactor. In their work, the Box-Behnken design was applied for analysis and modeling the interactive effects of the three variables (COD_{in}, HRT, and temperature) on the responses. Based on the obtained results, under optimum conditions (COD_{in}: 6212 mg/L, HRT: 23 h, and temperature: 35 °C), the highest values of COD removal percentage (84.3%), COD removal rate (230.9 mg/L h), and biogas production (21.2 l/d) were achieved.

Operating a UASB reactor for anaerobic treatment of a bleaching stream can lead to more satisfactory results than the total effluents generated from a P&P mill; as bleaching streams typically contain a higher concentration of organic substances or, in other words lower volumes of water need tobe treated to achieve the same results. Larsson et al. (2015)[87] investigated the performance of two lab-scale UASB reactors working in mesophilic condition on the treatment of two types of alkaline kraft elemental chlorine-free bleaching wastewaters (hardwood and softwood). The results showed the filtered total organic carbon (fTOC) reduction of 43% and 60% as well as the biogas production of 120 NmL g TOC_{IN}^{-1} and 250 NmL g TOC_{IN}^{-1} for softwood (SW) and hardwood (HW) wastewaters, respectively. The methane content of the produced biogas was 75% for both reactors. Based on the results achieved, UASB application can be considered as an appropriate technique for anaerobic digestion of alkaline bleaching effluents produced in kraft PPMs.

Development of novel and advanced types of anaerobic reactors has also been a topic of high interest in recent studies. Some types of AD reactors such as static granular bed reactor (SGBR) without the need for mixing, and aiming to save energy, have been a subject of interest, but still at a lab-scale application [88]. Turkdogan et al. (2013)[89] compared the performance of a SGBR with a UASB reactor for the treatment of thermo-mechanical paper mill wastewater in a laboratory-scale experiment. This study was performed within 110 days with hydraulic retention times (HRTs) of 4, 6, 9 and 24 h. The results indicated that in both reactor systems the COD removal efficiency was improved with the increase in HRT, ranging from 67% to 92% for SGBR and 60% to 90% for the UASB reactor. Thus, SGBR exhibited not only exhibited approximately identical ability as UASB for the removal of organics from P&P mill wastewater, but was also slightly better than the UASB in terms of operational difficulties. So, SGBR system would be a proper alternative as conventional reactors for the anaerobic digestion of P&P mill effluents. Another type of anaerobic reactor applied to the treatment of P&P mills wastewater is the moving bed biofilm reactor (MBBR) which can result in an acceptable removal of organic matter and also in the biosynthesis of added-value products [90,91]. For example, Baeza et al. (2016)[92] treated a real PPMW by MBBR, aiming to evaluate the effect of different operational parameters (i.e. BOD_5/nitrogen (N)/phosphorus (P) ratio) on the Polyhydroxyalkanoate (PHA) biosynthesis rate during two experimental phases. In phase I, the best results for the accumulation of PHA (85.10%) and removal of organic matter (95.60%) were obtained using a BOD_5/N/P ratio of 100:5:1. However, for phase II, the highest PHA percentage (89.41%) and organic removal (97.10 %) were achieved with BOD_5/N/P ratios of 100:1:0.3 and 100:5:1, respectively. The results achieve can emphasize the efficiency of the membrane bioreactors to deal with highly polluted effluents.

Sequencing batch reactors (SBRs) are also among the suitable biological systems for the treatment of wastewaters such as PPME, due to their design simplicity and functional flexibility [93]. Muhamad et al. (2015)[94] treated a real recycled paper mill effluent using three forms of lab-scale aerobic bioreactors, containing two attached-growth SBR (AG-SBR) systems with or without additional biomass, and a suspended growth SBR (SG-SBR). Over a 300-days observation period, the attached-growth SBR with additional biomass showed the best operational stability and average removal performance of 95%, 82%, 95%, 92%, 86%, and 60% for the relevant parameters, namely COD, colour, turbidity, SS, NH_3-N, and $P0_4^3$-P, respectively.

The manipulation of anaerobic digestion reactors can also enhance biogas production and treatment efficiency for a given industrial effluent. The main problem here is that in some cases, the effluents have high COD (e.g., in case of black liquor) or high concentrations of toxic materials (e.g., AOXs). As a promising strategy, co-treatment approach can encompass many potential benefits including dilution of inhibitory and toxic compounds, establishing a balance between nutrients as well as increasing the diversity and synergistic effect of microorganisms in the system. Also, economic benefits may be obtained from equipment sharing [95,96]. However, despite the numerous advantages of co-treatment strategies, nowadays very few facilities have been adopted for the process due to some concerns such as the need for upgrading or strengthening the existing facilities, process instability, unsuccessful operation arising from undesirable suspended impurities, and digester overloading which can lead to foaming problems and unexpected failure of the process [97,98]. According to the above shortcomings, so far only few studies have been conducted on the use of co-treatments in P&P industry. Most of the published work have concentrated their attention on the combination of P&P primary and secondary sludge with substrates such as food waste, municipal sewage sludge and monosodium glutamate waste liquor [5]. Co-treatment with microalga is another candidate to enhance the overall performance of the anaerobic digestion process. Gentili (2014)[99] mixed the effluents from municipal and industrial sources. Afterwards, three microalgal strains (*Scenedesmus dimorphus*, *Selenastrum minutum* and *Scenedesmus sp.*) were grown in three wastewater mixtures (P&P influent 4:1 dairy sludge; P&P influent 1:1 municipal influent; P&P influent

2:1 dairy final effluent), named as a, b and c wastewaters, respectively. Based on the results, the highest lipids yield, up to 37% of the dry matter was obtained in the wastewater mixture (a) by *Selenastrum minutum*. In addition, the highest COD removal (92.7%) was attained in the wastewater mixture (a) with the *Scenedesmus sp*. Therefore, mixing the P&P wastewater with dairy and municipal wastewaters was found effective not only in wastewater treatment but also for the production of biomass with high amounts of lipids.

Photofermentation process, as one of the most desirable biological approaches for biohydrogen production from organic substrates [100], is another option to deal with P&P mill effluents. However, the practical applicability of this approach for lignocellulosic-based wastewaters, such as PPMW, has been restricted with a degradation deficiency and low hydrogen yield due to their complicated and resistant structure to microbial enzymatic attacks [101]. Budiman et al. (2015)[102] investigated the potential of co-treatment approach by combining palm oil mill wastewater (POMW) and P&P mill effluent for bacterial growth and biohydrogen production using photofermentation. The results revealed that with a mixture of wastewater containing 25% (v/v) POME and 75% (v/v) PPME the maximum biohydrogen yield of 4.670 mL H_2/mL can be achieved. Moreover, in this study the highest COD_{total} removal (up to 28.8%) was observed during 72 h of photofermentation using *R. sphaeroides* NCIMB8253. Thus, co-treatment of POME with PPME was found to be effective for reducing turbidity as well as for improving the visibility of wastewaters during photofermentation process. Furthermore, by mixing a proper ratio (9:1) of PPME and brewery wastewater (BW), Hay et al., (2017)[103] achieved a biohydrogen yield of 0.69 mol H_2/L_{medium} from photofermentation process. This combination also led to SCOD removal, soluble carbohydrate consumption, and light efficiency of 36.7%, 32.1%, and 1.97%, respectively. Table 2.2 presents a summary of the very recent publications on non- additives processes for the treatment of pulp and paper mill effluents.

Table 2. 2. A summary of the very recent non-additive based methods applied for the treatment of pulp and paper mill wastewater.

Method	Experimental conditions					Production efficiency				Removal efficiency of parameters/substances							Ref.
	Effluents origin	Time	pH	Other conditions		Gaseous products	Value	Other products	Value (%)	COD_{total}		BOD		Other parameters			
				Parameter	Value					Initial (mg/L)	Removal (%)	Initial (mg/L)	Removal (%)	Parameter / Substance	Initial	Removal (%)	
Membrane (microfiltration followed by ultrafiltration)	Alkaline bleaching		10.65	Tem.	60 °C					10400	35-45			TOC Lignin	4000 (mg/L)	 60-73	[65]
Microalgae cultivation		28 days	5.41							3000.15	75	2944	82	NO_3-N PO_4-P	9.932 (mg/L) 30.25 (mg/L)	65 71.29	[75]
Bacterial treatment			4.5							7768	53.23	160	81.25	TS Cu Cd Fe Cr Ni	39.33 (mg/L) 0.12 (mg/L) 0.05 (mg/L) 3.96 (mg/L) 0.57 (mg/L) 0.33 (mg/L)	81.19 16.67 40 39.14 77.19 39.39	[73]
HSSF constructed wetland		5.9 days	7.7							1011	87.86	248	93.14	AOX Chlorophenolics	16.5 (mg/L) 40 (mg/L)	89.1 67-100	[78]
Vertical flow constructed wetlands			7.80							981.7	55.38	230.2	45.35	Colour Fe Cu Mn Zn Ni Cd Phenol	2553 (Pt-Co) 1.56 (mg/L) 0.246 (mg/L) 0.21 (mg/L) 0.39 (mg/L) 0.06 (mg/L) 0.013 (mg/L) 4.93 (mg/L)	96.05 74 80 60 70 71 70 43.20	[79]
UASB	Bagasse	23 h	4.5-5.5	Tem.	35 °C	Biogas	21.2 l/d			6212	84.3						[86]
UASB	Alkaline kraft elemental chlorine-free bleaching (SW)		8			Biogas	120 NmL g $TOCIN^{-1}$							fTOC	6300 (mg/L)	43	[87]
	Alkaline kraft elemental chlorine-free bleaching (HW)					Biogas	250 NmL g $TOCIN^{-1}$							fTOC	610 (mg/L)	60	
SGBR	Thermo-mechanical	4-24 h	7.14	Tem.	35 °C					1133.9	67-92						[89]
UASB											60- 90						
MBBR	Pressure ground wood pulping		6.83	OLR BOD_5/N/P	2.99 kg $BOD_5 m^{-3}$ day^{-1} 100:5:1			Polyhydroxyalkanoate	85.10	839		441	95.60				[92]
	Thermo mechanical pulping		6.77	OLR BOD_5/N/P	2.83 kg $BOD_5 m^{-3}$ day^{-1} 100:1:0.3			Polyhydroxyalkanoate	89.41	2970		1670	97.10				

Table 2.2. Continued.

Method	Experimental conditions					Production efficiency				Removal efficiency of parameters/substances							Ref.
	Effluents origin	Time	pH	Other conditions		Gaseous products	Value	Other products	Value (%)	COD_{total}		BOD		Other parameters			
				Parameter	Value					Initial (mg/L)	Removal (%)	Initial (mg/L)	Removal (%)	Parameter/ Substance	Initial	Removal (%)	
AG-SBR with additional biomass	Dissolved air flotation recycled PPMW	24 h	8							1057	95%			Colour Turbidity SS NH_3-N PO_4^{3-}-P	121 (Pt-Co) 735 (NTU) 149 (mg/L) 4.1 (mg/L) 0.03 (mg/L)	82 95 92 86 60	[94]
Microalgae cultivation	Mixtures of PPMW with dairy wastewater		7.37	Tem.	27.5 °C			Biomass yield	>37	1905	92.7			NH_4-N NO_3-N PO_4-P	22.35 (mg/L) 1.06 (mg/L) 10.1 1 (mg/L)	99 25-55 >95	[99]
Photo fermentation	PPMW with POME (3:1)	72 h	7.00	Tem.	30 °C	Biohydrogen yield	4.670 mL H_2/mL			22 900	28.8						[102]
Hybrid UFBAB reactor and SSF		24 h	8.9							2912	99	1280	90	Sulfate Phenols TDS Chloride	207 (mg/L) 2.3 (mg/L) 1270 (mg/L) 365 (mg/L)	>50 >70 66.5 >50	[104]
UI and Photo fermentation		45 min	6.9	Tem.	30 °C	Biohydrogen yield	0.041 – 0.077 mL H_2/mL			1441	No change			SCOD	318 (mg/L)	25.9	[105]
UI and Photo fermentation	Mixtures of PPMW with POME (3:1)	45 min	7.00	UI[a] amplitude Tem. UIamplitude	60 30 °C 70	Biohydrogen yield	8.72 mL H_2/mL medium			22,900	36.9			SCOD	5725 (mg/L)	34.2	[106]
UI and Photo fermentation		10 min	6.9	Tem.	30 °C	Biohydrogen yield	9.62 mL H_2/mL			1441							[107]
		15 min		UI amplitude Tem.	30 30 °C									SCOD	318 (mg/L)	18	
Bacterial treatment	Synthetic PPMW	5 days	7	UI amplitude Tem.	15 37 °C					500	69			Colour lignin AOXs	1000 (Pt-Co) 15(mg/L)	47 37 39	[71]
Bacterial and fungi treatment		9 days	9	Tem.	26 °C					935-1005	94.7	130-136	87.2	Lignin	1.958(mg/L)	97	[72]

a. Ultrasonication.

2.1.3.2.2 Combined physico-biological treatment methods

Due to the insufficient treatment output of the single treatment methods, various studies have claimed the necessity of combining biological and physico-chemical methods [5,9]. Considering the benefits of such combinations, either in terms of economical-environmental aspects as well as the potential synergistic effects, Mishra et al. (2016)[104] studied the efficiency of an integrated system including upflow fixed-bed anaerobic bioreactor (UFBAB) and slow sand filter (SSF) for the removal of pollutants from PPMW (Fig. 2.4) as compared to a single UFBAB. At different HRTs, the hybrid system showed a very high removal efficiency of 90%, 99%, 100%, and 100% for BOD, COD and total dissolved solids and total suspended solids, respectively. Similarly, in the case of sulfate and phenols removal, a relative high efficiency was attained, indicating a very good performance for such combined system.

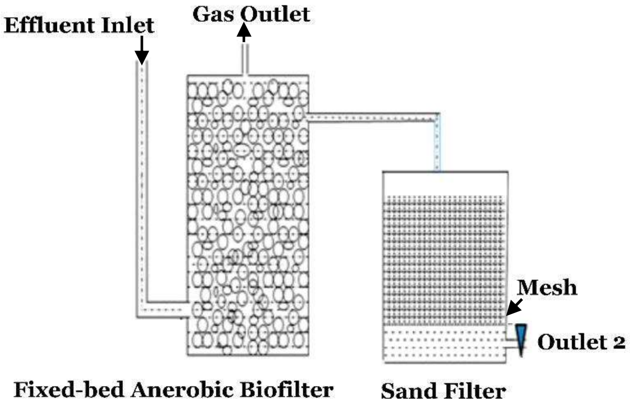


Fig. 2. 4. A scheme of a biofilter designed for P&P mill effluent treatment, adopted from Mishra et al. (2016)[104].

Recent studies have also demonstrated that pre-treatment of lignocellulosic materials by moderate ultrasound irradiation could break down their complex composition via the development and collapse of cavitation bubbles, which can lead to a positive effect on the biohydrogen production from the fermentation process [108,109]. In this regard, Hay et al. (2015)[105] investigated the effects of ultrasonic power (30%-90%) and duration (15 min-60 min) on the photofermentation process of PPMW. Based on the results obtained, the biohydrogen yield of all PPMWs pretreated by ultrasonication was higher than the ones obtained with the raw substrate, ranging between 0.041-0.077 mL H_2/mL. The maximum cumulative biohydrogen production (430%) and SCOD removal efficiency (25.9%) were achieved at the amplitude of 60% and time of 45 min (A60:T45), respectively. Moreover, economic assessment conducted in this research showed that ultrasonic pretreatment prior to biofermentation of PPMW could have a positive net saving in comparison with raw PPMW, due to the higher incomes from selling the biohydrogen and further reduction in costs related to the COD removal. Once more, Hay et al. (2016)[107] applied various ultrasound irradiation times (5, 10 and 15 min) and amplitudes (15%, 30%, and 45%) to specify the optimal ultrasonication conditions for pretreatment of *Rhodobacter sphaeroides*. As indicated in Fig. 2.5(a) moderate ultrasonic pretreatment could stimulate the generation of pores in the cell membrane of *R. sphaeroides* or slightly disrupt surface of cell, whilst higher-frequency ultrasonic was able to create more pores in cell surface, thereby resulting in further change of the cell morphology as compared to the untreated bacteria cell. Thus, highest hydrogen yield (9.62 mL bioH_2/mL) was attained at A30:T10 due to the fact that moderate ultrasonic applied to *R. sphaeroides* could improve the enzymatic activities of the cell with modification of membrane permeability and resistance, leading to increase degradation of large-size molecules into smaller ones. However, the higher release of intracellular products in the ultrasonic-pretreated PPMW caused a lower SCOD removal efficiency after biohydrogen production process as compared to the control substrate.

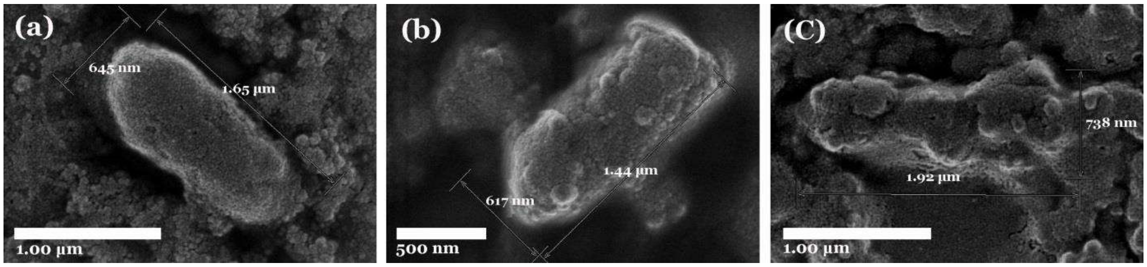


Fig. 2. 5. FE-SEM images of R. sphaeroides NCIMB8253 after undergoing (a) no ultrasonication; (b) ultrasonication with amplitude 30% and 10 min; (c) ultrasonication with amplitude 45% and 15 min, adopted from Hay et al. (2016)[107].

In another effort to improve the biohydrogen production, Budiman and Wu (2016)[106] evaluated the performance of ultrasound pretreatment (amplitudes of 30%-90% and duration of 5 min to 60 min) on a combined substrate consisting of PPMW and POME. The maximum hydrogen production rate (8.72 mL H_2/mL$_{medium}$) and COD removal efficiency (36.9%) were achieved by using A70:T45 ultrasonication. The improvement of biohydrogen production was linked to the positive effect of ultrasound irradiation on the release of lignin and cellulose from the structure of substrates, leading to increased bioavailable nutrients which could be simply degraded by fermentation bacteria.

2.1.3.3 Combined additive and non-additive treatment methods

2.1.3.1.1 Physico-chemical combined treatment methods

Application of various physical stimulates such as vibration, electricity flow, temperature, photo irradiation, filtration, and pressure, etc. can potentially enhance the performance of methods based on the addition of chemicals for the treatment of industrial effluents. For instance, the combination of ultrasonic irradiation with AOPs can be an interesting solution for the removal of recalcitrant pollutants from P&P mill effluents. Generation of powerful hydroxyl groups as a result of ultrasonic irradiation can facilitate the oxidation of complex organic materials especially when combined with methods such as Fenton-like oxidation treatments. Eskelinen et al. (2010)[110] studied the treatment of bleaching effluents from a P&P mill using a combination of ultrasonic irradiation in combination with Fenton-like oxidation (Fe^{3+}/H_2O_2) or photo-Fenton degradation ($Fe^{2+}/H_2O_2/UV$). Such an integration resulted in COD removals of 12%, 20%, and 28% from effluents by using Fenton-like oxidation, photo-Fenton's oxidation or electro-oxidation treatment, respectively, at the reaction conditions of dose of Fe(III)-1 g/L; dose of H_2O_2-3 g/L, pH-6.9, agitation speed: 200 rpm, and contact time-60 min. It has been also reported that ultrasonic irradiation can facilitate the coagulation process especially when combined with electricity. Asaithambi et al. (2016)[111] showed that the application of sono-electrocoagulation can yield 95% and 100%, for the removal of COD and color, respectively, at a current density of 4 A/dm^2, electrolyte concentration of 4 g/L, initial pH of 7, COD concentration of 3000 mg/L, electrode combination of Fe/Fe, inter-electrode distance of 1 cm, and reaction time of 4 h. Although filtration is not able to treat highly polluted industrial effluents, as in the case of PPMW, its combination with methods based on the addition of chemical additives can be considered as a good candidate to promote the overall efficiency of wastewater treatment plants. For instance, Gholami et al. (2017)[112] applied a hybrid system assembled with ultrafiltration (UF) membrane and AOPs in order to treat an effluent from fiber sewer collection unit. They indicated that the UF permeate quality was not sufficient to satisfy the related environmental regulations. As the next step, they applied AOPs under which sulfate and hydroxyl radicals were generated through the activation of persulfate ($S_2O_8^{2-}$) and H_2O_2 by Fe(II) to deal with the pollutants. Under optimized operational conditions, ($[H_2O_2]$=15 mM, [Fe (II)]=6 mM, and pH=3), the removal efficiency of COD, UV_{254}, and UV_{280} were 95.02%, 86.74% and 87.08%, respectively. Additionally, in order to reduce the reaction time and costs, Salazar et al. (2015)[44] combined AO-H_2O_2 with UF, nanofiltration (NF) and reverse osmosis (RO) treatments. The results for TOC removal by integrated filtration/AO-H_2O_2 indicated that the best pair-treatments for acid and alkaline bleaching effluents were UF/AO-H_2O_2 (68% of TOC removal) and NF/AO-H_2O_2 (96% of TOC removal), respectively. AOPs can also compensate the deficiency of electro-coagulation for the complete treatment of PPMW. Jaafarzadeh et al. (2016)[113] mixed electro-coagulation with UV oxidation for the removal of organic compounds from a P&P mill wastewater (COD=1537 mg/L). Under optimum conditions (natural pH, time=33.7min and current density=5.55 mA/cm^2) they achieved 61% of the COD removal. In a recent study, Abedinzadeh, Shariat and Masoud (2018)[114] applied an SBR method in combination with AOPs for the treatment of P&P wastewaters. Using a response surface methodology (RSM), they achieved an optimum COD and colour removals of 98% and

94%, respectively, under Fe^{2+} and H_2O_2 dosages of 3 mM and 9 mM, respectively at pH of 3.0 and 30 min.

For a sustainable treatment of industrial effluents, there is also a need for cheap and environmentally friendly additives. So far, some attempts have been made in this regard. As shown by Zhuang et al., (2018) [115] who used waste rice straw and iron-containing sludge to prepare catalytic particle electrodes. Electro-Fenton (EF) oxidation applied to real paper mill wastewater using the prepared electrodes under optimized treatment conditions (current density of 10 mA/cm^2, a catalytic particle electrodes dosage of 1.0 g/L, and an aeration rate of 5 L/min) reached allowed 86% of SCOD removal.

Due to the fact that sun is a renewable energy source that is free but dependent on the season and geographical conditions, it can be used as a source of light for treatment processes. It can also be combined with other physico-chemical methods to enhance the overall treatment efficiency. As a good example, a multi-barrier treatment (MBT) comprising the steps of filtration, photolysis of hydrogen peroxide (H_2O_2/UVC) and catalytic wet peroxide oxidation (CWPO) using granular activated carbon (GAC) as catalyst demonstrate a remarkable efficiency for synthetic industrial effluents post-treatment, particularly because of the possibility of removing residual H_2O_2 and some by-products generated during H_2O_2/UVC process through subsequent filtration by GAC column [116,117]. Accordingly, Rueda-Márquez et al. (2016)[118] investigated the viability of a MBT process for post-treatment of plywood mill effluent on a pilot scale. As a result, over the MBT process, the concentration of COD and TOC decreased by 88.5% and 76%, respectively, while SS and turbidity decreased by 89% and 70%, respectively. Moreover, an almost complete H_2O_2 removal (95%) was achieved after CWPO process (1.5 min of contact with GAC). On the other hand, the operation and maintenance cost for this MBT process was estimated as 0.95 €/m^3

2.1.3.1.2 Bio-chemical combined treatment methods

Former studies have clearly indicated that the application of either a single biological or a single chemical method would not be enough to complete treatment of the P&P mill effluents in order to satisfy legal requirements and protect the environment[5]. Besides some species of single bacteria, mixed culture acclimated biomass as well as biofilms can partially or completely degrade adsorbable organic halides (AOX). Considering the fact that AOX has a severe toxic effect on the growth of microorganisms, combining two process; adsorption and biofilms, more satisfactory results can be achieved for AOX treatment. On the other hand, HRT is one of the most important parameters that should be considered for achieving optimal conditions for wastewater treatment. Osman et al. (2013)[119] by combining adsorption and biological processes at a lab-scale granular activated carbon sequencing batch biofilm reactor (GAC-SBBR) under aerobic conditions, tried to evaluate the effect of HRT on the GSC-SBBR performance in terms of the simultaneous removal of AOX and COD from a recycled paper mill wastewater. For this purpose, the reactor was packed with 80 pieces of cylindrically shaped plastic media with GAC of sizes in the range of 6-8 mm. These packing materials played two roles, both as adsorption medium and as a medium for biofilm growth. The results indicated that just a meagre efficiency can be achieved in the COD removal when HRT reduces from 48h to 8 h. The results also demonstrated that the treatment efficiency for the reduction of COD and AOX from P&P mill effluents with GAC-SBBR can be obtained were as high as 92% and 99%, respectively, at an HRT of 48 h.

Addition of trace elements to the biological treatment systems has also been a solution to enhance the efficiency of the treatment, especially when facing with a highly polluted and complex effluent [120], as also previously observed for other types of industrial effluents [121,122]. This idea was tested by Barnett et al. (2015)[123] to promote the effluents from a TMP process by adding trace metals including Ca, Co, Cu, Fe(III), and Mg to an activated sludge (AS) plant as one of the common biological treatment to deal with P&P mill effluents [124]. They indicated that such trace elements are capable to enhance the COD removal from 82% to 86% (1.0 mg/L). Table 2.3 provides a summary of the recent studies on the application of non-additive methods for the treatment of pulp and paper mill effluents.

Table 2. 3. A summary of recent non-additive methods applied for the treatment of pulp and paper mill wastewater.

Method	Experimental Conditions					Parameters									Ref.
	Effluents origin	Time	pH	Additive(s)	Temperature (ºC)	COD		BOD		Colour		Other parameters			
						Initial (mg/L)	Removal (%)	Initial (mg/L)	Removal (%)	Initial (pt-Co)	Removal (%)	Parameter Substance	/Initial	Removal (%)	
UI&F[a]	Raw bleaching effluent	60 min	6.9	Fe(III): 1 g/L H_2O_2: 3 g/L		1510	12								[110]
PF[b]							20					Abietic acid Linoleic acid β-sitosterol		93 84 87	
Electrochemical treatment							28					Abietic acid Oleic acid β-sitosterol		51 76 83	
Sono-electrocoagulation		4 h	7.5	Fe/Fe-electrodes		3000	95	1000	95	Dark brown	Color-less	TSS Odor	2000 (mg/L) Burnt sugar	87.5 Nil	[111]
Filtration fenton like oxidation	Fiber sewer collection unit effluent		3	H_2O_2=15 mM, Fe (II) =6 mM		1943	95.02	250				Lignin UV_{254} UV_{280}		>90 86.74 87.08	[112]
Filtration/ $S_2O_8^{2-}$ /Fe(II)			6	$S_2O_8^{2-}$ =7 mM Fe (II) =2 mM			94.96					Lignin UV_{254} UV_{280}		>85 92.04 90.16	
UF and AOP	Acidic bleaching effluent		2.5	H_2O_2 BDD Anode	25	1250		563				TOC	499 (mg/L)	68	[44]
NF and AOP	Alkaline bleaching effluent		10.5	H_2O_2 BDD Anode	25	1500		595				TOC	594 (mg/L)	96	[44]
Electro-coagulation and UV/persulfate or UV/peroxymonosulfate			8.2	Persulfate Peroxymonosulfate	23–27	1537	61	410							[113]
Filtration and AOPs	Plywood mill effluent	5 min		H_2O_2: 200 mg/L		230	88.5					SS TOC Turbidity	26(mg/L) 70(mg/L) 8.3	89 76 70	[118]
Adsorption and aerobic process (GAC-SBBR reactor)	Recycled paper mill (Dissolved air floatation)	48 h	7.1	Granular activated carbon		1152	92					AOX		99	[119]
Electrocoagulation		60 min	5	Iron & Aluminum	Room temperature	657	85			Brown	Completely	Lignin	1,155 (mg Phenol/L)	78.5	[125]
Electrocoagulation	Tissue paper wastewater		7.4	Iron, Aluminum and Sludge		1220	92.6								[126]

2.1.4 Challenges and Opportunities

Currently, P&P mills continue to seek sustainable management solutions to overcome their difficulties in production processes and also to deal with economic and environmental management issues [127]. It is also of high importance for a good solution to establish a logic connection between the process engineering and economic considerations in line with the adoption of the best suited treatment process. Several techno-economic analysis have been carried out recently in order to optimize the production processes to have less environmental drawbacks while providing more quality for the products in an economic perspective [1,128–133]. But, industry is not yet able enough to minimize the pollution load in final effluents and it is expected for effluents from P&P industry to remain as one of the most polluted industrial wastewaters through the world containing recalcitrant and complex organic compounds [134]. There are a number of evidence for the soil pollution of the pulp and paper mills surrounding environment and severe toxic effects for the local biotic communities if discharging their wastewaters without efficient treatment [120,135–140]. In this situation, the end of pipe treatment of the wastewater will be considered, at least in the forthcoming years, as the main way to satisfy environmental protection communities. The stages involved in the treatment of such highly polluted and complex effluents are currently subjects of negotiations among the scientific communities. Some studies emphasizes that a series of biological treatments are good candidates to achieve the treatment goals regarding the stringent environmental protection standards and regulations [141]. For instance, Buyukkamaci & Koken in the year of 2010 [142] by comparing ninety-six treatment plants (in Turkey) having a single physical treatment, chemical treatment, aerobic and anaerobic biological processes or their combinations according to economic criteria including investment, operation, maintenance and rehabilitation costs tried to suggest an optimum treatment method for the P&P industry. They concluded that an extended aeration activated sludge process is the best option for low strength effluents, while extended aeration activated sludge process or UASB followed by an aeration basin can act efficiently for medium strength effluents, and finally UASB followed by an aeration basin or UASB followed by a conventional activated sludge process can optimize the techno-economic considerations for the treatment of high strength P&P effluents. However, the necessity of allocating a relatively large area for biological treatments, relatively long-time treatment requirements as well as uncompleted treatment and local issues such as the bad smell resulting from the bacterial activities are the main drawbacks of such systems. In addition, conventional biological treatments have shown a limited efficiency for the treatment of recalcitrant and complex pollutants such as AOXs which can remain in the treated effluents, causing several environmental and health problems [143,144]. Hence, there is also a need to perform further life cycle assessment studies for the biological treatment methods applied to this type of effluents [145,146]. The scientific orientation observed by the researchers in very recent literature emphasizes that the emerging novel technologies could considerably eclipse the idea of using sequential biological treatments. Economic analysis performed in some physico-chemical treatments methods, such as Fenton process [147,148], indicated their cost-effectiveness.In addition, with respect to adsorption processes it has been reported in the literature that activated carbons, among the existing adsorbents, can offer a high adsorption performance due to its specific characteristics such as large surface area and pore volume, high-speed kinetics and coarse texture [13,14]. However, although in comparison with relatively expensive adsorbents such as silica, activated carbon can contribute to minimize the overall treatment cost, it may be here suggested the need to develop the application of cheap materials that are by-products of other natural or artificial chemical-based processes as adsorbents. Hence, it is also recommend wider applications of biochar not only because of its low cost and high performance but also due to its potential to reduce toxicity to the environment (such as soil) [18]) after the treatment process. In this regard, ashes can also be a good candidate to this end, containing relatively high amounts of metallic elements such as Fe, Ca, Na, etc. Besides their ability to adsorb contaminants from the polluted effluents, they readily release relevant cations to the media. This can promote the treatment efficiency via inducing chemical reactions with the release of electrons from the metallic elements in the media such as those (such as iron ions) used for the removal of toxic materials from the effluents such as nitrate [149–151]. They can also provide enough nutrients in the final sludge content, making them suitable for land-use utilizations, for instance for agricultural applications which may need a sludge with a minimum content of toxic substances and enough amounts of nutrient elements [152,153]. The wastes from wastewaters treatment plants (such as secondary sludge) can also be considered as a low cost solution to adsorb recalcitrant compounds. However, the final sludge after the adsorption process can be harmful to the environment due to the attachment of toxic compounds to its surface. In this case, probably the incineration is the only existing way to deal with the final wastes, which will cause some environmental drawbacks [154]. In the other hand, some novel technologies such as the application of mesoporous nanomaterials with high adsorption capacity [154–156] can also make a revolution in the treatment of highly polluted and complex effluents from pulp and paper industry. In this regard, enough engineering efforts must be done to maximize the efficiency of such materials for better treatment results. This can be achieved by adopting optimization techniques such as surface response methodology [154–156] to reach best results in a cost-effective manner. Such efforts can also be made for the synthesis of materials with high optical properties to reduce the need for irradiation of light to the reaction medium during the processes such as oxidation of effluents. In this way, economic considerations of the treatment process can be also satisfied.

The combination of various additives can also result in the promotion of the treatment efficiency. Also, the combination of various additive-based methods with biological methods have shown attractive results for the elimination of recalcitrant pollutants from P&P mill effluents such as AOXs and to promote the overall efficiency of COD and BOD removals, which can result in a better quality for the final effluents. There is also a need to design combined reactors to join physico-chemical and biological methods by taking into consideration that such systems must not only enhance the overall treatment performance, but also be technically and economically feasible enough to encourage investors. This latter item is currently the main obstacle for the rapid commercialization of the lab-scale developed novel methods, especially in developing countries.

Application of chemical additives can generally raise some concerns on their toxic effects when released to environment [157]. Furthermore, the review of recent studies on the treatment of P&P mill effluents reveals a trend for the use of chemical additives but without enough eco-toxicological studies. This issue is of high importance because recently the concern on the effects of the remaining toxic chemicals after the treatment process has increased considerably in the scientific community. Hence, there is an urgent need to carry out life cycle assessment studies for emerging additive-based technologies for the treatment of highly polluted and complex industrial effluents such as those released to environment from the P&P industry.

It is also worthy to mention that the selection of a sustainable method to deal with effluents from pulp and paper industry is a complex task, requiring the consideration of various technical, environmental and economic as well as social criteria. Hence, application of multi-criteria decision making systems (MCDM) [158,159] is highly recommended in this regard to find the best available technologies for the treatment of pulp and paper mill effluents.

2.1.5 Conclusion

This paper presents very recent results achieved on the treatment of pulp and paper mill effluents based on the application of chemical additives alone or in combination with other physical or biological treatment methods. Moreover, recent developments on single biological and physical treatments or their hybrid application have been critically reviewed. As a result the interest of the scientific community to promote additive-based treatment methods in combination with conventional or novel physical or biological treatment methods could be highlighted. The overall trend in this field, as realized by the authors, is to promote techno-economic benefits of treatment processes. Furthermore, taking into account toxicology and environmental safety issues this review calls for joint studies or complementary studies on the subsequent environmental impacts of the novel combined technologies towards an efficient treatment method.

2.2 Anaerobic Digestion for sustainable treatment of industrial effluents, Case Study: Anaerobic digestion of Pulp and Paper Mill Wastes - An Overview of the Developments and Improvement Opportunities

2.2.1 Abstract

Various organic and inorganic hazardous substances are commonly originated during the processing of virgin or recovered fibers (RCFs), when the pulp and paper (P&P) are produced. Hence, the pulp and paper industry (PPI) strongly need to employ advanced waste treatment methods which make them powerful to comply with the stringent environmental regulations in one hand, and to increase their profitability in the current declining P&P markets, on the other hand. Anaerobic digestion (AD), as an interesting cost-effective alternative with a small environmental footprint has been increasingly adopted by the PPI to this goal. However, the applications of AD to deal with wastes generated in P&P mills has been restricted due to the number of limitations in the anaerobic reactor design, and the operating conditions. Hence, the optimization of the AD performance would be an essential step in order to increase the economic benefits, and to satisfy the strict environmental protection standards. To this end, this paper presents an overview on the current state of the developments associated with AD treatment of P&P mill wastes to assess the applicability of this treatment process for the management of this type of complex wastes. In this context, suggestions are provided to maximize both biogas production and removal efficiency in order to enhance methane capture, hence contributing to prevent global warming.

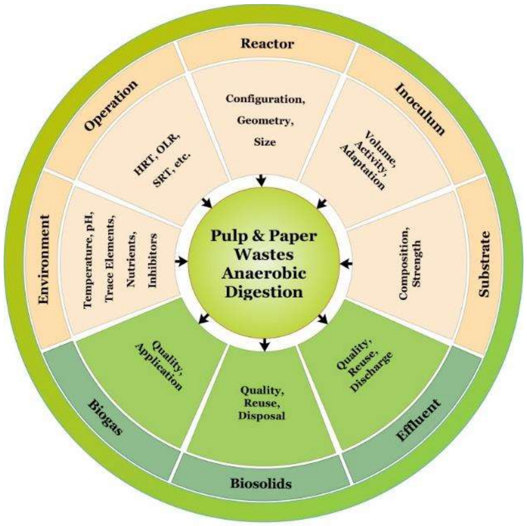


Fig. 2. 6. Graphical Abstract.

Keywords: Pulp and paper industry, wastewater, sludge, anaerobic digestion, methane production.

2.2.2 Introduction

Various wood or non-wood materials are the main raw materials for the production of pulp and paper (P&P) in many countries through the world (Fig. 2.7). Moreover, P&P manufacturing from recovered fibers (RCFs) has been increased during recent years [160]. After preparation of stock materials, steps including pulping, bleaching, and P&P making are applied, respectively, to yield pulp or paper (Fig. 2.8). Based on the raw materials used and the P&P manufacturing process adopted, P&P industry (PPI) produce relatively large amounts of both wastewater and solid wastes [5]. On-site, reuse and recycling, and modifications in the technology [161] are among the most efficient economic and environmental options dealing with the produced residues. In this regard, measures for minimizing the produced wastes, and recovery of the energy and unavoidable wastes have been introduced [162] and adopted by PPI [163]. However, the external treatments are still the main ways to deal with the residues from PPIs, especially for small and medium size units which generally do not benefit of infrastructures for the recovery of chemicals [164]. So far, various types of treatments (primary, secondary, and tertiary) have been developed and applied in order to enhance the treatment efficiency of both pulp and paper mill wastewater (PPMW) and sludge (PPMS) with the aim of reducing the amount of the produced final wastes, and also to prevent the probable subsequent toxic effects induced by hazardous compounds when released into the receiving environments [165].

Anaerobic digestion (AD), defined as the biological degradation of organic compounds into different end products, including methane (50-75%), carbon dioxide (25-50%), hydrogen (5-10%), and nitrogen (1-2%) [166] by a microbial consortium in the absence of air [167], has been widely employed for primary or secondary treatment of various industrial residues. The development of methods for the AD process control and monitoring [168] as well as the operational conditions set-up has raised a large interest in recent studies. This is mainly due to the advantages of AD over conventional biological P&P waste treatment, such as a significant reduction of the produced wastes and the production of biogas, mainly composed by methane. Despite these advantages, some improvements in the stability of the process, in methane yields, and regarding inhibition problems are still necessary to enhance the AD performance, especially when dealing with non-biodegradable and recalcitrant pollutants such as halogenated organic compounds present in P&P residues. Hence, when AD is used to treat wastes from P&P industry, the adoption of appropriate anaerobic reactor configuration and operating conditions can potentially promote methane production. Framed by this concern, the present study critically reviews the recent developments on AD bioreactor technologies used for the treatment of wastes generated by P&P mills and their relationship with the specific characteristics of the PPMW and waste sludge produced, depending on the P&P production process. In this context, previously published review papers addressing the various concepts of AD in general [169–175] or specific aspects of the AD of P&P mill wastes [176,177] have also been taken into consideration to provide a broader overview and to emphasize that a choice among various available technologies are likely to be case specific, needing also an economic evaluation. However, to focus on the technology with the highest potential for implementation in the PPI, it is important to discuss the recently developed high-rate anaerobic reactors together with the impact of the various environmental factors on the performances of the AD process. Hence, these aspects and their possible improvements are also discussed aiming at the optimization of the AD process and its adoption in the treatment of such high-strength complex wastes. Furthermore, considering the remaining weaknesses and the developments of anaerobic reactors for the treatment of other streams, suggestions for further studies in the form of future outlook are presented in the manuscript.

2.2.3 Historical Background

It is believed that biogas was used for the first time in Assyria in the 10th century B.C for bath water heating [178]. However, it was during the period 1804-1808 that John Dalton and Humphrey Davy discovered that the flammable gas in the biogas composition is methane [179]. Although the production of methane through the anaerobic conversion or digestion of animal and human wastes, as a source of energy, has a long history in many areas of the world [168], the first anaerobic digester was built in 1859 in a leper colony in Bombay, India, with the aim of converting the wastes to energy [180]. Afterwards, some studies were conducted to understand the mechanisms involved in the production of methane during the AD process. Bechamp (1868) and Popoff (1873) stated that biological processes are responsible for methane formation [181]. Omelianski, in the 1890s, and Sohngen in 1910 stated that the reaction between hydrogen and carbon dioxide, induced by biological agents is the probable pathway for methane formation [182].

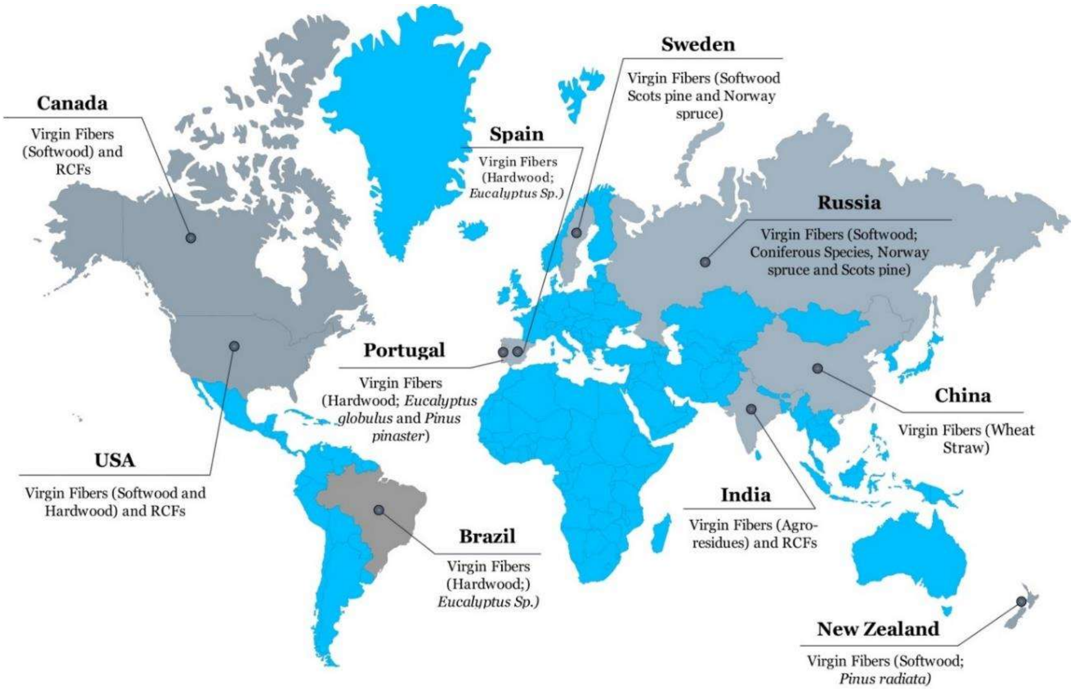


Fig. 2. 7. Predominating raw materials for P&P production in some main [23] P&P producers [24]–[33].

Since the beginning of the 20th century, AD has been widely used in many parts of world, and China has had the largest number of AD systems since the late nineteenth century [183]. In the mid-20th century, this technology was mainly used for the treatment of sewage sludge rather than industrial effluents [184]. Since then, the AD systems have been rapidly developed, especially after the first energy crisis back in the 1970's [185], with an increasing interest to optimize the AD process to treat high strength industrial wastes [186]. Upflow anaerobic sludge blanket reactor (UASB) was developed during 1970's and applied by Dutch sugar industry. However, the development of the high rate generation of anaerobic digesters only took place in 1980's, in order to decrease the hydraulic retention time (HRT), which was the main weakness of such systems. Since 1990's, the development and application of AD systems for simultaneous treatment and methane production from PPMW and sludge have found a considerable success [187]. Nowadays, AD, as a mature technology in most of European countries, is utilized for household energy production [188], as well as for the treatment of various organic wastes such as agricultural wastes, sewage treatment, and different industrial wastes such as textile industry wastewater, etc.. Although P&P mills generally produce a large amount of wastewater and solid wastes that contain various pollutants (Table 2.4), the effluents from mechanical pulping (MP), RCFs processing, chemical pulping process (CPP) and semi-chemical pulping (SCP), as well as from both primary and secondary sludge originated by PPMW treatment plants are not commonly toxic to methanogenic bacteria. Hence, adoption of AD process for the treatment of P&P mill wastes has raised a large interest during the two recent decades. Designing new generations of anaerobic reactors, improving reactors operational conditions, and developing effective consortia of anaerobic bacteria have significantly enhanced the performance of the AD process for the treatment of various industrial wastes containing high levels of organic matter during the last decades [189].

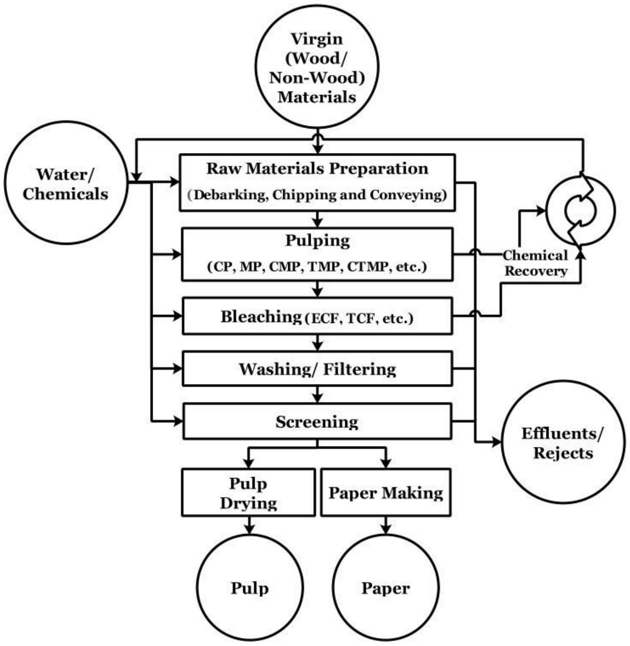


Fig. 2. 8. A schematic P&P production process from virgin fibres.

2.2.4 Wastewater and sludge from P&P industry

It is well-known that the P&P industry is among the large consumers of resources including raw materials (water and wood materials) and energy (i.e. fossil fuels). Depending on the final products of the mill (Pulp and/ or paper), the process(es) applied for manufacturing the final products, additives applied for various process stages, production scale, amount of the water consumed and the wood raw materials used, P&P mills have the potential to release various types of hazardous and non-hazardous substances in the content of the effluents, before applying the treatment process, or sludge, after physico-chemical or biological treatments or a combination of them. Accordingly, P&P production is considered a major source of environmental contaminants in both traditional and emerging P&P producers.

2.2.4.1 Water cycle in P&P mills

P&P is a relatively high water-dependent industry compared to many of other industries and, according to the stringent environmental regulations, responsible for the management of the water resources they use. Such resources are generally being received from the surface and ground waters and after being used in almost all the major process stages (Fig. 2.8), also for cooling the machines, cleaning the equipment, etc., form the main part of the rejects (effluents) from a P&P industry (Fig. 2.9).

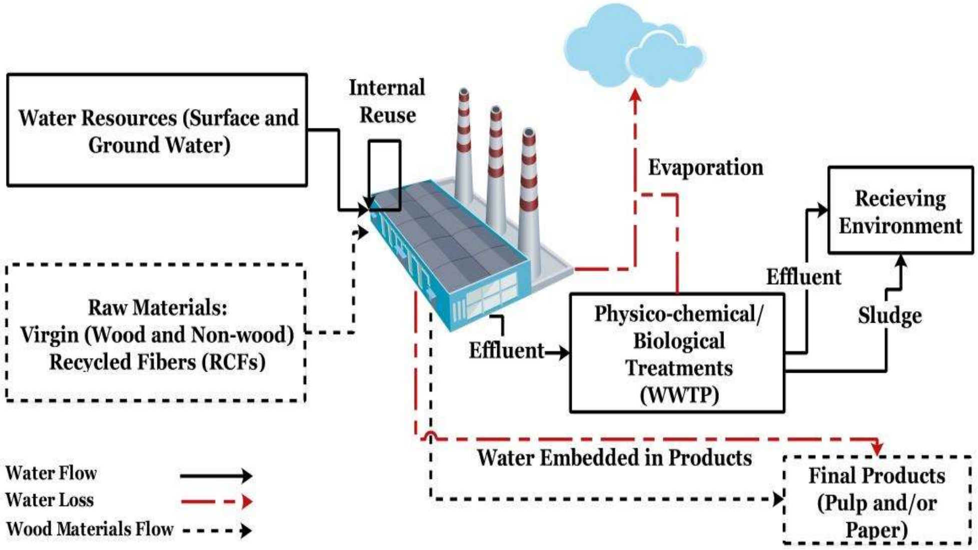


Fig. 2. 9. A schematic of the raw materials flow, use and fate at a typical P&P mill.

Due to the growing global concerns on the scarcity of water resources, the water management in water intensive industry, like PPI is of high importance and hence tough environmental regulations have been developed to ensure the sustainable use of the water resources in industrial water users. Although at the beginning of the last century the manufacturing processes in addition to other internal use required high amount of water (200-1000 m^3/tone paper), this amount has been considerably decreased due mainly to the technological advances occurred in the P&P production processes. As an example, German P&P industry has succeeded to reduce the water required for the production of a ton paper produced to just 13 m^3 [190]. Moreover, in many countries such as USA and Canada, the volume of recovered paper produced has significantly increased in the past two decades (e.g., from 17.4 million metric tons to 49.3 million metric tons in USA) [191] leading to a decrease in the amount of the wastewater generated for the production of P&P, due to the RCF mills being less water intensive when compared with virgin P&P producers [192].

Although the industry is a large user of water resources, only a small part of the water resource they use is consumed during the manufacturing related activities in a typical P&P mill. For instance, in United States, about 88% of the intake water is returned to the surface waters after being treated, while just 11% of it is evaporated and 1% is embedded in products or in solid wastes (Fig. 2.9) [193]. Accordingly, advanced treatment processes applied to the P&P mill wastes can significantly aid P&P producers to improve the quality of the effluents satisfying the environmental regulations. Moreover, some internal treatment processes can be provided in order to re-use the water during the manufacturing processes. For instance, Wang, Chen, Wang, Yuan, & Yu (2011) [194] through the application of aluminum chloride as a coagulant and a modified natural polymer (starch-g-PAM-g-PDMC) as a flocculant at the optimal conditions (coagulant dosage of 871 mg/L, flocculant dosage of 22.3 mg/L and pH 8.35) recovered 72.7% of water as a result of the treatment of a PPMW from a primary sedimentation tank.

2.2.4.2 Wastewater and sludge form P&P production processes

Virgin or RCFs are used as raw materials for the production of P&P. Pulp making, pulp processing, and paper-making are the main steps involved in the production of P&P from virgin wood raw materials. For this, a variety of chemical, mechanical or a combination of both methods have been applied so far. Debarking is the initial stage for the pulp making followed by pulping process which can be applied as MP and its derivatives (e.g., thermo-mechanical pulping (TMP), chemo-mechanical pulping (CMP), and chemical thermo-mechanical pulping (CTMP)) or CP processes like a widely used alkaline process called Kraft pulping process. Bleaching process is usually applied afterwards in order to increase the stability and brightness and to decrease the kappa number of the produced pulp. Paper-making is the final stage of P&P production applied in papermaking factories in which the produced pulps are converted to the paper sheets after dewatering. The fabrication of RCFs has also gained increasing attention in recent decades due to related environmental and economic benefits. Recovered pulp is produced through fiber recovering processes including pulping the waste paper (i.e., office paper wastes, newsprint papers and old paper containers), screening and deinking stages. Deinking stage, as the main RCFs recovering stage, is applied to remove the ink particles from the RCFs after being prepared through pulping process, followed by screening which removes large-diameter particles having high and medium density.

The amount of the wastewater produced from a P&P mill is strongly dependent on the P&P production stages and the method applied in each stage. Chemical additives are used in the several stages of P&P production process due to some reasons such as the reduction of the water consumption and saving the energy and raw materials. Table 2.4 summarizes the main rejects in the content of PPMW generally produced during several stages of P&P making processes. However, through the recovery of the chemical used for the manufacturing processes of P&P, the mills are able to reuse a portion of the required chemical raw materials. For instance, the black liquor from bleaching process can be concentrated and burned in order to recover inorganic smelt of Na_2CO_3 and Na_2S to be re-used for cooking the unbleached pulps [195]. However, such strategies would require the infrastructures for the chemical recovery and many of the small and some of medium scale P&P mills (> 100t/d) lack such facilities and, as a result, they discharge the rejects directly into the receiving environments [196]. In addition to the production method applied, the nature and origin of the raw materials used can cause the presence of some toxic and non-toxic substances such as resin acids (from conifer species), sterols (mainly β-sitosterol), waxes, and β-sitosterol esters (from the Kraft cooking and oxygen pre-bleaching of Eucalyptus sp.) in the content of the wastes produced from the P&P making processes [138], [197].

So far, some types of physico-chemical and biological treatments have been developed in order to deal with the wastes from P&P industry. However, the adoption of an effective and economic method by P&P industry still remains a main problem when dealing with their wastes. Table 2.5 presents the results of some recent studies indicating the performance of physicochemical and biological P&P treatments methods. Various approaches applied for the treatment of PPMW have shown different capabilities to remove the generated pollutants from the PPMW. However, there are main drawbacks that have restricted their adoption by the mills. For instance, in spite of the acceptable performance of physico-chemical methods for the improvement of various wastewater parameters (e.g., chemical oxygen demand (COD), biochemical oxygen demand (BOD), adsorbable organic halogens (AOXs), TSS, and lignin), being relatively expensive as well as maintenance requirements and technical barriers such as membrane fouling (for membrane reactors) are main limitations restricting their wider applications. Biological methods also have shown the feasibility for the treatment of wastewater from many types of P&P production processes. Although activated sludge processes are currently the major treatment for P&P mill effluents, AD has attracted a great amount of attention in recent years due to its inherent merits such as biogas production and minimizing the solid wastes production which has made it an attractive candidate for the treatment of PPMW. However, the toxic effects of some P&P effluents (e.g., kraft bleaching effluents) for the bacterial communities as well as the sensitivity of the biological systems to the environmental and operational conditions (e.g., restriction of AD and the fungal activity under high pH) are among the main problems of such systems to deal with PPMW. Having this, optimization the efficiency of such systems is the most important step to achieve the desired efficiency and facilitation of transferring these technologies from lab-scale to full-scale applications [163,198,199].

However, the treatment of P&P wastewater normally produces a large amount of primary and secondary sludge which management and disposal are contributing to about 60% of the total PPMW treatment cost [200]. In a typical P&P mill biological treatment is generally preceded by primary treatment (either sedimentation or flotation), resulting in the formation of primary sludge in the primary clarifier. The secondary sludge is subsequently produced in the secondary clarifier after treatment of the wastewater either by aerobic or anaerobic treatments or their combination. The characteristics of the primary and secondary sludge are highly dependent on the raw materials used, P&P production process, and the applied subsequent wastewater treatment process(es). Primary sludge mainly consists of the higher size rejects such as fibrous materials (cellulose, hemicellulose and lignin), as well as the rejects from paper making process such as fillers, and metallic components, sand, coatings, fillers, etc, in the case of paper making from RCFs. However, non-biodegradable compounds and other rejects from P&P production processes, based on the efficiency of the applied wastewater treatment processes [198], as well as the biomass from involved microbial communities and the cell-decay materials are the main constituent of the secondary sludge [201]. The common management ways to deal with the PPS are the incineration and landfilling. However incinerating the primary and secondary sludge after being mixed and thickened is not energy efficient. Also, land filling is being restricted by the environmental rules. Moreover, some other constrains such as land availability, public opinion and the cost are involved in the utilization of land filing [202]. So, AD of PPS can be considered as a long-time solution, in line with the increasing interest to promote the production of renewable energy, to convert the rejects from PPMS into the biogas, and to minimize the final wastes from the P&P industry.

2.2.5 Developments and improvement opportunities

Hydrolysis, acidogenesis, acetogenesis and methanogenesis are the main steps involved in the AD process. While the first three steps are performed by various bacterial species, methanogenesis is performed by methanogens, a group of Archaea [203]. During hydrolysis, hydrolytic bacteria secrete enzymes to break organic polymers (carbohydrates, proteins and fats) into smaller parts, such as sugars, amino acids and fatty acids. At the next stage, these products are converted to compounds like acetic acid and intermediate products such as ethanol, hydrogen and carbon dioxide by fermentative or acidogenic bacteria. Then, acetate, hydrogen and carbon dioxide are produced as a result of the acetogenic bacterial activity. Finally, the methanogenic bacteria produce methane from acetate, hydrogen, and carbon dioxide [204,205] (see Fig. 2.10).

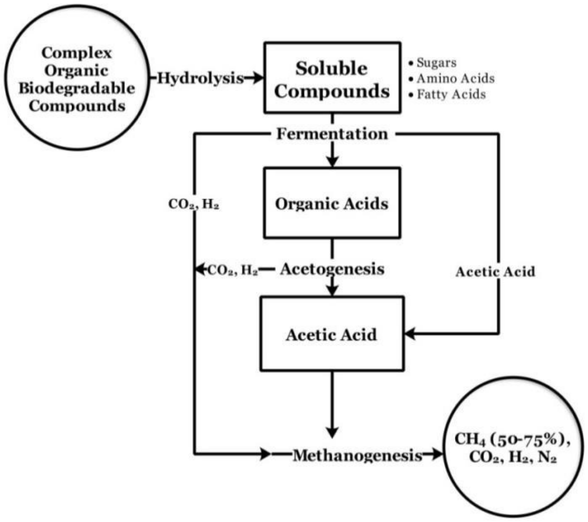


Fig. 2. 10. A schematic of the AD steps.

Table 2. 4. Main rejects from P&P making processes using virgin or RCFs to the PPMW.

Fibrous raw materials	Operation	Main processes	Main rejects	Typical effluents parameters							Reference
				Process	pH	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	Other parameters		
									Type	Quantity	
Virgin fiber	Raw materials operation	Debarking, chipping and conveying	Bark, tannin, lignin, hemicelluloses and some large amounts of organic compounds such as resin acids as well as soil and dirt.	Wood yard and chipping	7	1275	556	7150	-	-	[206–209]
	Pulping (paper grade or dissolving grade)	Sulfate pulping (kraft) and sulfite pulping, TMP CTMP MP CMP	Knots, uncooked woods, bark particles, soluble wood materials Color, resin acids (Including Isopimaric, sandacopimaric, levopimaric, abietic, dehydroabietic, neoabietic and palustric acids), fatty acids, BOD, COD, and dissolved inorganics, Lignin, and hemicelluloses, also some chemical additives such as soluble silicates ($3SiO_2$ Na_2O).	Kraft cooking	13.5	1669.7	460	40	-	-	[80,195,206,209–215]
				TMP	4.0–4.2	3343–4250	-	330–510	TN[a] TP[b]	0.01-0.02 (mg/L) 1.31–1.47 (mg/L)	
				APMP[c]	7.43	7521	3000	350	Lignin MTBE extractives	516 (mg/L) 147 (mg/L)	
				CTMP	12	25000	6800	-	Color	42000 (C.U.)	
				MP[d]	6.1-8.1	91-1150	6-69	3-45	-	-	
	Bleaching	Chemical or mechanical pulp bleaching	Chlorophenols, AOX, EOXs, polychlorinated biphenyls, polychlorinated dibenzodioxines, dioxins, furans, chlorinated lignosulfonic acids, chlorinated resin acids, residual lignin, color, COD, carbohydrate, inorganic chlorines, VOCs, and halogenated hydrocarbons.	Kraft pulp Bleaching	8.50	426	25.50	-	Lignin Phenol AOX	50.00 (mg/L) 0.535 (mg/L) 2.82 (mg/L)	[80,206,208,216–220]
				Bleaching[e]	8.2	3680	352	950	Residual chlorine Chloride content	9040 (mg/L) 1340 (mg/L)	
	Washing	Bleached pulp washing	Residual lignin, bleaching agents and some hardly biodegradable organic compounds.	-	-	-	-	-	-	-	[208]
	Paper-making	Dewatering, pressing and drying, finishing	Mineral additives, AOXs, resins, BOD, COD, resin acids, particulate wastes, etc.	Paper machine	6.5	1116	641	645	-	-	[210][221][222]

Table 2.4. Continued.

Fibrous raw materials	Operation	Main processes	Main rejects	Typical effluents parameters							Reference
				Process	pH	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	Other parameters		
									Type	Quantity	
RCFs	Pulping/ deinking	RCFs pulping	Metallic components, sand, glass, plastic, coatings, fillers, organic compounds from the paints and printing inks such as 2,4,7,9-Tetramethyl-5-decyne-4,7-diol, pulping additive chemicals, compounds like Si and Ca, higher amounts of organics[i], thermoplastic resins[j], TCMTB, chlorophols, etc.	Newsprint mill	-	3500	-	250	Color	1000 (Pt-Co)	[198,210,223–228]
				Recycled paper mill	6.2–7.8	3380–4930	1650–2565	1900–3138	-	-	
				Recycled paper mill	6.36	4328	669	645	VFA	501(mg/L)	
									VSS[k]	850 (mg/L)	
	RCFs	De-inking	Deinking additives and ink particles, fibers, fines, fillers, ash, etc.	De-inking effluents	7-8	-	-	-	Moisture	98.7 (%)	[225,229–231]
									Ash[l]	0.54 (%)	

a. Total nitrogen.
b. Total phosphorus.
c. Alkaline peroxide MP.
d. Effluents from seven Canadian mills.
e. Chlorination and alkaline extraction stages.
f. e.g., clay, titanium dioxide, calcium carbonate.
g. e.g., rosin, starch and styrene copolymers.
h. Wet strength additives like synthetic resins (such as Urea formaldehyde and melamine formaldehyde) and Epichlorohydrin (ECH)-derived compounds (such as polyamine-epichlorohydrine resin (PAE)) as wet strength additives.
i. From light-weight coated paper, because of the coating binders.
j. In case of laser printing papers.
k. Volatile fatty acids.
l. Ash (after ignition at 900° C) consisted of SiO_2 (16.70 %), Al_2O_3 (16.53 %), CaO (22.46 %), TiO_2 (32.39%), BaO (5.43%), CuO (2.59%), S_2O_3 (1.17%), Fe_2O_3 (0.92%), Na_2O (0.33%).

Table 2. 5. Efficiency of physicochemical and biological processes for the treatment of PPMW.

Type	Process	Parameters				Reference
		COD removal (%)	**BOD removal (%)**	**Other Parameters**		
				Type	**Removal (%)**	
Physicochemical	Electrocoagulation (Al)	75	70	Lignin Phenol	80 70	[232]
	Flocculation (polydiallyldimethylammonium)	> 90	-	Turbidity TSS	> 90 > 90	[233]
	Ozonation	~ 20	-	DOC Color	> 15 > 50	[234]
	Fungi+solar photo-Fenton (Cryptococcus+Fe^{2+}/H_2O_2)	> 90	-	DOC	90	[235]
Biological	Fungal (*Aspergillus niger*)	60	-	MTBE extracts	97	[236]
	Aerated stabilization basins	67	90	-	-	[237]
	Aeration pond	-	-	2,4-DCP	56.0- 77.6	[238]
	Multiple stage activated sludge	65	95	-	-	[239]
	Activated sludge	76	-	Color	76	[164]
	Activated sludge	-	-	Sterols	> 90	[240]
	Upflow anaerobic filter[a]	-	-	AOX	90.7	[241]
	Modified anaerobic baffled reactor	71	71	VFA	-32	[227]

a. UAF

AD is considered an attractive candidate to deal with a broad range of wastes with high levels of biodegradable materials, such as the residues from PPI. Nonetheless, lignocellulosic materials present in P&P wastes have the potential to slow the hydrolysis step of the AD process. In addition, the overall performance of AD systems can be strongly affected by several types of factors. Anaerobic configuration, operational and environmental conditions (i.e., HRT, pH, temperature), and the presence of inhibitory compounds like ammonia, sulfide, chlorides, heavy metals, and hardly biodegradable compounds in the wastewater or sludge contents can potentially contribute to slow the AD process, resulting in a low methane yield and process instability [169]. The factors that critically affect the performance of AD for the treatment of P&P wastewater and sludge are reviewed and discussed in the next sections.

2.2.5.1 AD of PPMW

2.2.5.1.1 Reactor configuration

After innovation of high rate generations of AD digesters, several types of such reactors have been developed, and some of them have been adopted by the PPI for the treatment of PPMW. The achievement of a short HRT, when a relatively high OLR is introduced to the system, was a focus of large attention in order to minimize the volume of the reactor, as well as to improve the methane production. Among the high rate anaerobic reactors, UASBs, anaerobic filters (AFs) and anaerobic membrane bioreactors (AnMBRs) have been mainly applied to treat the P&P mill effluents.

2.2.5.1.1.1 AFs

AFs are earlier types of high-rate anaerobic reactors with relatively simple configuration, compared with other types of AD reactors such as fluidized bed reactors (FBRs) and UASB reactors [242]. Show & Tay (1999) [243] showed that the texture and the porosity of the media surface can significantly influence the removal of the chemical oxygen demand (COD) by anaerobic filter reactors.

In recent years, novel filter media such as sludge-fly ash ceramic particles [244], clay ceramic particles [245], and pumice stone [246] have been successfully applied in order to improve the AD by using AFs.

So far, AFs has shown an acceptable performance, especially to deal with municipal and other low-strength effluents at the ambient temperature [247]. There are also evidences indicating an acceptable performance of AFs to deal with high- strength effluents [248]. However, the application of such systems for the treatment of wastewater from P&P mills is limited, when compared to reactors with internal settlers, such as UASB reactors. Satyawali, Pant, Singh, & Srivastava (2009) [249] applied an upflow anaerobic packed bed reactor (UAPBR) with brick ballasts as packing material for the treatment of rayon grade pulp drain effluents. They observed 74.5% and 81% reductions in COD and BOD respectively, at an optimum HRT of 12 h. Deshmukh et al. (2009) [241] reported AOX degradation from a PPM bleaching effluent by using an AF with upflow. They observed 88% and 28% removals of AOX at initial concentrations of 28 mg AOX/L and 42 mg AOX/L, respectively, and HRT of 20 days. Bakhshi et al. (2011) [250] studied the removal of phenol from a synthetic wastewater by using a pilot-scale UAPBR. Under mesophilic conditions and HRT of 24 h, the maximum biodegradation of phenol and biogas production achieved were 98% and 3.57 L/d, respectively. Jong & Parry (2003) [251] achieved more than 82% removal of sulfate from contaminated waters by using a bench-scale UAPBR filled with silica sand at an organic and sulfate loading rates of 7.43, and 3.71 kg/d/m^3, respectively. Moreover, they observed removals of Cu and Zn >97.5%, removals of Ni of 77.5%, and removals of As and Fe >82%.

Technical considerations are the main limiting factors for wider applications of AFs. The performance of such reactors is mainly impaired by clogging due to the presence of high amount of suspended solids leading to short circuiting of the wastewater [252]. Although some improvements have been proposed to solve this problem such as biological pre-treatment [253] and utilization of the filtering media packing method, in which filtering media blocks prepared by filling the filtering media with cross-flow type filtering media are inputted into the anaerobic reactor, further research and developments are critical in order to find out technical and economical solutions for this problem.

2.2.5.1.1.2 UASBs

Among the several types of anaerobic reactors, UASB has been commonly adopted by pulp and paper industry since 1980's, due to its advantages when compared with other types of high-rate anaerobic reactors, such as low investment requirements [171]. Buzzini & Pires (2002) [254] reached 80% on average removal of COD when treating diluted black liquor from a kraft pulp (KP) mill by using an UASB reactor. The performance of a bench scale UASB was also investigated by Buzzini, Gianotti, & Pires (2005) [255] for the treatment of simulated bleached and unbleached cellulose pulp mill wastewaters. They achieved 76% on average removal of COD and 71-99.7% on the removal of chlorinated organics. They also observed no inhibitory effect of the chlorinated organics on the removal of COD during the experiments. Chinnaraj & Rao (2006) [85] reported 80-85% reduction in COD, while producing 520 L/Kg COD of biogas, after the replacement of an anaerobic lagoon by an UASB installation (full-scale) for the treatment of an agro-based PPMW. Moreover, they achieved a reduction of 6.4 Gg in CO_2 emissions through the savings in fossil fuel consumption, and 2.1 Gg reduction in methane emissions from the anaerobic lagoon (equal to 43.8 Gg of CO_2) in nine months. Zhenhua & Qiaoyuan (2008) [256]achieved 98% and 85.3% reductions in BOD_5 and COD, respectively, from pulping effluents by using a combination of UASB and sequencing batch reactors (SBRs), while the removal efficiency when the substrate was just treated by a UASB reactor was considered to be 95% and 75% for BOD_5 and COD, respectively at an HRT of 1 day. Rao & Bapat (2006) [257] achieved 70-75% and 85-90% reductions of COD and BOD, respectively, and a methane yield of 0.31–0.33 m^3/kg of COD reduced, when using a full-scale UASB for treating the pre-hydrolysate liquor from a rayon grade pulp mill. Puyol, Mohedano, Sanz, & Rodríguez (2009) [258] studied the effective removal of 2,4-DCP by using both UASB and anaerobic expanded granular sludge bed reactor (EGSB). Moreover, they indicate that EGSB reactor exhibited a better efficiency for the removal of both COD and 2,4-DCP (75% and 84%, respectively), when compared with UASB reactor (61% and 80%, respectively), at loading rates of 1.9 g COD/L/d and 100 mg 2,4-DCP /L/d.

2.2.5.1.1.3 AnMBRs

In recent years, AnMBRs which combine the advantages of AD process and membrane separation mechanisms have received considerable attention due to their advantages for wastewater treatment such as lower sludge production and energy requirements over conventional anaerobic treatment methods [259]. By adopting anaerobic membrane technologies, it is possible to achieve complete solid-liquid phase separation and, as a result, complete biomass retention [260]. Since 1990s, some studies have been carried out to investigate the efficiency of such systems for the treatment of PPMW, and have shown 50-96% removal of COD [261]. Xie et al. (2010) [262] investigated the performance of a submerged anaerobic membrane bioreactors (SAnMBRs) for the treatment of kraft evaporator condensate at mesophilic conditions. They reached 93-99% COD removal under an OLR of 1-24 kg COD/m^3/day. Moreover, the methane production rate was observed to be 0.35 ± 0.05 L/g COD reduced. Lin et al. (2009) [263] achieved 97-99% COD removal from a kraft evaporator condensate at a feed COD of 10000 mg/L in two pilot-scale (thermophilic and mesophilic) submerged AnMBRs. Gao, Lin, Leung, & Liao (2010) [264] observed about 90% COD removal during the steady period (22nd-33rd day) of the performance of a submerged AnMBR, treating thermomechanical pulping (TMP) whitewater.

However, despite the acceptable performance of AnMBRs for the removal of COD from the P&P substrates and good methane production, the maintenance and operational costs arising from membrane fouling are considered the main obstacles of such treatment systems dealing with various types of wastewaters. After studying the fouling mechanisms in AnMBRs, Charfi et al. (2012) [265] concluded that the cake formation is the main mechanism responsible for membrane fouling in

AnMBRs. Such findings were also corroborated by other studies [263]. Although some measures such as feed pre-treatment, optimization of operational conditions, broth properties improvements, and membrane cleaning have already been applied to control the membrane fouling process [172], this issue demands further studies on AnMBR performance.

The applications of other types of anaerobic reactors have also been investigated for the treatment of PPMW, although the number of such studies is scarce in the literature. For instance, Grover et al. (1999) [266] achieved a maximum of 60% COD removal from black liquor by using an anaerobic baffled reactor (ABR) at an organic loading rate (OLR) of 5 kg /m^{3}/d, a HRT of 2 d, a pH 8.0 and a temperature of 35°C.

Table 2.6 summarizes the observed performance of various reactor configurations for anaerobic treatment of PPMWs.

Table 2. 6. Performance of various reactor configurations for anaerobic treatment of PPMWs.

	Effluents Origin	**Parameters**					**Refe.**
Reactor Configuration		**COD**		**Other parameters**			
		Initial (mg/L)	**Removal (%)**	**Parameter/ substance**	**Initial (mg/L)**	**Removal (%)**	
UAPBR, (brick ballasts as packing material)	Rayon grade pulp drain effluent	3200[a]	74.5	BOD	-	81	[249]
				TSS[b]	-	62.7	
				TDS[c]	-	52	
UAF	Bleach composite wastewater	-	-	AOX	28	88	[241]
				AOX	42	28	
UAPBR	Synthetic phenolic wastewater	-	-	Phenol	1000	98	[250]
UAPBR, filled with silica sand	-		-	Sulfate	2280	82	[251]
		-		Cu	10.8	>97.5	
				Zn	10.3	>97.5	
				Ni	9.5	82	
				As	10.6	82	
				Fe	11.6	82	
UASB	Diluted black liquor	1400	76-86	-	-	-	[254]
UASB	Diluted black liquor	1400	76	chlorinated organics	15	71-99.7	[255]
UASB	Bagasse-based P&P mill	2000–7000	80-85	-	-	-	[85]
				VFA	500-3500	-	
				SS	400-1000		
UASB+SBR UASB	Wheat straw explosion pulping effluent	-	85.3	BOD_5	-	98	[256]
		-	75	BOD_5	-	95	
UASB	Synthetic wastewater containing 2,4-DCP	1900	61	2,4-DCP	100 (mg/L/day)	80	[258]
EGSB	Synthetic wastewater containing 2,4-DCP	1900	75	2,4-DCP	100 (mg/L/day)	84	
UASB	Pre-hydrolysate liquor from a rayon grade pulp mill	2500	70-75[d]	BOD	-	85-90	[257]
UASB	P&P mill	1,133.9±676	~ 81	TSS	1,063±537	~ 67	[89]
				VFA	397±347.7	~ 87	
SGBR[e]	P&P mill	1,133.9±676	~ 82	TSS	1,063±537	~ 57	[89]
				VFA	397±347.7	~ 53	
Submerged AnMBR	Kraft evaporator condensate	2500-2700	93-99	-	-	-	[262]
Submerged AnMBR	Kraft evaporator condensate	10000	97-99	-	-	-	[263]

Table. 6.2. Continued.

Reactor Configuration	Effluents Origin	Parameters					Refe.
		COD		Other parameters			
		Initial (mg/L)	Removal (%)	Parameter/ substance	Initial (mg/L)	Removal (%)	
Submerged AnMBR	TMP whitewater	2782-3350	90	-	-	-	[264]
ABR	Cornstalk fibrous pulp wastewater	4000	81.9^{f}	-	-	-	[267]
	Cornstalk fibrous pulp	4002	81.1^{g}	-	-	-	
ABR	wastewater	6560	75.7^{g}	-	-	-	[267]
ABR	Black liquor	10003±69	60	-	-	-	[266]
ABR	Recycled paper mill effluents	3380–4930	Up to 71	BOD	1650–2565	~ 70	[227]
				VFA	455–490	~-31	
				TSS	1900–3138	~ 45	

a. The rate of the effluent generation was 6000-7000 m^3/day.
b. Total dissolved Solids
c. Total suspended Solids
d. Full-scale installation with an optimum OLR of 10 and a methane yield of 0.31–0.33 m^3/kg of COD reduced.
e. Static granular bed reactor.
f. HRT 18 h.
g. HRT 24 h.

2.2.5.1.2 Operating conditions

2.2.5.1.2.1 HRT

HRT is one of the most significant influencing factors that can potentially affect the performance of an anaerobic reactor. In UASB reactors type, at high HRTs, the upflow velocity (V_{up}) decreases, and, as a result, the efficiency of the reactor for the removal of the suspended solids increases [268]. Moreover, elevated HRT can enhance the COD removal through the elevation of the contact time. Parker, Hall, & Farquhar (1993) [269] reported 27 to 65% removal of adsorbable organic halogens (AOX) when treating a kraft-mill bleach wastewater by using a UASB reactor, depending on the HRT (3 to 48 h). Since then, the developments on the design and operational conditions of high rate reactors have led them to treat P&P mill wastes more efficiently. Turkdogan et al. (2013) [89] achieved 60% and 81% removals of COD by using a pilot-scale UASB reactor at 4 and 9 h HRT, respectively. Moreover, they observed that the performance of a static granular bed reactor (SGBR) was better than that of a UASB reactor, with more than 70% COD removal at 4 h HRT. In addition, at 24 h HRT, the suspended solids removal was observed to be slightly higher in the SGBR. Sun et al. (2009) [267] investigated the effect of different HRTs on the performance of an ABR when treating the cornstalk fibrous pulp wastewater. They observed that with the initial COD of 4000 mg/L, when HRT decreased from 40 h to 19 h, the COD removal efficiency decreased from 81.9% to 75.7%, respectively. The performance of AD systems under various HRTs may also be affected by the operating temperature. Ahn & Forster (2002) [270] stated that with an increase in the HRT from 11.7 to 26.2 h, the performance of the thermophilic digestion increases, while no significant HRT-related improvement in the mesophilic digester is observed in terms of COD removal when treating a simulated paper mill wastewater.

The presence of 2,4 dichlorophenol (2,4 DCP) can negatively affect the methanogenic phase [258]. Sponza & Uluköy (2008) [271] evaluated the removal of 2,4 DCP and COD from a synthetic wastewater at different HRTs ranging from 2 to 20 h using an UASB reactor. They observed a decrease in the COD removal from 83% to 65% when the HRT was decreased from 20 to 2 h. In these conditions, the removal of 2,4 DCP was 99% and 83%, respectively. Sponza & Cigal (2008) [272] identified *Methanobacterium bryantii*, *Methanobacterium formicicum*, *Methanobrevibacter smithii*, *Methanococcus voltae*, *Methanosarcina mazei*, *Methanosarcina acetivorans*, *Methanogenium bourgense*, and *Methanospirillum hungatei* as the microorganisms involved in the treatment of 2,4 DCP, when using a UASB reactor. Table 2.7 presents the results from some studies investigating the effects of the HRT on the performance of anaerobic reactors for the treatment of PPMW.

Table 2. 7. The effect of HRT on the performance of AD for the treatment of PPMWs

Reactor	Effluents origin	Parameters						Referece
		COD			Other parameters			
		Initial (mg/L)	Removal (%)	HRT (h)	Parameters	Initial (mg/L)	Removal (%)	
UASB	Black liquor	1400	76	24	BOD	800	-	[254]
					Sulfide	8.8	-	
					P_{total}	6.5	-	
UASB	Black liquor	1400	86	14.4	-	-	-	[273]
		1400	75	24	BOD	660	-	
					P_{total}	4.0	-	
					VFA	-	30	
UASB	Black liquor	1400	78	30	VFA	-	29	
UASB	Synthetic effluents	514	83	20	2,4 DCP[a]	12	99	[271]
		2000	65	2	2,4 DCP	232	83	
UASB	Segregated kraft bleaching effluents	-	-	3	AOX	-	27	[269]
		-	-	48	AOX	-	65	
UASB	TMP paper mill wastewater	1,133.9	60	4	TSS	1,063	92	[89]
					VFA	397	71	
		1,133.9	85	9	TSS	1,063	55.57	
					VFA	397	84	
		1,133.9	81	24	TSS	1,063	50	
					VFA	397	88	
ABR	Cornstalk fibrous pulp wastewater	4000	81.9	40	-	-	-	[267]
			75.7	19	-	-	-	
AF[a]	Simulated paper mill wastewater		85	13	-	-	-	[270]
			>90	23	-	-	-	
MAHB[b]	RCFs	1000-4000	97.69	-[d]	VFA	35[e]	-	[274]
			78.37	-[f]	VFA	~10[g]	-	

a. Thermophilic conditions (55 °C).
b. Anaerobic hybrid baffled.
c. Prepared by paper- pulp liquors and corrugated paper- pulp liquors.
d. OLR of 1.33 gm COD/lit/day.
e. VFA concentration at OLR of 2.00 gm COD/lit/day.
f. OLR of 2.00 gm COD/lit/day.
g. VFA concentration at OLR of 1.33 gm COD/lit/day.

2.2.5.1.2.2 Environmental Conditions

a) Temperature

AD is generally designed and conducted in psychrophilic (<25°C), mesophilic (25-40°C), and thermophilic (>45 °C) conditions [136]. Suihko et al. (2005) [275] concluded that the most common thermophile and mesophilic anaerobic bacteria in paper mill environments are *T. thermosaccharolyticum* and *C. magnum*, respectively, among a total of 177 anaerobically grown bacterial isolates.

The operating temperature is a significant variable that can potentially affect the efficiency of the COD removal and biogas production from various wastewaters through, for instance, an increase in the microbiological activity [276]. This process is generally carried out at mesophilic conditions (35-37 °C). However, several studies on the AD of various substrates have clearly indicated that the thermophilic conditions allow a better COD removal and biogas production [277]. Moreover, benefits like higher maximum specific growth rate of microorganisms (μ_{max}), and therefore better organic matter degradation in a shorter operating time [276], higher colour removal efficiency [278], more favorable disinfection capability, improved AD steady state stability [279], and being more feasible for co-digestion approaches than mesophilic processes [280] can be expected by operating under thermophilic conditions.

Yilmaz et al. (2008) [242] studied the performance of two AFs under mesophilic (35 °C) and thermophilic (55 °C) conditions for the treatment of a paper mill wastewater. They observed no significant differences at OLRs up to 8.4 g COD/L d. At higher OLRs, slightly better COD removal and biogas production were observed in the thermophilic reactor, which also denotes the effect of the OLR on the performance of the AD process. Ahn & Forster (2002) [270] showed that the specific methane production obtained in an AF treating a simulated paper mill wastewater under thermophilic digestion was higher than the one obtained at a mesophilic temperature under all the studied HRTs from 11.7 to 26.2 h. In the same study, they also indicated that the performance of the two mesophilic and thermophilic upflow AFs treating a simulated paper mill wastewater can be affected either by a drop or an increase in the operating temperature. They showed that the performance of both digesters, in terms of COD removal efficiency and biogas production at an OLR of 1.95 kg COD/m^3/day, was negatively affected by a drop in the operating temperature to 18-24°C and to 35°C for mesophilic and thermophilic digesters, respectively. When the temperature was increased to 55 and 65°C in mesophilic and thermophilic digesters, respectively, they also observed an immediate decrease in the treatment efficiency [281]. However, some studies have also shown that anaerobic biomass have a potential for good recovery after undergoing thermal shock [254]. The effect of the variations in the operating temperature can be significantly affected by the configuration of the reactor. SAnMBR seems to be more resistant to temperature variation when compared with other high-rate conventional anaerobic digesters. Lin et al. (2009) [263] observed no significant difference between the thermophilic and mesophilic AD, when treating pulping wastewater by using a pilot-scale SAnMBR. They also observed that the mesophilic SAnMBR can exhibit a better filtration performance in terms of filtration resistance. Gao et al. (2011) [260] investigated the effect of the temperature and temperature shock on the performance of a SAnMBR treating TMP pressate. Their results indicated that the COD removal at 37 and 45 °C was slightly higher than that at 55 °C. However, they observed no significant differences between the methane productions at the various temperatures. They also indicated that temperature shock can affect the diversity and richness of the species. A COD removal efficiency of 97–99% was observed at a feed COD of 10000 mg/L in both SAnMBRs. In spite of the advantages of conventional mesophilic and thermophilic treatments, low-temperature AD has emerged in recent years, as an economic method to deal with cool, dilute effluents which were considered as inappropriate substrates for AD [282]. McKeown, Hughes, Collins, Mahony, & O'Flaherty (2012) [283], by reviewing the basis and the performance of the low-temperature AD for wastewater treatment, concluded that the adoption of effective post treatments for low temperature anaerobic digestion (LTAD) is a way to satisfy the stringent environmental regulations. Some recent studies have also indicated that LTAD can be more efficient by adopting the co-digestion approach (in pilot-scale application) [284]. However, significant physical, chemical and biological improvements should be applied to high-rate AD under low-temperature conditions to enhance the efficiency of the present AD systems, and to improve the amount of the methane produced during the related anaerobic processes.

b) pH

In addition to the temperature, the pH of the system is of great significance to identify the predominant type of microorganisms and their growth rate. The anaerobic digesters are very sensitive to changes in the pH of the system. This occurs mainly due to the restriction of the methanogens growth below pH 6.6 [285] (Table 2.8). Methanogens are more sensitive to pH, compared to fermentative microorganisms which can survive in a wider pH range between 4.0 and 8.5 [286]. By inhibiting the methanogens, VFAs are produced and converted to acetic acid, hydrogen and carbon dioxide and thus they are accumulated in the medium. As a result, the pH will decrease leading to a further inhibition of the microbial activities [287]. Allowing methanogens to be reproduced by stopping the substrate feeding is considered to be one of the possible ways [173] In order to correct the pH failure. Moreover, co-digestion of the main substrate with an appropriate ratio of another (co)substrate is an applicable way to provide the system with a suitable pH, and to increase its buffering capacity [288]. However, the most appropriate pH range for such reactors is between 6 and 8 [289]. The variation in the pH can also influence the activities of the microorganisms including metabolism and degrading efficiency of the system [290]. Moreover, the morphology of the bacterial communities may be influenced by the changes in the pH. Sandberg & Ahring (1992) [291] stated that disintegration of microbial granules can be expected at alkaline pH values. This is a very important issue because the kraft wood pulping effluent is alkaline [292] which may lead to the failure of the system. Moreover, the ECF acidic effluents from the KP mills have been shown to be very toxic to the AD microorganisms [293] and this can directly affect the methane production from such effluents. Gao et al. (2010) [264] indicated that although a pH shock of 8.0 had no important adverse effects on the performance of a SAnMBR in terms of COD removal, biogas production and membrane filtration, the long lasting negative effects of pH shocks of 9.1 and 10.0 were significant. They also observed that after providing the normal pH (7.0), it took approximately 30 days for the total recovery of the reactor performance after the pH shock of 10, compared with 1, and 6 days for pH shocks of 8.0 and 9.1, respectively.

Table 2. 8. Optimal conditions for the growth of some methanogenic bacteria [173,289,294].

Genus	Optimal temperature range	Optimal pH range
Methanobacterium	37-45	6.9-7.2 (*Methanobacterium bryantii*)
Methanobrevibacter	37-40	7.8-8 (*Methanobrevibacter arboriphilus*) ~7 (*Methanobrevibacter smithii*)
Methanosphaera	35-40	~7
Methanolobus	35-40	~7
Methanococcus	35-40	5-7 (*Methanococcus voltae*)
Methanosarcina	30-40	6.5-7.5 (*Methanosarcina acetivorans)*
Methanocorpusculum	30-40	6.4-7.2 (*Methanocorpusculum aggregans*)
Methanoculleus	35-40	~7
Methanogenium	20-40	6.2-6.6 (*Methanogenium cariaci*)
Methanoplanus	30-40	6.6-7.2 (*Methanoplanus endosymbiosus*)
Methanospirillum	35-40	-
Methanococcoides	30-35	~7
Methanolobus	35-40	~7
Methanohalophilus	35-45	~7
Methanohalobium	50-55	~7
Methanosarcina	50-55	6.5-7.5 (*Methanosarcina acetivorans*)

Table 2.9 presents the results of some studies on the performance of AD under various operating conditions, especially temperature and pH, for the treatment of PPMWs.

Table 2. 9. Performance of some AD systems for the treatment of PPMWs.

Reactor	Effluents origin	Parameters						Considerations	Ref.
		Temp.	pH	COD		Biogas production (L/day)	Methane yield (L CH_4/g COD)		
				Initial (mg/L)	Removal (%)				
AF	Paper mill wastewater	Mesophilic	7-7.6	3144	77	2.957	0.274	At HRT of 6 hr	[242]
		Thermophilic	7-7.6	3144	80	3.204	0.291	At HRT of 6 hr	
SAnMBR	kraft evaporator condensate	Mesophilic	7.0	10000	97-99	-	0.35	-	[263]
		Thermophilic	7.0	10000	97-99	-	0.35	-	
Serum bottles	ECF bleaching process effluents at kraft mills (softwood)	Mesophilic	3.2	1700	-	-	0.35[a]	-	[293]
	Kraft cooking effluent (softwood)	Mesophilic	10.0	620	-	-	0.660	-	
SAnMBR	TMP whitewater	Mesophilic	7.0	2782-3350	~90	-	0.41	-	[264]
		Mesophilic	8.0	2782-3350	83	-	0.38	pH shocks from 7 to 8, 9.1, and 10, respectively	
		Mesophilic	9.1	2782-3350	75	-	~0		
		Mesophilic	10	2782-3350	30	-	~0		
AF	Simulated paper mill wastewater	Thermophilic		-	93		~ 0.25	At HRT of 25.1 hr	[270]
		Mesophilic		-	77		~ 0.18	At HRT of 26.2 hr	

a. NL CH4/g TOC, COD/TOC: 2.3.
b. NL CH4/g TOC, COD/TOC: 6.5.

2.2.5.1.3 Inhibitory elements

The efficiency of an AD system may be limited by the presence of some elements. Relatively high amounts of soluble forms of nitrogen and phosphorous are required to ensure the sufficient growth and activity of all microorganisms, involved in all AD stages. This is considered a significant feature for the treatment of PPMW, due to the low amount of nitrogen, as a key nutrient, which normally occurs in such type of residues [295]. In addition, the ratio of key elements is of high importance to avoid the failure of the AD process. Bouallagui (2003) [296] applied an optimum ratio of 100-130:4:1 for COD:N:P, as an optimal condition for AD of vegetable biomasses. Qu et al. (2012) [213] reported the adjustment of this ratio to 100:5:1 for appropriate biomass growth. The successful adoption of this ratio has been also indicated by other studies [270]. Furthermore, the ratio of carbon to nitrogen (C:N) is of importance to ensure the desirable efficiency of an AD system. In this regard, a low C:N ratio may cause the accumulation of total ammonia nitrogen or VFAs, which are inhibitor factors for AD performance. Moreover, the inhibition of the methane production is considered to be a result of a high C:N ratio, through the rapid consumption of the nitrogen by methanogens. The optimal amount of 25:1 has been determined for C:N [297].

In addition, the PPMW often contains high amounts of sulfide compounds which may inhibit the AD process. Air purging is considered an effective way to increase the efficiency of the system and to remove the adverse toxic effects caused by sulfide compounds. Lin et al. (2014) [298] achieved a considerable improvement in the COD removal (from 20-30% to 65-75%) by using a UAPBR anaerobic digester, when a foul condensate from a PPI was purged with air for at least 2 h before the pre-digestion stage. Zhou, Imai, Ukita, Li, & Yuasa (2007) [299] achieved a 40% increase (from 40% to 80%) in the removal of COD from a sulfite pulp mill evaporator condensate, by applying a direct limited aeration in the UASB, at an OLR of 8 kg COD m^3/d and a HRT of 12 hr. This extra COD removal occurred due to sulfide oxidation and H_2S removal, which can lead to the methanogens improvements.

2.2.5.1.4 Pre-treatment strategies

Although many attempts have been made to enhance the removal of the persistent pollutants from PPMWs (Table 2.10), the number of published papers investigating the direct effects of the physico-chemical and biological pre-treatments on the performance of AD facilities is still scarce. Kim, Yeom, Ryu, & Song (2004) [300] achieved 60% removal of the calcium hardness in the CO_2-stripper when a UASB/CO_2-stripper system was used for the treatment of liner paper wastewater. In this situation, more than 60% removal efficiency for the anaerobic process of COD was also observed. Yue, Li, & Yu (2013) [301] by reviewing the performance of the rumen microorganisms for AD of lignocellulosic biomass showed the higher hydrolytic and acidogenic activity of such microbial inoculums, compared to other microorganisms. Yuan et al. (2012) [302] indicated that pre-treatment of the filter paper, office paper, newspaper, and cardboard with a microbial consortium, containing *Clostridium straminisolvens* CSK1 and *Clostridium* sp, resulted in a significant increase in the soluble chemical oxygen demand (SCOD) and, as a consequence, an improvement in the methane production with all studied substrates. Baba, Tada, Fukuda, & Nakai (2013) [303] achieved a 2.6 times higher methane production (73.4% of the theoretical methane yield), when the waste paper was soaked with rumen fluid for 6 h at 37 °C before treatment in a semi-continuous AD, compared to that of untreated paper.

Table 2. 10. AD performance with physico-chemical methods for pre-treatment of PPMWs.

Wastewater	Pre-treatment method	Parameters				Reference
		COD		Biodegradability		
		Initial (mg/L)	Removal (%)	Initial	Final	
Bleaching effluent	Precipitation	1510	Up to 90	0.11	0.26	[303]
Blending black liquor	Coagulation+ Flocculation	358	--	--	--	[194]
Synthetic wastewater	Electrocoagulation	2500	~ 95	-	-	[304]
Effluents from equalization tank	Flocculation	2900±90	>90	-	-	[233]
Cardboard industry wastewater	Flocculation	500–1800	>80	-	-	[305]
Effluents from aerated lagoons	Electrocoagulation	426	75	-	-	[233]
TCF effluents	Fungi-solar photo-Fenton	1802	>90	-	-	[235]

2.2.5.1.5 Anaerobic-aerobic combinations

In recent decades, the combination of anaerobic-aerobic treatment methods has received a great attention for the treatment of various types of municipal wastewaters [306] and various types of industrial wastes such as textile industry [307], healthcare production [308], metal manufacturing processes [309], etc.. This is mainly due to the advantages of such combinations over conventional aerobic and AD processes including lower energy requirements, low sludge production [310], less consumption of chemicals and the potential of rich-methane biogas production [175].

According to most references [311] a system consisting of an anaerobic followed by an aerobic process is a better option for the removal of COD, AOX and colour from P&P mill streams. Tezel, Guven, Erguder, & Demirer (2001) [312] observed 91% and 58% removals of COD and AOX, respectively, by using sequential anaerobic and aerobic digestion systems to treat a PPMW, at a HRT of 5 h and 6.54 h for the anaerobic and aerobic processes, respectively. Bishnoi, Khumukcham, & Kumar (2006) [313] achieved a maximum methane production up to 430 mL/day. Moreover, a COD removal up to 64% was obtained, while VFAs increased up to 54% at a pH of 7.3, a temperature of 37 °C and 8 days HRT during AD. Afterwards, COD and BOD removals were 81% and 86%, respectively, at 72 h HRT in activated sludge process. It also seems that a combination of fungal and bacterial strains can help for a more effective removal of recalcitrant pollutants from streams. For instance, a treatment of the combined effluent of a PPM by using a sequential anaerobic and aerobic treatment in two steps bioreactor was studied by Singh & Thakur (2006) [314]. They observed 70%, 42% and 39% removals of colour, COD and AOX, respectively, in 15 days. However, using a mixture of fungi and bacteria (*Paecilomyces sp.* and*Microbrevis luteum*) for the treatment of anaerobically treated PPM effluents, it was observed 95%, 67%, and 88% reductions in colour, AOX, and COD after 7 and 3 days in the anaerobic and aerobic treatment of the effluents, respectively. Combination of a UASB reactor (step I) and two-step sequential aerobic reactor, involving *Paecilomyces sp.* (step II) and *Pseudomonas syringae pv myricae* (CSA105) (step III), as aerobic inoculums for the treatment of PPM effluents, has been also investigated by Chuphal, Kumar, & Thakur

(2005) [315]. They indicated that by using such three-step fixed film sequential bioreactors, 87.7%, 76.5%, 83.9% and 87.2% removals of colour, lignin, COD, and phenol, respectively, can be achieved. Balabanič & Klemenčič (2011) [316], by using full-scale aerobic and combined aerobic-anaerobic treatment plants, reached removal efficiencies of 87% and 87% for dimethyl phthalate, 79% and 91% for diethyl phthalate, 73% and 88% for dibutyl phthalate, 84% and 78% for di(2-ethylhexyl) phthalate, 86% and 76% for benzyl butyl phthalate, 74% and 79% for bisphenol A and 71% and 81% for nonylphenol from paper mill effluents, respectively. In a study carried out by Sheldon, Zeelie, & Edwards (2012) [317], a pilot plant EGSB reactor effectively lowered the COD by 65 to 85% over a 6 month period. The overall COD removal efficiency after the combination of an EGSB with a modified Ludzack–Ettinger process coupled with an ultra-filter membrane was consistent at 96%. Lin et al. (2014) [298] observed 50–65% COD removal from four different KP wastewaters (Table 2.11) under AD by using a pilot-scale packed bed AD column at an OLR of 0.2 to 4.8 kg COD/m^3/d. The overall COD removal efficiency after combining with completely mixed activated sludge process (ASP), as anaerobic-aerobic sequential system, was 55-70%. Moreover the methane production yield was 0.22–0.34 m^3 CH_4/ kg COD, with the biogas containing 80% of methane.

Table 2. 11. Changes in the P&P mill rsidues parameters after treatment by anaerobic-aerobic combinations.

Process	Parameters					Reference
	COD		Other parameters			
	Initial (mg/L)	Removal (%)	Parameter	Initial (mg/L)	Removal (%)	
EGSB+MLE+UF	1600-4400	96	-	-	-	[317]
Packed bed AD column +ASP	2973±142[a] 2886±381[b] 3901±1940 4498±2020	55-70				[299]
Sequential anaerobic - aerobic process	-	42	Colour	-	70	[314]
			Lignin	-	25	
			AOX	-	15	
			Phenol	-	39	
Sequential anaerobic - aerobic[e] process	-	88	Colour	-	95	[314]
			Lignin	-	86	
			AOX	-	67	
			Phenol	-	63	
UASB + Two-step sequential aerobic reactor[f]	5280	83.9	Colour	5205.5 cu	87.7	[315]
			Lignin	6380.56 mg/L	76.5	
			Phenol	54 mg/L	87.2	

[a] Foul condensates.
[b] Chlorine dioxide bleaching effluents.
[c] Alkaline extraction reinforced with oxygen and peroxide bleaching effluents.
[d] Dewatering operation of plant wasted sludge.
[e] A combination of fungal and bacterial strains.
[f] Involving *Paecilomyces sp.* and *Pseudomonas syringae pv myricae* (CSA105), respectively.

2.2.5.1.6 AD of PPMW: criticisms and future outlook

Inherent capabilities of AD reactors can play a significant role in their adoption by P&P mill to treat various types of PPMW. UASB reactors are currently the dominant full-scale facilities adopted by P&P mills through the world. In spite of Their moderate efficiencies for the removal of COD, BOD, TSS, etc, from PPMWs, originated from wood based and non-wood based fiber processing processes, and high levels of stability (based on the ratio of VFA/Alk indicator), they mainly fail to treat recalcitrant compounds such as AOX released to the content of the wastewater from the processes involving the use of chlorinated compounds during the bleaching sequences. The pre-treatment methods have been applied so far for the remediation of wastes containing AOXs, are also mainly unable to degrade and remove these compounds from the wastes content. In this sense, state of the art technologies, especially application of engineered nanomaterials (ENMs), can assist the degradation of AOXs from the PPMW, and enhance the biodegradability of the streams, providing a potentially cost effective and efficient solution. It is also of high importance to develop novel methods for the green fabrication of ENMs having enhanced and modified properties for such application as well as the facile and applicable methods for the collection of the used ENMs. Lab-scale observations have also introduced AFs (i.e. UAFs and anaerobic fixed film reactors), as good candidates for the efficient removal of AOXs from the P&P mill effluents, mainly those from ECF bleaching processes. AFs also have shown the applicability for the removal of sulfate, dominant in the kraft mill effluents, as well as other trace metallic materials which can be found in the effluents from RCFs processing processes. In spite of inherent advantages of AFs, such as negligible power requirements, remained technical difficulties including clogging (as a result of the presence of high amount of suspended solids in P&P mill effluents), and the cost of the packing materials must be overcome to facilitate their transfer from lab-scale to full-scale applications. Some innovations such as periodical irradiation of ultrasound waves and fabrication of low-cost and high efficiency filters (i.e. biotrickling filters [318]), can be proposed as the domains for further studies to overcome such deficiencies.

Relatively long HRT requirement of UASBs, can also affect their efficiencies when operating in low HRTs which is an urgent need for the P&P industry to deal with a large amount of the wastewater produced. These can reflect the importance of the adoption of corrective measures such as adoption of appropriate pre-treatments before AD by UASB reactors. Recent studies have introduced low operating cost reactor configurations such as SGBR, having better efficiencies than UASBs at low HRTs in the lab-scales, although not yet widely used to test their performance in full-scale treatment of PPMWs.

Submerged anaerobic membrane reactors can be also an acceptable choice for treatment of highly polluted wastewaters such as kraft evaporator condensate and TMP whitewater if their main technical difficulties, especially for treatment of PPMW having high TSS and fibrous materials, membrane fouling, will be overcome. Low-cost methods such as back-flush cycles or relaxation are not able to remove the cake sludge (as the dominate cause of the membrane fouling). So, innovation of applicable and economic ways to deal with this phenomenon, like optimization the most important operating conditions such as transmembrane pressure can help their wider application by P&P mills. Such improvements are especially of high importance because SAnMBR exhibit better stability and resistance to temperature variation compared with conventional high-rate anaerobic digesters for the treatment of PPMW and, hence, can be a promising alternative for the conventional high-rate anaerobic digesters to be used by P&P mills.

ABRs have been also rarely applied for the treatment of PPMW, despite having inherent advantages including simplicity, no requirement for gas separation system, low bacterial washout, and the adaptability to the changing operational conditions such as HRT and OLR, which can make them favorable choices, especially in the low-income countries. It is because any drop in the upflow velocity (Vup) in conventional AD systems (i.e. UASB reactors) resulting in decrease in the OLR and increase in the efficiency of the reactor, will increase the treatment and maintenance costs. However, for the existing UASB systems some measures can be proposed in order to maintain the removal efficiency of the anaerobic system while decreasing the HRT. Partial recirculation of the effluent, or cultivation of specific microbial strains [272] are among the tested methods in lab-scale [273] which need precise cost-benefit evaluations to be applicable by the P&P mills. Thermophilic digesters can also give a superior stability compared to mesophilic digesters for a wide range of highly polluted PPMWs like those from CP (especially ECF), CMP, CTMP, etc.. However, utilization of high-temperature conditions may alter the energy saving strategies of P&P mills. In this regard, it would be also of high importance for future studies to evaluate the performance of LTAD by adopting some strategies like co-digestion with other substrates for the treatment of PPMW.

Some other features of the PPMW such as the alkaline nature of the wastes from some P&P production processes (such as Kraft pulping) or toxic effects of the acidic effluents, like those from ECF may considerably restrict the efficiency of the AD. Innovation of multi-stage AD reactors, able to separate the hydrolysis/acidification (and acetogenesis/methanogenesis phases) (Fig. 4) with acceptable performance criteria (i.e. HRT, OLR, removal efficiency, etc.), and adopting the strategies such as co-digestion with the appropriate substrates in order to increase the buffering capacity and neutralization of the P&P effluents are the subject for further studies in this field. Sequential bioreactors including anaerobic and aerobic (especially a combination of fungal and bacterial strains) digestion systems has been also of high effectiveness for the removal of COD, to some extent AOXs, lignin and colour from PPMWs. This could be used as a solution for the problems of the conventional anaerobic digesters (such as UASB) when the HRT decreases; because the experimental analysis have shown relatively high performance for the combined systems in a relatively low HRTs. For the environmental conditions and their effects on the AD process it should be also mentioned that the performance of the AD systems for the treatment of PPMW when exposed to shocks in the operating conditions, and their recovery potential has not been well documented so far.

Besides the reactor configurations and operating conditions, PPMW AD can be limited at the rate which is permitted by the most limiting elements (i.e. nitrogen phosphorous), according to the Liebig's law [319]. An applicable method for compensation of the nutrient deficiency seems to be co-digestion of PPMW with the appropriate substrates. However, real applications of such strategies are highly scarce, whereas it can be a very interesting choice in order to integration of different treatment plants. However, in some cases, such as the effluents from *Eucalyotus sp.* P&P making processes, there may be relatively high amounts of phosphorous which may need the innovation of novel techniques to prevent discharging the phosphorus-based compounds, higher than their limits according to the environmental protection standards. However, the presence of some compounds can limit the AD of P&P mill wastes. For sulfide, some measures such as pre oxidization [298] can be a possible solution which, however, can be compensated by the presence of sulfate-reducing bacteria and releasing H2S, as the most toxic form of the sulfide species for the microbial communities. Such species can also promote the corrosion of the concrete in full-scale reactors, caused by the hydrogen sulfide released in the media, or interrupting the methane yield through anaerobic oxidation of the methane for instance through the following equation [320]:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \qquad \text{(Eq. 1)}$$

However, studies on the conversion or removal of sulfide from the P&P mill effluents are scarce. Multi-stage reactors may be a good option for this purpose. Moreover, there is a lack for studies on the presence of sulfate-reducing bacteria in the AD microbial population and their effects on the inhibition of the methane yield. For other inhibitory elements, such as tannins, which are considered as the main portion of the P&P mill effluents, AOXs, resin acids, etc., in spite of their evident toxic effects on the microbial communities, there is still a need for further comparative studies to quantify their exact effects on the methane production, as well as the economic and effective innovative methods for the degradation (or removal) of these compounds from the streams. One effective way to deal with the inhibitors and also with non-biodegradable compounds is applying a physico-chemical and biological pre-treatment. However, there is a lack of knowledge on the direct effects of such methods on both the methane yield and AD removal efficiency. Coagulation, flocculation, precipitation, oxidation, adsorption, and filtration are the main physico-chemical techniques that have been applied so far for the treatment of P&P wastewater. However, several technical and economic considerations have limited their wider application at full-scale. Membrane-based technologies are mainly struggling with technical deficiencies (such membrane fouling) and conventional oxidation processes are of high expense to be adopted economically by the P&P mills. Moreover, applying methods such as sedimentation can remove high-weight fibrous materials from the content of P&P wastewater which may affect the yield of the following AD. In spite of innovation of some economic and theoretically applicable methods such as advanced oxidative processes (AOPs) by using nano catalytic materials, they have not been used for the pre-treatment of PPMW. Ultrasonic irradiation (20 KHz–10 MHz), which has been used previously as a pre-treatment for some types of effluents, such as municipal wastewaters [321] can also be applied before AD of PPMW. It may increase the homogeneity of the effluents and transform some hardly biodegradable fractions, as a result of direct high-intensity energy of ultrasonic irradiation or, indirectly, under the effect of high-speed jets or shock waves (400 km/h) produced by collapsing the bubbles which form and grow under ultrasonic irradiation, and experience instantaneous implosive collapse [64].

Although pre-treatment methods have been applied so far for the remediation of wastes containing AOXs, they are also mainly unable to degrade and remove these compounds from the wastes content. In this sense, an evolution had occurred in the state of the art technologies, especially the application of engineered nanomaterials (ENMs), which can assist the degradation of AOXs from the PPMW, and enhance the biodegradability of the streams, providing a potentially cost effective and efficient solution. In this area of study, it is also of high importance to develop novel methods for the green fabrication of ENMs having enhanced and modified properties for such application as well as to develop facile and applicable methods for the collection of the used ENMs.

2.2.5.2 AD of PPMS

Pre-treatment methods and co-digestion strategies are the main approaches used so far to enhance the AD of PPMS.

2.2.5.2.1 Pre-treatment strategies

In case of PPMS, pretreatment technologies aim at disintegration of sludge cells, and, as a result, at enhancing the biogas production from primary and secondary sludge. Because of that, the accessibility and/or solubilization of the organic compounds present in the sludge substantially increases. It seems that such methods are very effective in order to reduce the residence time and to enhance the performance of the AD systems, and, hence, to reduce the treatment costs. Thermal, chemical, and mechanical pre-treatments methods have been successfully applied to primary and secondary sludge, mostly generated by municipal treatment plants. However, there are just a limited number of papers on the application of such pre-treatment methods to PPMS. Yunqin et al. (2009) [322] investigated the effects of the pre-treatment of the PPMS with NaOH, prior to AD. They observed that by performing this pre-treatment, the SCOD of the sludge increased, and, as a consequence, a 54-88% improvement in the methane production was achieved. Ultrasonic is another method that has been successfully applied to municipal wastewaters [321]. However, reports about the application of this method for the pre-treatment of PPMS are scarce in the literature. Park et al. (2012) [200] achieved no significant methane production improvement when the thickened PPMS (65 g/kg TS) was subject to a pre-treatment with NaOH (0.261 g/g TS), or to an ultrasonic pre-treatment (16.8 MJ/kg TS) before AD. However, the initial rate of methane production increased and, as a result of the pre-treatment, 80% of total methane yield was reached 5.5-6.5 days faster. Moreover, Bayr et al. (2013) [323] indicated that ultrasound method could not improve the methane yield, when used as pre-treatment for AD of secondary PPMS. They investigated 12 different pre-treatment methods in this regard and concluded that hydrothermal pretreatment (150 °C, 10 min), alone or in combination with enzymatic and/or ultrasound pretreatment can result in the highest methane yield. Wood et al. (2009) [324] achieved similar results with respect to the efficiency of the thermal pre-treatment of the kraft and sulfide sludge samples, when compared to other studied pre-treatments, including thermochemical (caustic) and sonication. Saha et al. (2011) [325] studied the effects of the microwave (2450 MHz, 1250 W), ultrasonic (20 kHz, 400 W) and chemo-mechanical (MicroSludge® with 900 mg/L NaOH followed by 83,000 kPa) pre-treatments on the methane production from pulp mill wastewater treatment sludge. They observed that the microwave pretreatment was the most effective method, resulting in a 90% increase in the specific methane yield, when compared to controls after 21 days under mesophilic digestion of secondary sludge. Moreover, although sonication showed a better effect on the COD solubilization, it resulted in soluble non-biodegradable compounds. Table 2.12 summarizes the results of the recent studies on the PPMS pre-treatments.

Table 2. 12. The AD performance with pre-treatment methods for treatment of PPMS.

Sludge	Method	SCOD (Before pre-treatment) (mg/L)	SCOD (AD)		Methane production improvement (%)	Reference
			Initial (mg/L)	Removal (%)		
Mixture of primary and secondary sludge	Alkali pre-treatment (8 g NaOH/100 g TS_{sludge})	-	14778.6	93	83	[322]
Secondary sludge (TMP)	Alkali + Ultrasound pre-treatment	-	~ 13000	-	3-7	[200]
Secondary sludge (KP)[a]	Hydrothermal pretreatment	800	9000	-	54	[323]
	Hydrothermal + Enzymatic pretreatment	800	9000	-	41	
	Ultrasound + Hydrothermal pretreatment	800	9000	-	52	
	Ultrasound + Hydrothermal + Enzymatic pretreatment	800	10000	-	57	
Secondary sludge (pulp mill[b])	Thermal pretreatment	1.4 ± 0.03	8.5 ± 1.0	-	50	[324]
	Thermochemical pretreatment	1.4 ± 0.03	9.7 ± 1.0	-	18	
Mixture of primary and secondary sludge[c]	Microwave pre-treatment (175 °C)	1926	- [d]	- [e]	~ 80[f]	[325]
	Ultrasonic (90 °C)	1926	- [g]	- [h]	~ 90[c]	

a. Integrated bleached (chlorine dioxide, oxygen) KP (softwood and birch) and paper mill (producing coated magazine paper).
b. Ammonium sulfite mill, and a kraft mill.
c. Pulp mill WAS and WAS + PS (40:60% v/v) mixed sludge.
d. SCOD/ total chemical oxygen demand (TCOD): 41 ± 2.1%.
e. TCOD removal: 30%.
f. Based on the specific methane yield (mL/mg $TCOD_{added}$) after 21 days.
g. SCOD/TCOD: 42 ± 2.1%.
h. TCOD removal: 30%.

Moreover, there is a potential improvement in the treatment process through the application of advanced materials and technologies such as ENMs which experienced a rapid transfer from laboratory to field-scale applications in various scientific fields [326]. Such novel materials are used to remove trace elements such as Ni, Cd, and Pb [327] which may be found in PPMS [328], mainly through sorbtive techniques [329]. Moreover, they seem to be able to break down non-biodegradable compounds like cellulosic biomass (i.e., cellulose, hemicellulose, and lignin [330] which resists the hydrolytic enzymes [331]. This may lead to enhance the biodegradability index (BI), and an improvement in the yield of the biological treatment.

2.2.5.2.2 Co-digestion

Co-digestion of substrates such as animal manure [332], sewage sludge [333], and municipal solid wastes [334] with various co-substrates has been well documented in recent years [174], in order to overcome the weaknesses of mono-digestion, related to substrate characteristics, and to enhance the profitability of the treatment plants. Nutrient deficiency, and also lignin and sulphur containing substances are considered the main drawbacks which may cause an incomplete anaerobic treatment of P&P mill wastes. Hagelqvist (2013) [335] indicated the feasibility of the secondary sludge from CTMP, from KP process, and from food packaging board to be co-digested with municipal sewage sludge, without significant reduction in methane production, but a small increase in the solid residue's cadmium content. Bayr & Rintala (2012) [201] achieved methane yields of 150-170 $m^3/t\ VS_{fed}$ by anaerobic co-digestion of primary and secondary sludge with OLR of 1 $kgVS/m^3d$ and HRT of 25-31d. In order to do adjustments of the C/N ratio, Lin et al. (2011) [297] investigated co-digestion of the PPMS with monosodium glutamate waste liquor by using a bench-scale anaerobic digester under mesophilic conditions. They observed no inhibitions due to VFAs and ammonia on the anaerobic co-digestion process, with an accumulative methane yield attained of 200 $mL/g\ VS_{added}$ and a peak value of daily methane production of 0.5 m^3. Y. Lin et al. (2013) [172] designed a mesophilic anaerobic bio-hydrogen production and a mesophilic anaerobic process for methane production, for co-digestion of PPMS and food wastes. They achieved 64.48 $mL/g\ VS_{fed}$ and 432.3 $mL/g\ VS_{fed}$ yields for hydrogen and methane production, respectively, at an optimal ratio of PPS and food wastes (1: 1 VS), as the feedstock. In this situation, a maximum of 87% removal efficiency on the SCOD was achieved.

2.2.5.2.3 AD of PPMS: criticisms and future outlook

AD has been traditionally utilized for decades, as an attractive way to stabilize primary, secondary and mixed sludge having high levels of biodegradable materials, especially the sludge from municipal wastewater treatment plants, and to produce biogas, as a source of renewable energy form these types of wastes. However, compared to PPMW, there are a limited number of reports about AD of PPMS, especially for the (semi) continuous AD of P&P primary sludge (Table 2.13). This may be to the fact that the primary sludge from P&P mill production processes are rich in fibrous materials and, hence, is recovered instead of being anaerobically digested. However, the PPMS is generally low in organic matters, especially biodegradable compounds; they have typically low methane potentials. It is mainly attributed to the fact that they have been already degraded by physico-chemical or biological treatments. In this regard, application of pre-treatment technologies, especially chemical (e.g., alkali) ones as cost-effective ways, can promote the biogas production, through the disintegration of sludge cells and enhancing the availability of the biodegradable compounds for AD microorganisms. However, it seems that in order to achieve the maximum energy production, in line with environmental considerations, the main priority must be to develop and promote the efficient methods to AD treatment of PPMW to maximize the biogas production resulting in a low sludge production which can meet discharge standards to be used, for instances, in land applications safely.

In spite of the recent advances in the anaerobic digestion of the P&P mill wastes, digested streams may still contain compounds like lignin, tannin, etc. (Table 2.4); contributing to color of the leachate/ effluents, as well as microorganisms, suspended solids and other pollutants including non-biodegradable compounds and relatively low quantities of remained biodegradable organics [234,336]. Hence, tertiary treatments such as membrane separation [234], adsorption [337], ion exchanging [338], and chemical oxidation process [117,336,339] may be vital if the sludge (or wastewater) is desired to be recycled in the manufacturing processes. Composting for the AD residual to form a soil conditioner can also be performed on the AD residuals [340].

Table 2. 13. Characteristics of the primary, secondary and mixed PPMS.

Sludge type	Characteristics					Reference
	COD (mg/L)	TS (%)	VS (% of TS)	pH	C/N ratio	
Primary sludge[a]	-	3.4	86	6.2	-	[201]
Secondary sludge[a]		4.0	82	7.6	-	[201]
Secondary sludge[b]	29800	24.2	77.0	7.3	10.5:1	[200]
Secondary sludge[c]	-	4.7	83	-	-	[323]
Secondary Sludge[d]	11700	11.1 (mg/L)	-	-		[324]
Secondary Sludge[e]	27000	24.4 (mg/L)	-	-		[324]
Secondary Sludge	39579	2.50	80	6.5		[325]
Promary + secondary sludge	34229	2.21	83	6.2		[325]
Promary + secondary sludge	-	31.45	62.3	7.82	30.05	[322]

a. integrated bleached kraft pulp (softwood and birch) and paper mill.
b. Bleached CTMP and TMP.
c. integrated bleached kraft P&P mill.
d. Sulfite mill.
e. Kraft mill.

2.2.6 Conclusion

High COD concentrations contributing to the 55-60% of the original weight of the wood [169] and additives used (Table 2.4) can strongly support the idea of the AD of P&P mill wastes in order to reduction of pollution load, and production of biogas, as a renewable source of energy. However, several factors are involved in the AD of P&P mill wastes (graphical abstract) which should be taken into consideration carefully to achieve the desirable methane production and treatment efficiency for this process. Anaerobic digesters having internal settlers such as UASB reactors are the dominant reactor systems for the treatment of PPMWs. Such reactors have shown a moderate to high performance to reduce the COD and various removal efficiencies for other parameters including BOD, TSS, AOX, etc., depending on the reactor design, operating conditions and the properties of the streams. While the relatively long HRT has been the main shortfall in the performance of UASB systems, the maintenance and the additional costs are considered the most significant obstacles for AnMBRs. In addition, the cost of the packing materials has been considered the cause of the limited applications of AFs to deal with PPMWs. The microbial activity and its impact on the overall performance of the AD reactors for methane production and COD (and other pollutants) removal can be highly influenced by the reactor operating conditions including HRT, OLR, operating temperature, and pH, as well as the presence of inhibitory elements such as sulfide compounds. Nevertheless, the performance of the AD systems for the treatment of P&P mill wastes when exposed to shocks in the operating conditions, and their recovery potential has not been well documented so far. In addition, the development of reliable sensing systems for a continuous measurement and adjustment of the operating conditions would be an essential need to promote the methane yield from AD, especially when applied to P&P mill wastes as complex high-strength substrates. In addition, there is a lack in the investigation of the direct effects of physico-chemical and biological pre-treatments on both the methane yield and removal efficiency of AD reactors. The research on the PPMS has clearly indicated that chemical (e.g., alkali) pre-treatments are acceptable and cost-effective ways to enhance the AD of both primary and secondary sludge, when compared to other studied methods. Combination of aerobic and anaerobic technologies have also been identified as a promising way to enhance either the overall performance of the treatment process for P&P mill wastes, or to satisfy the stringent environmental regulations. However, most of the developments in the AD of P&P mill wastes which have been reviewed in this paper have not been implemented in full-scale applications. In this regard, further work is required to evaluate and enhance the performance of these promising lab-scale technologies for large-scale operation in P&P mills.

Chapter 3: Selection the Most Appropriate Treatment Technology to Deal with Industrial Effluents

- Mohammadreza Kamali, Kenneth M. Persson, Maria Elisabete Costa, Isabel Capela, Sustainability Criteria for Assessing Nanotechnology Applicability in Industrial Wastewater Treatment: Current Status and Future Outlook, Accepted for publication in Environment International Journal (IF5=7.72).
- Kamali, M., Persson, K.M., Costa, M.E.V., Aminabhavi, T.M., Capela, I., Sustainability of Treatment Technologies for Industrial Biowastes Effluents, Under review in Chemical Engineering Journal (IF_5 = 6.74).

3.1 Sustainability Criteria for Assessing Nanotechnology Applicability in Industrial Wastewater Treatment

3.1.1 Abstract

Application of engineered nanomaterials for the treatment of industrial effluents and to deal with recalcitrant pollutants has been noticeably promoted in recent years. Laboratory, pilot and full-scale studies emphasize the potential of this technology to offer promising treatment options to meet the future needs for clean water resources and to comply with stringent environmental regulations. The technology is now in the stage of being transferred to the real applications. Therefore, the assessment of its performance according to sustainability criteria and their incorporation into the decision-making process is a key task to ensure that long term benefits are achieved from the nano-treatment technologies. In this study, the importance of sustainability criteria for the conventional and novel technologies for the treatment of industrial effluents was determined in a general approach assisted by a fuzzy-Delphi method. The criteria were categorized in technical, economic, environmental and social branches and the current situation of the nanotechnology regarding the criteria was critically discussed. The results indicate that the efficiency and safety are the most important parameters to make sustainable choices for the treatment of industrial effluents. Also, in addition to the need for scaling-up the nanotechnology in various stages, the study on their environmental footprint must continue in deeper scales under expected environmental conditions, in particular the synthesis of engineered nanomaterials and the development of reactors with the ability of recovery and reuse the nanomaterials. This paper will aid to select the most sustainable types of nanomaterials for the real applications and to guide the future studies in this field.

Keywords: Sustainability, Nanotechnology, Industrial wastewater treatment, Fuzzy-Delphi method.

3.1.2 Introduction

Water is among the most abundant natural resources on the earth, although less than 1% of water resources are directly usable for human consumption [341–343]. Problems associated with human activities such as rapid industrialization, growth of population and urbanization are stressing the available resources [344–347]. Generation and discharge of industrial effluents are polluting water worldwide, not least in developing countries [5]. In addition, stringent environmental regulations are forcing many industries all over the world to apply efficient treatment technologies to reach the standards for discharging the influents. In this context, the major challenge for the industries is the adoption of the most efficient, economic, and environmentally friendly methods to ensure their ability for managing wastewaters in a sustainable manner. Traditional treatment methods have evidenced some drawbacks, which limit their wider application. For instance, biological treatments are mainly limited to biodegradable compounds, being sometimes hampered by the presence of toxic materials in effluents such as complex halogenated organic compounds (e.g., AOXs) [9]. Physicochemical methods have also some drawbacks: most of them are relatively expensive and may pose some undesired environmental consequences. As an example, the application of filtration or adsorption processes may result in the generation of a highly concentrated sludge and thus transfering the toxic environmental contaminants from one phase to another.

Among the emerging technologies, the application of various types of engineered nanomaterials (ENMs) actually available has gained a particular attention in recent years [348–350]. In this regard, a number of metallic and non-metallic compounds has been synthesized and used to deal with various environmental contaminates [351–353]. Although this technology has shown an incredible potential for water and wastewater treatments, various aspects of its sustainability remain to be discussed. For instance, Tan et al., (2015) [354] reviewed various types of ENMs that has been synthesized and utilized so far for the removal of dyes from polluted waters and concluded that the sustainability of the use of advanced ENMs in water and wastewater treatments is still an open question.

In this paper a Delphi-based methodology is utilized in order to identify and to rank the sustainability criteria recommended for the selection of the industrial wastewater treatment technology to be adopted. A critical discussion of the performance of ENMs according to the criteria is also presented. Developing opportunities and future directions are also discussed in details.

3.1.3 Methodology

Delphi methodology is based on a group decision-making process among experts with sufficient experience and knowledge on the same field. In the Delphi approach, a complex problem with many interplaying variables is divided into a number of smaller domains, within which the variables are identified and weighted. The weights are ranked in such a way that it is possible to screen the variables allowing a decision to be made based on their quantification. In a fuzzy-Delphi methodology, a set of fuzzy numbers is used to rank the variables in order to make it more precise. A fuzzy number is a formalism normally used when uncertain information needs to be quantified or characterized. As an example, an entity (A) may be expressed by a fuzzy number $\tilde{A}=(a_1, a_2, a_3,.. a_i,.. a_n)$ when its quantification through a_i is subordinated to certain conditions (membership functions) that determine the choice of a_i within the fuzzy interval $(a_1, a_2, a_3,.. a_i,.. a_n)$ [355]. This methodology can be applied for screening the criteria required to evaluate a certain technology and furthermore, to evaluate the performance of the technology itself [356]. There is a number of reports in the literature about the application of fuzzy-Delphi methodology for making sustainable decisions in various fields [357–359]. In the present study, the fuzzy-Delphi methodology was selected for finding and ranking the criteria that influence the performance of industrial wastewater treatment processes in general, and in particular the application of engineered nanomaterials. The results provide a basis for the evaluation of this technology.

A review allowed to identify the most important criteria for the adoption of a sustainable industrial effluent treatment. In this regard, technical, environmental, economic and social parameters were expressed in terms of 17 criteria, as described in Figure 3.1. The descriptions for each studied criteria are presented in supplementary information.

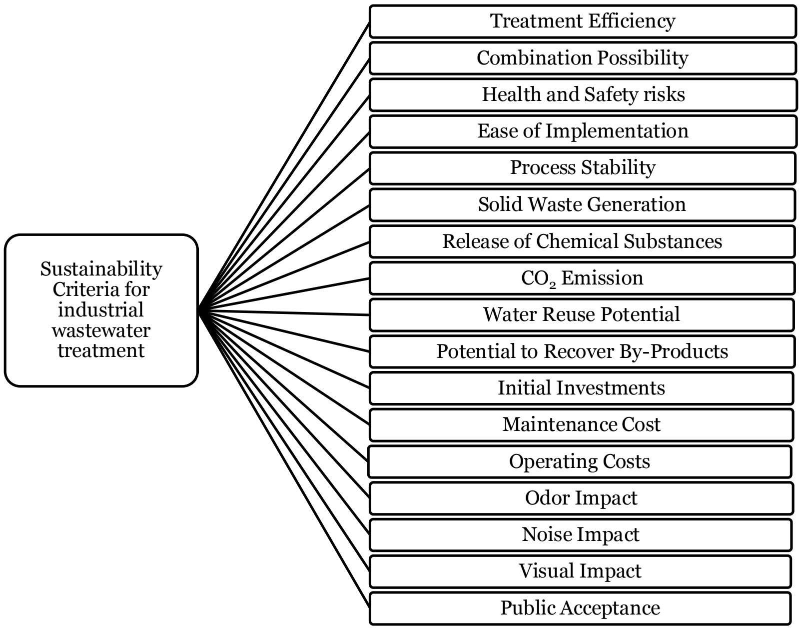


Fig. 3. 1. Sustainability criteria for the selection of appropriate industrial wastewater treatment.

Professional questionnaires (see supplementary information) were elaborated based on these criteria and then used to assist in gathering the opinion of a target group. The identification of the target group, i.e. the selection of the participants to be enquired was carefully performed by inviting experts with excellent academic and/or industrial experience in the field of industrial effluents treatment in general. In order to determine the importance of each studied criteria the linguistic variables and triangular fuzzy numbers (Tables 3.1 and 3.2) were utilized. A triangular fuzzy number is a fuzzy number which is represented with three points as follows: $\tilde{A} = (a_1, a_2, a_3)$. The membership functions which can be used to interpret this representation hold the following conditions [360]:

$$y = m(x) = \begin{Bmatrix} 0 & x < a_1 \\ \frac{x-a_1}{a_2-a_1} & a_1 \leq x \leq a_2 \\ \frac{a_3-x}{a_3-a_2} & a_2 \leq x \leq a_3 \\ 0 & x > a_3 \end{Bmatrix} \qquad \text{Eq. 1}$$

The consensus among the experts was estimated using the vertex method (Eq. 2). For that, the distance ($d(\widetilde{m},\tilde{n})$) between the aggregated fuzzy numbers (m_L, m_M, m_U) computed from Eq. 3 and the triangular fuzzy numbers (n_L^i, n_M^i, n_U^i) expressed by each expert in the form of linguistic terms were computed.

$$d(\widetilde{m},\tilde{n}) = \sqrt{(m_L - n_L^i)^2 + (m_M - n_M^i)^2 + (m_U - n_U^i)^2} \quad \text{Eq. 2}$$

If the calculated value of $d(\widetilde{m},\tilde{n})$ is less than 0.2, this indicates that a consensus has been achieved among the experts [361]. The stability of the results requires that 75% of group consensus among the experts is achieved [362]. The geometric mean (Eq. 3) [363] was used in order to calculate the fuzzy weights of the criteria, where L, M and U express the fuzzy number components.

$$L_j = \underset{i}{\mathrm{Min}}\{L_{ij}\}, \quad M_j = 1/n\sum_{i=1}^{n} M_{ij}, \quad U_j = \underset{i}{\mathrm{Max}}\{U_{ij}\} \quad \text{Eq. 3}$$

This equation is used to calculate the relative importance of the element no. j allocated by expert no. i. In order to defuzzification of the final triangular fuzzy numbers, Eq. 4 is utilized.

$$df = 1/4(L + 2M + U) \quad \text{Eq. 4}$$

Table 3. 1. Linguistic variables and the relevant fuzzy scale for the relative importance of the criteria.

Linguistic variable	**Fuzzy Scale (L, M, U)**	$df = \frac{1}{4}(L + 2M + U)$
Extremely high	(0.9, 1.0, 1.0)	0.975
Very high	(0.7, 0.9, 1.0)	0.875
High	(0.5, 0.7, 0.9)	0.7
Fair	(0.3, 0.5, 0.7)	0.5
Low	(0.1, 0.3, 0.5)	0.3
Very Low	(0.0, 0.1, 0.3)	0.125
Extremely low	(0.0, 0.0, 0.1)	0.025

3.1.4. Results and Discussion

3.1.4.1 Criteria prioritization

A total of 50 experts from 19 countries participated in the survey by expressing their opinion on the importance of the proposed criteria. Fig. 3.2 shows the world distribution of the experts participating in the study. After achieving a consensus in the second round of questionnaire distribution, the fuzzy weights of each studied criteria for selecting the most sustainable industrial wastewater treatment were ranked as presented in table 3.2 and Fig. 3.3. According to the defuzzified values, all the criteria studied received the importance values higher than “Fair” (Table 3.1). This can be interpreted as the necessity of including all the criteria in the decision making process. Among the technical criteria (i.e., treatment efficiency, combination possibility, health and safety considerations, ease of implementation and process stability), the criteria of “treatment efficiency” and “health and safety risks” were evaluated as the most important parameters among all. This conveys the idea that a technology to be adopted for the treatment of industrial effluents has to be not only efficient but also safe enough. However, despite a number of comparative studies on the efficiency of various treatment technologies available in the literature [174,198,364,365], the risks (i.e., noise, electricity, biological agents, etc.) associated with the implementation of the technology to the workers in the treatment factory have not yet been well documented and analyzed.

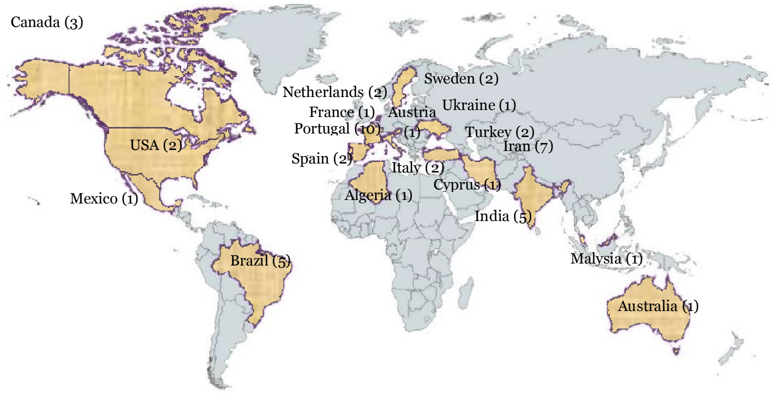


Fig. 3. 2. World distribution of the experts participating in this study.

Table 3. 2. Fuzzy values and defuzzified values for the studied criteria.

Criteria	**Fuzzy values**			**De-fuzzy values**
	L	**M**	**U**	$df = \frac{1}{4}(L + 2M + U)$
Treatment Efficiency	0,50	0,90	1,00	0,83
Ease of Implementation	0,30	0,79	1,00	0,72
Combination Possibility	0,25	0,72	1,00	0,67
Process Stability	0,30	0,83	1,00	0,74
Health and Safety Risks	0,50	0,90	1,00	0,83
Solid Waste Generation	0,10	0,79	1,00	0,67
Release of Chemical Substances	0,00	0,90	1,00	0,70
CO_2 Emission	0,00	0,74	1,00	0,62
Water Reuse Potential	0,10	0,79	1,00	0,67
Potential to Recover By-Products	0,25	0,75	1,00	0,69
Initial Investments	0,10	0,77	1,00	0,66
Maintenance Costs	0,10	0,80	1,00	0,67
Operating Costs	0,30	0,84	1,00	0,75
Odor Impact	0,10	0,74	1,00	0,64
Noise Impact	0,10	0,70	1,00	0,63
Visual Impact	0,00	0,64	1,00	0,57
Public Acceptance	0,00	0,75	1,00	0,63

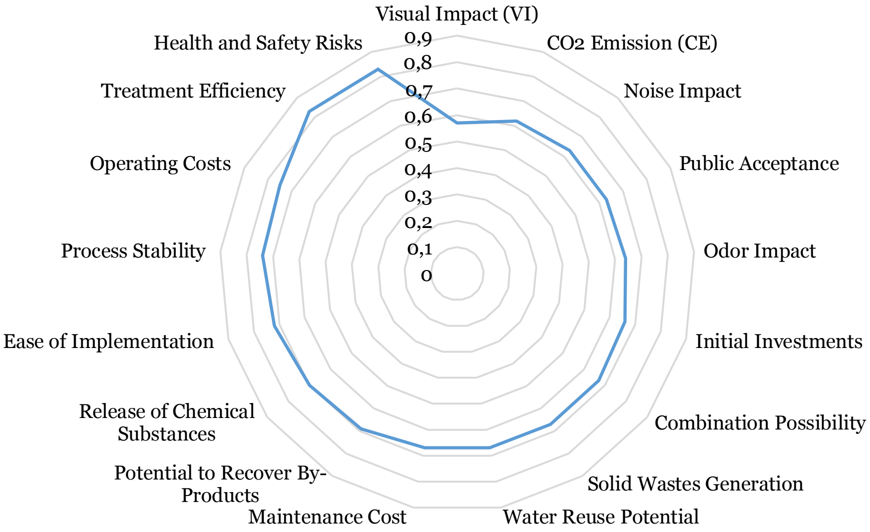


Fig. 3. 3. Calculated weights of the sub-criteria and criteria, measured as the average of the respective sub-criteria.

Economic criteria (i.e., initial investments, operation and maintenance costs) have shown to be also important when selecting the best industrial wastewater treatment option. For many industries, such as pulp and paper industry, there is currently a competitive market for their product [1] where they also need to comply with stringent environmental regulations. In this context, they obviously prefer to select the more economic solutions to deal with the produced effluent treatment. Criteria which reflect the environmental performance of the wastewater treatment technique such as solid waste generation, release of chemical substances, CO_2 emission, water reuse potential, and the potential to recover by-products were also evaluated as important in the decision making process although the emission of CO_2 received the least importance among the studied criteria. Social criteria which describe the impacts (visual, odor, and noise) of the treatment technique on the local communities together with the public acceptability of the technology received the least importance among the studied criteria. However, according to the weights allocated to the social criteria, they should be considered when deciding on the selection of the most appropriate alternatives for the treatment of industrial effluents. In the next section, the opportunities for the application of nanotechnology on industrial effluents treatment and the main challenges for improvement will be discussed in details.

3.1.4.2 Challenges and opportunities

3.1.4.2.1 Technical considerations

3.1.4.2.1.1 Treatment efficiency

The results of the fuzzy-Delphi methodology carried out in this study indicated that the treatment efficiency is of the highest importance among the studied criteria. In the past decade, various types of ENMs have been synthesized and tested for their efficiency to deal with various contaminants in polluted water and wastewaters. It is well-documented in the literature that the efficiency of nanomaterials based treatments is highly dependent on various parameters including the type of the materials used, the properties of the ENMs such as crystalline structure, particle morphology (shape, size, specific surface area), surface concentration of active sites and surface electrical charge of a specific material, and also the mechanisms involved in the degradation/ removal of the contaminants. Adsorption and oxidation are the two main phenomena involved in the removal/ degradation of environmental contaminants by ENMs. The following sections are aimed to provide an overview on the application of ENMs to deal with recalcitrant pollutants according to the mentioned mechanisms.

a) Adsorption on nanomaterials

The easiness of the heavy metals adsorption on nanomaterials surface is quantified by the adsorption coefficient (K_d) of the specific pollutant which may be followed by the redox reactions of the heavy metals on the ENMs to change the heavy metals oxidation state [366]. Metallic and non-metallic nanomaterials have been used for the adsorption of heavy metals. Activated carbon and carbon nanotubes are the main examples of non-metallic compounds and TiO_2, ZnO, MnO and iron-based nanomaterials are the main types of metallic oxide nanomaterials that have been used so far for this purpose. Regarding non-metallic compounds, functionalized carbon-based nanotubes and graphene-based nanomaterials with high specific surface areas which provide large amount of adsorption sites may be cited as representative examples. For instance, in the review of Xu et al., (2018) [351] it was reported that functionalized carbon-based nanomaterials which are used for aqueous heavy metals removal show various adsorption capacities ranging from 1.29 ($mg_{contaminant}/g_{ENMs}$) for raw carbon nanotubes [367] up to 479 ($mg_{contaminant}/g_{ENMs}$) for EDTA-RGO (ethylene diamine tetra acetic acid-reduced graphene oxide) corresponding up to 95% of the Pb(II) (100 mg/L) adsorption after 120 min of reaction time [368]. Some polymeric nanoparticles are also non-metallic compounds examples worthy of mention. For instance, Tan et al., (2015) [354] stated that the polymeric nanomaterials such as chitosan [369,370] can be categorized among the best options for the adsorption of dyes, although they have not been extensively studied for such purposes, especially for real wastewater treatments. For instance, Peng et al.(2015) [371] achieved upto 95% removal of methylene blue dye using chitosan–halloysite nanotubes composite hydrogel beads. The presence of amino and hydroxyl groups in the surface structure of chitosan may explain its high ability for pollutants adsorption [372]. It is believed that mechanisms such as surface interaction between the heavy metal and the surface of nanomaterials for instance via ion exchange process [351] account for the physical adsorption of heavy metals on nanomaterials which depends on the specific nanomaterial and the type of the pollutant under consideration. However, the efficiency of the ENMs for adsorbing environmental pollutants is highly dependent on environmental factors, such as contact time, pH, temperature, and the dosage of nanomaterials being their best performance achieved within a narrow range of environmental conditions [373]. For instance, Mehdizadehet al. (2014) [374] achieved the optimal adsorption of heavy metals (99%) at pH 7, 0.1 g/10 mL dosage and 30 min contact time using zeolite and platinum/Zeolite nanoparticles.

There has also been much interest in the use of metal oxides for the adsorption of heavy metals in contaminated waters. There is a number of reports in the literature for the application of various types of metal oxide nanomaterials, alone, or supported on non-metallic nanomaterials [375–379]. In this regard, magnetic oxide nanomaterials have been used efficiently due to their attractive characteristics such as high adsorption capacity and their collectability using a magnetic field [380]. As an example, Fe_3O_4 nanomaterials have been successfully applied for the removal of a variety of heavy metals [381]. Bakather et al., (2017) [375] also achieved 111 mg_{Se}/g_{ENMs} removal of Se (100%) using iron oxide impregnated carbon nanotubes (CNTs) indicating the super adsorption capacity of the materials used towards heavy metals.

b) Oxidation with ENMs

Oxidative degradation of complex organic compounds is another field of research that has gained a lot of interest in recent years. So far, some types of photo-oxidation processes have been developed and applied such as ozone/hydrogen peroxide/UV radiation, photo-Fenton system and photocatalytic decomposition of organic pollutants [382]. Heterogeneous photocatalysis, as an oxidation process, occurs when a semiconductor catalyst is illuminated with a suitable wavelength radiation ($\lambda < 380$ nm) providing a certain energy, greater than the band gap of the semiconductor used. So far, several semiconductors have been tested for their ability for heterogeneous photocatalysis such as TiO_2, Fe_2O_3, ZnO, CuO, etc. [383]. Among the studied semiconductor materials, TiO_2 has demonstrated the greatest potential for the degradation of environmental contaminants, especially the modified generations have shown further advantages. As an example, the use of carbonaceous materials as supports of TiO_2 can increase the activity of these materials towards environmental contaminants, providing high specific surface areas and preventing the agglomeration of nanomaterials after being introduced to the aqueous media [384]. For instance, Orha et al., (2017) [385] achieved 92% of humic acid (10 mg/L) degradation and mineralization using TiO_2-Acticated carbon nanomaterials. Iron-based nanomaterials have also gained a great attention in recent years, bringing many advantages when compared to the micro sized generation. For instance, they have been used successfully for the treatment of contaminated groundwater [386,387], due to their large surface area and high reactivity [24]. Nano sized zero valent iron and its modifications have been successfully applied for the removal of a number of environmental contaminants [388–391]. The main advantage of using some iron-based nanomaterials (such as Fe_3O_4 [392], Fe^0 [393], α-Fe_2O_3 [394]) for environmental clean-up purposes is the possibility of collecting them easily with a magnet after being used, allowing its re-use in further treatment cycles. However, not all the types of iron nanomaterials (ex: ferrihydrite) may present appropriate magnetic properties [395] for easy recovery. It must be stated that the performance of ENMs can be optimized through the manipulation of operating conditions. Among the most important studied parameters including pH, temperature and NMs dosage, the effect of pH have been emphasized in the literature. Some studies have indicated that slightly acidic pH is the optimum to achieve a high treatment efficiency [396]. Basic conditions do not favour hydroxyl radicals which play an important role in ENMs based oxidation processes whereas acidic pH may contribute for catalysts dissolution. For instance, Zyoud et al., (2015) [397] achieved the highest removal of aqueous methyl orange using nano-ZnO catalyst under slightly acidic conditions. It is important to stress that the reported judgments on the efficiency of many types of ENMs are supported mainly by laboratory experiments. This is the case of the findings and remarks from very recently published review papers on the application of various types of nanomaterials for the treatment of polluted waters and wastewaters which are summarized in Table 3.3. The reports on scaling-up the application of these nanomaterials are very few [398]. At this stage, it is very important to design larger scale processes to test the performance of nanomaterials with real effluents.

3.1.4.2.1.2 Ease of implementation

In spite of the huge progresses in the synthesis and application of various types of ENMs to the treatment of polluted waters and wastewaters, there are still few examples of the commercialization of nanotechnology for such purposes. Many treatment plants still rely on the traditional technologies such as coagulation and membrane filtration for the chemical treatment of the influents. In general, there are some barriers for introducing a new technology in the industry, mainly because of the high capital costs and stringent environmental regulations which require the technology to be well proven in terms of its efficiency before commercialization. Literature clearly indicates that nanotechnology can bring a number of advantages over conventional technologies, including both the possibility to decrease the size of the reactors and to improve the treatment efficiency [399]. However, there are still some issues to be addressed for accelerating the commercialization of these technologies. Currently only few nanomaterials have already entered the market and are ready for large-scale applications. Nano-sized TiO_2 and iron oxides are among these materials. Large-scale production of the nanomaterials with the desired properties for treatment purposes is critical, because it can considerably facilitate the whole process. Designing the proper configurations of the reactors to enable the use of nanomaterials is another step to overcome, in order to commercialize this technology. An ideal configuration has to ensure the possibility to provide (i) the necessary light (ultraviolet, visible, or both) in case of advanced oxidation processes with nano photocatalysts, (ii) enough contact time between the materials and the pollutants, and (iii) to recover the nanomaterials after being used. Nanomaterials can also be activated, either by an external source of light or by using oxidizing agents such as hydrogen peroxide (non-irradiated), as a new insight for the application of nanomaterials to deal with emerging environmental pollutants [400]. In addition, providing an external source of energy is of high importance for reactors which are dependent on the light illumination [351]. Effective penetration of the light into the system to provide enough reactive zone in the media is a barrier that needs to be addressed in such reactors. In this regard, solar light mediated processes have attracted recently a significant attention. Hence, the development of visible-light active materials can considerably help to overcome this barrier. It can be stated that the methods for the synthesis of visible light active nanomaterials (such as nitrogen doped TiO_2 NMs [401]) have been sufficiently developed and are ready to be used in such reactors [402–404] but still need scaling-up to be more economic. Recovery of the nanomaterials after being used is another issue which demands further efforts. For instance, the application of ceramic membranes to recover the nanomaterials [399], incorporation of the nanomaterials on the surface of the membranes [405], and also the application of magnetic nanomaterials easily collected after use can be considered as attractive solutions [24]. However, no magnetic separation reactor has been yet commercialized for the treatment of polluted water and wastewater, so far.

3.1.4.2.1.3 Combination with other methods

Effluents generated in many industries such as textile, pulp and paper, etc. generally have a high COD and low degree of biodegradability [5,9]. They may also induce some toxic effects in the aquatic microorganisms. Although common biological treatment techniques have shown to have an acceptable performance for a wide range of industrial effluents, they may face difficulties while dealing with non-biodegradable or hardly biodegradable and other emerging pollutants such as phthalates, pharmaceuticals compounds [406,407], PAHs, PCBs, etc. [408]. In these cases, a physico-chemical treatment using ENMs (either through adsorption or by using advanced oxidation processes) could be an attractive solution to remove such complicated compounds from industrial effluents. There are some pieces of evidence on the successful combination of nanomaterials with biological treatment systems. Algal biomass harvesting with wastewater treatment has also been an interesting research field in recent years for the production of renewable biofuels [409,410]. Recovery of algal biomass is facilitated when nanomaterials are incorporated in the structure of the membranes. This procedure is able to enhance the hydrophilicity of the membrane and minimize membrane fouling. So, such membranes can be effectively used for the recovery of the algal biomass [411,412]. Successful application of polyvinylidene fluoride (PVDF) hollow fiber membranes decorated with TiO_2 nanoparticles was reported for instance by Hu et al., (2015) [412] in an algal membrane bioreactor (A-MBR) for wastewater treatment. Self-cleaning ability is another advantage of using nanomaterials in the structure of the membranes. For instance, such a mechanism has been studied for photocatalytic self-cleaning under UV irradiation [413].

Table 3. 3. Application of ENMs for water and wastewater treatment: used nanomaterials, mechanisms, remarks and future perspectives.

Materials	Mechanism(s)	Remarks and future perspectives	Ref.
- Functionalized carbon nanotubes - graphene	- Adsorption	- Higher removal can be achieved after functionalization of nanomaterials. - Operating parameters i.e. temperature, pH, ionic strength, etc. are of high importance.	[351]
- Carbon-based nanomaterials - Metal oxide-based nanomaterials	- Adsorption	- Carbon-based nanomaterials have shown acceptable performances for the removal of heavy metals and dyes due to their nontoxicity, abundance, ease of preparation, high surface area and porosity, stable structure and high sorption capacities. - Carbon nanomaterials have shown significantly higher sorption efficiency compared to commercial activated carbon (AC).	[414]
- Carbonaceous nanomaterials - Metallic nanomaterials - Bionanomaterials	- Adsorption (dyes)	- Application of cheaper and less toxic materials, such as nZVI is highly recommended. - Chitosan nanoparticles seem to have the largest potential to be used as a commercial adsorbent for dyes, because it is both non-toxic and low cost. - The sustainability of the application of nanomaterials to be used for water and wastewater treatment remained unanswered yet.	[354]
- Modified chitosans	- Adsorption (dyes, metals/ions, etc.)	- Chitosan modified by grafting, cross-linking or composite functionalization is effective to deal with various pollutants.	[372]
- Carbon-based nanomaterials - Metal oxide-based nanomaterials	Adsorption (arsenic)	- Carboxymethyl cellulose (CMC)-stabilized Fe-Mn showed highest capacity for arsenic adsorption (372 $mg_{pollutants}/g_{ENMs}$) at pH=3. - Magnetite was very efficient for the removal of As (III) (188.69 $mg_{pollutants}/g_{ENMs}$) at neutral pH.	[415]
- Carbonaceous-TiO_2 composites	- Advanced oxidation process (AOP), photocatalysis	- Carbonaceous -TiO_2 materials have shown better performance when compared to bare TiO_2 such as high photocatalytic activity, activity under solar irradiation, and easy separation. - Many methods developed for the synthesis of carbonaceous-TiO_2 composites are expensive, complicated, and time consuming.	[384]
- $Y_xFe_yZr_{1-x-y}O_2$ coated TiO_2	- AOP, photocatalysis	NMs combined with polymer membranes can enhance the hydrophilic and antifouling properties of the membrane.	[416]

Table 3.3. Continued.

Materials	Mechanism(s)	Remarks and future perspectives	Ref.
- Nanoscale TiO_2 film	- AOP, photocatalysis	- It remained unclear yet which synthesis method for TiO_2 nanoscale films can give better performance with lower costs.	[417]
- TiO_2, CdS, WO_3, SnS and ZnO based composites	- AOP, photocatalysis	- Modification of crystallinity, morphology, band gap, particle size and surface area of the catalyst can considerably improve the photocatalytic activity of the composite catalysts. - Combined with other suitable catalytic composites may reduce the band gap of the nanocomposite and hence enhances the photocatalytic decomposition of complex organic molecules.	[418]
- Zero valent iron nanoparticles	- Fenton-like oxidation (textile dyes)	- nZVI dosage, initial dye concentration, pH, etc. are the main factors involved in the treatment of dyes by nano zero valent iron. - Green supports were recommended to enhance the stability of iron nanoparticles. - Adequate dye decolorization of 67-100% has been achieved in the first 10 min using nZVI particles. - Integration of nZVI with other techniques can considerably increase the efficiency of organic matters removal from textile dye wastewaters.	[419]
- Copper-based nanomaterials	- AOP, photocatalysis	- Morphology and crystalline structure are the main factors determining the reactivity of the nanomaterials. - Development of economic and technical synthesis methods is required to improve the band gap energy of the nanomaterials. - Doping another metallic compound to the structure of nanomaterials is a possible way to increase their efficiency and to decrease the release of the ions to the medium.	[353]
- Biochar-based nano-composites	- Adsorption/ degradation	- Nanomaterials can be impregnated onto raw biochars to promote the environmental applications of biochar and nanotechnology. - There are some study gaps including the effect of the operating parameters, the development of the synthesis methods, etc.	[420]
- Carbonaceous nanomaterials/ Metal and metal oxides/ Magnetic-core composite nano/micro particles	- Adsorption/ degradation	- Nanotechnology can offer a promising alternative to the traditional treatments of polluted waters and wastewaters. - Nanotechnology can be especially promising for the removal of emerging environmental contaminants. - Treatment cost using nanotechnology can be comparable to that of traditional methods for water and wastewater treatment.	[421]
- Carbon based materials/ Metal oxide based nanomaterials	- Adsorption/ degradation	- Although nanotechnology can be considered as a promising technology for water and wastewater treatment, there are some challenges such as providing large amounts of nanomaterials at an economically viable price.	[422]

Application of nanomaterials in the structure of microbial fuel cells (MFCs) is another possibility to accelerate the commercialization of MFCs which currently suffer from relatively low performance when compared to other fuel cell technologies [423]. There have been some interesting reports in the literature for the improvement of the performance of MFCs [424–427]. Nanomaterials can also be used to improve the conductivity of the electrode region to facilitate oxygen reduction reactions [428]. In this regard cheap nanocomposite materials such as carbonaceous nanocomposites can be further studied and applied to improve the performance of MFCs.

3.1.4.2.1.4 Process Stability

The presence of compounds such as heavy metals, sulfide, chlorides, and hardly biodegradable compounds in the content of industrial effluents can result in process instability when they are being treated by biological processes [9,169]. For instance, textile wastewater dyes can cause problems during biological treatment.[429]. Especially, such systems are very sensitive to any change in the quality of the effluents in terms of the type and the concentration of the pollutants. Therefore, the application of ENMs can considerably contribute to handle the treatment process with a high degree of stability required for continuously generated effluents from industrial activities. Hence, ENMs may be used efficiently to ensure a stable treatment efficiency for the effluents.

3.1.4.1.2.5 Health and safety risks

Along with the progress in the development and implementation of ENMs for the treatment of industrial effluents, the evaluation of the exposure of workers in the various stages of manufacturing, handling and application of ENMs is of high importance. In this regard, various nanomaterials have been the subject for toxicological studies in order to have a better understanding of the probable health and safety (H&S) risks they may bring. Various modes have been reported regarding workers exposure to ENMs in their workplace. Fig. 3.4 presents a summary of the predominant exposure routes, i.e., dermal, oral, inhalation and ocular. Basinas et al., (2018) [430] through a recent and systematic review on the available evidence about ENMs exposure routes, concluded that there is a likelihood to expose the workers to ENMs through all the above- mentioned exposure routes. However, Yokel and MacPhail, (2011) [431] in their review concluded that inhalation is a route of great concern when the workers are exposed to airborne ENMs. In this regard, more research is necessary to have a conclusion on the most important exposure routes which could benefit the design and implementation of appropriate protective actions. These research studies may help to apply safer materials with minimum subsequent H&S effects [432].

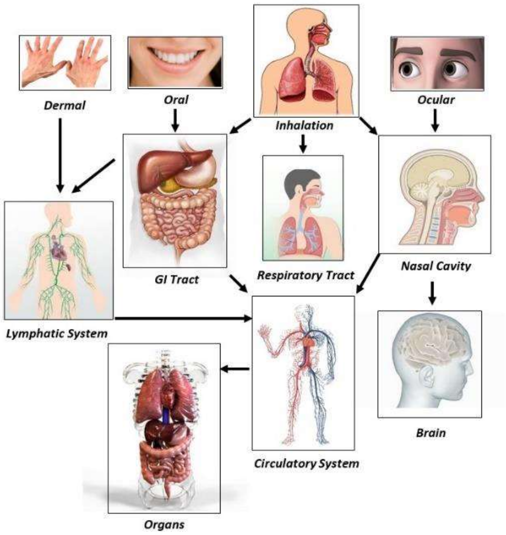


Fig. 3. 4. The key routes of ENMs exposure and uptake and their translocation potential in the human body. Dermal, oral, inhalation and ocular are the primary routes of ENMs exposure. The arrows show their probable translocation pathways, redesigned from Yokel and MacPhail, (2011) [431].

The exposure routes and properties of the nanomaterials such as shape, size, surface charge, solubility, together with their concentration may condition their subsequent toxic effects. Some types of ENMs may cross biological membranes under specific circumstances (particle size and shape, surface functionalization) and may cause harmful effects to living organisms by inducing cell oxidative stress and inflammation [433]. Some comparative studies [434] showed that toxicity of oxide nanoparticles may depend on the oxide type: ZnO and TiO_2 can induce more severe toxic effects when compared to MgO. In this case ROS (reactive oxygen species), which are able to oxidize and degrade cell membrane [433], are reported to account for the toxicity of ZnO and TiO_2 nanoparticles. In addition, nanoparticles accumulation facilitated by blood systemic circulation may cause adverse effects on pulmonary system and other organs such as kidneys, liver, spleen or even on the brain, as found for TiO_2 nanomaterials in rats and mouse [435]. Despite this knowledge, there is still a lack of consensus on the toxic effects of some types of nanomaterials. For AgNPs in consumer products, although there is no evidence for the direct adverse effects of such particles to human cells, their bioaccumulation in the environment can increase the probability of their toxicity [436–438]. Regarding carbon-based nanomaterials, Ema et al. (2017)[439] reported very low pulmonary toxicity for graphene and graphene oxide nanomaterials after inhalation. Simon-Deckers et al., (2008) stated that carbon nanotubes are more toxic when compared to nano-TiO_2 towards A549 human pneumocytes [54] whereas Tsuda, et al (2009) concluded that no carcinogenic effects were observed for single-walled carbon nanotubes (SWCNT) and fullerenes [441]. Rodriguez-Yañez et al. (2013) [442] reviewed the mechanisms of carbon nanotubes toxicity, and concluded that their toxic effects to living cells are attributed to their morphology allowing their cell membrane penetration as well as to impurities and functional groups attached to them.

In the context of toxicity, inorganic and organic (polymer) nanomaterials have been ranked in terms of their toxic effects. Iron-based nanomaterials such as Fe_3O_4, and especially zero valent iron appear to have low levels on toxicity on freshwater and marine organisms [443]. There are several reports on the application of Fe_3O_4 in medical field. As an example, magnetite has been used to treat lung cancer [444]. Diamond ENMs have also shown low levels of toxicity in human kidney cells [445]. Regarding organic based nanomaterials, chitosan may be cited as example of an efficient drug carrier being extensively used in drug delivery systems [446] with unreported toxicity [354]. However, knowing the mechanisms involved in the toxicity of specific types of nanomaterials, modifications in their structure can be used to considerably reduce their toxic effects. For instance, Khalaj, et al., (2018) [353] based on in vivo and in vitro studies concluded that copper-based nanomaterials may bring some toxic effects to aquatic and terrestrial organisms. However, by modifying the material structure either through crystallinity improvement, which may limit the material solubility and thus decrease the release of ions to the media, or by doping the structure with another metal, their toxicity can be considerably reduced [39].

It can be stated that the toxicological studies carried out so far have used different in vitro and in vivo experimental models and also different experimental conditions such as different ENMs concentrations. Therefore, it is still difficult to interpret and compare the existing data in order to have a conclusion on the real toxic effects of nanomaterials on living organisms as the conditions difference can be the source of different results achieved for the toxicity ofENMs such as carbon nanotubes. Although some legislation has been already implemented by national organizations in order to minimize the risks associated with the application of nanomaterials, there is no specific international regulation covering the issues related to the production, handling or application of nanomaterials [447]. Therefore, there is a need for a regulatory framework considering all the health and safety aspects of working with nanomaterials [148,448]. In conclusion, more toxicological studies are necessary in order to create a poule of recommendations for framing the development of safer ENMs with minimum health and safety issues and also to strict engineering control in workplaces which has not been addressed so far. Meanwhile, engineered controls (including treatment process change, controlling the dispersion of the ENMs in the workplace, isolation of the workers, the use of robots, etc), as well as administrative controls (when engineering controls are not feasible) such as implementation of an ENMs hygiene plan, training the workers, reducing the exposure time to ENMs, and precise housekeeping practices should be implemented to minimize the probable adverse effects of ENMs on the safety and health of the workers. Educated utilization of personal protective equipment such as respirators, gloves and protective clothing are also of high importance to block the exposure routes to ENMs [431]. Considering that health and safety issues are of high importance according to the performed fuzzy-Delphi results obtained in this study, urgent actions seem to be required to provide a safe workplace for the workers.

3.1.4.2.2 Economic Considerations

3.1.4.2.2.1 Initial investments

Initial investments, including the cost of land, civil works, equipment, etc. are of significant importance to decide whether a technology will be adopted by an industry or not, as is the case of industries dealing with the treatment of wastewaters [449–453]. There is a limited number of studies on the economic feasibility of various treatment technologies, especially for the emerging ones. Buyukkamaci and Koken (2010)[142] studied the optimum treatment processes for various types of pulp and paper mill effluents based on detailed analysis of initial investment costs. They concluded that the most appropriate method in terms of economic and technical considerations for medium strength effluents is an upflow anaerobic sludge blanket (UASB) method followed by an aeration basin. For high strength effluents they proposed a UASB method followed by an aeration basin or by a conventional activated sludge process. Regarding the development of nano-based wastewater treatment technology, there is a need for more studies on the required initial investments. However, there is no report in the literature on the investments required by nano-based wastewater treatment plants. In this regard, technical specifications can be helpful to determine the amount of the initial investment required. As an example, the kinetics of the treatment process may be used as an indicator for the design of the reactor size considering the type of the nanomaterials used [454].

From a technical perspective, assuming that the capital costs, including total direct plant cost (i.e., land, equipment, buildings, etc.) and indirect investment required (i.e., engineering supervision, etc.), associated to the nano-enabled treatment plants are comparable to the treatment plants that utilize advanced oxidation processes, especially Fenton treatment process, some rough cost estimations can be made. Cañizares et al., (2009) [455] conducted a comparative study on the investment costs of various chemical oxidation processes for the treatment of the effluents from olive oil mills and from a fine-chemical manufacturing plant. They concluded that although the nature of the effluents can influence the investments required, the capital costs related to the electrochemical oxidation ($15x10^3$ €/m^2) is comparable to the Fenton process. This capital cost, $15x10^3$ €/m^2, can thus be roughly assumed to stand for ENMs based treatments as well. Furthermore, assuming that the efficiency of ENMs based treatments might be enhanced over time [421], the size of the reactors can then be reduced, thus contributing to lower the capital costs.

3.1.4.2.2.2 Operating costs

When nanotechnology-based treatments are to be implemented, different contributions arising from the purchase or synthesis of ENMs, from energy (such as electricity required for instance for photocatalysis treatments using ENMs), and from labor should be altogether considered for the estimation of operating costs. The costs of the nanomaterials is highly dependent on material type and the desired properties such as purity level (wt. %), surface functionalization, and particle size. TiO_2 nanoparticles are available at prices ranging from \$0.03/g to \$1.21/g, with treatment costs ranging from \$0.50 to \$1.00 per gram of pollutant [421]. The costs of nano zero valent iron (nZVI) particles have decreased with the improvement of technology used for their production, being currenty around \$0.05–0.10/g. However, micro and bulk zero valent iron are still considerably cheaper (\$0.001/g) in terms of production [456].The cost of magnetite nanoparticles (in a continuous flow system) has been reported as well: Simeonidis et al., (2015) [457] estimated a synthesis cost around 0.0035 €/g. Despite these large scale production costs, there is still an urgent need not only to find cheaper feedstocks but also to develop green and cost effective methods to synthesize ENMs at a reasonable price. Application of nanomaterials with the possibility of their recovery and reuse can also potentially decrease their total production cost. Recovery and recirculation of nanomaterials can be implemented through the use of ceramic membranes [458]. Another possibility which is now raising a large interest is the use of magnetic nanoparticles to facilitate their separation under an applied magnetic field.

For a specific type of contaminant, when various appropriate ENMs are available for the treatment, it is crucial to proceed with an individual evaluation. For instance, for phenol contaminant, Pires et al., (2015)[459] compared the cost of different types of synthesized nanomaterials, i.e., copper oxide catalysts on different supports such as γ-Al_2O_3, pillared clay and TiO_2. They concluded that CuO on γ-Al_2O_3 is the most cost effective material with an estimated treatment cost of 0.07 \$ at 0.175/g of metal) for a pollutant load removal of 80%. In this regard, further comparative studies on treatment costs with different nanomaterials are mandatory in order to have a final conclusion about the optimized cost, allowing to leverage ENMs technologies among other competitors and potentially push them for commercialization.

Regarding energy costs, there are also some estimation for the price of the electricity as is the case of ENMs based photocatalysis processes which are much dependent on electricity consumption. Pirkarami et al., (2014) [460] indicated that treating 1 m^3 of a dyed solution using UV/Ni–TiO_2 system may consume 4 kWh/m^3 of electricity. According to the local electricity price (Iran, 0.042 USD/kWh), the total price of the energy required was estimated as 0.168 USD/m^3. In regions where the electricity price is high, application of visible light active nanomaterials such as N-TiO_2 or consumption of solar energy are adviced as prefered solutions [461].

Labour costs are scarcely reported or inexistent in the literature. Given the total absence of data on the labour costs associated with ENMs treatment processes, traditional industrial treatments of effluents will be here considered while attempting to rank labour cost among the various contributions to total operating costs. Long et al., (2018)[462] reported that in industrial parks in Taihu and Haihe water basins (China) the operating costs of centralized wastewater treatment plants may be ranked as electricity > labor > used chemicals. Li, et al. (2017) [463] stated that the average energy consumption for a treatment process (0.20 ± 0.06 kWh/t) in China, calculated on the basis of the cost of traditional treatment technologies is much less as compared to that of some developed countries, referring that the relatively low cost is related to the use of the advanced installations newly constructed and the low-quality requirements of wastewater treatment in Shenzhen, China. Therefore, assuming that ENMs based treatments will not substantially diverge from the tradional treatment methods in terms of the comparative weight of electricity, labor and chemical reagents in the overall operating costs, labor cost contribution is anticipated to be ranked between energy and nanomaterials cost, safeguarding that this rank may vary with the region under consideration [463].

There are also some reports in the literature on the operating costs of some traditional industrial effluents treatment processes which can be used for a rough comparison of the operating costs using nanomaterials with other wastewater treatment technologies. For instance, Weschenfelder et al., [465] stated that the operating costs of a full-scale ceramic membrane plant for the treatment of oilfield produced water can be estimated around US$ 0.23/m^3. Electrocoagulation is also a widely applied method for the treatment of industrial effluents. Various operating costs (e.g., US$ 3.4 /m^3 [466] to US$ 5.43 /m^3 [467] for the treatment of heavy metals from industrial effluents. However, the operating cost may be varied based on the treatment plant scale. For instance, Niu et al., (2016)[468] stated that the operating costs for the treatment of paper mill effluents using a combination of conventional physico-chemical and biological treatment methods can be ranged from US$ 0.029 (100000 thousand m^3/y) to US$ 0.99 (150 thousand m^3/y), depending on the treatment scales. Hence, for the application of nanomaterials some factors such as treatment scale and also the potential of the recovery and re-use the nanomaterials can determine the final operating costs of the large-scale treatment plants.

3.1.4.2.2.3 Maintenance costs

The application of ENMs for industrial wastewater treatment purposes may contribute to a substantial reduction of the maintenance costs of treatment plants. As an example, when using membrane systems, fouling by inorganic suspended solids, dissolved organic compounds or biofilms due to biological activities are major contributor to maintenance costs. A pre-treatment with nanomaterials or the incorporation of nanomaterials in the structure of the membrane are the possible ways to mitigate fouling concerns. For instance, Lifen et al. (2012)[469] indicated that incorporation of TiO_2 into polyvinyl alcohol (PVA) can considerably enhance the hydrophilicity and anti-fouling property of the composite membrane. Also, less solid waste generation can potentially lead to costs mitigation required for the maintenance of the sludge dewatering and thickening facilities.

However, the negative effects of the ENMs application for the treatment of industrial effluents have not been addressed so far in the literature, especially under real conditions. Studies are thus encouraged in this regard to allow a more realistic evaluation of the overall maintenance costs of the systems using this technology.

3.1.4.2.3 Environmental considerations

3.1.4.2.3.1 Solid wastes generation

So far, various treatment technologies included in primary, secondary, and tertiary treatments have been examined for their efficiency for the treatment of industrial effluents and also for their capability to reduce the amount of final waste generated. Activated sludge as one of the most common treatment technologies for the treatment of industrial effluents [5], generally produces a large amount of waste activated sludge. Generation of solid wastes has been also considered a potential for the improvement of some physicochemical methods such as coagulation [470]. Due to the remarkable sludge disposal costs [471] and subsequent environmental drawbacks, the development of methods with a minimum solid waste production is of high importance. It is evident that the mechanisms involved in the removal and degradation of the environmental pollutants contained in the industrial effluents can determine the extent of the solid waste generated. When adsorption processes are involved, the pollutants, mainly heavy metals, get attached to the surface of the nanomaterials, being thus transferred from the liquid to the solid phase. The recovery of the adsorbed elements may prompt the reusability of the nanomaterials, thus raising a significant interest. There are some reports in the literature for the successful recovery of adsorbed pollutants. For instance Yang et al., (2014)[472] recovered Os(IV) adsorbed on the γ-nano-Al_2O_3 in the pH range of 3-7 which could be easily recovered with 0.1 mol L^{-1} HCl. They stated that the chloride ion with smaller size can be easily exchanged with Os. As an another example, carbon nanotubes (CNTs) and nZVI were utilized in order to recover hexavalent chromium, selenium and cobalt, from aqueous solutions [473]. In contrast, the degradation mechanism involved in the decomposition of organic compounds either through catalytic activity of nanomaterials or Fenton-like processes may lead to final products including carbon dioxide and water. In such circumstances no, or negligible, solid waste is expected to be generated. For instance, Sudha & Sivakumar, (2015)[418] stated that the photocatalytic degradation of industrial effluents containing dyes generates negligible amounts of solid waste. The disposal of the nanomaterials can also be considered as a likelihood for the solid waste generation. However, there is not currently an estimation on the amount of the nanomaterials released form the wastewater treatment plants using this technology. The disposal of the nanomaterials can be conditioned by several factors such as the properties of the nanomaterials (e.g., magnetic properties to allow magnetic separation), the initial amounts of the nanomaterials used, etc. In addition to the environmental concerns, the disposal of nanomaterials can be prevented or minimized using innovative techniques (nanomaterials separation by membranes) to allow the nanomaterials to be re-used, rendering the process more cost-effective.

3.1.4.2.3.2 Release of chemical substances

The release of by-products into the effluent by the treatment process itself is another important issue to be addressed when evaluating a treatment method of industrial effluents. Recently, chemical methods based on the production of hydroxyl radicals which are powerful agents to deal with recalcitrant organic pollutants, have received an enormous attention. Among the chemical methods applied so far, Fenton reactions and oxidation with ENMs are among the most widely investigated technologies. The basis of Fenton process is the reaction between iron ions and hydrogen peroxide [474] to generate hydroxyl radicals. In spite of the inherent advantages of this method, such as short reaction time [475], there are some drawbacks including the generation of secondary pollutants through the release of ferric ions to the treated effluent [476]. As a result, additional treatments may be required [477]. In order to overcome this issue, heterogeneous Fenton reactions based on the application of iron oxide(s) nanomaterials or other types of inorganic nanomaterials such as TiO_2, copper-based nanomaterials, etc. have been developed in recent years.

The dissolution of nanomaterial particles is the phenomenon that may account for the ions released to the effluent during the treatment process [478]. However, recent studies have indicated that some parameters can be used to control the extent of ion release. pH, particle size, crystalline structure, and temperature are among the most important parameters. Schmidt and Vogelsberger (2009)[479] concluded that amorphous TiO_2 NMs are more soluble than crystalline TiO_2. They also stated that pure nano-anatase was more soluble than a mixture of nano-anatase and nano-rutile phases. Mudunkotuwa et al. (2012)[480] also concluded that ZnO nanoparticles with lower particle size may show a higher tendency for dissolution. Avramescu, et al. (2017) [481] indicated that the pH of the media can also influence the solubility of metallic zinc, ZnO and TiO_2 nanoaparticles. They observed that all particles show higher solubility at pH 1.5 as compared to pH 7. Recent studies have also indicated a higher dissolution of nanomaterials by increasing the temperature of the media [482]. Considering the importance of the solubility of ENMs, especially for risk assessment purposes, there is a need for specific standard methods to assess their solubility [483]. The release of the nanomaterials itself is also considered as another subject to be addressed. Although some techniques such as magnetic field separation [24] can be a good solution to prevent the release of magnetic nanomaterials, the successful application of such methods for real application should be examined. In addition, development of other technologies, such as membrane separation to prevent the release of nanomaterials, especially non-magnetic nanomaterials, is highly recommended.

3.1.4.2.3.3 CO_2 emission

The mechanisms involved in the process used for the treatment of industrial effluents can also determine the extent of carbon dioxide production and release. In this regard, various final products can be expected when different treatment methods are applied. For instance, in traditional nanomaterials free methods, methane and/or carbon dioxide are the main final products of anaerobic and aerobic treatment processes, respectively [175]. In addition, pond systems, as one of the most widely used methods for the treatment of industrial effluents in some developing countries [484] are partially aerobic and partially anaerobic, thus probably resulting in the emission of both carbon dioxide and methane. However, when using nanomaterials, the catalytic activity of nanomaterials themselves may also account for the generation of carbon dioxide as a final product in case of complete degradation. In this regard, the development of carbon dioxide capturing methods can help to control its emission from nano enabled reactors.

There are several options to reduce CO_2 emissions from wastewater treatment plants. For instance, the application of photosynthetic bacteria to consume the CO_2 produced can be adopted for this purpose [485]. Recently, some innovative techniques have also been developed aiming to capture carbon dioxide and CH_4 through the use of advanced ENMs. The most important mechanism is the adsorption of these gases on the nanomaterials previously stabilized on porous supports. As an example, Fe_3O_4-graphene provides very promising results [486]. However, scaling up challenges and capturing costs are still the main barriers to the commercialization of these technologies.

Additionally, the synthesis and handling of ENMs may also account for CO_2 emission. Some factors such as the synthesis route used, the need for further treatments such as thermal treatment of as-prepared nanomaterials, etc. can determine the amount of the carbon dioxide release into the atmosphere. For instance, sol-gel method, as a conventional process for the synthesis of titanium dioxide nanoparticles, generally results in amorphous nanomaterials [487]. Calcination of the freshly prepared nanoparticles to provide the nanomaterials with the desired degree of crystallinity can be a source of CO_2 release. Some methods have been recently developed without the need of calcination. For instance, Wei et al., (2018)[488] Prepared Sn-TiO_2 aerogel without the need for annealing using an ultrasonic-assisted sol-gel method.

3.1.4.2.3.4 Water reuse potential

The potential of an industrial effluent to be re-used after the treatment process is highly dependent on factors like the treatment method(s) applied, the involved treatment stages (primary, secondary or tertiary), the type of effluent, and the quality needed for reuse. ENMs processes can be used as a pre-treatment stage of industrial effluents in order to increase their biodegradability, as a single treatment or as a tertiary treatment to polish the treated effluents coming from biological treatment steps. The ability of nanomaterials to deal with non-biodegradable contaminants is one of the most important features of the application of this technology. For instance, nanomaterials such as zero valent iron have been successfully applied to treat chemically complex effluents, such as those from metalworking [489] including highly toxic compounds. As stated before (section 3.2.1.1), treatment with ENMs may involve various mechanisms which can deal with various types of contaminants [382]. Adsorption and oxidation may allow to remove and degrade various complex organic compounds (such as AOXs) and toxic inorganic compounds (such as heavy metals) which concentration has to decrease below a standard limit in order to ensure the quality of water resources [490,491].

In addition, some types of industrial effluents contain some specific microbial communities [492] with high resistance to conventional disinfection methods. Nanomaterials such as CuO [493], ZnO [494], Ag [495], and TiO_2 [496] can show strong antimicrobial activity. Although some single-phase nanomaterials such as nano-WO_3 (for disinfection of *Escherichia coli*) [497], and nanocomposites such as carbon nanotubes/silver nanoparticles (for disinfection of *Escherichia coli* and *Staphylococcus aureus*) [498] have been used for polluted waters disinfection, literature reports on the application of engineered nanomaterials for the disinfection of real effluents are yet rare. Moreover a pre-treatment with nanomaterials can significantly reduce the microbial contamination load of the effluents when discharged into receiving water bodies. Some recent studies have also indicated that biologically treated effluents can be considered as a source of microbial pollution on surface water resources [499]. To overcome this drawback, a tertiary treatment with nanomaterials can be used to improve further the treatment efficiency of the system and make the effluents suitable for re-use purposes. Although the potential of the water to be re-used is preliminarily attributed to the quality of the effluents after being treated with nanomaterials, in terms of COD, BOD and other influencing parameters, economic considerations should be taken into account to provide clean water resources at reasonable costs. In section 3.2.2 economic considerations on the application of this technology for the treatment of industrial effluents have already been mapped out, although the link between the treatment costs and the quality of the treated water for various applications is still to be addressed, thus warranting further studies.

3.1.4.2.3.5 Potential to recover by-products

The potential of a process for the recovery of materials from industrial effluents or to convert organic compounds into energy can considerably prevent the release of the chemicals into the environment. The implementation of this strategy may also bring some economic benefits when contributing to the reduction of the overall treatment costs, thus being an important economic feature to be considered. In this context, anaerobic digestion of industrial effluents among the biological treatments, can lead to the production of methane as an energy carrier [9]. Additionally, membrane technologies, as leading wastewater treatment strategies [500] have shown high efficiency for the treatment of industrial effluents [501], and also in the recovery of organic [502] and inorganic materials[503,504]. Modifications in the structure of the membranes by the addition of low-cost nanomaterials have improved their overall performance while decreasing the treatment costs. For instance, Scheibler et al. (2015)[505] developed a low-cost multilayer γ-Al_2O_3 ceramic membrane for ultrafiltration pre-treatment of oily wastewater. They achieved a high oil/water separation capability using the developed membrane. There are also other reports in the literature for the successful separation of oil/water using ENMs ZnO [506], SiO_2 [507], and nano-aluminum films on stainless steel meshes [508] which demonstrate their potentional for treating oily wastewaters [506–508]. However, the recovery of the chemicals using nanomaterials depends on the mechanisms involved. In this regard, adsorption is the recommended mechanism for the recovery of the chemicals from polluted effluents. In the case of advanced oxidation processes, no organic matter recovery can be expected. Nevertheless, there are many evidence for the successful application of ENMs for the recovery of inorganic materials from effluents.

3.1.4.2.4 Social considerations

3.1.4.2.4.1 Odor impact

In some biological treatments such as pond systems, which is a common technology for industrial wastewater treatment especially in some developing countries [484], the treatment process may result in the formation of malodorous compounds such as volatile fatty acids (VFA) with harmful olfactory impacts [509]. The release of volatile organic compounds (VOCs) which is typical in effluents from industries such as pulp and paper production is normally high from the open surface of the biological treatment systems[510]. The ability of a method for minimizing the odor impacts can increase its acceptability by local communities. There are some reports about the successful application of ENMs for the mitigation of odorous compounds such as TiO_2 [511] and ZnO [512] nano photocatalysts. According to the mechanisms involved in the degradation of organic compounds, the formation of malodorous compounds is not expected when using such nanomaterials because malodorous compounds can be easily decomposed by the powerful hydroxyl radicals generated under the activity of these nanomaterials. Designing closed-surface reactors with the ability to prevent the escape of odorous compounds can also be considered depending on the distance of the industry to the local communities and on the probable negative impacts they may bring. Such designs can also aid to improve the visual characteristics of wastewater treatment plants which have adopted this technology. Some studies have also indicated that the application of caps with an internal layer of nanomaterials (zeolites) can help to mitigate the odorous compounds released from the effluents [513].

3.1.4.2.4.2 Noise and visual impact

Recent studies have clearly indicated that “less crowded neighbourhoods” may bring both social and environmental advantages [514]. Noise nuisance for the nearby residents can be produced by several process units in a wastewater treatment plant. So far, some models have been developed for the assessment of the sound effects [515]. However, the noise level of a treatment plant depends on several factors such as the operational process units, the sequences of treatment steps (biological, physicochemical, or their combinations) and the distance of the treatment plant from local residents. Currently, the noise impacts from the industrial treatment plants using nanotechnology has not yet been well documented. Risk assessment can help to have a better understanding on the extent of the noise pollution that the nano-reactors may induce in the surrounding environment. The mitigation of such pollution source may help to attract social supports for such novel technologies.

Visual characteristics of an industrial wastewater treatment facility are highly dependent on the design parameters of the reactors such as the size, shape, etc. As stated before, the application of nanotechnology for the treatment of industrial effluents may lead to reactor size reduction and while mitigating the need for sludge collection and processing. Although this criterion has received the least importance among the studied criteria, it should be considered when designing the industrial wastewater treatment plants using nanotechnology.

3.1.4.2.4.3 Public acceptance

Social acceptability is one of the important criteria to push a technology for commercialization. So, in order to achieve a sustainable development of wastewater treatment plants it would be necessary to consider social benefits, besides technical, environmental and economic performance of a given technology [516]. However, the current society has still a lack of knowledge on nanotechnology, and public debates on nanotechnology for water and wastewater treatment are rare according to literature [509]. Gupta, et al. (2012) [517] conducted structured interviews to identify opinion makers in the North West Europe and the factors that may influence the societal response to various applications of nanomaterials. They concluded that a technology should be beneficial, useful, and necessary enough to attract the support of the society. According to experts judgment, the drug delivery and water treatments are the most beneficial and necessary applications among the studied fields. Cook & Fairweather (2006) [518] by distributing questionnaires to randomly selected household addresses in New Zealand examined the acceptability of 12 potential applications of nanotechnology. They concluded that the treatment of wastewater using nanomaterials was assessed as acceptable by the community. However, the public acceptance towards a technology for the treatment of industrial wastewater can be highly influenced by other factors. The effectiveness of a technology can positively affect the perception of the general public which may result in the improvement of the economic situation. In case of the treatment of industrial effluents using nanotechnology, the large-scale production of the nanomaterials, transportation and application of nanomaterials in the treatment process may produce new job opportunities. However, there is a need for realistic estimations of the extent of the opportunities that can be created by the commercialization of this technology. Awareness of the general public on the footprint(s) of the nanotechnology for effluents treatment can also aid to reinforce the scientific-based orientation of the community towards this technology. In this regard, there is also a need to trace the effects of the nanomaterials in case they are released into the environment from the wastewater treatment plants and to perform comparative studies on the effects of various types of nanomaterials after being released. However, there is not yet a consensus among the scientific community on the release, fate, environmental concentrations and nanomaterials behaviour in real environmental conditions. Table 3.4 presents the current status of the release, fate, environmental expected concentrations of some widely used nanomaterials based on recently published review papers.

Table 3. 4. Release, fate, and environmental expected concentrations of some widely used ENMs.

ENMs	Application	Comments on the release, fate, and environmental concentrations of ENMs	Ref.
- CeO_2, CuO, TiO_2, and ZnO	- General applications[a]	- There is a possibility even for soluble metal oxides to accumulate in the environment. - The NMs concentrations may exceed the minimum toxic threshold, especially for high production materials such as TiO_2 and ZnO.	[519]
- Ag, Au, Cu, ZnO, TiO_2, F_xO_y	- Not specified	- The behaviour of ENMs in the environment is not yet fully understood. - It is important to distinguish the source of differences in the results of various studies on the toxicity of nanomaterials in the environment. - Toxic effects of the nanomaterials in the environment is not yet a common problem. - It is necessary to determine and standardize the toxic dose of nanomaterials in the environment.	[520]
- Graphene-Based NMs	- Biomedical Applications	- The majority of the toxicological studies is at the cellular level rather than genetic level. - More studies on the fate, transport and ecological risks of nanomaterials are required to provide a basis to control the use of NMs.	[521]
- Not specified	- Not specified	- There is a knowledge gap on environmental concentrations of NMs. - There are some evidence on the specific effects of some types of NMs on the environment in terms of fate, bioavailability and toxic effects. - ENMs seem to be less toxic than equivalent dissolved materials.	[522]
- Metal and metal oxides NMs	- Not specified	- The fate of NMs in the atmosphere has not yet been well understood. - It seems that NMs may have limited transport in the atmosphere because of rapid settling. - The stability of ENMs in freshwater and stormwater is higher than that in seawater or groundwater. It may enhance the transportation of ENMs in freshwaters.	[523]
- CeO_2, SiO_2, and Ag	- Commercial activities	- The concentrations of CeO2-ENMs in freshwater may range from 1 pg/l (2017) to a few hundred ng/l (2050). - The concentrations of SiO2-ENMs are estimated to be 1,000 times higher than CeO_2. - The concentrations of Ag-ENMs are estimated the 10 times lower than CeO_2. - The risks of the nanomaterials in most environmental conditions are relatively low.	[524]

Table 3.4. Continued.

ENMs	Application	Comments on the release, fate, and environmental concentrations of ENMs	Ref.
- Not specified	- Not specified	- There is a need for alternative methods to assess the environmental exposure to NMs to decrease the uncertainty in ecological risk assessment.	[525]
- TiO_2, ZnO, Ag, fullerenes, CNT and CeO_2		- Five different types of NMs including ENMs, bulk-derived NMs, and abrasion produced NMs, combustion-generated NMs and natural NMs are present in the environment. - The current methods predict the concentration of NMs are only based on the release of ENMs. So, the expected the concentration may be higher than predicted.	[526]

3.1.5 Conclusion

The application of nanotechnology for water and wastewater treatment needs to be transferred from lab and pilot scale to real applications. At this stage, the evaluation of the technology, according to the criteria that may lead to its sustainable development and implementation, is inevitable. In this study, it was adopted a fuzzy-Delphi approach to have a better understanding of the criteria involved in the selection of an industrial wastewater treatment process, based on the consensus of experts. 17 criteria were ranked according to their relative importance, being the treatment efficiency and health and safety risks associated with the application of the most important criteria, although the importance of all the studied criteria were ranked above “Fair”. It was also clear that all criteria should be included in the decision making process. Although nano-based techniques are in general very important and beneficial for the removal of emerging pollutants, enough attention should be paid to the selection of the appropriate type of nanomaterials. For instance, low-cost and non-toxic materials such as chitosan and iron based nanomaterials seem to be good candidates considering all the aspects of sustainability. At this stage, the community will welcome studies focused on the sustainability aspects of ENMs in the treatment of environmental contaminants to facilitate the application of this technology to real situations.

3.2 Best Available Technologies for the Treatment of Industrial Effluents

3.2.1 Abstract

In spite of the huge efforts to develop efficient technologies for the treatment of recalcitrant compounds and emerging pollutants, selecting the most sustainable methods among possible alternatives is still a very complex and debating task. This is mainly due to the fact that an integration of technical, economic, environmental, and social criteria must be considered in the decision-making process. Traditionally, various multi-criteria decision-making approaches have been adopted to integrate various criteria for environmental applications. In this study, it was examined a fuzzy-Delphi approach to rate 17 factors integrating technical, economic, environmental and social criteria and also to rank 9 treatment technologies divided in two categories (physico-chemical and biological treatments). The results of this study indicated that although the efficiency of the treatment methods is the most important criterion, the contribution of other sustainability criteria should also be considered because they are of high importance for the selection of sustainable wastewater treatment methods. The proposed framework indicated that membrane technologies (among the physico-chemical methods) and anaerobic sludge blanket technology (among the biological treatment methods) are the most promising technologies for the treatment of highly polluted industrial effluents, being these findings supported by a consensus achieved by a group of 50 experts from 19 countries. The opportunities for the improvement of the mentioned methods according to the results achieved have also been discussed in the present study.

Keywords: Sustainability, Fuzzy-Delphi methodology, Physico-chemical methods, Biological methods.

3.2.2 Introduction

The quality of the final discharged effluents from industrial activities has been the subject of significant efforts over several decades to improve the performance of the methods applied for their treatment, either by physico-chemical, biological, or a combination of these processes. On the other hand, industries around the world, such as textile or pulp and paper industries are struggling with their economic profitability [1]. In this situation, stringent environmental regulations have also forced industries, especially those releasing recalcitrant compounds in their effluents, to adopt efficient treatment technologies. Hence, it is vital to consider both the importance of technical and economic factors when selecting the most appropriate treatment technologies [2]. In addition, long-term sustainability considerations enforce industries to include environmental and health [3] as well as social criteria in the decision-making process for the selection of the best treatment strategies [4]. Integration of all these aspects while selecting the most appropriate techniques for the treatment of recalcitrant compounds in industrial effluents is a complex task which needs a multi-criteria analysis framework to identify among a set of existing technologies the most suitable one.

Due to the inherent advantages of multi-criteria decision making (MCDM) approaches [158,527], such as their strong structure and logic [528], they have been effectively applied to support the decision makers to choose the most appropriate alternatives to solve a number of environmental problems [529]. Delphi, as a branch of MCDM processes, is basically conducted through a group decision-making among experts with different experiences and knowledge on the same application domain. Two main applications of this process are screening the criteria and forecasting (or evaluating) the performance of a method or technology [356]. Fuzzy-Delphi method (FDM) has been developed by the application of traditional Delphi methodology in a fuzzy environment. This technique has been previously applied for making sustainable decisions in various fields [357–359]. In this study, we utilized an FDM in order to assess the current opinion of experts in the field of various conventional and emerging technologies for the treatment of recalcitrant organic compounds from industrial effluents.

3.2.3 Methodology

3.2.3.1 Problem description

Selecting the most appropriate technologies to deal with recalcitrant compounds and emerging pollutants in the content of industrial effluents to satisfy stringent environmental standards while considering various technical, environmental, economic and social aspects is a complex task [5]. Multi-criteria decision analysis, as a set of methods allows to identify the most important criteria and to rank the available alternatives [530]. Although these methods have been extensively used to rank the relevant criteria and to select the most suitable alternatives in various scientific fields, only a few reports are available in the literature regarding the application of MCDAs to the selection of wastewater treatment technologies. Arroyo and Molinos-Senante (2018)[2] used choosing-by-advantages (CBA) approach to select the most suitable municipal wastewater treatment technology among the widely used methods (constructed wetlands, pond systems, extended aeration, membrane bioreactor, rotating biological contactor, trickling filter and sequencing batch reactor), considering several criteria including treatment efficiency, energy consumption, land area required, sewage sludge production, potential for water reuse, potential to recover by-products, reliability, odor impact, noise impact, visual impact, public acceptance, and complexity of operation. According to the opinions of 19 participants, odor impact was identified as the most important sustainability criterion and the extended aeration together with sequencing batch reactor were ranked as the most promising treatment technologies. A “technique for order of preference by similarity to ideal solution” (TOPSIS) approach was also used in some studies. For instance, Dursun (2016)[531] using this technique indicated that sustainability is the most important parameter among the studied factors (i.e., cost, global warming, eutrophication, land requirement, manpower requirement, reliability, sustainability and flexibility) and sequencing batch reactors (SBRs) method is the best technology among the studied technologies (i.e., activated sludge, upflow anaerobic sludge blanket followed by a facultative aerated lagoon, sequential batch reactor, constructed wetlands). Analytical hierarchy process (AHP) has also been used in recent years in its conventional and advanced forms (e.g., AHP fuzzy approach) in order to select the best wastewater treatment technologies. For instance, Ouyang et. al (2015)[532] applied an integrated fuzzy analytical hierarchy process for the selection of natural wastewater treatment alternatives. However, the fuzzy-Delphi method for ranking the most suitable technologies to deal with industrial effluents loaded with recalcitrant compounds has not been employed so far considering both conventional and novel treatment technologies for industrial effluents.

3.2.3.2 Study design

In this study, expert questionnaires were assisted for collecting the current opinion of experts on the performance of the studied treatment methods. A careful process was followed to invite experts with excellent academic and/or industrial experience in the field of the study. Linguistic variables and triangular fuzzy numbers (Tables 3.5 and 3.6) were utilized in order to determine the importance of the evaluation criteria and to rate the studied alternative methods. The questionnaire used in order to collect the opinion of the experts have been provided in supplementary information. The vertex method was used to estimate the consensus among the expert group (Eq. 1) through computing the distance between the aggregated fuzzy numbers (m_L, m_M, m_U) and the triangular fuzzy numbers expressed by each expert in the form of linguistic terms.

$$d(\widetilde{m},\widetilde{n}) = \sqrt{(m_L - n_L^i)^2 + (m_M - n_M^i)^2 + (m_U - n_U^i)^2} \qquad \text{Eq. 1}$$

According to Cheng and Lin [361], a value of $d(\widetilde{m},\widetilde{n})$ less than 0.2 indicates the consensus among the experts. The stability of the results achieved necessitates achieving 75% of group consensus among the experts [362]. The geometric mean (Eq. 2) [363] was utilized to calculate the fuzzy weights of the criteria and the relative efficiency of the industrial effluents treatment methods.

$$L_j = \underset{i}{\mathrm{Min}}\{L_{ij}\}, \quad M_j = \frac{1}{n}\sum_{i=1}^{n} M_{ij}, \quad U_j = \underset{i}{\mathrm{Max}}\{L_{ij}\} \qquad \text{Eq. 2}$$

This equation is used to calculate the relative importance of the element no. j allocated by expert no. i. In order to do the defuzzification of the final triangular fuzzy numbers, Eq. 3 was utilized.

$$df = \frac{1}{4}(L + 2M + U) \qquad \text{Eq. 3}$$

Table 3. 5. Linguistic variables and the relevant fuzzy scales for the relative importance of the criteria.

Linguistic variable	Fuzzy Scale (L, M, U)	$df = \frac{1}{4}(L + 2M + U)$
Extremely high	(0.9, 1.0, 1.0)	0.975
Very high	(0.7, 0.9, 1.0)	0.875
High	(0.5, 0.7, 0.9)	0.7
Fair	(0.3, 0.5, 0.7)	0.5
Low	(0.1, 0.3, 0.5)	0.3
Very Low	(0.0, 0.1, 0.3)	0.125
Extremely low	(0.0, 0.0, 0.1)	0.025

Table 3. 6. Linguistic variables and the relevant fuzzy scales for the evaluation of the methods efficiency.

Linguistic variable	Fuzzy Scale (L, M, U)	$df = \frac{1}{4}(L + 2M + U)$
Very good	(0,75, 1, 1)	0.937
Good	(0,5, 0,75, 1)	0.75
Fair	(0,25, 0,5, 0,75)	0.5
Bad	(0, 0,25, 0,5)	0.25
Very bad	(0, 0, 0,25)	0.0625

Aggregation of the fuzzy evaluations for each method was carried out according to Eq. 4.

$$\tilde{A} = \begin{bmatrix} \tilde{A}_1 \\ \tilde{A}_2 \\ \tilde{A}_3 \\ . \\ . \\ . \\ \tilde{A}_m \end{bmatrix}, \tilde{A}_1 = \sum_{i,j=1}^{n} r_{ij} \times w_j \qquad \text{Eq. 4}$$

Where, r_{ij} is the rating of alternative i with respect to criteria j and w_j is the j_{th} criterion weight.

3.2.4 Results and discussion

Due to the inherent complexity in the selection of the most appropriate industrial effluents treatment methods, it is not feasible to rely only on a single aspect such as the technical characteristics. An international panel consisting of 50 high-quality experts from 19 countries (all over the world with academic and/or industrial experience contributed in this study to determine the importance of each criterion and to rate the treatment methods according to their previous experience on the application of the different methods for industrial effluents treatment.

3.2.4.1 Prioritization of the criteria

Fig. 3.5 and table 3.7 present the fuzzy weights of the studied criteria and sub-criteria after achieving consensus among the experts in the second round of questioning. According to the results achieved, technical considerations received the highest importance among the studied criteria, with high relevance allocated to the “treatment efficiency” and “health and safety risks”. These results can reflect the fact that a technology to be chosen for the treatment of industrial effluents must be efficient and safe. Although there are a number of publications in the literature on the performance of various industrial effluents treatments [174,198,364,365], the health and safety issues attributed to the workers using those treatment technologies have not yet been well investigated. Exposure to biological agents (including bacteria, viruses, fungi (yeasts and mould) and parasites) is considered as one of the most important factors which affect the safety and health of workers. The entrance of the spores in human body via many ways such as respiratory tract, damaged skin, eye, etc. can cause severe health problems for the workers in the working place. In addition, environmental conditions such as humidity and temperature or their combination can also provide a favorable environment for the growth of biological agents. The nature of the treatment method applied, and the associated facilities can also pose some risks to the workers.

Table 3. 7. Linguistic variables and the relevant fuzzy scale for the relative importance of the criteria.

Criteria	Sub-Criteria	Fuzzy values			De-fuzzy
		L	M	U	
Technical	Treatment Efficiency (TE)	0,50	0,90	1,00	0,83
	Ease of Implementation (EI)	0,30	0,79	1,00	0,72
	Combination Possibility (CP)	0,25	0,72	1,00	0,67
	Process Stability (PS)	0,30	0,83	1,00	0,74
	Health and Safety Risks (HSR)	0,50	0,90	1,00	0,83
Environmental	Solid Wastes Generation (SWG)	0,10	0,79	1,00	0,67
	Release of Chemical Substances (RCS)	0,00	0,90	1,00	0,70
	CO_2 Emission (CE)	0,00	0,74	1,00	0,62
	Water Reuse Potential (WRP)	0,10	0,79	1,00	0,67
	Potential to Recover By-Products (PRB)	0,25	0,75	1,00	0,69
Economic	Initial Investments (II)	0,10	0,77	1,00	0,66
	Maintenance Cost (MC)	0,10	0,80	1,00	0,67
	Operating Costs (OC)	0,30	0,84	1,00	0,75
Social	Odor Impact (OI)	0,10	0,74	1,00	0,64
	Noise Impact (NI)	0,10	0,70	1,00	0,63
	Visual Impact (VI)	0,00	0,64	1,00	0,57
	Public Acceptance (PA)	0,00	0,75	1,00	0,63

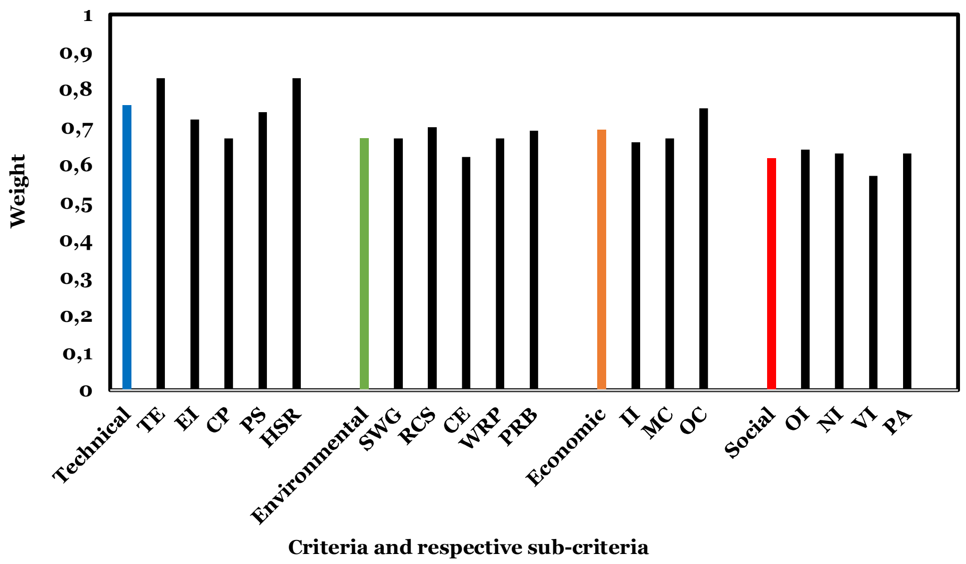


Fig. 3. 5. Calculated weights of the criteria and sub-criteria, measured as the average of the respective sub-criteria. The results indicate that the technical criteria are of the most importance for selecting the most sustainable industrial effluents treatment technologies. Economic criteria are in the second place of importance followed by environmental and social parameters. Also, treatment efficiency and health and safety risks are the most important among the influencing criteria. The abbreviations are described in Table 3.7.

The results of the fuzzy-Delphi method for the studied physico-chemical and biological treatment methods are summarized in tables 3.8 and 3.9, respectively. Various physico-chemical treatment methods have been so far applied for the treatment of industrial effluents. Coagulation and precipitation, membrane technologies, adsorption and oxidation processes are among the most effective and widely applied techniques.

Biological treatments, used as a single treatment or as a combination with other physico-chemical methods have also been widely applied for the treatment of industrial effluents [5]. Although they have a number of advantages, including being eco-friendly and cost-effective, they exhibit a lack of efficiency for the removal of recalcitrant compounds due to their low biodegradability in highly polluted industrial effluents. However, scientific efforts are in progress to promote their efficiency for such applications. Pond Systems, aerated lagoons, activated sludge and anaerobic sludge blanket technologies are the main biological treatments that have been applied so far for the treatment of industrial effluents around the world.

As summarized in table 3.8, the most sustainable method for the treatment of industrial effluents is membrane-based technologies followed by adsorption, oxidation with nanomaterials and Fenton process. Membrane-based technologies gained the highest scores in technical criteria (2.79) as well as in environmental criteria (2.27). While adsorption-based technologies are the most efficient in terms of economic and social criteria. However, considering all the various criteria, membrane-based technologies have been identified as the most sustainable technology to deal with industrial effluents. It can be highly correlated with the advances in the fabrication of novel membrane structures, mainly inorganic membranes and those decorated with engineered nanomaterials to increase the treatment efficiency and to decrease fouling properties of the membranes [500].

Novel technologies such as oxidation with nanomaterials are also moderately sustainable due in their current situation due to some existing barriers which need to be overcome. Due to the high potential of such technologies to satisfy the future need for clean water resources, more efforts are required, especially in terms of economic (i.e., operating cost) and social considerations (i.e., social acceptance) to push these technologies for commercialization. Development of cheaper nanomaterials, with the ability of recovery and re-use and low toxic effects [23], are highly welcome as the strategic steps for the development of oxidation with nanomaterials. Fenton-based technologies are also suffered from weaknesses such as the release of relatively high amounts of chemicals. Development of facilities to recover the chemical before discarding can also push this technology by reducing both subsequent environmental risks and operating costs.

Among the biological treatment methods (Table 3.9), activated sludge has been identified the most promising technology in terms of technical criteria (score: 2.47). However, considering all the criteria technical, environmental, economic and social), anaerobic sludge blanket was identified as the most sustainable technology (overall score: 6.82).

Table 3. 8. The average fuzzy values and de-fuzzy numbers allocated by the experts to the studied physico-chemical methods.

Main Criteria	Sub-Criteria	Fuzzy weights of sub-criteria				Physico-chemical methods																			
						Electrocoagulation				Membrane Technologies				Adsorption				Fenton Process				Oxidation with nanomaterials			
		Fuzzy values			De-fuzzy	Fuzzy values			De-fuzzy	Fuzzy values			De-fuzzy	Fuzzy values			De-fuzzy	Fuzzy values			De-fuzzy	Fuzzy values			De-fuzzy
		L	M	U		L	M	U		L	M	U		L	M	U		L	M	U		L	M	U	
Technical	TE	0,50	0,90	1,00	**0,83**	0,50	0,85	1,00	**0,80**	0,50	0,90	1,00	**0,83**	0,25	0,79	1,00	**0,71**	0,25	0,76	1,00	**0,69**	0,25	0,78	1,00	**0,70**
	EI	0,30	0,79	1,00	**0,72**	0,00	0,64	1,00	**0,57**	0,25	0,69	1,00	**0,66**	0,25	0,75	1,00	**0,69**	0,00	0,73	1,00	**0,62**	0,25	0,63	1,00	**0,63**
	CP	0,25	0,72	1,00	**0,67**	0,25	0,75	1,00	**0,69**	0,25	0,78	1,00	**0,70**	0,25	0,82	1,00	**0,72**	0,00	0,79	1,00	**0,64**	0,25	0,74	1,00	**0,68**
	PS	0,30	0,83	1,00	**0,74**	0,25	0,76	1,00	**0,69**	0,25	0,71	1,00	**0,67**	0,25	0,78	1,00	**0,70**	0,00	0,72	1,00	**0,61**	0,25	0,68	1,00	**0,65**
	HSR	0,50	0,90	1,00	**0,83**	0,25	0,72	1,00	**0,67**	0,50	0,89	1,00	**0,82**	0,50	0,83	1,00	**0,79**	0,25	0,76	1,00	**0,69**	0,25	0,73	1,00	**0,68**
Environmental	SWG	0,10	0,79	1,00	**0,67**	0,00	0,63	1,00	**0,56**	0,00	0,70	1,00	**0,60**	0,00	0,57	1,00	**0,53**	0,00	0,58	1,00	**0,54**	0,25	0,75	1,00	**0,69**
	RCS	0,00	0,90	1,00	**0,70**	0,00	0,64	1,00	**0,57**	0,00	0,80	1,00	**0,65**	0,00	0,82	1,00	**0,66**	0,00	0,64	1,00	**0,57**	0,25	0,69	1,00	**0,66**
	CE	0,00	0,74	1,00	**0,62**	0,25	0,73	1,00	**0,68**	0,25	0,74	1,00	**0,68**	0,25	0,79	1,00	**0,71**	0,25	0,74	1,00	**0,68**	0,25	0,71	1,00	**0,67**
	WRP	0,10	0,79	1,00	**0,67**	0,49	0,80	1,00	**0,77**	0,25	0,95	1,00	**0,79**	0,00	0,75	1,00	**0,63**	0,25	0,73	1,00	**0,68**	0,25	0,79	1,00	**0,71**
	PRB	0,25	0,75	1,00	**0,69**	0,00	0,55	1,00	**0,52**	0,25	0,74	1,00	**0,68**	0,25	0,64	1,00	**0,63**	0,00	0,63	1,00	**0,56**	0,25	0,59	1,00	**0,61**
Economic	II	0,10	0,77	1,00	**0,66**	0,25	0,63	1,00	**0,63**	0,00	0,57	1,00	**0,53**	0,00	0,67	1,00	**0,58**	0,00	0,64	1,00	**0,57**	0,00	0,55	1,00	**0,52**
	MC	0,10	0,80	1,00	**0,67**	0,00	0,56	1,00	**0,53**	0,00	0,54	1,00	**0,52**	0,00	0,63	1,00	**0,57**	0,00	0,60	1,00	**0,55**	0,00	0,55	1,00	**0,53**
	OC	0,30	0,84	1,00	**0,75**	0,00	0,58	1,00	**0,54**	0,00	0,57	1,00	**0,54**	0,00	0,62	1,00	**0,56**	0,00	0,56	1,00	**0,53**	0,00	0,51	1,00	**0,51**
Social	OI	0,10	0,74	1,00	**0,64**	0,25	0,73	1,00	**0,68**	0,25	0,83	1,00	**0,73**	0,25	0,82	1,00	**0,72**	0,00	0,75	1,00	**0,63**	0,25	0,81	1,00	**0,72**
	NI	0,10	0,70	1,00	**0,63**	0,00	0,70	1,00	**0,60**	0,25	0,83	1,00	**0,73**	0,25	0,83	1,00	**0,73**	0,25	0,77	1,00	**0,70**	0,25	0,76	1,00	**0,69**
	VI	0,00	0,64	1,00	**0,57**	0,25	0,75	1,00	**0,69**	0,25	0,86	1,00	**0,74**	0,25	0,85	1,00	**0,74**	0,25	0,77	1,00	**0,70**	0,25	0,78	1,00	**0,70**
	PA	0,00	0,75	1,00	**0,63**	0,25	0,76	1,00	**0,69**	0,25	0,89	1,00	**0,76**	0,50	0,86	1,00	**0,81**	0,25	0,73	1,00	**0,68**	0,25	0,73	1,00	**0,68**
Sum									10,88				11,63				11.48				10.64				11,02
Fuzzy Value									7,48				7,99				7,87				7,29				7,55
Rank									**(4)**				**(1)**				**(2)**				**(5)**				**(3)**

Table 3. 9. The average fuzzy values and de-fuzzy numbers allocated by the experts to the studied biological methods.

Main Criteria	Sub-Criteria	Fuzzy weights of sub-criteria				Biological methods															
						Pond Systems				Aerated Lagoons				Activated Sludge				Anaerobic sludge blanket technologies			
		Fuzzy values			De-fuzzy	Fuzzy values			De-fuzzy	Fuzzy values			De-fuzzy	Fuzzy values			De-fuzzy	Fuzzy values			De-fuzzy
		L	M	U		L	M	U		L	M	U		L	M	U		L	M	U	
Technical	TE	0,50	0,90	1,00	**0,83**	0,00	0,58	1,00	**0,54**	0,25	0,68	1,00	**0,65**	0,25	0,76	1,00	**0,69**	0,25	0,63	1,00	**0,63**
	EI	0,30	0,79	1,00	**0,72**	0,25	0,75	1,00	**0,69**	0,25	0,72	1,00	**0,67**	0,25	0,73	1,00	**0,68**	0,00	0,60	1,00	**0,55**
	CP	0,25	0,72	1,00	**0,67**	0,25	0,63	1,00	**0,63**	0,25	0,66	1,00	**0,64**	0,25	0,73	1,00	**0,68**	0,00	0,65	1,00	**0,58**
	PS	0,30	0,83	1,00	**0,74**	0,00	0,64	1,00	**0,57**	0,25	0,70	1,00	**0,66**	0,25	0,68	1,00	**0,65**	0,00	0,60	1,00	**0,55**
	HSR	0,50	0,90	1,00	**0,83**	0,00	0,65	1,00	**0,58**	0,00	0,63	1,00	**0,57**	0,00	0,64	1,00	**0,57**	0,25	0,60	1,00	**0,61**
Environmental	SWG	0,10	0,79	1,00	**0,67**	0,00	0,53	1,00	**0,52**	0,00	0,55	1,00	**0,52**	0,00	0,51	1,00	**0,51**	0,00	0,63	1,00	**0,57**
	RCS	0,00	0,90	1,00	**0,70**	0,00	0,59	1,00	**0,55**	0,25	0,58	1,00	**0,60**	0,00	0,65	1,00	**0,58**	0,00	0,63	1,00	**0,57**
	CE	0,00	0,74	1,00	**0,62**	0,00	0,47	1,00	**0,48**	0,00	0,45	1,00	**0,47**	0,00	0,54	1,00	**0,52**	0,00	0,58	1,00	**0,54**
	WRP	0,10	0,79	1,00	**0,67**	0,00	0,52	1,00	**0,51**	0,00	0,59	1,00	**0,54**	0,00	0,68	1,00	**0,59**	0,00	0,55	1,00	**0,53**
	PRB	0,25	0,75	1,00	**0,69**	0,00	0,47	1,00	**0,48**	0,00	0,44	1,00	**0,47**	0,00	0,59	1,00	**0,54**	0,00	0,79	1,00	**0,64**
Economic	II	0,10	0,77	1,00	**0,66**	0,00	0,67	1,00	**0,58**	0,00	0,68	1,00	**0,59**	0,00	0,64	1,00	**0,57**	0,00	0,57	1,00	**0,54**
	MC	0,10	0,80	1,00	**0,67**	0,00	0,72	1,00	**0,61**	0,00	0,59	1,00	**0,55**	0,00	0,62	1,00	**0,56**	0,00	0,68	1,00	**0,59**
	OC	0,30	0,84	1,00	**0,75**	0,25	0,79	1,00	**0,71**	0,00	0,58	1,00	**0,54**	0,00	0,58	1,00	**0,54**	0,25	0,74	1,00	**0,68**
Social	OI	0,10	0,74	1,00	**0,64**	0,00	0,37	1,00	**0,43**	0,00	0,38	1,00	**0,44**	0,00	0,44	1,00	**0,47**	0,00	0,48	1,00	**0,49**
	NI	0,10	0,70	1,00	**0,63**	0,00	0,61	1,00	**0,56**	0,00	0,46	1,00	**0,48**	0,00	0,54	1,00	**0,52**	0,25	0,69	1,00	**0,66**
	VI	0,00	0,64	1,00	**0,57**	0,00	0,44	1,00	**0,47**	0,00	0,49	1,00	**0,49**	0,00	0,52	1,00	**0,51**	0,00	0,65	1,00	**0,57**
	PA	0,00	0,75	1,00	**0,63**	0,00	0,52	1,00	**0,51**	0,00	0,61	1,00	**0,55**	0,00	0,65	1,00	**0,57**	0,25	0,63	1,00	**0,63**
Sum									9,42				9,43				9,75				9,93
Fuzzy Value									6,50				6,54				6,78				6,82
Rank									**(4)**				**(3)**				**(2)**				**(1)**

This technology has gained the highest score in environmental criteria (1.90), compared to other studied biological technologies. It means that anaerobic sludge blanket is a green biological technique to deal with industrial effluents. It also achieved the highest score (1.45) in social criteria which can indicate that this technology can be selected as a socially acceptable technique. In addition, while pond systems are the most economic biological technique (score: 1.32), it cannot be selected as the most sustainable technology for the treatment of industrial effluents. It can clearly reflect the fact that considering all the sustainability criteria can highly affect the decision-making process to identify the most sustainable technology to deal with industrial effluents.

However, it can be stated that the biological treatment methods are not generally sufficient enough to deal with recalcitrant compounds such as AOXs. The effluents with high loads of such environmental contaminants may interrupt the performance of such systems. In order to overcome this issue, a combination of biological methods, as the post-treatment to oxidation with nanomaterials can be an attractive solution. However, the reports in the literature are rare on such combinations which need further efforts to make the treatment methods more sustainable to deal with industrial effluents.

3.2.4.2 Development opportunities

According to the results achieved, the main potentials for improvement for each method are briefly presented and discussed in the next sections.

3.2.4.2.1 Physico-chemical methods

Currently, membrane technologies are still the leading wastewater treatment methods to overcome the global water pollution challenge [500]. Besides the high treatment efficiency of these technologies [501], they can contribute to the recovery of organic [502] and inorganic compounds [503,504] present in the effluents. Recent studies have mainly focused on the development of polymeric and inorganic membranes. Goh and Ismail (2018)[500] reviewed the latest progress in the fabrication of a new class of inorganic nanostructures (i.e. ceramic membranes (such as metal oxide membranes, zeolite membranes, metal organic framework membranes), and carbon-based membranes (such as carbon nanotubes membranes, and graphene membranes)), as promising materials for industrial treatment purposes. They concluded that the operating cost is still the main barrier for the rapid commercialization of new branches of membrane technologies. In this regard, the reduction of production costs through the development and use of cheap raw materials and the development of efficient and cost-effective fabrication methods for the membranes can be considered as interesting fields of study. There are some evidences for such approaches in the literature. For instance, Scheibler et al. (2015)[505] developed an ultrafiltration process composed of a low-cost multilayer γ-Al_2O_3 ceramic membrane for the pre-treatment of oily wastewater. Zhu et al. (2016)[533] prepared a titanium dioxide membrane supported on mullite hollow fiber synthesized from industrial solid waste coal fly ash as a low-cost alternative for the treatment of oily effluent. In addition to the operating costs associated with the membrane preparation, fouling is considered another drawback on the application of these technologies. Bagheri and Ahmad (2018)[534] reviewed the fouling mitigation technologies and concluded that the application of nanomaterials (Fig. 3.6), electrical and mechanical based methods, ultrasonic irradiation, and their combination with biological treatments (Fig. 3.7) can be considered as effective strategies to deal with this problem. However, none of these methods has yet been used in full-scale technologies to prove their efficiency with real industrial effluents. Table 3.10 resents the main advantages and disadvantages of various physico-chemical treatment methods for the treatment of recalcitrant compounds and emerging pollutants from the content of industrial effluents.

Table 3. 10. Some literature reports on the advantages and disadvantages of the studied physico-chemical methods.

Method	Advantages	Disadvantages	Reference
Electrocoagulation	No need for chemical reagents. Relatively low operating costs. Low secondary pollution. Low sludge generation. No moving parts.	Maintenance is required. Electrode passivation occurs over time. High water conductivity is required. The lack of reactor systematic design	[535]
Membrane technologies	High treatment efficiency. Small footprint. High potential of the treated water to be re-used. Ease of implementation. Fast start-up.	Process stability due to membrane fouling. Relatively high operating costs.	[364,536–538]
Fenton Process	High treatment efficiency. Non selectivity. No need for especial reactor configuration (especially in case of non-UV irradiated systems.	Secondary pollution which requires additional treatments. Relatively high operating costs.	[539–541]
Oxidation with engineered nanomaterials	High treatment efficiency. Non-selectivity. Low operating costs for some types of ENMs. No need for complicated reactor configurations. Ease of implementation. Stability of the process.	Probable secondary health and safety risks. Availability of some efficient nanomaterials and nano-composites in the current market.	[342,344,353]
Adsorption	High treatment efficiency. The potential of material recovery. Ease of implementation. Process stability.	Relatively high treatment costs. Selective removal of the contaminants. High sludge generation.	[148,354,378]

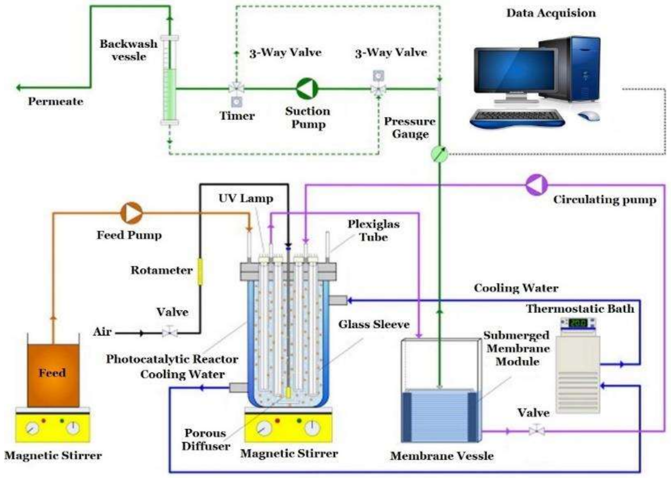


Fig. 3. 6. An example of the combination of nano-treatment technologies with membrane technologies to form a photocatalytic membrane reactor (PMR), adapted from Sarasidis et al., (2014) [542].

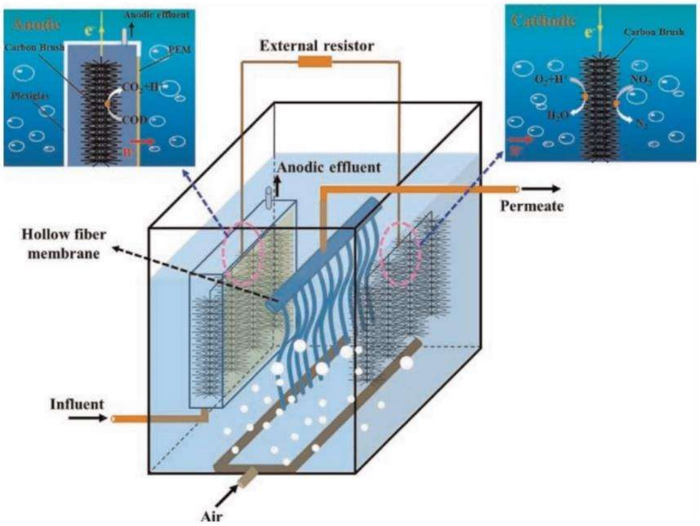


Fig. 3. 7. A schematic of an in-situ integration of microbial fuel cell with hollow-fiber membrane bioreactor in order for treatment of wastewaters. Such a combinaion is also very effective for the mitigation of the membrane fouling due to the biological decomposition of organic compounds responsible for the membrane fouling, reprinted with permission from Tian et al., 2015 [543].

Adsorption has also been widely studied as one of the most efficient and effective treatment technologies [544], easy to operate and well suited for materials recycling of nutrients and materials [545]. Activated carbon is a widely used material for this process. However, such a conventional material is very expensive especially for high quality products [546]. Hence, finding low-cost alternatives has been the subject for a number of recent studies. Castro et al. (2018) [547] indicated that the application of cork granules is a cheap material for the treatment of textile effluents. Especially, the operating costs will significantly increase when a highly polluted effluent is subjected to treatment. For instance, Wang et al. (2017) [548] used a combination of adsorption (wooden activated carbon) at a dosage of 10 g/L, and 1500 mg/L of polymeric magnesium ferric sulfate for the subsequent coagulation process. This combination increased significantly the efficiency of the system to treat highly polluted effluents. This possibility derivating from activated carbon (AC) can be economically beneficial when compared to conventional AC processes. Agriculture wastes have also been studied as the economic alternative material to be used in the treatment of industrial effluents. As an example, acid-washed coconut shell based activated carbon (CSAC) has been used successfully for the treatment of palm oil mill effluents [548]. Bello et al. (2018) [546] used banana pseudo-stem, a plant waste of banana, as a cheap source of cellulose for the removal of dyes from industrial effluents. In recent years, some nanostructured materials have also been developed for the adsorption of complex organic pollutants in the content of effluents. For a nanomaterial to be used for the adsorption applications, some properties such as specific surface area is considered a determinant factor [353]. For instance, Heydartaemeh (2018) [544] prepared a nanocomposite (Ni_XZn_X–X Fe_2O_4) with a specific surface area of 120 m^2/g having a maximum of 90% of green malachite adsorption after 120 min. Being low-cost is a main advantage for these materials in terms of their application for industrial treatment purposes.

Advanced oxidation processes have been identified in recent years as efficient methods to deal with recalcitrant pollutants. The generation of powerful hydroxyl radicals in the medium are the basis of the oxidation of recalcitrant pollutants. Fenton reactions and oxidation with engineered nanomaterials are the main processes based on the generation of hydroxyl radicals. The reaction between iron salts and hydrogen peroxide is the basis of Fenton process [474]. The short reaction time is the main advantage of the Fenton process [475]. Photo-Fenton process using ultraviolet irradiation (UVI) offers higher removal efficiency when compared to conventional Fenton process, although it may bring some safety issues and higher operating costs [549]. The main drawback of Fenton processes is the generation of secondary pollutants by releasing ferric ion to the effluents [476]. As a result, additional treatment is required for instance by precipitation of the ferric ions through a pH increase of the effluents [477]. This additional treatment can result in the generation of iron containing sludge. Treatment of this sludge is expensive and needs a high amount of chemicals [550,551].

In order to overcome these drawbacks, heterogeneous Fenton reactions based on the application of iron oxide nanomaterials or other types of inorganic nanomaterials such as titanium dioxide, copper-based nanomaterials, etc. have gained a huge attention in recent years [23,24,552]. However, the reaction kinetics of these processes are slower than those with Fenton process [476]. The properties of the nanomaterials such as high specific surface area and agglomeration state can play a critical role in the nano-catalytic processes. The main mechanisms involved in the removal or degradation of the pollutants using nanomaterials consist on the chemisorption of the pollutants on the surface of the materials, transformation of hydrogen peroxide to hydroxyl radicals on the surface of the materials followed by the decomposition of the adsorbed pollutants [553]. UVI can also assist in the generation and decomposition of hydrogen peroxide to hydroxyl radicals on the surface of the nanomaterials. In recent years, a trend can be seen in the literature for the synthesis of low-cost catalytic materials with the ability to work under visible light irradiation, for instance by introducing nitrogen into the structure of titanium dioxide nanomaterials, as one of the most widely applied nanomaterials for wastewater treatment purposes [554]. In spite of the inherent advantages on the application of engineered nanomaterials for the treatment of industrial effluents, the subsequent health problems arising from the possible toxic effects of the nanomaterials are now under debate [555–558]. Although some in vitro and in vivo studies have shown that some types of nanomaterials such copper oxide nanoparticles [353] can cause some toxic effects on terrestrial and aquatic organisms, the probable health problems associated to the use of nanomaterials are not yet widely investigated and understood.

Electrocoagulation has also been successfully applied in recent years for the treatment of a variety of parameters chemical oxygen demand (COD), color, recalcitrant compounds, etc.) from industrial effluents. The basis of the coagulation is to introduce the metal salts to the stream in order to generate larger flocs from small particles. In the electrocoagulation process, the metal cations are dissolved from the anode resulting in the simultaneous formation of hydroxyl radicals and hydrogen in the form of gas in the cathode (Eq. 5, 6).

$$M \rightarrow M^{+} + ne^{-} \qquad \text{Eq. 5}$$

$$2H_2O(l) \rightarrow OH^{-} + H_2(g) \qquad \text{Eq. 6}$$

While in the conventional coagulation methods, coagulants such as aluminium chloride [194] are used, in the electrocoagulation there is no need for any coagulant to be added to the effluents. Hence, the main advantage of this process is to mitigate the release of chemical substances into the treated effluent [559]. This method has been considered as an efficient solution for a sustainable industrial wastewater treatment. However, several parameters such as current density, operating pH, electrolyte type and passivation, reactor design, etc. can determine its efficiency for the treatment of highly polluted industrial effluents. These factors can determine the electrical energy and operating costs including the costs of electrodes, electrode replacement, chemicals used for pH and electric conductivity adjustment, etc. Recently, some measures have been applied in order to reduce the operating costs of this process such as the use of Fe electrodes instead of other metals such as aluminium [5].

For electrocoagulation process to be more economic, there is a need to increase the efficiency of the energy used in the system. For instance, Cheng-ChunHe et al. (2018) [560] indicated that chloride addition and ultrasonic processing can increase the energy efficiency of the system by removing the passivation layer on the electrodes used for the electrocoagulation. Reducing the sludge generation in coagulation processes is another potential for improvement in the application of this technology. Considering that the cost of sludge disposal is remarkable [471], the related costs should be included in the design of the treatment facilities using electrocoagulation techniques. Hence there is a need for more studies on the reduction of the sludge volume in this technology.

3.2.4.2.2 Biological Treatments

Stabilization ponds, as an artificial ecosystem, consist on the co-existence of biological communities such as bacteria, protozoa, alga, fungi, and crustacean larvae. Generally, stabilization ponds are partially aerobic and partially anaerobic in a basin with a depth of about 1 to 2 meters. These systems have been used for the treatment of a variety of industrial effluents, especially in under developed countries. For instance, in Malysia, stabilization ponds are the most widely used methods for the treatment of palm oil production mill effluents [484]. In fact, they are good options when large land areas are available for such treatment installations. Although they have shown to some extent an acceptable treatment efficiency, there are some drawbacks for the application of such systems. Large amounts of greenhouse gases such as carbon dioxide and methane are released from the open ponds into the atmosphere. In addition to the effects of these systems on the global warming, the recovery of energy in the form of methane gas is highly limited from such systems [561,562]. Sia et al. (2017) [484] stated that by 2020 ponding systems in Malysia will release 7.2 million tonnes of CO_2 into the atmosphere. Although some measures such as the application of photosynthetic bacteria to recover CO_2 in the form of bacterial cell [485] have been adopted for capturing carbon dioxide, this problem is still considered as the major deficiency of these systems. The odor impact is another problem in pond systems. There are some studies available in the literature to mitigate this problem. Truppel et al. (2005) [563] achieved a reduction of odor of a treatment plant located near a populated area by recirculation of the effluent followed by aeration of the pond. The combination of pond systems with other treatment facilities can also be considered as an effective solution to deal with this problem and also to increase the quality of the treated effluents. As an example, Liu et al. (2014) [510] applied a combination of a pond system and a wetland to increase the overall efficiency of the system for the treatment of refractory organic pollutants in petrochemical industrial wastewater.

Aerated lagoons have been extensively used for the treatment of industrial effluents such as kraft mill effluents [564,565]. They can present acceptable performance for the removal of biological oxygen demand (BOD) from theses industrial effluents [5]. However, some studies have shown that their performance for the removal of color from the effluents is considered as one of the drawbacks of these systems. Also, energy input and daily maintenance costs are the main challenges of using these systems which require the development of efficient aeration and mixing technologies with acceptable energy efficiency. However, by increasing the efficiency of the system in order to promote biodegradation, the sludge accumulation will occur as one of the main disadvantages of such systems. These may themselves lead to the increase of the suspended biomass which needs a final treatment such as filtration with an increase of the treatment cost.

Since last decade, many industries have started upgrading their aerated lagoons to activated sludge systems due to the advantages of such systems [565]. Xavier et al. (2009) [565] compared aerated lagoon with activated sludge processes and concluded that the activated sludge system can present a better efficiency for the treatment of kraft pulp and paper mill effluents, except for phenolic compounds.

In addition to activated sludge processes, anaerobic sludge blanket processes, as the most widely used anaerobic treatment methods in many industries [566,567], have been designed and implemented. From table 3.9 it is evident that although the treatment efficiency of the activated sludge process has received a higher value (0.69) compared to that of anaerobic sludge blanket technology (0.63), the latter technology was identified as more sustainable to deal with industrial effluents. It represents the importance of other sustainability criteria to take a final decision for the adoption an industrial wastewater treatment method. However, in spite of the acceptable performance of both the mentioned biological systems, they are now struggling with some certain disadvantages such as relatively high sludge production, especially in case of activated sludge. Although the degradation mechanism of the recalcitrant pollutants in anaerobic digestion processes leads to the formation of biogas (mainly methane), and hence reduces the emission of greenhouse gases, they are sensitive to some inhibitory elements such as sulfide and toxic substances [9]. Considering that methane is an important greenhouse gas with a potential 34 times higher than carbon dioxide, the production of this gas can significantly contribute to the emission of greenhouse gases. However, by the utilization of the produced gas as a source of energy, the anaerobic process can be more cost-effective when compared to activated sludge processes. However, the need for the supply of alkalinity may increase the energy consumption and greenhouse gases (GHGs) generation in anaerobic treatment process. The average alkalinity required in anaerobic processes is in the range of 2000-4000 mg $CaCO_3$/l to maintain a basic pH. Hence, the production and transportation of the required alkalinity agents can be considered as significant up-stream sources of CO_2 emission [198].

3.2.5 Conclusion

The main goal of this study was to provide a framework for making a sustainable decision for the selection of suitable wastewater treatment technologies considering the integration of multi-criteria (technical, environmental, economic and social). The application of fuzzy-Delphi method indicated that technical criteria, especially treatment efficiency and health and safety risks in the treatment plant are the most important among the studied criteria. The results also revealed that there are other criteria (i.e., technical, economic, environmental and social) that have enough significance to be also considered when deciding on the most suitable industrial effluent treatment technology. The results obtained in this study demonstrate that the selection of the treatment methods to deal with industrial effluents cannot be based only on treatment efficiency to satisfy the requirements of sustainable development. Among the treatment methods, membrane technology was identified as the most suitable physico-chemical method for recalcitrant compounds removal whereas anaerobic sludge blanket technology was identified as the most sustainable biological method to deal with highly polluted industrial effluents. The opportunities for improvements of each treatment method have also been discussed while providing a general perspective for the future.

3.3 Supplementary Information

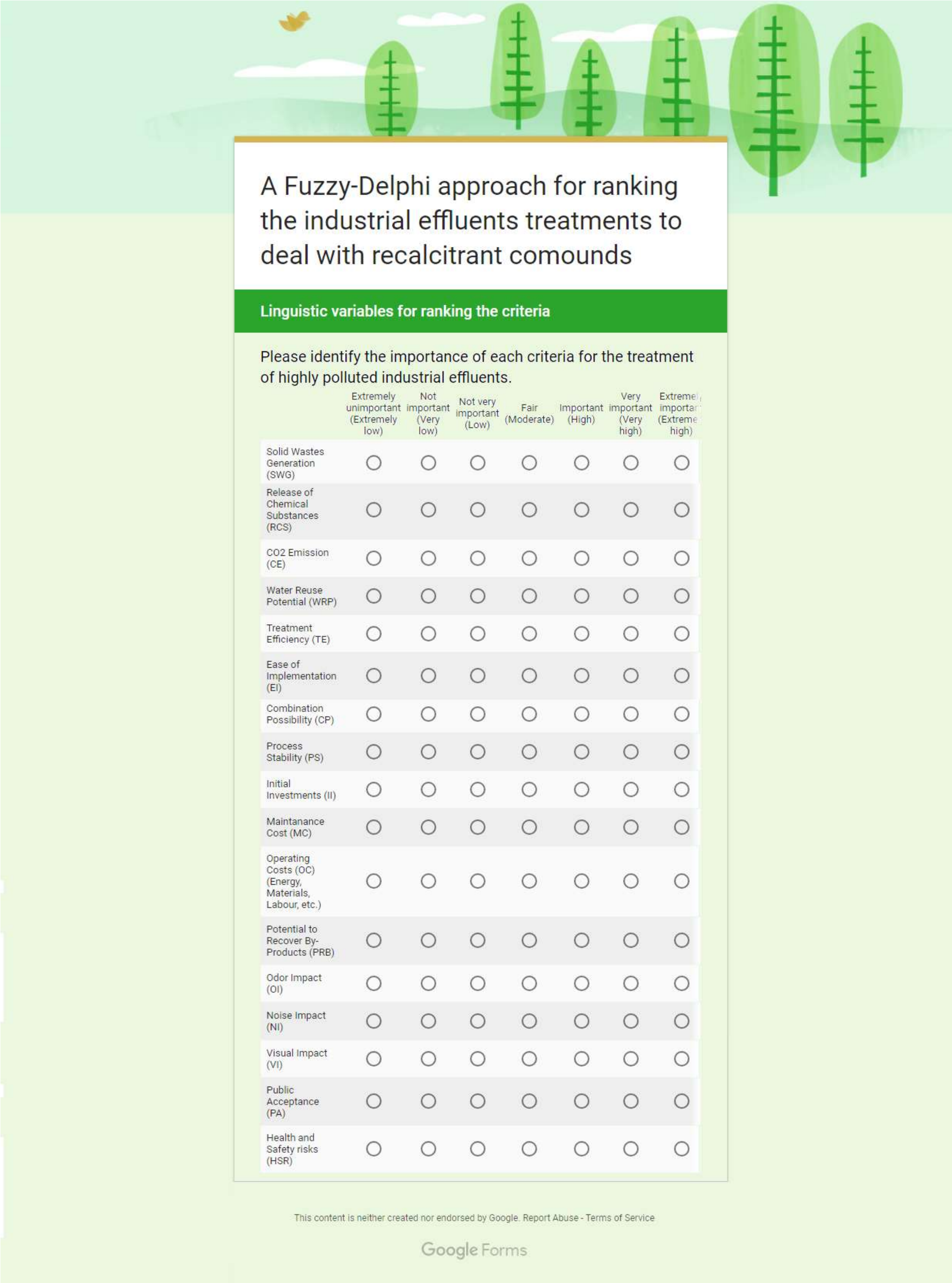
3.3.1 Supplementary Information

Descriptions of the studied criteria

Table 3. 11. The descriptions of the studied criteria.

Criteria	Description
Treatment Efficiency	The potential of the method for the treatment of industrial effluents, considering all the treatment variables such as duration, operating conditions, etc.
Ease of Implementation	The complexity level of the method in terms of equipment, expertise, etc. required for treatment process.
Combination Possibility	The potential of the method to be combined with other physicochemical or biological methods in order to optimize the quality of the final effluents.
Process Stability	The degree of reliability of the method against the failures and the ease of re-establishment of the method after any probable failure.
Health and Safety risks	The risks (noise, electricity, biological agents, etc.) associated with the implementation of the method to the workers in the treatment working place.
Solid Wastes Generation	Generation of the solid wastes as a result of treatment process; either by chemical or biological treatments.
Release of Chemical Substances	The release of chemical additives used for the treatment process into the effluents content which may appear in the final treated effluents.
CO_2 Emission	The direct (from the treatment process) and the indirect (from the treatment facilities, etc.) emissions of CO_2 to the atmosphere.
Water Reuse Potential	The effects of the method on all the water quality parameters, other than the amount of the organic pollutants load.
Potential to Recover By-Products	The potential of the method for the recovery of the by-products including energy and materials.
Initial Investments	The initial investments required in terms of land area, equipment, infrastructures, certificates, etc. required for the establishment of the method.
Maintenance Cost	The costs required for maintaining the facilities operational.
Operating Costs	The costs of energy, materials, labour, etc. required for the treatment process to be performed.
Odor Impact	The odor from the treatment process which may affect the surrounding local communities.
Noise Impact	The noise of the process with potential effects on the surrounding local communities.
Visual Impact	The effects of the treatment facilities on the visual properties (such as beauty) of the local environment.
Public Acceptance	The overall perception of public communities about the usefulness of the method for their routine life.

3.3.2 The format and structure of the questionnaires

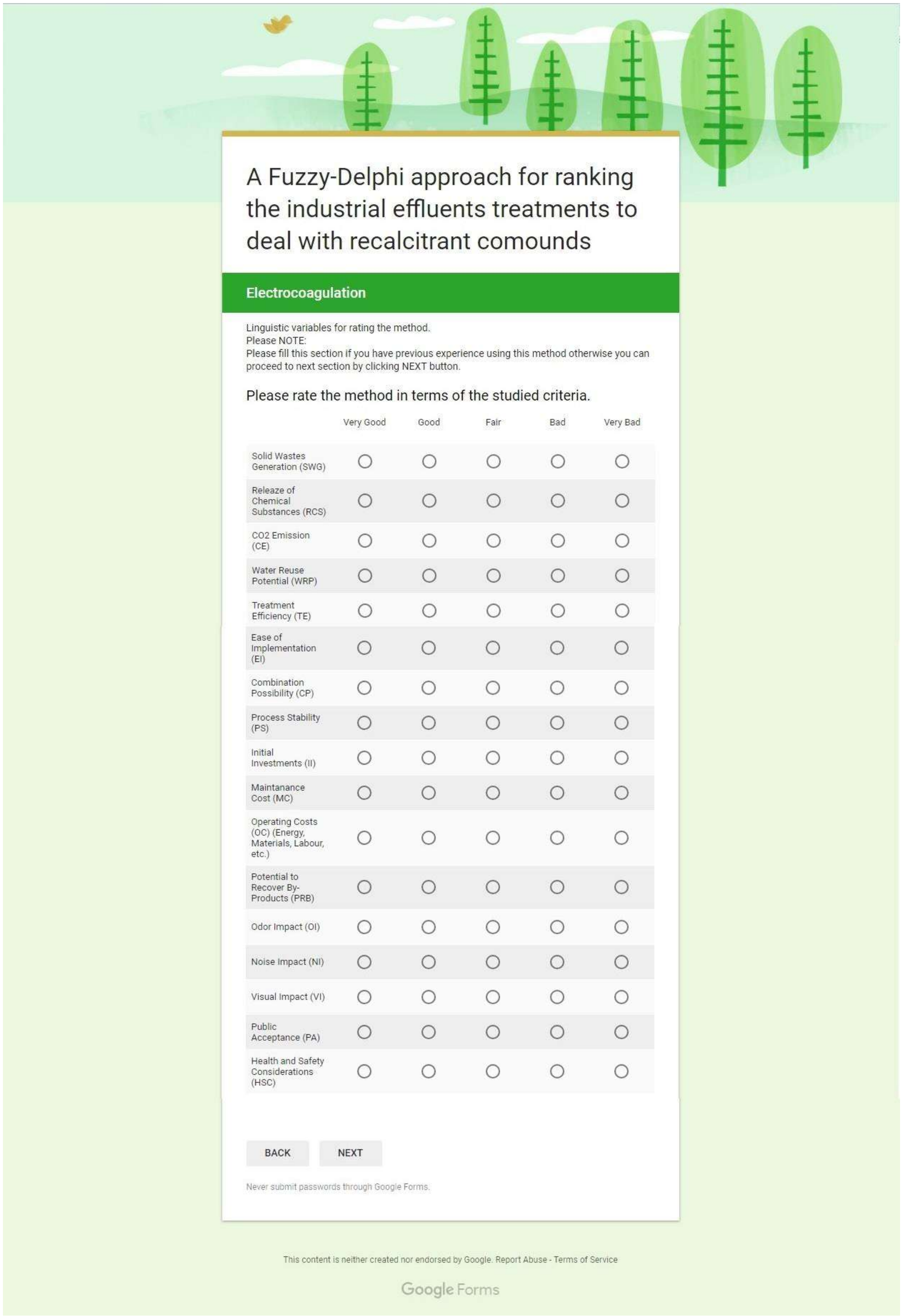


A Fuzzy-Delphi approach for ranking the industrial effluents treatments to deal with recalcitrant comounds

Linguistic variables for ranking the criteria

Please identify the importance of each criteria for the treatment of highly polluted industrial effluents.

	Extremely unimportant (Extremely low)	Not important (Very low)	Not very important (Low)	Fair (Moderate)	Important (High)	Very important (Very high)	Extremel importar (Extreme high)
Solid Wastes Generation (SWG)	○	○	○	○	○	○	○
Release of Chemical Substances (RCS)	○	○	○	○	○	○	○
CO2 Emission (CE)	○	○	○	○	○	○	○
Water Reuse Potential (WRP)	○	○	○	○	○	○	○
Treatment Efficiency (TE)	○	○	○	○	○	○	○
Ease of Implementation (EI)	○	○	○	○	○	○	○
Combination Possibility (CP)	○	○	○	○	○	○	○
Process Stability (PS)	○	○	○	○	○	○	○
Initial Investments (II)	○	○	○	○	○	○	○
Maintanance Cost (MC)	○	○	○	○	○	○	○
Operating Costs (OC) (Energy, Materials, Labour, etc.)	○	○	○	○	○	○	○
Potential to Recover By-Products (PRB)	○	○	○	○	○	○	○
Odor Impact (OI)	○	○	○	○	○	○	○
Noise Impact (NI)	○	○	○	○	○	○	○
Visual Impact (VI)	○	○	○	○	○	○	○
Public Acceptance (PA)	○	○	○	○	○	○	○
Health and Safety risks (HSR)	○	○	○	○	○	○	○



A Fuzzy-Delphi approach for ranking the industrial effluents treatments to deal with recalcitrant comounds

Electrocoagulation

Linguistic variables for rating the method.
Please NOTE:
Please fill this section if you have previous experience using this method otherwise you can proceed to next section by clicking NEXT button.

Please rate the method in terms of the studied criteria.

	Very Good	Good	Fair	Bad	Very Bad
Solid Wastes Generation (SWG)	○	○	○	○	○
Releaze of Chemical Substances (RCS)	○	○	○	○	○
CO2 Emission (CE)	○	○	○	○	○
Water Reuse Potential (WRP)	○	○	○	○	○
Treatment Efficiency (TE)	○	○	○	○	○
Ease of Implementation (EI)	○	○	○	○	○
Combination Possibility (CP)	○	○	○	○	○
Process Stability (PS)	○	○	○	○	○
Initial Investments (II)	○	○	○	○	○
Maintanance Cost (MC)	○	○	○	○	○
Operating Costs (OC) (Energy, Materials, Labour, etc.)	○	○	○	○	○
Potential to Recover By-Products (PRB)	○	○	○	○	○
Odor Impact (OI)	○	○	○	○	○
Noise Impact (NI)	○	○	○	○	○
Visual Impact (VI)	○	○	○	○	○
Public Acceptance (PA)	○	○	○	○	○
Health and Safety Considerations (HSC)	○	○	○	○	○

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Chapter 4: Ultrasonic irradiation as a green production route for coupling crystallinity and high specific surface area in iron nanomaterials

- Mohammadreza Kamali, Maria Elisabete V. Costa, Gonzalo Otero-Irurueta, Isabel Capela, Ultrasonic irradiation as a green production route for coupling crystallinity and high specific surface area in iron nanomaterials, Journal of Cleaner Production, 211 (2019), 185-197. IF_5=6.35 https://doi.org/10.1016/j.jclepro.2018.11.127

4.1 Abstract

Coupling high crystallinity with high specific surface area in engineered nanomaterials is imperative whenever both chemical endurance regarding particle dissolution and a large specific surface area are needed for environmental clean-up purposes. Gathering both properties in the same particulate system is not trivial. In this work, A L-9 orthogonal array of experiments was used to assist a liquid-phase reduction method aiming to synthesize zero valent iron nanoparticles (nZVI) that could offer a large specific surface area while presenting a well-developed crystalline structure. The experimental variables included the reductant addition rate, the precursor (Fe^{+3}) concentration, the (reductant/Fe^{3+}) ratio, (R), and also the application of ultrasonic irradiation (UI) to the precipitating medium. The results show that $NaBH_4/FeCl_3$ ratio and Fe^{+3} concentration have opposite effects on the specific surface area of the synthesized particles whereas the effect of reductant addition rate is negligible. Moreover, the introduction of UI in the precipitation process benefits considerably the surface area of the particles while preserving or even enhancing the crystallinity of the precipitated nanomaterials. The effects of UI were interpreted in the frame work of the classical nucleation theory. This work raises the potential of UI as an environmentally friendly method to be applied to other precipitation systems which could end up in finer powder particles with better crystallinity.

Keywords: Nano zero valent Iron, Iron oxide nanoparticle, Ultrasonic irradiation, Crystallinity, Specific surface area, Taguchi method.

4.2 Introduction

In recent years, iron-based nanoparticles have gained a considerable attention due to their enhanced properties, which make them attractive candidates to replace conventional materials for various purposes such as environmental applications for the removal of contaminants [568,569] and biomedical applications such as drug delivery, enzyme immobilization, specific cell labelling and medical imaging among others [570]. In the specific case of environmental and industrial applications dealing with liquid effluents, the solubility of the nanomaterial helps to predict particle toxicity and fate and also the lifetime of the nanoparticles when used as decontamination agents. Generally, the solubility of a particle reflects various energy contributions associated not only to the particle crystal lattice itself but also to the interaction of the particle surface with the surrounding liquid (solvation energy) and the proper liquid-liquid entities. Therefore, for the same liquid, the crystallinity of the particle matters a lot when dissolution is concerned. As a rough rule of dumb, it can be said that crystalline structures are 1 to 10^3 fold less soluble than their amorphous counterparts. When iron-based nanoparticles are to be used as cleaning agents targeted to liquid effluents it is crucial to ensure not only particle crystallinity for minimizing particle solubility but also a particle size as small as possible to provide a high specific surface area that could warrant a high number of active surface sites. However, both particle properties, i.e. crystallinity and small size are difficult to reconcile in the same particulate system.

Various methods based on both "top-down" [571] and "bottom-up" strategies [572] have been used for the synthesis of nanoscale iron-based materials. Among them, chemical precipitation based on borohydride reductant is the most used method for the synthesis of zero valent iron nanoparticles (nZVI), mainly due to its simplicity and high yield [572]. Literature results have shown that the properties of the particles synthesized by this method are highly dependent on the schedule of experimental variables that assist the precipitation, such as the the cation (Fe^{3+}) and/or solvent concentration, the reductant addition rate, the ratio between both the reductant and the cation, among others. Hence, critical properties of nZVI such as chemical composition, particle size and shape and specific surface area may be controlled by adequate manipulation of the above-mentioned variables. Therefore, exploring facile, economic, effective and, ideally, green methods to enhance crystallinity while preserving the nanometric dimensions of the synthesized particles is highly relevant, either technically or economically, for an efficient utilization of nanomaterials.

Green chemistry principles may assist the design of nanomaterials synthesis processes for obtaining cheaper and more eficient materials while minimizing subsequent environmental effects [573–577]. For instance in the case of iron or iron oxide based nanomaterials, green principles have for instance fostered the quest for more sustainable raw materials for the synthesis of iron and silica-iron oxide-composite based nanoparticles, respectively [574–576]. Aligned with the benefits of green chemistry principles, ultrasonic irradiation (UI) appears as a cost-effective approach that can be easily coupled to many synthesis procedures. Being an environmentally friendly procedure [26,578–580], UI is based on the supply of powerful ultrasound irradiation (20 KHz–10 MHz) to the medium [581]. Such irradiation may trigger a direct interaction between molecules (e.g., precursors) in the medium, or induce indirect effects through the growth and implosive collapse of bubbles created by UI [25]. Sound waves with sufficient amplitude create dynamic tensile stress in the liquid resulting in a density change with alternating expansive and compressive waves. Pre-existing impurities in the medium will produce bubbles oscillating with the applied sound field. When reaching a critical size, bubbles couple strongly to the acoustic field resulting in a rapid inertial overgrowth during expansion followed by a catastrophic collapse in less than 500 μS, thus accounting for localized transient conditions of high temperature and pressure (> 5000 K and 1000 atm, respectively) [578]. Such hot spot points together with the shock wave and micro-jet (400 km/h) induced by cavitation seem to have the ability to alter the properties of the produced nanomaterials. These alterations can either happen inside the collapsing bubbles (primary sonication) or as a result of the energy produced from the collapsing bubbles in the medium (secondary sonication) [25]. Various studies have successfully reported the synthesis of nanostructures with different dimensionality by UI such as zero-dimensional (0D) [582], one-dimensional (1D) [583], two-dimensional (2D) [581] or three-dimensional (3D) [584] nanometric sized particles with controlled morphology to be utilized in a variety of applications. Coexistence of high crystallinity with high specific surface area in engineered nanomaterials is vital whenever both chemical endurance regarding particle dissolution and a large specific surface area are needed for environmental clean-up purposes. However, gathering both properties in the same particulate system is not a trivial achievement by conventional methods. Hence, a procedure able to couple the mentioned properties is highly welcome, warranting further studies.

In this work, a liquid-phase reduction method is combined with UI aiming to obtain nanomaterials with both enhanced surface area and high crystallinity for ensuring high reactivity and stability for the treatment of specific environmental contaminants. For that purpose, a statistical design of experiments (DOE) relying on Taguchi method with an L-9 orthogonal array of experiments is firstly used for identifying the impact of various experimental conditions on specific properties of the synthesized nanomaterials including the particle size, specific surface area and crystallite size. According to literature DOE strategy has been used to optimize the properties of some nanomaterials [585], but iron-based nanomaterials were not yet covered so far, hence remaining a fertile field to be exploited. Once the better conditions for obtaining iron-based nanoparticles having large surface area or high crystallinity are identified by DOE, the experimental synthesis process is then modified by coupling it with UI. This novel procedure allows producing zero valent iron nanoparticles (nZVI) that offer a large specific surface area while presenting a well-developed crystalline structure.

4.3 Experimental

4.3.1 Experimental design

Taguchi L-9 statistical design [586] was employed in order to identify the effect of experimental variables on the chemical composition, particle size and specific surface area of the products. In this study we used the signal-to-noise ratio (S/N) as a variable for qualifying the significance of the results: the larger S/N the better. Details on the Taguchi design and associated variables may be found on the supporting information. Based on literature reports [587–591] and as summarized in Table 4.1, three experimental variables have been selected for the present study, i.e. the cation concentration, the injection rate of the reductant and the (reductant/cation) ratio (hereafter named I and R, for the last two variables, respectively). The complementary information about Taguchi method calculations can be accessed in the appendix.

Table 4. 1. L-9 orthogonal array of experiments including as studied variables the reductant injection rate (I, mL/min), the (Fe^{+3}) concentration (mM), and the ($NaBH_4/FeCl_3$) ratio, R.

Run	**Sample Identification***	**Experimental variables**		
		Reductant injection rate (I, mL/min)	**Fe^{+3} concentration (mM)**	**($NaBH_4/FeCl_3$) ratio (R)**
1	I5-Fe100-R2	5	100	2
2	I5-Fe67-R5	5	67	5
3	I5-Fe40-R8	5	40	8
4	I10-Fe100-R5	10	100	5
5	I10-Fe67-R8	10	67	8
6	I10-Fe40-R2	10	40	2
7	I15-Fe100-R8	15	100	8
8	I15-Fe67-R2	15	67	2
9	I15-Fe40-R5	15	40	5

Sample Identification*: the label in the first position (I5 to I10) stands for the reductant injection rate, the second position label (Fe40 to Fe100) stands for Fe^{3+} concentration and the third position label (R2 to R8) stands for ($NaBH_4/FeCl_3$) ratio.

Chemical reagents including iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) (99%) and sodium borohydride ($NaBH_4$) (≥98.0%) were purchased from Sigma-Aldrich (St. Louis, MO) and used as received without further purification. Ethanol (99.0%) was purchased from Fisher scientific, and deionized water was obtained from distilled water using an ultra pure water purification system (EASYpure RF - Barnstead/Thermolyne). All samples were synthesized in a 500 mL three-open neck flask reactor where central neck housed a mechanical overhead stirrer (IKA Eurostar 40), operating at 250 rpm.

For the synthesis of the particles according to Taguchi design (Table 4.2), selected amounts of sodium borohydride dissolved in 100 ml of deionized water were added to 30 mL of an ethanol solution (24 mL of ethanol + 6 ml of deionized water) containing ferric ion (Fe^{3+}) which pH was ~ 1.8. The amounts of sodium borohydride were varied in order to achieve different values of R. A Watson Marlow 120U/R peristaltic pump was used to ensure the desired values of the injection rate (I) of the sodium borohydride solution. After completing the delivery of the borohydride solution, the final mixture was stirred in the reactor for more 10 minutes. All samples were synthesized at room temperature. For a schedule of specific conditions (I5-Fe100-R2 and I15-Fe100-R8) the precipitation process was repeated but under UI (I5-Fe100-R2-UI and I15-Fe100-R8-UI, Table 4.2). For that purpose, an ultrasonic cleaning bath (Branson, 1510E-MT) with a theoretical dissipation rate of 70 W and operating at 42 KHZ ± 6% was used.

Table 4. 2. Experimental conditions used for the synthesis of nZVI under UI.

Sample Identification*	Operating Variables			
	Injection rate (I) (mL/min)	[Fe^{+3} concentration] (mM)	[$NaBH_4/FeCl_3$] ratio(R)	UI
I15-Fe100-R8-UI	15	100	8	Yes
I5-Fe100-R2-UI	5	100	2	Yes

*The label UI stands for ultrasonic irradiation

After being synthesized, the particles were washed three times with absolute ethanol to remove water. Magnet collection with a permanent magnet was utilized to separate the precipitated particles from the liquid phase. The particles were subsequently dried overnight, in air at 50 °C and then characterized; for storage, the remaining particles were covered with a thin layer of ethanol.

4.3.2 Characterization

The crystal phase composition of the synthesized particles was evaluated using X-ray diffraction analysis (Rigaku, Geigerflex, Japan). The analysis was conducted in the 2θ range from 30° to 100°, using a goniometer speed of 2°/minute. The crystallite size of the particles was determined through Scherrer equation (Eq. (2)).

$$d = K\lambda/\beta\cos\theta \qquad (2)$$

where d is the average crystallite size, K is a dimensionless shape factor, λ is the wavelength of the X-ray used, β is the full-width at half maximum intensity (FWHM) of the sample, and θ is the Bragg angle. A transmission electron microscope (Hiatchi H9000na, Japan) operated at 300 kV acceleration voltage was utilized in order to assess the morphology of the prepared nanoparticles. Sample specimens were prepared by ultrasonic dispersion of the nanoparticles in ethanol. The suspensions were dropped onto a carbon-coated copper grid, and the solvent allowed to fully evaporate. TEM images were used to determine the average particle size of the synthesized particles: about 500 particles of each sample were randomly counted using Image-J software. Particles specific surface area (SSA) and porosity were assessed by gas adsorption. Adsorption/desorption isotherms were obtained with a Micromeritics Gemini V2 (USA) equipment, being the powder samples degasified at 120 °C overnight before measurement. The adsorption data were fitted to Brunauer, Emmett, Teller (BET) isotherm equation to determine the specific surface area of the particles. Barrett, Joyner, Halenda (BJH) method, derived from Kelvin equation [592], was used to estimate the pore size distribution curves. To characterize the particle thermal behavior thermo-gravimetric (TG) and differential thermal (DTA) analysis were performed using a Labsys (TG-DSC16) TG/DTA analyzer. Samples were heated from 25 to 800 °C with a 5 °C/min heating rate in steady atmospheric air. XPS spectra were acquired in an Ultra High Vacuum (UHV) system with a base pressure of $2x10^{-10}$ mbar. The system is equipped with a hemispherical electron energy analyzer (SPECS Phoibos 150), a delay-line detector and a monochromatic AlKα (1486.74 eV) X-ray source. High resolution spectra were recorded at normal emission take-off angle and with a pass-energy of 20 eV, which provides an overall instrumental peak broadening of 0.5 eV. Aliphatic adventitious hydrocarbon C(1s) peak at 284.6 eV was used in order to calibrate the binding energies of the photoelectrons [593].

4. 4 Results

4.4.1 Taguchi experimental design

4.4.1.1 Statistical analysis

Table 4.3 presents the values of the response data (specific surface area) and the calculated S/N ratios corresponding to Taguchi L9 orthogonal array (table 4.1). For each variable, the higher S/N ratio will define the optimal level of the variable [585]. Among three possible S/N ratios ("smaller is better", "higher is better" and "nominal is better"), the "larger is better" S/N ratio was selected for evaluating SSA as higher values of SSA are desirable. Fig. 4.1 illustrates the variation of the calculated S/N ratios with the values of the different variables. In Table 4.4, the highest S/N ratio together with the highest effect factor (E_f), being E_f the difference between the maximum and the minimum S/N ratio, are presented for the various studied experimental variables. E_f is a statistically important output that quantifies the relative importance of each variable. According to the obtained results, the variation of R has the highest impact on E_f (E_f = 18.6) while the variation of I (E_f = 0.91) has a minor effect on the response data.

Table 4. 3. Values of specific surface area (response data) measured for the samples prepared under the experimental conditions scheduled according to L9 orthogonal array (table 4.1).

Sample Identification	Response data Specific surface area (m²/g)	S/N ratio (decibel (dB))
I5-Fe100-R2	110 ± 5.5	40.8
I5-Fe67-R5	33 ± 1.6	30.3
I5-Fe40-R8	19 ± 0.9	25.5
I10-Fe100-R5	17 ± 0.8	24.7
I10-Fe67-R8	18 ± 0.9	25.0
I10-Fe40-R2	229 ± 11.4	47.2
I15-Fe100-R8	21 ± 1.0	26.2
I15-Fe67-R2	171 ± 8.5	44.6
I15-Fe40-R5	27 ± 1.3	28.5

Table 4. 4. Signal to noise ratio (S/N), effect factor (E_f) and ranking (Rank) for each variable corresponding to the various studied experimental conditions

Factor/ Levels	Reductant injection rate (I,mL/min)	S/N (dB)	Fe^{+3} concentration (mM)	S/N	$NaBH_4/FeCl_3$ ratio (R)	S/N (dB)
	5	32.22	40	33.74	2	44.20
	10	32.31	67	33.33	5	27.85
	15	33.13	100	30.59	8	25.60
E_f		0.91		3.15		18.6
Rank		3rd		2nd		1st

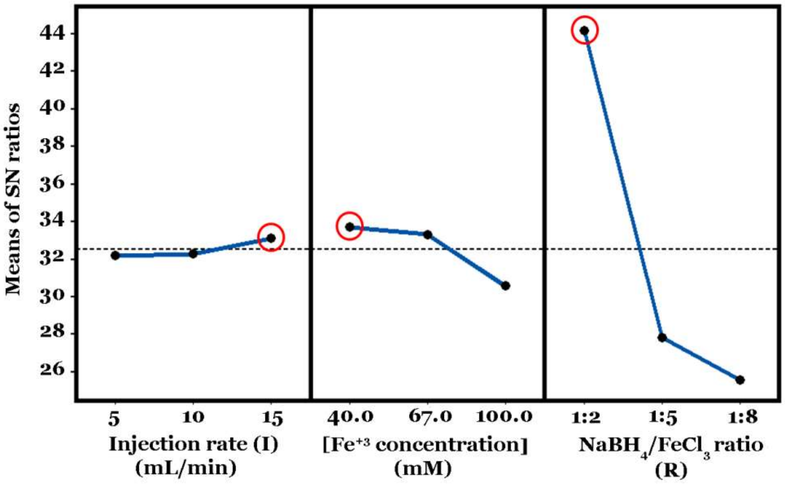

Fig. 4. 1. Variation of the calculated S/N ratios. For each variable, the optimal level of the S/N ratio (its highest value) is highlighted in circles.

The validation of the method was accomplished by comparing the experiments executed under the optimal conditions with the prediction generated by Minitab 17 using T-test. The method is validated if P value is greater than 0.05. The generated P-value is 0.076, greater than 0.05 [594,595]. Hence, the optimal conditions obtained by using different approaches are verified (see supplementary data).

4.4.1.2 Chrystal phase composition of precipitates

The XRD patterns of the 9 samples prepared under Taguchi design are presented in figure 4.2 (a, b, c and d), being grouped in terms of their similarity regarding crystal phase composition. As observed, the XRD profiles shown in figure 4.2(a) pertain to the samples precipitated under the highest (I5-Fe40-R8, I10-Fe67-R8 and I15-Fe100-R8) and medium R (I5-Fe67-R5 and I10-Fe100-R5). Those XRD profiles display a peak centered at 44-45° 2θ, and other peaks centered at 64-65° and 82-83° 2θ which were assigned to ZVI. No other crystalline phase could be detected in this group of samples. The samples precipitated under the lowest values of R but with high or moderate [Fe^{3+}], i.e. samples I5-Fe100-R2 and I15-Fe67-R2, figure 4.2(c), are composed by a mixture of ZVI and magnetite. Regarding the sample I15-Fe40-R5 which XRD profile is shown in figure 3.2(b), peaks attributed to ZVI are clearly identified but humps centered at 35° and 60-65° 2θ suggest that incipient magnetite could also be present. Figure 4.2(d) refers to the sample I10-Fe40-R2 (lowest R coupled to the lowest [Fe^{3+}]) which XRD peaks were assigned to Lepidocrocite.

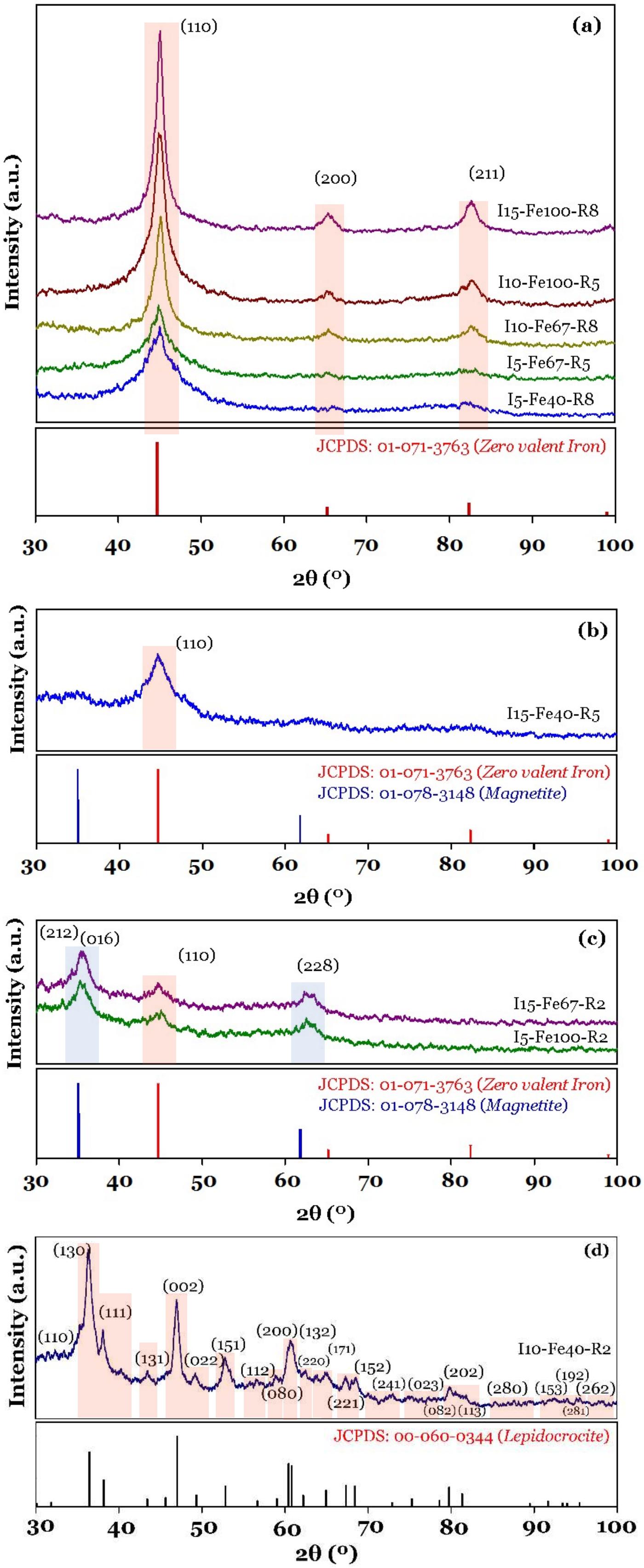
(a)
(110)
(200)
(211)
I15-Fe100-R8
I10-Fe100-R5
I10-Fe67-R8
I5-Fe67-R5
I5-Fe40-R8
JCPDS: 01-071-3763 (*Zero valent Iron*)
Intensity (a.u.)
30 40 50 60 70 80 90 100
2θ (°)
(b)
(110)
I15-Fe40-R5
JCPDS: 01-071-3763 (*Zero valent Iron*)
JCPDS: 01-078-3148 (*Magnetite*)
Intensity (a.u.)
30 40 50 60 70 80 90 100
2θ (°)
(c)
(212)
(016)
(110)
(228)
I15-Fe67-R2
I5-Fe100-R2
JCPDS: 01-071-3763 (*Zero valent Iron*)
JCPDS: 01-078-3148 (*Magnetite*)
Intensity (a.u.)
30 40 50 60 70 80 90 100
2θ (°)
(d)
(130)
(111)
(110)
(131)
(002)
(022)
(151)
(112)
(080)
(200)(132)
(220)
(171)
(221)
(152)
(241)(023)
(082)(113)
(202)
(280)
(153)
(192)
(262)
(281)
I10-Fe40-R2
JCPDS: 00-060-0344 (*Lepidocrocite*)
Intensity (a.u.)
30 40 50 60 70 80 90 100
2θ (°)

Fig. 4. 2. XRD patterns of the samples obtained under varied synthesis conditions. Single-phase ZVI is obtained under moderate or high [Fe^{3+}] and high NaBH4/FeCl3 ratio (R)(a), but as R or [Fe3+] decrease a trend for magnetite precipitation is noticed. For low values of both [Fe^{3+}] and R, precipitation of lepidocrocite takes place (d).

4.4.1.3 Particles morphology

Figures 4.3 and 3.2.4 present TEM images of the particles prepared according to the Taguchi design. The morphologies of the powders vary considerably with the synthesis conditions. In the samples consisting of pure nZVI (Fig. 4.2(a)), chain-like aggregates of individual spherical shape particles like those presented in figure 3.3 (a and b) are predominant. Regarding the samples combining low R and moderate or high [Fe] or moderate R and low [Fe], it was observed that enchained spherical particles could also be detected but coexisting with transparent sheet-like structures few nanometers thick (nanosheets) and tubular-like structures, as shown in the TEM micrograph of Fig. 4.4(a). As referred before, these samples are mostly composed of a mixture of nZVI and magnetite (Fig. 4.2 (b and c)), being the spherical particles assigned to ZVI and both the nanosheet and tubular structures to magnetite.

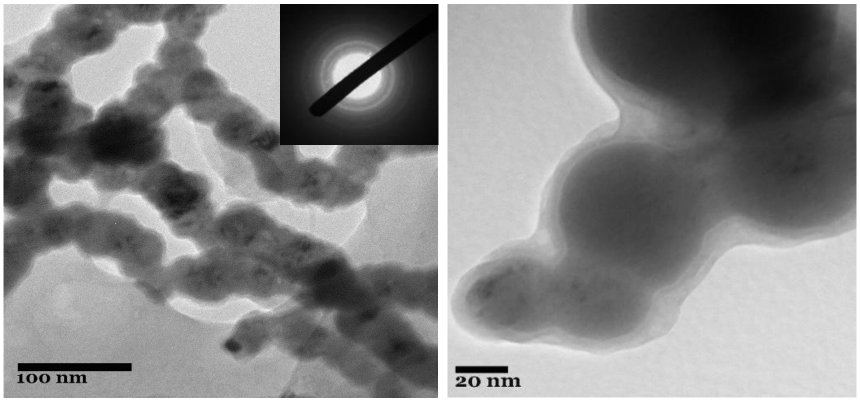

Fig. 4. 3. TEM images of the sample I15-Fe100-R8. The chain-like aggregates of individual spherical shape particles were predominant.

Also, among these samples, it could be noticed that in the case of I15-Fe67-R2 with a very high specific surface area (SSA=170 m^2/g), the nanosheet and tubular structures are predominant whereas in sample I15-Fe40-R5 (SSA=27 m^2/g) which consists mainly of nZVI (Figure 4.2 (b)), the chain-like aggregates of spherical particles are the prevailing ones. When a low [Fe] is combined with a low R as in the case of the sample I10-Fe40-R2 corresponding to Lepidocrocite, only thin nanosheet-like particles and tubular shapes are observed, some of which clearly bounded by parallel walls that contrast to the particle core with few nanometers width, hence suggesting the presence of nanotubes (Figure 4.4(b)).

4.4.2 Ultrasonic assisted optimization

In order to enhance the properties of the prepared nanomaterials using a liquid-phase reduction process, two samples were selected and synthesized utilizing UI while maintaining their synthesis conditions. The analysis of the results achieved under the Taguchi experimental design (Fig. 4.1 and Table 4.4) revealed that the reductant injection rate (I) does not have a significant effect on the response data whereas the ratio (R) between the precursors [$NaBH_4/FeCl_3$] had a considerable impact. Moreover, under the highest concentration of the cation, [Fe^{+3}], spherical nZVI particles with high crystallinity and relatively low SSA were prepared when providing high [$NaBH_4/FeCl_3$] ratio (sample I15-Fe100-R8). On the other hand, although the sample prepared under a low R (sample I5-Fe100-R2) exhibits a very high specific surface area, it is not well crystalized. Hence, the experimental conditions underlying these two samples, i.e. I15-Fe100-R8 and I5-Fe100-R2, were the ones selected for the synthesis under UI aiming to explore the potential of UI to improve both properties, i.e. the particle SSA and the crystallinity. The synthesis results concerning the corresponding samples obtained under UI, i.e. I15-Fe100-R8-UI and I5-Fe100-R2-UI, respectively (Table 4.2), are presented in the next sections.

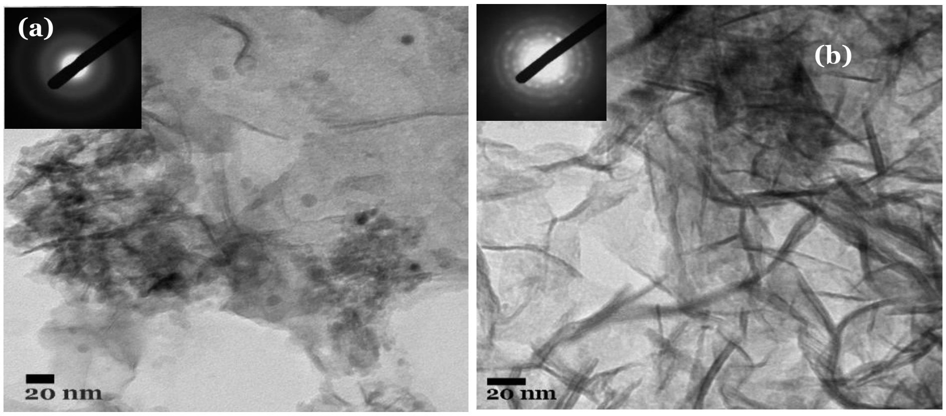

Fig. 4. 4. TEM image of the precipitated samples: (a) I15-Fe67-R2, showing few enchained spherical particles coexisting with nanosheet and nanotube-like structures and (b) I10-Fe40-R2, consisting of thin sheets and nanotubes.

4.4.2.1 Chrystal phase composition of UI precipitates

The X-ray diffraction (XRD) patterns of the particles prepared under the more intense synthesis conditions, with and without UI (I15-Fe100-R8 and I15-Fe100-R8-UI, respectively) are presented in Fig. 4.5. Both samples are composed of ZVI (JCPDS No. 07-71-3763), without any evidence of secondary phases. Based on Sherrer equation (Eq. 1), the crystallite sizes of the I15-Fe100-R8 and I15-Fe100-R8-UI samples were determined as 12.2 nm and 23.9 nm, respectively indicating the sample prepared under UI to have a better developed crystalline structure. Regarding the samples prepared under low R, with (I5-Fe100-R2-UI) and without UI (I5-Fe100-R2), their XRD patterns (Fig. 4.5) still denote the presence of ZVI but accompanied by another phase, magnetite (JCPDS No. 01-078-3148). In this case, no crystallinity improvements attributed to UI could be noticed in the XRD results.

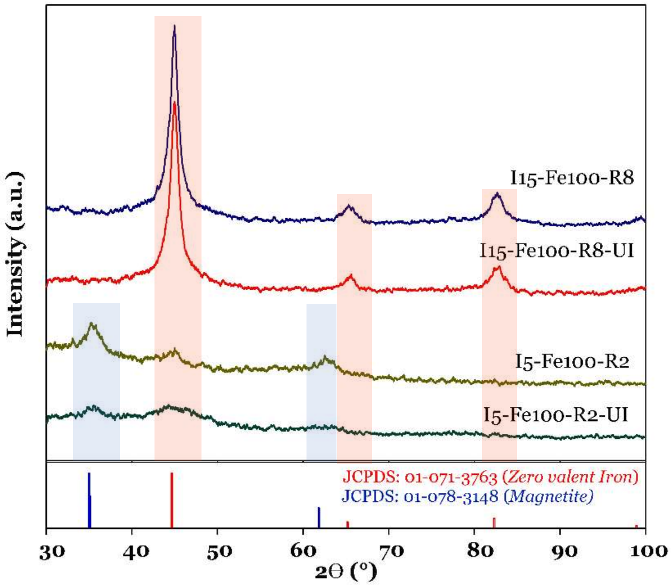

Fig. 4. 5. XRD patterns of the samples prepared with and without UI.

4.4.2.2 Morphology of UI precipitates

The TEM micrographs of the nZVI samples prepared under high R and UI (I15-Fe100-R8-UI) are presented in Fig. 4.6. The sample consists of aggregates of enchained spherical particles, similar to those prepared without UI (Fig. 4.3). The individual particles clearly present a core-shell structure, in which a dark core (nZVI) is covered with a thin bright layer. The particle size distributions of both irradiated and non-irradiated samples are presented in Fig. 4.7. An average particle size around 27 nm is evidenced for I15-Fe100-R8-UI which compares to 43 nm, the average size found for the non-irradiated particles (I15-Fe100-R8), hence indicating that the sonication of the precursors did result in smaller sized nanoparticles. These findings are also well-supported by the BET SSA of both types of particles which values are 20.5 m^2/g and 50.6 m^2/g for I15-Fe100-R8 and I15-Fe100-R8-UI, respectively. Furthermore, the SAED images obtained from TEM (Fig. 4.6) denote a higher intensity of spots in the case of I15-Fe100-R8-UI as compared to I15-Fe100-R8 (Fig. 4.3), hence indicating a better-developed crystal structure of UI sample, in line with the calculated crystallite sizes for both samples.

Regarding the samples prepared under low R, I5-Fe100-R2 and I5-Fe100-R2-UI, Fig. 4.8 (a - d) allows comparing the effects of UI on particle's morphology. As observed both types of samples show the presence of spherical particles but enveloped by veil-like particle structures among which some nanotubes can be identified. Also there is a tendency for the spherical particles to be smaller in the case of the UI sample (Fig. 4.8- a and b). Furthermore, the veil-like particles appear to be smaller and thinner in the UI sample (Fig. 4.8- c and d), seeming predominantly packed around the spherical particles (Fig. 4.8-d). Combining these morphology results with the corresponding XRD data (Fig. 4.5, samples I5-Fe100-R2 and I5-Fe100-R2-UI), the spherical morphology is here attributed to nZVI particles whereas veil-like and tubular morphologies are considered to pertain to magnetite. The SAED images of both samples (Fig. 4.8-a and b) denote an amorphous structure, without any significant benefit from UI.

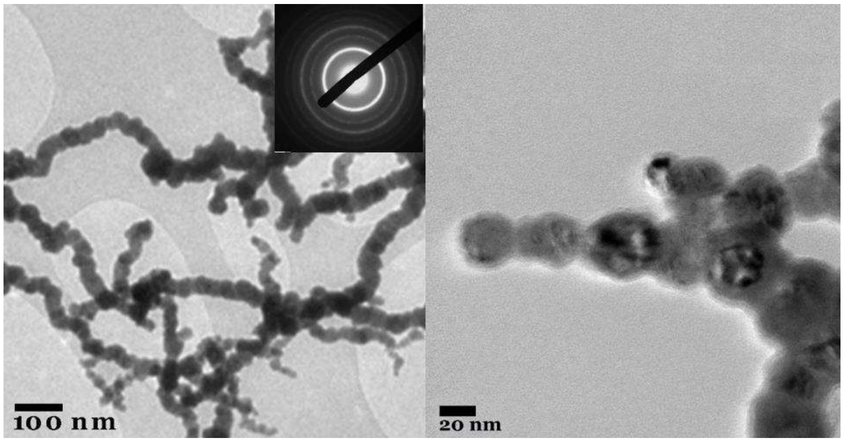

Fig. 4. 6. TEM and SAED images of the sample I15-Fe100-R8-UI indicating the chain-like aggregates of individual spherical.

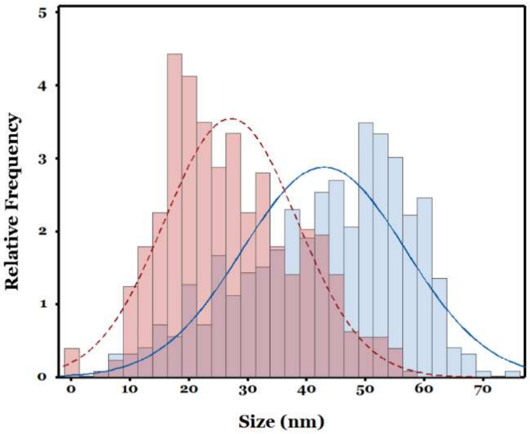

Fig. 4. 7. The number-frequency histogram of the samples I15-Fe100-R8 (mean: 42.95 nm, StDev: 13.87) and I15-Fe100-R8-UI (mean: 27.11 nm, StDev: 11.26) particle sizes.

The results of surface area analysis for these two types of samples were 108 m²/g for I5-Fe100-R2 and 167 m²/g for I5-Fe100-R2-UI. A clear tendency for the increase of particle surface area when UI is applied is thus observed again.

Adsorption/desorption isotherms were measured for both type of particles (irradiated and non-irradiated). The obtained results are presented in Fig. 4.9 (a and b). In contrast to the absence of hysteresis noticed in the case of samples I15-Fe100-R8 and I15-Fe100-R8 (results not shown) a hysteric behaviour typical of mesoporous materials is clearly evidenced by both samples I5-Fe100-R2 and I5-Fe100-R2-UI. Furthermore, the shape of both isotherms suggests the presence of slit-like pores which are thus considered to account for the large surface areas of both samples. Also, the amount of adsorbed/desorbed gas is larger in the case of the irradiated particles (≈ 7 mmole/g) as compared to the non-irradiated ones (≈ 5 mmole/g).

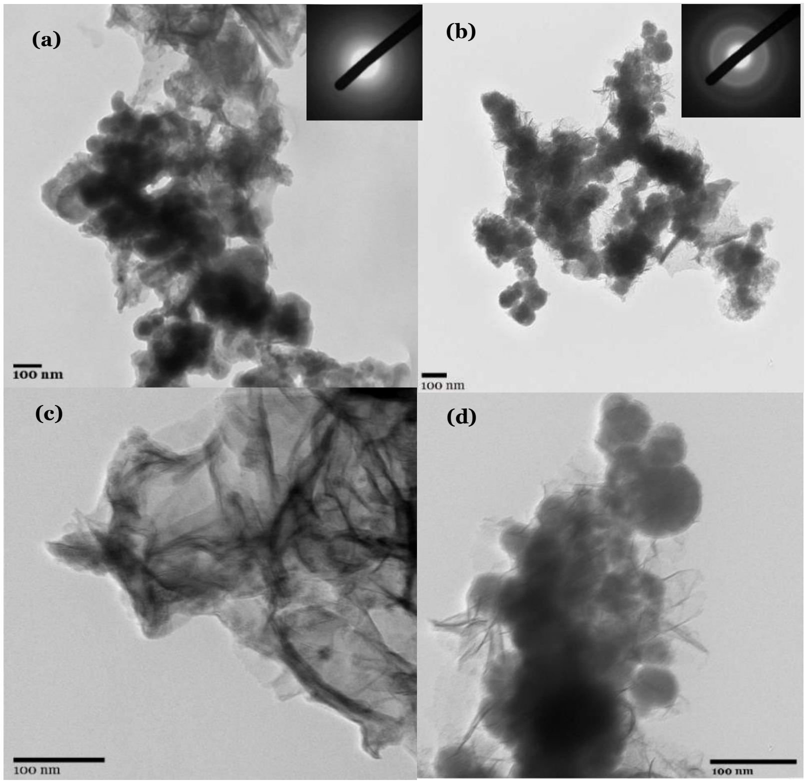

Fig. 4. 8. TEM and SAED images of the samples I5-Fe100-R2 (a, c), and I5-Fe100-R2-UI (b, d).

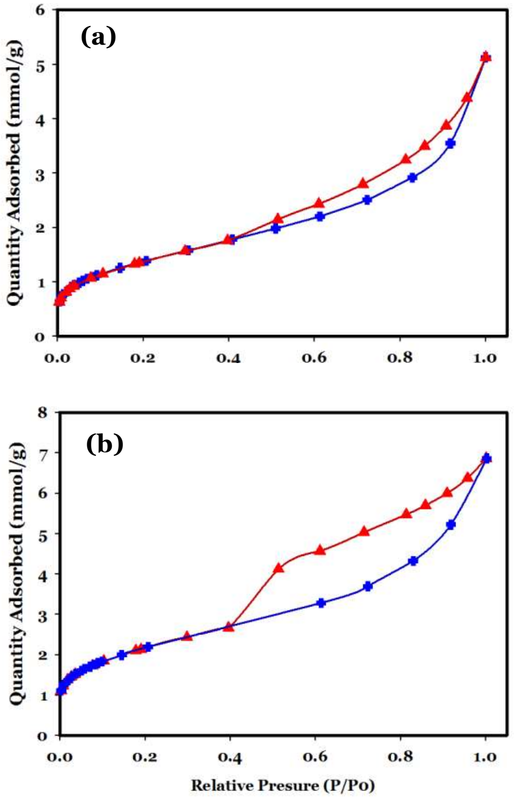

Fig. 4. 9. Adsorption and desorption isotherms of the samples I5-Fe100-R2 (a) and I5-Fe100-R2-UI (b). (adsorption and ◆ desorption ▲ data).

The pore size distribution curves of these two samples, determined according to BJH method are shown in Fig. 4.10. In the case of I5-Fe100-R2-UI, the intense peak centered at ~50 Å indicates that pores with an average size of 5 nm are the main contributors for the specific surface area of the sample. Regarding the non-irradiated sample curve, a maximum of much weaker intensity is also associated to a similar pore size. Altogether, these results suggest that despite the similar pore size of both samples, a larger amount of pores is likely accounting for the larger surface area of I5-Fe100-R2-UI.

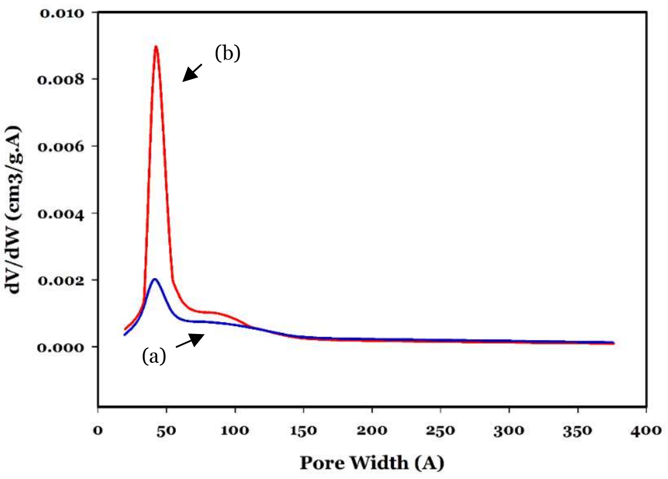

Fig. 4. 10. Pore size distribution curves of the samples I5-Fe100-R2 (a) and I5-Fe100-R2-UI (b).

4.4.3 Thermal behavior and oxygen uptake

Fig. 4.11 compares the thermogravimetric (TG) curves of the ZVI samples obtained under UI (I5-Fe100-R8 –UI) and without UI (i.e. I5-Fe100-R8) which were recorded in air. Both curves show that the two samples undergo a weight gain when exposed to a temperature increase, from 200 to 500 °C. The weight increase is larger for the particles synthesized under UI. From 500 up to 800°C, a weak but continuous weight loss takes place. The derivative curves corresponding to both TG plots (inserted in Fig. 4.11) display a similar temperature dependence, with a peak around 330°C which indicates that the maximum rate of weight gain occurs at the same temperature in both samples regardless the use of UI during particle synthesis. The XRD analysis of the samples after being heat treated at 330 °C (Fig. 4.12) reveals that, in addition to the peaks pertaining to ZVI, new peaks attributed to magnetite are identified in both cases, thus indicating that oxidation of the initial samples did take place during heat treatment. Therefore, the weight gain detected in both TG curves (Fig. 4.11) is assigned to the uptake of oxygen from air, which maximum rate occurs at 330 °C in both samples. According to TG results, 5.7% of weight gain is observed for the sample I15-Fe100-R8 at T = 330 °C, being the total gain of ~11% after the thermal treatment up to 800 °C. Regarding the sample I5-Fe100-R8-UI, 12.5% of mass gain is observed at T = 330 °C, being the total mass gain of 20% at 800°C. These results are summarized in Table 4.5.

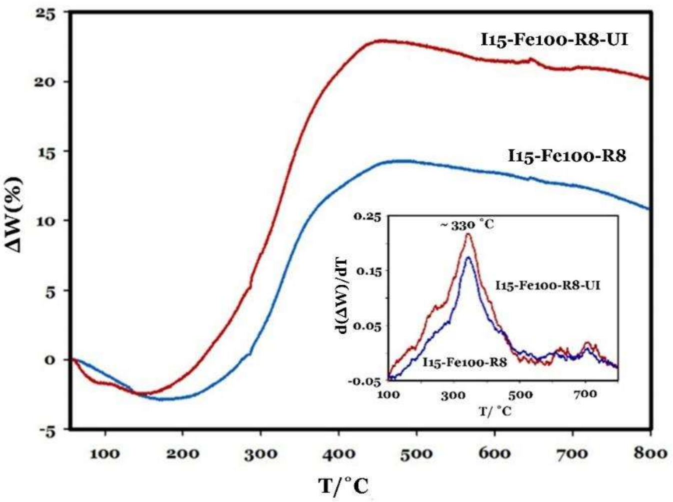

Fig. 4. 11. Thermal gravimetric analysis of samples I15-Fe100-R8 and I15-Fe100-R8-UI which respective derivative curves (dΔw/dT) are presented in the inset figure.

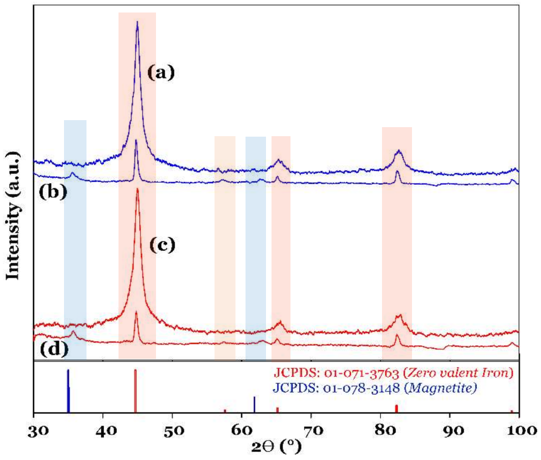

Fig. 4. 12. XRD patterns of the sample I15-Fe100-R8 (a and b) and I5-Fe100-8R-UI (c and d) before and after thermal treatment at 330 °C, respectively.

Table 4. 5. TG analysis data of the nZVI samples prepared with and without UI.

Sample identification	**T_{MR}^{a} (°C)**	**Δ_{WG}^{b} (%)**	**SSA of the starting sample (g/m^2, at room temperature)**
I15-Fe100-R8	327	11	21
I5- Fe100- R8-UI	329	20	51

[a] Temperature of maximum weight gain rate
[b] Total weight gain.

4.4.4 XPS analysis

Fig. 4.13 shows the XPS signal from Fe*2p* core level electrons for the samples I5- Fe100- R8-UI and I15-Fe100-R8.

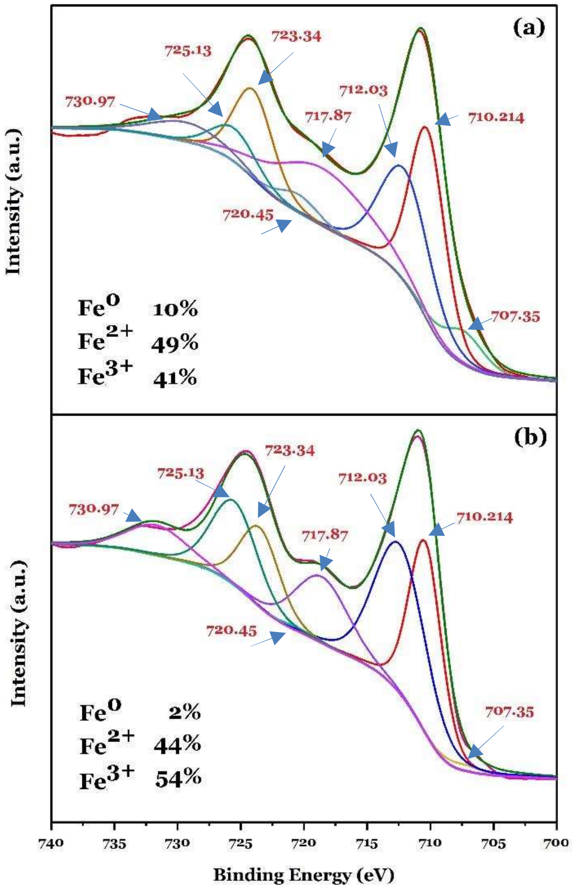

Fig. 4. 13. XPS signal from Fe2p core level electrons for the samples I5- Fe100- R8-UI (a) and I15-Fe100-R8 (b).

The main contributions to the total signal originate from Fe^0 and iron oxides (Fe^{2+} and Fe^{3+}) expressed as three synthetic peaks due to Fe^0: Fe$2p_{3/2}$ at 707.35 eV and Fe$2p_{1/2}$ at 720.45 eV, Fe^{2+} ions: Fe$2p_{3/2}$ at 710.214 eV and Fe$2p_{1/2}$ at 723.34 eV, and Fe^{3+} ions: Fe$2p_{3/2}$ at 712.03 eV and Fe$2p_{1/2}$ at 725.13 eV. The signals from Fe^{2+} and Fe^{3+} ions are overlapped due to strong multiplet splitting and shake up phenomena (satellites)[596]. The relative surface amounts of Fe^0, Fe^{2+} and Fe^{3+} species in the two samples are unequal: 10, 49 and 41 % for the sample prepared under UI (I5- Fe100- R8-UI) and 2, 44 and 54 % for the sample prepared without UI (I15-Fe100-R8), respectively. Accordingly the total amount of surface iron species that may undergo oxidation (59%) is larger in the sample I5-Fe100-R8-UI as compared to that (46%) of sample I15-Fe100-R8.

4.5 Discussion

4.5.1 Precipitation without UI

The results achieved in the framework of Taguchi approach revealed that both variables the ratio R=[$NaBH_4$/$FeCl_3$] and the cation concentration [Fe^{3+}] have determinant effects on the phase composition of the precipitated particles. High R values (R=10) combined with high or moderate values of [Fe^{3+}] clearly result in the precipitation of nZVI particles. On the other hand, a low value of

R (R=2) favors the precipitation of iron oxides which phase composition depends on [Fe^{3+}]. These trends are also identified among literature data as magnetite particles are often reported for R≈3 whereas nZVI particles are precipitated when R≥5 [1-8], as observed in the present study. A survey of literature data together with the present results is presented in table A.1 (see annex A) being the observed trends graphically expressed in figure 4.14.

The reduction reaction of $Fe^{3+}$by sodium borohydride may be described by Eq. 2 [587,597]),

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2 \qquad \text{Eq. (2)}$$

Another possibility may be also considered according to Eq. 3 [598],

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2(g) \qquad \text{Eq. (3)}$$

which implies the formation of the complex iron(III) hexahydrated ion ($Fe(H_2O)_6^{+3}$). Our experimental results seem to be in line with this alternative reaction path. This complex hydrated ion is well- known for its acidic behaviour, accounting frequently for solutions with low pH, close to 2 [599]. This was the case of the present study where the starting aqueous solutions of the iron precursor reagent ($Fecl_3.6H_2O$) showed a pH of ~1.8.

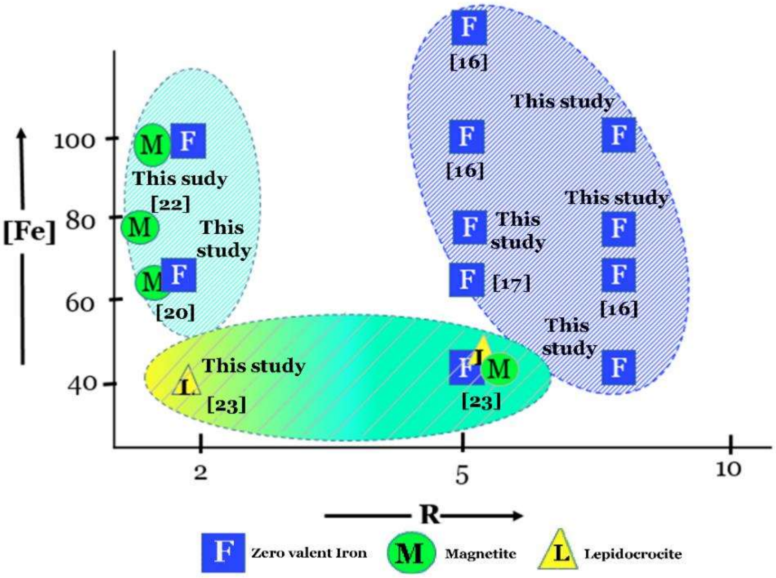

Fig. 4. 14. A schematic of the effects of synthesis conditions on the composition of iron based nanomaterials: data from the present study and from the literature.

Regardless the adopted mechanism (Eq. 3 or 4), a certain stoichiometric proportion of reductant to iron ion can be anticipated for ensuring the total reduction of the cation, being (3:4) or (3:1) for equations 3 or 4, respectively. Our results evidence that the experimental ratio R that is requested exceeds even the highest proportion (3:1) as an R=5 was necessary to avoid precipitation of iron oxides. This deviation may be explained by the procedure followed in the reagents mixture. As the reductant $NaHB_4$ is dissolved in water prior to its addition to the cation solution, a substantial amount of the boron hydride ion $BH4^-$ may undergo spontaneous hydrolysis [602] before cation reduction takes place. The hydrolysis reaction of $NaBH_4$ can be described by the following equation [603]:

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2 \qquad \text{Eq. (4)}$$

Thus, according to Eq. (4) a certain amount of the initial sodium borohydride is converted to $BO2^-$, hence becoming unavailable to play further as a reductant. Although the process of liquid-phase reduction has been widely reported in the literature for the synthesis of nZVI (Hwang et al., 2011; Woo et al., 2014), these molecular-scale phenomena underlying the preparation of the sodium borohydride aqueous solution have not been addressed so far.

The morphology of the powder particles varies significantly with the precipitate composition. When the amount of reductant is high enough (R≥5) to allow the precipitation of ZVI particles, nanosized spherical particles aggregated as chain-like structures are formed. The reasons accounting for the assembly of magnetic nanoparticles in a chain-wise manner have been addressed by Zhang and Manthiram (1997)[604]. The authors concluded that the magnetic interaction between adjacent nanosized iron particles is a primary factor guiding the chain formation. The results of the present study also revealed that increasing R from 5 to 8, the crystallinity of the nZVI particles is improved while the aggregation of the spherical particles is reinforced. Xu et al. (2013) [605] showed that crystallinity improvements benefit the magnetic properties. In line with this reasoning, it is here suggested that ZVI particles with better crystallinity will have enhanced magnetic properties that may contribute to a stronger particle aggregation.

When the synthesis is run under a low R (R=2) while keeping a moderate or high cation concentration (Fe = 67 or 100), the presence of magnetite among the precipitates indicates that instead of a complete reduction of Fe^{3+} to Fe^o, a partial reduction occurred to Fe^{2+} which concentration together with that of the still unreacted Fe^{3+} met the supersaturation requirements for the nucleation and growth of magnetite. Among the various iron oxides which are characterized by different solubility products, magnetite is known for its extremely low solubility [606]. So, the precipitation of magnetite can be expected under the used low R (R=2) where no sufficient $BH4^-$ is available to convert totally the Fe^{3+} cations to Fe^o.

Most of the methods reported in the literature for magnetite synthesis rely on two main precursors which provide Fe^{3+} to Fe^{2+} separately [607,608]. Also, the resulting particles usually present a spherical or irregular shape which contrasts to the nanosheets and tubular structures obtained in this study. Table A-2 (annex A) documents these observations (see appendix). Magnetite tubular structures were already reported in the literature but via synthesis routes that require the use of tubular templates assisting the formation of tubular structures that need to be eliminated at a later stage [609,610]. However, non-templated precipitation of tubular structures is found in the literature for some oxide systems as is the case of trititanate oxide. For that particular oxide the formation of $H_2Ti_3O_7$-type nanotubes was attributed to a scrolling up process of trititanate layers peeled off from trititanate plates under the interaction of OH^- species from the surrounding solution with the surface of the plate [611]. In the present work which is free of tubular templates, a borohydride reduction enabled nanosheets and tubular structures of magnetite to be formed. Contrarily to lepidocrocite, magnetite is not a layered structured oxide hence making it unlikely to precipitate as a sheet-like particle unless some intermediate lamellar parental phase could act as a temporary template. This possibility of a transient precursor of magnetite such as a green rust was raised by the observation of a turbid and greenish solution that preceded the final dark brown coloured suspension. Green rust (GR) has a mixed-valent iron layered structure consisting of positively charged sheets of Fe(II) and Fe(III) hydroxide intercalated with layers of water molecules and anions (like chloride, sulphate, or carbonate) [612], being chloride the most likely structural anion in the present case. GR has been reported as very thin lamellar shaped particles [613,614] which are here hypothesized to act as templates of magnetite. The formation of tubular shapes could be viewed as resulting from a rolling process of thin sheets triggered by some built-in strain induced by the structural changes accompanying the transformation of GR into magnetite [615,616]. The combination of low R (R=2) with a low amount of Fe^{+3} as is the case of sample I10-Fe40-R2, leads to the precipitation of lepidocrocite (γ-FeOOH) particles shaped as nanotubes (Fig. 4.4, b). Lepidocrocite finds a large number of applications such as in the purification of contaminated waters with heavy metals [617], as a catalyst for organic reactions [618], or as a precursor for the synthesis of ferromagnetic maghemite (γ-Fe_2O_3) or magnetite (Fe_3O_4) used as engineering materials in the manufacturing of magnetic devices [619]. There are few reports in the literature for the synthesis of lepidocrocite nanotubes with a large specific surface area (~105 m^2/g) [620,621]. However, this study offers a simpler and low-cost method for the fabrication of lepidocrocite nanotubes with a very high specific surface area (229 m^2/g).

4.5.2 Precipitation under UI

The results achieved under UI reveal that higher specific surface area was achieved for both I15-Fe100-R8-UI and I5-Fe100-R2-UI samples (50.6 m^2/g and 167 m^2/g, respectively), as compared to their counterparts I15-Fe100-R8 (20.50 m^2/g) and I5-Fe100-R2 (108 m^2/g) without UI. In the case of Fe100-R8-UI which showed smaller sized particles than I15-Fe100-R8 a higher nucleation rate could explain these results. According to the classical nucleation theory, the nucleation rate J is expressed as $J = A \exp(-\Delta G^*/KT)$, where ΔG^* is the free energy change required for the critical nucleus formation, K the Boltzmann constant, T the temperature and A a pre-exponential factor reflecting kinetic considerations, i.e. the molecular mobility affecting the rate of attachment of molecules to the critical nucleus [63,64].

It is here suggested that the formation, growth, and instantaneous implosive collapse of bubbles and the shock wave and micro-jet (400 km/h) induced by cavitation during UI [62–64] enhance the agitation of the solution species in the medium [622–624] thus increasing the statistical probability of chemical entities collision with the critical nuclei surface which ultimately favors the nuclei growth rate. A similar mechanism might also explain the apparently precipitation of the smaller sized spherical particles of the nZVI phase in the case of the sample I5-Fe100-R2-UI as compared to I5-Fe100-R2. The nucleation rate enhancement effect of UI may also apply to magnetite phase: this possibility aligns well with the smaller and thinner veil-like particles of magnetite which seem to wrap the spherical nZVI particles under UI. The significant increase of porosity due to slit-like pores revealed by the adsorption desorption isotherms of I5-Fe100-R2-UI (Fig. 4.9) compared to the non-irradiated sample, also supports the picture of very thin particles stacking around a larger amount of smaller sized nZVI particles, thus giving rise to a larger amount of slit-like pores. In addition to the benefits of UI for the enhancement of the specific surface area of the synthesized nanomaterials it is worthy to be mentioned that the crystallinity of the crystalline precipitates was maintained. This is an important achievement when considering the potential application of ZVI in the treatment of contaminated wastewaters as it helps minimizing ZVI undesired dissolution whenever recycling and reuse operations are implied. With regard to the effects of UI on the crystal structure of the obtained NP, positive effects were reported in the literature for some particular systems. For instance, Barbosa et al [625] indicated a better developed crystalline structure for nanohydroxyapatite (nHAp) (HAp:$Ca_{10}(PO_4)6(OH)_2$) powders prepared under UI where the crystallite sizes of the particles increased from 12 to 40 nm. In addition, their results showed an increase in the yield of the reaction when assisted by UI. Also, ultrasonic cavitation was able to avoid particles agglomeration while providing conditions for the precipitation of particles uniformly sized [626,627]. Such observations in addition to the relatively high yield of the products and in many cases without any need of surfactants or additional chemical reagents render UI a green synthesis route for a wide range of NMs. Moreover, room-temperature possibility for the ultrasonic synthesis highlights this method as an economic and clean route to large scale production of various dimensionalities of NMs.

The application of UI modifies the oxidation state of the iron species localized in the near surface region. According to XPS results the surface distribution of Fe^0, Fe^{2+} and Fe^{3+} is affected by UI: the total amount of oxidized iron species decreases when introducing UI (from 98% to 90%) and the content of species wich potentially may undergo further oxidation increases (from 46% to 59%) . Some literature data based on nZVI prepared under conventional liquid-phase reduction methods without UI also show that Fe^{3+} peaks are dominant as compared to Fe^{2+} [628,629], in line with the findings for the non irradiated sample .The present results substantiate the idea that UI provides ZVI nanoparticles with less oxidized surfaces hence with a larger oxidation potential. It is here hipothesized that the local agitation and heating induced by UI contributes to the depletion of the oxygen dissolved in medium [62–64]; in adition, as the specific surface area of UI sample is larger, the amount of oxygen available for interacting with its surface area unit becomes lesser under UI. For real applications, nanomaterials are expected to display high reactivity. In environmental clean-up applications the reactivity of nZVI materials reflects its ability towards surface oxidation [630]. When decomposing organic pollutants, nZVI reacts with H_2O molecules and become oxidized while generating radicals ($H^{\bullet}$) that degrade the organic molecular structure [419,631–633].

This work indicates that UI enhances the reactivity of ZVI. A higher reactivity will positively influence the treatment efficiency and the total treatment cost by reducing the amount of the material needed. In developing countries, where the treatment of polluted water and wastewater are among the main existing challenges [5], the reduction of treatment cost by applying UI assisted synhesis techniques might be of huge importance. The technology can also provide the ability of large scale production thus resulting in the reduction of nanomaterials costs. The thermal behavior of the prepared ZVI nanomaterials with and without UI (Fig. 4.11) allowed to evidence that despite their differences in terms of available surface area, the temperature at which both particles (I15-Fe100-R8 and I15-Fe100-R8-UI) undergo a maximum oxidation rate remains the same (~ 330°C). This indicates that UI benefits the particles with a larger surface area for catalytic activity without detrimental effects on their thermal stability regarding oxidation. Such nanomaterials profiting from this compromise of properties could be valuable options for applications in enhanced catalytic activities [634] to face with ongoing environmental problems such as purification of drinking waters and treatment of highly polluted industrial effluents.

Further studies are required to identify the efficiency of the proposed system in large-scale applications taking into consideration economic parameters. This may help to overcome the existing barriers on the commercialization of the technologies based on engineered nanomaterials.

4.6 Conclusion

Sustainable development of nanomaterials for various applications demands specific properties to enhance their performance while minimizing subsequent drawbacks. This study addresses in the same particulate system the combination of two characteristics that usually do not go together, i.e. crystallinity and high specific surface area, both of which are fundamental when using engineering nanomaterials for environmental clean-up applications. A Tagguchi approach provided the identification of parameters that control the properties of iron-based nanoscale particles synthesized by a liquid-phase reduction process. Both the (reductant/Fe^{3+}) ratio, (R), and the Fe^{3+}concentration, [Fe_3^+], are the parameters that determine critical characteristics including particle crystalline phase composition, crystallinity and surface area although R has been revealed as the most important one. The addition of ultrasonic irradiation (UI) to the synthesis process proved to be a successful approach for synthesizing nZVI particles with smaller size, hence with a higher surface area, but without sacrificing their crystallinity or their thermal stability regarding oxidation. Furthermore, the surface composition of nZVI produced under UI appears populated by iron species with a higher ability to undergo oxidation which render them better suited to environmental clean-up applications. Thus UI benefits smaller sized crystalline particles with more reactive surface which role in polluted water treatment warrants to be considered for optimizing efficiency and associated costs.

Chapter 5: Treatment of Recalcitrant Contaminants

- Kamali, M., Capela, I. and Costa, M. E. (2018) ‘Ultrasonic Synthesis of Zero Valent Iron Nanoparticles for the Efficient Discoloration of Aqueous Solutions Containing Methylene Blue Dye’, in Ul-Islam, S. and Butola, B. S. (eds) *Nanomaterials in the Wet Processing of Textiles*, pp. 261–284. Hoboken, NJ, USA.: John Wiley & Sons, Inc., https://doi.org/10.1002/9781119459804.ch8
- Mohammadreza Kamali, Maria Elisabete V. Costa, Isabel Capela, Boosting the Biodegradation of Phenolic Wastewaters with Acclimatized Activated Sludge - A kinetic Study, under submission.

5.1 Ultrasonic Synthesis of Zero Valent Iron Nanoparticles for the Efficient Discoloration of Aqueous Solutions Containing Methylene Blue Dye

5.1.1 Abstract

Dyes are complex toxic and non-biodegradable aromatic compounds used as colorants in many industries such as textile, pulp and paper, printing, leather, etc. For environment safety purposes, the separation of dyes from polluted effluents is a major concern. The current study aims at ultrasonic synthesis of nano-sized zero valent iron (nZVI) particles and their application for the removal of methylene blue (MB) from aqueous solution. The removal of MB dye can be optimized by varying the operating pH and the contact time between the dye molecules and nZVI particles. UV-Vis spectroscopy, employed to study the MB removal efficiency and the underlying mechanisms, indicates high efficiency of the nanomaterials regarding MB removal as compared to literature data. The synthesized nanomaterials possess an excellent removal potential for the treatment of industrial wastewater containing dyes.

Keywords: Nano zero valent iron (nZVI), Ultrasonic irradiation, Methylene blue, Wastewater treatment.

5.1.2 Introduction

Dyes are major organic compounds of effluents discharged from industries such as textile, pulp and paper, cosmetic and pharmaceuticals, food and packaging, etc. [635,636]. Methylene Blue (MB), i.e. methylthioninium chloride (Fig. 5.1.1), is a member of the thiazine class of dyes with many applications [637–639] which was firstly prepared by Heinrich Caro in 1876 [640]. The toxic effects from thiazine dyes have been previously investigated and documented [641]. Severe toxic effects (1%) on Iris epithelium and corneal endothelium [642], and toxic effects on human luteal cells [643], on the fetus [644], and on erythroleukemic cells [645] are only few examples of the harmful impacts on living organisms when exposed to MB. Hence the toxicity and carcinogenic effects of these dyes raise major concerns about human health and aquatic environments where dyes contaminated effluents might end up [646–648].

The removal of MB from industrial effluents is an important environmental issue because most of the conventional biological, physical, and chemical treatment methods are not able to efficiently degrade this compound [649]. In this context, exploring efficient methods and optimizing its operating conditions for MB removal are goals of high significance. The application of engineered nanomaterials (NMs) has proved to be a successful route for the removal of MB dye from contaminated environments when appropriate conditions are met. Recent studies have shown that the performance of the nanomaterials is highly conditioned by the experimental conditions, i.e. contact time, pH, and temperature among others, being the removal efficiency very dependent on the combination of used conditions. In addition, the application of additional measures such as UV irradiation has shown the ability to improve the final removal efficiency when assisted by nanomaterials. Table 5.1.1 summarizes literature data supporting these findings. Despite this pool of knowledge, there is still a need to find out the optimum conditions under which maximum removal efficiency can be achieved under reasonable investments of time, materials and input energy.

As an emerging technology, the application of iron-based nanomaterials for the treatment of polluted waters and wastewaters underwent a fast development in recent years. Within this context, iron oxides such as magnetite (Fe_3O_4) [650,651], hematite (Fe_2O_3) [652–654] and maghemite (γ-Fe_2O_3) [655,656], and iron hydroxides such lepidocrocite (α-FeOOH) [601] are of a particular interest to degrade and remove various types of environmental contaminants. Zero valent iron (ZVI) is another type of iron-based material with a potential to be widely adopted in real scale applications as an effective, non-toxic and low-cost alternative for conventional clean-up technologies [657,658]. Application of micro-sized ZVI particles in permeable reactive barriers [386,387] is a good example of the utilization of this material as a well-known strategy for the treatment of highly polluted ground waters. However, ZVI particles if used as nanosized particles (nZVI), they may provide a significantly larger surface area to volume ratio, and also a higher surface energy which result in a significant improvement of their reactivity towards contaminants [659]. Nano-scale zero valent iron has been recently applied for the removal of a variety of environmental contaminates [388,389,391,660–664] due to the enhanced reactivity of nZVI towards organic pollutants as compared to conventional micro-scale ZVI powders. In addition, various attempts have been made in order to enhance the properties of these nanomaterials in terms of specific surface area (SSA), crystallinity, etc. [664–666]. However, there is still field for improvements. For instance, the simultaneous enhancement of nanomaterials properties like crystallinity and surface area and the optimization of the nZVI synthesis conditions still remain to be explored. For optimizing the MB removal efficiency, nZVI synthesized with enhanced surface area and crystalline structure via a combined liquid phase reduction-ultrasonic irradiation technique is here proposed. Also, the MB removal can be maximized by correlating the conditions allowing optimum degradation of the MB with the properties of the used nanomaterials. The reactivity of the synthesized nZVI towards MB can be traced with a photometric analysis which allows to identify the mechanisms involved as well.

Table 5.1. 1. Performance of nanomaterials used for the removal of MB from dye solution.

Nanomaterials	Operating conditions							Removal Efficiency (%)	Ref.
	Dye conc. (mg/L)	NMs dosage. (g/L)	Time (min)	Temp. (˚C)	pH	Reactor type	Other conditions		
Ti/Sb–SnO$_2$-TiN[1]	50	NG[2]	60	23	NG	Three-electrode cell	-	73.9[3]	[667]
	50	NG	120	23	NG	Three-electrode cell	-	100	
Ti/Sb-SnO$_2$	50	NG	60	23	NG	Three-electrode cell	-	34.3	
	50	NG	120	23	NG	Three-electrode cell	-	65.1	
Fe$_2$O$_3$/TiO$_2$	1×10^{-5} mol/L	1	60	NG	7	NG	UV irradiation	95	[646]
Poly Acrylonitrile	5	4	60	30-70	5-9	NG	-	70	[668]
Hydroximated poly Acrylonitrile	5	4	60	30-70	5-9	NG	-	90	
h-MoO$_3$	10	1	180	Room	NG	NG	Dark	67	[669]
h-MoO$_3$	10	1	180	Room	NG	NG	UV light[4]	71	
h-MoO$_3$	10	1	120	Room	NG	NG	Visible light[5]	98	
h-MoO$_3$	10	1	180	Room	NG	NG	Without catalyst	4	
β-Cyclodextrin Multi-Conjugated Magnetic Graphene Oxide	40	0.7	150	Room	13	Vial reactor	-	93	[670]
NixZn$_{1-x}$Fe$_2$O$_4$[6]	200	0.3	90	Room	3	Photocatalytic reactor	UV irradiation		[671]
MnO$_2$	100	0.35	90	Room	11	Flask reactor	-	90	[672]
CuO/nano TiO$_2$	10	0.2	300	NG	NG	Total reflection quartz reactor	UV irradiation	99	[673]
SiO$_2$[7]	100	2.3	180	20	5.5	NG	-	9.4 (mg/g)[8]	[674]

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1. Supporting electrolyte: 0.25 M Na2SO4 solution.
2. NG: Not Given.
3. The removal process was carried out using electrodes.
4. 6 W, λ= 365 nm.
5. 350 W, λ >400 nm, 833×100 lux.
6. X=0.0 to 1.0.
7. Silica nano-sheets derived from vermiculite.
8. mg of MB to g of nanomaterials.

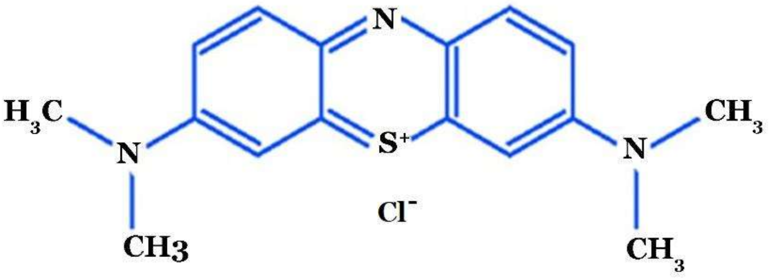

Fig. 5.1. 1. Chemical structure of MB.

5.1.3. Materials and Methods

5.1.3.1 Materials

Chemicals reagents including iron (III) chloride hexahydrate ($FeCl_3.6H_2O$ from Sigma-Aldrich, St. Louis, MO) (99%) and sodium borohydride ($NaBH_4$ from Sigma-Aldrich, St. Louis, MO) (≥98.0%) without further purification are used as precursor and reductant for the synthesis of nZVI. Ethanol from Fisher scientific (99.0%), and deionized water supplied by an ultrapure water purification system (EASYpure RF-Barnstead/Thermolyne) are also used for experiments. Methylene blue (MB) (99%) is from Sigma-Aldrich (St. Louis, MO). pH adjustments are performed with H_2So_4 (>95%, Fisher Scientific, UK) and NaOH (JMGC co., Portugal).

5.1.3.2 Synthesis and characterization of nanomaterials

The synthesis of nZVI is performed in a 500 mL three-open neck flask reactor installed inside an ultrasonic cleaning bath (Branson, 1510E-MT) with a theoretical dissipation rate of 70 W and operating at 42 KHZ ± 6%. Mechanical overhead stirring (at 250 rpm) with IKA Eurostar 40 stirrer is utilized to continuously stir the reaction medium. Certain amounts of a sodium borohydride solution (0.91 g g of sodium borohydride dissolved in 100 ml of deionized water) are injected in 30 mL of an ethanol/deionized water solution (24 mL of ethanol + 6 ml of deionized water) containing the precursor (0.81 g of $FeCl_3.6H_2O$) at room temperature. A Watson Marlow 120U/R peristaltic pump is utilized to control the injection rate of the reductant. After completing the injection of the reductant solution, the final mixture is stirred for more 10 minutes in the reactor. The black precipitates are then collected, washed and dried before characterization.

Crystallographic characterization of the synthesized particles is carried out by X-ray diffraction (XRD) analysis (Rigaku, Geigerflex, Japan) in the 2θ range from 30° to 100° with a goniometer speed of 2°/minute. Scherrer equation (Eq. 2) is used to determine the crystallite size of the particles:

$$d = K\lambda/\beta\cos\theta \qquad \text{Eq. 1}$$

where d is the average crystallite size, K is a dimensionless shape factor, λ is the wavelength of the X-ray used, β is the full-width at half maximum intensity (FWHM) of the sample, and θ is the Bragg angle. Transmission electron microscopy by Hiatchi H9000na, Japan operated at 300 kV acceleration voltage is utilized to study the morphology of the synthesized particles. Particle size distribution of the particles is obtained by counting more than 500 individual particles selected randomly using photoshop and Image J software programs. Particles specific surface area (SSA) is assessed by gas adsorption with a Micromeritics Gemini V2 (USA) equipment. The SSA is calculated based on the Brunauer–Emmett–Teller (BET) isotherm. Zeta potential measurements are carried out using a zetasizer (Zetasizer Nano ZS, Malvern, UK) for assessing the electrical charge characteristics of the particles surface. For that dilute aqueous suspensions of the nanomaterials (10 mL) are prepared under ultrasonic irradiation in an ultrasonic cleaning bath (Model Sonoswiss 6lt, Switzerland). The pH of the nanoparticle suspensions is adjusted in the acidic and alkaline ranges using HCl or NaOH respectively. The magnetic hysteresis measurements are performed using vibrating sample magnetometer-VSM (CryogeniceCryofree). The Hysteresis curve is recorded at 5K under a magnetic field up to 10 T.

5.1.3.3 Discoloration of methylene blue

Reactivity of the ZVI nanomaterials prepared under ultrasonic irradiation ($nZVI^{UI}$) is determined using MB, as a model contaminant [675,676]. The reactions are performed under visible light at 720 lux assisted by a multi-function environment meter (ST-8820, REED, USA) under ambient temperature. Based on a set of preliminary experiments (data not shown), the optimum dosage of the nanomaterials for the removal of MB was identified as 1 g/L. $nZVI^{UI}$ particles are suspended in a 100 mL aqueous solution containing 25 mg/L of MB. The absorbance behavior of MB solution under various pHs ranging from 4 to 10 at room temperature is monitored for 30 min with a UV-Vis spectrometer (T80+, PG Instruments, UK), from 200 to 750 nm. When the MB (green color) is dissolved in water, a blue color solution yields. The intensity of the blue color measured at wave lengths of maximum absorption, i.e. 665 and 605 nm (related to monomeric (0-0 band) and dimeric (0-1 band) forms of MB, respectively [677]) is used to follow the removal process and its efficiency.

5.1.4 Results and discussion

5.1.4.1 Materials characterization

The XRD pattern of the particles prepared under ultrasonic irradiation is presented in Fig. 5.1.2. The sample is composed of ZVI (JCPDS No. 07-71-3763), without any evidence of secondary phases. Based on Sherrer equation (Eq. 1), the crystallite size of the powders was determined as 23.9 nm.

A TEM micrograph of the $nZVI^{UI}$ samples prepared under ultrasonic irradiation is presented in Fig. 5.1.3. The sample consists of aggregates of enchained spherical particles. The particles clearly present a core-shell structure consisting of a dark core (nZVI) covered with a thin bright layer. Figure

5.1.4 shows the particle size distribution of the prepared particles. As observed, the average particle size is around 27 nm. The BET specific surface area of this sample was determined as 50.6 m²/g; this large value is in line with the relatively low average particle size calculated for the sample (Fig. 5.1.4). Also, the SAED image obtained from TEM denotes a relatively high intensity for spots indicating well-developed crystalline structure.

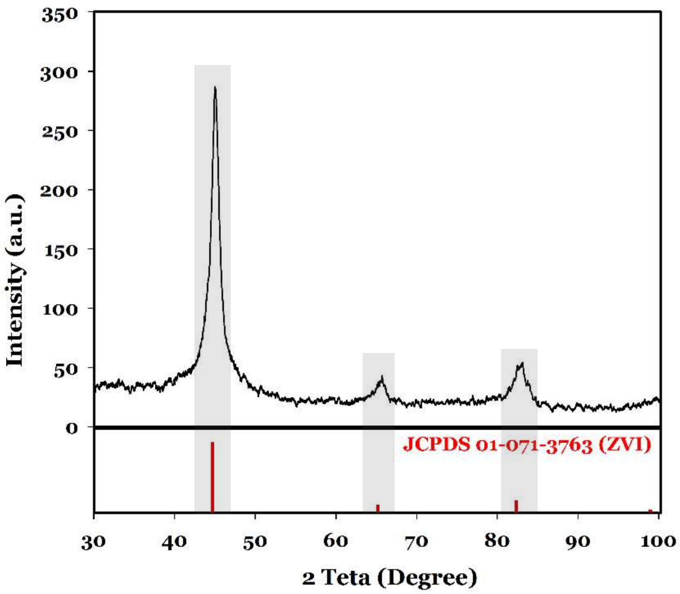

Fig. 5.1. 2. XRD pattern of the synthesized nZVI^{UI} particles. A ZVI single-phase can be identified according to the JCPDS database.

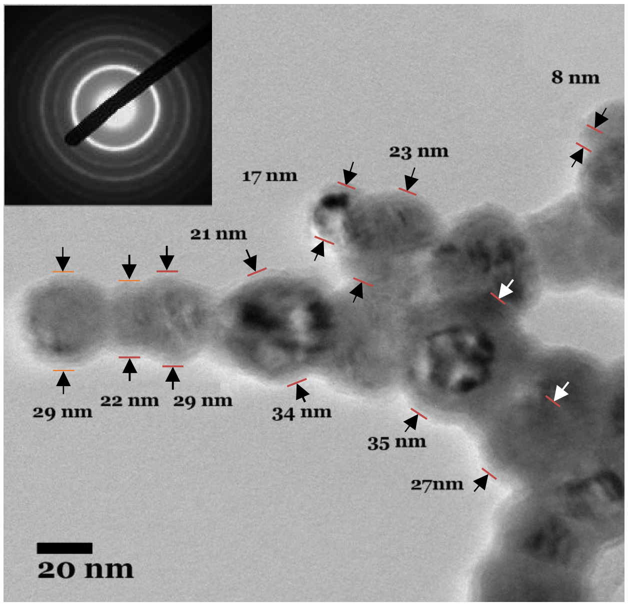

Fig. 5.1. 3. TEM and SAED images of the nZVI^{UI} particles.

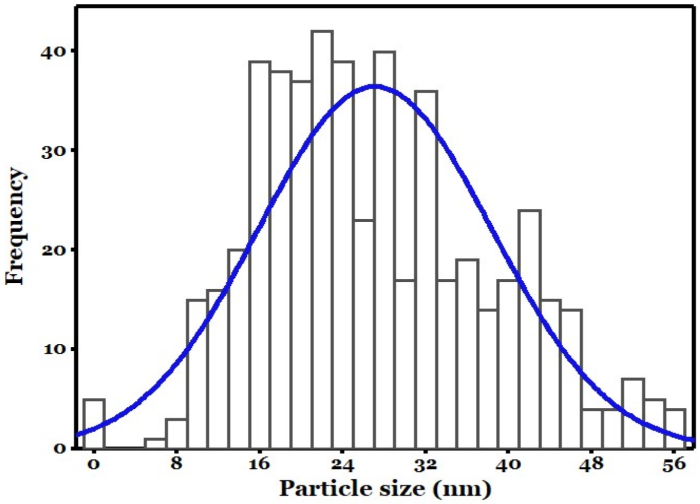

Fig. 5.1. 4. Particle size distribution of the synthesized nZVI^{UI}. The average particle size is around 27 nm.

The pH dependence of nZVI^{UI} zeta potential is shown in Fig. 5.1.5. The results indicate that the zero charge point (ZPC) is ~8 and that the surface of the particles is negatively and positively charged at pH above and below 8, respectively.

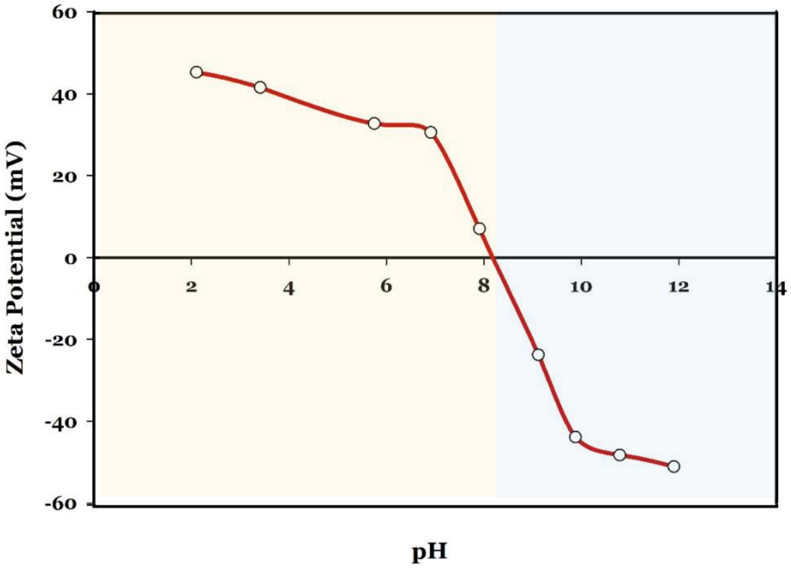

Fig. 5.1. 5. pH dependence of the zeta potential of nZVI^{UI}. The zero charge point is around 8.

Vibrating sample magnetometer (VSM) analysis was performed in order to study the magnetic properties of the prepared nZVI^{UI} nanomaterial [670]. In Fig. 5.1.6 the magnetic hysteresis (M-H) loop of the sample is presented. According to this figure, saturation magnetization (Ms) of the sample was found very high (~100 emu/g). This characteristic of the nanomaterials can offer an economic advantage of using this type of nanomaterials for the treatment of polluted aquatic environments because they can be recovered and recycled readily after being used in treatment operations [678–

683]. The materials can be easily separated from the treated effluents by applying an external magnetic field e.g., using a permanent magnet.

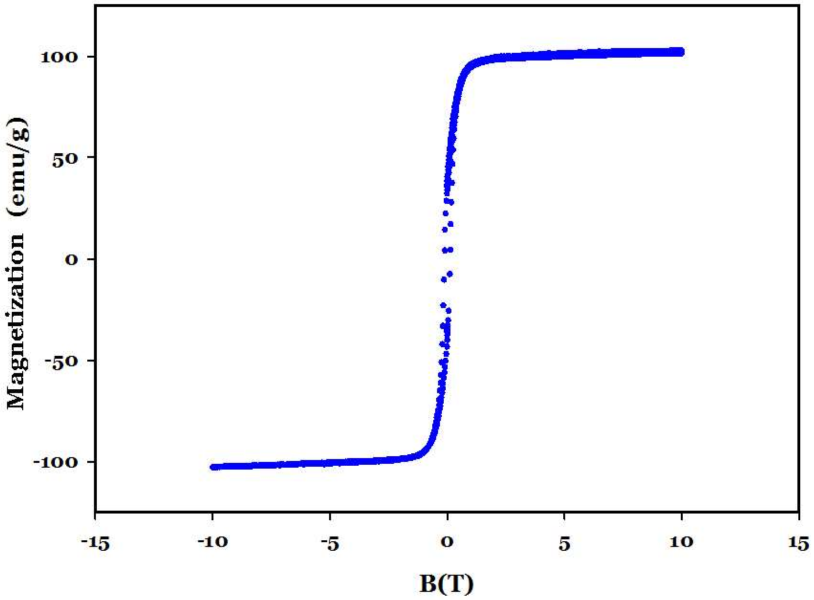

Fig. 5.1. 6. Magnetic hysteresis loop of nZVI^{UI} at T=5K.

5.1.4.2 Discoloration studies

5.1.4.2.1 MB Discoloration in acidic conditions

A photometric assay is employed for assessing the concentration of MB in synthetic solutions. Adsorption spectra of MB solutions with different concentrations are detailed in Fig. 5.1.7. As observed, two absorption maxima of MB are detected at 610 and 664 nm [684–687], being their intensity difference attenuated as MB concentration increases. In this study, the conversion of MB to any colorless products such as MLB is termed as discoloration whereas the irreversible conversion of MB to products like CO_2 or H_2O is referred as MB degradation [688].

In order to study the extent of MB discoloration using nZVI particles prepared under ultrasonic irradiation and also the mechanisms involved in the process, assays at various pHs of the reaction medium, ranging from 4 to 10 are important in order to cover the effects of pH variation.

The assay at pH=4 is used to assess the effects of acidic conditions on the process of MB discoloration. Under this condition the percentage of color removal (here identified as the percentage of the reduction of the adsorption intensity measured at 664 nm) from the solution reached only 29% after 30 min of reaction and the pH slightly increased to 4.1. Moreover, after re-collecting the nanoparticles from the reaction medium, the solution becomes rapidly re-colored suggesting that there should be a reversible reaction for the removal of MB under acidic conditions where the MB molecules are not attached to the surface of the nanomaterials considering the zeta potential of the synthesized nZVI^{UI}.

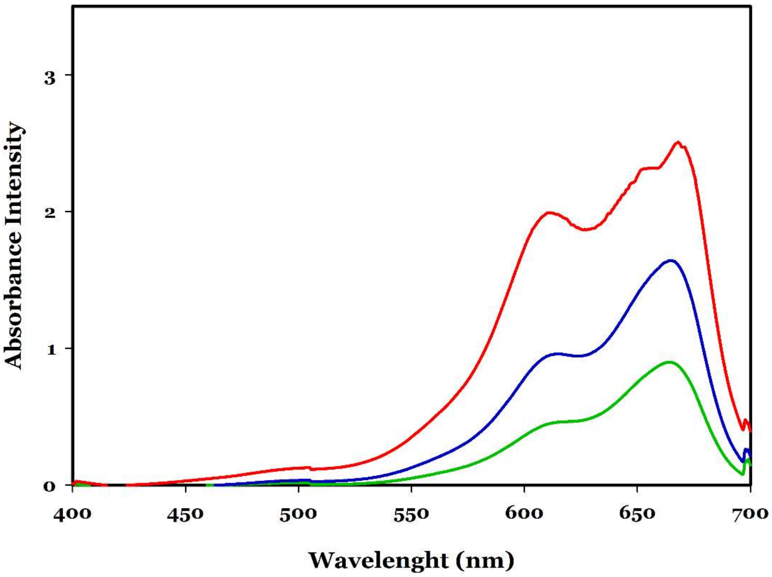

Fig. 5.1. 7. The absorption spectra of various concentrations varying from 5 mg/L to 25 mg/L.

MB is widely applied for optical oxygen sensing especially in the food industry [689,690]. It is well known that MB is reduced to leuco methylene blue (LMB) which is a colourless compound in the absence of oxygen. This compound is readily re-oxidized (to MB) by introducing oxygen to the system [691]. When the MB is subjected to the treatment with nZVI particles, it is here proposed that the surface layer of ZVI particles undergoes oxidation according to (Eq. 2) [692–695]:

$$Fe^{0} \rightarrow Fe^{2+} + 2e^{-} \qquad \text{Eq. 2}$$

The released electrons are subsequently used to reduce the MB to LMB, under acidic conditions. A schematic of the involved mechanism is presented in Fig. 5.1.8.

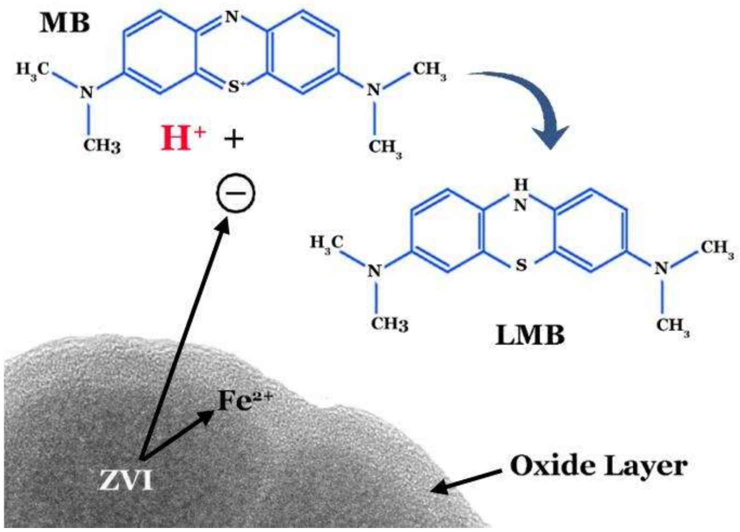

Fig. 5.1. 8. Mechanism involved in the discoloration of MB under acidic conditions. The electrons released by the oxidation of the surface layer of the ZVI nanoparticles are used in the reduction of MB to the colourless LMB.

According to Fig. 5.1.5, the point of zero charge (PZC) of the prepared nZVI particles is reached approximately at pH 8. Below this pH, the surface of $nZVI^{UI}$ particles is positively charged, while above this pH it is negatively charged. Hence, under acidic conditions, repulsive electrostatic interactions between ZVI particles and the positive ions of MB do not favor the adsorption of MB on the surface of ZVI particles. Therefore, the hypothetic contribution of MB adsorption on ZVI particles for the chemical pathway of MB discoloration is considered negligible within the considered acidic pH window.

As referred, rapid re-coloration of the solution takes place suggesting that in acidic condition LMB does not degrade to simpler intermediate compounds or to final products (CO_2+H_2O) [696]. This suggestion is supported by the photometric results obtained after 30 min of reaction presented in Fig. 5.1.9. The results show that the difference between the two maximum absorbances at 290 and 664nm becomes enhanced with the reaction time, being this considered as an evidence for the decrease of MB in the reaction medium. Also the intensity of the adsorption peak at 243 nm which is attributed to LMB [697] becomes enhanced with the reaction time, in line with the reasoning here proposed.

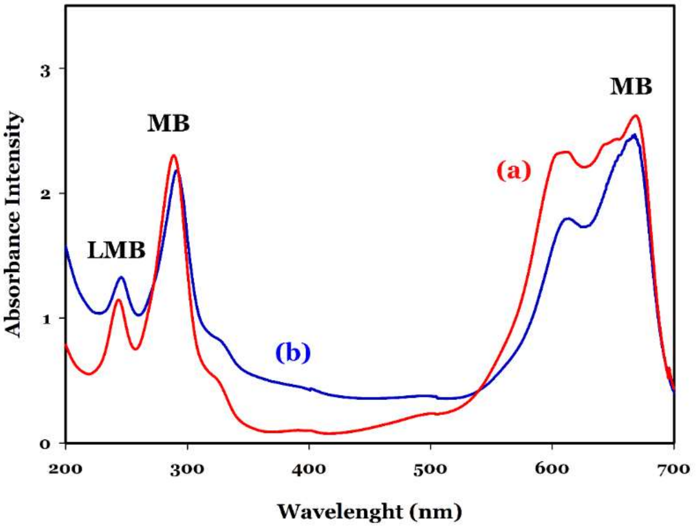

Fig. 5.1. 9. The UV-Vis adsorption spectra of the solution containing MB (25 mg/L) at the beginning (a) and after treatment with nZVIUI (1 g/L) for 30 min under acidic condition, pH=4 (b).

5.1.4.2.2. MB Discoloration in quasi-neutral conditions

In order to study the effects of increasing the pH till the vinicity of the pzc of the nZVI particles, the pH of the MB solution is adjusted to 7.5 immediately after the addition of the nanomaterials to the suspending medium (water) (1 g/L). The photometric results obtained in a 30 min time interval are presented in Fig. 5.1.10. As observed in this figure (a), an apparent effective removal of MB is observed after 5 min of reaction time (blue line), in line with the loss of blue color observed after 5 min. During this short period, the pH of the medium raised slightly to ~8.5. A shoulder at 664 nm (Fig 5.1.10) indicates that the discoloration of MB was almost achieved but not complete. The shoulder does disappear after 30 min of reaction (Fig. 5.1.10, b) (green line), thus indicating that a 100% discoloration of MB was achieved (Fig. 5.1.11). However, a narrow peak observed at 250 nm indicates that part of the organic dye (MB) is converted to LMB. Fig. 5.1.10 (c) presents the UV-Vis adsorption of the solution with regard to 24 hrs, after collecting the nanomaterials. At this time (red line), a small peak is found at 664 nm, corresponding to a concentration of 3.9 mg/L, which is 15% of the initial amount of the MB. It is also observed a decrease in the LMB peak at 250 nm denoting the transformation of the existing LMB to MB in the presence of oxygen in the medium.

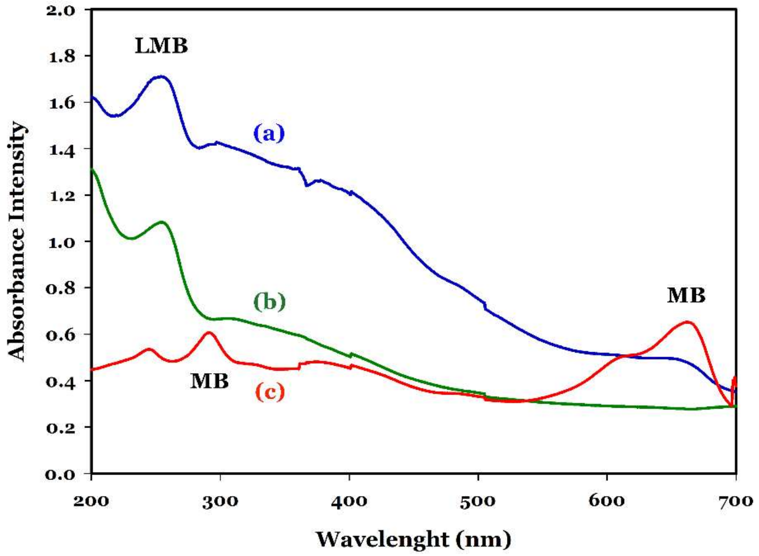

Fig. 5.1. 10. UV-Vis spectra of the reaction medium under initial pH=7.5 after 5 min (a), 30 min (b), and 24 hrs being the nanomaterials already separated from the reaction solution (c).

When the pH of the medium gets close to the pzc of nZVI particles, MB gets more easily adsorbed on the surface of nZVI particles as the repulsive forces between the surface of the nanoparticles and MB molecules are now much weaker or inexistent. In these conditions, it is assumed that MB complexes are formed on nZVI particles surface [696] being very susceptible to chemical attack by species originated at the surface layers of the nZVI particles. According to equations 3 to 7 which describe the reactions possibilities of the nZVI particles surface layers, namely with the surrounding H_2O molecules, H radicals are generated which may induce the cleavage of the MB molecules [419,631–633]. This can be suggested as a main reason for the higher efficiency of the MB degradation and cleavage at pH=7.5 compared to acidic conditions. A schematic of the involved mechanism under quasi-neutral conditions is presented in Fig. 5.1.12.

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad \text{Eq. 3}$$

$$Fe^0 + H_2O \rightarrow Fe^{2+} + H^+ + OH^- \qquad \text{Eq. 4}$$

$$Fe^0 + H^+ \rightarrow Fe^{2+} + H^{\cdot} + 2e^- \qquad \text{Eq. 5}$$

$$Fe^{0} + 2H^{+} \rightarrow Fe^{2+} + H_{2} \qquad \text{Eq. 6}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \qquad \text{Eq. 7}$$

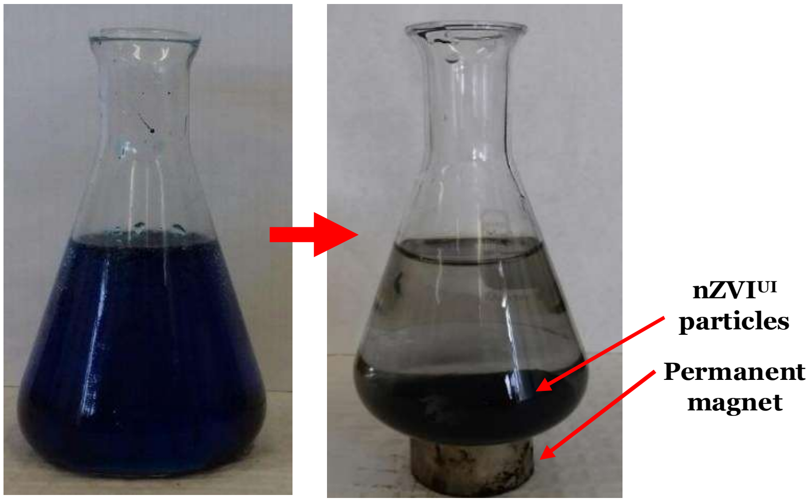

Fig. 5.1. 11. Initial MB solution (25 mg/L) (left) and the solution after 30 min of reaction under initial pH=7.5 using nZVI particles (1 g/L) (right).

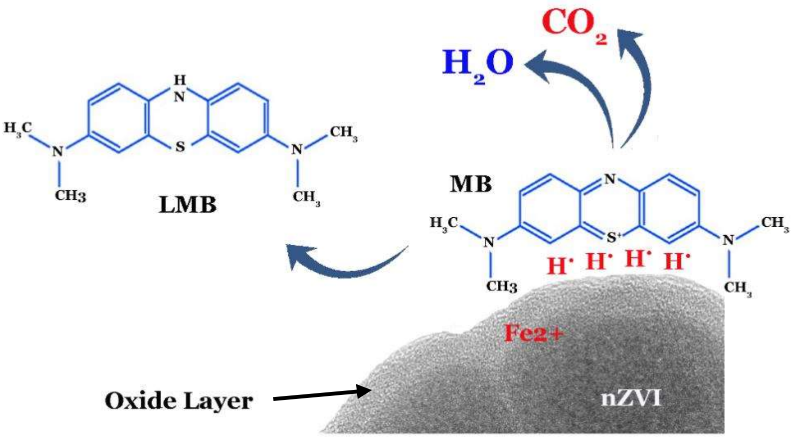

Fig. 5.1. 12. Mechanism involved in the discoloration of MB under quasi-neutral conditions. Attachment of MB to the surface of the nanomaterials facilitates the degradation of MB molecules.

5.1.3.2.3 MB Discoloration in basic conditions

Fig. 5.1.13 presents the results of the discoloration of MB carried on at an initial pH of 10. As observed, the extent of the discoloration reached only 26% after 5 min (blue line) which is a much lower than that recorded at initial pH=7.5. After 15 min of reaction (red line), the discoloration of MB reached 61% and it increased further to 100% after 30 min of reaction (green line).

Under high pH values, an extensive adsorption of MB on the surface of the used nanomaterials, helped by electrostatic attractive forces, can be expected. Such adsorption provides a favourable condition for the degradation of MB. A lower removal of MB in basic conditions as compared to quasi-neutral conditions can be attributed to the mechanisms involved in the discoloration of MB in alkaline medium. According to eq. 4, the production of H^+ is a key step for the generation of hydrogen radicals which can subsequently degrade and remove MB from the solution. Nonetheless, the presence of abundant OH^- in basic conditions may play a scavenging role leading to the readily consumption of the produced H^+ near the surface of the nZVI particles. Hence, the reactions for the cleavage of MB are restricted.

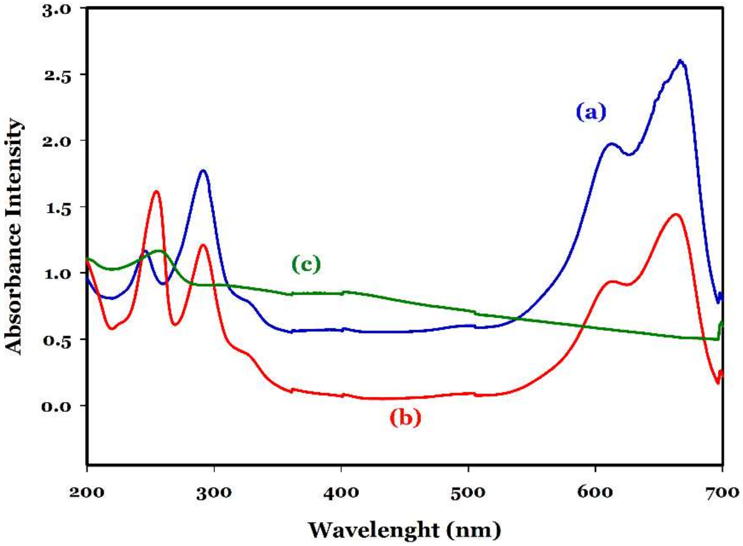

Fig. 5.1. 13. UV-Vis spectra of the reaction media under initial pH=10 after 5 min (a), after 15 min (b), and after 30 min (c) of reaction for the removal of MB (25 mg/L) with ZVI nanomaterials (1 g/L).

It has been well documented in the literature that the performance of nanomaterials for the removal of persistent phenolic compounds increases under acidic conditions [698–701]. Most of the phenolic compounds such as chlorophenols are negatively charged which facilitates their attachment to the surface of nanomaterials positively charged as frequently observed in acidic media. Therefore, it can be suggested that the better efficiency of nanomaterials under acidic pH for the removal of such contaminants is probably associated to the formation of pollutants-nanomaterials surface complexes which might be more effective players in the process of pollutants degradation than the release of electrons to the reaction medium by the reduction of Fe nanoparticles with subsequent chemical attack to pollutants.

The results of this study show that the attachment of MB molecules to the surface of nZVI particles under neutral or basic conditions facilitates the degradation of the dye due to the positive charge of MB specie. So, it can be anticipated that the available surface area of the nanomaterials is a key factor, because it can critically determine their efficiency when dealing with complex organic pollutants. The results of this study also indicate that the efficiency of the reactions that occurred in the bulk solution (not on the surface of the nanomaterials) is negligble. So, limiting the release of electrons from the nZVI materials to the reaction medium for the purpose of increasing the life time of nZVI particles will probably not affect their efficiency.

Table 5.1.2 provides the results of some recent studies for the removal of MB using ZVI nanomaterials comparing the efficiency of Fe nanoparticles towards the discoloration of MB, under different operating conditions. In most of the cases, the characteristics of the used nanomaterials has not been fully provided in the respective reports. In the present study, the very high efficiency of the nanomaterials for the degradation of MB can be attributed to the enhanced properties (high crystallinity and large specific surface area) of the used nanoparticles which provide a good condition for the rapid degradation of MB in a short period of time (100% discoloration in 5 min) in appropriate pH conditions.

5.1.4 Conclusions

nZVI particles with enhanced properties may be successfully synthesized by utilization of ultrasonic irradiation. Such nanomaterials present an efficient performance regarding the degradation of MB and discoloration of MB solutions. The pH of the solution medium is a critical parameter for determining the MB removal efficiency of the synthesized nanomaterials. While acidic pH allows achieving 30% discoloration of MB, quasi-neutral conditions of pH=7.5 permit the complete removal of the dye color. The properties of the nanomaterials including zeta potential, size and specific surface area and crystallinity are the main factors determining the efficiency of the nanomaterial for environmental clean-up purposes.

Table 5.1. 2. Some recent studies for the removal of MB using nZVI materials.

Nanomaterials	Nanomaterials properties			Operating conditions				Discoloration (%)	Reference
	Size (nm)	Surface area (m^2/g)	Crystallite size (nm)	Dye conc. (mg/L)	pH	NMs dosage (mg/L)	Time (min)		
nZVI^{UI}	27	50	23.9	25	4	1	30	29	This study
	27	50	23.9	25	7.5	1	5	100	This study
	27	50	23.9	25	10	1	5	26	This study
	27	50	23.9	25	10	1	15	61	This study
	27	50	23.9	25	10	1	30	100	This study
Iron nanoparticles[1]	40-60	NG[2]	NG	10	3-4[3]	1	60	100	[702]
ZVI	NG	NG	NG	20	3	1	30	77	[696]
	NG	NG	NG	20	6	1	40	90	[696]
nZVI	NG	33.7	NG	100	6	0.7	60	96	[702]
nZVI	NG	33.7	NG	100	NG	0.2	60	76	[702]
nZVI-Clinoptilolite	40-60	16.1	NG	100	5	0.1	420	91	[703]

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1. A mixture of ZVI, FeOOH and Fe_3O_4.
2. NG: Not Given.
3. Using 5 ml in 50 ml H_2O_2.

5.2. Removal of AOXs from Pulp and Paper mill Effluents using Fe_3O_4/ZnO nanocomposite

5.2.1 Abstract

The discharge of complex industrial effluents without effective treatments can cause serious environmental problems, such as increased pollution of water resources. Phenol and phenol derivatives are highly toxic compounds for human and animal health and are therefore considered important contaminants. AOX is a phenolic organic compound released into the environment through wastewater from many industrial activities, such as pulp and paper, petrochemical, plastics and polycarbonate industries. Thus, the strict environmental criteria forced industries to treat their effluents and limit the release of these compounds into the environment. So far, some physico-chemical treatment methods such as advanced oxidation, and biological processes such as aerobic and anaerobic digestion have been applied to the degradation and removal of these compounds from polluted waters. However, there is a need to develop more efficient and cost-effective methods to replace conventional methods. In this study, Fe_3O_4/ZnO nanometrials were synthesized by chemical precipitation. The nanomaterials obtained were used to remove the AOX from the effluents. The obtained results showed an effective AOX removal with the synthesized nanomaterials.

5.2.2 Introduction

The pulp and paper (P&P) industry is now challenging to comply with the restricted environmental regulations. The effluents generated from pulp and paper industry commonly have a high chemical oxygen demand (COD). Moreover, they represent very low biodegradability (defined as the ratio of BOD_5/COD) [217] which make them very hard to be removed by the conventional treatment methods [5] For instance, treatment of the effluents from a pulp and paper mill by using a sequential anaerobic and aerobic treatment in two steps bioreactor resulted 70%, 42% and 39% removals of colour, COD and adsorbable organic halides (AOX), respectively, in 15 days [314].

The amounts of the effluents produced and the concentration of AOX in the produced effluents are highly dependent to some parameters such as the pulping process applied, the extent of the chemical additives, and the amount of water consumed during the production of bright pulp. In many countries through the world, in both traditional and emerging P&P producers [704] such as United States [705], China [706], and India [707], the effluents from pulp and paper mills are considered a major source of environmental pollutants. The presence of AOXs as well as other toxic substances in the content of pulp and paper mill effluents can potentially induce toxicity in the receiving environment, especially in the aquatic environments [165,708,709]. Although the developments occurred in the pulp and paper mill effluents treatment methods have drastically reduced the toxicity of the final discharged effluents however, pollutants such as AOXs continue to be found in the final treated effluents [710].

In recent years, nanomaterials have been widely used in many applications such as for the removal of environmental contaminants. Hence, various methods have been developed for the synthesis of nanomaterials with especial properties. Magnetite (Fe_3O_4), a member of spinel type ferrite, has been widely used in many applications. Various methods have been applied so far for the synthesis of magnetite. The main advantages of magnetite for environmental applications is the magnetic properties of these materials. Combination of these materials with high efficiency materials such as zinc oxide [711] can considerably enhance the efficiency of these materials to benefit from the cumulative advantages of such combinations.

In this study, a composite consisting of magnetite and zinc oxide have been prepared to remove the AOXs from a Kraft pulping process using Taguchi experimental design methodology.

5.2.3 Materials and Methods

All the reagents including Ferric chloride ($FeCl_3.6H_2O$), ferrous sulfate ($FeSO_4.7H_2O$), zinc acetate ($ZnAC_2.2H_2O$), ammonium carbonate ($(NH_4)_2CO_3$), aqueous ammonia (NH_4OH), Sodium citrate, acetone and ethanol, hydrogen peroxide used were all reagent grade.

5.2.3.1 Synthesis of Fe_3O_4 MNPs

A co-precipitation from a mixture of Fe(II) and Fe(III) salt solutions with the addition of ammonia solution was used to synthesis the magnetite nano particles. The reaction for the synthesis of magnetite is as follows:

$$Fe^{2+} + 2Fe^{3+} + 8NH_3.H_2O \rightarrow Fe_3O_4 \downarrow + 8NH^{4+} + 4H_2O$$

The synthesis was performed in a 500 mL three-open neck flask reactor. The central neck was housed with a mechanical overhead stirrer (IKA Eurostar 40), fixed at 250 rpm. The reactor was placed in a water bath to provide a temperature of 35◦C during the synthesis process. The reaction was performed under aerobic condition to allow the partial oxidation of Fe(II) to Fe(III). In experiments, 6.1 g $FeCl_3{\cdot}6H_2O$ and 4.2 g $FeSO_4{\cdot}7H_2O$ were dissolved in 100 mL of deionized water. 20 mL of base in the form of 30% ammonia: water was added to initiate synthesis process at the rate of 10 mL/min using a Watson Marlow 101U/R peristaltic pump. After addition of the base, the stirring was continued for 30 minutes whilst keeping the reactor at stable temperature condition. By finishing the precipitation of the black precipitate, the mixture was cooled to room temperature, and the magnetite nanoparticles was collected using a permanent magnet and washed three times with 50 mL of deionized water

5.2.3.2 Sodium citrate modification of Fe_3O_4 MNPs

The surface of Fe_3O_4 MNPs was modified by the reaction of the magnetite nanoparticles with sodium citrate. In the typical procedure, 4 g of magnetite nanoparticles and a solution of sodium citrate (200 ml, 0.5 M) were mixed well the reactor. The ultrasonic irradiation using an ultrasonic cleaning bath for 30 min. Then, the mixture was stirred for 12 h under a temperature of 60 ˚C. After collection the precipitates, they washed with acetone 3 times.

5.2.3.3 Synthesis of Fe_3O_4/ZnO nanocomposite

The surfaced modified magnetite nanomaterials were dispersed in 100 ml deionized water. Ultrasonic irradiation was applied for 30 min to achieve a stable ferrofluid as a precursor for the synthesis of Fe_3O4/ZnO nanocomposite. Then, 30 mL of the precursor was transferred to a three-neck reactor. In parallel, 12.16 g of zinc acetate dihydrate and 7.6 g ammonium carbonate were separately dissolved in 100 mL od deionized water. The two solutions, were introduced to the magnetite precursor using a peristaltic pump under a rate of 15 mL/min. The final precipitates were collected and washed with water, aqueous ammonia and ethanol. The last phase of the synthesis was the calcination of the prepared powders under 350 ˚C for 3 h.

5.2.3.4 Characterization

Crystallographic characterization of the prepared nanomaterials was performed using X-ray diffraction (XRD) analysis (Rigaku, Geigerflex, Japan) in the 2θ range from 20° to 100° with a goniometer speed of 2°/minute.

Transmission electron microscopy (TEM) by Hiatchi H9000na, Japan operated at 300 kV acceleration voltage was assisted to study the morphology of the synthesized composite nanomaterials. Particles specific surface area is assessed by gas adsorption with a Micromeritics Gemini V2 (USA) equipment. Brunauer–Emmett–Teller (BET) isotherm was used to calculate surface area of the materials.

5.2.3.5 AOX removal experiments

The effluents were obtained from a local pulp and paper mill which uses Kraft pulping process for the production of pulp and paper. The effluent was characterized before the experiments. Batch experiments for the removal of AOX were carried out in the 250 mL flasks equipped with overhead mechanical stirring (IKA Eurostar 40) at 250 rpm. The nanomaterials were dispersed into 100 ml of effluent. The temperature was controlled using a heating bath. Various operational conditions according to Table 5.2.1 were studied for their effects on the removal of AOX from the effluents.

Table 5.2. 1. Studied experimental variables.

Conditions	Time (min)	NMs dosage (g/L)	Light	H_2O_2 Conntration (mL/L)
Levels	15	0.5	UV	1
	30	1	Visible	2,5
	60	2	Dark	5

A Taguchi L-9 statistical design [712] (Table 5.2.2) was designed to study the effect of operational conditions on the removal of AOX from the effluents. The larger S/N the better (Eq. 1) was utilized to determine the relative importance of the studied parameters. five experimental variables i.e. reaction time, light, hydrogen peroxide concentration, and the effect of nanomaterials dosage in the reaction medium were studied in order to identify the relative importance of the variables.

$$\frac{S}{N}[dB] = -10\log\frac{1}{n}\left(\sum_{i=1}^{n}(\frac{1}{Y_i})^2\right) \qquad \text{Eq. 1}$$

In this equation, Y_i is the response data of the Taguchi statistical design, and n is the number of runs [585,713].

Table 5.2. 2. The L-9 Taguchi experimental design for this study.

Runs	Time (min)	Light	H_2O_2 (ml/L)	NMs dosage (g/L)
1	15	UV	1	0,5
2	15	Visible	2,5	1
3	15	Dark	5	2
4	30	UV	2,5	2
5	30	Visible	5	0,5
6	30	Dark	1	1
7	60	UV	5	1
8	60	Visible	1	2
9	60	Dark	2,5	0,5

5.2.4 Results and discussion

5.3.4.1 Nanomaterials Characterization

The XRD pattern of the prepared Fe_3O_4 nanoparticles is presented in Fig. 5.2.1. The sample was composed of two different phases which were indexed for Fe_3O_4 (JCPDS No. 01-078-3148) and ZnO (JCPDS No. 01-089-0511). The TEM photograph of the Fe_3O_4 (Fig. 5.2.2) illustrated the formation of small Fe_3O_4/ZnO particles less than 10 nm in diameter. A remarkable increase in particle size from 10 nm (Fe_3O_4 MNPs) to 30 nm (Fe_3O_4/ZnO) can also be observed in Fig. 5.2.2. The BET specific surface area of Fe_3O_4/ZnO sample was determined as 25 m^2/g.

5.2.4.2 Effluent Characteristics

The results of the characterization of the D0 sample is presented in Table 5.2.3.

Table 5.2. 3. Characteristics of the effluents.

Characteristics	Values
Effluent	D0
COD	2925 (mg/L)
VFA	162 (mg/L)
BOD_5	77
pH	1.9
AOX	135 (mg/L)

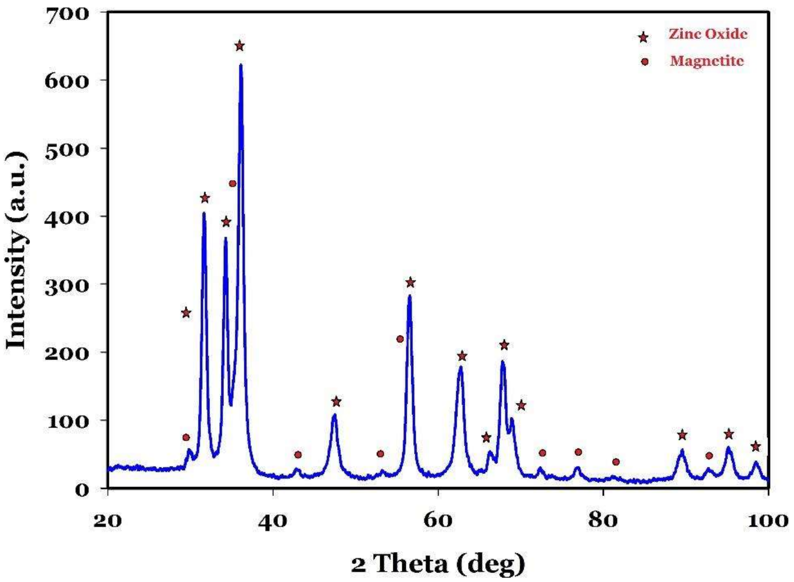

Fig. 5.2. 1. XRD pattern of the Fe_3O_4/ZnO nanocomposite. Two different phases can be identified according to the JCPDS database.

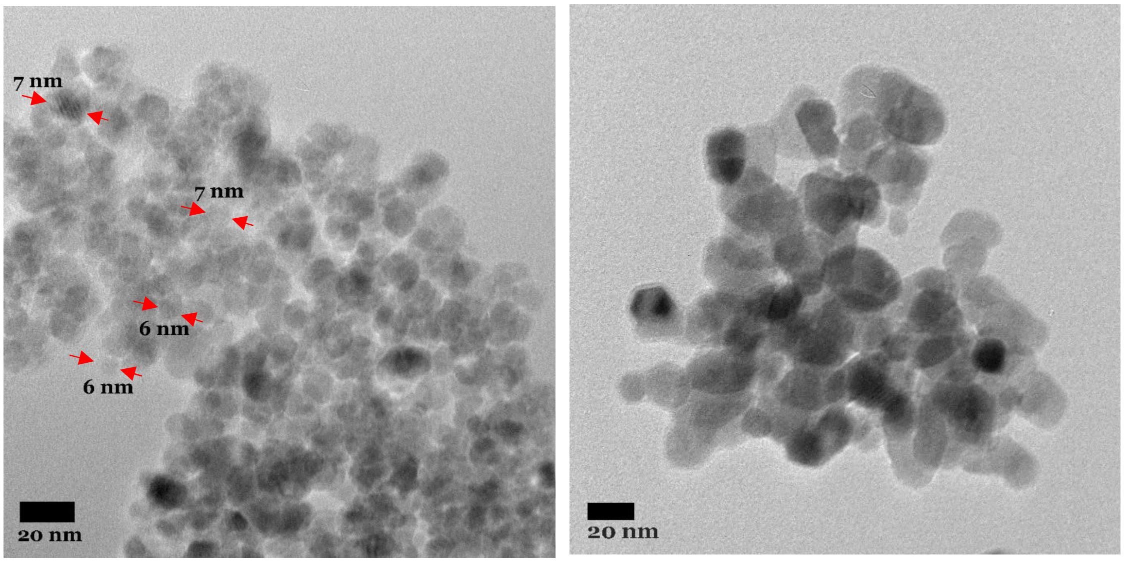

Fig. 5.2. 2. TEM images of Fe_3O_4 nanoparticles (left) and Fe_3O_4/ZnO nanocomposite (right).

5.2.4.3 Optimization of AOX removal with Fe_3O_4/ZnO nanocomposite

Table 5.2.4 represents the results of the removal of AOXs according to the L-9 experiments designed according to the Taguchi approach. In this table, the signal to noise ratios of the runs have been also presented.

Table 5.2. 4. Values of AOX removal (%) as the response data according to the L-9 Taguchi experimental design.

Runs	Time (min)	Light	H_2O_2 (ml/L)	NMs dosage (g/L)	Removal (%)	S/N ratio

1	15	UV	1	0,5	29	29,39
2	15	Visible	2,5	1	39,0	31,82
3	15	Dark	5	2	41,0	32,26
4	30	UV	2,5	2	46,0	33,25
5	30	Visible	5	0,5	35,0	30,88
6	30	Dark	1	1	42,0	32,47
7	60	UV	5	1	51,0	34,15
8	60	Visible	1	2	49,0	33,80
9	60	Dark	2,5	0,5	38,0	31,59
Optimum	60	UV	5	2	64	

Fig. 5.2.3 shows the L-9 orthogonal array of the studied factors and their combined effects on the removal of AOXs from the D0 effluents. The strongest statistical relevance is for the NMs dosage followed by the reaction time, hydrogen peroxide concentration and the light. The highest S/N ratio difference between various levels of an individual parameter belongs to the S/N (NMs dosage 1 g/L) – S/N (NMs dosage 0.5 g/L). It means that the removal reaction performed very fast in the presence of higher dosages of the nanomaterials. This can illustrate the effect of providing higher surface area for the generation of strong hydroxyl radicals in the presence of catalyst [714]. The hydroxide radicals are normally produced on the surface of the catalyst facilitating the decomposition of the AOX compounds.

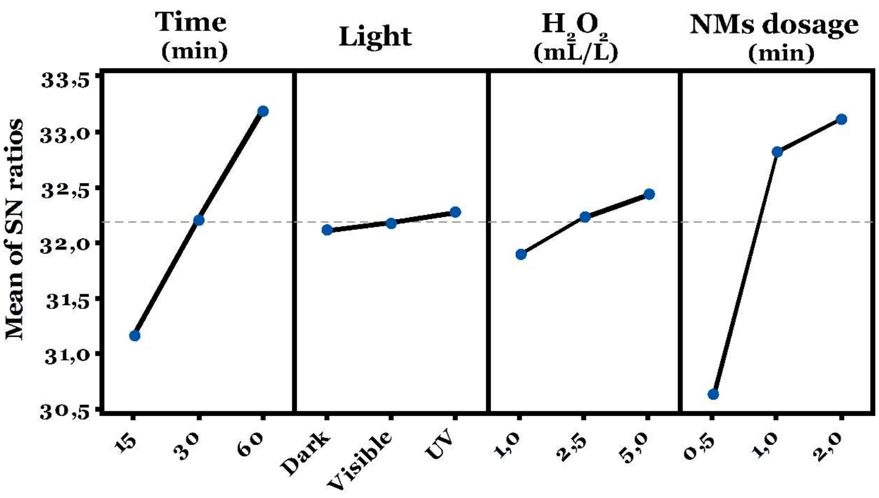

Fig. 5.2. 3. Variation of the calculated S/N ratios for the studied experimental conditions.

The reaction time has also a significant role in the removal of AOXs from the effluents. In fact, the removal efficiency was doubled when the reaction time increased from 15 min to 60 min. the importance of the reaction time on the removal of complicated organic compounds has been also reported by other recent studies [34]. The concentration of hydrogen peroxide and the light had also increasing impacts on the removal of AOX due to the generation of higher amount of reactive hydroxyl species. However, the relative importance of these two factors was evaluated less compared to the dosage of the nanomaterials and the reaction time. Under optimum conditions, Table 5.2.4, 64% of the AOXs were removed from the effluents (Fig. 5.2.4).

Fig. 5.2. 4. Effluents before treatment with nanomaterials (left) and the sample of the treated effluents under optimum conditions (right).

This is the first report for the removal of AOX using Fe_3O_4/ZnO nanocomposite indicating efficient removal of AOX from the effluents. There are a limited number of reports in the literature for the removal of AOX using nanomaterials. For instance, Sharma & Kumar, (2016) [716] achieved maximum 48% of AOX removal from a paper industry effluent using 1 g/L of Mn_3O_4-CeO_2 after 2 h of reaction. Due to their magnetic properties, Fe_3O_4/ZnO nanocomposite can be recovered using a magnet after treatment of the effluents.

5.2.5 Conclusion

In this study, magnetite nanomaterials were synthesized and characterized to be applied in the removal of AOX from pulp and paper mill effluents. The results of this study clearly indicated the efficiency of catalytic removal of this highly toxic compounds by using the advanced oxidation system with the application of Fe_3O_4 / ZnO nanoparticles.

5.3 Boosting the Biodegradation of Phenolic Wastewaters with Acclimatized Activated Sludge - A kinetic Study

5.3.1 Abstract

This paper reports the biodegradation of phenol with promoted efficiency in a sequencing batch reactor (SBR) after a precise acclimatization procedure with mixed culture activated sludge. The effects of parameters such as initial temperature, initial phenol concentration, and acclimatization on the phenol biodegradation were studied during the experiments. Acclimatization greatly enhanced the biodegradation rate of phenol, whereas temperature showed no significant effect on the biodegradation rates over the studied conditions. After 60 days of acclimatization, the activated sludge was able to degrade phenol at the maximum rate of 1.20 (g phenol/g VSS/h) at pH ~6 and 18-20 °C. Other kinetic parameters were also estimated as the half-saturation constant (K_S) = 1869.99 mg/L and the inhibition constant K_I= 85.80 mg/L, calculated according to the Haldane kinetic model. These results represent the highest phenol biodegradation efficiency reported so far, based on our best knowledge. In addition, the inhibitory effects were identified at concentrations higher than 500 mg/L. The system was also showed a high degree of stability and resistance to a load shock by the initial concentration of phenol from 500 to 1000 mg/L.

Keywords: Phenolic wastewater, Activated sludge, Sequencing batch reactor, Kinetic study.

5.3.2 Introduction

Although water is considered an abundant natural resource, only less than 1% can be used for human consumption [342,343]. Rapid industrialization is responsible for the generation and discharge of a huge amount of industrial effluents all over the world [9,566]. A major compound in the effluents from various industries (such as textile, oil refining, pharmaceuticals, etc.) is phenol and its derivatives [717–719]. Various studies have indicated that discharging phenolic effluents without efficient treatment can lead to severe toxic effects to aquatic organisms [720,721] and it can also lead to serious human health problems [8,722,723]. It has been demonstrated in the literature that such compounds can induce toxic effects for both human and aquatic life even at relatively low concentrations (9-25 mg/L)[724]. Hence, discharging the industrial wastewater without appropriate treatment method(s) applied may lead to subsequent environmental and health problems. Hence, the development of sustainable treatment methods to deal with phenolic compounds in the content of industrial effluents is highly welcome. Treatment efficiency is considered as one of the most important sustainability criteria [2] and as an essential need for the treatment technologies to deal with industrial effluents. In this regard, various physicochemical (e,g., coagulation, adsorption, oxidation, etc.) and biological methods (e.g., fungal treatment, aerobic treatment, anaerobic digestion, etc.)[5,353,552,725,726] have been developed and applied so far for the treatment of industrial effluents and have shown various efficiencies for the degradation or removal of phenolic compounds. Among the conventional methods for the treatment of industrial effluents, activated sludge (AS) have been widely adopted by various industries. However, promoting their efficiency for the treatment of phenolic effluents is considered a field of interest among the researchers [727]. Promoting the efficiency of such systems to deal with high strength industrial effluents can both increase the reliability of these methods to satisfy the ongoing need for clean water resources and to decrease the treatment operating costs, as one of the main criteria considered by the industries [565]. Xavier et al. (2009) [565] in their comparative study concluded that the activated sludge can present a high degree of efficiency for the treatment of Kraft pulp and paper mill effluents (higher than aerated lagoons), except for the treatment of phenolic compounds. Such finding can reflect the need for promotion AS efficiency for the treatment of phenolic compounds and can offer an opportunity for their wider application for the treatment of real industrial effluents.

This work aimed to apply an acclimatization procedure for the seeding activated sludge in order to enhance the phenol removal efficiency at high concentrations up to 1,000 mg/L. A kinetic study according to Haldane kinetic model clearly indicated a high degree of efficiencies of the acclimatized sludge to deal with high concentrations of phenol (up to 1000 mg/L) and also to tolerate the shock in the initial concentrations of phenol in the influent.

5.3.3 Materials and Methods

5.5.3.1 Acclimatization

Acclimatization can give rise to enhanced biomass population which could be adapted to the toxic compounds [728]. Acclimatization of activated sludge towards increasing phenol concentration, including 50 mg/L (days 1-3), 100 mg/L (days 4-6), 200 mg/L (days 7-12), 300 mg/L (days 13-18), 400 mg/L (days 19-24), 500 mg/L (days 25-30), 600 mg/L (days 31-36), 700 mg/L (days 37-42), 800 mg/L (days 43-48), 900 mg/L (days 49-54) and 1000 mg/L (days 55-60) was carried out using a cylindrical reactor with an operating volume of 5 L under batch mode. The seed sludge for acclimatization was brought from a full-scale sewage treatment plant located in Aveiro, Portugal. Activated sludge was acclimatized with nutrient water (base mix) as reported by Hussain et al., (2015) [729] with the composition including bactopeptone (188 mg/L), ammonium chloride (172 mg/L), magnesium sulfate (49 mg/L), dipotassium hydrogen phosphate (250 mg/L), and sodium bicarbonate (14.7 mg/L). At the end of the acclimatization period, micrographs of the sludge were achieved using ZEISS (imager A.2) microscope.

5.3.3.2 Phenol volatilization

Volatilization of phenol was carried out without biomass in order to determine the potential of phenol loss under aerated condition [730]. Phenol (Riedel-de Haën, 33517) was used in all experiments. Hence, any loss in phenol concentration can be attributed to air stripping from aeration. Tests were performed in a 5 L reactor with phenol containing effluent at various concentrations of 250, 500, and 1000 mg/L. Simultaneous aeration (using air stone diffusers) to keep the dissolved oxygen over 1 mg/L, and mixing (using a mechanical overhead stirrer (IKA Eurostar 40), operating at 100 rpm) was applied to the effluents in all experiments. 10 mL of the sample was collected from the reactor at the beginning of the test and then after every one hour for phenol analysis. The total duration of the test was six hours. The phenol content of the collected samples was determined to examine any loss of phenol by volatilization. A UV-vis spectrophotometer (T80+, PG Instruments, UK) was utilized for monitoring the absorption intensity at 500 nm, as an indicator for the phenol concentration in the medium, according to 4-aminoantipyrene method [731]. 10 mL of sample was drawn in each sampling point and was analysed after vacuum filtration. Volatile suspended solids (VSS), chemical oxygen demand (COD) and sludge volume index (SVI) was measured in accordance with the standard methods [731].

5.3.3.3 Phenol biodegradation experiments

Upon the completion of acclimatization phase, the reactor was set to operate under sequencing batch reactor (SBR) mode. The reactor was operated sequentially within a 12 h cycle, including 15 min of influent filling, 660 min of aeration, 30 min of settling, and 15 min of effluent discharging. The effluent was drawn from the middle port of the reactor column (2.5 L), and the resulting hydraulic retention time (HRT) was 24 h. The reactor was operated for 5 days under SBR mode at 250 mg/L of phenol, and then for 5 days at 500 mg/L and finally phenol concentration was increased to 1000 mg/L at the last day of experiments. Samples were taken from the reactor at pre-determined time intervals. The desired SRT during SBR mode was set by controlling the amount of sludge wasted from the reactor in each cycle. The initial desired mixed liquor suspended solids (MLSS) concentration was provided by incubating a certain amount of seeding sludge into the reactor. Parallel batch tests were also carried out in order to study the effects of the initial temperature (15-18 °C and 30 °C) and the effects of acclimatization process on the performance of the mixed microbial community for the biodegradation of phenol.

5.3.3.4 Kinetic study

Haldane equation (Eq. 1) was used in order to study the Kinetic of the phenol biodegradation data and to compare them with the results achieved so far in the literature. This equation is used to describe the biodegradation rate of an inhibitory substrate [732,733].

$$q = \frac{q_{max} S}{K_S + S + \frac{S^2}{K_I}} \qquad \text{Eq. 1}$$

In this equation, q and q_{max} are the specific substrate biodegradation rate (SSBR) and maximum substrate biodegradation rate (MSBR) (g phenol/ g VSS/h), respectively. S, K_s, and K_I are the substrate concentration, half-saturation constant and the inhibition constant (mg phenol/L), respectively. The least-square error methodology was assisted in order to estimate the kinetic parameters including K_S and K_I. q_{max} was accordingly calculated according to the Eq. 2, $\hat{q}$ refers to the maxium value of q when there is an inhibition [734].

$$\hat{q} = \frac{q_{max}}{1+2\sqrt{\frac{K_S}{K_i}}} \qquad \text{Eq. 2}$$

5.3.4 Results and Discussion

Fig. 5.3.1 shows micrographs of the activated sludge community after the acclimatization process. Based on these images, it can be stated that the activated sludge after acclimatization is mainly consisted of microorganisms' flocks forming dense colonies which may belong to phenol degrading microorganisms (Fig. 5.3.1, a and b).

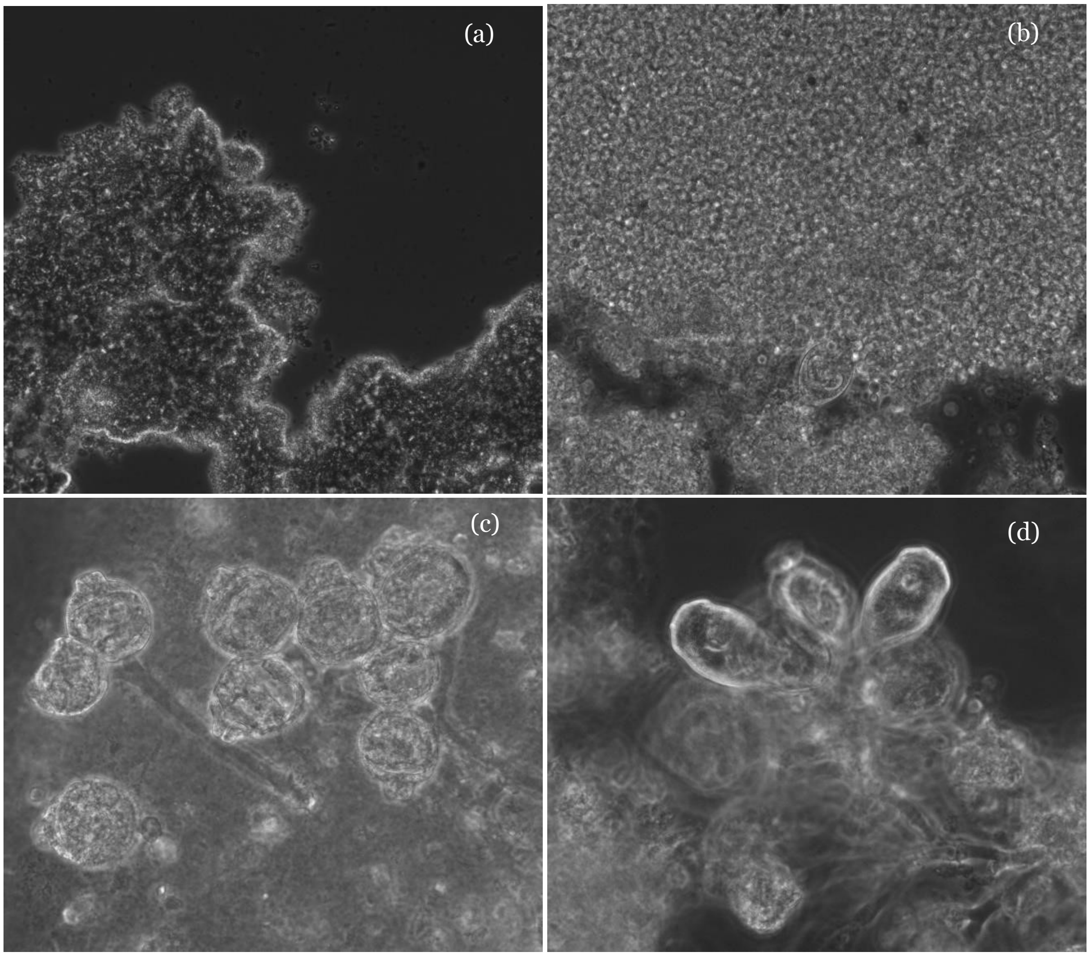

Fig. 5.3. 1. Micrographs of the acclimatized activated sludge mixed culture, mainly consisted of microorganisms' flocks forming dense colonies (a and b), and some identified species including *Opercularia sp.* species (c) and *Vorticella sp.* (d).

Some species such as *Opercularia sp.* [735](Fig. 5.3.1, c) and *Vorticella sp.* [736](Fig. 5.3.1, d) can also be identified in the activated sludge content. Kachieng & Momba, (2018) [737] indicated that the synergistic effect of such species can also enhance the biodegradation of wastewaters contaminated with polycyclic aromatic hydrocarbons. According to these findings, it can be suggested that the enhanced activated sludge consortium is well-acclimatized for the biodegradation of phenol.

5.3.4.1 Phenol volatilization

Based on the phenol volatilization tests, it was observed that there was negligible loss of phenol at the studied phenol concentrations (<5% in all cases). The results are in agreement with the results previously reported in the literature for volatilization of phenol [729,738].

5.3.4.2 Phenol biodegradation tests

5.3.4.2.1 Effect of temperature

Phenol degradation experiments at room temperature (15-18 °C) and a higher temperature of 30 °C were carried out in order to explore the effect of temperature on the biodegradation of phenols by the acclimatized mixed enhanced culture under batch reactor mode. Fig. 5.3.2 shows the effect of the operating temperature on the phenol biodegradation. As can be observed in this figure, at phenol concentration of 250 mg/L it was completely biodegraded in both experimental conditions after 150 min of biodegradation test. There was no noticeable difference between the phenol biodegradation extent over studied operating temperatures. Similar results were achieved in the literature. For instance, Duan, (2011) [732] studied the effects of operating temperature on the biodegradation of phenols over a range of 25 °C to 40 °C using a mixed culture of microorganisms. They concluded that under optimum pH around 6, the temperature had no significant impact on the biodegradation rate. Similarly, Adav et al. (2007) [739] indicated that various operating temperatures (25-40 °C) had no considerable effect on the biodegradation performance using *Candida tropicalis* isolated from an aerobic granule. However, there are some reports in the literature for a better performance of the phenol biodegradation performance under higher temperatures [740]. The difference in the sludge characteristics and microbial communities can be considered as a reason for the difference in the results achieved in literature [732]. According to the results achieved in this study, effective biodegradation of phenol can occur under room temperature (18-20 °C) which can suggest a high ability of the acclimatized community for the phenol biodegradation. According to the results obtained, room temperature condition was selected for the phenol biodegradation tests under SBR conditions.

5.3.4.4.2 Effect of initial phenol concentration

A sequencing batch reactor was utilized in order to test the phenol biodegradation using acclimatized activated sludge with phenol concentrations of 250-1000 mg/L at pH ~6 and room temperature conditions. According to Fig. 5.3.3, the acclimatized mixed culture sludge almost completely degraded the phenol in 150, 180, and 390 min respectively, corresponding to COD removals of 85, 83 and 86%. The SVI of the sludge also increased during the tests from 102 cm^3/g (day 1) to 80.7 cm^3/g in day 5 and to 69.5 cm^3/g at the final day of the SBR experiments, indicating that the sludge became denser with improved settleability characteristics.

kinetic parameters were estimated according to the Haldane kinetic model. Fig. 5.3.4 presents the SSDR plotted against various initial phenol concentration in ASBR experiments.

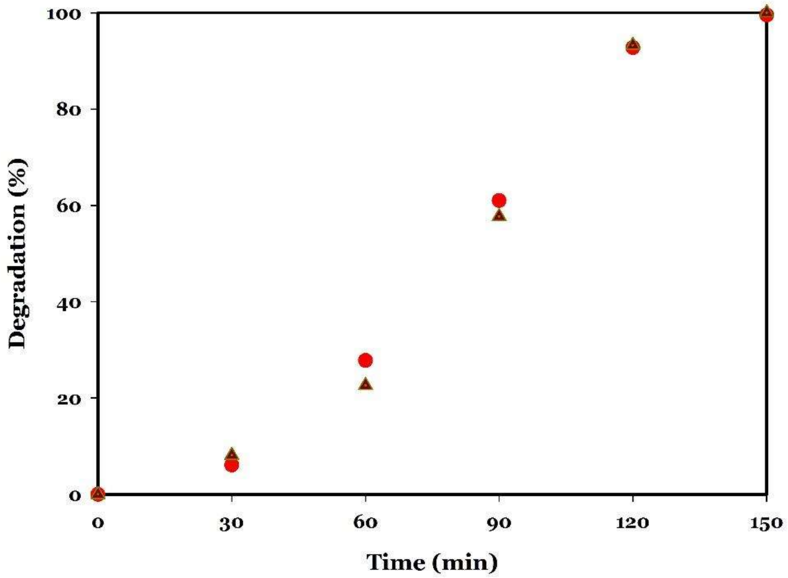

Fig. 5.3. 2. Batch tests for phenol degradation by the acclimatized mixed enhanced culture under various temperature, i.e., 15-18 °C (●), and 30 °C (▲), MLVSS=1 g/L, and initial phenol concentration of 250 mg/L.

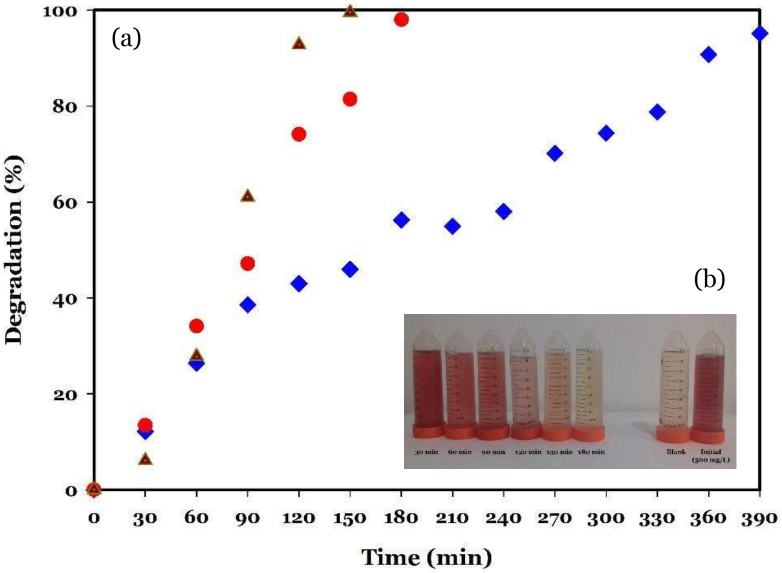

Fig. 5.3. 3. Sequencing batch tests for phenol biodegradation with the enhanced mixed culture under various initial phenol concentrations, i.e., 250 mg/L (▲) (MLSS=1 g/L), 500 mg/L (●)(MLSS=1.4 g/L) and 1000 mg/L (MLSS=2 g/L) (◆) (a). The sharp decrease in the colour of the samples prepared according to the 4-aminoantipyrene method [731] **(Initial phenol concentration=500 mg/L), (b).**

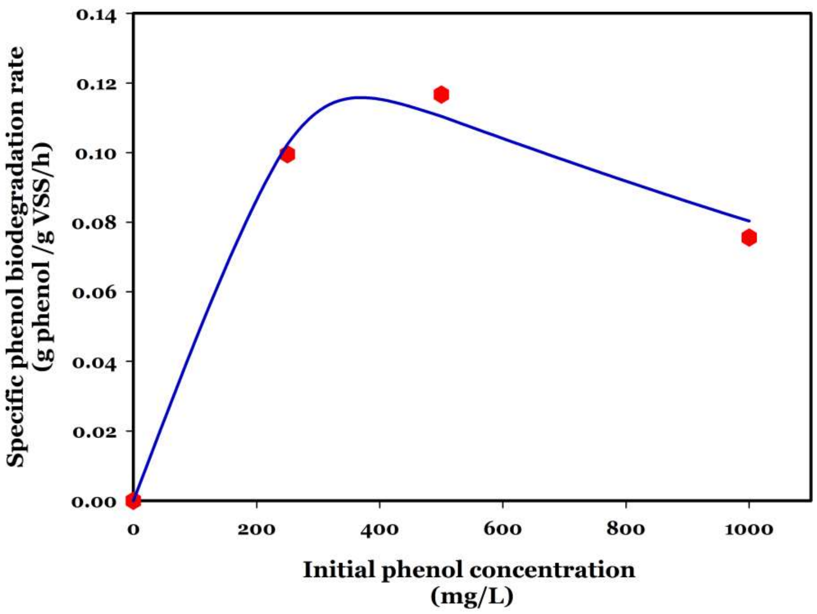

Fig. 5.3. 4. Specific phenol biodegradation rate versus initial phenol concentration. The kinetic parameters are q_{max}=1.205 (g phenol/g VSS/h), K_I=85.80 mg phenol/L, K_S=1869.99 mg phenol/L and R^2=0.98.

Fig. 5.3.4 shows that SSDR increases with an increase in the initial phenol concentration from 250 to 500 mg/L, and reaches a maximum value at 0.117 (g phenol/g VSS/h). However, SSDR decreases with increasing the initial phenol concentration to 1000 mg phenol/L (SSDR=0.076 (g phenol/g VSS/h)). These results can suggest that the concentration of phenol only higher than 500 mg phenol/L could slightly inhibit the biodegradation behaviour of the acclimatized microorganisms. Modelling the phenol biodegradation data according to the Haldane equation was utilized in order to evaluate the phenol biodegradation kinetics. The kinetic parameters were extracted as q_{max} = 1.205 (g phenol/g VSS/h), K_I = 85.80 mg/L, and K_S = 1869.99 mg/L with the correlation coefficient (R^2) of 0.98. The obtained values in this study are much higher than those reported so far in the literature. For instance, Hussain et al. (2015) [729] achieved a q_{max} = 0.355 (g phenol/g VSS/h) and Duan, (2011) [732] reached a q_{max}=0.4695 (g phenol/g VSS/h).

Table 5.3.1 presents a summary of the kinetic parameters achieved in this study and a comparison of them with results obtained from various similar studies.

Table 5.3. 1. A summary of the Kinetic constants calculated by studies considering aerobic phenol biodegradation using pure or mixed cultures.

Initial phenol Conc. (mg/L)	q_{max} (g/g/h)[a]	K_s (mg/L)	K_I (mg/L)	Strain	Ref.
100-500	NA	NA	NA	*B. thermoleovorans sp. A2*	[741]
0-1970	NA	NA	NA	Mixed culture[b]	[742]
250, 500, 1000	0.39	NA	NA	*Candida tropicalis*	[739]
2500	0.438	29.5	72.4	Mixed culture	[724]
23.5–659	0.3095	74.65	648.13	Mixed culture	[727]
0-1500	0.4695	603.9869	28.4860	Mixed culture	[732]
25-1450	0.143	87.44	107.06	Mixed culture	[743]
100–700	0.150	51.8	404.04	Mixed culture	[744]
500-3000	0.355	603.80	40	Mixed culture	[729]

250, 500, 1000	1.20	1869.99	85.80	Mixed culture	This study

a. g phenol/g VSS/h
b. Extracted from polluted soil

5.3.4.4.3 Effects of acclimatization

In parallel to sequencing batch tests (initial phenol concentration of 500 mg phenol/L), a batch test was operated with the as-received sludge from the same wastewater treatment plant (Aveiro, Portugal), in order to compare the phenol biodegradation efficiency using acclimatized activated sludge with as-received sludge at pH ~6 and room temperature conditions. The results of the phenol biodegradation tests under the studied conditions are presented in Fig. 5.3.5.

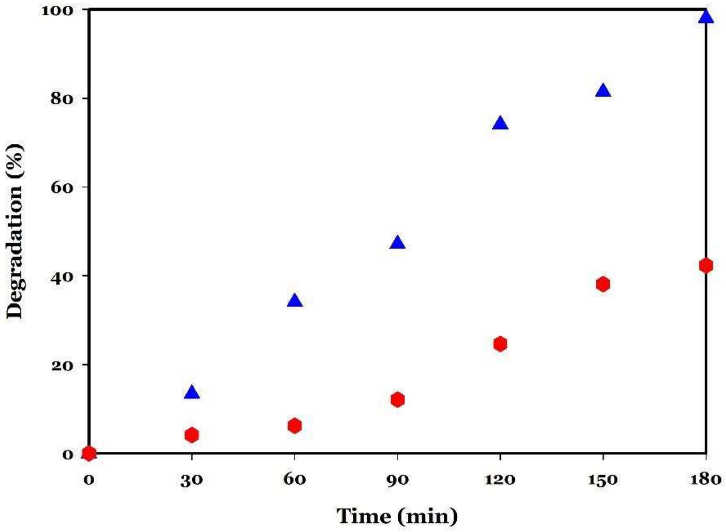

Fig. 5.3. 5. Batch tests for phenol degradation by the enhanced mixed culture (▲) (SVI=80.71 cm3/g) and as-received sludge (⬢)(239.28 cm3/g). Initial phenol concentration of 500 mg/L, at 15-18 °C, MLVSS=1.4 g/L.

According to Fig. 5.3.5, the acclimatized mixed culture sludge almost completely degraded the phenol in 180 min, while with as-received sludge only 42% of the phenol degradation was achieved at the same time interval. The results achieved can support the hypothesis that the sludge has been well adapted for the degradation of phenolic effluents.

5.3.5 Conclusion

This study reports the highest (in our best knowledge) phenol removal kinetics with a mixed enhanced culture of activated sludge after 60 days of acclimatization process. While the effect of temperature at 15-18 °C and 30 °C had no noticeable effect on the biodegradation of phenol with the acclimatized activated sludge, the effect of various initial concentrations on the extent of the phenol biodegradation using a sequencing batch reactor were considerable. The maximum biodegradation rate (q_{max}) of 1.20 (g phenol/g VSS/h) at pH ~6 and 18-20 °C was achieved in this study according to the Haldane kinetic model, much higher than previously reported in the literature. The inhibitory effects identified at concentrations higher than 500 mg/L. The resistance of the system to the shock load by the increase of the initial phenol concentration from 500 to 1000 mg/L without considerable drop on the phenol biodegradation rate can suggest the ability of the acclimatized sludge to be applied for the treatment of industrial effluents laden with high concentrations of phenolic compounds in very short degradation time. The acclimatized sludge also showed much higher biodegradation efficiency when compared to as-received activated sludge with higher settleability characteristics.

Chapter 6: General Conclusion and Future Outlook

6.1 General conclusion

The present study aimed to assess the sustainability of various physico-chemical and biological treatment methods to deal with industrial effluents. From the results of this thesis, the following conclusions can be driven:

- The microbial activity for the treatment of polluted industrial effluents can be highly influenced by the operating conditions including HRT, OLR, operating temperature, and pH, as well as the presence of inhibitory elements such as chlorinated organic compounds (AOXs). The effective application of physico-chemical and biological pre-treatments to enhance the biodegradability of the effluents from industrial activities can be considered a good solution to reduce the sensitivity of biological treatment technologies and to enhance the overall treatment performance.
- Application of advanced types of engineered nanomaterials can open a window to deal with highly polluted industrial effluents. sustainable development of nanomaterials for various applications demands specific properties to enhance their performance while minimizing subsequent drawbacks. In the present thesis, it was indicated that the application of green and effective methods such as ultrasonic irradiation can result in the combination of two characteristics that usually do not go together, i.e. crystallinity and high specific surface area, both of which are fundamental when using engineering nanomaterials for environmental clean-up applications.
- It was demonstrated in this thesis that the application of Tagguchi approach can considerably aid to control the properties of iron-based nanoscale particles synthesized by a liquid-phase reduction process. Working with this system revealed that both the (reductant/Fe^{3+}) ratio, (R), and the Fe^{3+}concentration, $[Fe_3^+]$, are the parameters that determine critical characteristics including particle crystalline phase composition, crystallinity and surface area although R has been revealed as the most important one. Furthermore, the surface composition of nZVI produced under UI appears populated by iron species with a higher ability to undergo oxidation which render them better suited to environmental clean-up applications. Thus, UI benefits smaller sized crystalline particles with more reactive surface which role in polluted water treatment warrants to be considered for optimizing efficiency and associated costs. It was also demonstrated in this thesis that ultrasonic irradiation phenomena can be considered a capable technology for the synthesis of ultrapure materials which can be used in environmental clean-up purposes, as well other related scientific fields. As an example, this thesis reported the growth of metallic copper using ultrasonic irradiation which can offer an environmentally friendly and efficient method for the synthesis of nanomaterials, especially for the applications which need to use high purity and well-developed crystalline structure of the metallic compounds.

- This thesis also aimed to assess the application of nanotechnology for water and wastewater treatment (which is currently in the stage to be transferred from lab and pilot scale to real applications) according to the sustainability criteria. Adoption of a fuzzy-Delphi approach aimed to rank the 17 identified according to their relative importance. Although the treatment efficiency and health and safety risks associated with the application of nanomaterials were identified the most important criteria, importance of all the studied criteria were ranked above “Fair”. Although nano-based techniques are in general very important and beneficial for the removal of emerging pollutants, enough attention should be paid to the selection of the appropriate type of nanomaterials. For instance, low-cost and non-toxic materials are very welcome for the environmental clean-up applications. The results of the study also indicated that magnetic based nanomaterials (such as zero valent nanoparticles) are preferable materials due to their high efficiency, low toxicity, relatively low cost and the ease of the recovery.
- According to the results achieved, nZVI particles with enhanced properties, synthesized by utilization of ultrasonic irradiation was tested to degrade organic dyes (methylene blue, as a case study) which are dominant in the wastewater from some industries such as textile factories. Such nanomaterials present an efficient performance regarding the degradation of the dye in a short reaction time. The pH of the reaction medium was also identified as a critical parameter for determining the dye removal efficiency of the synthesized nanomaterials.
- Recovery of the nanomaterials after being applied for the treatment purposes is also among the most important parameters for the selection and synthesis of the most sustainable nanomaterials for environmental applications. A novel ZnO/Fe_3O_4 on Bentonite nanocomposite prepared in this thesis showed acceptable photocatalytic decomposition of 2,4 dichlorophenol besides the ability to be recovered after being used. Magnetic nanocomposites were also tested for the degradation of AOXs from pulp and paper mill effluents and showed acceptable performance in such applications.
- Besides the attempts for the development of novel treatment technologies (such as oxidation with engineered nanomaterials) a framework was developed for the sustainability assessment of the best available technologies to deal with industrial effluents. Among the treatment methods studied, membrane technology was identified as the most suitable physico-chemical treatment method for recalcitrant compounds removal and anaerobic sludge blanket technology was identified as the most sustainable biological method to deal with highly polluted industrial effluents. The opportunities for each treatment method improvements have also been discussed in order to provide a

general future perspective, while activated sludge technology was identified as the most efficient technology to deal with industrial effluents.

- However, the biological methods have some limitations (such as process instability) to deal with complex compounds such as phenolic compounds which may be found in the most industrial effluents. Hence, this thesis was also aimed to develop the activated sludge treatment method to deal with high concentrations of phenol. After 60 days of acclimatization process, the sludge showed very high efficiency for the biodegradation of phenol with a high degree of resistance to the shock of initial phenol concentration increase.
- For the future studies, a critical review was also performed in this thesis in order to study the possible improvements in the membrane-based technologies in terms of treatment costs and process stability (which can be caused by membrane fouling process). The results indicated the possibility of integration of engineered nanomaterials and also biological treatment with the membrane technologies in order to overcome the existing barriers for the rapid development of membrane technologies for the treatment of industrial effluents.

6.2 Future Outlook: Membrane-based Technologies for Desalination and Industrial Effluents Treatment

New generations of membrane-based technologies, including the combination of membranes with other physico-chemical or biological methods have also proven their efficacy to deal with the industrial effluents. Luo et al. [746] suggested that an acceptable nitrogen and phosphorous removal can be achieved (up to 97% and 93%, respectively) using the submerged membrane photobioreactor (MBPR), consisting of an enclosed photobioreactor (PBR) [747,748] with a submerged or side stream membrane filtration process. Even though various studies have indicated the successful application of membrane technologies to deal with a wide range of toxic materials (such as chlorinated organic compounds [749,750]), it must be stated that this technique has some weaknesses regarding some dissolved organic compounds (DOCs), especially low molecular weight organic compounds, e.g., in the UF/MF range. On the other hand, advanced oxidation processes (AOPs) have proved their efficiency for the degradation of DOCs. For instance, TiO_2 modified with carbonaceous nanomaterials [751] has shown excellent performance in terms of high photocatalytic activity, good performance under solar irradiation, and easy to be collected for re-use. It has been well documented in the literature [106–109] that the generation of hydroxyl radicals, as powerful oxidation agents, are the basis of AOPs. Hence, a combination or integration of membrane separation technologies with AOPs (e.g., photocatalytic membrane reactors (PMRs), seems to be an appropriate solution to enhance the overall efficiency of the process and to overcome the limitations of both AOPs and membranes systems. Ganiyu et al. [753] reviewed the literature on the combination of AOPs with membrane technologies for the treatment of pharmaceutical residues and indicated the suitability of AOPs (i.e., ozonation, peroxone using O_3 and H_2O_2, UV/H_2O_2 system, photo-Fenton process, photocatalysis and electrochemical AOPs (EAOPs)) as pre-treatment stages for degradation of organic materials to prevent membrane fouling or as post-treatment stages in order to polish the treated effluents in the membrane systems. Li et al. [754] reviewed the degradation of dyes in the content of industrial effluents by a separation membrane coupled to an electrochemical advanced oxidation process (EAOP). They indicated that such an integration might improve the separation process as long as the operating parameters such as initial dye concentration, current density or electric field intensity, supporting electrolyte nature and concentration, pH, and temperature of the solution are suitably controlled. Furthermore, some important features have to be addressed for the successful combination of membrane technologies with other physico-chemical or biological treatments.

The application of pre-treatment step before membrane treatment can potentially enhance the overall efficiency and, may even prevent the system failure caused by membrane fouling. Such combinations were initiated in the 1980s. Canepa et al. [593] applied an integrated three-phase process (UF to adsorption to RO) at pilot scale to deal with OME. The interest in using membrane processes for the separation of volatile fatty acids (VFAs) from the fermentation broth has been well documented [755]. Among the membrane processes, ED has been tested by Scoma et al. [756] for the first time to separate the VFAs enriched effluent from the pre-treated fermentation of olive mill wastewater. Stoller and Bravi [758] studied various methods including coagulant-flocculants, photocatalysis (PC) using titanium dioxide nanomaterials (anatase) under UV light irradiation, and aerobic digestion (AD) to pre-treat OME before batch MF, UF and NF processes in sequence, with a final RO step. They concluded that all the pre-treatment processes are successful leading by UV/TiO_2 PC. Lu et al. [759] summarized the results of the studies on the combination of membrane-ozonation processes for the removal of PhACs. They highlighted that a post-treatment to NF by ozone (UV_{245}/O_3) (4 mg/L) [760] could result in <99% PhACs removal using such a combination. They also emphasized the successful combination of membrane technologies with Fenton and photo-Fenton processes [761], membrane/photocatalytic processes (e.g., with TiO_2 nanoparticles) [762], as well as electrochemical treatment processes [759].

Mitigation of membrane fouling has been considered another reason for the combination of membrane technologies with other physico-chemical or biological methods. For instance, the integration of MBRs with FO (to form an osmotic membrane bioreactor) has contributed to reduce membrane fouling by applying osmotic pressure difference, which is driven from FO [763–766]. Such a combination has shown enhanced efficiency for the treatment of EFs [766]. Another innovative combination is the coupling of MBRs with other biological methods, such as microbial fuel cells (MFCs) to form bioelectrochemical membrane reactors (BECMRs) [767]. Using such a technology, biological treatment of industrial effluents can be coupled with electricity harvesting. Anaerobic dynamic membrane bioreactors (AnDMBRs) [537,768,769] are another successful combination of membrane technologies with the biological treatment techniques, which have demonstrated a number of advantages over AnMBRs. Some of the advantages of these techniques include lower nutrient requirement, lower energy requirement, lower temperature sensitivity, higher potential for bioenergy recovery and better overall treatment efficiency [770,771].

In conclusion, membrane-based technologies have historically received extensive great deal of attention as the promising methods to deal with the polluted waters. Combination of Membrane-based technologies with other methods such as engineered nanomaterials can also make the treatment process more economically feasible and sustainable. Such advanced methods can considerably contribute to the overcoming of the traditional bottlenecks of membrane technologies (such as fouling properties) to deal with complex industrial effluents in order to focus on further enhancement of effluent quality towards the holistic concept of “one water” approach. At this stage, more studies on sustainability aspects of membrane technologies for the treatment of environmental contaminants will be needed. Technical, environmental, economic and social aspects of new combinations of membrane technologies have to be addressed for accelerating their transferring from the lab-scale and pilot-scale studies to real-scale applications.

Annex A: Ultrasonic irradiation as a green production route for coupling crystallinity and high specific surface area in iron nanomaterials -Supplementary information

- Mohammadreza Kamali, Maria Elisabete V. Costa, Gonzalo Otero-Irurueta, Isabel Capela, Ultrasonic irradiation as a green production route for coupling crystallinity and high specific surface area in iron nanomaterials, Journal of Cleaner Production, 211 (2019), 185-197. IF_5=6.35 https://doi.org/10.1016/j.jclepro.2018.11.127

A.1 Statistical Analysis

A.1.1 Signal to noise ratio

Taguchi experimental design, as a statistical method was developed by Genichi Taguchi. At first, it was mostly applied to improve the manufactured products quality. Recently, it has been applied in many fields such as engineering [712]. In this study, a Taguchi L-9 statistical design was designed to study the effect of operational conditions on the surface areas of the prepared iron-based nanomaterials, as response data. The larger is better algorithm was selected in order to optimize the surface area of the produced nanomaterials according to equation S-1:

$$\frac{S}{N}[dB] = -10\log\frac{1}{n}\left(\sum_{i=1}^{n}\left(\frac{1}{Y_i}\right)^2\right) \qquad \text{(S-1)}$$

In this equation, Y_i is the response data of the Taguchi statistical design, and n is the number of runs [585,713].

A.1.2 Verification

Verification test was carried out to confirm the validity of the predicted value of the optimum condition compared to the relevant experimental data. Minitab 17 was utilized to predict the result of the optimum settings. Experimental conditions of I=15 mL/min, Fe^{+3} concentration=40 mM and R=2 were selected as the optimal conditions according to the means of means graph (Fig. B.1). This results are in agreement with the achieved S/N ratios where R in the most important parameter and there is no significant difference was determined between various S/N ratios of I (P=0.912). The prediction result is 206.33 m^2/g (S/N ratio: 45.13) with no significant difference with the obtained experimental results with P-value of 0.076 greater than acceptable rang (0.05).

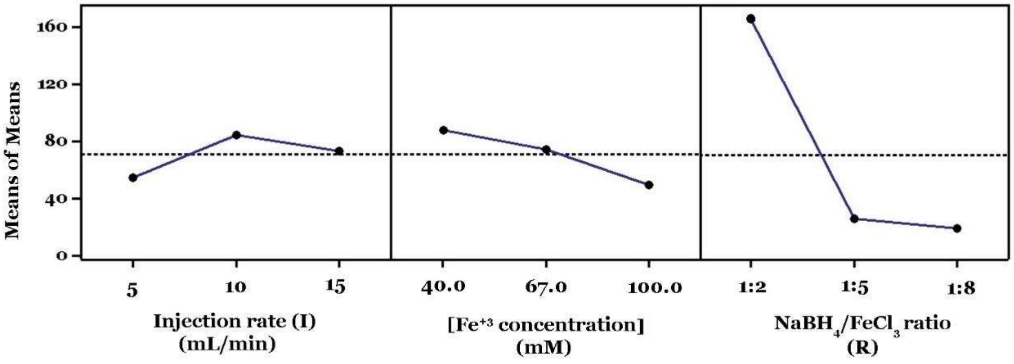

Fig. A. 1. Variation of the calculated means of means.

Table A. 1. The effect of the synthesis conditions on the morphology, shape, and specific surface area (BET) of nZVIs.

Synthesis Conditions				Properties		Crystallinity	Reference
[Fe^{+3}] (mM)	[Fe^{+3}] (mM)	Injection rate (mL/min)	Ethanol portion[a] (%)	Shape (TEM image)	BET (m^2/g)		
100	1:8	15	80	Spherical	20.50	Relatively high	This study
100	1:8	15	80	Spherical	50.60	Relatively high	
100	1:5	5	80	Spherical	41	Moderate	
71.7	1:5	2	-	Spherical	8.4	Relatively high	[587]
71.7	1:5	20	-	Whiskers	45.4	Moderate	
71.7	1:5	5	-	Spherical	8.55	N.G.	
71.7	1:5	10	-	Spherical	18.30	N.G.	
67	1:5	-[b]	80	Spherical	25	Moderate	[588]
18	1:3.7	~6.15	0	Spherical	13.30	Amorphous	[589]
18	1:3.7	~6.15	70	Irregular	47.49	Amorphous	
45	1:5.5	-	-	-	N.G.	N.G.	[590]
69	~1:2	1	-	Spherical	7.3[c]	N.G.	[591]
69	~1:2	1	-	Spherical	20[d]	N.G.	
69	~1:2	1	-	Spherical	24[e]	N.G.	

[a] The portion of the ethanol in the reaction medium.

[b] Vigorous hand stirring.

[c] The washing solution was deionized water, and the sample was dried under anaerobic condition.

[d] The washing solution was acetone, and the sample was dried under aerobic condition.

[e] The washing solution was ethanol, and the sample was dried under aerobic condition.

Table A. 2. Recent reports for the synthesis of magnetite nanomaterials.

Method	Compound	Precursors	Reductant	Properties			Crystallinity Crystallite size	Reference
				Shape (TEM image)	Size (nm)	BET (m^2/g)		
Hydrothermal	Magnetite-graphite oxide	$FeCl_3.6H_2O$, $FeCl_2.4H_2O$, $NH_3.H_2O$	-	Spherical	-	-	-	[607]
One step controlled precipitation	Magnetite	FeSO4.7H2O, NaOH	-	Cubic	35	-	31.4	[650]
Aqueous to toluene phase-transfer	Magnetite	$FeSO_4$, KOH, $C_{19}H_{42}NBr$, C6H5-CH		Cubic	18	-	-	[772]
Solvothermal method	Cluster and nano magnetite	$FeCl_3.6H_2O$	NaOAc		3-10		-	[773]
Solvothermal process[a]	Magnetite	$FeCl_3.6H_2O$, $CO(NH2)_2$		From hollow sphere, to pinecone-like, and finally into cracked nanostructures	A few hundreds to several tens[b.]	5-21	-	[772]
Ultrasonic assisted deposition method[c]	Magnetite	$FeCl_3$, $EDTA(C_{10}H_{16}N_2O_8)$[d], NH_4OH	KI	Spherical	104	-	-	[600]
Precipitation	Magnetite	$FeCl_3.6H_2O$, NH_4OH	KI	Spherical	5-12			
Co-precipitation	Magnetite	$FeCl_3{\cdot}6H_2O$, $FeCl_2 \cdot 4H_2O$, NH_4OH		Spherical	30.5[e]	-	-	[651]
Weakly magnetic field-assisted synthesis [f]	Magnetite	NaOH, $FeCl_2$	H_2O_2	Irregular	20-40	-	-	[774]
Liquid-phase reduction	Magnetite	$FeCl_3$	$NaBH_4$	Rod-like microstructures	555-1555 (length), 333-444 (wight)	-	-	[775]
Co-precipitation	Magnetite	$FeCl_2.4H_2O$, $FeCl_3.6H_2O$, $NH_3.H_2O$	-	Irregular to spherical	48-64	-	-	[608]
Liquid-phase reduction	Lepidocrocite	FeCl3.6H2O	NaBH4[g]	Spherical	15-30	-	10.94	[601]
Liquid-phase reduction	Magnetite	FeCl3.6H2O	NaBH4[g]	Spherical	20-30	-	18.10	[601]
Liquid-phase reduction	Magnetite/nZVI mixture	$FeCl_3.6H_2O$	$NaBH_4$[h]	Nanotubes/ Spherical	-	110	-	This study
Liquid-phase reduction	Magnetite/nZVI mixture	$FeCl_3.6H_2O$	$NaBH_4$[i]	Nanotubes/ Spherical	-	171	-	This study
Liquid-phase reduction	Lepidocrocite	$FeCl_3.6H_2O$	$NaBH_4$[j]	Nanotubes	-	229	-	This study

a. With ethylene glycol as reaction medium.

b. By increasing urea dose tuned.

c. To assist the deposition of nanoparticles on the porous BiMnOx nanotubes.

d. As capping agent.

e. The average size of the encapsulated nano-magnetite particles.

f. $Fe(OH)_2 \rightarrow \alpha - FeOOH \rightarrow Fe_3O_4$.

g. $[Fe^{+3}]$: 45 mM and [FeCl3:NaBH4] = ~1:5.5).

h. Sample I5-Fe100-R2.

i. I15-Fe67-R2.

j. I10-Fe40-R2.

A.2 TEM images of the whole samples

A.2.1 TEM images of the samples prepared under I=2

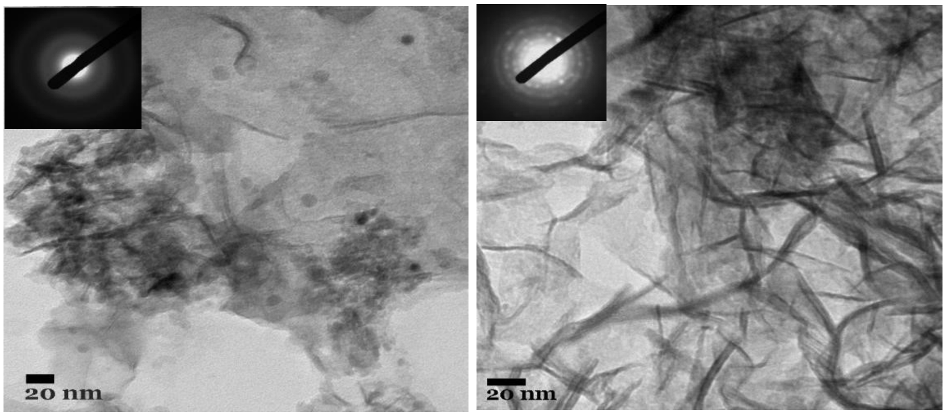

Fig. A. 2. TEM image of the precipitated samples: (left) I15-Fe67-R2, and (right) I10-Fe40-R2.

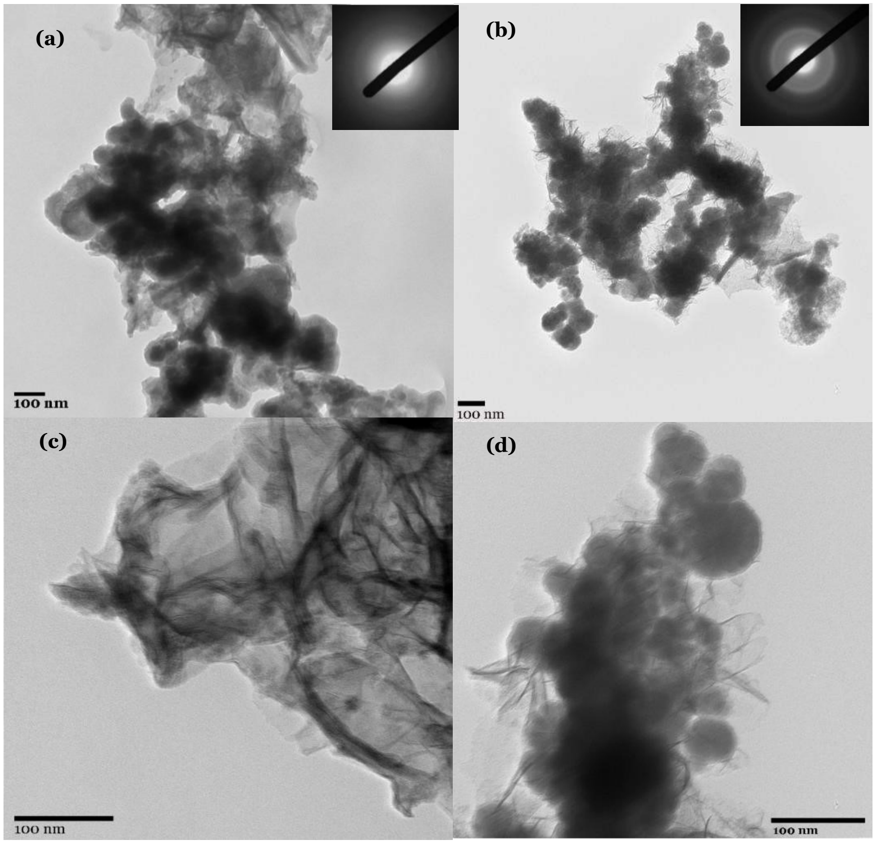

Fig. A. 3. TEM and SAED images of the samples I5-Fe100-R2 (a, c), and I5-Fe100-R2-UI (b, d).

A.2.2 TEM images of the samples prepared under I=5

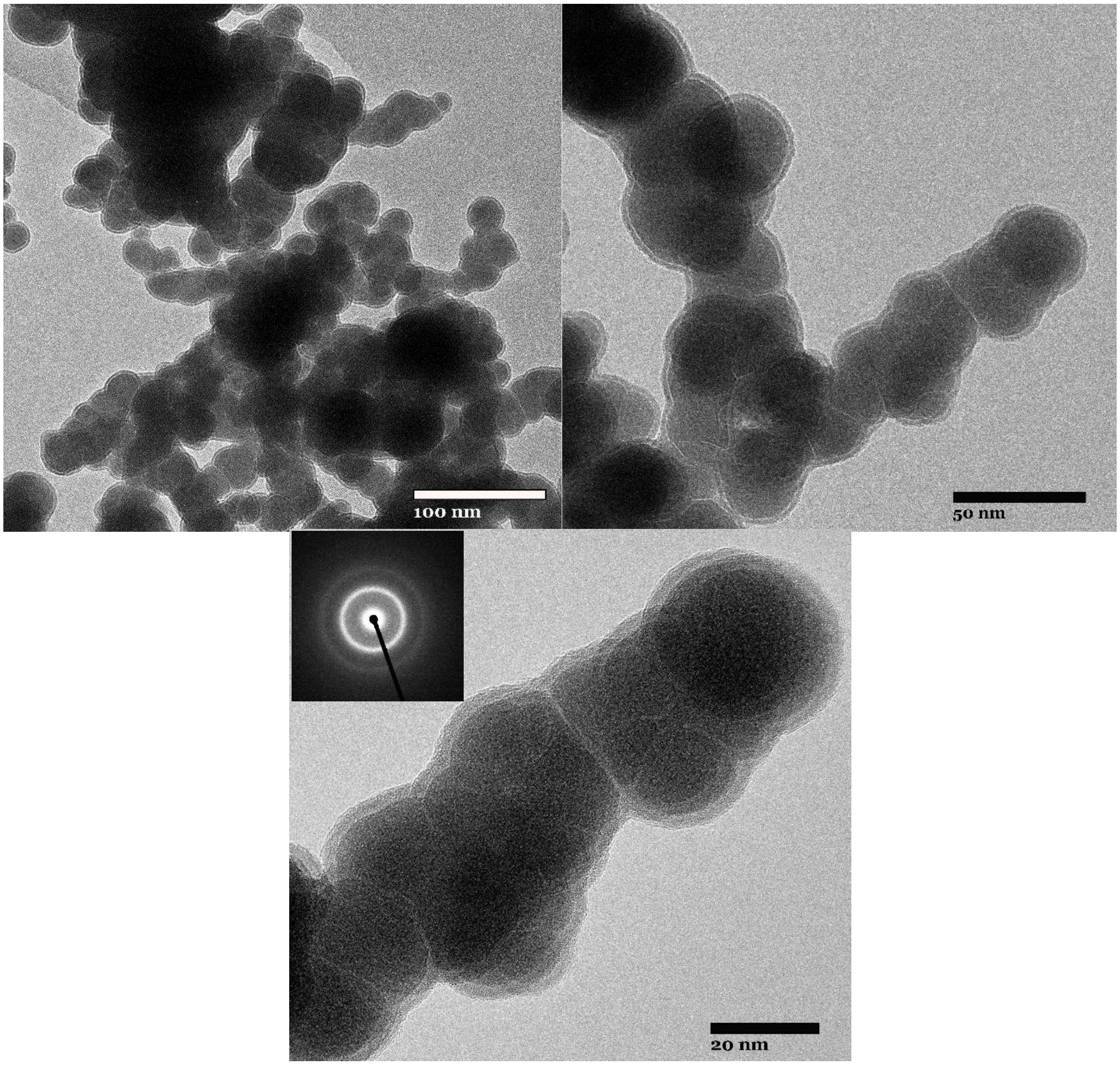

Fig. A. 4. High resolution TEM and SAED images of the sample I5-Fe67-R5.

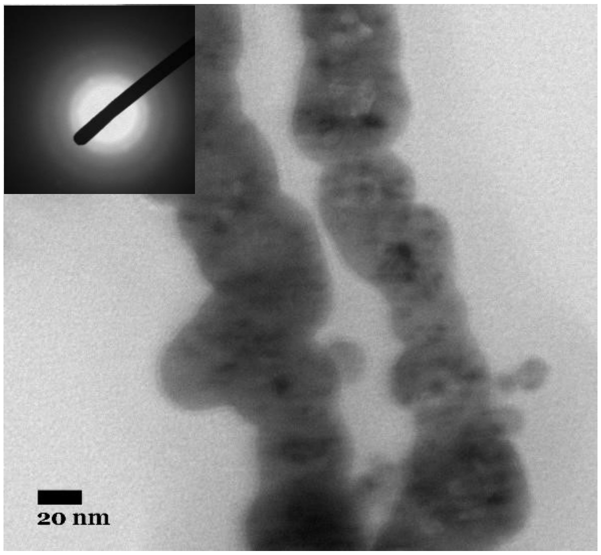

Fig. A. 5. TEM and SAED images of the sample I10-Fe100-R5.

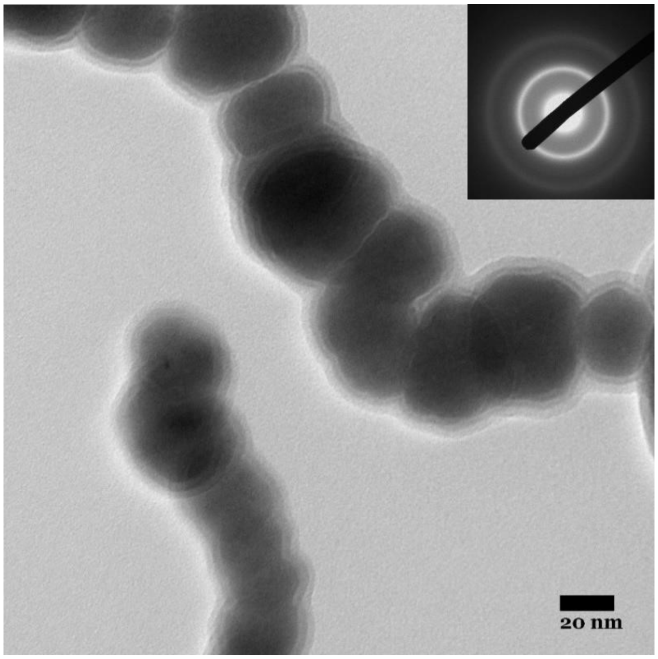

Fig. A. 6. TEM and SAED images of the sample I15-Fe40-R5.

A.2.3 TEM images of the samples prepared under I=5

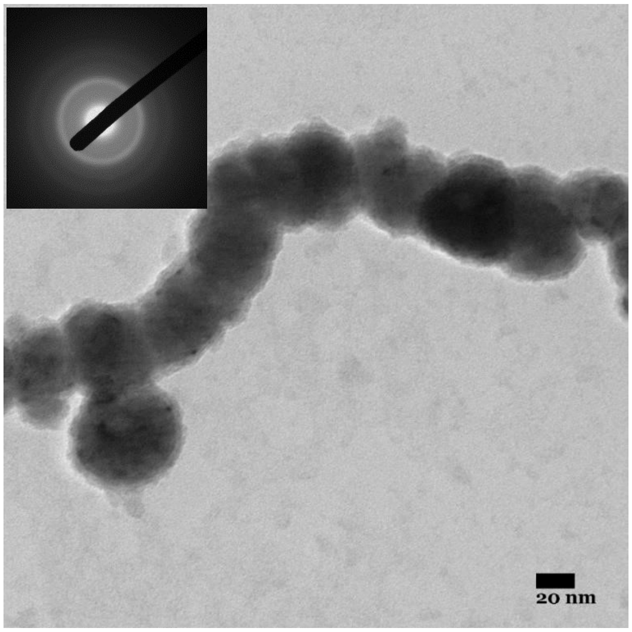

Fig. A. 7. TEM and SAED images of the sample I5-Fe40-R8.

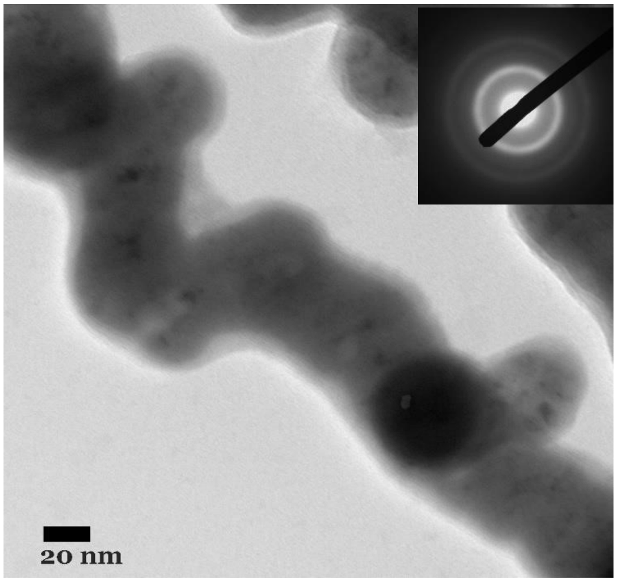

Fig. A. 8. TEM and SAED images of the sample I10-Fe67-R8.

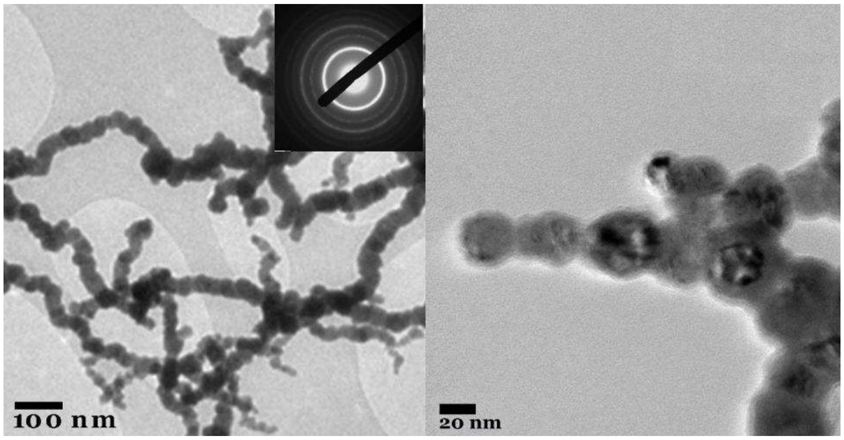

Fig. A. 9. TEM and SAED images of the sample I15-Fe100-R8-UI.

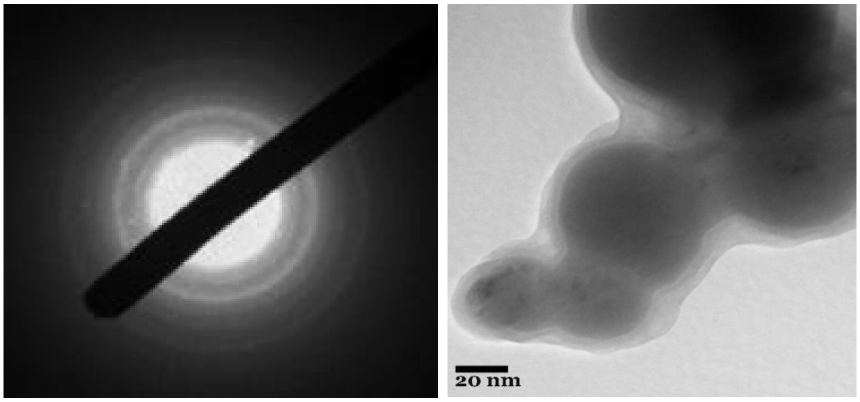

Fig. A. 10. TEM images of the sample I15-Fe100-R8.

Annex B: Equipment used

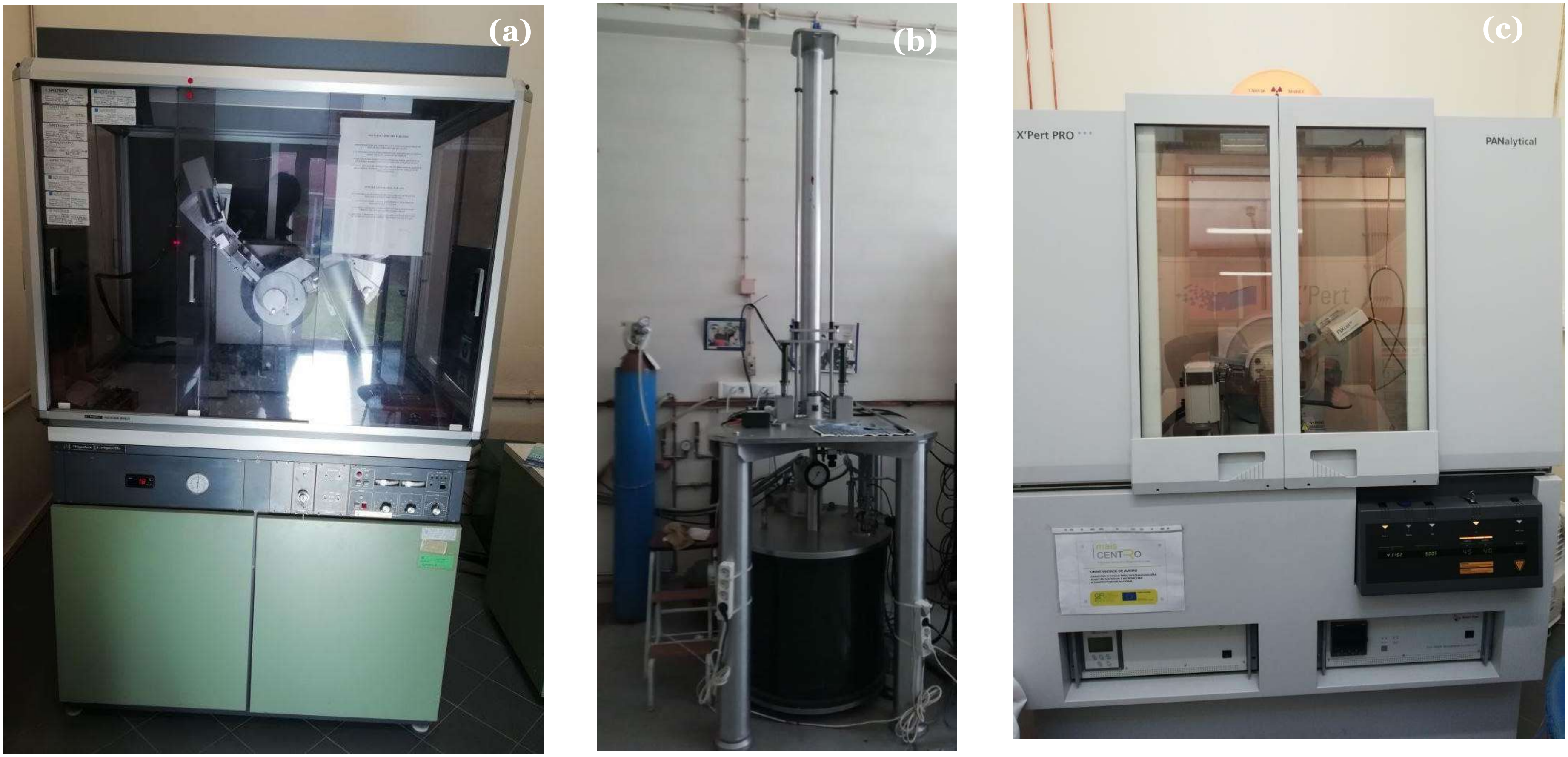

Fig. B. 1. A Rigaku, Geigerflex, Japan reflectometer (a), a vibrating sample magnetometer-VSM (CryogeniceCryofree) (b), a panalytical X'Pert Pro X-ray reflectometer (c).

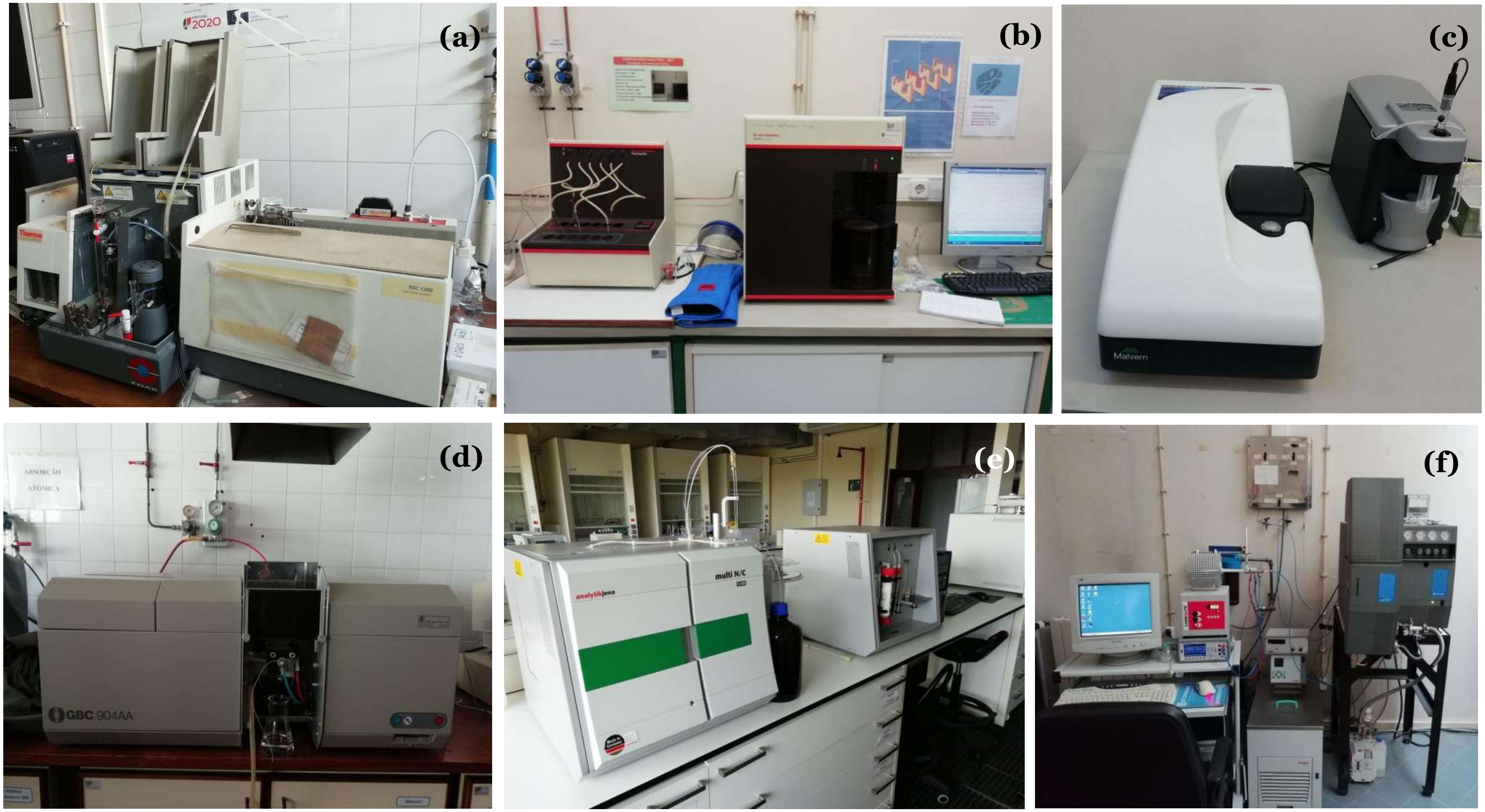

Fig. B. 2. A ECS 1200 (TOC, AOX) Analyzer (a), a Gemini V2 (USA) equipment (b), a Zetasizer Nano ZS, Malvern (c), an atomic absorption spectrometers (GBC 904 AA) (d), a total organic carbon (multi N/C, analytikjena) analyser (e), and a Labsys (TG-DSC16) TG/DTA analyzer (f).

Fig. B. 3. A scanning electron microscopy (SEM) (Hitachi S4100) coupled to energy dispersive X-ray spectroscopy (EDS) (a), a HD2700 STEM microscope (b).

Fig. B. 4. **A Transmission electron microscopic (TEM) (Hiatchi H9000) (a), an Ultra High Vacuum (UHV) system w equipped with a hemispherical electron energy analyzer (SPECS Phoibos 150), a delay-line detector and a monochromatic AlKα (1486.74 eV) X-ray source (b).**

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