HELIO-PHOTOCATALYTIC ENHANCEMENT OF THE BIODEGRADATION OF BIORECALCITRANT POLLUTANTS IN WATER: PHYSICOCHEMICAL AND TECHNICAL ASPECTS

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ABSTRACT

The importance of the photocatalytic treatment of water is continuously growing since the 80s. In spite of the well management of the existing biological water treatment plants and the constant reinforcement of the wastewater discharge standards, the development of new water depolluting processes among which the photocatalysis is still relevant.

It is recognized that certain chemicals mostly from the synthetic chemistry are not or could only be biodegradable under very critical conditions. When these "biorecalcitrant" pollutants are rejected in a biological wastewater treatment plant, they very often cross it without being degraded and thus, they accumulate in the environment and/or in the living beings. Some of them like the phthalates and the pesticides are known for their carcinogenic and mutagen effects or, they induce hormonal disruptions in the animals, including humans.

In general, all the Advanced Oxidation Processes (AOP) whose characteristic is to generate hydroxyls radicals ($^{\bullet}OH$) are able to degrade most of the organic molecules including the biorecalcitrant chemicals.

As a technology using the photons emitted by a light source to excite a catalyst and facilitate the generation of the $^{\bullet}OH$ radicals, the photocatalysis would be a more environmental compatible and less expensive process for depolluting such chemicals, if the light source is natural: the sun.

For the first time, a study of potential application in the field of helio- photocatalysis was explored in a sub-Saharan Africa country (Burkina Faso), making profitable the significant solar radiation present in that country, to validate certain results obtained using appropriated experimental and analytical methods at the Laboratory for Environmental Biotechnology (LBE) at the Ecole Polytechnique Fédérale de Lausanne (EPFL) in Switzerland.

The main objective of this thesis was to contribute to evaluate some physicochemical and technical rules which guide the scaling up processing of the helio-photo-Fenton process.

To achieve this, the work was organized in several phases of laboratory work at the EPFL and field apply work at the Ecole Inter-Etats d'Ingénieurs de l'Equipement Rural (EIER) of Ouagadougou in Burkina Faso. To mitigate the deficit of sophisticated analytical material during the field work's periods, a simple analytical method requiring relatively modest equipment was developed and validated in the laboratory and on the field.

This thesis is organized in 5 chapters of which the first focuses on the problems of this research and presents the fundamental principles of the photocatalytic processes.

Chapter 2 presents the systematic development of a low cost analytical method built up and validated in the laboratory for field's applied studies on three phthalates: the dimethyl phthalate (DMP), the diethyl phthalate (DEP) and the Diallyl phthalate (DAP).

The chapter 3 focuses on the study of the optimal parameters influencing the helio-photo-degradation of the DEP.

In the chapter 4, two case studies on the enhancement of the biodegradability of some biorécalcitrants wastewaters of which, the first evaluates the possibility of integrating the photocatalysis into a global strategy of managing the effluents of a chemical industry and the other treat problem of the depollution of the water polluted by a pesticide are presented.

The last chapter presents some modelling approaches allowing to evaluate the solar UVA energy (needed for the helio-photocatalysis) basing on the equation of the solar UVA irradiation which was proposed and tested with the one year solar data of Ouagadougou.

Keywords: Wastewater treatment, biorecalcitrant pollutants, advanced oxidation process, helio-photo-Fenton, biodegradation, compound parabolic collector, modelling, solar UVA, sub-Saharan country.

RÉSUMÉ

La dégradation progressive de la qualité des eaux douces n'est pas freinée par l'utilisation des systèmes d'épuration des eaux usées par voie biologique. Ceci est dû au fait que de nombreuses substances chimiques issues de la chimie de synthèse et massivement utilisées dans l'industrie et les ménages, ne sont pas biodégradables et/ou ne le sont que dans des conditions particulièrement drastiques. Ces substances dites "biorécalcitrantes" s'accumulent dans l'environnement et par la suite dans les êtres vivants qui les ingèrent. Certaines de ces substances tels que les phthalates et les pesticides, sont aujourd'hui reconnues pour leurs effets cancérigènes, mutagènes ou de disruptions hormonales chez les êtres vivants.

Pour faire face à cette problématique, des traitements tels que l'incinération, l'oxydation par voie humide et l'adsorption sur charbon actif sont souvent utilisées. Malheureusement, ces techniques s'avèrent très coûteuses et restent controversées du point de vue environnemental.

D'autres alternatives pour dégrader ces molécules font aujourd'hui l'objet d'études; notamment les Procédés d'Oxydation Avancée (POA) dont la particularité est de générer des radicaux hydroxyles (${}^{\bullet}OH$), puissants oxydants capables de dégrader la plus part des molécules organiques. La photocatalyse est un de ces procédés qui consiste à induire la génération de radicaux (${}^{\bullet}OH$) par l'excitation d'un catalyseur par des photons. Ce procédé serait encore plus environnementalement compatible et moins coûteux si la source photonique utilisée est le soleil.

Cette étude est une contribution à la compréhension de quelques aspects physico-chimiques et techniques qui influencent le processus hélio-photo-Fenton en vue de l'amélioration de la biodégradabilité d'un effluent biorécalcitrant réel.

La partie fondamentale de l'étude à l'échelle du laboratoire a été réalisée à l'Ecole Polytechnique Fédérale de Lausanne (EPFL) en Suisse et les études à l'échelle pilote utilisant le rayonnement solaire direct ont eu lieu à l'Ecole Inter-Etats d'Ingénieurs de l'Equipement Rural (EIER) de Ouagadougou au Burkina Faso.

Cette thèse est subdivisée en cinq chapitres dont le premier expose la problématique de l'étude et présente les principes fondamentaux des procédés photocatalytiques.

Le chapitre 2 présente la systématique de développement et la validation au laboratoire, d'une méthode analytique simple permettant d'étudier l'hélio-photocatalyse Fenton sur le terrain au Burkina Faso sur trois phthalates: le diméthyl, le diéthyl et le diallyl phthalate.

Le chapitre 3 présente les résultats de l'étude des conditions optimales de dégradation hélio-photo-Fenton du DEP et de fonctionnement du photo-réacteur de type CPC.

Le chapitre 4 présente deux études de cas contextuelles dont la première réalisée à l'EPFL, évalue la possibilité d'intégrer la photocatalyse à une stratégie globale de gestion des effluents d'une industrie chimique en Suisse. La deuxième effectuée à l'EIER, étudie l'utilisation du traitement hélio-photo-Fenton pour détruire un stock de pesticides obsolètes dont la matière active est l'Endosulfan.

Le 5ème chapitre présente la caractérisation de l'ensoleillement UVA à Ouagadougou et une approche de sa modélisation qui a été testée avec les moyennes mensuelles de l'irradiation et de l'énergie accumulée au mètre carré. Enfin, une évaluation du calcul des coûts de traitement solaire d'un important stock de pesticides obsolète (Endosulfan) a été faite, tenant compte des conditions optimales de traitement obtenues au chapitre 4, et des données de l'ensoleillement UVA locale de Ouagadougou.

Mots Clés: Traitement des eaux usées, polluants biorécalcitrants, procédé d'oxydation avancé, hélio-photo-Fenton, amélioration de la biodégradabilité, collecteur parabolique local, modéliser, UVA solaire, pays sub-saharien, pesticide obsolète.

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SYMBOLS

AOP	Advanced Oxidation Process
BOD	Biological Oxygen Demand
$\mathbf{C_i}$	Initial concentration
COD	Chemical Oxygen Demand
CPC	Compound Parabolic Collector
TOC	Total Organic Carbon
HPLC	High Pressure Liquid Chromatography
k	(First order) photodegradation rate
L	Litre
LBE	Laboratoire de Biotechnologie Environnementale
λ	Wavelength
h	Planck Constant
ν	Light frequency
PSA	Plataforma Solar de Almeria
t	time
V	Volume
POP	Persistent Organic Pollutant
Vtot	Total volume
UVA	Ultra Violet A
$\mathbf{Rad_{UVA}}$	Solar UVA radiation
$\mathbf{E_{UVA}}$	Solar UVA energy
VB	Valence Band
DEP	Diethyl phthalate
DMP	Dimethyl phthalate
DAP	Diallyl phthalate
EIER	Ecole Inter-Etats d'Ingénieurs de l'Equipement Rural
EPFL	Ecole Polytechnique Fédérale de Lausanne
EDC	Endocrine Disrupting Chemical
NCCR-NS	National Centre of Competence in Research North-South
EPA	Environmental Protection Agency (US)

PVC	Polyvinyl chloride
FDA	Food and Drug administration (US)
OECD	Organisation for Economic Co-operation and Development
K_{ow}	Octanol-Water Partition Coefficient
LD_{50}	Lethal Dose
CE	Concentrate Emulsifier
WHO	World Health Organization
mM	Milli Molar
nm	nanometre
C_v	Variation coefficient
DDC	Direction du Développement et de la Coopération Suisse
SAPHYTO	Société Africaine des Produits Phytosanitaires

TABLE OF CONTENTS

ABSTRACT

RÉSUMÉ

ACKNOWLEDGMENT

SYMBOLS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1. BACKGROUND 1

1.1 A Global view of the water crisis in the world 2

1.1.1 Environmental and health related risks to water pollution 4

1.1.2 Common wastewater treatment techniques and their limits: The biodegradability and biorecalcitrancy concepts 5

1.2 The importance of the environment pollution of the phthalates and pesticides 8

1.2.1 Phthalates 8

1.2.1.1 The sources of phthalates in the environment 8

1.2.1.2 The environmental and health risks related to phthalates 9

1.2.1.3 The phthalates and the legislation 12

1.2.2 Pesticides in water and environmental pollution 13

1.2.3 The biodegradability and biorecalcitrancy concepts as tools in the environmental chemical risk assessment 15

1.3 Advanced oxidation processes 19

1.3.1 Reaction mechanisms and mode of action of the hydroxyl radicals 22

1.3.1.1 Electrophilic addition reactions on double bonds…………………………...23
1.3.1.2 Abstraction of one hydrogen atom……………………………………………23
1.3.1.3 Electron transfer………………………………………………...……….23
1.3.2 Advanced photochemical oxidation processes…………………………………....24
1.3.2.1 Heterogeneous photocatalysis………………………………………………25
1.3.2.2 Homogeneous photocatalysis……………………………………………….28
1.3.2.3 Factors influencing the effectiveness of the iron photo-assisted processes.32
1.4 Objectives and outlines of the thesis……………………………………...34
References ……………………………………………………………………...38

CHAPTER 2: A SYSTEMATIC DEVELOPMENT OF A FIELD MONITORING METHOD FOR THE STUDY OF THE HELIO-PHOTO-FENTON DEGRADATION OF THREE PHTHALATES……………………………………………49

2.1 Introduction……………………………………………………………...50
2.2 Materials and procedures…………………………………………….....53
2.2.1 The Suntest and the CPC pilot photo-reactor…………………………...…..53
2.2.2 Chemicals……………………………………………………………...…56
2.2.3 HPLC and UV-visible analytical methods……………………………………...57
2.3 Results and discussions……………………………………………………57
2.3.1 Monitoring the photodegradation of the DEP following a HPLC analytical protocol…………………………………………………………………………57
2.3.2 The spectrophotometric monitoring of the photodegradation of the DEP and the validation of the analytical method ...……………………………………………...60
2.3.3 The test of the developed analytical method at the field experimentation …….63
2.4 Conclusion………………………………………………………………66
References……………………………………………………………………66

CHAPTER 3 STUDY OF SOME PHYSICAL AND CHEMICAL PARAMETERS AFFECTING THE HELIO-PHOTO-FENTON DEGRADATION OF THE DIETHYL PHTHALATE ON A CPC PHOTO-REACTOR……………....71

3.1 Introduction……………………………………………………………...72

3.2 Experimental………………………………………………………..……...75

3.2.1 Chemicals…………………………………………………………...……....75

3.2.2 Experimental device and procedures…………………………………….…....75

3.2.3 Analytical methods…………………………………………….…………76

3.3 Results and discussions……………………………………………………...76

3.3.1 Study of the optimal physicochemical parameters influencing the helio-photo-Fenton degradation of the DEP…………………………………………………….....77

3.3.1.1 The initial concentration of the DEP……………………………………77

3.3.1.2 The pH …………………………...…………………………………..78

3.3.1.3 The concentration of the hydrogen peroxide (H_2O_2) and iron (Fe^{3+})…….81

3.3.1.4 The nature of the iron source……………………………………….....82

3.3.2 Influence of some physical and technical parameters ……………………….....83

3.3.2.1 The solar irradiance flux……………………………………………….....83

3.3.2.2 The flow rate……………………………………………………………......86

3.4 Conclusion…………………………………………………………………….88

References…………………………………………………………………….89

CHAPTER 4: PHOTO-FENTON STUDY OF THE DEPOLLUTION OF REAL BIORECALCITRANT WASTEWATERS: CASE STUDIES……………………………………………………......93

4.1 Introduction…………………………………………………………………...94

4.1.1 The case study of some real biorecalcitrant wastewaters from a chemical industry in Switzerland……………………………………………………………...…….95

4.1.2 The problem of POPs and obsolete pesticides in Burkina Faso……………..……95

4.2 Experimental……………………………………………………………97
4.2.1 Materials……………………………………………………………....97
4.2.2 Procedures……………………………………………………………98
4.2.3 Analytical methods…………………………………………………99
4.3 Results and discussions……………………………………………..100
4.3.1 Study of the management of the chemical industry effluents…………………100
4.3.1.1 Diagnosis: Physicochemical and biological characterization of different type of effluents resulting from the processing of LQV……………………..…….100
4.3.1.2 Fenton and photo-Fenton treatment of the CHPYR polluted wastewater…………………………………………..…………………..101
4.3.1.3 Optimisation of the H_2O_2 and Fe^{2+} concentrations…………………..….103
4.3.1.4 Biodegradability of the photo-treated effluent…………………………..104
4.3.1.5 Recommendations……………………..……………………………..105
4.3.2 Helio-photo-Fenton study of the degradation of Endosulfan………..…......106
4.3.2.1 Influence of the aeration (O_2) and the photolysis………….……………106
4.3.2.2 Influence of iron and H_2O_2 concentrations…………….……………......108
4.3.2.3 Evolution of the biodegradability of the phototreated Endosulfan wastewater……………………………….…………………………...109
4.4 Conclusion…………………………………………………………....111
References…………………………………………………………………...112

CHAPTER 5. SOLAR UVA RADIATION AND ENERGY MEASUREMENTS AND MODELLING 113

5.1 Introduction…………………………………………………...…..114
5.2 Materials and procedures……………………...………………………117
5.3 Results and discussions…………………………………………...…...119
5.3.1 Analysis of the solar UVA data measurements…...…………………………..119
5.3.2 Statistical models for evaluating the solar UVA radiation and UVA energy…...122
5.3.3 A simplify adjustment modelling approach for evaluating the solar UVA energy in a specific site: The applied case on the solar UVA of Ouagadougou …………..…..127

5.4 Cost estimation of the helio-photo-Fenton treatment of 4 m^3 of commercial Endosulfan in Ouagadougou……………………………131

5.5 Conclusion……………………………………………………..………133

References…………………………..…………………………………………..134

GENERAL CONCLUSION AND RECOMMENDATIONS…………137

CURRICULUM VITAE…………………………………………………..143

LIST OF FIGURES

Figure 1. 1: Global annual water withdrawal by sector, 1900-2000 (Abromovitz, 1996). 2

Figure 1. 2: Fresh water distribution in the world 3

Figure 1. 3: The diversity of AOPs 19

Figure 1. 4: Classification of the photo-initiated AOPs according to their active wavelength and spectral domains of excitation 21

Figure 1. 5: Domains of suitability of biorecalcitrant wastewater treatment according to COD contents (Andreozzi R. 1999). 22

Figure 1. 6: TiO_2 absorption spectrum (in green) 25

Figure 1. 7: TiO_2-semiconductor photocatalytic process: Scheme of some chemical events which may occur at the surface of an irradiated TiO_2 particle. 26

Figure 1. 8: Scheme of the chemical reactions occurring in the photo-Fenton process. 31

Figure 1. 9: Schematic representation of the suggested wastewater management strategy including the helio-photochemical treatment 35

Figure 2. 1: A Hanau Suntest Simulator containing Pyrex flask samples during a laboratory experiment at the LBE-EPFL, Lausanne, Switzerland…….…………………..53

Figure 2. 2: A Picture and the technical design of the CPC photo-reactor used for the experiments at the EIER in Ouagadougou, Burkina Faso……………………..55

Figure 2. 3: A series of superimposed chromatograms of a solution of 0.3 mM DEP phototreated using the Hanau suntest simulator, sampled at 15 minutes period……………………………………………………………………....58

Figure 2. 4: Spectra of the three regular picks generated from the chromatogram of a sample of a DEP phototreated sample after 15 minutes of the treatment. (4a) shows the superimposition of the DEP spectrum with those of the two by-products. (4c) is the spectrum of the DEP, (4a) and (4d) are the spectra of the by-products at 253.4 and 301.3 nm respectively. During the field work, the absorbance measures were made at 301 nm………………………………………………….59

Figure 2. 5: Molecular structure of two by-products of photodegradation of the DEP: (P_1) absorbs maximum at 256 nm and (P_2) absorbs at 302 nm. (Mailhot et al., 2002). In our work, we assume that the by-products observed with maximum absorption at 253.4 nm and 301.3 nm are the same as P_1 and P_2 respectively. The slight differences of data (253.4 # 256 nm) and (301.3 # 302 nm) could be due to the difference of the analytical procedures or devices……………………....60

Figure 2. 6: A series of superimposed spectra of two DEP photo-treated solutions sampled at 15 minutes period: The initial concentrations were: (a) 0.3 mM and (b) 0.47 mM...61

Figure 2. 7: Correlation of the absorbance at (▲) 301 nm and (×) 254 nm of the by-products, (●) 273 of the DEP and (■) the concentration of the DEP. 63

Figure 2. 8: Solar UVA radiation and energy at Ouagadougou during the three days of the 44th week (3-9th November 2003)..64

Figure 2. 9: Comparing the solar-photodegradation of three phthalates during the field study, using an initial concentration of 0.6 mM of each: (■) for DMP, (▲) for DEP, (×) for DAP and (●) for the average of the solar UV energy during the same operating period of the day (10h00 – 13h30)....................................65

Figure 3. 1: Photo-Fenton degradation of a series of successive increasing concentrations of DEP. (□) for 0.16 mM.L^{-1}, (Δ) for 0.3 mM.L^{-1}, (●) for 0.6 mM.L^{-1} and (+) for 0.9 mM.L^{-1} as a function of the accumulated energy. The inserted figure is the energetic rate (mM x 10^3 J^{-1}) of the 90% degradation of the DEP in two hours (Energy at the point $A/A_0=1$, with $t\neq t_0$)...78

Figure 3. 2: Photodegradation of the DEP at various initial pH. It's plotted the relative evolution of the absorbance of the by-product for (●) pH=1.5; (×) pH=3; (■) pH=5.5; (▲) pH=8.5. The initial DEP concentration is 0.6 mM and initial H_2O_2 concentration: 3.6 mM...80

Figure 3. 3: Influence of the concentration of H_2O_2 (▲) and Fe^{3+}(■) on the photo-Fenton degradation of the DEP. The optimal concentration is obtained with 3.6 mM of H_2O_2 and there is no optimum in the range of the tested Fe^{3+} concentrations....81

Figure 3. 4: Influence of the iron ion source...83

Figure 3. 5: Influence of the period of the day on the photodegradation of the DEP: (■) Photodegradation rate of 90% of DEP and (▲) Energy needed to degrade 90% of DEP at each of the three periods of the day ("Morning": 08h00-10h30; "Noon": 10h30-13h30"; "Afternoon": 13h30-16h30)..86

Figure 3. 6: Influence of the water flow rate in the photoreactor: (▲) for 14.4 L.min^{-1}; (■) for 19.1 L.min^{-1} and (●) for 24.2 L.min^{-1}. Experiments were carried out at the three periods of the days to confirm the conclusion of Fig.3.5. 24.2 L. min^{-1} is the most effective circulation rate and the noon is the most favourable period.........87

Figure 4. 1: A schematic representation of the helio-photocatalytic decontamination of some pesticide containers...98

Figure 4. 2: The spectrum of a diluted commercial Endosulfan solution (0.36 mM) showing a maximum at 218 nm...99

Figure 4. 3: Biodegradability after 07 (☐) and 14 days (▨) of the three raw chemical industrial wastewaters..101

Figure 4. 4: HPLC chromatograms of the CHPYR effluent before and after the Fenton (left) and the photo-Fenton (right) processes...102

Figure 4. 5: Kinetic of mineralisation of the CHPYR at various iron concentration: (■) for 3mM; (▲) for 5.2 mM and (●) for 9.6 mM, as a function of the H_2O_2 concentration during the Photo-Fenton process on a 50% diluted effluent 103

Figure 4. 6: Chromatograms of a series of photo-treated samples of CHPYR taken at 30 min period.....104

Figure 4. 7: Biodegradability of a CHPYR photo-treated effluent.....105

Figure 4. 8: A Schematic presentation of the global strategy for the studied wastewater management in the company.....106

Figure 4. 9: Influence of (O_2 from air) and photolysis on the degradation of the Endosulfan: (■) only O_2 from air; (▲) for (O_2 + hν)=photolysis and (●) for helio-photo-Fenton. 108

Figure 4. 10: Relative absorbance of the phototreated water as a function of the volumetric energy. The H_2O_2 is varied from: (●) 8 mM, (■) 12 mM to (▲) 16 mM. The insert is percentage of relative degradation of the Endosulfan (monitored at 218 nm) when 6 x 10^3 $J.L^{-1}$ energy is accumulated in the photoreactor for the three tested H_2O_2 values. 109

Figure 4. 11: Evolution of the biochemical parameters of the Endosulfan polluted water during the helio-photo-Fenton treatment; (■) for the COD, (▲) for BOD_5 and (●) for the BOD_5/COD ratio. 110

Figure 5. 1: Global solar energy per capita (from the World Energy Council 27.11.01).....116

Figure 5. 2: A view of the radiometer used for the solar UVA data measurement.....118

Figure 5. 3: Monthly average daily UVA radiation at midday and UVA energy from 08.00 am to 04.00 pm.....121

Figure 5. 4: Monthly average daily UVA radiation and UVA energy at Ouagadougou – Burkina Faso.....123

Figure 5. 5: Monthly average daily UVA energy values recorded by various ways: (■) "real" measured values; (▲) statistical model; (♦) Adjustment model; (×) average values between the "real" values and the calculated values through the adjustment model. 130

Figure 6. 1: Schematic diagram of the state of the art in the field of wastewater treatment including the photochemical processes.....140

LIST OF TABLES

Table 1. 1: Overview of the acute toxicity of key Endosulfan compounds in (Guerin 2001)...15

Table 1. 2: Oxidation potential of various currently used oxidant...20

Table 1. 3: Characteristics of some common semiconductors in aqueous solution at pH=1..27

Table 1. 4: Main characteristics of the chemicals studied..37

Table 2. 1: Quality of the tap waters used for the experiments at the EIER, (Burkina Faso); November 2003…………………………………………………………...56

Table 4. 1: Results of the surveys of POPs and obsolete pesticides in Burkina Faso (2001 and 2004)……………………………………………………………………………96

Table 4. 2: Synthesis of the characteristics of the three industrial effluents studied................100

Table 5. 1: Monthly average daily solar UV-A radiation and the monthly average daily Solar UV-A energy accumulated from 08.00 am to 04.00 pm………………………..121

Table 5. 2: List of coefficients of the equations of the monthly average daily solar UVA radiation and energy accumulated from 08.00 am to 04.00 pm at Ouagadougou.125

Table 5. 3: Abacus of conversion of the time values (from 08.00 am to 04.00 pm) into scalar values in the reference frame used in this thesis...126

Table 5. 4: Comparison to the "really" monthly average daily measured values of the UVA data to those from the statistical and adjustment models 130

Table 5. 5: Cost estimation of the helio-photo-Fenton treatment of 4 m^3 of Endosulfan in Ouagadougou..132

Chapter 1

Background

1.1 A Global view of the water crisis in the world

Although water is the most widely occurring substance on earth, the evolution of the world population, the agricultural and industrial activities, as well as changes of human behaviours, constitute today a real threat to its infinite availability.

One estimates that the total volume of water available at an invariant cycle on earth is about 1.4 billion km^3 of which 97% is salted water in oceans and ≈ 2% is locked up in glaciers. Hence, one could imagine that the remaining 1% would be available to satisfy the water requirements of all human activities; however, it happens that the 90% of this is located far in the deepest ground and finally, only 0.1 % of the all water is easily available.

The rising water demand for domestic (municipal) consumption, agriculture and industry, has been constantly increasing for about 700-850% within the last century (**Fig.1.1**) and are forcing stiff competition over the allocation of scarce water resources among both areas and types of use.

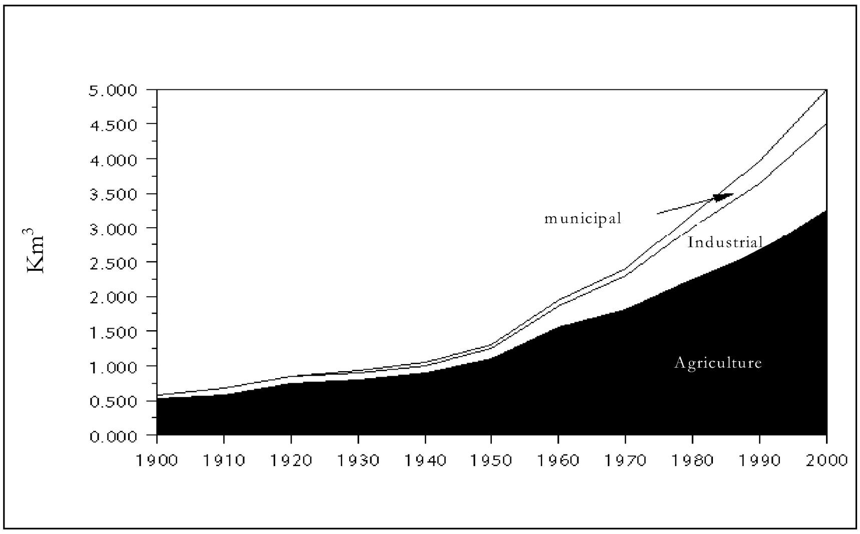
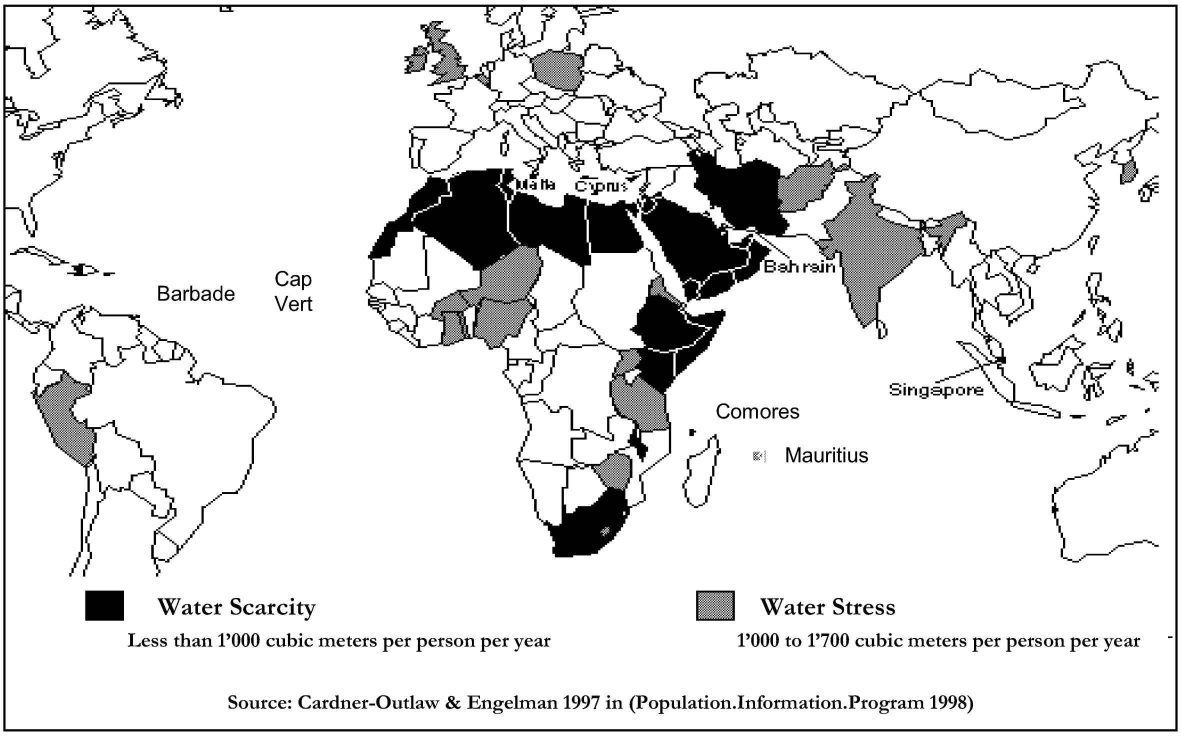


Figure 1. 1: *Global annual water withdrawal by sector, 1900-2000 (Abromovitz, 1996).*

Due to the difference of the hydroclimatic and the geomorphology among the regions of the world, the available water flows are different from one country to another.

The world's available freshwater is distributed regionally as shown in **Fig.1.2**. Today more than 30 countries accounting for about 8-10% of the world population face chronic freshwater shortages and according to reasonable perspectives, 48 other countries are expected to face water shortages by the year 2025, affecting more than 2.8 billion people - 35% of the world's projected population. In Burkina Faso where the field's part of this research was carried out is one of the few countries (e.g. Ghana, Togo, Ethiopia, Niger, Burundi, Kenya, Nigeria…etc.) likely to have water shortage in the next 20 years (Population.Information.Program 1998).



Source: Cardner-Outlaw & Engelman 1997 in (Population.Information.Program 1998)

Figure 1. 2: *Fresh water distribution in the world*

Scarce and unclean water supplies are critical public health problems in most parts of the world. It's estimated that polluted water and water shortages which are sources of unsanitary living conditions kill over 12 million people per year. For some time now, the water crisis has become worst because of the occurrence of new sorts of chronic diseases (cancers, endocrine disruptions…etc.) which result from water pollution by some micro-pollutants (Geschwind, Eiseman et al. 1999; Centre for Disease Control (CDC) 2001).

Among the current main causes of water shortage are: (i) the increase of the population while the water resources are limited; (ii) the decrease level of rain and desertification; (iii) the weak management of the Transborder Rivers; and of course, (iv) the anthropogenic hazardous pollution of water.

1.1.1 Environmental and health related risks to water pollution

Each year, around 1500 new chemical products join the 70'000 already existing ones on the market, and the trend is still increasing (Toepfer 2004). It's estimated that some 2 million tons of waste per day are disposed of within receiving waters, including industrial wastes and chemicals, human waste and agricultural wastes (fertilizers, pesticides and pesticide residues) (WHO-UNDP 2004). Many of these pollutants are known to be hazardous for living organisms, and there is a growing concern about the impact of the chemical pollution on the environment. The *Stockholm convention* on Persistent Organic Pollutants (POPs) which entered into force in 2003 banned the use of nine pesticides and polychlorinated biphenyls (PCBs) and the generation of two by-products of incineration. In 1996, the European Integrated Pollution Prevention and Control (IPPC) directive was set out, with the objective of minimizing pollution from specific industrial activities (listed in the Annex I of the Directive) throughout the European Union (EU 1996).

The lack of best available on-site treatment technologies (BAT) and their high cost has made it difficult for industries to fulfil the requirements. In this context, simple and low cost solutions are still strongly required.

In developing countries, the production of hazardous chemicals is increasingly shifting whereas the needs of cost affordable and appropriate techniques for the treatment of wastewater are strongly required (Cissé 1997; Koné 2003). Developing countries depend on high amounts of pesticides and fertilisers for their agriculture and their share of the worldwide chemical consumption was 20 percent in 2002 and is set to increase (Watfa T.N, Awan S. et al. 1998; Kogi 2002). The lack of public awareness on the potential risks and the in appropriation of adequate mechanisms of protection, combined with the non existence of water treatment techniques, increased the negative impact on peoples' health and their living standards. The main problem with POPs is that they are hardly or even not degradable by microorganisms and thus, accumulate in the environment all along the years. Long-term consequences of this accumulation of xenobiotic compounds in aqueous and terrestrial ecosystems are hard to predict, but some alarming findings have already been made; relatively high concentrations of some pollutants have been detected in fish, seals and in mother's milk (Geschwind, Eiseman et al. 1999; DiGangi 2002; Zhang, Hong et al. 2003; Ali 2004).

1.1.2 Common wastewater treatment techniques and their limits: The biodegradability and biorecalcitrancy concepts

In general, the conventional water treatment processes are classified as pre-treatment, primary, secondary and tertiary treatments (Horan 1990).

- ✓ The pre-treatment is designed to remove the coarse remains and sandy material from the wastewater.

- ✓ The primary treatment is the step in which suspended matters and greases are separated from wastewater. In general, flocculent and some polymers are added in wastewater at this stage
- ✓ The secondary treatment is referred to as biological treatment and is designed and managed to remove dissolved organic matter from wastewater. The microorganisms absorb organic matter for their metabolism. This step of wastewater treatment produced quantity of sludge when died and still alive microorganisms decant in the basin.
- ✓ The tertiary treatment generally focuses on the removal of nitrogen, phosphorus (principal causes of the eutrophication of lakes and rivers) and other disease-causing organisms from wastewater.

Since the main principle of these processes is based on degrading the pollution by natural means, the biodegradability as a concept is an important parameter in water chemical risk assessment, because it directly influences the predicted environmental concentrations and thus, the possible exposure of biota to the chemical pollution.

Biodegradation is defined as the biologically mediated breakdown of chemical compounds. Complete biodegradation of organic molecules to CO_2, H_2O and/or other inorganic end products, is called mineralization. This is most often accomplished by microbial consortia, even if individual reactions may be carried out by a single organism. Compounds that are not biodegradable are referred to as biorecalcitrant.

The biodegradability and the biodegradation rate of a chemical compound depend mainly on:

- ✓ the concentration of the substance in the system
- ✓ the structure of the molecule
- ✓ the microbial population

- ✓ and the bioavailability of the compound

At different concentrations, completely different biodegradation rates can be observed. At high concentrations a biodegradable compound can be degraded as a primary substrate, i.e. it gives the degraders sufficient energy and carbon to support growth. In that case the involved microorganisms grow exponentially, leading to an acceleration of the degradation rate, following Monod kinetics. At low concentrations the substance will not serve as a primary substrate, but will be degraded by means of co-metabolism. The microorganisms degrade the substance without deriving carbon or energy from it. In this case, degradation does not fuel population growth, and the degradation rate remains constant (zero order kinetics) (Banerjee, Howard et al. 1984).

Generally, a xenobiotic resembles a natural substrate; the more likely it is to be degraded. Functional groups that are often found in nature usually increase the biodegradability, whereas newly synthesized man-made groups often make the molecule more persistent. In aromatic rings, electron-withdrawing constituents (e.g. halogens and nitro-groups decrease the biodegradability, whereas electron-donating constituents (carbonyl groups and phenols) increase it.

The microbial population, their relative concentrations and the induction of their enzymes depend strongly on the environmental conditions such as pH, temperature, redox potential, oxygen concentration and concentrations of other relevant substances for microbial growth. Consequently, the biodegradation rates vary remarkably, depending on the environment. A microbial community can also adapt to a compound, which will ameliorate the biodegradation rate.

Within the framework of this thesis, the depollution of two important groups of biorecalcitrant pollutants (the phthalates and pesticides) was investigated.

1.2 The importance of the environmental pollution of the phthalates and pesticides

1.2.1 Phthalates

1.2.1.1 The sources of phthalates in the environment

Phthalates are a principal component of flexible PVC products, plastic packaging, cosmetics, pesticides, building maintenance products, lubricants, and personal care goods that surround consumers.

Approximately 90% of global plasticizer production is destined for use in polyvinyl chloride plastic (PVC) (Bizzari 2000). The remaining 10% is used in adhesives, caulks, skin creams, detergents, electrical capacitors, hairsprays, inks, solvents, lubricating oils, lotions, nail polish, paints, fragrances, and pharmaceuticals (Houlihan and Wiles 2000; Centre for Disease Control (CDC) 2001; Phthalate Esters Panel 2002).

The benzene ring based structure of phthalates helps reduce their viscosity but also makes them harder to degrade; since they are not covalently bound to the polymer, they are fairly easily released to air, water, saliva, blood, nutritional formulae, and other extracting materials (EU Scientific Committee on Toxicity 1998.). Since phthalates tend to be fat soluble, they leach more readily into lipid-containing solutions. Depending on the circumstances of use, 2% - 50% of the phthalate content can emerge from products over their service life (Kemi 2001).

The Diethyl phthalate (DEP), the dimethyl phthalate (DMP) as well as the dibutyl phthalate (DBP) are used as solvent in the perfumes and support of the active ingredient in the cosmetics. The concentration of DEP in these products varies from 0.1% to 50% in weight, which in DBP does not exceed 10 %. The annual production of DEP in Europe rose in 1999 with roughly 10' 000 tons for its use as plasticizer. In parallel, 4' 000 t/year were used in perfumery (Api 2001;

WHO 2003). Human are directly exposed to a considerable quantity of phthalates when those are used in cosmetics. American studies (Blount 2000; Brock 2002) bearing on the presence of phthalates in the urines showed concentrations going of a few µg/g of creatin to more than 300 µg /g of creatin. In a study of Blount et al. (Blount 2000), six of the eight higher concentrations were observed among pregnant women. An assumption plausible, but not checked is that this contamination is related to beauty products since it is about the principal use of the phthalate measured during study (the DBP). The presence of phthalates in the human urines has been reported in many papers (Blount 2000; Brock 2002; DiGangi 2002; Houlihan J. 2002), arguing that the concentration in DEP increases with the age of the studied people. The use of these phthalates could explain these different behaviours since DEP is especially used in the cosmetic products and the perfumes.

1.2.1.2 The environmental and health risks related to phthalates

The release of the phthalates in the environment can occur at each phase of their cycle of life; in the case of their use as plasticizer, during the production of the plastics (wastewater of plastic manufactures), of their use but especially by leaching in the discharges where the plastic wastes are stored (Api 2001).

The manufacture, the use and the disposal of PVC and other phthalate-containing products have resulted in extensive environmental releases of phthalates. Consequently, phthalates are now one of the most abundant industrial pollutants in the environment, and are widely present in air, water, soils, and sediments (Agency for Toxic substances and disease registry 1995; Danish Environmental Protection Agency 1995; Staples 1997).

In Sweden, Italy, Germany and the UK, various phthalates and their metabolites have also been detected in landfill leachates. Phthalate concentrations for phthalic acid, DEP, and DMP were 18.900 µg/kg, 540 µg/kg, and 300 µg/kg respectively.

Compared with other phthalates, the Diethyl phthalate (DEP) has the worst capacity to bind with the sediments. It is thus in majority (70 to 90%) in the aqueous phase (WHO 2003); this enables it to move in the environment and it's likely to accumulate in the natural water tanks as attested by a study in several American cities carried out by the Environmental Protection Agency of the USA (EPA 2001).

In the case of its use in cosmetic, the contamination by the DEP on Human does not depend only on its concentration in the products used but also on the frequency of use and the number of products. According to an England studies', women use an average of 26 cosmetic products per day, but several studies show that many products of high standard may contain a considerable quantity of phthalates (DiGangi 2002).

The study of Colón, 2000 (Colón 2000) bearing on children of California showed that they have a concentration in different phthalates higher than the American average monitored by Blount et al. (Blount 2000). The types of phthalates observed (DBP, DEP) tend to show that the contamination is made via cosmetic products. But the presence of DEHP proves also that there was as contamination via PVC products, as are of the toys or edible packing of products.

Among 120 pollutants considered as priority and being indexed by the American agency of environmental protection (EPA) within the framework of the American policy of protection of the water quality, the DEP and DMP respectively occupy the 79thand 80th position. This classification is not due to a proven acute toxicity of these substances but quite to the contrary to a chronic toxicity. Indeed, acute toxicity is very low since only irritations can occur in the event of direct contact with the skin and the risk of pure ingestion of phthalates which is very limited.

The chronic toxicity of the phthalates is characterized by disruptions of the hormonal system. Hashimoto et al. 2003 showed through studies carried out on cells proliferating in the presence of estrogens, that some phthalates support the growth of these cells and are thus assimilated by these to hormones (Hashimoto, Kawaguchi et al. 2003). These substances thus affecting the hormonal system of the alive beings constitute the family of the endocrine disruptors whose many contemporary studies on the human beings are worried some (Colón 2000; Rozati, Reddy et al. 2002; Latini, Felice et al. 2003).

American and Italian studies bearing on adults show that women from 20 to 40 years present the strongest contamination; however it is in this age group that the women are most numerous to have children. Studies showed that the phthalates can cause a reduction in the time of gestation which can be responsible for later disorders for the child if is not to increase the infant mortality (Duty, Silva et al. 2003; Duty, Singh et al. 2003; Latini, Felice et al. 2003).

However, these results cannot be interpreted as a proof of the causality which exists between the phthalates and the various affections. On the other hand, scientists at the origin of this research, as well as the American Academy of the Podiatrist joined together at the time of a debate in June 2003 agreed on the fact that it is significant to increase the number of studies on the subject. By then, it is significant that on a world level, the principle of precaution should be applied, as that was done in Europe since December 7, 1999, date on which 6 phthalates (DEHP, DBP, DINP, DIDP, DNOP and BBP) were prohibited in the manufacture of PVC toys for the children of less than 3 years. With the sight of the various studies that should as apply to the cosmetic products, at the same time as of the technical solutions making it possible to cleanse water of their contents in phthalates and other substances biorecalcitrant must be developed. It is to this end that the present study is registered.

In general, the monoester metabolite of the parent phthalate compound is thought to be responsible for adverse reproductive and developmental effects of phthalates. In animal testing, impacts include decreased fertility in females, foetal defects, and reduced survival of offspring, birth defects, altered hormone levels, and uterine damage (Lamb, Chapin et al. 1987; Field, Price et al. 1993).

In males, phthalates cause prostate damage, female like areolas/nipples, and reproductive malformations in infants, including altered hormone levels, testicular atrophy, reduced sperm production and motility, undescended testes, hypospadias, Sertoli cell damage, and Leydig cell tumours (Brown 1978; Lamb, Chapin et al. 1987; Jones, Garside et al. 1993).

1.2.1.3 The phthalates and the legislation

Phthalates have been identified as a priority for action in Europe. In 1998, the Oslo and Paris Commission (OSPAR) listed DBP and DEHP among substances for priority action. The 13 countries named as Contracting Parties agreed to make "every endeavour to move towards the target of cessation of discharges, emissions and losses of hazardous substances by the year 2020.

In 1999, the European Community (EC) took restrictive measures as for the use of some phthalates in the toys for children. These measurements were based on the precaution principle and had a limited duration. The purpose was to limit the risks when taking the time to acquire sufficient knowledge on the effective toxicity of the phthalates.

The first regulation dating from 7 December 1999 (decision 1999/815/CE) prohibited the use of some phthalates in the plastics used for the manufacture of toys intended for children of less than three years. This prohibition was limited to 3 months duration but since then, this regulation was prolonged three months in three months until today, because of the lack of certainty and the need for thorough research (Byrne 2003).

For the phthalates present in the cosmetics, no legislation exists to date within the European Union but certain organizations like Women' S Environmental Network, Swedish Society for Nature Conservation and Health Care Without Harm, proposed a series of measurement in order to improve the consumer protection and the public health (DiGangi 2002). Among those a private bill appears prohibiting the use of the phthalates in the cosmetics. This idea is justified by the fact that in the trade there are cosmetics having the same properties, but not containing a phthalate; which proves that the industrialists, if the legislation imposed such a restriction on them, would remain able to satisfy the request of their customers.

The US Food and Drug Administration (FDA) requires some labelling of cosmetic ingredients, but the law does not require listing of phthalates or other ingredients considered fragrance components nor does the law require labelling of products sold to professional salons (US Food and Drug Administration 2001).

According to a voluntary reporting system used by the FDA, DEP-containing products include 42 colognes, 7 powders, 8 aftershaves and 8 skin creams (US Food and Drug Administration 2001). The Agency also lists DMP in 11 hair preparations and DBP in 120 nail basecoats, polishes and enamels and 27 other manicuring preparations. As the Health Canada panel concluded, *"the status quo is not an acceptable option"* (Digangi 2002).

Regulatory agencies charged with protecting medical patients, public health, and the environment must substantially revise procedures and protocols to consider the potential impacts of phthalate exposures cumulatively, rather than as single chemical exposures.

1.2.2 Pesticides in water and environmental pollution

A pesticide is generally a drug use for the mitigation, control or elimination of plants, animals or microorganisms, detrimental to human health or the economy (ca. agriculture products).

Depending on the target, pesticides can be classified to: (i) insecticides act against insects, (ii) herbicides against weeds, (iii) fungicide against fungi agents, (iv) rodenticides against rodents…..Etc.

The application of pesticides into agriculture has significantly increased the global food production and, their production and use are likely to increase, in order to meet the needs of the growing world population. Unfortunately, pesticides are nowadays a serious cause of water resources, soil and air pollution. 70% of the twelve listed Persistent Organic Pollutants (POPs) are pesticides.

Most pesticides used in agriculture have the potential to affect non-targeted organisms and, once in the environment, pesticides may be transformed into a large number of degraded products, commonly defined as metabolites and most of them are toxic or at less harmful to the biota. Many studies reported the presence of pesticide metabolites in groundwater since the 1950s (Malato, Blanco et al. 2002) and since they most often are biorecalcitrant, they will keep accumulating, with unpredictable consequences to the environment. Endosulfan has been found to have endocrine disrupting effects on the wildlife (Gomes, Scrimshaw et al. 2003). Within the framework of this research, the helio-photo-Fenton degradation of one of the known biorecalcitrant insecticides was studied. Endosulfan is a cyclodiene organochlorine possessing a labile, cyclic sulfite diester group. It is currently used throughout the world for the control of numerous insects in a wide variety of food and non-food crops.

Endosulfan has been ubiquitously detected in the atmosphere, soils, sediments, surface waters, rainwaters, and foodstuffs (Turner 1997). Endosulfan comprises two parent isomers, α- and β-Endosulfan; the α to β ratio of technical endosulfan is about 7:3 (Geobel 1982), and both isomers are extremely toxic to aqueous organisms (National Research Council of Canada 1975). Of key concern regarding its widespread distribution, particularly in water environments, is its high acute toxicity to fish (**Table 1.1**). The toxicity of the Endosulfan in aquatic animals under laboratory conditions has been attributed to the fact that it has very low water solubility and a high bioaccumulation factor (Sonnenschein and Soto 1998).

Because of its widespread use, its migration and persistence in the environment, the Endosulfan is listed in the EEC directive 76/464/EEC of very toxic chemicals for water and environment (EEC 1976).

Table 1. 1: *Overview of the acute toxicity of key Endosulfan compounds (Guerin 2001)*

Compound	Toxicity LD50 (mg.kg-1)			
	Insects	Fish	birds	Mammals
Endosulfan α	5.5	0.001-0.01*	26-1000	9.4-40
Endosulfan β	9.0	0.001-0.01	26-1000	177
Endosulfan sulphate	9.5	0.001-0.01	-	8-76
Endosulfan diol	>500	1-10	-	>1500

*) The lower the lethal dose (LD_{50}), the higher the toxicity

1.2.2 The biodegradability and biorecalcitrancy concepts as tools in the environmental chemical risk assessment

The biodegradability is an important parameter in chemical risk assessment since it directly influences the predicted environmental concentrations and thus the possible exposure of biota to a chemical. Biodegradation is defined as the biologically mediated breakdown of chemical compounds. Complete biodegradation of organic molecules to CO_2, H_2O and/or other inorganic end products, is called mineralization.

This is most often accomplished by microbial consortia, even if individual reactions may be carried out by a single organism. Compounds that are not biodegradable are referred to as biorecalcitrant.

As described previously in § 1.1.2, the biodegradability is affected by many factors which makes its prediction very complex. The existing OECD biodegradability tests (among which the most applied Zahn Wellens test), are designed to determine weather a chemical has the potential to be easily biodegraded. This is done by measuring the decrease of organic carbon, carbon evolution or oxygen demand during the test. If 60-70 % degradation occurs during the first 10 days, the chemical is regarded as readily biodegradable in the OECD regime (OECD 1996; Ahtiainen 2003). Yet, the test results often do not reflect what actually happens in the environment. The problem with most biodegradability tests is that they are performed at high substrate concentrations, sometimes simulating the functioning of an activated sludge wastewater treatment plant, whereas the concentrations of chemicals in the environment usually are in the range of ng-μg carbon per litre (Ahtiainen 2003). That is why the biodegradation rates obtained in the tests are often higher than the actual rates in the environment.

The degree of biodegradability can also be estimated, using the chemical and the biochemical oxygen demand (COD and BOD). Both BOD and COD are used to measure decomposition of chemicals. COD is a measure of the theoretical amount of oxygen required to convert the material to carbon dioxide and water, whereas the BOD measures the actual amount of oxygen consumed by microorganisms decomposing organic matter. It also measures the chemical oxidation of inorganic matter i.e. the extraction of oxygen from water via chemical reaction. The ratio BOD/COD can be considered as a measure of biodegradability. For completely biodegradable compounds it is near to one and for totally biorecalcitrant compounds it is zero.

During biological wastewater treatment, the value of the BOD/COD ratio decreases, since the fraction of biorecalcitrant matter becomes more important. Photocatalytic treatment in turn leads to an increase of the BOD/COD ratio, since biorecalcitrant compounds are oxidised by •OH radicals generated within the process, which very often leads to more biodegradable intermediate by products.

For a chemical to be degraded, it is necessary that it can reach the active site of the degrading enzyme. Several studies have shown that although a chemical is easily degradable, when freshly added to the soil, the biodegradation can become very slow when it has been there for a long time. This is due to sequestration, which makes the molecules unavailable to degraders. The bioavailability of a chemical also depends on its physical and chemical properties. Generally, more water-soluble molecules are more easily degraded. In 1984, Banerjee et al. reported that the correlation of the octanol-water partitioning coefficient (K_{ow}) with biodegradation rate depends on the type of the molecule. For hydrophobic compounds the adsorption rate on the cell membrane increases with K_{ow}, whereas the rate of penetration through the membrane is inversely proportional to K_{ow}. Depending on which of these steps is rate-determining, the overall biodegradation rate can either increase or decrease with the K_{ow}. For hydrophilic substrates, the biodegradation rates are independent of K_{ow}, since the molecules enter the cell via hydrophilic pores in the membrane (Banerjee, Howard et al. 1984).

In the industrial wastewater management strategy, two fundamental reasons for biorecalcitrance have been identified: (i) the microorganisms present in the system do not possess the enzymes needed for the degradation of the substances in question; (ii) the wastewater contains substances which are bactericidal or strong inhibitors to the metabolism of microorganisms (Rodriguez, Sarria et al. 2002; Sarria 2003). In one way or another, the actually designed mostly biological wastewater treatment plants, wherever they exist, have shown their incapability to remove effectively many biorecalcitrant or toxic pollutants. In this context, there is a strong need for the development of new adequate water treatment systems and/or water management strategies.

Among the plausible water management strategies, one can quote:

- ✓ The rational use of water by the various stakeholders; this will lead to the reduction of water consumption and prevent water pollution.
- ✓ The development of tools for the better management of water catchments and rivers basins
- ✓ The prevention and control by means of cleaner technologies, of industrial wastewater pollution and,
- ✓ The development of efficient and friendly environmental processes for the depollution of waters containing toxic or biorecalcitrant pollutants.

Within the past 30 years, research on water detoxification techniques had been extensively growing simultaneously with implementation of water management legislations in Europe (EEC, 1992; (EEC 1992; Conseil fédéral Suisse 1998) in order to improve the existing water treatment technologies and develop new and more efficient ones.

Within the framework of this awakening, a great interest had been spread on the development of Advanced Oxidation Processes (AOPs), pointing out their prominent role in the water and air purification (Ollis and Ekabi 1993; Pulgarin and Kiwi 1995; Malato, Blanco et al. 1999; Blake 2001).

Some of these AOPs among the photo-Fenton process (which is the main focus process in this thesis), are extensively described in the following paragraph.

1.3 Advanced oxidation processes

The most recent challenges in the domain of water decontamination are focused on the oxidation of hardly biodegradable chemicals, as well as the disinfection of drinking water by other means than using chlorine, as it's generally the case. In this concern, methods based on the chemical and photolytic catalysis; generally referred to as Advanced Oxidation Processes (AOPs) involving the production of highly oxidative $^{\bullet}OH$ radicals, have shown to be very attractive (Malato, Blanco et al. 2004; Dominguez, Beltran et al. 2005).

Generating $^{\bullet}OH$ radicals is possible via several ways: Chemical, photochemical, electrochemical….etc .as illustrated below.

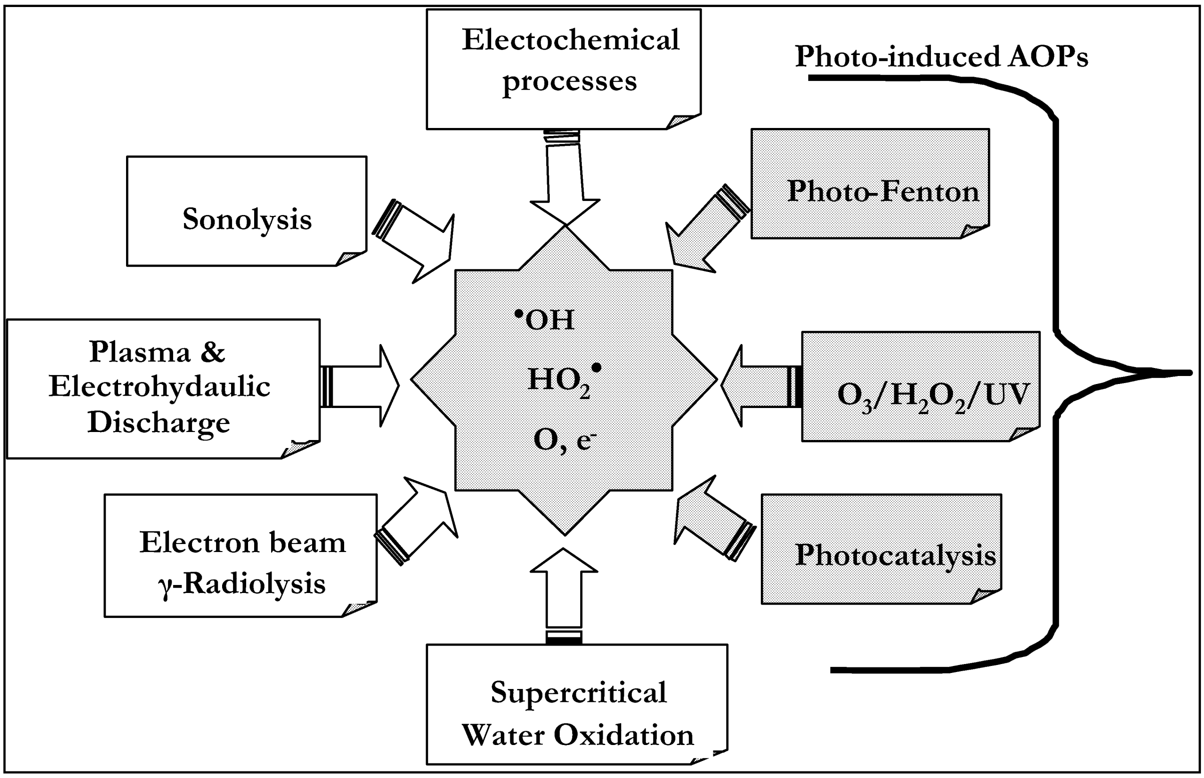


Figure 1. 3:*The diversity of AOPs*

Promoting the use of the $^{\bullet}OH$ radicals for the detoxification of water pollutants presents two main advantages:

- ✓ $^{\bullet}OH$ radicals attack mostly all organic pollutants with rate constants usually in the order of 10^6-10^9 $M^{-1}.s^{-1}$ (Hoigne 1997).
- ✓ The way of production of $^{\bullet}OH$ radicals can be chosen in a better compliance with the specific required treatment process.

Table 1.2 presents the oxidation potential of various oxidant mostly used and, it is evident to notice that the $^{\bullet}OH$ radical is quite the most oxidative species.

Table 1. 2: *Oxidation potential of various currently used oxidant*

Oxidant	Oxidation potential (eV)
$^{\bullet}OH$	2.8
O (^{1}D)	2.42
O_3	2.07
H_2O_2	1.77
$HO^{\bullet}_2$	1.70
MnO_4^-	1.67
ClO_2	1.50
Cl_2	1.36
O_2	1.23

Source: (CRC 1985)

Among the panel of AOP presented in **Fig.1.4**, extensive studies and very recent industrial applications of AOP for the treatment of biorecalcitrant pollutants are concentrated on the sonochemical, the electrochemical and very more on the advanced photochemical oxidation processes. In fact, the photo-induced AOPs which involve the use of photons generated by a UV-visible light source in order to modify or break very high energetic chemical bonds, have shown to be of great environmental concern especially if the sunlight could be used as the photons generator.

As presented in **Fig.1.4**, each of the known photo-induced catalytic process is optimally efficient only within a characteristic wavelength range of excitation.

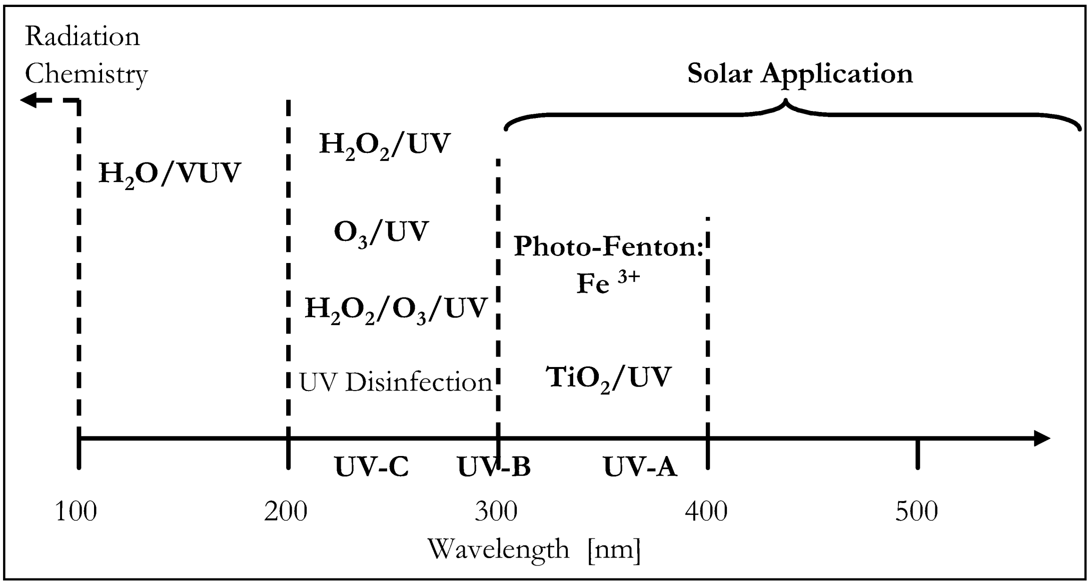


Figure 1. 4: *Classification of the photo-initiated AOPs according to their active wavelength and spectral domains of excitation*

A report of Blake, 2001 presents a review of thousands of works on the photocatalytic removal of hazardous chemicals in water and air, is a relevant proof that AOPs could successfully solve the problem of biorecalcitrant pollutants in water(Blake 2001). However, most of the cost assessment operations made on the photochemical AOP developed up to now show that they could advantageously be used only for relative small amount of industrial biorecalcitrant wastewaters (onsite pre-treatment) or if they are proposed in combination to the well established biological water treatment techniques (Ollis 1988; Pulgarin, Invernizzi et al. 1999; Parra 2000; Sarria, Parra et al. 2002; Sarria 2003; Sarria 2005).The flexibility in use of the AOPs is related to the possibility of producing $^\bullet$OH radicals by different techniques. The potentialities offered by the AOPs can be combined with the biological treatments when oxidizing the refractory toxic substances entering or getting out of a biological stage (Malato, Blanco et al. 1999; Pulgarin, Invernizzi et al. 1999). However the application of such processes is limited to wastewaters with COD lower than 5.0 g/L (Mantzavinos, Lauer et al. 1997; Andreozzi R. 1999). Biorecalcitrant wastewaters with higher COD values would require the consumption of significant quantities of the reagents. This is why such wastewater should more effectively be treated by other processes such as wet oxidation or incineration.

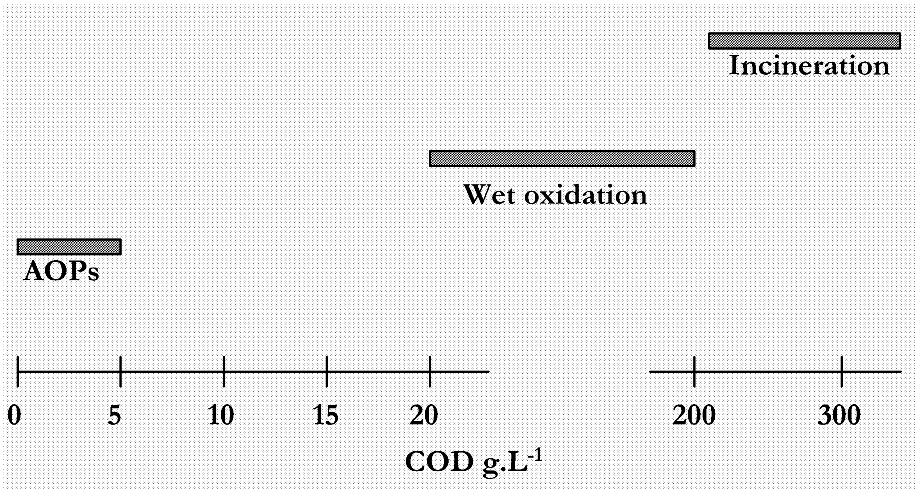


Figure 1. 5: *Domains of suitability of biorecalcitrant wastewater treatment according to COD contents (Andreozzi R. 1999).*

1.3.1 Reaction mechanisms and mode of action of the hydroxyl radicals

The AOP are mainly based on the chemistry of the hydroxyl radical. The $^\bullet$OH radicals are the most significant intermediate reagent responsible of the oxidation of the organic compounds. Due to its strong oxidative power, the $^\bullet$OH radical can attack the organic compound by three main mechanisms: electrophilic addition **(Eq.1.1)**, hydrogen abstraction **(Eq.1.2)** or electron transfer **(Eq.1.3).**

1.3.1.1 Electrophilic addition reactions on double bonds

$^{\bullet}OH + PhX \rightarrow HOPhX^{\bullet}$ **(Eq.1. 1)**

$HOPhX^{\bullet} + n\ (O_2/^{\bullet}OH) \rightarrow HPh + x\ CO_2 + y\ H_2O$, where X a carbonyl group **(Eq.1. 2)**

1.3.1.2 Abstraction of one hydrogen atom

$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$ **(Eq.1. 3)**

The free R$^{\bullet}$ radical reacts after with molecular oxygen to give the peroxyle radical ROO$^{\bullet}$, initiating a sequence of oxidizing reactions which can lead to the complete mineralization of the pollutant.

$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ **(Eq.1. 4)**

$ROO^{\bullet} + n\ (O_2/^{\bullet}OH) \rightarrow\rightarrow x\ CO_2 + y\ H_2O$ **(Eq.1. 5)**

1.3.1.3 Electron transfer

$^{\bullet}OH + RH \rightarrow (RH)^{+\bullet} + HO^{-}$ **(Eq.1. 6)**

In some non favourable conditions of oxidative reactions involving the hydrogen peroxide, $^{\bullet}$OH radicals could react with H_2O_2 leading to the production of hydroperoxyl radicals **(Eq.1.7)**, which are very less powerful than the OH radicals or they could even recombined to form H_2O_2 **(Eq.1.8)**.

$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet}$ **(Eq.1. 7)**

$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$ **(Eq.1. 8)**

Cater et al, 1990 and Haag et al, 1992 had demonstrated that the reactivity of the hydroxyl radical is:

- ✓ Faster for non saturated ethyl and aromatics compounds than for aliphatic compounds;
- ✓ Faster for aromatic compounds with activated phenolic and aniline derivatives than deactivate radicals,
- ✓ Lower for aliphatic compounds than for organic acids.

As a consequence of its high reactivity, the half-life of the $^{\bullet}OH$ radical is obviously very short (e.g. the half life of the $^{\bullet}OH$ in an aqueous solution containing 1 mM of an organic chemical which the kinetic constant is 108 $M^{-1}.s^{-1}$ is 6.9 μs). This thesis focuses on the solar application of the Fenton/photo-Fenton process, one of the most attractive in the group photochemical oxidation processes.

1.3.2 Advanced photochemical oxidation processes

A common limits to most of the AOP is their high demand of electricity either for ozonation, sonication, electrochemist,….etc. At the opposite of that, the energy cost of the photochemical oxidation processes, characterized by the generation of $^{\bullet}OH$ radicals initiated by the interaction of the photons on a catalyst, could be reduced by the use of solar irradiation as the photonic source. Depending on the used catalyst's form (soluble or solid), photochemical processes had been subdivided in two main groups: the homogeneous catalysis which mostly used iron aqua-complex as catalyst and the heterogeneous catalyst leaded by the Titanium dioxide (TiO_2) mediated photocatalysis.

1.3.2.1 Heterogeneous photocatalysis

The first work related to the photoelectrochemical behavior of the metallic oxide semiconductors was initiated by Fujishima and Honda in 1972. These two authors were interested in the dissociation of water photoinduced by the TiO_2 electrodes (Fujishima and Honda 1972).

In spite of the strong passion in this research which involves the activation of the TiO_2 by a photonic light source (sun or lamp), effective conversion into hydrogen by the sun did not exceed a few per cent because the fundamental absorption range of the TiO_2 is located in the area of the UVA.

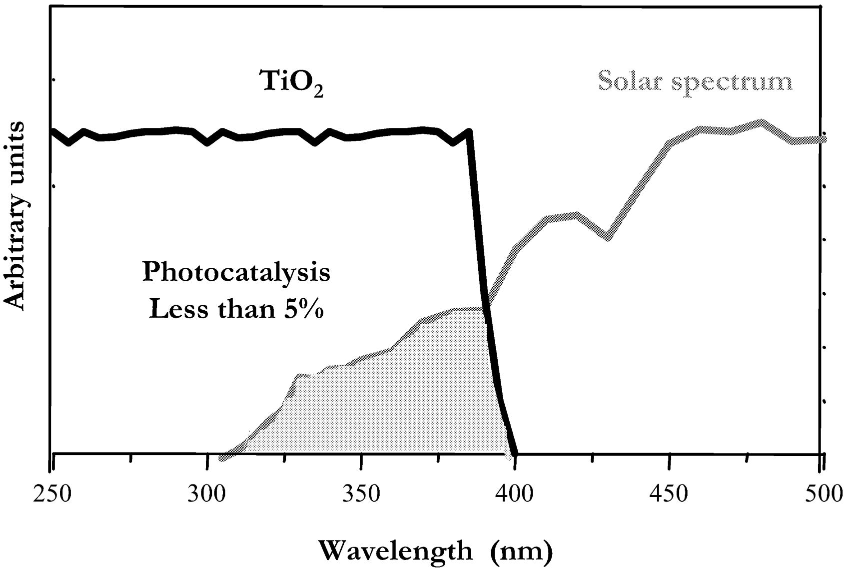


Figure 1. 6: *TiO_2 absorption spectrum (in green)*

In the middle of the 1980s, the interest went on other applications of metallic oxide semiconductors. Research turned to the photocatalytic degradation of water pollutants photoinduced by semiconductors, and more specifically by the TiO_2.

In general, heterogeneous photocatalysis is based on the photo-excitation (by irradiation) of a catalyst, usually a semiconductor, which forms electron-donor sites (Valence band: VB) and electron acceptor-site (conduction band: CB), providing great scope as redox reagents. CB and VB are separated by an energy distance referred to as the band gap (E_{bg}); when the semiconductor is irradiated with light (n*hν) of higher energy than that of the used semiconductor's band gap, n*e are promoted from the VB to the CB leaving a positive hole in the VB. The generated pair of electron (e^-)/hole (h^+) may recombine to generate heat or can be involved in chemical reactions (addition reactions, electron transfer reactions or substitution reactions) with other species in solution as illustrated in **Fig.1.7.**

The process is heterogeneous because there are two active phases: the solid catalyst immerged in the liquid (water in the case of water detoxification).

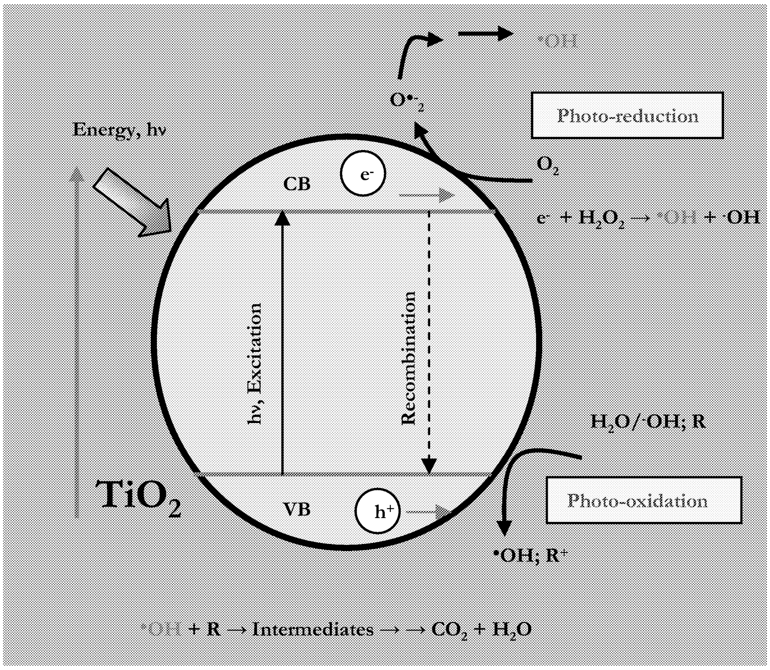


Figure 1. 7: *TiO_2-semiconductor photocatalytic process: Scheme of some chemical events which may occur at the surface of an irradiated TiO_2 particle.*

Among the semiconductors which have been tested for photocatalytic purposes listed in **Table 1.3**, TiO_2 has proven to be the most suitable for widespread environmental applications. TiO_2 is stable light and chemical corrosion and also, its appropriate energetic separation between the VB and CB (+3.1 and -0.1 eV) can be surpassed by the photonic solar energy, leading to the use of sunlight for TiO_2 photocatalytic application.

Table 1. 3: *Characteristics of some common semiconductors in aqueous solution at pH=1.*

Semiconductor	Valence Band	Conduction band	Band Gap (eV)	Band gap wavelength
TiO_2	+ 3.1	-0.1	3.2	387
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	387
ZnS	+ 1.4	-2.3	3.7	335
WO_3	+3.0	+0.2	2.8	
CdS	+2.1	-0.4	2.5	
CdSe	+ 1.6	-0.1	1.7	
GaAs	+1.0	-0.4	1.4	
GaP	+1.3	-1.0	2.3	

Blake D. updated in 2001 a list of over thousands of different contaminants including alcohols, carboxylic acids, phenols, dyes, aromatic hydrocarbons, alkanes, halogenated alkanes, surfactants, pesticides….etc. which have been successfully degraded by TiO_2 photocatalysis (Blake 2001).

Among the possible mechanisms presented in **Fig.1.7** and which may take place on an irradiated particle of TiO_2, there are evidence supporting the idea that hydroxyl radical ($^{\bullet}OH$) is the main responsible of the photo-oxidation of the chemicals because of its powerful oxidation potential; its production in the medium followed the generation of the pair electron/hole shown in the **Fig.1.7**.

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^- + h^+) \qquad \textbf{(Eq.1. 9)}$$

Since H_2O_2 is an electron acceptor, its generation in the medium or its addition, limits the recombination of the electron-hole pair and generate more $^{\bullet}OH$ radical.

$H_2O_2 + e^-_{CB} \rightarrow {}^\bullet OH + OH^-$ **(Eq.1. 10)**

1.3.2.2 Homogeneous photocatalysis

The former application of the homogeneous photocatalysis (single phase system) to treat contaminated waters concerned the use of UV/H_2O_2 and UV/O_3. The use of the UV light for the degradation of water pollutants can be classified in two categories: (i) photolysis (direct excitation of the pollutant by UV light and (ii) photo-oxidation in which light is a propagator agent of an oxidative process initiated by hydroxyl radicals. Hence, this second process involves the use of an oxidant to generate the hydroxyl radicals; for this purpose, three main reagents are commonly used: H_2O_2, O_3 and the photo-Fenton (H_2O_2/Fe^{3+}) reagents.

The photolysis of hydrogen peroxide (H_2O_2)

The couple UV/H_2O_2 was first used for water detoxification by Koubeck (Koubeck 1975). The aqueous hydrogen peroxide solution absorbs the light at wavelengths lower than 360 nm. The optical density of the hydrogen peroxide solution increases with the pH because the dissociated form of hydrogen peroxide (HO_2^-) absorbs the light better than the molecular form H_2O_2.

$H_2O_2 + H_2O \leftrightarrow HO_2^- + H_3O^+$ **(Eq.1. 11)**

The most common accepted mechanism of the photolysis of the H_2O_2 is the cleavage of the molecule into two hydroxyl radicals per quantum of radiation absorbed, by the homolytic breakdown of the O-O bond (Nicole, De Laat et al. 1990). These radicals can then initiate a radicalising feedback path:

$H_2O_2 + h\nu \rightarrow 2\,{}^\bullet OH$ **(Eq.1. 12)**

$2\,(H_2O_2 + {}^\bullet OH) \rightarrow H_2O + HO_2^\bullet$ **(Eq.1. 13)**

$2\,HO_2^\bullet \rightarrow H_2O_2 + O_2$ **(Eq.1. 14)**

Finally, $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$ **(Eq.1. 15)**

Even if Baxendale and Wilson confirmed that the quantum yield of the global reaction is important at 254 nm, its weak extinction coefficient (18.6 $L.mol^{-1}.cm^{-1}$) and the high energy need to run the necessary mercury lamps for the process are some of the limitative factors (Baxendale 1957).

The photolysis of Ozone (O_3)

O_3/UV is an advanced oxidation process widely used in the elimination of the toxic and refractory organic pollutants in drinking waters (Hoigné 1998). The generation of OH radical process is more complex because it holds through various pathways:

$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2$ **(Eq.1. 16)**

$H_2O_2 + h\,\nu \rightarrow 2^{\bullet}OH$ **(Eq.1. 17)**

$H_2O_2 + 2\,O_3 \rightarrow 2^{\bullet}OH + 3\,O_2$ **(Eq.1. 18)**

The molar absorption coefficient of ozone at 254 nm (3600 L^{-1} $mol.^{-1}$. cm^{-1}) is largely higher than that of hydrogen peroxide (18.6 L^{-1}. $mol.^{-1}$. cm^{-1}); thus, the photolysis of ozone does not have the same limitations as that of the hydrogen peroxide. Mercury UV lamps with low pressure can easily be used. One of the main disadvantages of the technique is that when there are many pollutants in the same solution, the reaction is so slow (Fan, Lioy et al. 2003; Reisz, Schmidt et al. 2003; Pera-Titus, Garcia-Molina et al. 2004; Dominguez, Beltran et al. 2005) that for all practical purposes, the process is non viable. Alternatives in order to improve the application of ozone for water refractory pollutants detoxification are promoted by means of combination of ozone with other oxidant such as (i) H_2O_2 (Safarzadeh-Amiri 2001), (ii) Fe^{3+} (Contreras 2001), (iii) Cu(I) (Canton 2003) or (iv) TiO_2 (Beltrán 2005). However, the same as the H_2O_2/UV process, the O_3/UV is limited to the artificial UV light applications since ozone does not absorb at wavelengths higher than 300 nm; thus, the use of sunlight could not be optimal in this process.

The Fenton and photo-Fenton processes

The Fenton reaction was discovered in 1894 by H.J.H. Fenton. In 1934, the Haber-Waiser postulate revealed the mechanism of the reaction, pointing out the hydroxyl radicals as the oxidative agent responsible of the degradation of the chemicals (Fenton 1894; Haber and Weiss 1934). Since then, many scientists have tried to elucidate the whole mechanism (Wailling 1975; Prousek 1995; Sychev and Isak 1995). The Fenton reaction is often modelled as follows:

$$Mn+ + H_2O_2 \rightarrow M^{(n+1)+} + OH^- + OH \qquad \textbf{(Eq.1. 19)}$$

Where M is a transition metal as Fe or Cu

Under the optimum pH conditions (pH=2.5 -4), Fe^{3+} is mainly under its form $Fe(OH)^{2+}$ (Faust and Hoigné 1990; Waite 2002). In absence of light and any other complexing ligand than water, the decomposition of H_2O_2 leads to the formation of hydroxyl radical $^\bullet OH$ and the hydroxylperoxyl ($HO_2^\bullet/O_2^-$) (Gallard H. 2001). Once in solution, the $^\bullet OH$ radical can attack the organic chemicals. The regeneration of iron ion can follow different paths as described in the following equations (Sychev and Isak 1995).

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

$$Fe(OH)^{2+} + H_2O_2 \longrightarrow Fe^{2+} + {}^\bullet O_2H + H^+ + OH^- \qquad \textbf{(Eq.1. 20)}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^\bullet OH + OH^- \qquad \textbf{(Eq.1. 21)}$$

$$^\bullet OH + H_2O_2 \longrightarrow HO_2^\bullet + H_2O \qquad \textbf{(Eq.1. 22)}$$

$$Fe^{3+} + {}^\bullet O_2H \longrightarrow Fe^{2+} + H^+ + O_2 \qquad \textbf{(Eq.1. 23)}$$

$Fe^{2+} + HO_2^{\bullet} \longrightarrow Fe^{3+} + HO_2^{-}$ **(Eq.1. 24)**

The iron aqua-complex $Fe(OH)^{2+}$ absorbs UV light in the region $250 < \lambda < 400$ nm; thus the Fenton rate reaction is strongly increased by UV/Visible light irradiation (Zepp, Faust et al. 1992; Ruppert 1993; Sun 1993; Sarria 2003). The reaction which is referred to as the "photo-Fenton reaction" is modelled as follow:

$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$ **(Eq.1. 25)**

Three possible pathways presented in **Fig. 1.8** have been recognized for the production of the hydroxyl radicals during the photo-Fenton process:

- ✓ The direct photo-reduction of the ferric aqua-complex
- ✓ The Fenton reaction
- ✓ The photolysis of hydrogen peroxide

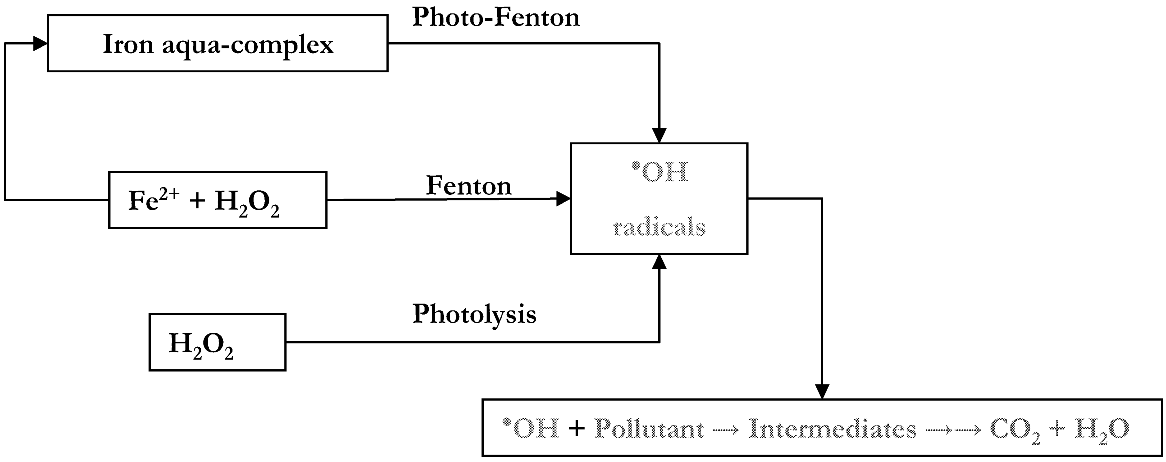


Figure 1. 8: *Scheme of the chemical reactions occurring in the photo-Fenton process.*

Fenton and photo-Fenton processes have been used with great success for the degradation of several organic and inorganic pollutants including pesticides (Malato, Blanco et al. 1999; Parra, Malato et al. 2002; Farre et al. 2005), dyes and dyes-precursors (Sarria 2003; Kositzi, Antoniadis et al. 2004), plasticizers (Muneer 2001; Mailhot 2002; Xue-Kun Zhao 2004; Li, Zhu et al. 2005) and various alkanes and alkenes hydrocarbons (Park, Joo et al. 2003; Kasprzyk-Hordern, Andrzejewski et al. 2004; Burbano 2005) in water.

The main advantage of the photo-Fenton process is the light sensitivity up to 600 nm (35% of the sunlight spectrum)(Safarzadeh-Amiri, Bolton et al. 1997). The closely contact between the pollutant and the oxidizing agent and the high penetration of light (in comparison to heterogeneous photocatalyst) are the important factor of the high effectiveness of the photo-Fenton process (Fallmann, Krutzler et al. 1999).

1.3.2.3 Factors influencing the effectiveness of the iron photo-assisted processes

Several parameters influencing the degradation rate of the Fenton/photo-Fenton processes have been studied: iron species and concentration (Minero, Pelizzetti et al. 1996); pH (Scott, William et al. 1995; Malato, Blanco et al. 2002); initial pollutant concentration (Ruppert 1993; Malato, Blanco et al. 1999); temperature (Sagawe, Lehnard et al. 2001; Rodriguez, Sarria et al. 2002; Lee, Lee et al. 2003); ratio iron-H_2O_2 (Sarria 2003). Some of these factors are discussed below.

(i) Effect of the reagents ratio (H_2O_2/Fe^{2+})

An increase in the iron concentration will accelerate the oxidation rate without influencing the process yield. In the contrary, a rise of the amount of hydrogen peroxide involves an increase in the effectiveness of degradation without notable influence on the process rate (Parra 2000; Neyens E. 2003). An optimal degradation can thus be obtained by increasing the concentration of the two reagents. However, operating in the presence of a great excess of reagents can become a limiting factor, since the ferrous irons and/or the hydrogen peroxide can behave like hydroxyl radicals scavengers. For both reagents, the increase of the initial concentration can only be possible up to an optimum. In the case of iron, the turbidity of the solution increases with an excess of iron and this hinders the light absorption. An optimum H_2O_2/iron ratio of 10-25 has been proposed by (Tang and Huang 1996). Even if iron is not counted as harmful chemical, environmental regulations are becoming restrictive on the use of all chemicals because once they are discharge in the environment, they can react with other chemicals, leading to toxic or harmful chemicals. In Switzerland for example, the norms of iron in wastewaters at the entrance of a biological wastewater treatment plant is 20 $mg.L^{-1}$ while the norm for the treated wastewaters discharging in natural waters is 2 $mg.L^{-1}$ (Conseil fédéral Suisse 1998).

The recent promotion of the Fenton catalyst supported on inert material (Gumy, Fernandez-Ibanez et al. 2005) could be of a great interest for the widespread application of the Fenton/photo-Fenton processes since this would avoid the limitation of discharging high amount of iron into natural waters. Also, different possibilities for heterogeneous iron photo-assisted processes such as the use of zero valent iron, iron oxide and iron load zeolithe for the treatment of wastewaters have been explored

(ii) Influence of the pH

The optimal application of the Fenton/photo-Fenton processes holds at pH between 2.5 and 4 (Gallard H. 1998), with a maximum around 3. At pH below 2.5, three plausible mechanisms decrease the effectiveness of the processes: (a) the formation of ferrous complex which makes the Fe^{2+} unavailable; (b) the inhibition of the Fenton reaction (Sanz J 2003); (c) the increase at weak pH of the scavenging role of the hydrogen peroxide for $^{\bullet}OH$ radicals. In the other hand, beyond pH= 5, the precipitation of iron can also inhibit the reaction (Faust and Hoigné 1990; Ghaly M. Y. 2001).

(iii) Influence of the temperature

Few works have yet been carried out in order to evaluate the influence of the temperature on the Fenton/photo-Fenton processes. While some of these works (Rodriguez, Sarria et al. 2002) evoked a remarkable increase of the process rate when increasing the temperature up to 70°C, Rivas et al., 2001 observed that the temperature in the range of 11 to 41°C do not significantly influence the oxidation of the p - hydro benzoic acid. This can be explained by the fact that at low temperature, for the initiation of the radicalizing mechanism, only weak energy of activation is required (Rivas J.F. 2001).

1.4 Objectives and outlines of the thesis

This research focused on the iron photo-assisted processes, with the aim to contribute to the comprehension of some physicochemical skills involved on the helio-photo-Fenton process and the technical rules guiding the scaling up processing from the laboratory to the field's apply studies. The specific objective is not to reach the complete mineralization of the pollutants within the photocatalytic process, but to transform the biorecalcitrant pollutants into more biodegradable by-products which could be mineralized in any of the known biological water treatment process. Thus, the photochemical treatment of biorecalcitrant pollutants could be integrated in a new global strategy for the management of the water pollution as illustrated in the figure below.

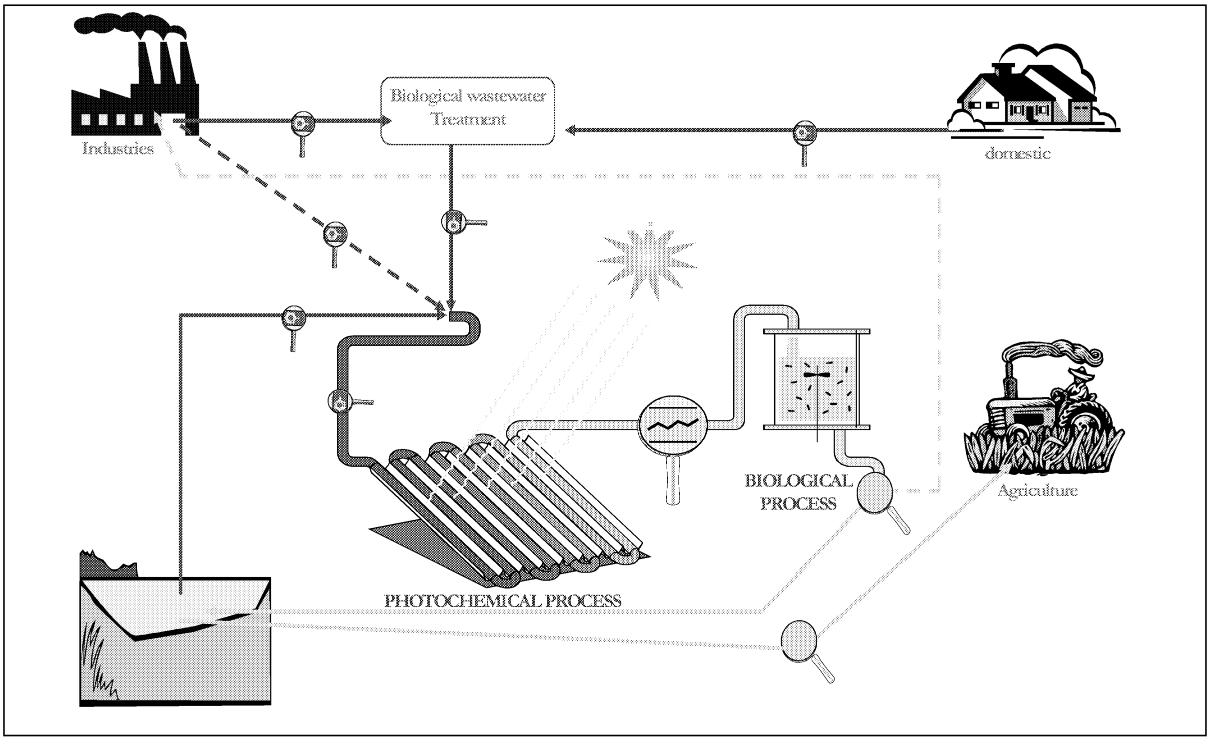


Figure 1. 9: *Schematic representation of the suggested wastewater management strategy including the helio-photochemical treatment*

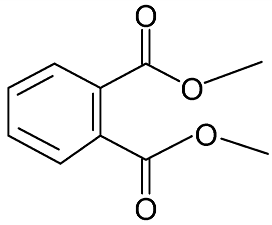
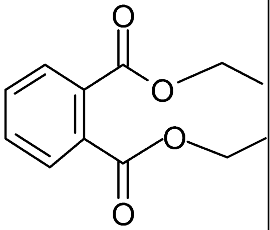
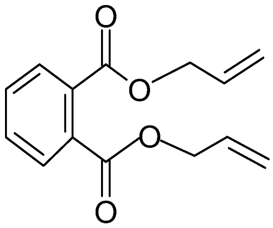
In order to achieve the main goal of this thesis, the following specific tasks were carried:

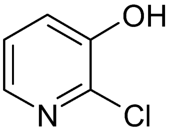
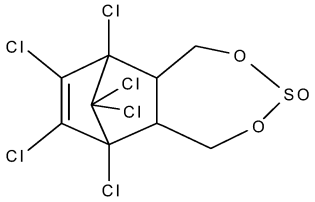
- ✓ The choice of some pollutants of particular scientific and environmental interest for model and field studies,
- ✓ The development of a realistic and cost efficient analytical skills for the field studies,
- ✓ The study of the optimal conditions for operating the helio-photo-Fenton process on a pilot photo-reactor,
- ✓ The study of applying the photo-Fenton process for the remediation of real environmental cases of contamination by biorecalcitrant pollutants.
- ✓ The evaluation and modelling of the solar UV radiation in order to design the photo-remediation processes of water using sun light.

The model's part of this study was carried out using the Diethylphthalate (DEP) as the main biorecalcitrant pollutant with a comparison to the photocatalytic degradation of two others phthalates: the Dimethyl (DMP) and the Diallyl phthalate (DAP). This was followed by two applied case studies carried out: One in the laboratory on a pyridin polluted wastewater from a Swiss chemical company and the other explored the use of the direct sunlight at Ouagadougou, in Burkina Faso, for the destruction of an obsolete stock of the pesticide Endosulfan. **Table 1.4** shows the 2d representation and the main characteristics of the chemicals involved in this study.

The field's part study took on in Burkina Faso, a West Africa sahelian landlocked country located at 12° 20' of latitude North and 1° 40' longitude west. It is located in the moderately favourable belt for solar energy that gets ca 2500 hours of solar radiation per year. Hence, it is a real place where solar applications including the detoxification of biorecalcitrant pollutants can take place.

Table 1. 4: *Main characteristics of the chemicals studied*

PHTHALATES			
Molecular structure	 Dimethyl phthalate	 Diethyl phthalate	 Diallyl phthalate
Molecular Formula	**$C_{10}H_{10}O_4$**	**$C_{12}H_{14}O_4$**	**$C_{14}H_{14}O_4$**
Weight [$g.mol^{-1}$]	194.19	222.24	246.3
Density	1.190	1.118	1.121
Solubility in water [$mg.l^{-1}$]	4000	1080	182
Log K_{ow}	1.6	2.42	3.23

PYRIDIN AND PESTICIDE		
Molecular structure	 2-Chloro-3-hydroxypyridin	 ENDOSULFAN
Molecular Formula	**C_5H_5ClNO**	**$C_9H_6C_{16}O_3S$**
Weight [$g.mol^{-1}$]	129.6	406.9
Solubility in water [$mg.l^{-1}$]	13700	0.325
Log K_{ow}	0.97	3.83

Source: (***http://www.syrres.com/esc/physdemo.htm***

The presentation of this work is organized in five chapters. The introductive chapter include a general view of the water problematic in the world, with a focus on the case of the Burkina Faso where an important part of this work was carried out. A general background on the specific AOPs studied in this work is also presented. The second chapter presents an original analytical method which was developed in the framework of this research in order to follow up model studies at the field's pilot scale in Ouagadougou. Chapter 3 focuses on the helio-photo-Fenton degradation of the diethyl phthalate (DEP), the model chemical pollutant on which optimal chemical and engineering parameters of the photocatalytical process were investigated. Chapter 4 is regarding an applied case study of the helio-photocatalytical depollution of wastewaters of a pesticide manufacture in Burkina Faso and finally, the chapter 5, reports the modelling assay of solar energy in Ouagadougou, the capital city of Burkina Faso.

References

Agency for Toxic substances and disease registry (1995). Toxicological profile for diethylphthalate. Sciences International, US department of Health and Human service.

Ahtiainen, J., Aalto, Miia. and Pessala, Piia (2003). "Biodegradation of chemicals in a standardized test and in environmental conditions." Chemosphere **51**(6): 529-537.

Ali, N. A. A., Mohammed; Sunahara, Geoffrey I.; Robidoux, Pierre Yves (2004). "Phytotoxicity and bioaccumulation of copper and chromium using barley (Hordeum vulgare L.) in spiked artificial and natural forest soils." Ecotoxicology and Environmental Safety **57**(3): 363-374.

Andreozzi R., C. V., Insola A., and Marotta R. (1999). "Advanced oxidation process (AOP) for water purification and recovery." Catal Today **53**: 51-59.

Api, A. M. (2001). "Toxicological profile of diethyl phthalate: a vehicle for fragrance and cosmetic ingredients." Food and Chemical Toxicology **39**(2): 97-108.

Banerjee, S., P. H. Howard, et al. (1984). "Development of a General Kinetic Model for Biodegradation and Its Application to Chlorophenols and Related Compounds." Environ. Sci. Technol. **18**: 416-422.

Baxendale, J. H., and Wilson, A. J. (1957). "The photolysis of hydrogen peroxide at high light intensities." Transactions of the Faraday Society **53**: 344-356.

Beltrán, F. J., Rivas, Francisco J., Gimeno, Olga and Carbajo, María (2005). "Photocatalytic Enhanced Oxidation of Fluorene in Water with Ozone. Comparison with Other Chemical Oxidation Methods." Ind. Eng. Chem. Res. **44**(10): 3419 - 3425.

Bizzari, S., Oppenberg, B. and Iskikawa, Y. (2000). Plasticizers. Chemical Economics Handbook. Palo Alto, CA., SRI International.

Blake, M. D. (2001). Bibliography of work on the heterogeneous photocatalytic removal of hazardous compounds from water and air.

Blount, B. C. (2000). "Levels of Seven Urinary Phthalate Metabolites in a Human Reference Population." Environ. Health Persp. **108**: 979-982.

Brock, J. W. (2002). "Phthalate Monoester Levels in the Urine of Young Children". Bulletin of Environmental Contamination and Toxicology. **68:** 309-314.

Brown, D., Butterworth, K.R. and Gaunt, I.F. (1978). "Short-term oral toxicity study of diethylphthalate in rat." Food Cosmet. Toxicol. **16**(5): 415-422.

Burbano, A. A., Dionysiou, Dionysios D., Suidan, Makram T. and Richardson, Teri L. (2005). "Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent." Water Research **39**(1): 107-118.

Byrne, D. (2003). Décision de la commission 2003/610/CE du 19 Août 2003. Journal officiel de l'Union européenne. L210/35. Brussel, CE**:** 1389-1399.

Canton, C., Esplugas, Santiago and Casado, Juan (2003). "Mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light." Applied Catalysis B: Environmental **43**(2): 139-149.

Centre for Disease Control (CDC) (2001). National Report on Human Exposure to Environmental Chemicals." USA.

Cissé, G., . (1997). Impacts sanitaires de la réutilisation des eaux usées en agriculture dans le contexte sahélien: Cas du maraîchage à Ouagadougou,. Génie Rural, EPFL, Lausanne, Switzerland.

Colón, I., Doris, Caro., Carlos , J. Bourdony and Osvaldo, Rosario (2000). "Identification of Phthalate Esters in the Serum of Young Puerto Rican Girls with Premature Breast Development." Environmental Health Perspectives . **108**: 895-900.

Conseil fédéral Suisse (1998). Ordonnance sur la protection des eaux. Suisse.

Contreras, S., Rodriguez, Miguel., Chamarro, Esther. and Esplugas, Santiago (2001). "UV- and UV/Fe(III)-enhanced ozonation of nitrobenzene in aqueous solution." Journal of Photochemistry and Photobiology A: Chemistry **142**(1): 79-83.

CRC (1985). CRC Handbook of chemistry and physics (CRC Handbook). Boca Raton, Florida, Weast R C, Astle M J and Beyer W H CRC Press.

Danish Environmental Protection Agency (1995). Male reproductive health and environmental chemicals with estrogenic effets.

Digangi, J., Norin H., Schettler, MD., Cobbing, M. and Rossi, Mark (2002). aggregate exposure to phthalates in humans. USA, Health Care Without Harm.

DiGangi, J. a. N., Helena (2002). Pretty and Nasty: Phthalates in European cosmetic products. Sweden, Women's Environmental Network, Health Care Without Harm, USA and Swedish Society for Nature Conservation**:** 26 p.

Dominguez, J. R., J. Beltran, et al. (2005). "Vis and UV photocatalytic detoxification methods (using TiO2, TiO2/H2O2, TiO2/O3, TiO2/S2O82-, O3, H2O2, S2O82-, Fe3+/H2O2 and Fe3+/H2O2/C2O42-) for dyes treatment." Catalysis Today **101**(3-4): 389-395.

Duty, S., M. Silva, et al. (2003). "Phthalate exposure and human semen parameters." Epidemiology **14**(3): 269-277.

Duty, S., N. Singh, et al. (2003). "The relationship between environmental exposures to phthalates and DNA damage in human sperm using the neutral comet assay." Source: ENVIRONMENTAL HEALTH PERSPECTIVES **111**(9): 1164-1169.

EEC (1976). Directive 76/464/EEC-Water pollution by discharges of certain dangerous substances.

EEC (1992). List of council directives 76/4647,. E. E. Community. Brussels, Belgium.

EPA (2001). Removal of endocrine disruptor chemicals using drinking water treatment processes. O. o. r. a. d. publication. Washington, USA.

EU (1996). "COUNCIL DIRECTIVE 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control." http://europa.eu.int/smartapi/cgi/sga_doc?smartapi!celexapi!prod!CELEXnumdoc&lg=en&numdoc=31996L0061&model=guichett.

EU Scientific Committee on Toxicity, E. a. t. E. C. (1998.). Phthalate migration from soft PVC toys and child-care articles. Opinion expressed at the CSTEE third plenary meeting. Brussels, EU.

Fallmann, H., T. Krutzler, et al. (1999). "Applicability of the Photo-Fenton method for treating water containing pesticides." Catalysis Today **54**(2-3): 309-319.

Fan, Z., P. Lioy, et al. (2003). "Ozone-Initiated Reactions with Mixtures of Volatile Organic Compounds under Simulated Indoor Conditions." Environ. Sci. Technol. **37**(9): 1811-1821.

Farre, M. J., M. I. Franch, et al. (2005). "Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation." Chemosphere **58**(8): 1127-1133.

Faust, B. C. and J. Hoigné (1990). "Photolysis of Fe(III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain." Atmos. environ. **24 A**(1): 79-89.

Fenton, H. J. H. (1894). "Oxidation of tartaric acid in presence of iron.." J. of chem. soc. Trans. **65**: 899-910.

Field, E. A., C. J. Price, et al. (1993). "Developmental toxicity evaluation of diethyl and dimethylphthalate in rats." teratology **48**: 33-44.

Fujishima, A. and K. Honda (1972). "Electrochemical photolysis of water at a semiconductor electrode." Nature **238**(7): 37-38.

Gallard H., D. L., J. (2001). "Kinetics of oxidation of chlorobenzenes and phenyl-ureas by Fe(II)/H2O2 and Fe(III)/H2O2. Evidence of reduction and oxidation reactions of intermediates by Fe(II) or Fe(III)." Chemosphere **42**(4): 405-413.

Gallard H., D. L. J., Legube B. (1998). "Effect of pH on the oxidation rate of organic compounds by FeII/H2O. Mechanisms and simulation." New J Chem.: 263-268.

Geobel, H., Gorbach, S., Knauf, W., Rimpau, R.H. and Huttenbach, H. (1982). "Properties, effects, residues and analytics of the insecticide endosulfan." Residue Rev. **83**: 1-122.

Geschwind, A. A., E. Eiseman, et al. (1999). The impact of endocrine disrupting chemicals on wildlife: A review of literature 1985-1998. Washington D.C, Science and Technology policy Institute**:** 69.

Ghaly M. Y., H. G., Mayer R., Haseneder R. (2001). "photochemical oxidation of p-chlorophenol by UV/H2O2 and photo-Fenton process. A comparative study." Waste management **21**: 41-47.

Gomes, R. L., M. D. Scrimshaw, et al. (2003). "Determination of endocrine disrupters in sewage treatment and receiving waters." TrAC Trends in Analytical Chemistry **22**(10): 697-707.

Guerin, T. F. (2001). "A biological loss of endosulfan and related chlorinated organic compounds from aqueous systems in the presence and absence of oxygen." Environmental Pollution **115**(2): 219-230.

Gumy, D., P. Fernandez-Ibanez, et al. (2005). "Supported Fe/C and Fe/Nafion/C catalysts for the photo-Fenton degradation of Orange II under solar irradiation." Catalysis Today **101**(3-4): 375-382.

Haber, F. and J. Weiss (1934). "The Catalytic Decomposition of Hydrogen Peroxide by Iron Salts." J. Proc. Roy. Soc. London A, Mathematical and Physical Sciences > Vol. **147**(861): 332-351.

Hashimoto, Y., M. Kawaguchi, et al. (2003). "Estrogenic activity of tissue conditioners in vitro." Dental Materials **19**(4): 341-346.

Hoigne, J. (1997). "Inter-calibration of oh radical sources and water quality parameters." Water Science and Technology **35**(4): 1-8.

Hoigné, J. (1998). Chemistry of aqueous ozone and transformstion of pollutanst by ozone and advanced oxidation process. The Handbook of Environmental Chemistry, part C: Quality and treatment of drinking water, part II. Berlin, Springer. **5**.

Horan, N. J. (1990). Biological wastewater treatment systems. Theory and operation. Chichester, England, John Wiley & Sons Ltd.

Houlihan, J. and R. Wiles (2000). Beauty Secrets: Does a common chemical in nail polish pose risks to human health? Environmental Working Group.

Houlihan J., B. C., and Schwan B., (2002). Not too pretty: Phthalates, beauty products & the FDA. USA, Health care without harm, FDA and Coming Clean.

Jones, H. B., D. A. Garside, et al. (1993). "The influence of phthalic esters on Leydic cell structure and function in vitro and in vivo." Exp. Mol. Pathol. **58**: 179-193.

Kasprzyk-Hordern, B., P. Andrzejewski, et al. (2004). "MTBE, DIPE, ETBE and TAME degradation in water using perfluorinated phases as catalysts for ozonation process." Applied Catalysis B: Environmental **51**(1): 51-66.

Kemi, N. C. I. (2001). Risk assessment: bis(2-ethylhexyl) phthalate. EINECSNo. 204-211-0. C.-N. 117-81-7;.

Kogi, K. (2002). "Work Improvement and Occupational Safety and Health Management Systems: Common Features and Research Needs." Industrial Health **40**: 121–133.

Koné, D. (2003).

Kositzi, M., A. Antoniadis, et al. (2004). "Solar photocatalytic treatment of simulated dyestuff effluents." Solar Energy **77**(5): 591-600.

Koubeck, E. (1975). "photochemical induced the oxidation of refractory organics with hydrogen peroxide." Ind. Eng. Chem. Process des. Dev. **14**: 348.

Lamb, J. C. t., R. E. Chapin, et al. (1987). "reproductive effects of four phthalic esters in the mouse." toxicol. Appl. Pharmacol. **88**: 255-269.

Latini, G., D. C. Felice, et al. (2003). "In utero exposure to di-(2-ethylhexyl)phthalate and duration of human pregnancy." Env. Health Persp. **111**((14):): 1783-1785.

Lee, Y., C. Lee, et al. (2003). "High temperature dependence of 2,4-dichlorophenoxyacetic acid degradation by Fe3+/H2O2 system." Chemosphere **51**(9): 963-971.

Li, L., W. Zhu, et al. (2005). "Photocatalytic ozonation of dibutyl phthalate over TiO2 film." Journal of Photochemistry and Photobiology A: Chemistry **175**(2-3): 172-177.

Mailhot, G., Sarakha, M., Lavedrine, B., Caceres, J. and Malato, S. (2002). "Fe(III)-solar light induced degradation of diethyl phthalate (DEP) in aqueous solutions." Chemosphere **49**(6): 525-532.

Malato, S., J. Blanco, et al. (2002). "Photocatalytic treatment of water-soluble pesticides by photo-Fenton and TiO2 using solar energy." Catalysis Today **76**(2-4): 209-220.

Malato, S., J. Blanco, et al. (1999). "Pre-Industrial Experience in Solar Photocatalytic Mineralization of Real Wastewaters. Application to Pesticide Container Recycling." Water Sci. Technol. **40**(4-5): 123-130.

Malato, S. R., J. G. Blanco, et al. (2004). "Photocatalysis." Solar Energy **77**(5): 443-444.

Mantzavinos, D., E. Lauer, et al. (1997). "Wet oxidation as a pretreatment method for wastewaters contaminated by bioresistant organics." Water Science and Technology **36**(2-3): 109-116.

Minero, C., E. Pelizzetti, et al. (1996). "Large solar plant photocatalytic water decontamination: Degradation of atrazine." Solar Energy **56**(5): 411-419.

Muneer, M., Theurich, J. and Bahnemann, D. (2001). "Titanium dioxide mediated photocatalytic degradation of 1,2-diethyl phthalate." Journal of Photochemistry and Photobiology A: Chemistry **143**(2-3): 213-219.

National Research Council of Canada (1975). Endosulfan: Its effects on environmental quality. Pesticides and related compounds. Report 11. Ottawa, ON: 1-100.

Neyens E., B. J. (2003). "A review of classic Fenton's peroxidation as an advanced oxidation technique." J Hazard Matter **98**(33-50).

Nicole, I., J. De Laat, et al. (1990). "Utilisation du rayonnement ultraviolet dans le traitement des eaux: mesure du flux photonique par actinometrie chimique au peroxyde d'hydrogene: Use of u.v. radiation in water treatment: measurement of photonic flux by hydrogen peroxide actinometry." Water Research **24**(2): 157-168.

OECD (1996). Guidelines for testing of chemicals, test 302B.

Ollis, D. F. (1988). " Process economics for water purification: A comparative assessment." in Photocatalysis and environment: 663-677.

Ollis, D. F. and H. A. Ekabi (1993). photocatalytic purification and treatment of water and air. Amsterdam.

Park, S. E., H. Joo, et al. (2003). "Photodegradation of methyl tertiary butyl ether (MTBE) vapor with immobilized titanium dioxide." Solar Energy Materials and Solar Cells **80**(1): 73-84.

Parra, S., S. Malato, et al. (2002). "New integrated photocatalytic-biological flow system using supported TiO2 and fixed bacteria for the mineralization of isoproturon." Applied Catalysis B: Environmental **36**(2): 131-144.

Parra, S., Sarria, V., Malato, S., Peringer, P. and Pulgarin, C. (2000). "Photochemical versus coupled photochemical-biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon." Applied Catalysis B: Environmental **27**(3): 153-168.

Pera-Titus, M., V. Garcia-Molina, et al. (2004). "Degradation of chlorophenols by means of advanced oxidation processes: a general review." Applied Catalysis B: Environmental **47**(4): 219-256.

Phthalate Esters Panel (2002). How are phthalates used? American Chemistry Council, http://www.phthalates.org.

Population.Information.Program (1998). "Solutions for a water-short world." 1-31.

Prousek, J. (1995). "fenton reaction after a century." Chem. Lisy **89**: 11-21.

Pulgarin, C., M. Invernizzi, et al. (1999). "Strategy for the coupling of photochemical and biological flow reactors useful in mineralization of biorecalcitrant industrial pollutants." Catalysis Today **54**(2-3): 341-352.

Pulgarin, C. and J. Kiwi (1995). "Iron Oxide-Mediated Degradation, Photodegradation, and Biodegradation of Aminophenols." Langmuir **116**: 519-52.

Reisz, E., W. Schmidt, et al. (2003). "Photolysis of Ozone in Aqueous Solutions in the Presence of Tertiary Butanol." Environ. Sci. Technol. **37**(9): 1941 - 1948.

Rivas J.F., B. J. F., Gimeno O., and Frades J. (2001). "Treatment of olive oil mill wastewater by Fenton's reagent." J Agric Food Chem **49**: 1873- 1880.

Rodriguez, M., V. Sarria, et al. (2002). "Photo-Fenton treatment of a biorecalcitrant wastewater generated in textile activities: biodegradability of the photo-treated solution." Journal of Photochemistry and Photobiology A: Chemistry **151**(1-3): 129-135.

Rozati, R., P. P. Reddy, et al. (2002). "Role of environmental estrogens in the deterioration of male factor fertility." Fertility and Sterility **78**(6): 1187-1194.

Ruppert, G., Bauer, R. and Heisler, G. (1993). "The photo-Fenton reaction: an effective photochemical wastewater treatment process." Journal of Photochemistry and Photobiology A: Chemistry **73**(1): 75-78.

Safarzadeh-Amiri, A. (2001). "O3/H2O2 treatment of methyl-tert-butyl ether (MTBE) in contaminated waters." Water Research **35**(15): 3706-3714.

Safarzadeh-Amiri, A., J. R. Bolton, et al. (1997). "Ferrioxalate-mediated photodegradation of organic pollutants in contaminated water." Water Research **31**(4): 787-798.

Sagawe, G., A. Lehnard, et al. (2001). "The Insulated Solar Fenton Hybrid Process: Fundamental Investigations." Helv. Chem. Act. **84**: 3742-3759.

Sanz J, L. J. I., De Louis A.M, Ortueta M and Varona F. (2003). "Microwave and fenton's reagent oxidation of wastewater." Environ Chem lett, **1**: 45-50.

Sarria, V. (2003). Coupled advanced oxidation and biological processes for wastewater treatment. Institute of Environmental science and Technology. Lausanne, EPFL**:** 150.

Sarria, V., Deront, M., Peringer, P. and Pulgarin, C. (2003). "Degradation of a biorecalcitrant dye precursor present in industrial wastewaters by a new integrated iron(III) photoassisted-biological treatment." Applied Catalysis B: Environmental **40**(3): 231-246.

Sarria, V., Kenfack, Simeon., Guillod, Olivier. and Pulgarin, Cesar (2003). "An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants." J. of photoch. and photobiol. A: Chem. **159**: 89-99.

Sarria, V., Kenfack, Simeon.,Malato, Sixto., Blanco, Julian. and Pulgarin, Cesar (2005). "New helio-photocatalytic-photovoltaic hybrid system for simultaneous water decontamination and solar energy conversion." Solar Energy **79**(4): 353-359.

Sarria, V., S. Parra, et al. (2002). "Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds." Catalysis Today **76**(2-4): 301-315.

Scott, M. A., J. H. William, et al. (1995). "Degradation of Atrazine by Fenton's Reagent: Condition Optimization and Product Quantification." Environ. Sci. Technol. **29**(8): 2083 - 2089.

Sonnenschein, C. and A. M. Soto (1998). "An updated review of environmental estrogen and androgen mimics and antagonists." The Journal of Steroid Biochemistry and Molecular Biology **65**(1-6): 143-150.

Staples, C. A., Peterson, Dennis R., Parkerton, Thomas F. and Adams, William J. (1997). "The environmental fate of phthalate esters: a literature review." Chemosphere **35**(4): 667-749.

Sun, Y. F., and Pignatello J.J. (1993). "Photochemical Reactions Involved in the Total Mineralization of 2,4-D by Fe3+/H,0,/UV." Environ. Sci. Technol. **27**: 304-310.

Sychev, A. Y. and V. G. Isak (1995). "Iron compounds and the mechanisms of the homogeneous catalysis of the activation of O2 and H2O2 and the activation of organic substrates." Russian chemical Reviews **64**(12): 1105-1129.

Tang, W. Z. and C. P. Huang (1996). "2,4-Dichlorophenol Oxidation Kinetics by Fenton's Reagent." Environ. Techn., **Volume 17,**(12): 1371-1378.

Toepfer, K. (2004). " Speech of the Director of the United Nations Environment Programme: Statement on the occasion of the Stockholm Convention on Persistent Organic Pollutants coming into Force." UNEP.

Turner, K. O., Syvanen, M. and Meizel, S. (1997). "The human acrosome reaction is highly sensitive to inhibition by cyclodiene insecticides. ." J. Androl. **18**: 571-575.

US Food and Drug Administration (2001). Frequency of use. O. o. c. a. colors, Centre for food safety and applied nutrition.

US Food and Drug Administration (2001). Phthalates and cosmetic products. O. o. c. a. colors, Centre for food safety and applied nutrition.

Wailling, C. (1975). "Fenton's reagent revisited." Acc. chem. Res. **8**: 125-131.

Waite, T. D. (2002). "Challenges and opportunities in the use of iron in water and wastewater treatment." reviews in Environmental Science and Biotechnology **1**: 9-15.

Watfa T.N, Awan S., et al. (1998). Chemical risk assessment and occupational hygiene preventive measures in small and medium-sized enterprises (SMEs): A Contribution to the ILO Action Programme on Safety in the Use of Chemicals at Work. Geneva, International Labour Office.

WHO (2003). "Diethyl Phthalate" Concise International Chemical Assessment Document. 52. CICAD. Geneva 2003.

WHO-UNDP (2004). WHO -UNDP joint monitoring programme report.

Xue-Kun Zhao, G.-P. Y., Yu-Jue Wang, Xian-Chi Gao (2004). "Photochemical degradation of dimethyl phthalate by Fenton reagent." Journal of Photochemistry and Photobiology A: Chemistry **161**: 215-220.

Zepp, R. G., B. C. Faust, et al. (1992). "Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron(II) with hydrogen peroxide: the photo-Fenton reaction." Environ. Sci. Technol. **26**(2): 313 - 319.

Zhang, Z. L., H. S. Hong, et al. (2003). "Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China." Chemosphere **52**(9): 1423-1430.

Chapter 2

A systematic development of a field monitoring method for the study of the helio-photo-Fenton degradation of three phthalates

This chapter describes the analytical method which was developed in the laboratory at the LBE-EPFL in Switzerland, in order to facilitate the monitoring of the degradation of the diethyl phthalate (DEP) during field's experimentations at Ouagadougou in Burkina Faso. Another objective of this field work at Ouagadougou was to use the sunlight to provide photons in the photo-Fenton process instead of UV lamps as it was the case in the laboratory and to test the functioning of a Pilot Compound Parabolic Collector (CPC) photo-reactor.

2.1 Introduction

The photocatalytic detoxification of water is one of the new promoted research fields which up till now, have been carried out mostly in highly equipped laboratories. One of the important reasons is that the experimental and analytical devices which are needed for this research are very expensive. As the same as other Advanced Oxidation Processes (AOP), the photocatalysis is studied for the degradation pollutants which are refractory to the biodegradation and obviously, the effectiveness of such processes is limited to less polluted waters (only few grams of COD per litre) (Andreozzi 1999). Most of the photodegradation processes have been monitored by means of the following analytical methods: High Pressure Liquid Chromatography (HPLC), Gas Chromatography (GC), Total Organic Carbon (TOC) and/or Chemical Oxygen Demand (COD) (Ruppert 1993; Parra 2000; Utset 2000; Bajt 2001; Poulain 2003; Sarria 2003; Sarria 2003). However, these methods are time-consuming and they need highly qualified personnel, very expensive equipments and reagents to be run; therefore, they cannot be applied in contexts with technical, economical and educational limitations. On the other hand, the toxicity of some of the reagents used is detrimental to the environment (Cooper 2002; Stasinakis 2003; Gunaratnam and Grant 2004) and/or harmful to the operators (Wright 1994; Al-Ghamdi 2003).

Numerous works on the Fenton and photo-Fenton processes, have exhibited the ability to oxidize most of the hardly or non biodegradable organic pollutants in water and wastewaters (Kiwi 1993; Feng and Nansheng 2000; Waite 2002; Sarria 2003).

Very few studies reports of which the pollutants form complexes with iron during the process and thus absorb light in the wavelengths higher than 300 nm, have been monitored by measuring the absorbance of the complex (Nansheng 1996). By what we know, no study has yet explored the use of the measure of the absorbance of a degradation intermediates as the main procedure of monitoring the process.

Such indirect, rapid and cost effective methods are referenced as "Poor Man's" approaches (Ken 2000; Stephen 2003). They are widely used in various scientific fields and technological works in order to supply the lack of more sophisticated analytical or data acquisition devices (Idso 1997; Nijman and Bellussi 2000; Radzewicz 2000; Csikor 2001; Alhakimi 2003; Ai 2004; Ghule 2004; Tang 2004).

Recently, Shiyun Ai et al (Ai 2004) had suggested the monitoring of the COD using a nano-TiO_2–$K_2Cr_2O_7$ system based on the measure of the absorbance of Cr^{6+} initially in the solution or that of the Cr^{3+} which is released by the oxidation of $Cr_2O_7^{2-}$. The method was modelled as follow:

$$TiO_2 + h\nu \longrightarrow h^+ + e^- \quad \textbf{(Eq. 2.1)}$$

$$h^+ + H_2O \longrightarrow {}^\bullet OH + H^+ \quad \textbf{(Eq. 2.2)}$$

$$^\bullet OH + R \longrightarrow CO_2 + H_2O \quad \textbf{(Eq.2. 3)}$$

$$2Cr_2O_7^{\ 2-} + 28H^+ + 12e^- \longrightarrow 4Cr^{3+} + 14H_2O \quad \textbf{(Eq.2. 4)}$$

The TiO_2 photodegradation process was then monitored by measuring the absorbance of the photo-treated solution at 610 nm (the maximum absorption wavelength of Cr^{3+}) and correlating this to the COD of the solution. Since the principle of the method was based on the K_2CrO_7 fixed on the TiO_2, we assume that its utilization in the solar photodegradation process, could be limited to the monitoring of slightly polluted water because, the applicable concentration of the TiO_2 used in this field is mostly in the range of 0.2 to 1 $g.L^{-1}$ (Curco 2002)

The iron photo-assisted degradation of the DEP could be monitored by a similar method considering that, any variation of the absorbance of the phototreated solution at a wavelength higher than 295 nm should be linked to the appearance of a by-product; since the DEP and mostly all the phthalates do not absorb at the wavelengths higher than 295 nm; moreover, they do not complex with iron (Staples 1997; Mailhot 2002). The correlation of the absorbance at that identified wavelength, to the variation of the initial concentration of the DEP (analyzed by other means: HPLC, GC…) can thus be used to standardize the spectrophotometric monitoring method.

In the Fenton/photo-Fenton processes, Fe^{2+} and Fe^{3+} ions react with H_2O_2 in the presence or absence of photons to generate very powerful oxidative radicals $^{\bullet}OH$ (2.8 eV) according to the following fundamental equations (Fenton 1894; Faust and Hoigné 1990).

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + {}^{\bullet}OH \qquad \textbf{(Eq. 2.5)}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \qquad \textbf{(Eq.2. 6)}$$

The $^{\bullet}OH$ radicals have the ability to oxidize almost all organic compounds in aqueous solution (Huston and Pignatello 1999; Malato 2000; Blake 2001.) and a first-order equation of such reactions can be written as follows:

$$DEP + Fe^{3+} \xrightarrow{h\nu} \textit{by-products} \qquad \textbf{(Eq. 2.7)}$$

In general, there is no adsorption of the soluble pollutant or the by-products on the catalyst, the pollutant and the catalyst are both homogeneous in the system (homogeneous photocatalysis). Thus, the amount of the by-product formed within the process can be monitored using any of the conventional analytical methods among which, the measure of the absorbance at a specific wavelength is one of the most rapid, cost effective and does not need highly qualified personal to be carried out. But this approach is limited when the by-products do not absorb at any specific absorption band.

This paper reports the method that we developed in the Laboratory at the EPFL in Switzerland and was validated during a field work in Burkina Faso in the framework of a study of the evaluation of a CPC reactor.

The following steps were followed: (i) the monitoring of the photodegradation of the DEP by HPLC method and the identification of two photodegradation intermediates, (ii) the monitoring of the degradation of the DEP following the spectra evolution of the phototreated solution, (iii) the correlation of the DEP degradation to the absorbance of the intermediate products and (iv) the validation of the method at the field scale study on a CPC photo-reactor.

2.2 Materials and procedures

2.2.1 The Suntest and the CPC pilot photo-reactor

At the LBE-EPFL, the photocatalytic experiments were performed using a 50 ml Pyrex flask with a cut-off at λ=290 nm placed into a Hanau Suntest (**Fig.2.1**).

The radiation source was a Xenon lamp where the radiant flux (80 mW.cm^{-2}) was measured with a power meter of YSI Corporation. The lamp had a regular distribution of wavelengths with about 0.5% of the emitted photons at wavelengths shorter than 300 nm (UV-C range) and about 7% between 300 and 400 nm (UV-B range). The profile of the photons emitted between 400 and 800 nm (UV-A range) followed the solar spectrum.

Experiments were done at the light intensity of 560 W.m^{-2}, which corresponds to a relative UVA (300-400 nm) intensity of W.m^{-2}.

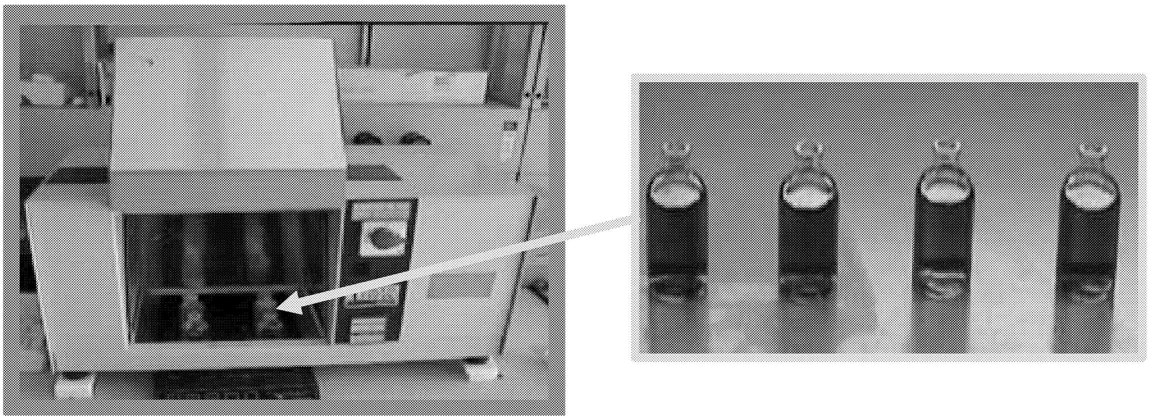


Figure 2. 1: *A Hanau Suntest Simulator containing 04 Pyrex flask samples during a laboratory experiment at the LBE-EPFL, Lausanne, Switzerland.*

The pilot plant, a SOLARDETOX ® ACADUS-2003 device model delivered by Ecosystem SA, Barcelona, Spain, basing on the engineering skills developed at the Almeria's solar platform in Spain (http://www.psa.es/webesp). It is a Compound Parabolic Concentrator (CPC) module (collector useful surface: 2.12 m^2, photo-reactor active volume 15.1 L within a total volume of 16.07 L) made of sixteen borosilicate cylindrical glass tubes. Each glass tube lies on a CPC aluminium mirror with one sun ratio of concentration. The total surface of the collector is 2.25 m^2.

The reactor plate is mounted on a two positions fixed platform inclinable at 10° and 35° allowing operating at the approximate local latitude of Ouagadougou-Burkina Faso (12.2° N), at 10° angle position for a wide period of time and at 35° angle position during the winter solstice if necessary. A picture of the CPC photo-reactor used and its technical design are shown in the **Fig. 2.2**.

From the operational point of view, the plant behaves as plug-flow reactor in the collector zone, connected in series with a 50 L polypropylene stirred tank (re-circulating tank or buffer tank) for wastewater preparation: pH adjustments, catalyst and oxidant feeding. The mixture is homogenized to achieve a fixed concentration in the system; by circulating the preparation in a closed loop circuit round the tank and centrifugal pump.

At the beginning of an experiment, a desired stock of commercial *"pure"* phthalate solution was solubilized in 2 litres of tap water in a Pyrex flask and stirred for at least 2 hours in the laboratory. Afterward, the solution was poured into the conditioning tank of the photo-reactor in which additional 23 litres of the same tap water were added. The characteristics of the used tap waters for field work at Ouagadougou, are giving in **Table 2.1**. The pH of the solution was adjusted to 3 by adding a concentrated HCl solution and the required amount of the catalyst ($FeCl_3$, $6H_2O$) was added. The entire system was homogenized by closing the valves **(1)** and **(3)**, and circulating the polluted water in a closed loop circuit round the pump and the tank for 15 min.

Once the solution is homogenised, the required amount of hydrogen peroxide was added and the feeding valve (1) was opened at a desired water flow rate (24.2 L.min^{-1}) for all the experiments.

The solar ultraviolet radiation was instantaneously determined during the experiments through a UV-A radiometer ACADUS 85 UV mounted on the reactor, at the same angle (10°) as its flat plate part. It provides data in terms of incident UV radiation per area unit (W.m^{-2}) and the accumulated UV energy in the reactor (in Wh). In this thesis, we reported the UV energy in kJ (the international system unit of energy).

The system operates in semi-batch mode and samples were collected at 10 minutes interval. For the testing and validation of the analytical method, all the field's experiments were carried out at the same period of the day: 10:30-13:30; thus, the influence of the sunlight rate fluctuations could be avoided.

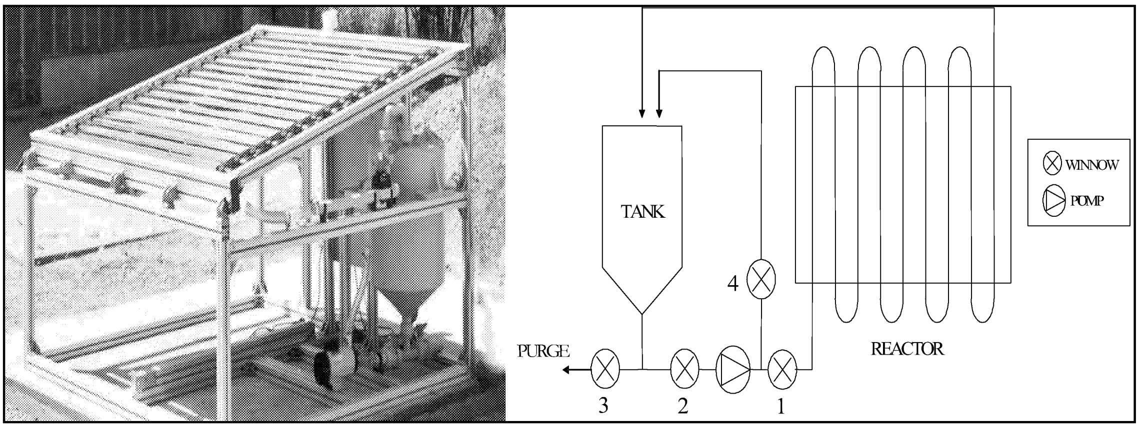


Figure 2. 2: *A Picture and the technical design of the CPC photo-reactor used for the experiments at the EIER in Ouagadougou, Burkina Faso*

Table 2. 1: *Quality of the tap waters used for the experiments at the EIER, (Burkina Faso); November 2003.*

Parameters	**Units**	***Water at the EIER***	***WHO Guidelines 1993***
pH	-	7.60	-
Conductivity at 20°C	$\mu S.cm^{-1}$	121	-
Turbidity	NTU	0.7	5
Chlorine	$mg.l^{-1}$	0.1–1.5	-
Hardness	$mg.l^{-1}$	4.0	-
Calcium (Ca^{2+})	$mg.l^{-1}$	9.6	-
Magnesium (Mg^{2+})	$mg.l^{-1}$	4.8	-
Sodium (Na^{+})	$mg.l^{-1}$	9.8	200
Potassium (K^{+})	$mg.l^{-1}$	10.0	-
Total iron (Fe)	$mg.l^{-1}$	0.1	0.3
Ammonium (NH_4^{+})	$mg.l^{-1}$	0	-
Carbonates (CO_3^{2-})	$mg.l^{-1}$	0	-
Bicarbonates (HCO_3^{-})	$mg.l^{-1}$	48.8	-
Chlorine ion (Cl^{-})	$mg.l^{-1}$	17.5	250
Sulphates (SO_4^{2-})	$mg.l^{-1}$	14.0	250
Nitrites (NO_2^{-})	$mg.l^{-1}$	0.01	3
Nitrates (NO_3^{-})	$mg.l^{-1}$	11.0	50
Orthophosphates (PO_4^{3-})	$mg.l^{-1}$	0.08	-

2.2.2 Chemicals

All chemicals were used as received from the commerce. The dimethyl phthalate, the diethyl phthalate and the diallyl phthalate were obtained from Fluka, Buchs, Switzerland. **Table 1.4** shows the characteristics of these chemicals. ($FeCl_3$, $6H_2O$), HCl and H_2O_2 (30% w/w) were also from Fluka (Switzerland). All were analytical grade (p.a.).

2.2.3 HPLC and UV-visible analytical methods

HPLC analyses were carried out in a Varian 9065 unit provided with a Varian 9012 solvent delivery system, an automatic injector 9100 and a Varian Pro Star Variable (200–400 nm) diode array detector: 9065 Polychromic. All modules were piloted with a computer on which the Varian Star 5.3 software is installed for liquid chromatography data delivery. A reverse phase spherisorb silica column ODS-2 and a (70/30) (v/v) mixture of acetonitrile/water mobile phase were used to run the chromatography in isocratic mode at a flow rate of 1 ml.min^{-1}. This technique allows the measuring of the DEP concentration in the solution and to follow the overall formation and decay of the aromatic and aliphatic by-products during the process.

A Hitachi UV-vis U-3010 and a Biomate 3 model spectrophotometers were used respectively at the LBE and at the EIER, with a 1.0 cm quartz cell. The Hitachi UV-vis U-3010 spectrophotometer allowed generating the characteristic spectra of phototreated samples in the wavelength range of 200-600 nm, so that all the chemicals and/or complexes contained in the solutions can be signalled at their maximum absorption wavelength. Once we identified the specific absorption wavelengths through the spectra, we chose these particular wavelengths for the analyses on the multi-wavelengths *Biomate 3* spectrophotometer during the field's experiments at the EIER at Ouagadougou, Burkina Faso.

2.3 Results and discussions

2.3.1 Monitoring the photodegradation of the DEP following a HPLC analytical protocol

The superimposed chromatograms of a consecutive series of the DEP phototreated solution sampled at 15 min period are presented in **Fig.2.3**. It was noticed that the DEP get out of the column at 3.8 minutes, when two by-products which absorption spectra are shown in **Fig.2.4,** get out of the column earlier at respectively 2.5 and 3.2 minutes. These spectra delivered by the HPLC managing software shows maximum at 253.4 and 301.3 nm respectively.

We did not observe any change of the DEP concentration in the "control" experiments (without iron, nor hydrogen peroxide, but at the presence of the light). This confirmed the difficult ability of the DEP to photolysis as it was observed by Staple et al (Staples 1997).

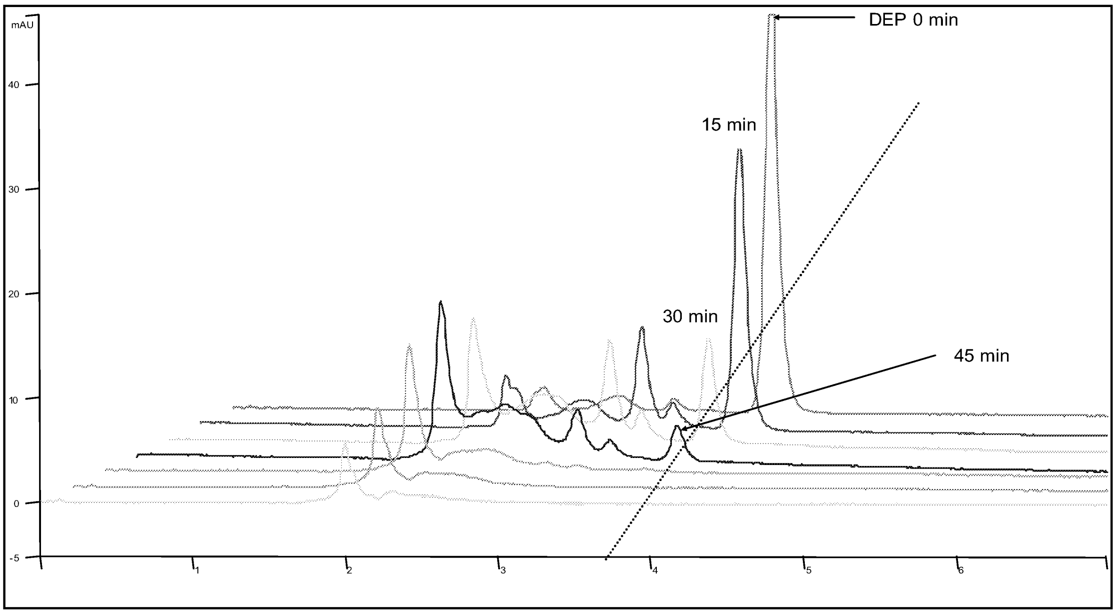


Figure 2. 3: *A series of superimposed chromatograms of a solution of 0.3 mM DEP phototreated using the Hanau suntest simulator, sampled at 15 minutes period.*

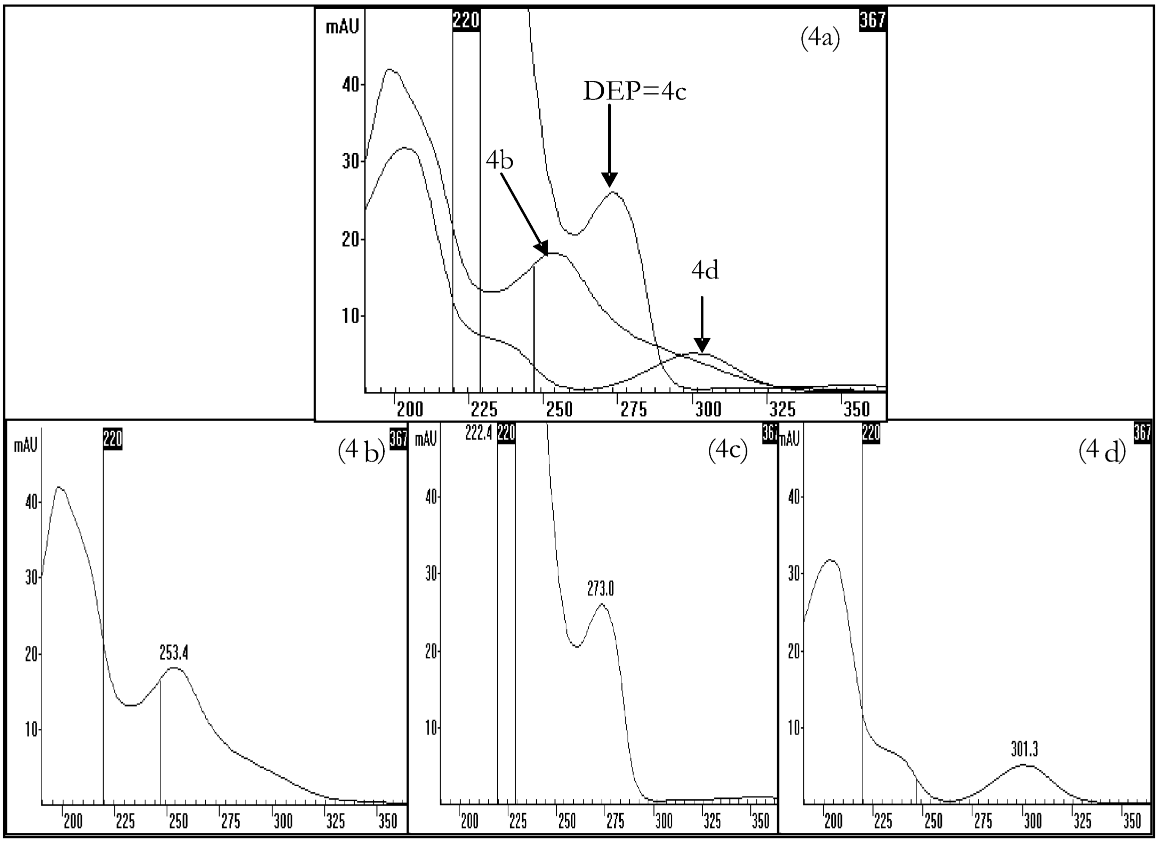


Figure 2. 4: *Spectra of the three regular picks generated from the chromatogram of a sample of a DEP phototreated sample after 15 minutes of the treatment. (4a) shows the superimposition of the DEP spectrum with those of the two by-products. (4c) is the spectrum of the DEP, (4a) and 4d) are the spectra of the by-products at 253.4 and 301.3 nm respectively. During the field work, the absorbance measures were made at 301 nm.*

In a recent work on the iron-photoassisted degradation of the DEP reported by (Mailhot et al 2002) two intermediate products showing maximum absorption at 254 and 302 nm (**Fig 2. 5**) where identified. We assume that the by-products that we observed in this study are the same. But since we were preparing for a field experimentation campaign in a context where there was no HPLC device, the need of another method was critical. We explore the spectrophometric analytical method so as to avoid the high cost of the COD or TOC analyses. Also; we were expected to develop a field instantaneous and rapid analytical method which could if necessary, be confirmed later (at specific steps of the process) by a more precise conventional method.

$\mathbf{P}_1$ P_2

Figure 2. 5: *Molecular structure of two by-products of photodegradation of the DEP:* (P_1) *absorbs maximum at 256 nm and* (P_2) *absorbs at 302 nm. (Mailhot et al., 2002). In our work, we assume that the by-products observed with maximum absorption at 253.4 nm and 301.3 nm are the same as* P_1 *and* P_2 *respectively. The slight differences of data (253.4 # 256 nm) and (301.3 # 302 nm) could be due to the difference of the analytical procedures or devices.*

2.3.2 The spectrophotometric monitoring of the photodegradation of the DEP and the validation of the analytical method

It is known that in the light UV-visible region, the absorbance (A) of a liquid containing a chemical at the concentration (c), is proportional to (c) as stated by the Lambert's law:

$$A = \varepsilon \cdot l \cdot c \qquad \textbf{(Eq.2. 8)}$$

Where (l) is the path length of the incident light in the liquid and (ε) is the absorption constant depending on the nature of the chemical. Hence, in the range of concentration in which A=f(c) is linear, the absorbance of a chemical polluted solution at a specific wavelength can be used to determine the concentration of the chemical in the media.

Recently, (Sarria 2003), used the measure of the absorbance at 549 nm to monitor the photo-Fenton degradation of AMBI[1], a dye precursor which complexes with iron in water. The decrease of the absorbance at 549 nm of the phototreated solution AMBI, followed

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[1] 5-Amino-6-methyl-2-benzimidazolone

the degradation of AMBI (Parra 2001; Sarria 2003). Unfortunately, in the case of this study, phthalates did not complex with iron within our experimental conditions; however, using the spectrophotometer 3010-U, we generated from 200 to 600 nm, the spectra of successive series of phototreated DEP, sampled at 15 min period. **Fig. 2.6** shows the results of two concentrations (0.3 mM and 0.47 mM) of the DEP carried out in the lab within the same conditions, when using the Suntest as light source.

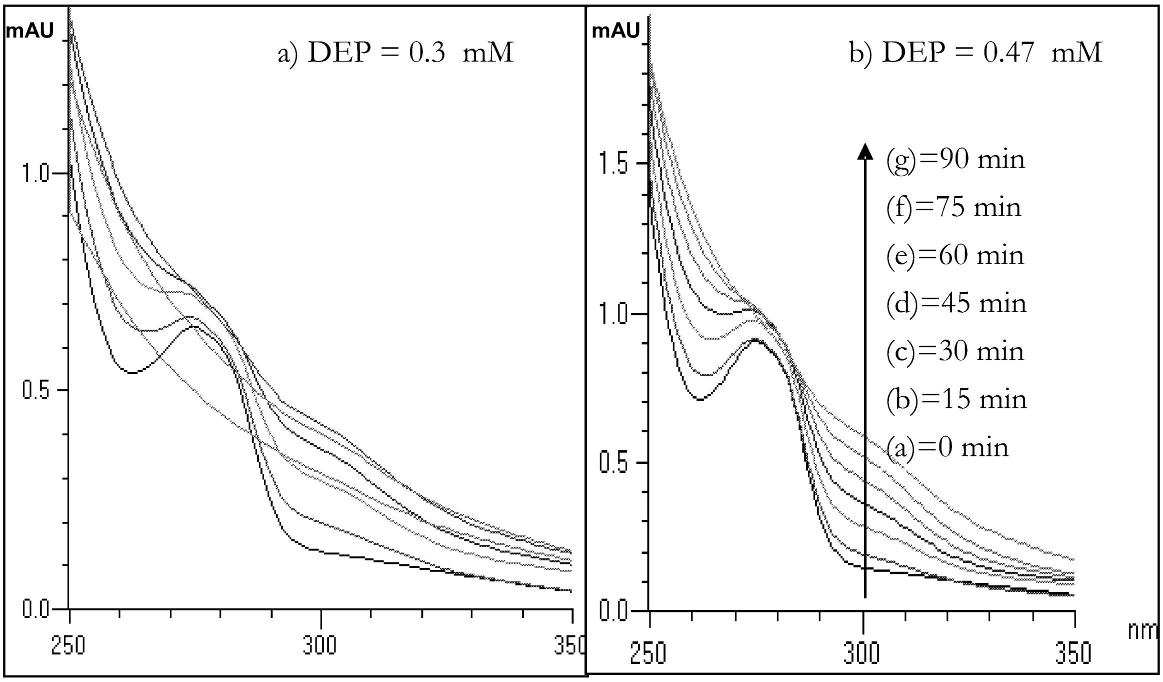


Figure 2. 6: *A series of superimposed spectra of two DEP photo-treated solutions sampled at 15 minutes period: The initial concentrations were: (a) 0.3 mM and (b) 0.47 mM.*

Using the managing software of the Hitachi UV-Vis model 330 spectrophotometer, we listed the values of the absorbance of the phototreated samples at 254, 273 and 301 nm and simultaneously, we analysed by using HPLC the concentration of the DEP.

The curves in **Fig 2.7** show that the absorbance of the solution at 273 nm remains relatively constant during the first 30 minutes while the absorbances at 254 and 301 nm of the phototreated solution present: (i) a first step of increasing values up to maxima, at the same time (phase I); then, (ii) the values decrease up to their initial values (where the curves cut the line of equation Y=1) (phase II) and finally, (iii) the phase III corresponds to the parts of the two curves after the line Y=1 in which the evolution of the absorbance is rather constant. We assumed that:

- ✓ The observations at 254 and 301 nm correspond to the evolution of the by-products P_1 which, the maximum absorption wavelength is 253.4 nm and P_2 of maximum absorption wavelength at 301.3 nm.
- ✓ Phase I is the step of the process in which the production rate of the by-products (due to the degradation of the DEP) is higher than their degradation rate.
- ✓ The maximum may correspond to equilibrium between the production and the degradation rates of P_1 and P_2; induced by the relative exhaustion of the DEP. The degradation curve of the DEP shows that only 10% of the initial DEP remain in the process.
- ✓ The phase II corresponds to the degradation of the by-products,
- ✓ The phase III may correspond to a slight degradation or mineralization of the organic constituents of the phototreated solution.

When the production of the by-products is maximal, 90% of the DEP is degraded. Consequently, the production of the by-products rather stops and their degradation become dominant; this is noticed by the decrease of the absorbance of the corresponding by-products at 254 and 301 nm.

From the **Fig 2.4**, we could conclude that the Meta by-product (P_1) absorption is higher than the one of (P_2); but due to the interference of the P_1 absorption at 301 nm (see **Fig. 2.4**, (4a), the relative evolution of the absorbance of the solution at 301 nm is higher than the one at 254 nm. Also, the P_1 by-product is more sensitive to the photo-Fenton process since it is the first by-product which is totally degraded in the medium (e.g. after 60 min); thus, we chose 301 nm as the reference wavelength to monitor when using a spectrophotometer.

For operational matter, It was decided to take a security margin and let the degradation of the by-product continue. This is noticed by the decrease of the absorbance curve in **Fig.2.7** in which the stop point corresponds to where the curve of $f(t)=A/A_0$ cuts the line of equation Y=1. This theoretically means that the by-product is totally degraded.

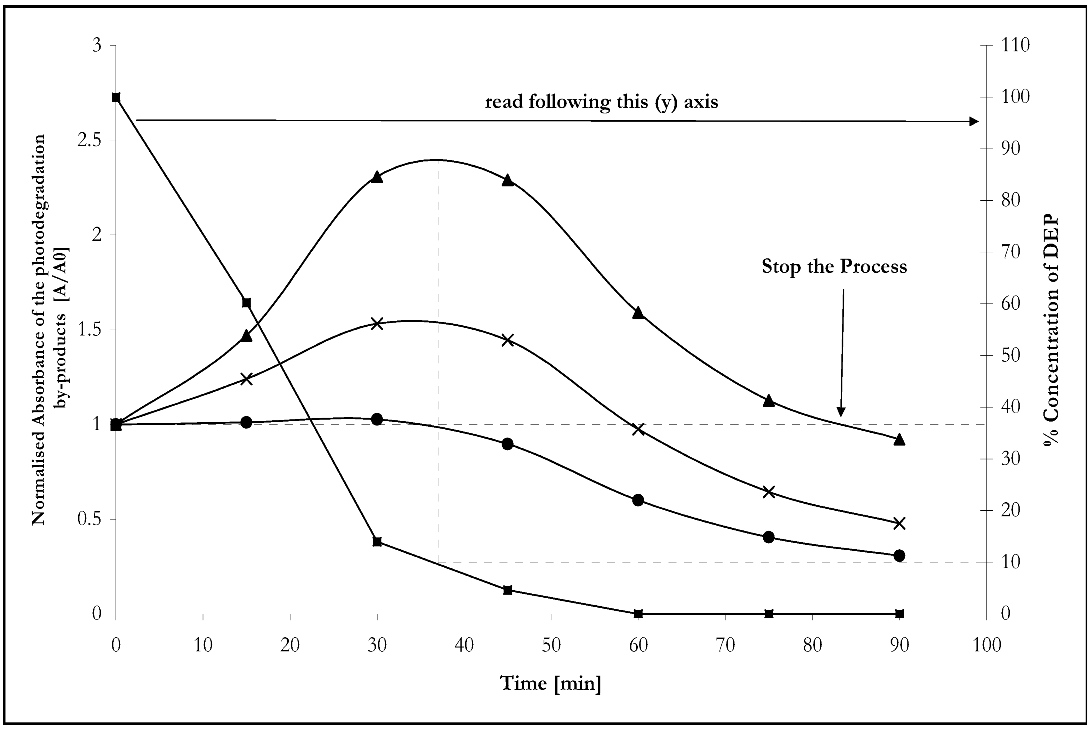


Figure 2. 7: *Correlation of the absorbance at (▲) 301 nm and (×) 254 nm of the by-products, (●) 273 of the DEP and (■) the concentration of the DEP*

2.3.3 The test of the developed analytical method at the field experimentation

The photo-Fenton degradation of three phthalates of the same chemical profile: the dimethyl phthalate (DMP), the diethyl phthalate (DEP) and the Diallyl phthalate (DAP) were followed during a field study at Ouagadougou in Burkina Faso, and monitored using the developed absorbance measurement analytical method. All the experiments were carried out for two hours each, at the same period of the day (10h30-13h30), so to limit the influence of the solar irradiation variation. This is shown by the curve of the accumulated solar UV energy per unit area (kJ.m^{-2}) on the photoreactor during the experiments (**Fig**

2.8). The following experimental conditions were observed: 0.6 mM of each phthalate; pH= 3; 0.071 mM of Fe^{3+} and 3.6 mM of H_2O_2; all in 25 L of tap water (see characteristics in **Table 2.1**). As seen in **Table 1.4**, the three chemicals have the same molecular structure apart from the length of their peripheral alkylic chains (see **Table 1.4**). The absorbance curves in **Fig 2.9** reveal that the method is applicable to the study of other phthalates. The calculation of the photodegradation rates of the three phthalates assuming the 90% degradation (when the absorbance at 301 nm is at the summit of the curve) depends of the length of the peripheral aliphatic group following the order: $k_{DAP}= 6 < k_{DEP}=13 < k_{DMP}=.$ 21 (10^{-3} $mol.s^{-1}$)

The longer the aliphatic chain is, the more the photodegradation rate is slow. In addition to the $^{\bullet}OH$ oxidation of the chemical bonds which can be easier on the benzene ring than on the alkylic bonds (ca. availability of the electrons on the benzene ring), one could imagine a combined photonic degradation effect which in contrary, would be efficient on the alkylic bonds than on the benzene ring (Edelahi 2004). As a consequence to this second plausible photo-effect, the calculated molecular bonds energy of three phthalates confirms that the DAP would be more stable than the DEP which would be also more stable than the DMP.

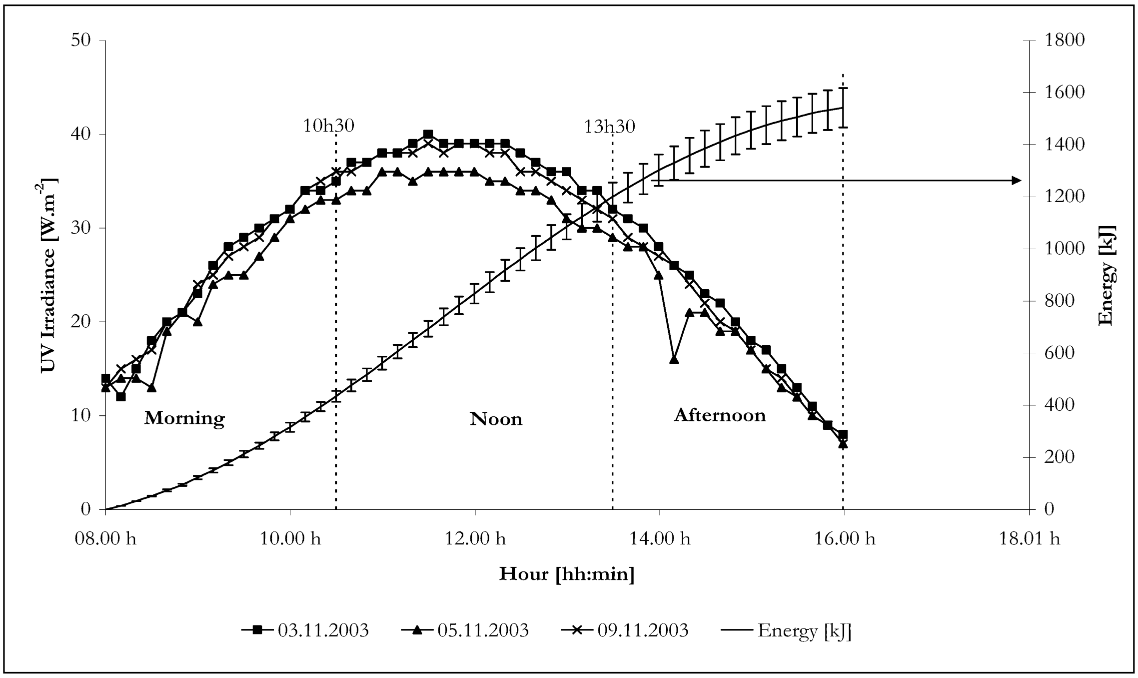


Figure 2. 8: *Solar UVA radiation and energy at Ouagadougou during the three days of the 44th week (3-9th November 2003).*

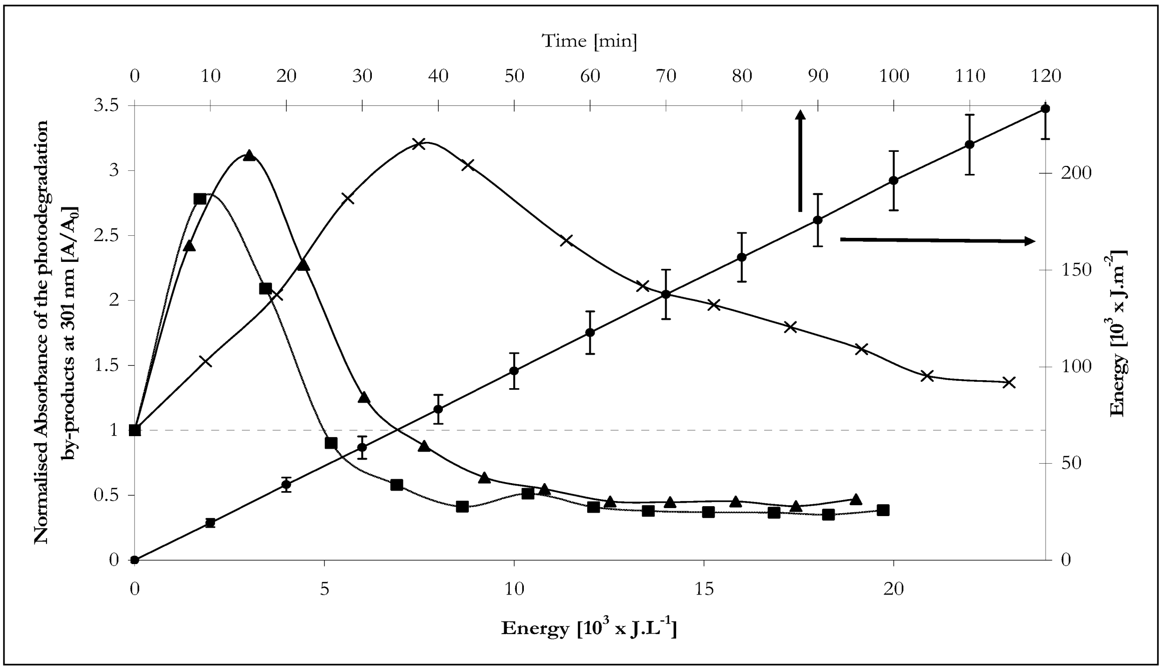


Figure 2. 9: *Comparing the solar-photodegradation of three phthalates during the field study, using an initial concentration of 0.6 mM of each: (■) for DMP, (▲) for DEP, (×) for DAP and (●) for the average of the solar UV energy during for the operating period of the days (10h00 – 13h30).*

2.4 Conclusion

In this part of our research, measuring the absorbance at 301 nm of the water solutions containing phthalates had shown to be a rapid analytical method for the monitoring of the photodegradation of the DEP and other phthalates. It was ensured that we could not directly monitor the process by measuring the absorbance of the DEP at its maximum absorption wavelength, since its absorbance does not change significantly during the first 30 minutes when most of the like-first-order photocatalytical reactions took place in the process. This was due to the interference of the absorption of other chemicals in the medium. Two by-products absorbing at maximum 253.4 and 301.3nm were identified and one of them was chosen to monitor the process with a more accurate security margin. We observed that the photodegradation rates of the tested phthalates follow the length of their peripheral alkyl chains in the following order: $k_{DAP} < k_{DEP} < k_{DMP}$. This analytical method could be used to carry out experiments in a context where sophisticated analytical devices are lacking.

References

Ai, S., Li, Jiaqing., Yang, Ya., Gao, Mengnan., Pan, Zhensheng. and Jin, Litong (2004). "Study on photocatalytic oxidation for determination of chemical oxygen demand using a nano-TiO2-K2Cr2O7 system." Analytica Chimica Acta **509**(2): 237-241.

Al-Ghamdi, S. S., Raftery, Martin J. and Yaqoob, Muhammad M. (2003). "Acute solvent exposure induced activation of cytochrome P4502E1 causes proximal tubular cell necrosis by oxidative stress." Toxicology in Vitro **17**(3): 335-341.

Alhakimi, G., Studnicki, Lisa H. and Al-Ghazali, Muftah. (2003). "Photocatalytic destruction of potassium hydrogen phthalate using TiO2 and sunlight: application for the treatment of industrial wastewater." Journal of Photochemistry and Photobiology A: Chemistry **154**(2-3): 219-228.

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

Bajt, O., Mailhot, Gilles. and Bolte, Michele (2001). "Degradation of dibutyl phthalate by homogeneous photocatalysis with Fe(III) in aqueous solution." Applied Catalysis B: Environmental **33**(3): 239-248.

Blake, D. M., . (2001.). Bibliography of work on the photocatalytic removal of hazardous compounds from water and air., National Technical Information service, US department of commerce, Springfield, VA, USA.

Cooper, G. R. C. (2002). "Oxidation and toxicity of chromium in ultramafic soils in Zimbabwe." Applied Geochemistry **17**(8): 981-986.

Csikor, F., Fodor, Z., Hegedus, P., Horvath, V. K., Katz, S. D. and Piroth, A. (2001). "The PMS project: Poor man's supercomputer." Computer Physics Communications **134**(2): 139-149.

Curco, D., Gimenez, J., Addardak, A., Cervera-March, S. and Esplugas, S. (2002). "Effects of radiation absorption and catalyst concentration on the photocatalytic degradation of pollutants." Catalysis Today **76**(2-4): 177-188.

Edelahi, M. C. (2004). Contribution to the study of the in situ degradation of pesticides by advanced oxidation processes involving the use of iron. application to the phenylureas herbicides. Chemistry. Marne-la-Vallée, Marne-la-Vallée**:** 173 pp.

Faust, B. C. and J. Hoigné (1990). "Photolysis of Fe(III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain." Atmos. environ. **24 A**(1): 79-89.

Feng, W. and D. Nansheng (2000). "Photochemistry of hydrolytic iron (III) species and photoinduced degradation of organic compounds. A minireview." Chemosphere **41**(8): 1137-1147.

Fenton, H. J. H. (1894). "Oxidation of tartaric acid in presence of iron.." J. of chem. soc. Trans. **65**: 899-910.

Ghule, A. V., Chen, Ren Kun., Tzing, Shin Hwa., Lo, Jim. and Ling, Yong Chien (2004). "Simple and rapid method for evaluating stickiness of cotton using thermogravimetric analysis." Analytica Chimica Acta **502**(2): 251-256.

Gunaratnam, M. and M. H. Grant (2004). "Damage to F-actin and cell death induced by chromium VI and nickel in primary monolayer cultures of rat hepatocytes." Toxicology in Vitro **18**(3): 245-253.

Huston, P. L. and J. J. Pignatello (1999). "Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction." Water Research **33**(5): 1238-1246.

Idso, S. B. (1997). "The poor man's biosphere, including simple techniques for conducting CO2 enrichment and depletion experiments on aquatic and terrestrial plants." Environmental and Experimental Botany **38**(1): 15-38.

Ken, M. (2000). Multi-model Ensemble, Poor Man's Ensembles and Super-Ensembles - a brief review, Prepared for the WMO Workshop on Applications of Ensemble Forecasting, http://www.wmo.ch/web/www/DPS/WS-EPS/PRES6-1-1UK.doc. **2004**.

Kiwi, J., Pulgarin, C., Peringer, P. and Gratzel, M. (1993). "Beneficial effects of homogeneous photo-Fenton pretreatment upon the biodegradation of anthraquinone sulfonate in waste water treatment." Applied Catalysis B: Environmental **3**(1): 85-99.

Mailhot, G., Sarakha, M., Lavedrine, B., Caceres, J. and Malato, S. (2002). "Fe(III)-solar light induced degradation of diethyl phthalate (DEP) in aqueous solutions." Chemosphere **49**(6): 525-532.

Malato, S., Blanco, J., Fernandez-Alba, A. R. and Aguera, A. (2000). "Solar photocatalytic mineralization of commercial pesticides: acrinathrin." Chemosphere **40**(4): 403-409.

Nansheng, D., Tao, Fang and Shizhong, Tian (1996). "Photodegradation of dyes in aqueous solutions containing Fe(II)-hydroxy complex I. Photodegradation kinetics." Chemosphere **33**(3): 547-557.

Nijman, E. J. M. and G. N. M. Bellussi (2000). "Helium as good as vacuum: the poor man's approach for accurate material damping measurements." Applied Acoustics **60**(3): 385-392.

Parra (2001). Coupling of photochemical and biological processes as a contribution to the detoxicication of water: Catalytic and technological aspects. LBE. Lausanne, EPFL: 148.

Parra, S., Sarria, V., Malato, S., Peringer, P. and Pulgarin, C. (2000). "Photochemical versus coupled photochemical-biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon." Applied Catalysis B: Environmental **27**(3): 153-168.

Poulain, L., Mailhot, Gilles., Wong-Wah-Chung, Pascal. and Bolte, Michele (2003). "Photodegradation of chlortoluron sensitised by iron(III) aquacomplexes." Journal of Photochemistry and Photobiology A: Chemistry **159**(1): 81-88.

Radzewicz, C., Wasylczyk, P. and Krasinski, J. S. (2000). "A poor man's FROG." Optics Communications **186**(4-6): 329-333.

Ruppert, G., Bauer, R. and Heisler, G. (1993). "The photo-Fenton reaction: an effective photochemical wastewater treatment process." Journal of Photochemistry and Photobiology A: Chemistry **73**(1): 75-78.

Sarria, V. (2003). Coupled advanced oxidation and biological processes for wastewater treatment. Institute of Environmental science and Technology. Lausanne, EPFL: 150.

Sarria, V., Deront, M., Peringer, P. and Pulgarin, C. (2003). "Degradation of a biorecalcitrant dye precursor present in industrial wastewaters by a new integrated iron(III) photoassisted-biological treatment." Applied Catalysis B: Environmental **40**(3): 231-246.

Sarria, V., Kenfack, S., Guillod, O., Pulgarin, C. (2003). "An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants." Journal of Photochemistry and Photobiology A: Chemistry **159**: 89-99.

Staples, C. A., Peterson, Dennis R., Parkerton, Thomas F. and Adams, William J. (1997). "The environmental fate of phthalate esters: a literature review." Chemosphere **35**(4): 667-749.

Stasinakis, A. S., Thomaidis, Nikolaos S., Mamais, Daniel, Papanikolaou, Evangelia C., Tsakon, Angeliki and Lekkas, Themistokles D. (2003). "Effects of chromium (VI) addition on the activated sludge process." Water Research **37**(9): 2140-2148.

Stephen, A., Stowers, and Richard, Umfrid (2003). "supine-prone SPECT myocardial perfusion imaging: The poor man's attenuation compensation." Journal of Nuclear cardiology: 338.

Tang, B., Zhang, Li., Hu, Ji-Xi., Li, Ping., Zhang, Hui. and Zhao, Yan-Xiu (2004). "Indirect determination of superoxide anion radical in the plant of red sage based on vanillin-8-aminoquinoline with fluorescence." Analytica Chimica Acta **502**(1): 125-131.

Utset, B., Garcia, Josep., Casado, Juan., Domenech, Xavier. and Peral, Jose (2000). "Replacement of H2O2 by O2 in Fenton and photo-Fenton reactions." Chemosphere **41**(8): 1187-1192.

Waite, T. D. (2002). "Challenges and opportunities in the use of iron in water and wastewater treatment." reviews in Environmental Science and Biotechnology **1**: 9-15.

Wright, P. F. A., Schlichting, L. M. and Stacey, N. H. (1994). "Effects of chlorinated solvents on the natural lymphocytotoxic activities of human liver immune cells." Toxicology in Vitro **8**(5): 1037-1039.

Chapter 3

Study of some physical and chemical parameters affecting the helio-photo-Fenton degradation of the diethyl phthalate on a CPC photo-reactor

After developing and validating the analytical method allowing to follow-up the degradation of phthalates in chapter 2, the diethyl phthalate (DEP) was chosen as the main model pollutant for more investigations on the various physicochemical and technical parameters influencing the solar photo-Fenton process. All the experiments were carried out at the EIER in Ouagadougou, Burkina Faso using the photo-reactor described in the §2.2.1, under sunlight irradiation. The optimal conditions for operating the helio-photo-Fenton treatment of the DEP were determined for the initial concentration of the DEP, the pH, the H_2O_2 and the Fe^{3+} concentrations. Also, the nature of the iron source, the solar irradiance flux, and the influence of water flow rate during the process were studied.

3.1 Introduction

The diethyl phthalate (DEP) is one of the most important chemical of the group of plasticizers used as softeners in a variety of plastic products such as PVC, including construction, car spare parts (car under-coating, car seats etc.), children's products (teething rings squeeze toys, clothing, rainwear…etc.). It is also widely used in cosmetics such as nail polishes (as plasticizer in order to reduce cracking by making them brittle), hair spray (to avoid stiffness) and as solvents and perfume fixative (Centre for Disease Control (CDC) 2001). Among the listed phthalates in 34 European most popular cosmetic products, the DEP is used in 68% of them (DiGangi 2002). As the result of such various usages, human exposure to the DEP is expected to be significant.

In general, phthalates have been detected in every environment in which they have been sought (Gian 1984) with the highest concentration detected adjacent to phthalate production or plastics processing facilities. It has been estimated that approximately 1% of the phthalate ester content of plastic materials in direct contact with water or other liquids may be released to the aquatic environment (Fiedler 1987). This is the case of the Chesapeake Bay where dialkyl phthalates had accumulated and persisted in the sediments for over a century. Surface water samples collected along the length of the Mississippi River in the USA, contained phthalates in significant concentrations and specifically, the DEP has been identified in drinking water in many cities of the USA (US. 2001).

In Africa and many other developing countries, plastic packing are mainly used at all level of the life cycle of goods (manufacture, commercialization, utilization…etc.). It is estimated that around 30'000 tonnes of plastic packaging are annually used in Burkina Faso (MINEFIB. 2000) where the final destinations of all these plastic packaging are the landfill discharges. In none of the Burkina Faso's cities, leachates from landfill discharges are collected and treated whereas wastewaters are used for garden vegetable irrigation in

Ouagadougou, even those from industries (Cissé G. 1997.; Kenfack 2000). Within such a context, the pollution of the surface and ground water by phthalates and other pollutants is highly risky. Although the acute toxicity of the diethyl phthalate seems to be very low (Api 2001), some sub-lethal effects of its contamination have been reported (Lovekamp-Swan T. and Davis 2002).

Several investigations suggest that phthalates may affect human sperm quality (Frericsson 1993; Staples 1997). A correlation with the impaired reproductive performance has been found in multigenerational studies in rodents. Up till now, various investigations and discussions are still being carried out on phthalates; while the EU in November 2002, had amended the Cosmetics Directive 76/768/EEC and prohibited the use of some of them (DiGangi 2002).

The diethyl phthalate is weakly biodegradable in natural water and even under activated sludge biological treatment conditions (Sugatt 1984; O'Grady 1985); as the result of such a weak biodegradation, it has been found to accumulate in the environment and its toxicity to a variety of aquatic and soil micro organisms of the natural food chain of fishes and fauna has been proved (Staples 1997).

Even if the endocrine disrupting effects associated to the DEP exposure in humans wildlife is not yet clearly defined, the caution principle should be applied and thus, efficient technologies and strategies for removing it and other phthalates from water should be developed.

For that issue, this part of my research focused on a detailed study of the photodegradation of the diethyl phthalate (DEP) sensitized by the Fenton reagent in aqueous suspension, under sunlight irradiation.

Up till now, the technology proposed for the removal of phthalates and other endocrine disrupting chemicals from drinking water is the very expensive Granular Activated Carbon (GAC) process (US. 2001). However, this approach consists only to transfer the pollutant from a medium to another, without destroying it. The new proposed approach should be friendly environmental since it could allow to detoxify polluted waters using a renewable energy free of charge.

In the recent years, Advanced Oxidation Processes (AOP) had exhibited the ability to oxidize most of the biorecalcitrant organic pollutants, especially under the photocatalytic processes conditions (Kawagushi 1994; Parra 2000). As sunlight is highly available in most of developing countries, it could be an alternative solution for the treatment of such pollutants, at specific conditions: (i) at the outlet of industries, (ii) as post-treatment of a wastewater treatment plant or (iii) as a drinking water treatment process for polluted surface and ground waters.

Some few studies carried at lab scale on the photocatalytic degradation of the diethyl phthalate using the heterogeneous TiO_2 catalyst (Hurtert 1988.; Muneer 2001; Ooka 2003.) and at pilot scale under photo-Fenton conditions (Mailhot 2002), have shown promising results; but to our knowledge, no study had yet been carried out at the field pilot scale, and never in the tropical African region.

In this chapter, the following topics are reported: (i) the effect of initial concentration of the DEP and the influence of the pH of the phototreated solution, (ii) the optimal Fe^{3+} and H_2O_2 concentrations for the efficient abatement of DEP in the process, (iii) the influence of the circulation flow rate of the solution in the photoreactor, (iv) the influence of the solar radiation imparted along the day (at morning, noon and afternoon), (v) the efficiency of the helio-photodegradation of the diethyl phthalate at these different periods of the day and finally, a relative cost evaluation for the scaling-up of the process is presented.

3.2 Experimental

3.2.1 Chemicals

All chemical products were used as received from the commerce. The diethyl phthalate (DEP) was obtained from Fluka, Buchs, Switzerland. Its molecular structure and some of the main characteristics have been presented in **Table 1.4** where we could notice that the DEP is fairly soluble in water. The catalysts: ($FeCl_3$, $6H_2O$), ($FeSO_4$, $7H_2O$) and ($Fe_2 (SO_4)_3$, $7H_2O$) the electron acceptor H_2O_2 (30% w/w) and HCl were all bought at Fluka (Switzerland). All were of analysis grade (p.a.).

3.2.2 Experimental device and procedures

All the experiments were carried out at the Ecole Inter-Etats d'Ingénieurs de l'Equipement Rural de Ouagadougou (EIER) in Burkina Faso, a tropical sahelian country located at the core of West Africa. It's an ideal place where solar experimentation researches can be carried out, as more than 300 days per year can be expected to be sunny, so to reach an average of 2'500 sunny hours per year (e.g. in Alméria, Spain, it's estimated up to 3'000 sunny hours per year (Blanco J. and Malato 2001))

The SOLARDETOX ® ACADUS-2003 pilot plant described in *paragraph 2.1.2* was used and the operating procedure was the same and the characteristics of the used tap water are the same as giving in **Table 2.1** at the EIER working station in Ouagadougou. The pH of the solution was adjusted to 3 by adding a concentrated HCl solution and the required amount of the catalyst ($FeCl_3$) was added.

Once the solution was ready, the required amount of hydrogen peroxide was added and the feeding Valve (1) was opened according to the water circulation flow rate needed for the operations. The water flow rate was varied at three values by regulating the valve (1) delivering relative flow rates of 14.4, 19.1 and 24.2 ($L.min^{-1}$); which corresponded respectively to water circulation speeds of 0.3, 0.4 and 0.5 m.s^{-1}. During each experiment the solar UVA radiation and the related accumulated energy on the photoreactor was determined registered through a UV-A radiometer ACADUS 85 UV mounted on the reactor, at the same angle (10°) as its plate part. It provides data in terms of incident UV radiation per area unit (W.m^{-2}) and the accumulated energy in the reactor (in Wh). In this thesis, all the energy values are reported in 10^3 x J so to conform to the international unit system.

All the experiments were run for two hours using 25 litres of polluted water and the sampling period was 10 minutes. Apart from the experiments which were carried out in order to evaluate the influence of the photonic flux on the treatment, all the experiments were done at the same period of the day (10h30-13h30).

3.2.3 Analytical methods

The monitoring of the DEP degradation process followed the analytical method developed as described in chapter 2; by measuring the absorbance of the phototreated solution at 301 nm using a spectrophotometer of the *Biomate 3* model. This technique allows measuring the light absorbance of the overall formation and decay of an oxidized aromatic by-products deriving from the DEP due to the process.

3.3 Results and discussions

Some previous works, mostly carried out at the lab scale on the photo-Fenton degradation of biorecalcitrant chemical pollutants have reported a significant influence of the initial concentration of the pollutant, as well as the catalyst and the electron acceptors (H_2O_2, O_2, O_3,…etc.) on the photodegradation rate of the process (Kiwi 1993; Sarria 2001; Sarria 2003). This was experienced in this part of our research.

3.3.1 Study of the optimal physicochemical parameters influencing of the helio-photo-Fenton degradation of the DEP

3.3.1.1 The initial concentration of the DEP

The operational initial concentration in two hours ($C_{i,2h}$) is defined in this paper as the maximal initial concentration of the DEP which can be treated in two hours so as to reach the total degradation of the DEP and that of the monitored by-product. According to the analytical procedure shown in **Fig.3.1**, the $C_{i,2h}$ corresponds to the concentration of the DEP which satisfies the following conditions:

$A/A_0=1$; (With $t\neq0$) **(Eq.3. 1)**

Where A_0 is the initial absorbance of the polluted solution (at the time t=0) and A is the absorbance of the phototreated solution at the time t.

Thus, the phototreatment includes the degradation of the DEP and that of the monitored by-product at 301 nm.

Fig.3.1 shows the relative evolution of the absorbance at 301 nm (A/A_0) of the phototreated solutions for four initial concentrations of the DEP, as a function of the accumulated solar energy received by the photoreactor. A_0 is the absorbance at time zero. Maxima of the curves are observed respectively at 36, 72, 108 and 126 kJ. At these maxima, it is assumed that the production rate of the monitored by-product is: $\frac{d[by-product]}{dt}=0$; meaning that, its degradation rate is equal to its production rate. Thus 0.6 mM shown to be the highest concentration of DEP which satisfy the conditions in **Eq. 3.4**, with the need of 3 $kJ.L^{-1}$ of energy for 90% degradation of DEP and up to 7 $kJ.L^{-1}$ for the degradation of the by products.

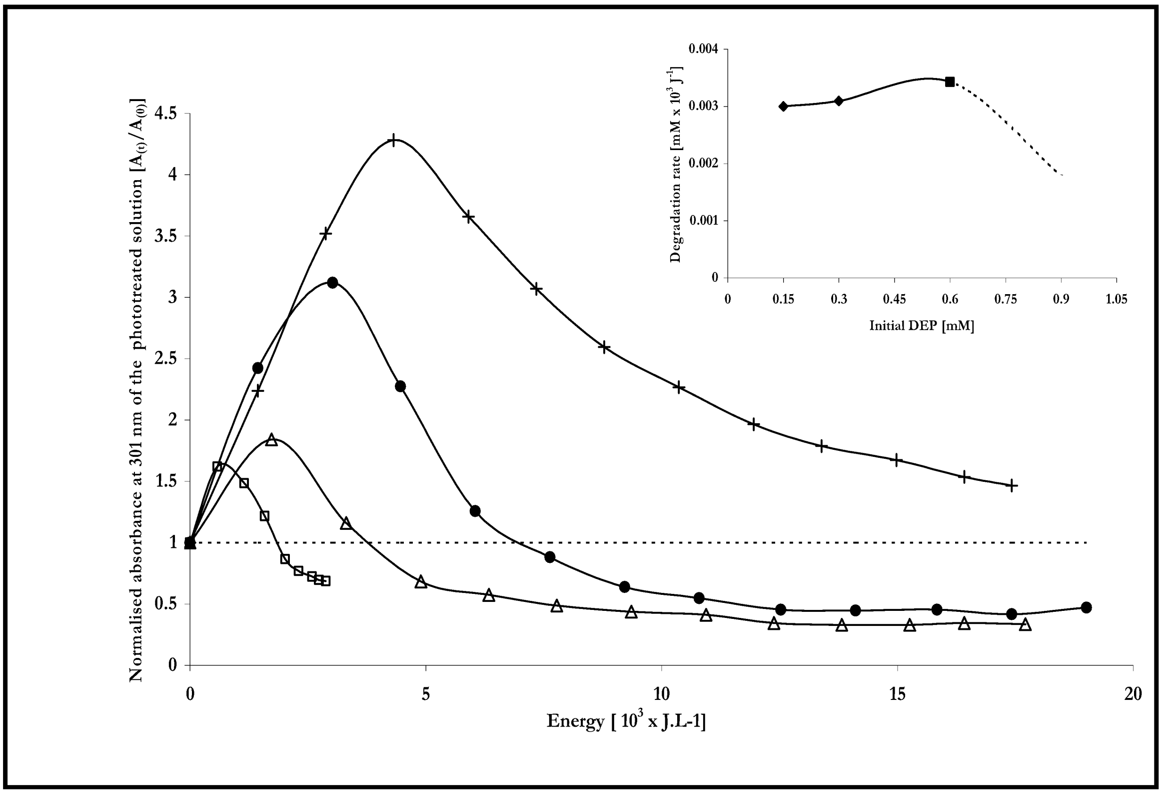


Figure 3. 1: *Photo-Fenton degradation of a series of successive increasing concentrations of DEP. (□) for 0.16 mM.L^{-1}, (Δ) for 0.3 mM.L^{-1}, (●) for 0.6 mM.L^{-1} and (+) for 0.9 mM.L^{-1} as a function of the accumulated energy. The inserted figure is the energetic rate (mM x 10^3 J^{-1}) of the 90% degradation of the DEP in two hours (Energy at the point $A/A_0=1$, with $t \neq t_0$).*

3.3.1.2 The pH

We investigated the helio-photo-Fenton degradation of the DEP at four pH values representative of: (i) strong acidic wastewaters (pH=1.5-3.5), (e.g. pesticides manufactures) (ii) natural waters (pH=5.5-7) and (iii) wastewaters at the inlet of a biological wastewater treatment plant (pH≈6.5–8.5). The DEP evolution was indirectly monitored by the absorbance of its by-product monitored at 301 nm and **Fig. 3.2** shows the plot of the relative evolution of the by-product. At pH=5 and 8.5, in two hours the photodegradation of the DEP is not significant. The slight reactivity of iron photoassisted systems at these pH values, was also observed previously by Kiwi et al (Kiwi 1993; Kwon 1999) and is attributed to the Fe^{3+} precipitation at high pH values, according to the following equations.

$Fe^{3+} + 3\ OH^- \rightarrow Fe(OH)_{3\ (s)}$ **(Eq.3. 2)**

$Fe^{2+} + 2\ OH^- \rightarrow Fe(OH)_{2\ (s)}$ **(Eq.3. 3)**

The pH=3 and 1.5 have shown to be more favourable because, in acidic waters iron is in solution in its ionic form Fe^{3+}, generating very reactive hydroxyl radicals ($^{\bullet}OH$), in the presence of photons and hydrogen peroxide, according to the following reactions (Fenton 1894; Baxendale 1957):

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + {}^{\bullet}O_2H + H^+ \quad \textbf{(Eq.3. 4)}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad \textbf{(Eq.3. 5)}$$

$$Fe^{3+} + H_2O \xrightarrow{h\nu} {}^{\bullet}OH + Fe^{2+} + H^+ \quad \textbf{(Eq.3. 6)}$$

$${}^{\bullet}OH + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O \quad \textbf{(Eq.3. 7)}$$

$${}^{\bullet}O_2H + H_2O_2 \longrightarrow {}^{\bullet}OH + H_2O + O_2 \quad \textbf{(Eq.3. 8)}$$

$$2{}^{\bullet}O_2H \longrightarrow H_2O_2 + O_2 \quad \textbf{(Eq.3. 9)}$$

$${}^{\bullet}O_2H + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad \textbf{(Eq.3. 10)}$$

$$2{}^{\bullet}OH \longrightarrow H_2O_2 \quad \textbf{(Eq.3. 11)}$$

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \quad \textbf{(Eq.3. 12)}$$

However, we observed that the process is less efficient at pH=1.5 than at pH=3. Xue-Kun Zhao et al, 2004 found that, even if the hydroxyl radicals are present in a medium, their oxidative potential decreases with the decrease of the pH. This observation was explained by Kwon et al, 1999, by the formation of the oxonium radical ($H_3O_2^+$) which may be less reactive than the peroxide (Kwon 1999; Xue-Kun 2004).

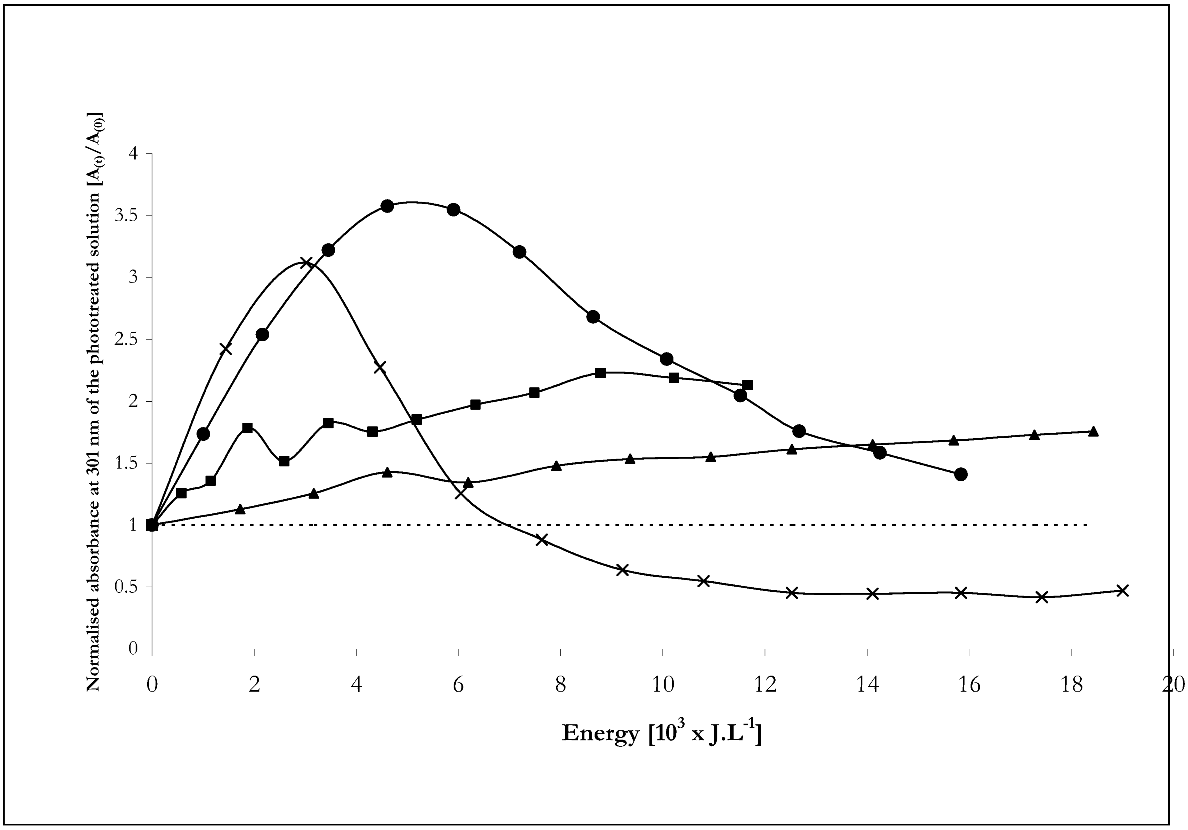


Figure 3. 2: *Photodegradation of the DEP at various initial pH. It's plotted the relative evolution of the absorbance of the by-product for (●) pH=1.5; (×) pH=3; (■) pH=5.5; (▲) pH=8.5. The initial DEP concentration is 0.6 mM and initial H_2O_2 concentration: 3.6 mM*

3.3.1.3 The concentration of the hydrogen peroxide (H_2O_2) and iron (Fe^{3+})

The variation of the initial concentrations of H_2O_2 and that of Fe^{3+} was investigated and four initial concentrations we experimented for each variable: (0; 2.04; 3.6 and 6.12 mM) for H_2O_2 when keeping the concentration of Fe^{3+} constant at 0.071 mM and afterward, we varied the concentration of the iron respectively at 0; 0.035; 0.071 and 0.142 mM when keeping the amount of hydrogen peroxide constant at 3.6 mM. **Fig.3.3** shows the plot of the photodegradation rate of 90% of the photodegradation of the DEP as a function of the concentration of H_2O_2 and **Fig.3.3** presents the influence of Fe^{3+} concentration in the process. All over, the initial pH was adjusted to 3, the initial concentration of the DEP was 0.6 mM and the volume of the polluted water was 25 L.

In **Fig.3.3,** it's noticed that the photodegradation rate of the process increases with the increase of H_2O_2 up to an optimum around 3.6 mM of H_2O_2, but the increase of the iron concentration shown in the same **Fig. 3.3** does not show a limit in the range of concentration that we tested (0.035–0.142 mM).

The decrease in **Fig.3.3** can be explained by the fact that, in the photo-Fenton process, $^{\bullet}OH$ radicals that are responsible for the degradation of the substrates can enter in competition (**Eq.3.10, 3.13**) or, when there is an excess of H_2O_2, molecules can dismute **(Eq.3.15)** and the increase of the reaction rate would not automatically follow the increase of the H_2O_2 concentration (Baxendale 1957).

When the concentration of H_2O_2 is kept constant in the presence of sunlight, the increase of the Fe^{3+} concentration in acidic water, may induce the increase of the degradation rate of the DEP because, all the pack of equations **(3.7-3.10)** are favoured. But in contrary to what we observed in the case of H_2O_2, the plot of **Fig.3.3** shows that the increase of the Fe^{3+} concentration between (0.035 and 0.142 mM) leads to a linear enhancement of the DEP photodegradation rate with R^2= 0.9993.

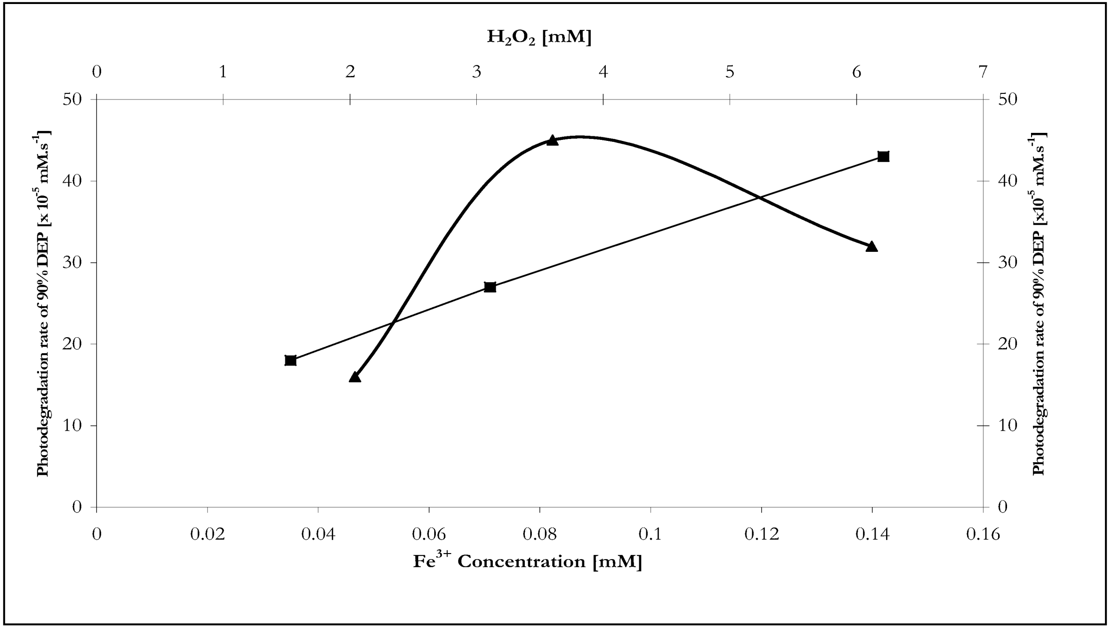


Figure 3. 3: *Influence of the concentration of H_2O_2 (▲) and Fe^{3+}(■) on the photo-Fenton degradation of the DEP. The optimal concentration is obtained with 3.6 mM of H_2O_2 and there is no optimum in the range of the tested Fe^{3+} concentrations.*

3.3.1.4 The nature of the iron source

A comparison between three different iron catalysts on the photodegradation rate of the DEP was studied and the results presented on **Fig.3.4** shows clearly that the degradation rate was highest with $FeSO_4$ followed by $Fe_2(SO_3)_2$ and the $FeCl_3$ gave the lowest degradation rate. This may be due to the fact that iron in $FeSO_4$ is in the form of Fe^{2+}, which can be directly oxidized by H_2O_2 in the photo-Fenton reactions, forming $^{\bullet}OH$ radicals. The Fe^{3+} ions in $FeCl_3$ and $Fe_2(SO_3)_2$ need to be reduced to Fe^{2+} first, which makes the beginning of the reaction slower; therefore, less energy was needed to accomplish the DEP photo-Fenton degradation when using the $FeSO_4$.

However, the highest photodegradation rate observed when using the $FeSO_4$ can also be justified by the effect of anions on the photo-Fenton process. Indeed, Lipczinska-kochany et al, 1994 showed that even if the influence of SO_4^{2-} and Cl^- on the Fenton process is weak when one compares it with that of HPO_4^{2-} and HCO_3^-, the delay of the process is higher with Cl^- than SO_4^{2-} (Lipczynska-Kochany, Sprah et al. 1995). Thus, this could justify the following decreasing order of the photo-Fenton degradation rates of the DEP: $FeSO_4 > Fe_2(SO_4)_3 > FeCl_3$.

Other observations have been made by Rodriguez et al, 2002 about the efficiency of Fe(II) compared to Fe(III) in a study about the photo-Fenton degradation of nitrobenzene. A faster start of the reaction was observed with the Fe(II) (Rodriguez 2002).

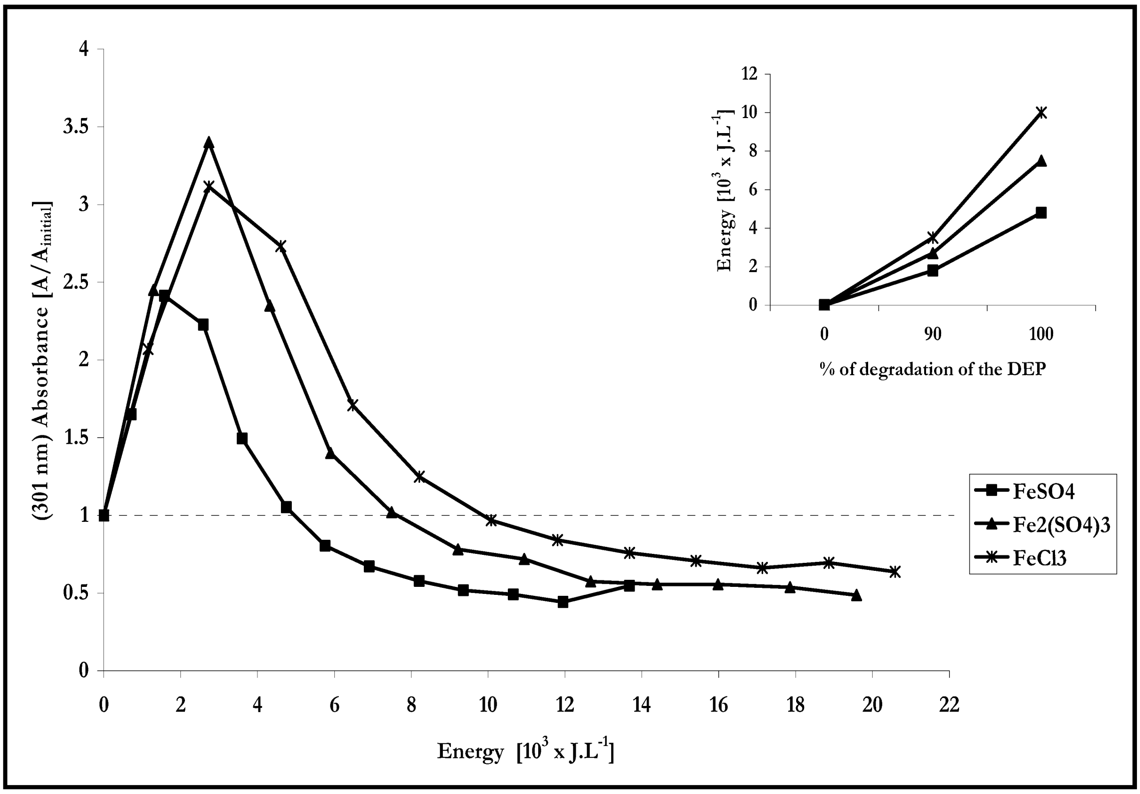


Figure 3. 4: *Influence of the iron ion source*

3.3.2 Influence of some physical and technical parameters of the helio-photo-process

3.3.2.1 The solar irradiance flux

Fig. 2.8 shows the variation of the radiation flux for three days during a clear sky sunny week: 03-09th November 2003 in Ouagadougou (Burkina Faso); from 08h00 to 16h00. In that period, the curve of the daily average of the solar UVA irradiance flux follows was in the form of parabola that a trend equation is written below:

Rad (t)= $- 974\ t^2 + 952\ t - 198$ **(Eq.3. 13)**

Where, Rad (t) is the radiation flux in (W.m^{-2}) at the hour t is given in (hh:min).

According to **Fig.2.8**, a sunny day can be subdivided in three sub-periods as follows: (i) the sunrise "morning" is considered from 08h00 to 10h30; (ii) the zenith "noon", from 10h30 to 13h30, and (iii) the sunset "afternoon", from 13h30 to 16h00. Before 08h00 and after 16h00, the solar irradiance flux values were less than 5 $W.m^{-2}$ and the photodegradation rate of the photo-process shown to be very low. Within the three respective sub-periods, the accumulated energies in the photoreactor, presented by the inserted curve in **Fig.2.8** (see second axis), have shown to follow the three partial trends equations given below, with the respective orders of 2, 1 and 2.

Morning: $\mathbf{E_m} = 19412\, t^2 - 10751\, t + 1425$ **(Eq.3. 14)**

Noon: $\mathbf{E_n} = 6209\, t - 2280$ **(Eq.3. 15)**

Afternoon: $\mathbf{E_a} = -19158\, t^2 + 26584\, t - 7658$ **(Eq.3. 16)**

((E_i) given here in 10^3 x $J.m^{-2}$, is the energy at the period (i) of the day and (t) the hour at the stop point of the process. In the frame, t takes respectively the values 10h30 (when $t_{initial}$ is 8h00: "morning"), 13h30 (when $t_{initial}$ is 10h30: "noon") and 16h00 (when $t_{initial}$ is 13h30: "afternoon").

It has been shown that the accumulated energy is an important parameter on which depends the photodegradation rate of the process (Blanco J. and Malato 2001); when using a CPC photoreactor, the accumulated energy per unit of the phototreated volume is linked to the instantaneous irradiance flux ($\overline{UV}$), the reactor total active area (A), the water volume (V) and the experiment duration (t) by the following relation:

$$E_{(t)} = E_{t0} + \Delta t * \overline{UV} * \frac{A}{V}$$ **(Eq.3. 17)**

The experiments were carried out within the same conditions, apart from varying the period of the day. **Fig. 3.5** presents the degradation rate of 90% of the DEP for each of the three sub-periods of the day, and the corresponding necessary energy. The photodegradation rate of 90% of 0.6 mM of DEP in the polluted water was calculated using the following formula:

$$Rate = \frac{C_0 * V}{t_{\max} - t_{initial}} \qquad \textbf{(Eq.3. 18)}$$

Where V is the total volume of the treated solution, $C_{initial}$ (mM) is the initial concentration of the pollutant and ($t_{max} - t_{initial}$) is the laps of time from the beginning (time zero) to the moment where the absorbance of the monitored (at 301 nm) by-product is at its maximum.

The results were 27, 50 and 38 x 10^{-5} $mol.s^{-1}$ respectively in the morning, at noon and in the afternoon; showing that noon is the most favourable period of the day to carry out the process, followed by the afternoon and the morning.

As expected in agreement with **Eq.3.20**, when all the variables are kept constant except $\Delta\overline{UV}$, the reactor should accumulate more energy at noon than at any of the two other periods (morning or afternoon); because at the noon, the radiation flux is at its maximum as shown in the **Fig.2.8**.

The second curve (see second axis) shows that relatively the same amount of energy is needed to degrade the 90% of DEP in the three cases. This observation should be considered for the automation of the system when designing a new plant. But in the case when a photoreactor is not provided with a radiometer, the database of the sunshine in Ouagadougou could provide the average of total energy per day, per month or a season so that, when knowing the energy necessary to degrade a pollutant per volume of water, and the Volumetric Treatment Factor (T*fv: Effective Energy per volume)*, one could design photoreactors for specific usages in Ouagadougou.

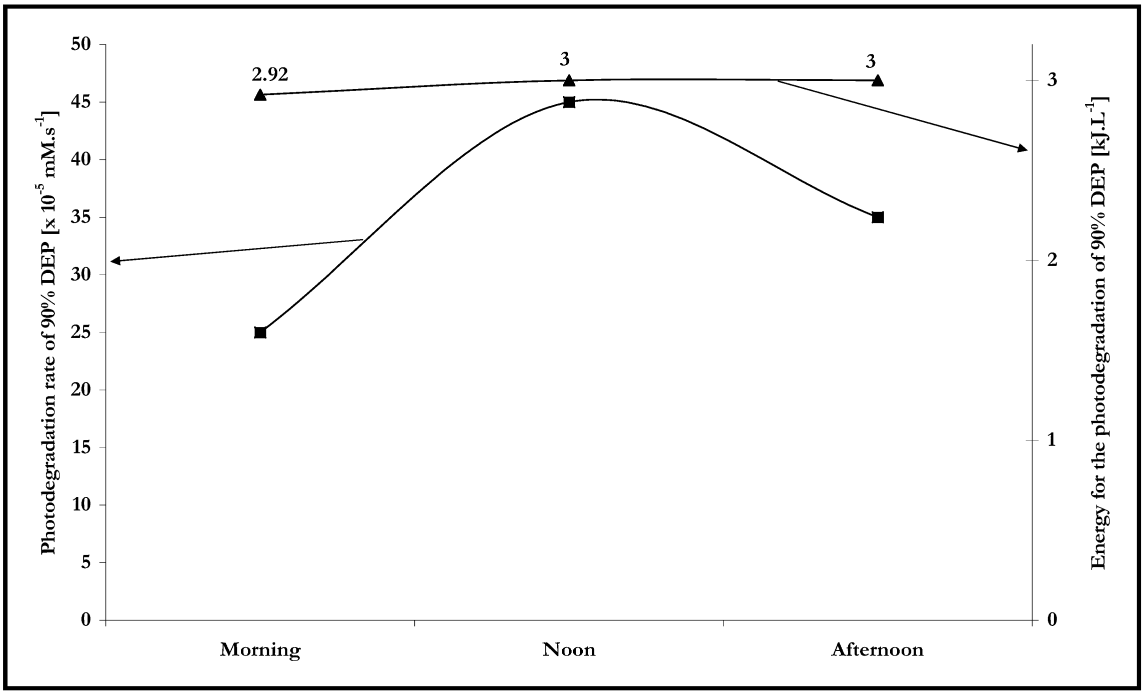


Figure 3. 5: *Influence of the period of the day on the photodegradation of the DEP: (■) Photodegradation rate of 90% of DEP and (▲) Energy needed to degrade 90% of DEP at each of the three periods of the day ("Morning": 08h00-10h30; "Noon": 10h30-13h30"; "Afternoon": 13h30-16h30).*

3.3.2.2 The flow rate

The water circulation rate was applied at three different values: 14.4, 19.1 and 24.2 L.s^{-1} (corresponding to the water circulation speeds of 0.3, 0.4 and 0.5 m.s^{-1} in the photoreactor) and the experiments were carried out in the morning, at noon and in the afternoon.

The results presented in **Fig 3. 6** shows that whenever the experiment was carried out (morning, noon or afternoon), the degradation rate followed the increase of the circulation rate. This observation can be due to the high aeration of the system which was visually noticed by the presence of more air bubbles in the photoreactor. Since the oxygenation takes place in the tank, we can assume that the aeration was maximal when water entered in the tank at the highest speed.

Several authors had investigated the effect of the dissolved oxygen within iron photo-assisted treatment of some organic pollutants in water (Zuo 1992; Sun 1993; Sarria 2003).

It was shown that oxygen participates in the generation of H_2O_2 by the formation of the hydroperoxyde, which recombines to generate the hydrogen peroxide according to the following reactions:

$$Fe^{2+} + O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}O_2H \qquad \textbf{(Eq.3. 19)}$$

$$2\ {}^{\bullet}O_2H \rightarrow H_2O_2 + O_2 \qquad \textbf{(Eq.3. 20)}$$

Thus, the Fenton and photo-Fenton processes can be activated, because of the continuous production under aeration of the hydrogen peroxide within the system.

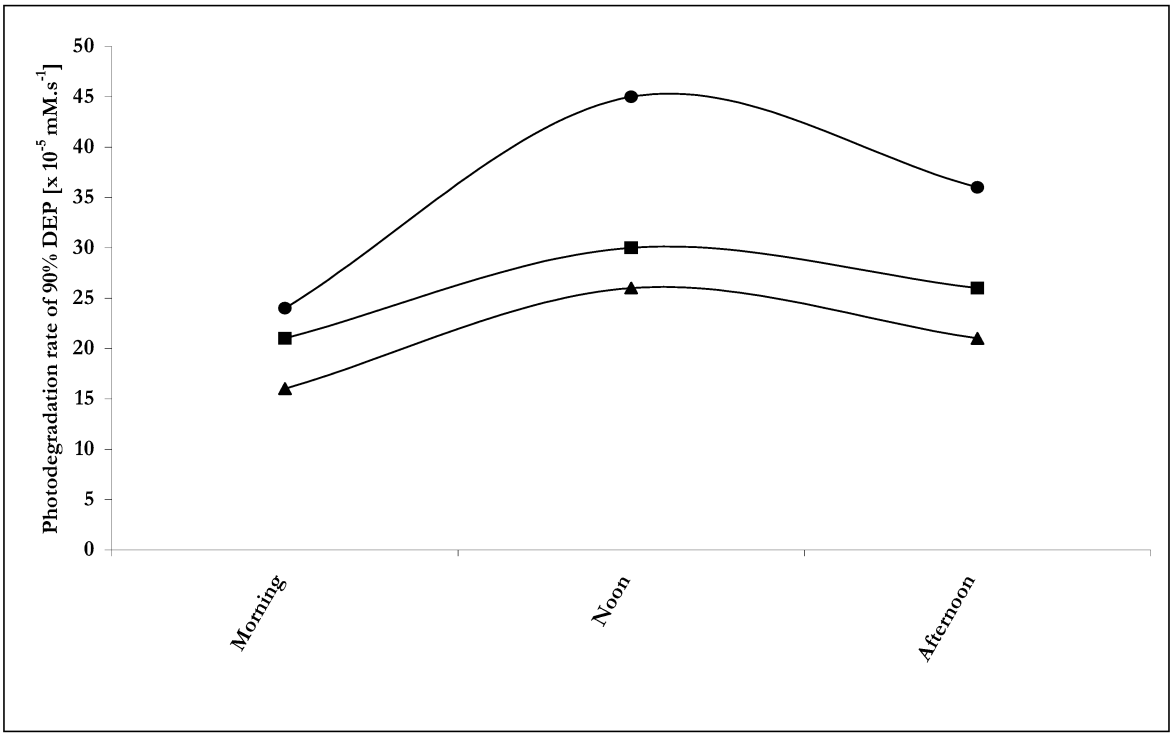


Figure 3. 6: *Influence of the water flow rate in the photoreactor: (▲) for 14.4 L.min^{-1}; (■) for 19.1 L.min^{-1} and (●) for 24.2 L.min^{-1}. Experiments were carried out at the three periods of the days to confirm the conclusion of Fig.3.5. 24.2 L. min^{-1} is the most effective circulation rate and the noon is the most favourable period.*

Practically, the operator should gain in operating the reactor at the maximal circulation rate so to diminish the duration of treatment per batch. Among the three flow rates which were tested, 24.2 L.min^{-1} had shown to be the optimal.

3.4 Conclusion

The photo-Fenton degradation of a potential Endocrine Disrupting Chemical, the diethyl phthalate is reported in this study carried on a field pilot Compound Parabolic Collector photoreactor using direct solar energy in Burkina Faso. It is observed that the DEP degradation rate depends on the period of the day and the water circulation speed. It is also influenced by the amount of Fe^{3+} and the initial H_2O_2 and DEP concentration. In the range of the Fe^{3+} concentrations tested (0.035-0.142 mM), the degradation rate of DEP is linearly proportional to the amount of the iron used. We then proposed some economical considerations to optimize the iron amount needed for the process.

The optimal efficiency of the photoreactor using a $UV/H_2O_2/Fe^{3+}/O_2$ (from air) system was observed at the following conditions: pH=3, Fe^{3+} concentration of 0.071 mM, initial H_2O_2 concentration, 3.6 mM. The most favourable period of the process was the mid day ("noon "), when applying to the pump a flow rate of 24.2 $L.min^{-1}$ with 25 litres of water containing 0.6 mM of DEP.

From the energetic point of view, it was observed that the photochemical process followed a similar 1st principle of the thermodynamic: "The energy necessary to degrade a constant amount of DEP doesn't depend on the period of the day".

References

Api, A. M. (2001). "Toxicological profile of diethyl phthalate: a vehicle for fragrance and cosmetic ingredients." Food and Chemical Toxicology **39**(2): 97-108.

Baxendale, J. H., and Wilson, A. J. (1957). "The photolysis of hydrogen peroxide at high light intensities." Transactions of the Faraday Society **53**: 344-356.

Blanco J. and Malato, S. R. (2001). Solar detoxification. Alméria, UNESCO/PSA.

Centre for Disease Control (CDC) (2001). National Report on Human Exposure to Environmental Chemicals." USA.

Cissé G. (1997.). Impacts sanitaires de la réutilisation des eaux usées en agriculture dans le contexte sahélien: Cas du maraîchage à Ouagadougou,. Génie Rural, EPFL, Lausanne, Switzerland.

DiGangi, J. a. N., Helena (2002). Pretty and Nasty: Phthalates in European cosmetic products. Sweden, Women's Environmental Network, Health Care Without Harm, USA and Swedish Society for Nature Conservation**:** 26 p.

Fenton, H. J. H. (1894). "Oxidation of tartaric acid in presence of iron.." J. of chem. soc. Trans. **65**: 899-910.

Fiedler, P., Rock, C. (1987). Quimica organica,.

Frericsson, B., Moller, L., Pousette, A. and Westerholm, R. (1993). "Human sperm motility is affected by plasticizers and diesel particle extracts." Pharmacol. Toxicol. **72,**: 128-133.

Gian, C. S., Atlas, E., Powers Jr., M.A. and Leonard, J.E. (1984). Phthalates ester. Anthropogenic chemicals, Springer-Verlag, Berlin**:** 67-142.

Hurtert, K., Moza, P.N. (1988.). "photkalytisher abbau von phthalten an titandioxid in wässriger phase,." chemosphere **17**(9): 1751-1754.

Kawagushi, H. (1994). "photodecomposition of bis-2-ethylhexyl phthalate. ." Chemosphere **28**(8): 1485-1493.

Kenfack, S., Mampouya, M. and Cissé, G. (2000). Eau-Environnement et santé. International colloquium "Water and health Ouaga-2000".

Kiwi, J., Pulgarin, C., Peringer, P. and Gratzel, M. (1993). "Beneficial effects of homogeneous photo-Fenton pretreatment upon the biodegradation of anthraquinone sulfonate in waste water treatment." Applied Catalysis B: Environmental **3**(1): 85-99.

Kwon, B. G., Lee, Dong Soo., Kang, Namgoo. and Yoon, Jeyong (1999). "Characteristics of p-chlorophenol oxidation by Fenton's reagent." Water Research **33**(9): 2110-2118.

Lipczynska-Kochany, E., G. Sprah, et al. (1995). "Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction." Chemosphere **30**(1): 9-20.

Lovekamp-Swan T. and Davis, B. J. (2002). "Mechanisms of phthalate ester toxicity in the female reproductive system." Environ Health Perspect.

Mailhot, G., Sarakha, M., Lavedrine, B., Caceres, J. and Malato, S. (2002). "Fe(III)-solar light induced degradation of diethyl phthalate (DEP) in aqueous solutions." Chemosphere **49**(6): 525-532.

MINEFIB. (2000). Registre Import-Export. Ouagadougou, Ministère de l'Economie et des finances du Burkina Faso,Etat burkinabé**:** 125.

Muneer, M., Theurich, J. and Bahnemann, D. (2001). "Titanium dioxide mediated photocatalytic degradation of 1,2-diethyl phthalate." Journal of Photochemistry and Photobiology A: Chemistry **143**(2-3): 213-219.

O'Grady, D. P., Howard, P. H., Werner, F. (1985). "Activated sludge biodegradation of 12 commercial phthalate esters,." Appl. And Environ. Microbial. . **49**: 443-445.

Ooka, C., Yoshida, H., Horio, M., Suzuki, K., Hattori, T. (2003.). "Adsorptive and photocatalytic performance of TiO2 pillared montmorillonite in degradation of endocrine disruptors having different hydrophobicity." Applied Catalysis B: Environmental **41**: 313-321.

Parra, S., Sarria, V., Malato, S., Peringer, P. and Pulgarin, C. (2000). "Photochemical versus coupled photochemical-biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon." Applied Catalysis B: Environmental **27**(3): 153-168.

Rodriguez, M., Timokhin,Vitaliy., Michel,Florian., Contreras, Sandra., Gimenez, Jaime and Santiago Esplugas. (2002). "The inffluence of different irradiation sourcesvon the treatment of nitrobenzene." Catalysis Today **76**: 291-300.

Sarria, V. (2003). Coupled advanced oxidation and biological processes for wastewater treatment. Institute of Environmental science and Technology. Lausanne, EPFL**:** 150.

Sarria, V., Parra, S., Invernizzi, M., Péringer, P. and Pulgarin, C. (2001). "Photochemical-biological treatment of a real industrial biorecalcitrant wastewater containing 5-amino-6-methyl-2-benzimidazolone." Wat. Sc. and Technol. **44**(5): 93-101.

Staples, C., Peterson, D., Parkerton, T. and Adams W., (1997). "The environmental fate of phthalate esters: A literature review." Chemosphere **35,**: 667-749.

Staples, C. A., Peterson, Dennis R., Parkerton, Thomas F. and Adams, William J. (1997). "The environmental fate of phthalate esters: a literature review." Chemosphere **35**(4): 667-749.

Sugatt, R. H., O'Grady, D. P., Banerjee, S., Howard, P. H. and Gledhill, W.E (1984). "Shake flask biodegradation of 14 commercial phthalate esters." Appl. And Environ. Microbial. . **47**: 601-606.

Sun, Y. F., and Pignatello J.J. (1993). "Photochemical Reactions Involved in the Total Mineralization of 2,4-D by Fe3+/H,0,/UV." Environ. Sci. Technol. **27**: 304-310.

US., E. P. A., U.S (2001). Removal of Endocrine Disruptor Chemicals Using Drinking Water Treatment Processes, EPA.

Xue-Kun, Z., Gui-Peng, Yang., Yu-Jue, Wang. and Xian-Chi Gao (2004). "Photochemical degradation of dimethyl phthalate by Fenton reagent." Journal of Photochemistry and Photobiology A: Chemistry **161**: 215-220.

Zuo, Y., and Holgn, J (1992). "Formation of Hydrogen Peroxide and Depletion of Oxalic Acid in Atmospheric Water by Photolysis of Iron(I I I)-Oxalato Complexes." Environ. sci. technol. **26**: 1014 -1022.

Chapter 4

Photo-Fenton study of the depollution of real biorecalcitrant wastewaters: Case studies

Chapter 3 investigated the optimal operational conditions to carry out the photo-Fenton treatment of "modelled" polluted water, using a Compound Parabolic Concentrator photo-reactor. The Chapter 4 explores the possibility of applying the same treatment in two real cases of industrial water pollution. The first one concerns a methodological study for integrating the photo-Fenton treatment in a general strategy of wastewaters management in a chemical industry in Switzerland; the second case investigates the application of the helio-photo-Fenton process for destroying an obsolete stock of a commercial Endosulfan in Burkina Faso.

4.1 Introduction

An estimation of the global world water pollution reveals that (60 -.70%) of the total pollution is due to the agricultural activities, (25 to 30%) by industries and the remaining 5 to 10% due to the domestic uses (Population.Information.Program 1998). The report showed that in the most optimistic cases, the water pollution from agricultural origin is mostly consisted of the residues of pesticide and contributes to at least 50% on the deterioration of the quality of natural waters (surface and subsoil waters). This is closely followed by the pollution of chemical industrial origin. In fact, more than 1000 new substances are marketed each year in the world whereas up to now, the toxicological information on only 1000 to 2000 of these products is accessible (Toepfer 2004).

Most of these substances are ***xenobiotic*** (c.a. foreign to the life) and very often they are synthetic products. Indeed, xenobiotic substances are in general not easily biodegradable and they cross the biological water treatment systems without being completely degraded or even sometimes not degraded at all.

Some of these substances such as the pesticides are recognized for their carcinogenic, mutagen effects or of hormonal disruptions on the fauna, wild life and human beings.

To face these problems, waste treatments such as the incineration, wet oxidation and activated carbon adsorption are often used. Unfortunately, these techniques are very expensive and the environmental virtues of some of them are discussed.

However, biological processes remain the most economical and environmentally compatible alternative for wastewater treatment. Thus, it would be important to confirm the biorecalcitrancy of a wastewater before the application of a photo-catalytic treatment. Moreover, biorecalcitrant wastewater could only be photo-catalytically treated up to the point where its biodegradability is enough to let the photo-treated water follows a biological treatment. Two methodological case studies were followed in this chapter to illustrate this strategy of enhancing the biodegradability of biorecalcitrant wastewaters by a photocatalytic process. Each of the studies is representative of a real situation of water pollution (One in Switzerland and another in Burkina Faso).

4.1.1 The case study of some real biorecalcitrant wastewaters from a chemical industry in Switzerland

A Swiss chemical company had just started the production of a significant chemical, following a three steps manufacturing process. Three types of effluent of a specific composition are generating at each step and, all the three effluents were mixed to the other effluents of many processes and treated in an activated sludge wastewater treatment plant. Before the new production, the yield of the wastewater treatment plant was efficient and it could respect the legal rejection norms. But since the production of the new chemical has started, the yield has fallen down and the plant could not any more respect the standards, even when the hydraulic capacity overshooting of the treatment plant was still very low. Within the framework of this thesis, we had to make a case diagnosis and identify the biorecalcitrant effluent and study its photo-Fenton treatment using a sunlight simulator in the laboratory. After all, I proposed a scheme integrating the studied treatment in a general global strategy of the wastewaters management in that company. This study using sunlight simulator was followed by another one using real sunlight, carried out at Ouagadougou in Burkina Faso, and contextualized with the problem of POPs and obsolete commercial pesticides stocks which is crucial in the country.

4.1.2 The problem of POPs and obsolete pesticides in Burkina Faso

In order to implement the national plan of the ***Stockholm's Convention*** on the persistent organic pollutants (POPs), the government of Burkina Faso carried out in 2001 and 2004 two inventories of stocks of POPs pesticides available on the extent territory of Burkina Faso. The results of these inventories are reported below.

Table 4. 1: *Results of the surveys of POPs and obsolete pesticides in Burkina Faso (2001 and 2004)*

Form	**Quantity**			
	2001	**2004**	**Nature of the pesticide in 2004**	
Contaminated empty containers (-)	1'450'000	120'000	**Cypermethrin**	**Endosulfan**
Powder (kg)	26'000	3'000		
Liquid (Litres)	250'000	130'000	85'700	4'000

Source: Rapport d'inventaires des pesticides POPs au Burkina Faso, 2004 (Ministère de l'Environnement et du Cadre de Vie 2005)

It was noticed that 90% of these pesticides were formulated with Cypermethrin (67%) and Endosulfan (3%) which are classified in the categories II and III (from the toxic to very toxic) by the WHO. The same report revealed that 13 contaminated sites of major importance are available in Burkina Faso. Since there is neither incinerator in Burkina Faso, nor a specialized hazardous waste treatment plant, the photo-Fenton process was tested in this study for the degradation of the pesticide made with Endosulfan. This study was carried out at the EIER, Ouagadougou, Burkina Faso, using the sunlight as the photonic source. The experimental and results of the two stated case studies are presented in the following sections.

4.2 Experimental

4.2.1 Materials

The solar simulator (Hanau Suntest) described in the **section 2.1.1** was used through out this work at the LBE-EPFL in Switzerland and the CPC photo-reactor described in **section 2.1.2** was used for the field applied case study in Ouagadougou (Burkina Faso).

All the chemicals ($FeCl_3$, $6H_2O$), HCl and H_2O_2 (30% w/w) were bought from Fluka (Switzerland). All were analytical grade (p.a.).

Three types of wastewaters (see **Table 4.2**) containing pyridine compounds were received from DLK Technology S.A; a Swiss company specialized in the development of specific plants for water and wastewater treatment.

The obsolete stock of pesticide was constituted of 1 litre of Endosulfan 350® EC, an insecticide made of 350 $g.L^{-1}$ pure Endosulfan supplied by the direction of the industrial pollution control of the ministry of environment and living standard of Burkina Faso. This insecticide is commonly used for the cotton pest control.

The commercial pesticide was diluted in tap water to constitute a raw polluted water stock of 370 $mg.L^{-1}$ of Endosulfan. This concentration could be characteristic of an effluent resulting from the rinsing of tanks and containers in a manufacture, where such pesticides are produced, or in the wastewater resulting from an industrial site of pesticide containers decontamination, such as it is illustrated in the scheme below.

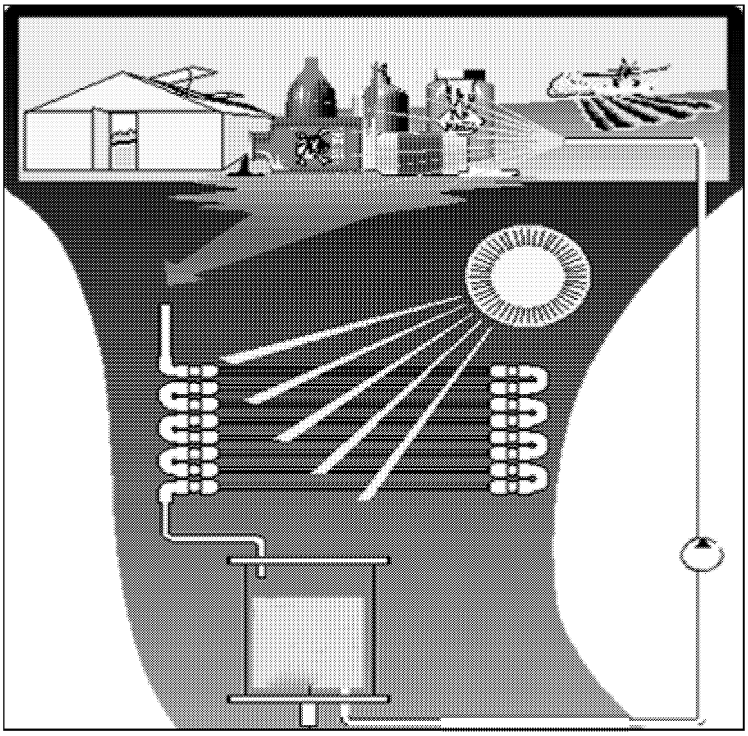


Figure 4. 1: *A schematic representation of the helio-photocatalytic decontamination of some pesticide containers.*

4.2.2 Procedures

In the laboratory, a systematic diagnosis including the characterisation of each of the three effluents received was first made and this was followed by the photo-assisted studies on the effluent containing the chloro-2-pyridin. 2 litres of the raw effluent was first acidified at pH=3. For the photodegradation processing, 50 ml of this preparation was put into a 60 ml of a Pyrex flask glass and reactants (iron and peroxide) were added. The flask glass was placed into the Suntest photo-reactor for a determined time of illumination. Samplings were made every 10 minutes for TOC, HPLC and spectrophotometric analyses and, during the Zahn Wellens tests, sampling were made daily.

For the experiments carried out at Ouagadougou, the CPC photo-reactor was processed as the same as described in **section 2.1.2.** Samplings were made every 10 min for the absorbance analyses and every 30 min for the COD and DBO_5 analyses.

In both cases (laboratory of field study) samples were each time neutralized with $NaHSO_3$ in order to quench the $^{\bullet}OH$ radicals so that the Fenton reaction could not continue in the dark.

4.2.3 Analytical methods

At the LBE, HPLC analyses were carried out using the same Varian 9065 unit device and the absorbance measurement of the samples were made using the Hitachi UV-vis U-3010 model spectrophotometer all described in § **2.2.3**.

The biological Zahn Wellens tests were carried out on the phototreated samples after 60% degradation of the TOC, following the OCDE standard method (OECD 1996).

At the EIER in Ouagadougou during the field work, the monitoring of the process was made using the Biomate spectrophotometer at the fixed wavelengths of 218 nm which is the maximal absorption wavelength of the Endosulfan as shown in **Fig.4.2**.

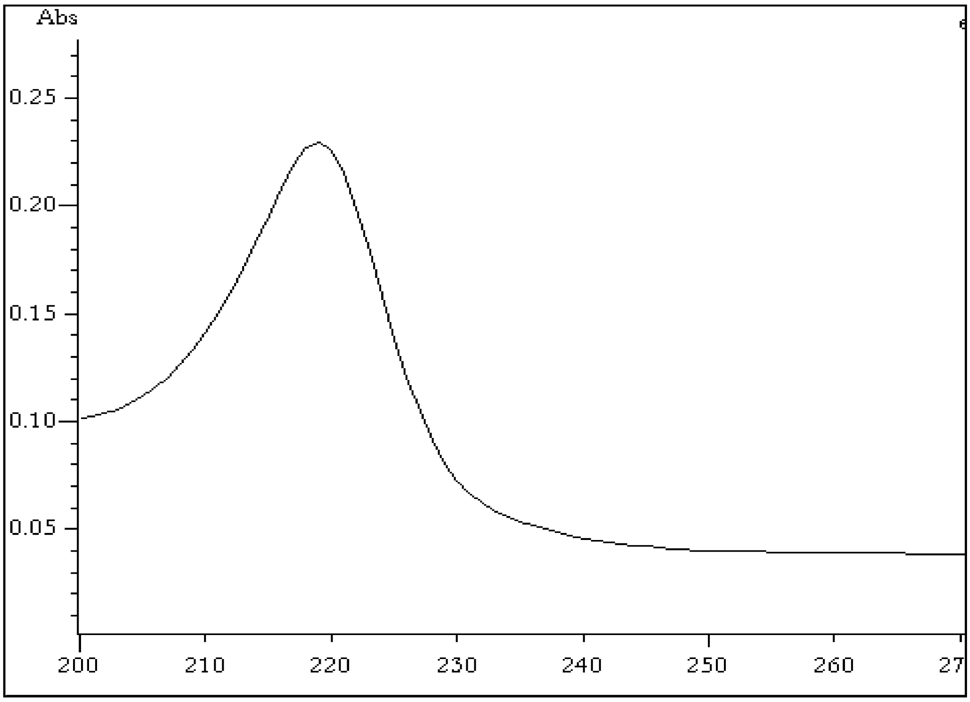


Figure 4. 2: *The spectrum of a commercial diluted Endosulfan solution at 0.36 mM showing a maximum at 218 nm*

The Chemical Oxygen Demand (COD) analyses were carried out via a Hach-2000 spectrophotometer using the dichromate solution as the oxidant in a strong acid medium. 2 ml of the samples were put into the low range kits (0-150 mg.L^{-1}) and digested at 150°C for two hours. Once the digested samples were cooled, their optical density was determined at $\lambda = 430$ nm, in comparison to a blank, prepared with 2 ml of distilled water. The Biological Oxygen Demand for five days (BOD_5) was measured by means of a Hg free WTW 2000 Oxytop unit thermostated at 20°C according to the standard method.

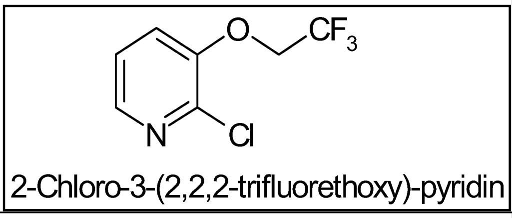
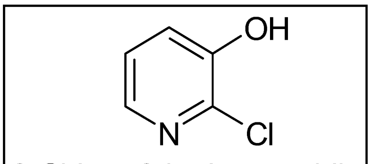
4.3 Results and discussions

4.3.1 Study of the management of the chemical industry effluents

4.3.1.1 Diagnosis: Physicochemical and biological characterization of different type of effluents resulting from the processing of LQV.

Table 4.2 presents the characteristics of the three effluents (WW_i) from the production of the LQV (its molecular formula of this chemical is confidential) and **Fig. 4.3** shows the results of the Zahn wellens tests carried out on the three effluents.

Table 4. 2: *Synthesis of the characteristics of the three industrial effluents studied*

Type of effluent	Main pollutant	Molecular structure	pH	TOC (g.L^{-1})
WW_1	CTFEP	 2-Chloro-3-(2,2,2-trifluorethoxy)-pyridin	8.3	45
WW_2	LQV	confidential	6	43.5
WW_3	CHPYR	 2-Chloro-3-hydroxypyridin	5.8	6.5

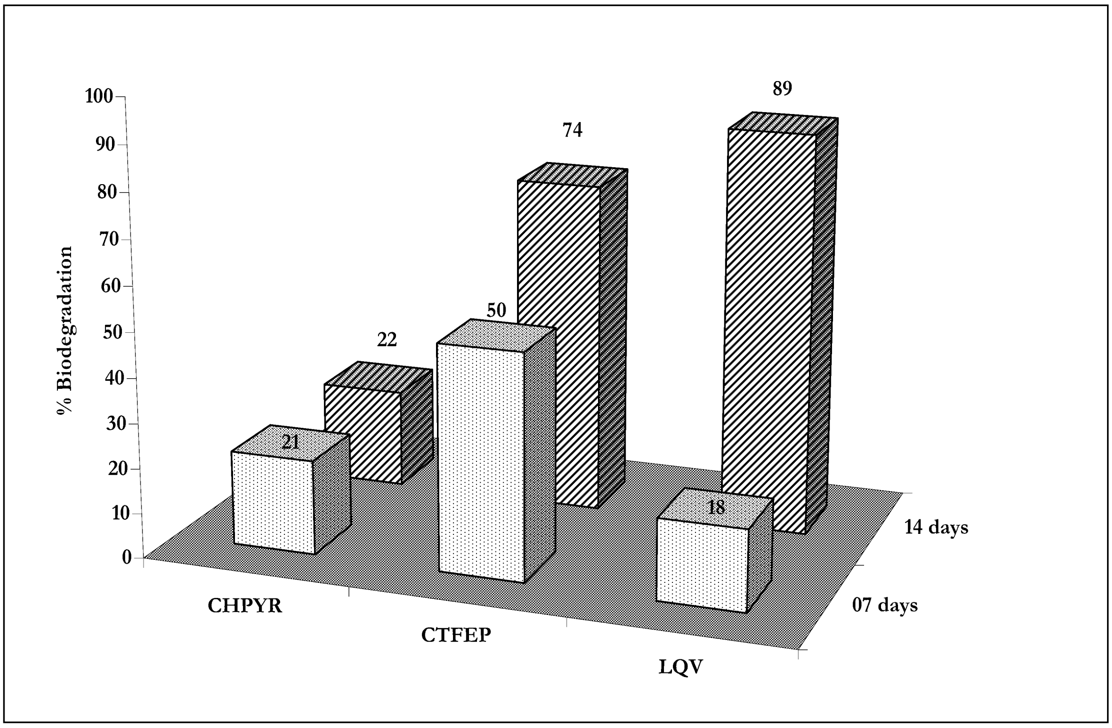


Figure 4. 3: *The biodegradability after 07 (☐) and after 14 days (▨) of the three raw chemical industrial wastewaters*

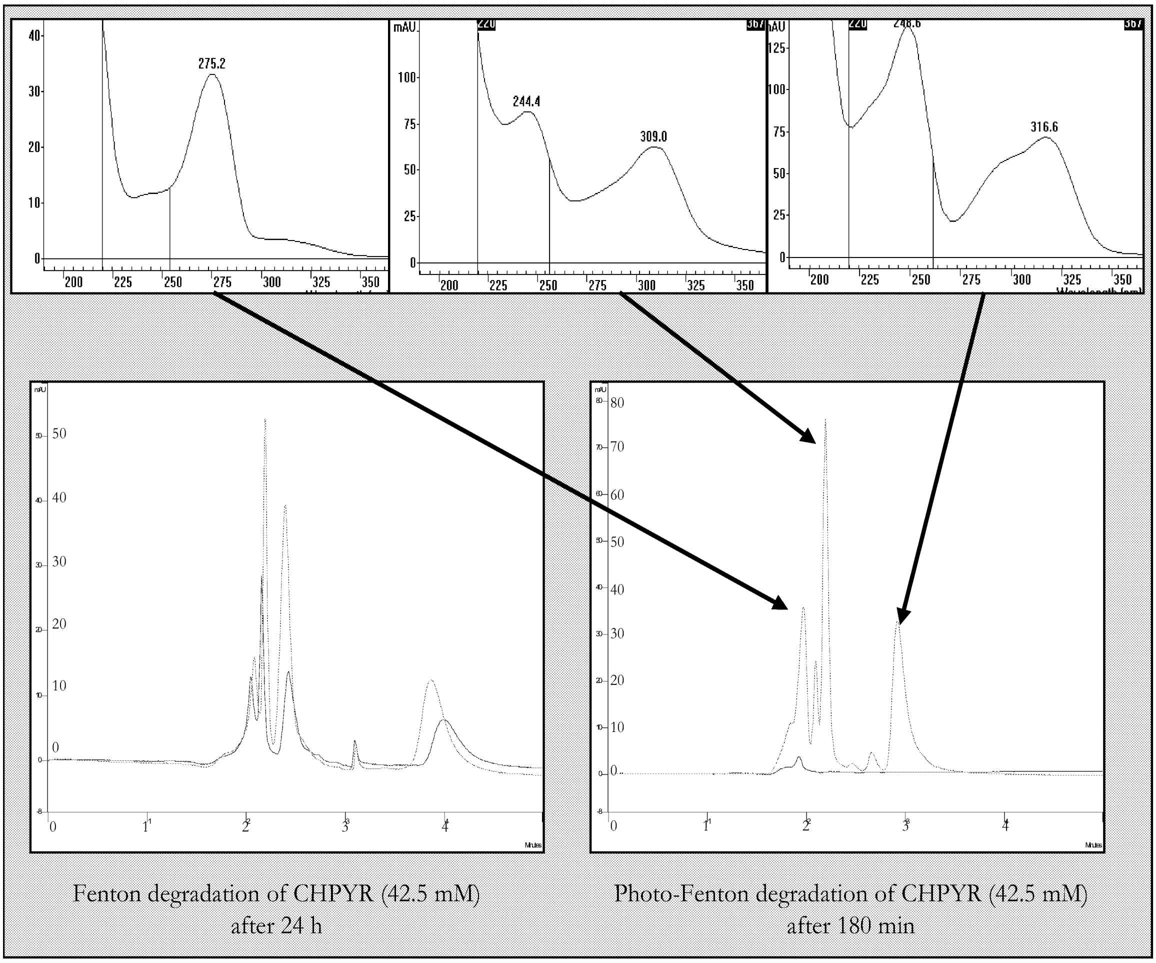
From these results, one can conclude that:

- ✓ The wastewater mainly containing CTFEP is easily biodegradable and that with LQV is biodegradable after a certain bacteria adaptation period.
- ✓ The wastewater mainly containing CHPYR is biorecalcitrant. No change in the degradation rate was observed from the 7th till 14th day, nor up to 28 days. The Fenton and photo-Fenton process was applied to WW_3 and the experimental conditions were optimized for the catalyst (Fe^{2+}) and the electron acceptor (H_2O_2).

4.3.1.2 Fenton and photo-Fenton treatment of the CHPYR polluted wastewater.

Fig. 4.4 shows the chromatograms of the CHPWR effluent carried out at times 0 and 24h (Fenton on 50% diluted CHPYR effluent) on the one hand, and 0 and 1h30 (photo-Fenton on the same effluent). The UV spectra of the three significant peaks before the treatment are shown. The two most important peaks of the chromatograms were completely degraded in the case of the photo-Fenton and the peak at 275.2 nm was 90%

degraded when compared to time 0 while all the peaks regressed to almost 50% in the Fenton process after 24 h.



Fenton degradation of CHPYR (42.5 mM)
after 24 h

Photo-Fenton degradation of CHPYR (42.5 mM)
after 180 min

Figure 4. 4: *HPLC chromatograms of the CHPYR effluent before and after the Fenton (left) and the photo-Fenton (right) processes*

From **Fig.4.4**, we confirmed that the CHPYR (maximum UV absorption at 309 nm) is the most important pollutant in the effluent. More so, we could conclude that the Fenton and photo-Fenton processes could lead to total degradation of the CHPYR within the tested condition. However, the Fenton process is not timely efficient.

4.3.1.3 Optimisation of the H_2O_2 and Fe^{2+} concentrations

Fig. 4.5 shows that the optimal conditions for the photo-Fenton treatment of the CHPYR effluent are obtained in 2 hours with an initial concentration of the solution of TOC = 2200 mg.L $^{-1}$, Fe $^{2+}$= 5.2 mM, H_2O_2 = 768 mM. The chromatograms of **Fig. 4.6** make it possible to note that under these conditions, 60% of the organic pollutants (main pollutants and their degradation intermediates) are mineralized when the CHPYR is completely exhausted in the solution within the two hours of photo-Fenton treatment. The OECD of Zahn Wellens test was then carried out to evaluate the biodegradability of the photo-treated effluent.

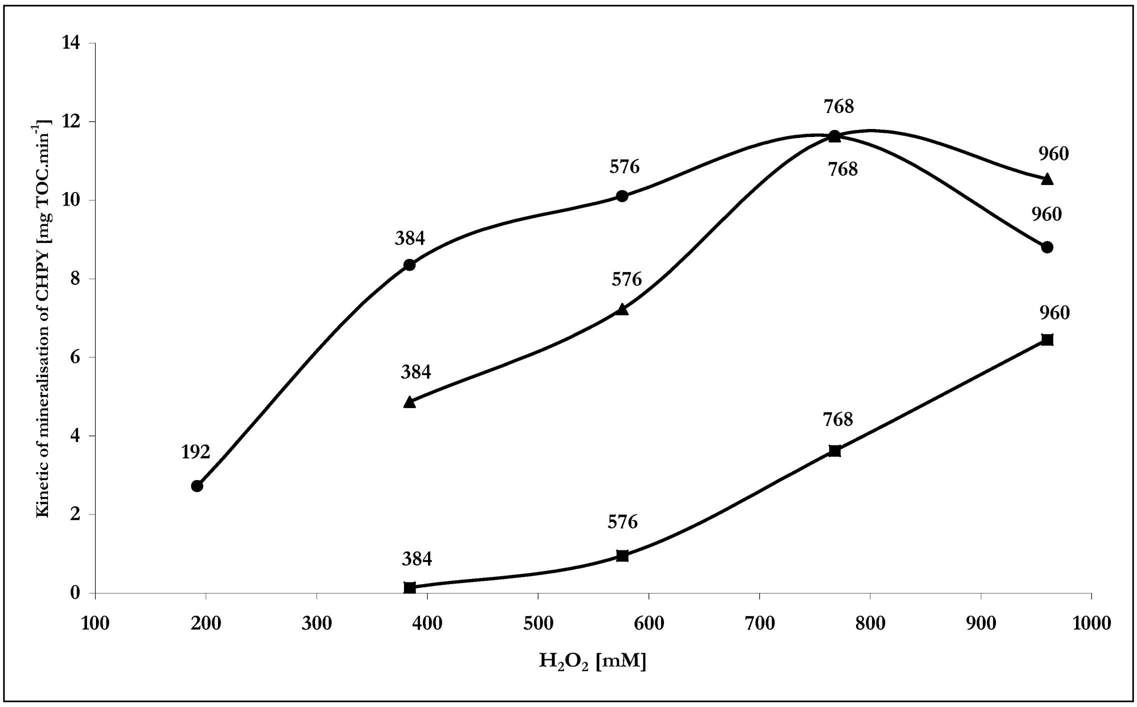


Figure 4. 5: *Kinetic of mineralisation of the CHPYR at various iron concentration: (■) for 3mM; (▲) for 5.2 mM and (●) for 9.6 mM, as a function of the H_2O_2 concentration during the Photo-Fenton process on a 50% diluted effluent*

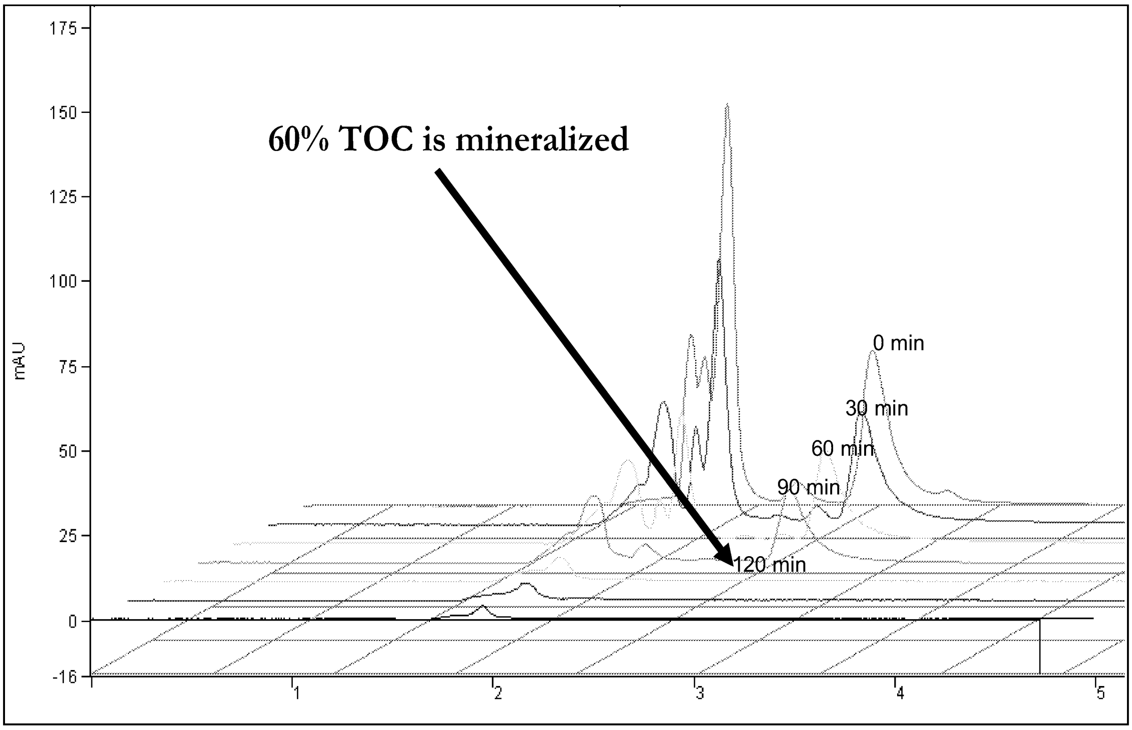


Figure 4. 6: *Chromatograms of a series of photo-treated samples of CHPYR taken at 30 min period.*

4.3.1.4 Biodegradability of the photo-treated effluent

Fig. 4.7 shows the results of the test of Zahn Wellens carried out on the photo-treated CHPYR affluent under the given optimal conditions (Fe^{2+} = 5.2 mM; H_2O_2 = 768 mM; pH = 2.8) with a folding back of 60% of the total organic carbon. The result obtained shows that, hardly 15 to 18% of biological degradation is reached at the end of the first weeks followed by a fold down at 12 % and stagnation until the 28th day. We assumed that the photo-generated intermediates of degradation of the CHPYR are also biorecalcitrant or toxic. Hence a total mineralization following the Fenton or photo-Fenton process is necessary.

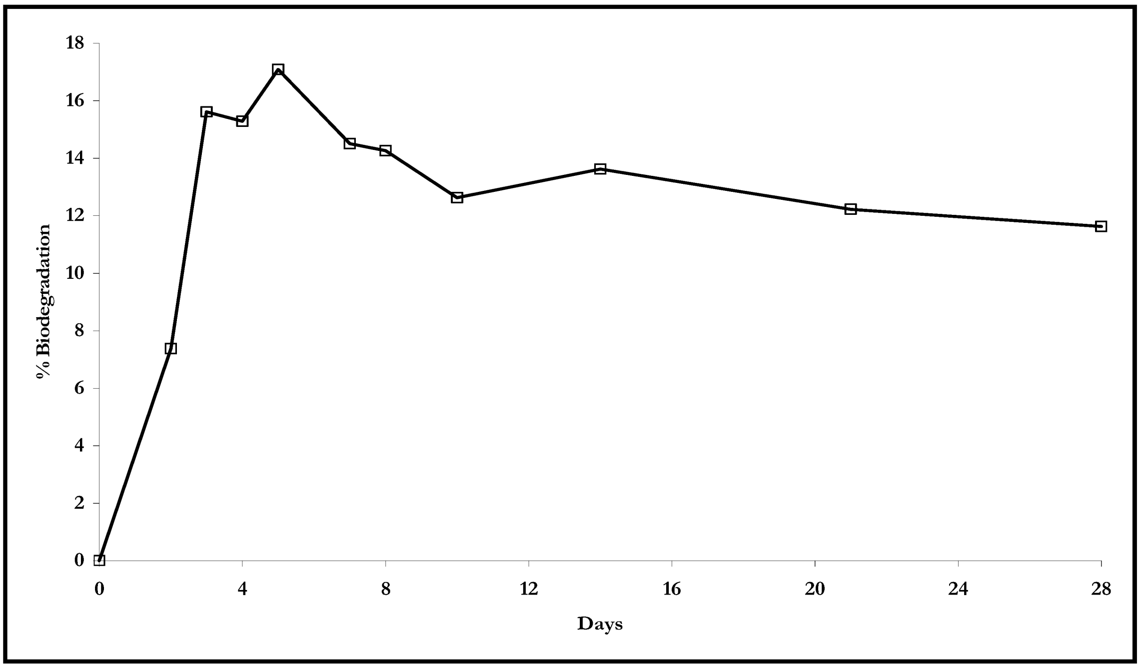


Figure 4. 7: *Biodegradability of the CHPYR photo-treated effluent following the Zahn Wellens test*

4.3.1.5 Recommendations

The studies carried out on the three types of effluents showed that the effluents mainly containing LQV and of the CTFEP are biodegradable and only the effluent with CHPYR is biorecalcitrant. However, the CHPYR effluent can be degraded through the Fenton and photo-Fenton processes, within the following optimal conditions: $[Fe^{2+}]$= 5.2 mM; $[H_2O_2]$= 768 mM for effluent concentrated at 2.2 $g.L^{-1}$ of CHPYR.

The Zahn Wellens tests carried out on photo-treated effluent at 60% TOC reduction do not show a significant biodegradability; hence it would be necessary to reach at least 90% of mineralization before stopping the photocatalytic process.

For a better management of the effluents resulting from this manufacture, we recommended the following diagram:

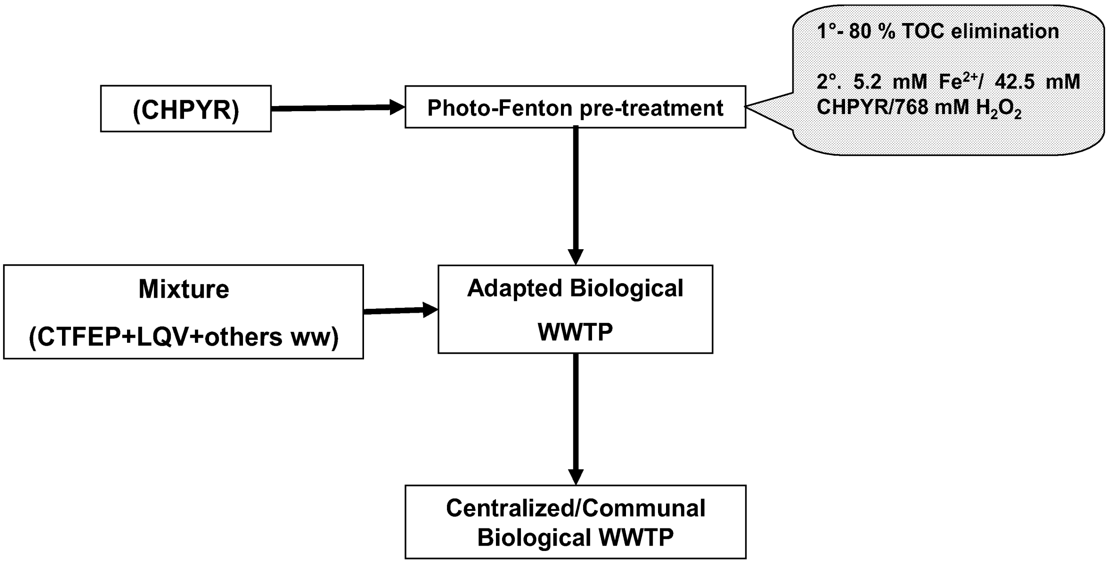


Figure 4. 8: *A Schematic presentation of the global strategy for the studied wastewater management in the company*

4.3.2 Helio-photo-Fenton study of the degradation of Endosulfan

4.3.2.1 Influence of the aeration (O_2) and the photolysis

To assess if the studied helio-photo-Fenton system allows an optimal degradation of the Endosulfan on the CPC photo-reactor, the polluted water samples were initially subjected to aeration without exposure to the solar radiation, then with solar exposure.

Previous studies (Zuo 1992; Malato et al. 2000; Waite 2002; Sarria 2003) revealed that O_2 (from air) applied alone or associated to UV light, was able to generate $^{\bullet}OH$ radicals following the equations **Eqs. 1.2, 1.4** and **1.5** described in the chapter 1, section 1.3.1. The degradation of the Endosulfan followed by a simultaneous measure of the absorbance of the phototreated samples at 218 nm (see **Fig. 4.2**) and the analyse of the COD presented in **Fig. 4.9** shows that the photolysis makes it possible to decrease by 40% the absorbance of the solution of Endosulfan and approximately 30% of the COD. The aeration alone could allow only a relative fall of 20% of the absorbance to 218 nm and any fall of the COD. On the other hand the photo-Fenton process applied under the following conditions: $[Fe^{2+}]$= 0.18 mM; $[H_2O_2]$= 12 mM on the polluted effluent at 0.36 mM of Endosulfan (135 mg.L^{-1}) leaded to a fall down of 80% of the absorbance at 218 nm and 85% decrease of the COD when applying an energetic treatment factor of ca. 20 x 10^3 J.L^{-1}. It is possible that, the chemical composition of the commercial pesticide which includes the active Endosulfan compound (solubility in water (0.325 mg.L $^{-1}$) and other additives such as the emulsifiers and the adhering agents which stabilizes the product on the plant once it is pulverized (Sethunathan 2002), some of these additives would be destroyed by photolysis and/or oxidation with oxygen from the air. The fall down up to 40% of the absorbance at 218 nm of the solution does not inevitably mean that the Endosulfan is degraded, since it was shown that the molecule of Endosulfan is stable with the solar radiation and the tests of stabilization for the commercial formulation of pesticides take into account the sunlight exposition aspects. We can allot the effect of photolysis and aeration on the Endosulfan solution to the degradation of the manufacturing additives.

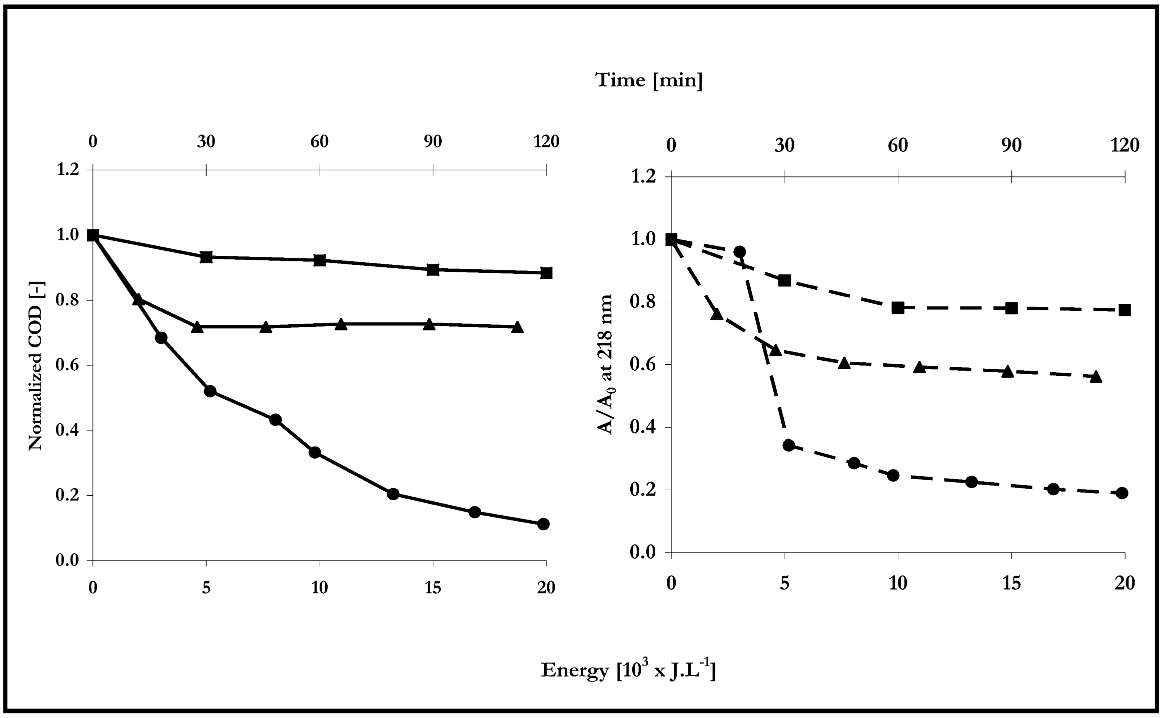


Figure 4. 9: *Influence of (O_2 from air) and photolysis on the degradation of the Endosulfan: (■) only O_2 from air; (▲) for (O_2 + hν)=photolysis and (●) for helio-photo-Fenton.*

4.3.2.2 Influence of the H_2O_2 concentration

As the same as in the former studies carried out on the model pollutants, the variation of the concentration of hydrogen peroxide was studied and its influence on the degradation of the Endosulfan is represented in **Fig. 4.10.**

It is noted that the more one increases the hydrogen peroxide concentration, the more the degradation is faster for the same concentration of the pesticide in the effluent. However, a threshold is reached around 12 mM of H_2O_2. Beyond that, it is noticed a decrease in the Photo-Fenton process activity. This fall could be related to the dismutation and competition reactions between the $^{\bullet}OH$ radicals, O_2 and $^{\bullet}O\,H_2$ as previously described in the **Eqs. 3.11 and 3.12**.

When taken into account the high cost of hydrogen peroxide on one hand, the technical choice of a treatment: photochemical total mineralization or coupling photochemical-biological processes on the other hand, it is necessary to make a compromise over the optimal concentration of H_2O_2 and the duration of the treatment, by evaluating the biodegradability of the phototreated effluent. In the case of this study, we chose the lowest concentration of the peroxide (8 mM) with 0.18 Fe^{2+} mM for an initial concentration of 0.36 mM of Endosulfan.

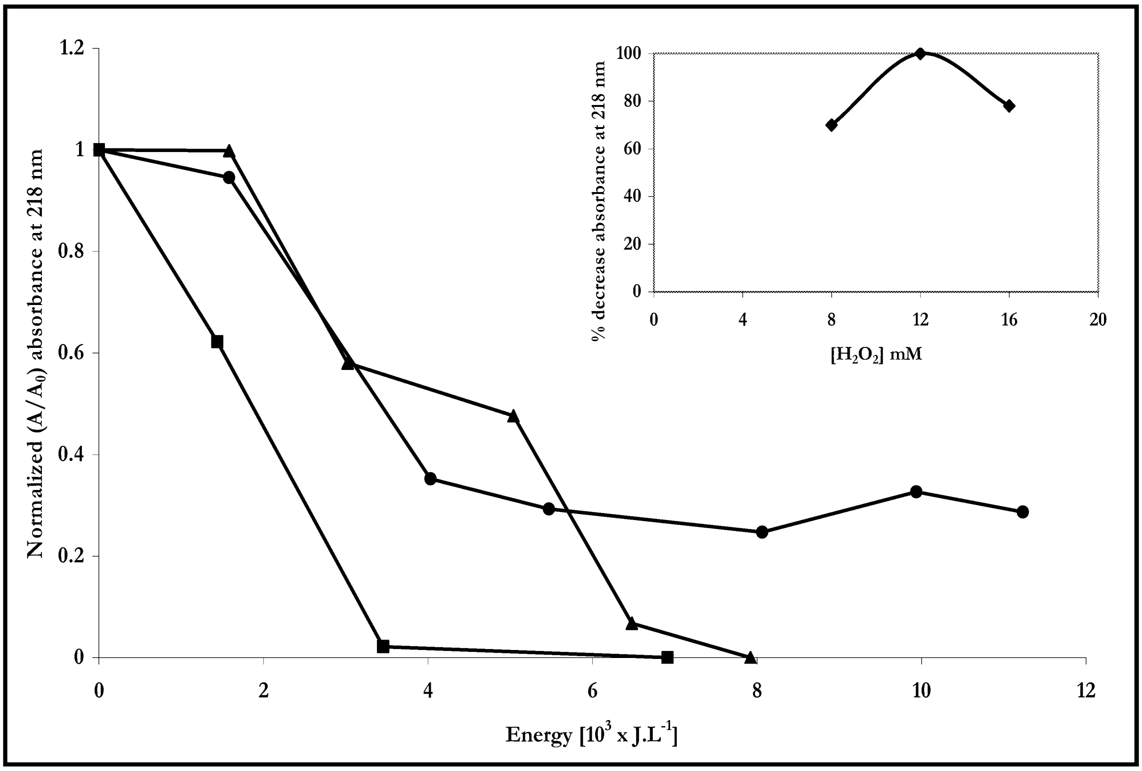


Figure 4. 10: *Relative absorbance of the phototreated water as a function of the volumetric energy. The* H_2O_2 *is varied from: (●) 8 mM, (■) 12 mM to (▲) 16 mM. The insert is percentage of relative degradation of the Endosulfan (monitored at 218 nm) when* 6×10^3 $J.L^{-1}$ *energy is accumulated in the photoreactor for the three tested* H_2O_2 *values.*

4.3.2.3 Evolution of the biodegradability of the phototreated Endosulfan wastewater

It is known that the photocatalytic treatment is not a cost effective process when compared to biological treatment (Ollis 1988; Pulgarin, Invernizzi et al. 1999; Blanco J. and Malato 2003; Sarria 2003). Therefore, the monitoring of the biodegradability of the phototreated effluent was conducted on 30 min sampled effluents. The results in **Fig. 4.11** show that the BOD_5 increases during the first 30 minutes of the treatment and decrease during the next one hour; after that it remains constant. At the same time, the COD is continuously decreasing up to one and half hour after which it remains constant. As a consequence of the evolution of these two parameters, the intrinsic biodegradability defined as the ratio BOD_5/COD is continuously increasing up to 50% where it became constant when the energetic treatment factor of the process is 15×10^3 J.L^{-1}.

Assuming this relatively high value of the BOD_5/COD ratio, one can conclude that the phototreated effluent of the Endosulfan pesticide is biodegradable in the natural environment. However, it would be necessary to throw such effluents into a biological wastewater treatment plant before they could be reused for any purpose or be rejected in the natural media (river, dam or lake) as illustrated in the (**Fig. 1.10**).

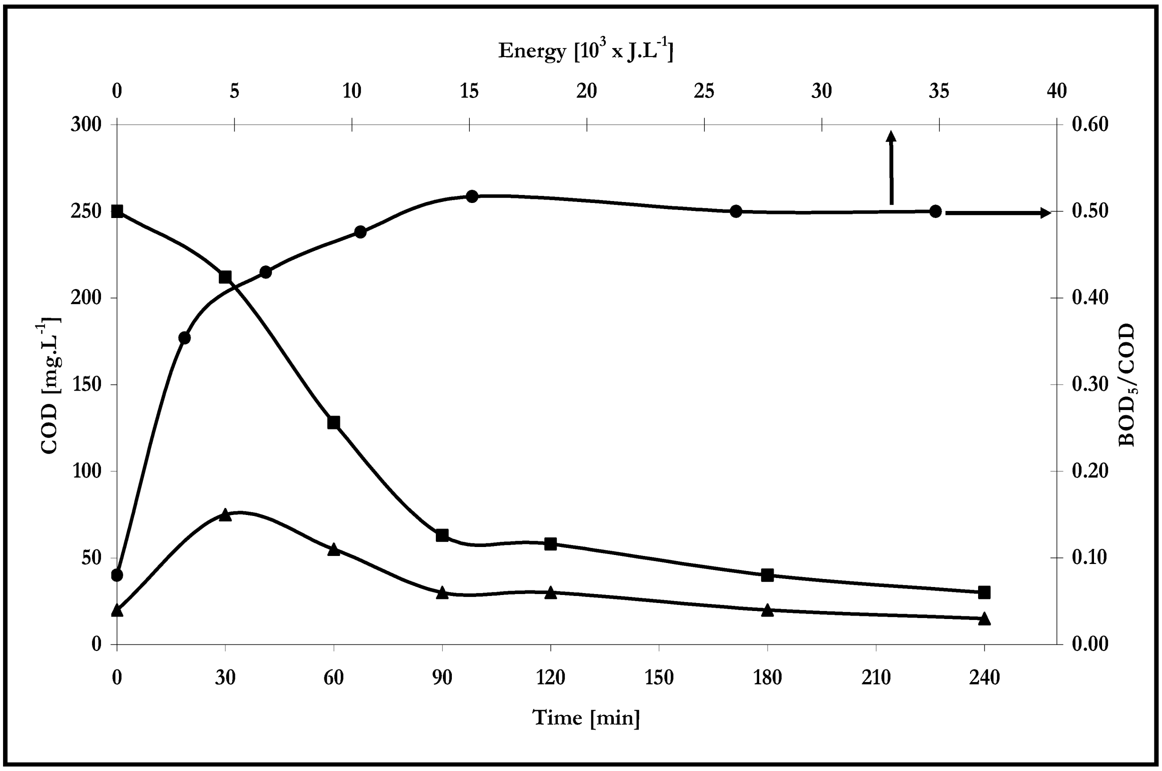


Figure 4. 11: *Evolution of the biochemical parameters of the Endosulfan polluted water during the helio-photo-Fenton treatment; (■) for the COD, (▲) for BOD_5 and (●) for the BOD_5/COD ratio.*

4.4 Conclusion

The difficulty and the complexity of treating real biorecalcitrant wastewaters were observed within the two studied cases. The increase of the biodegradability was observed after the photo-Fenton treatment of the effluent contaminated with Endosulfan, but not with the CHPYR effluent. Thus, we recommended a total mineralization in the latter case and rather an improvement of the biodegradability of the Endosulfan effluent.

The study on the pesticide effluent allow us to notice that the photolysis could lower by 30% the COD of the effluent compared to no COD decrease for a simply aeration.

In the two case studies, the helio-photo-Fenton process is effective proportionally to the amount of hydrogen peroxide added; but for economic reasons, a compromise was made between the highest kinetic of the treatment process of the Endosulfan effluent, and the overall objective (or strategy) of the treatment: namely the coupling photochemical and biological processes which is a cost minimization option in the treatment strategies of biorecalcitrant wastewaters.

Does the high DBO_5/DCO ratio in the case of the photodegradation of Endosulfan effluent necessarily be a good indicator to confirm the bio-treatability of the photo-treated effluent? Such a request could be looked out through very concise chemical analyses of the components of the effluents.

References

Blanco J. and Malato, S. R. (2003). Solar detoxification. Alméria, UNESCO/PSA.

Malato, S., J. Blanco, et al. (2000). "Optimization of pre-industrial solar photocatalytic mineralization of commercial pesticides: Application to pesticide container recycling." Applied Catalysis B: Environmental **25**(1): 31-38.

Ministère de l'Environnement et du Cadre de Vie, B. F. (2005). Rapport d'inventaires des pesticides POPs au Burkina Faso. Ouagadougou.

OECD (1996). guidelines for testing of chemicals, test 302 B.

Ollis, D. F. (1988). " Process economics for water purification: A comparative assessment." in Photocatalysis and environment: 663-677.

Population.Information.Program (1998). "Solutions for a water-short world." 1-31.

Pulgarin, C., M. Invernizzi, et al. (1999). "Strategy for the coupling of photochemical and biological flow reactors useful in mineralization of biorecalcitrant industrial pollutants." Catalysis Today **54**(2-3): 341-352.

Sarria, V. (2003). Coupled advanced oxidation and biological processes for wastewater treatment. Institute of Environmental science and Technology. Lausanne, EPFL: 150.

Sarria, V., Kenfack, Simeon., Guillod, Olivier. and Pulgarin, Cesar (2003). "An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants." J. of photoch. and photobiol. A: Chem. **159**: 89-99.

Sethunathan, N., Megharaj,M., Chen,Z., Singh,N., Kookana,R.S. and Naidu,R. (2002). "Persistence of Endosulfan and Endosulfan Sulfate in soil as affected by Moisture Regime and organic Matter addition." Environment contamination and Toxicology **68**: 725-731.

Toepfer, K. (2004). Statement on the occasion of the Stockholm Convention on Persistent Organic Pollutants Coming into Force., UNEP.

Waite, T. D. (2002). "Challenges and opportunities in the use of iron in water and wastewater treatment." reviews in Environmental Science and Biotechnology **1**: 9-15.

Zuo, Y., and Hoigné, J (1992). "Formation of Hydrogen Peroxide and Depletion of Oxalic Acid in Atmospheric Water by Photolysis of Iron (III)-Oxalato Complexes." Environ. sci. technol. **26**: 1014 -1022.

Chapter 5

Solar UVA data measurements and modelling

Chapter 4 described some helio-photocatalytic case studies applied for the depollution of industrial wastewaters. This chapter 5 presents the result of one year measurements of solar data monitored at the working station of Ouagadougou. A methodological approach for modelling solar UVA radiation and energy is given and tested on the solar data collected at the EIER, Ouagadougou. They could allow predicting the average solar UVA radiation rate for each month and the corresponding average solar UVA energy which is a determinant factor in the photocatalytic process.

5.1 Introduction

Solar irradiation is becoming increasingly appreciated because of its influence on living matter and the feasibility of its application for useful purposes. It is a perpetual source of natural energy that, along with other forms of renewable energy, has a great potential for a wide variety of applications because it is abundant and accessible. Solar radiation is gaining ground as a supplement to the non renewable sources of energy, which have a finite supply.

Recent developments in the areas of photochemistry and photobiology have also helped in bringing attention to solar radiation. Unfortunately, much more insufficiencies exist as well on the availability and the reliability of the data of solar radiations which arrive on the ground (Rivington 2005; Younes 2005).

Today, much of the solar radiation data are received from sensing instruments located far above the atmosphere. Satellite technology now contributes a significant proportion of the basic solar radiation information available worldwide; but it requires a considerable effort to make that information efficiently available for practical applications. At the 3rd international conference on measurement and modelling of solar radiation and daylight "challenges for the 21st century" held at Edinburgh in September 2003, it was clearly recognised that *"there are still enormous gaps in our knowledge concerning irradiative transfer through different types of clouds. Predictions of ground-level irradiance below clouds obtained using satellite observations have been hampered by lack of information about the transmission properties of the different cloud types involved"* (Page 2005). Since the solar data are much important for solar applications and, because of the existing constraints as stated below, the need to develop alternative ways of generating solar data is of great importance (Donatelli 2005; Janjai 2005; Muneer 2005). The availability of data from ground sites measurement, would be as much important as satellite technologies development, especially when these data are needed for specific applications such as the photochemistry in which mostly the UV part of the wide range of solar radiation is of great importance (Baxendale 1957; Hulstrom 1985; Curco 1996; Blanco and Malato 2001).

Historically, solar radiation studies were directed towards the issues of controlling the over-heating of buildings, in order to predict the thermal climate of buildings and adopt the concept of the design day (Kittler 1965). But after the world petrol crisis of the 1970s, much interest was focused on the need to develop alternative sources of energy. The solar energy research field became more attractive to scientists of other branches, and the development of new solar applications grew up: photovoltaic for electricity recovery, photochemistry, photobiology for medicine…etc. (Blanco and Malato 2001; Chow 2005; Häder and Rajeshwar 2005).

Since then, the need for taking measurements of solar irradiation and creating local and regional databases of irradiation and synoptic (meteorological) information has become crucial. However, depending on its application field, the nature and the quality of the solar data is different. For the thermal purpose, the infra red part of the sunlight would be more preferable while it would be obvious for other science (e.g. Photovoltaic); in the photochemistry, mostly the UV part of the solar radiation and more precisely its UVA part (Blanco 1999; Maldonado 2000; Blake 2001; Sarria 2003). The patterns of the availability of solar resource, in time, are important, as this dictates the design of energy storage systems or its applications. Accurate solar radiation data provides information on how much of the sun energy strikes a surface at a location on earth during a particular time period.

Obviously, in the African tropical areas which in contrast, is located in the most favourable solar belt of the world (latitude 35°S – 35° N) where up to 2500-3000 sunny hours could be registered per year (see **Fig. 5.1**), the very recent studies and measurements of solar data follows the history of colonies. In the early fifties, a few skilled scientists experienced in practical measurement in the African Belgium colonies and South Africa, with the aim of understanding the radiation climatology in humid tropical climates. One of the main achievements of these works was the impacts of dust pollution on dry-season radiation, which contrasted with the high atmospheric clarity of the wet seasons(Page 2005).

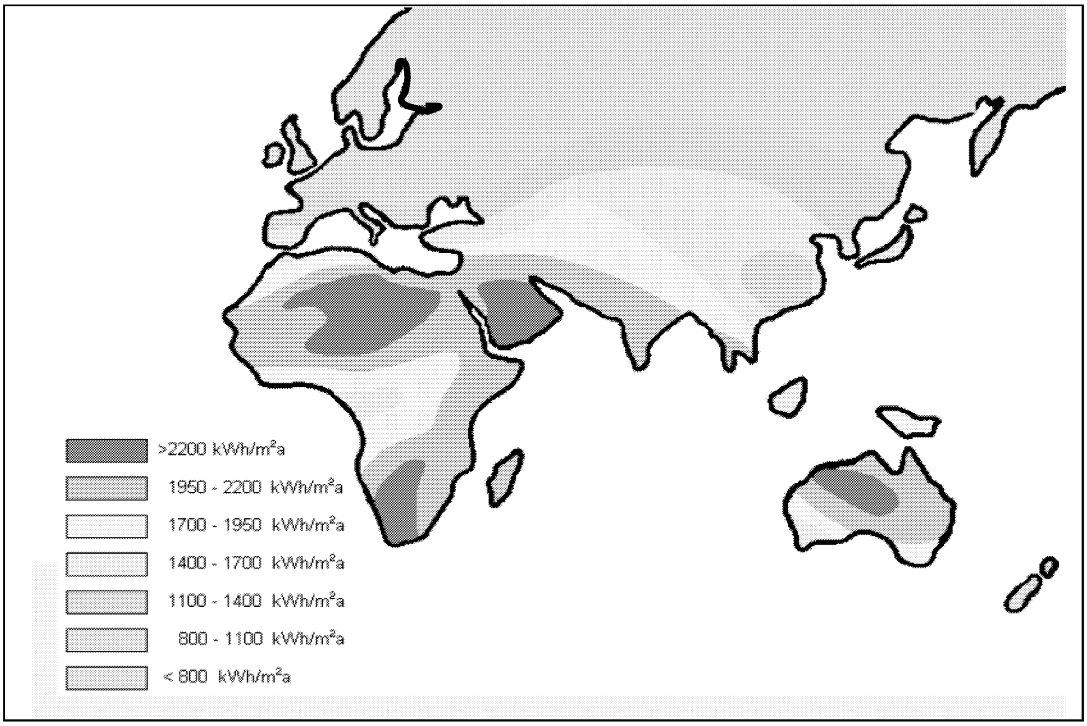


Figure 5. 1: *Global solar energy per capita (from the World Energy Council 27.11.01)*

Nowadays, even if there are gradually data from more sites, the lack of quality control meant that some of the data supplied by national meteorological offices (where they do exist) to the WMO[1], are unreliable.

This chapter 5 contributes to make available the solar UVA data for the city of Ouagadougou in Burkina Faso (12° N, 2.3° O) and proposes a simple approach for modelling ground solar data of a specific site. The following tasks were carried out:

(i) Acquisition and analysis of the daily solar UVA data recorded in term of the instantaneous radiation ($W.m^{-2}$) and the accumulated UVA energy per square

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[1] World Meteorological Office

meter (in 10^3 x $J.m^{-2}$) during the monitoring period (08:00 -16:00) for a year (January – December 2004).

(ii) Development of three simple models for (a) modelling the daily average hourly solar instantaneous radiation for each month of the year basing it on the statistical data collected, and (b) modelling the monthly average daily accumulated energy per meter square in a year basing it on the statistical database of solar energy registered and (c) proposing an adjustment model for evaluating the solar energy accumulated in a day, basing it on the solar radiation database where ever it is available.

(iii) Simulation of the dimensioning of a photo-reactor for the destruction of the obsolete pesticides stocks mainly made of endosulfan.

5.2 Materials and procedures

The solar ultraviolet data were determined through a UV-A radiometer ACADUS 85 UV (**Fig. 5.2**) mounted on the photo-reactor presented in **Fig.2.2**, at the same angle (10°) as its flat plate's part. The UVA radiometer ACADUS 85 has an analogical output range of 0-4.3 V DC, where each volt indicates 20.4 W/m^2, so its UV-A span is 87.7 W/m^2. This analogical signal is converted by means of an external device to another one with a span of 0-10 mA for a 0-5V DC input.

The PLC has an analogue expansion module for 0-20 mA inputs and digital output of 32.000 points. So the ratio among all electronic device spans is the Radiometer constant:

Radiometer constant= 20.4 $W.m^{-2}.V$ x 5V x 20mA /10 mA x 32000 pts=0.006375 $W.m^{-2}$. pts.

This constant is programmed into the PLC. For re-calibrating the radiometer gain or, if it is changed, a new constant must be introduced into the PLC.

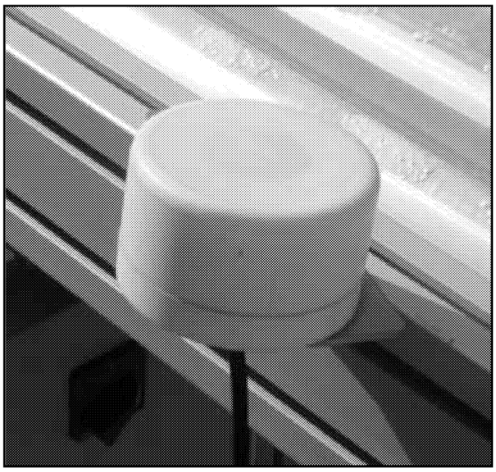

Figure 5. 2: *A view of the radiometer used for the solar UVA data measurement*

When operating, the radiometer provides solar data in the spectrum range of 300–400 nm (with a peak at 360 nm) in terms of incident UVA radiation per area unit ($W.m^{-2}$) and the accumulated UV energy (Wh) over the 2.12 m^2 of the active surface of the photo-reactor. Each 4 seconds, the PLC indicates the value of the UVA radiation which is automatically integrated at each 1/10 of a second and also, the output value of the accumulated energy is indicated 4 seconds following that of the solar radiation. From the PLC monitor, data were manually registered at 10 minutes intervals, then computed and stored in the Microsoft excel files. In this thesis, all the solar energy data are given in international unit system (J) by multiplying the output energy value in (Wh) by a factor of 3.6. The accuracy of the measurement is ± 2% for the daily total for both data.

The solar data measurements which are considered in this chapter were collected from April 2004 to May 2005 (one year). The data were registered three days a week for the whole period. The database has undergone an extensive analysis to give statistical evidence to the correctness of the calculated monthly average of the daily values. This was done by determining the coefficient of autocorrelation function and then using these values to determine the standard errors of both the monthly average of the daily values and the monthly average daily standard deviations.

For both solar radiation and energy values, it was determined that the standard errors are less than the inherent measurement. Consequently, the monthly average of the daily and hourly radiation intensities are representatives of the site.

The database for each type of data were then narrowed to include only those days for which the value of the radiation at the mid day and that of the energy at 04.00 pm do not exceed the average value of the month, ± a standard deviation of 3 $W.m^{-2}$ and 50 x 10^3 $J.m^{-2}$ respectively for the solar radiation and the solar energy. Consequently, the number of days for each month varies from one type of radiation to another.

5.3 Results and discussions

5.3.1 Analysis of the solar UVA data of Ouagadougou (Burkina Faso)

The result of the analysis of the 12 months database of the solar UVA at Ouagadougou from April 2004 to May 2005 is reported as monthly average for both daily radiation at midday and energy accumulated from 08.00 am to 04.00 pm. For each values, the coefficient of variation (Cv), reported as the ratio of the standard deviation to the mean value which gives an indication of the dispersion of the values is also shown in **Table 5.1**. The number of days within each monthly database is reported in the first column 1 of the table and a total of 80 days (≈ 22% of a year) have been considered in the database. A similar methodologies were recently adopted by Maldonado, Sarria, De Souza and Kudish et al in order to characterise the solar insolation respectively at the Plata forma solar de Almería-Spain, at the EPFL in Lausanne-Switzerland, at Maceió (Brazil) and in two meteorological sites at Beer Sheva and Neve Zohar in Israel (Maldonado 2000; Sarria 2003; De Souza 2005; Kudish 2005). From the plots of both values of the solar UVA characteristics present in the **Fig.5.3,** it was noticed that the accumulated energy is proportional to the radiation; in addition, it was observed that basing on this sunning database, the year can coarsely be divided into three seasons at Ouagadougou:

- ✓ The period (December-February) during which the average of radiation UVA at midday is below 30 W.m $^{-2}$ and the average energy accumulated in 08 hours (08.00-16.00) is lower than 600 x 10^3 J.m $^{-2}$. This corresponds to the Harmattan cold season in Ouagadougou.
- ✓ The period (March – May) during which the average of the midday radiations is 32 W.m $^{-2}$ and the UVA energy is in the range of 600 x 10^3 J.m $^{-2}$ but lower than 700 x 10^3 J.m^{-2}. This corresponds to the hot period of the year which proceeds the raining season.
- ✓ The period (June – November): This includes the raining and just after the raining season. At this period, the sky is very often clear and well blue; as a consequence of this, radiations at midday are at their higher values over 38 W.m $^{-2}$ and the accumulated energy is over 700 x 10^3 J.m $^{-2}$ with a peak at 816 x 10^3 J.m^{-2} in September.

Thus, from the solar database collected over a year, one can easily reconstitute the seasonal behaviour of the climate in Ouagadougou. In fact, the period from December to February corresponds to the Harmattan, a cold and dry wind which annually sweeps the West Africa sahelian zone and raises much dust which pollutes the air and then blocks the passage of the solar rays (Cissé 1997; Visser 2004).

Table 5. 1: *Monthly average daily solar UV-A radiation and the monthly average daily Solar UV-A energy accumulated from 08.00 am to 04.00 pm*

Month	Days	UVA radiation at midday (W.m^{-2})	Cv (%)	UVA energy (10^3 J.m^{-2})	Cv (%)
January (11)	6	28	3.6	552	4.5
February (11)	6	28	3.6	563	5.2
March (11)	6	34	5.9	638	7.2
April (14)	8	33	6.1	629	6.8
May (8)	8	32	9.4	601	6.7
June (7)	6	38	2.6	714	3.8
July (6)	6	39	5.1	746	4.4
August (16)	8	41	4.9	750	5.4
September (12)	7	41	2.4	816	3.3
October (11)	6	38	5.3	737	4.3
November (12)	6	39	2.6	740	3.9
December (11)	7	25	4.0	464	2.6
(130) - 35%	80 - 22%	-	Average:	-	Average:

(-): Number of days monitored; the percentage is calculated for a year (365 days).
The standard deviation of 3 W.m^{-2} for UVA radiation and 10 kJ for UVA energy were agreed.

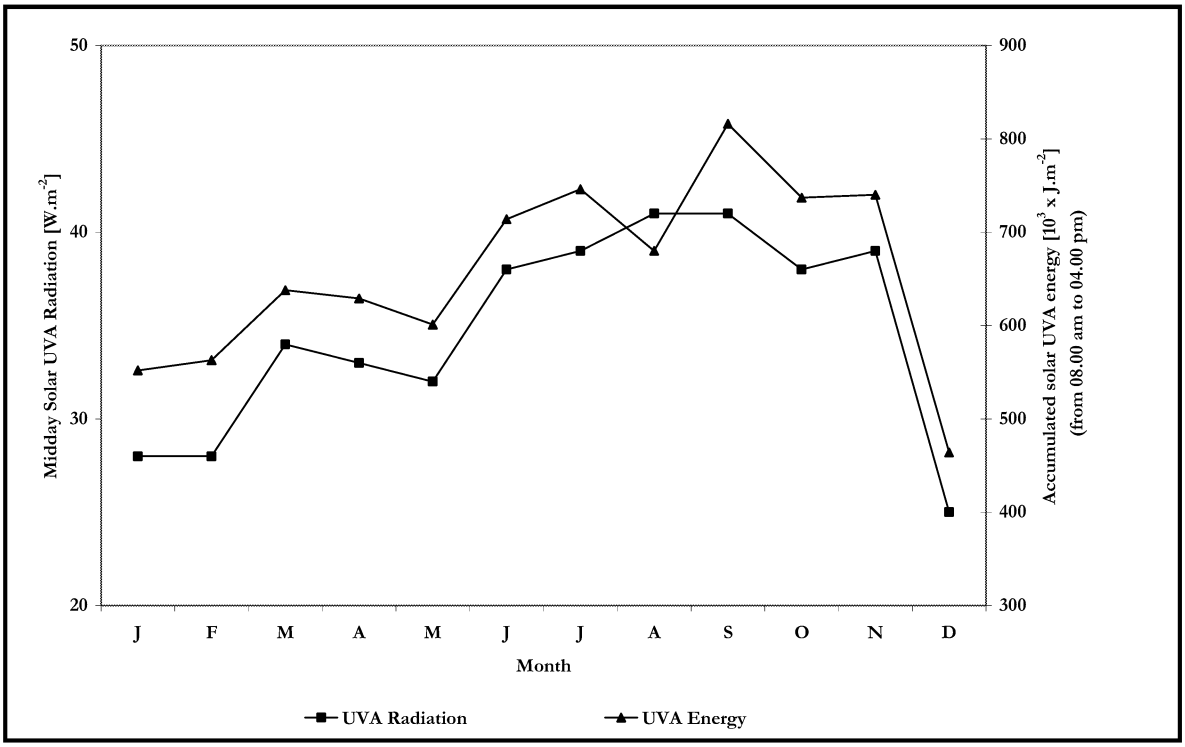

Figure 5. 3: *Monthly average daily UVA radiation at midday and UVA energy (08.00 am to 04.00 pm)*

5.3.2 Statistical models of evaluating the solar UVA radiation and UVA energy

In addition to the evaluation of the monthly average daily radiation and energy, the daily average of both the hourly solar radiation and energy accumulated from 08.00 am to 04.00 pm for each month of the whole measurement's period are plotted in **Fig. 5.4**. To each of the monthly curve of the daily solar UVA radiation in the **Fig.5.4,** it has been associated a tendency curve of order 2 with a general equation in the form of:

$$Rad(t) = at^2 + bt + c \qquad \textbf{(Eq.5. 1)}$$

Also, the monthly curves of the daily solar UVA energy (see the second y axis) have been approximated to the tendency curves of order 3, with the general equation in the form of:

$$E(t) = At^3 + Bt^2 + Ct + D \qquad \textbf{(Eq.5. 2)}$$

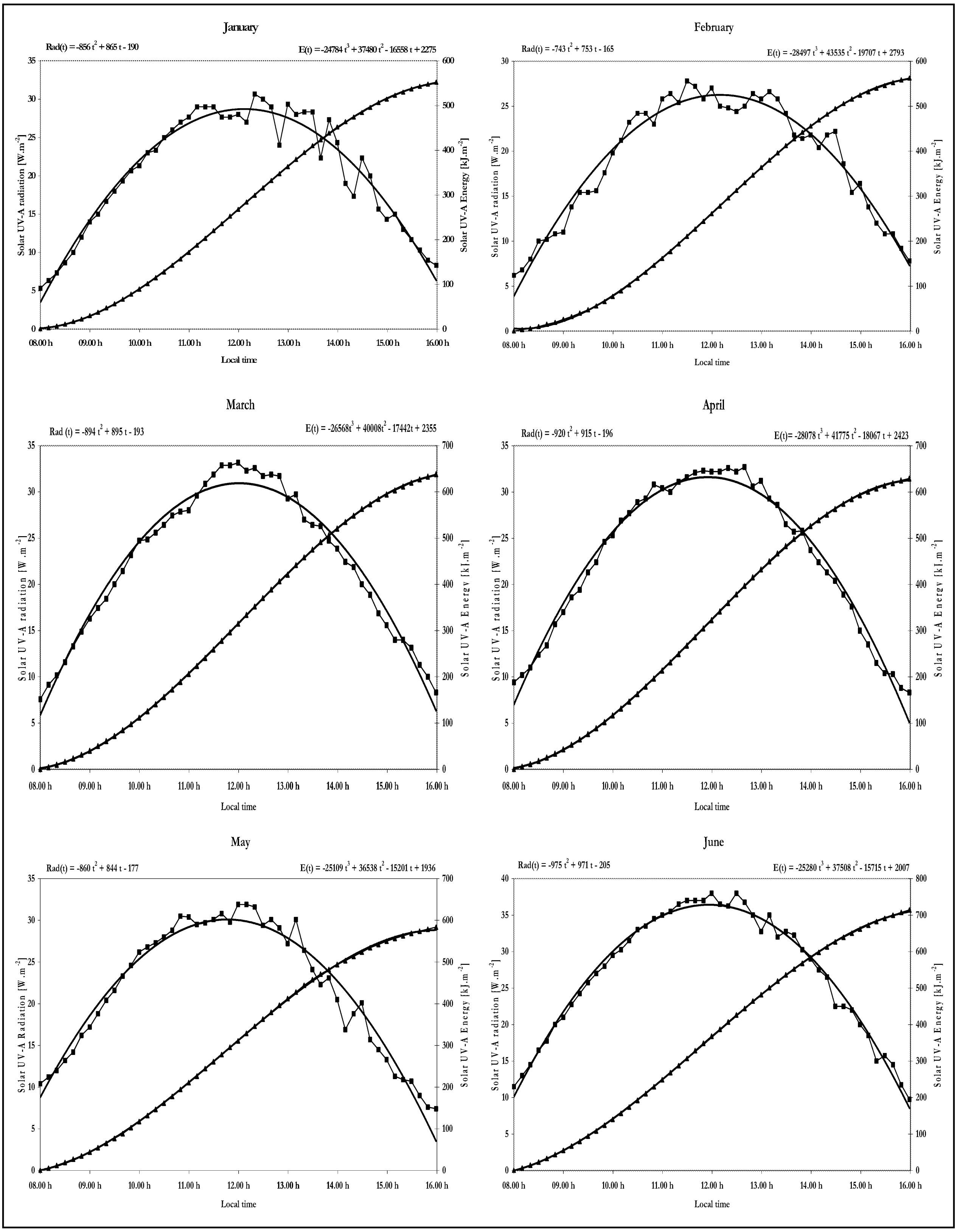

Figure 5. 4: *Monthly average daily UVA radiation and UVA energy at Ouagadougou – Burkina Faso*

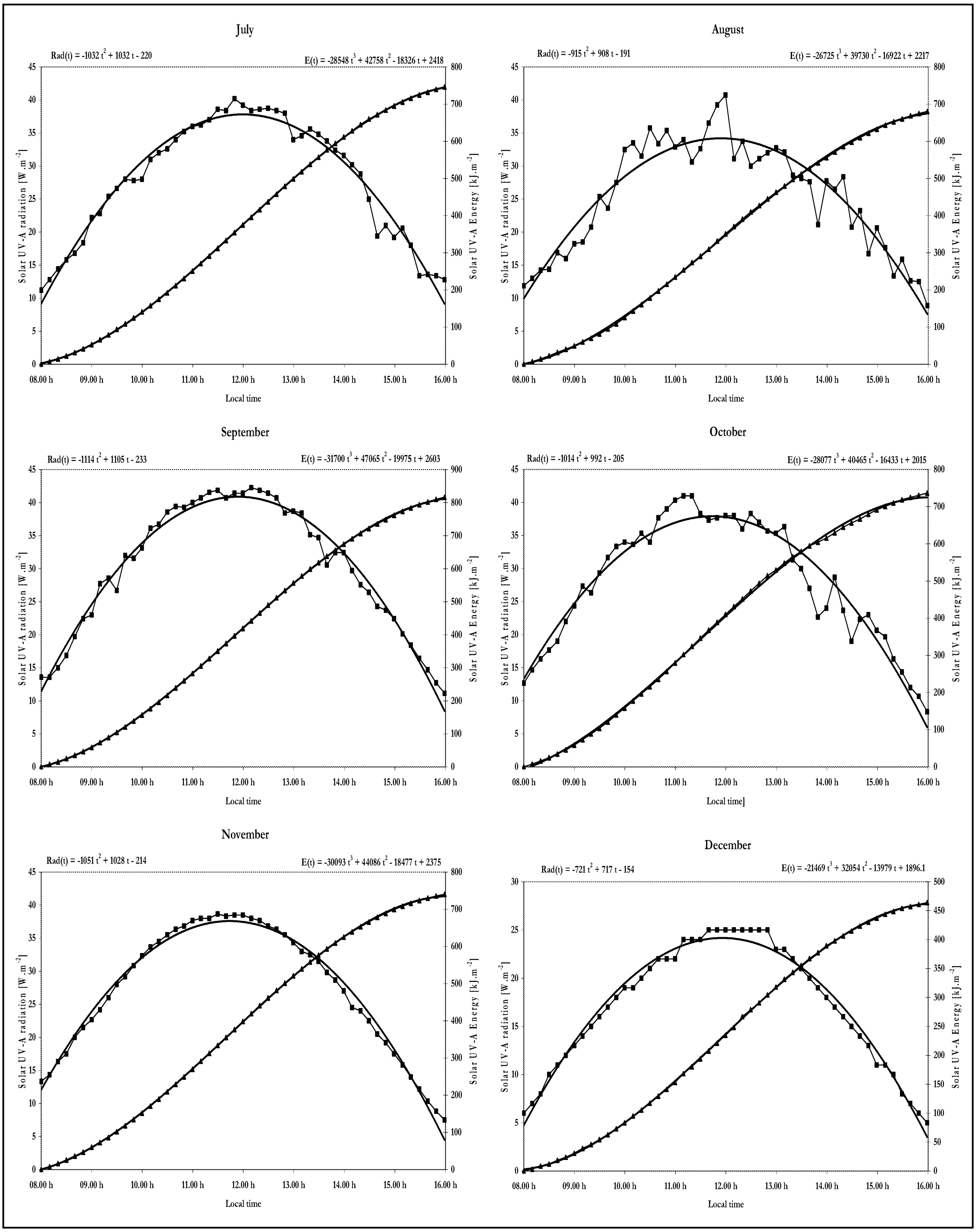

Figure 5. 4(next): *Monthly average daily UVA radiation and energy at Ouagadougou – Burkina Faso*

The values of the coefficients (a, b and c) in the one hand and (A, B, C and D) in the other hand, of the (**Eqs.5.1 and 5.2**) have been reported in the **Table 5.2** for the 12 months covering the one year measurement's period.

Table 5. 2: *List of coefficients of the equations of the monthly average daily solar UVA radiation and energy accumulated from 08.00 am to 04.00 pm at Ouagadougou*

Month	Coefficient of the solar UVA radiation second order equations			Coefficient of the solar UVA energy third order equations			
	a	b	c	A	B	C	D
January	-856	865	-190	-24784	37480	-16558	2275
February	-743	753	-165	-28497	43535	-19707	2793
March	-894	895	-193	-26568	40008	-17442	2355
April	-920	915	-196	-28078	41775	-18067	2423
May	-860	844	-177	-25109	36538	-15201	1936
June	-975	971	-205	-25280	37508	-15715	2007
July	-1032	1032	-220	-28548	42758	-18326	2418
August	-915	908	-191	-26725	39730	-16922	2217
September	-1114	1105	-233	-31700	47065	-19975	2603
October	-1014	992	-205	-28077	40465	-16433	2015
November	-1051	1028	-214	-30093	44086	-18477	2375
December	-721	717	-154	-21469	32054	-13979	1896

From the database of **Table 5.2**, it is possible to calculate the monthly average of the daily solar UVA radiation and energy for Ouagadougou at any month using the **Eqs. 5.1 and 5.2**. The exploitation of such equations would not only facilitate the dimensioning of the solar photo-reactors in the field of the solar photocatalysis but also, they could be useful to other fields of science. The influence of the irradiative energy in agriculture (photosynthesis, evapotranspiration, agricultural pests) and in medicine spreading of diseases, occurrence of skin cancers…etc. have been widely reported; moreover, studies on solar radiation have become an important issue for renewable energy and in the validation of general circulation models (Duchon and O'Malley 1999; Hansen 1999; Mariscal 2000). The equations 5.1 and 5.2 are easily applicable using the coefficients of the **Table 5.2**, the database of the time **(t)** values which are given in the graphs in (hh.min) should be converted into a scalar scale "without dimension" database. The current conversion factor has been graphically determined as follows:

1°- The origin of the time is midnight of the local time (00.00, LT)

2°- 1 min corresponds to t = 0.0006944

In this logical framework, the units of the coefficients (a, b, c, A, B, C and D) in the **Eqs 5.2 and 5.3**, the same as that of the time should be converted into the International Units System (IUS); then the calculated solar radiation or energy will be respectively in W.m^{-2} and 10^3 J.m^{-2}. However, the only one year of data measurement is not sufficient to definitely fix the monthly coefficients of the various equations of the solar radiation and energy. It would be interesting to use data for 5-10 years to standardize these values for more reliability in the calculations. The whole values of (t), for the period of the day ranging between 08.00 and 16.00 are given by the table below.

Table 5. 3: *Abacus of conversion of the time values (from 08.00 am to 04.00 pm) into scalar values in the reference frame used in this thesis*

Hour	t	Hour	t	Hour	t
08.00 h	0.33333	10.50 h	0.45131	13.30 h	0.56235
08.10 h	0.34027	11.00 h	0.45825	13.40 h	0.56929
08.20 h	0.34721	11.10 h	0.46519	13.50 h	0.57623
08.30 h	0.35415	11.20 h	0.47213	14.00 h	0.58317
08.40 h	0.36109	11.30 h	0.47907	14.10 h	0.59011
08.50 h	0.36803	11.40 h	0.48601	14.20 h	0.59705
09.00 h	0.37497	11.50 h	0.49295	14.30 h	0.60399
09.10 h	0.38191	12.00 h	0.49989	14.40 h	0.61093
09.20 h	0.38885	12.10 h	0.50683	14.50 h	0.61787
09.30 h	0.39579	12.20 h	0.51377	15.00 h	0.62481
09.40 h	0.40273	12.30 h	0.52071	15.10 h	0.63175
09.50 h	0.40967	12.40 h	0.52765	15.20 h	0.63869
10.00 h	0.41661	12.50 h	0.53459	15.30 h	0.64563
10.10 h	0.42355	13.00 h	0.54153	15.40 h	0.65257
10.20 h	0.43049	13.10 h	0.54847	15.50 h	0.65951
10.30 h	0.43743	13.20 h	0.55541	16.00 h	0.66645
10.40 h	0.44437				

5.3.3 A simplify adjustment modelling approach for evaluating the solar UVA energy in a specific site: the applied case on the solar data of Ouagadougou (Burkina Faso)

At the first conference on measurement and modelling of solar radiation and daylight held at Edinburgh on 15-16 September 2003, the low reliability of the solar radiations data currently register at numbers of the meteorological stations disseminated all over the world was recognized and, the need to "*combine ground-based information with satellite information*" was recommended (Page 2005). It was noted in the paragraph **5.3.2** that the characteristic equation of daily average of the UVA radiation is of a quadratic form. When integrating it as a function of the time within very shot intervals of time dt, one could evaluate by calculations, the accumulated energy rising from this radiation according to the first principle of thermodynamics:

$$\mathbf{E\ (t)\ = \int Rad(t).\ dt} \qquad \textbf{(Eq.5. 3)}$$

Therefore, in a given locality for which the solar radiation data are available, similar plots as presented in **Fig. 5.4** would make it possible to obtain the a, b and c coefficients of the monthly average daily radiation and, it could be feasible to predict by calculations, the available energy that could be obtained every month at that locality.

In order to test this option, a calculation test has been made using the solar data collected at Ouagadougou and, a comparison was made between the statistical results and the other obtained by calculation.

A simulation of the adjustment model for evaluation of the solar UVA energy basing on the solar UVA radiation (monthly average daily) is made below and applied on the case of Ouagadougou for January, April and August.

From **Eq.5.3**:

$$E(t) = \int Rad(t)dt$$

$$E_{UVA}(t) = \int_{t_0}^{t}(at^2 + bt + c)dt$$ **(Eq.5. 4**

$$E(t) = \frac{a}{3}t^3 + \frac{b}{2}t^2 + ct + d$$ **(Eq.5. 5)**

Supposing that $\frac{a}{3} \longrightarrow A'; \frac{b}{2} \longrightarrow B'; c \longrightarrow C' \, and \quad d \longrightarrow D'$ **(Eq.5. 6)**

This leads to the following equation:

$$E(t) = A't^3 + B't^2 + C't + D'$$ **(Eq.5. 7)**

The value of D' should be determined for the time t=0 (i.e. at the beginning of the monitoring period, when E =0; for this study, this corresponds to t= 08h00, i.e: 0.33333 as delivered by the **table 5.2** below).

We noted that **Eq. 5.7** was of the same polynomial order and form as the characteristic of **Eq 5.2** for the monthly average daily UVA energy obtained by the plots in **Fig. 5.4**. The equality of the two equations (**Eqs. 5.2 and 5.7**) implies that the following conditions should be satisfied:

$$A = A'; \quad B = B'; \quad C = C'; \quad D = D'$$ **(Eq.5. 8)**

Let's take the case of January with Rad (t): -865 t^2 + 865 t – 190

$$E(t) = \int Rad(t)dt = \ E(t) = \int(-865t^2 + 865t - 190)dt = A't^3 + B't^2 + C't + D'$$

From the **Eq.5.6**, $A' = \frac{a}{3} = -\frac{865}{3} = -288$ and by the same procedure, B'=433, C’=-190 and, when calculating E (t) = 0 for t= 0.33333, D'= 26. Thus,

$E(t) = -288t^3 + 433t^2 - 190t + 26$ in (W.min. m^{-2}) **(Eq.5. 9)**

In order to obtain the results in 10^3 J.m^{-2}, the informal unit of **Eq. 5.9** was converted by multiplying all the coefficients by 86.4= 24 * 3.6 (i.e: a day period is 24 hours and 3.6 is the conversion coefficient from Wh to 10^3 J).

Finally for January, the characteristic equations obtained by the two models (statistical and adjustment) in order to evaluate the UVA energy, are given below:

1) $E(t)_{Stat.} = -24784t^3 + 37480t^2 - 16558t + 2275$ **(Eq.5. 10)**

2) $E(t)_{Cal.} = -24912t^3 + 37411t^2 - 16416t + 2246$ **(Eq.5. 11)**

Both the **Eqs.5.10 and 5.11** are of 3rd order polynomial form and, when replacing t in both equations by its value at any interval of time e.g. from 08.00 am to 04.00 pm (i.e. for one day), the value of t given by the **Table 5.2** is 0.66645 and, the accumulated energy (10^3 J.m^{-2}) on a photo-reactor whose area is 1 m^{-2} for example can be calculated as follow:

$E(day)_{Stat.} = -24784 * 0.66645^3 + 37480 * 0.66645^2 - 16558 * 0.66645 + 2275 =$

551 x 10^3 J.m^{-2} **(Eq.5. 12)**

$E(day)_{Cal.} = -24912 * 0.66645^3 + 37411 * 0.66645^2 - 16416 * 0.66645 + 2246 =$

525 x 10^3 J.m^{-2} **(Eq.5. 13)**

The same calculations were done for all the months and the results, including their respective coefficient of variation (Cv) are shown in the **Table 5.3** below. 100% of them are less than 10%, with an average of 4.9%. This attests that the UVA energy values calculated by this adjustment model deducted from the proposed UVA radiation's statistical model are rather accurate. However, more solar data would be needed to implement the various coefficients (a, b, c, A, B, C and D) of the given models and thus, one could expect to get more reliable solar data of a specific site by this way.

Table 5. 4: *Comparison to the "really" monthly average daily measured values of the UVA data to those from the statistical and the adjustment models*

Month	"Real value"	statistical model		adjustment model	
	E	E (10^3 J.m^{-2})	Cv [%]	E (10^3 J.m^{-2})	Cv [%]
January	552	551	0.1	525	3.5
February	563	560	0.4	543	2.6
March	638	636	0.2	654	1.8
April	629	626	0.3	662	3.6
May	601	601	0.0	635	3.9
June	714	710	0.4	798	7.9
July	746	745	0.1	819	6.6
August	680	675	0.5	742	6.2
September	816	811	0.4	884	5.7
October	737	725	1.2	809	6.6
November	740	734	0.6	792	4.8
December	462	462	0.3	506	6.1
	-	-	Average.0.4	-	Average.4.9

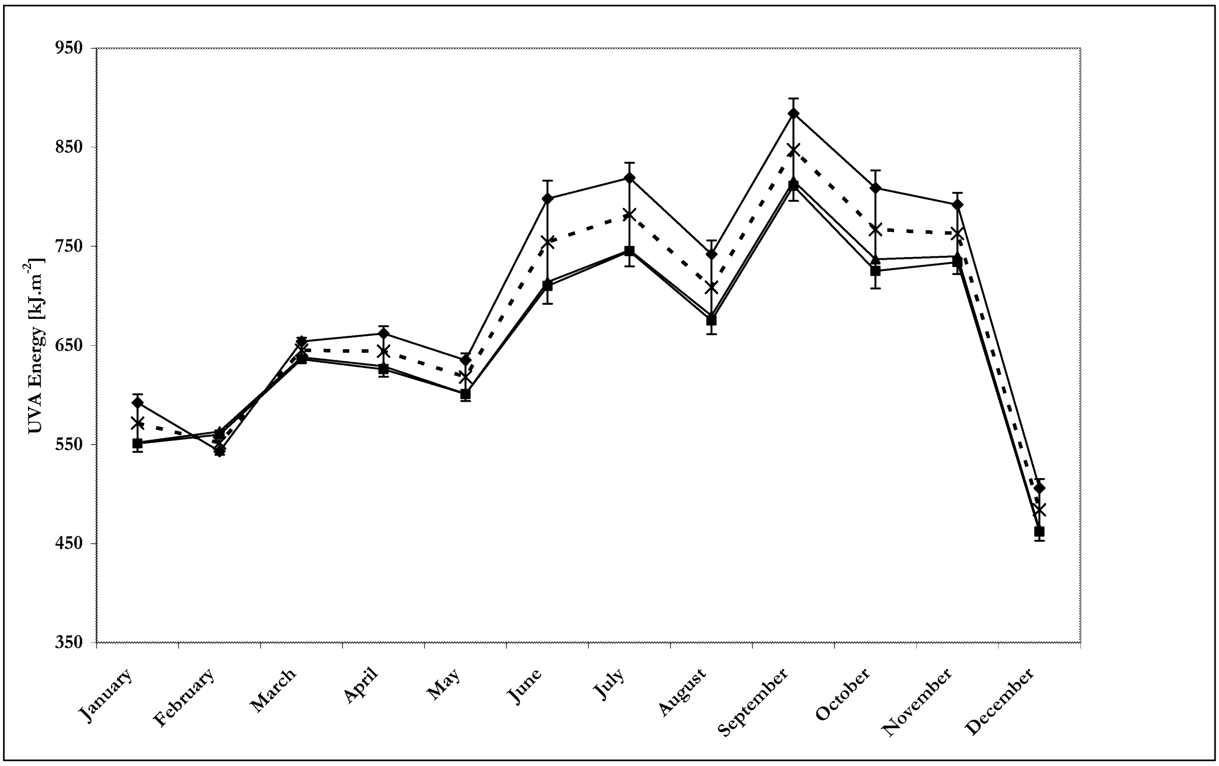

Figure 5. 5: *Monthly average daily UVA energy values recorded by various ways: (■) "real" measured values; (▲) statistical model; (♦) Adjustment model; (×) average values between the "real" values and the calculated values through the adjustment model.*

5.3.4 Cost estimation of the helio-photo-Fenton treatment of a stock of Endosulfan in Ouagadougou- Burkina Faso

In order to evaluate the cost of a practical application of the helio-photo-Fenton process for the treatment of 4 m^3 of obsolete Endosulfan stock disposal in Burkina Faso (**Table 4.1**) within the optimal condition observed in the **Fig. 4.11** and the sunny conditions observed in this chapter 5, we made the following considerations:

- ✓ The full-scale treatment plant is assumed to be a 300 m^2 CPC photo- reactor,
- ✓ The treatment objective is to enhance the biodegradability of the effluent by 50% as studied in the paragraph 4.3.2.3,
- ✓ The daily average UVA energy is 600 x 10^3 $J.m^{-2}$ within the treatment period (08:00 am to 04:00 pm)
- ✓ The treatment is conducted in batch. A batch of solution is reused for a month so to conserve the catalyst and acid used.

Taking into account these consideration and by analogy to (Vidal 1999; Sarria 2003), the treatment cost of the actual obsolete stock of Endosulfan in Burkina Faso (4 m^3) is estimated and presented in the **Table 5.5**.

We observe that the treatment of the hold stock of obsolete Endosulfan pesticide disposal in Burkina Faso could be carried out in three years of 300 working days per year, using a 300 m^2 CPC photo-reactor and when processing under the optimal condition studied in the **section 4.3.2.3**.

The total cost was calculated assuming banking fees of 2% over the treatment duration. The land cost was not considered since it is not significant in Burkina Faso; for such an environmental need, the government would offer the land as much as necessary.

After these helio-photo-Fenton treatments which allow enhancing by 50%, the biodegradability of the Endosulfan wastewater, the effluent can be sent toward a biological treatment. The treatment cost of 15 $US\$.m^{-3}$ when considering a wastewater containing 135 g.L^{-1} of Endosulfan (such as schematized in **Fig. 4.1**) is relatively very low when compared to the average cost of 200 US$.m^{-3} for the treatment of such effluents by alternative processes like incineration or wet oxidation in Switzerland (Sarria 2003).

Table 5. 5: *Cost estimation of the helio-photo-Fenton treatment of 4 m^3 of Endosulfan in Ouagadougou*

	INPUT DATA	
1	Volume of pure Endosulfan at 350 g.L^{-1} (L)	4'000
2	Total volume of diluted (at 135 mg.L^{-1}) Endosulfan = wastewater (m^3)	10'400
3	Average daily accumulated UVA on the 300 m^2 CPC photo-reactor in 8 hours : from 08:00 am to 04:00 pm (x 1000 J)	180
4	Specific Energy for 75% abatement of COD and 50% enhancement of the biodegradability of the diluted solution of Endosulfan (x 1000 J.L^{-1})	15
5	Daily treatment capacity (m^3.day^{-1})	12
6	Treatment duration (day)- years (assuming 300 days per year)	900 (3 years)
7	Number of batch of treatment	30
8	Quantity of water needed for dilutions (m^3)	720
9	$FeSO_4$ (kg)	18
10	H_2O_2 (L)	4500
11	HCl (L)	38
	COSTS ESTIMATION in US$	
12	**Equipment costs (EC)**	
13	Collectors of the Photo-reactor (200 m^2) at 200 US$.m^{-2}	40'000
14	Pipes and tanks (10% of the collectors cost)	4'000
15	Others (20% of the collectors cost)	8'000
16	Total EC (TEC)	52'000
	Indirect Costs (IC)	
17	Spare parts (2% TEC)	1'040
18	Contingencies (10% TEC)	5'200
19	Total Indirect Costs (TIC)	6'240
	Total Capital TC= (TEC+TIC)	**58'240**
	Functioning cost (FC)	
20	$FeSO_4$ (kg) 50 US$.L-1	900
21	H_2O_2 (L) 20 US$.L-1	90'000
22	HCl (L) 50 US$.L-1	1'875
23	Water for dilution (0.6 US$.m^{-3})	432
24	Operation and maintenance (5% TC)	2'912
25	Banking fees (2% of TC)	1'648
	Total functioning costs (TFC)	**97'767**
	Total treatment cost	**156'007**
Treatment cost of the pure commercial obsolete Endosulfan (US$.m^{-3})		**39**
Treatment cost of the assuming wastewater containing 135 mg.L^{-1} of Endosulfan (US$.m^{-3})		**15**

5.5 Conclusion

The characterisation of the solar radiation at Ouagadougou has been done and allows noticing that the period from December to February is the less sunny with an average of more or less 25 $W.m^{-2}$ of UVA radiation at midday. In contrary to what one could imagine, August which is heaviest raining month in Ouagadougou, is not the least sunny month; this is due to the clearness of the sky which is deprived of dusts by rains, and on the few sunny days, the irradiance flux is important (c.a 40 $W.m^{-2}$). As one would expect, the energy is proportional to the solar radiation in all the cases; hence, except in August, the months with the highest midday solar radiation are also the one with the highest energy per day values. In Ouagadougou, this corresponds to the period from June to November.

In order to estimate the solar UVA radiation and energy in a specific site, three novel models has been proposed in this study and, their validation has been made basing it on the solar data collected at Ouagadougou for one year:

a) The solar UVA radiation statistical model upon which: $Rad_{UVA}(t) = a*t^2 + b*t + c$ where $Rad_{UVA}(t)$ is the radiation at time t in the given site, a, b and c are scalar number depending on the locality and the month.

b) The solar UVA energy statistical model in which $E_{UVA}(t) = A*t^3 + B*t^2 + C*t + D$ where $E_{UVA}(t)$ is the accumulated UVA energy per meter square from an initial time (t_0) to a final time (t). The coefficients A, B, C and D have been statistically determined by the day's energy (from 08.00 am to 04.00 pm) at Ouagadougou, for all the months in a year.

c) A adjustment model linking the solar UVA radiation statistical and the solar UVA energy has finally been proposed and, according to this: $E_{UVA}(t) = \int Rad_{UVA}(t)\, dt$.

The calculation of the UVA energy delivered by the sun in a specific locality on the earth can be made when its solar database is available. In the case of Ouagadougou, it was observed that the accuracy of this adjustment solar UVA energy model could be admitted with a 5% coefficient of variation on monthly average daily. Although the database of the solar radiation was only made of 22% of days over one year of data requirement, the robustness of these models could be improved by using solar data for five to ten more years. However, the data obtained using these approaches could be compared and validated with those supplied by the meteorological stations where they do exist. Thus, the modelling approaches proposed in this study would be of a great importance when dimensioning photo-reactors for helio-photocatalytic applications in a specific site; also, these fast and easier ways for estimating solar data would benefit to scientific applications which are dependant to sunlight.

The feasibility study to carry out the helio-photo-Fenton process in a large scale CPC plant (300 m^2) in Burkina Faso showed that the degradation of 4 m^3 of a commercial obsolete stock of Endosulfan (350 $g.L^{-1}$) can be made in 3 years with an average cost of 39 $US\$.L^{-1}$.

References

Baxendale, J. H., and Wilson, A. J. (1957). "The photolysis of hydrogen peroxide at high light intensities." Transactions of the Faraday Society **53**: 344-356.

Blake, M. D. (2001). Bibliography of work on the heterogeneous photocatalytic removal of hazardous compounds from water and air.

Blanco, J. and S. R. Malato (2001). Solar irradiation. Solar Detoxification. Unesco**:** 1-13.

Blanco, J., Malato, S., Fernandez, P., Vidal, A., Morales, A., Trincado, P., Oliveira, J. C., Minero, C., Musci, M. and Casalle, C. (1999). "Compound parabolic concentrator technology development to commercial solar detoxification applications." Solar Energy **67**(4-6): 317-330.

Chow, T. T., Chan, A.L.S., Fong, K.F. and Lin, Z. (2005). "Hong Kong solar radiation on building facades evaluated by numerical models." Applied Thermal Engineering **25**(13): 1908-1921.

Cissé, G., . (1997). Impacts sanitaires de la réutilisation des eaux usées en agriculture dans le contexte sahélien: Cas du maraîchage à Ouagadougou,. Génie Rural, EPFL, Lausanne, Switzerland.

Curco, D., Malato, S., Blanco, J. and Gimenez, J. (1996). "Photocatalysis and radiation absorption in a solar plant." Solar Energy Materials and Solar Cells **44**(2): 199-217.

De Souza, J. L., Rosilene Mendonça Nicacio. and Marcos Antonio Lima Moura (2005). "Global solar radiation measurements in Maceio, Brazil." Renewable Energy **30**: 1203-1220.

Donatelli, M., Carlini, L. and Bellocchi, G. (2005). "A software component for estimating solar radiation." Environmental Modelling & Software **In Press, Corrected Proof**.

Duchon, C. and M. O'Malley (1999). "Estimating cloud type from pyranometer observations." J Appl Meteorol **38**(1): 32–41.

Häder, D.-P. and P. S. Rajeshwar (2005). "Solar ultraviolet radiation-incluced DNA damage in aquatic organisms:potential environmental impact." Fundamental and Molecular Mechanisms of Mutagenesis. **571**: 221-233.

Hansen, J. (1999). "Stocastic daily solar irradiance of biological modeling aplicatotions." Agric Forest Meteorol **94**: 53–63.

Hulstrom, R., Bird, R. and Riordan, C. (1985). "Spectral solar irradiance data sets for selected terrestrial conditions." Solar Cells **15**(4): 365-391.

Janjai, S., Laksanaboonsong,J., Nunez,M. and Thongsathitya,A. (2005). "Development of a method for generating operational solar radiation maps from satellite data for a tropical environment." Solar Energy **78**: 739-751.

Kittler, R. (1965). Standardization of outdoor conditions of calculation of the daylight factor with clear skies. Conference on sunlight in buildings, Newcastle.

Kudish, A. I., Lyubansky,V., Evseev,E.G. and Ianetz,A. (2005). "Inter-comparison of the solar UVB,UVA and global radiation clearness and UV indices for Beer Sheva and Neve Zohar (Dead Sea),Israel." Energy **30**: 1623-1641.

Maldonado, R. M. I. (2000). descontaminación de aguas de lavado de envases de plaguicidas mediante fotocatálisis solar. Departemento de Ingeniería Química. Almería, Universidad de Almería**:** 232.

Mariscal, M., Orgaz, F. and Villalobos, FJ (2000). "Modelling and measurement of radiation interception by olive canopies." Agric Forest Meteorol **100**(1): 83–97.

Muneer, T., Younes, S. and Munawwar, S. (2005). "Discourses on solar radiation modeling." Renewable and Sustainable Energy Reviews **In Press, Corrected Proof**.

Page, J. (2005). "First conference on measurement and modeling of solar radiation and daylight "Challenges for the 21st Century"." Energy **30**: 1501–1515.

Rivington, M., Bellocchi, G., Matthews, K.B. and Buchan, K. (2005). "Evaluation of three model estimations of solar radiation at 24 UK stations." Agricultural and Forest Meteorology **In Press, Corrected Proof**.

Sarria, V. (2003). Coupled advanced oxidation and biological processes for wastewater treatment. Institute of Environmental science and Technology. Lausanne, EPFL**:** 150.

Vidal, A., Diaz, A. I., El Hraiki, A., Romero, M., Muguruza, I., Senhaji, F. and Gonzalez, J. (1999). "Solar photocatalysis for detoxification and desinfection of contaminated water: pilot plant studies." Catalysis Today **54**(2-3): 283-290.

Visser, S. M., Sterk, Geert., and Snepvangers, Judith J. J. C. (2004). "Spatial variation in wind-blown sediment transport in geomorphic units in northern Burkina Faso using geostatistical mapping." Geoderma **120**(1-2): 95-107.

Younes, S., Claywell, R. and Muneer, T. (2005). "Quality control of solar radiation data: Present status and proposed new approaches." Energy **30**: 1533-1549.

General conclusion and recommendations

The general scope of this thesis is the detoxification of biorecalcitrant pollutants in water and, our general objective was to make a contribution for the development of a helio-photocatalytical process which is able to enhance the biodegradability of biorecalcitrant wastewaters.

In order to achieve this goal, model studies were first carried out in the lab and on field using respectively a sunlight simulator and the direct sunlight. In all the cases, the photo-Fenton process was studied on the diethyl phthalate which is known as an Endocrine Disrupting Chemical. The second step of the studies was made by following the photo-Fenton on real applied studies for the decontamination of an industrial wastewater in Switzerland mostly containing pyridine compounds and also for the degradation of an obsolete stock of commercial Endosulfan pesticide in Burkina Faso.

Finally, the monitoring and modelling of UVA radiation and Energy from the direct sunlight in the working site at Ouagadougou in Burkina Faso was done basing on a data base of one year solar data collected at the Ecole Inter-Etats d'Ingénieurs de l'Equipement Rural (EIER).

The work presented in this thesis let us observe that, the photochemical enhancement of the biodegradability of some biorecalcitrant pollutants is a viable process from the economic and environmental point of view and it appears as an alternative to the drastic and/or inefficient processes (incineration and wet oxidation) actually applied in biorecalcitrant pollutant elimination. However, the biocompatibility of the phototreated waters needs to be checked to ensure the beneficial effects of the photochemical treatment.

One important consideration of this thesis is that the studies were conducted in synergy between a highly equipped laboratory at the Ecole Polytechnique Fédérale de Lausanne (EPFL) in Switzerland and a moderate equipped laboratory at the EIER in Burkina Faso. This "two-contexts" study make it possible to observe that the results of photochemical studies carried out using UV-light generated by lamps (in Switzerland) were comparable with those obtained with the direct sunlight as the main photonic source (in Burkina Faso). The study was made possible through an original and realistic analytical simplified method which was first set up at the lab (in Switzerland).

From the fundamental physicochemical point of view, the measure of the absorbance at 301 nm is a relatively accurate analytical method (c.a << 10% error) for the monitoring of the photo-Fenton process carried out on phthalates polluted waters. The relatively less accuracy of this method do not significantly affect the global goal of the research, since this could be testified by other classical analytical methods such as the measure of the COD, BOD and the HPLC monitoring of the initial pollutant in the final treated effluent. This analytical method is cost effective and can allow using cost affordable and practical analytical devices during field experimentation in developing countries.

Within comparable experimental conditions, the study presented in the chapter 2 also reveals that the photo-Fenton degradation rates of the phthalates are strongly dependant to the length of their peripheral alkyl chains: the longer the chains are, the lower the degradation rates are.

The use of a pilot CPC photo-reactor (25 litres) has demonstrated the influence of various physicochemical and engineering parameters on the solar photocatalytic degradation of the DEP based on the Fe^{3+}/H_2O_2 and Fe^{2+}/H_2O_2. As main contribution, we observed that the DEP degradation rate depends on the period of the day which itself is linked to the intensity of solar radiation (radiation flux). Also, it was confirmed that by operating the CPC opened flow system at a higher water circulation flow, the aeration was very important and this increases the degradation rate of the photo-Fenton process. The influences of the amount of Fe^{3+}, the initial H_2O_2 and DEP concentration are also important.

From the energetic point of view, it was observed that the photochemical process followed a similar 1st principle of the thermodynamic: "The energy necessary to degrade a constant amount of DEP doesn't depend on the period of the day". As a consequence of this, the "noon" (10h30-13h30) is the most favourable period of the day to carry out solar photo-processes.

The investigations real applied studies presented in the chapter 4 shows the difficulty and the complexity of treating real biorecalcitrant wastewaters. The diagnosis step is one of great importance when facing the treatability of real industrial wastewaters as it was really observed in the case study on the real industrial effluent containing the chloro 2-hydroxy-pyridin. The non biocompatibility observed on the photo-treated effluents recommends the total mineralization of the industrial chloro 2-hydroxy pyridine wastewater through the photochemical, whereas the photodegradation of the commercial Endosulfan pesticide through the photo-Fenton process leads to a more biodegradable effluent.

Following these two case studies, we developed and recommend a general strategy (**Fig. 6.1**) which can be adapted in various contexts in order to combine photoassisted AOP and biological processes for biorecalcitrant wastewater treatment, so to fulfil the local legislation requirements on water and wastewater quality.

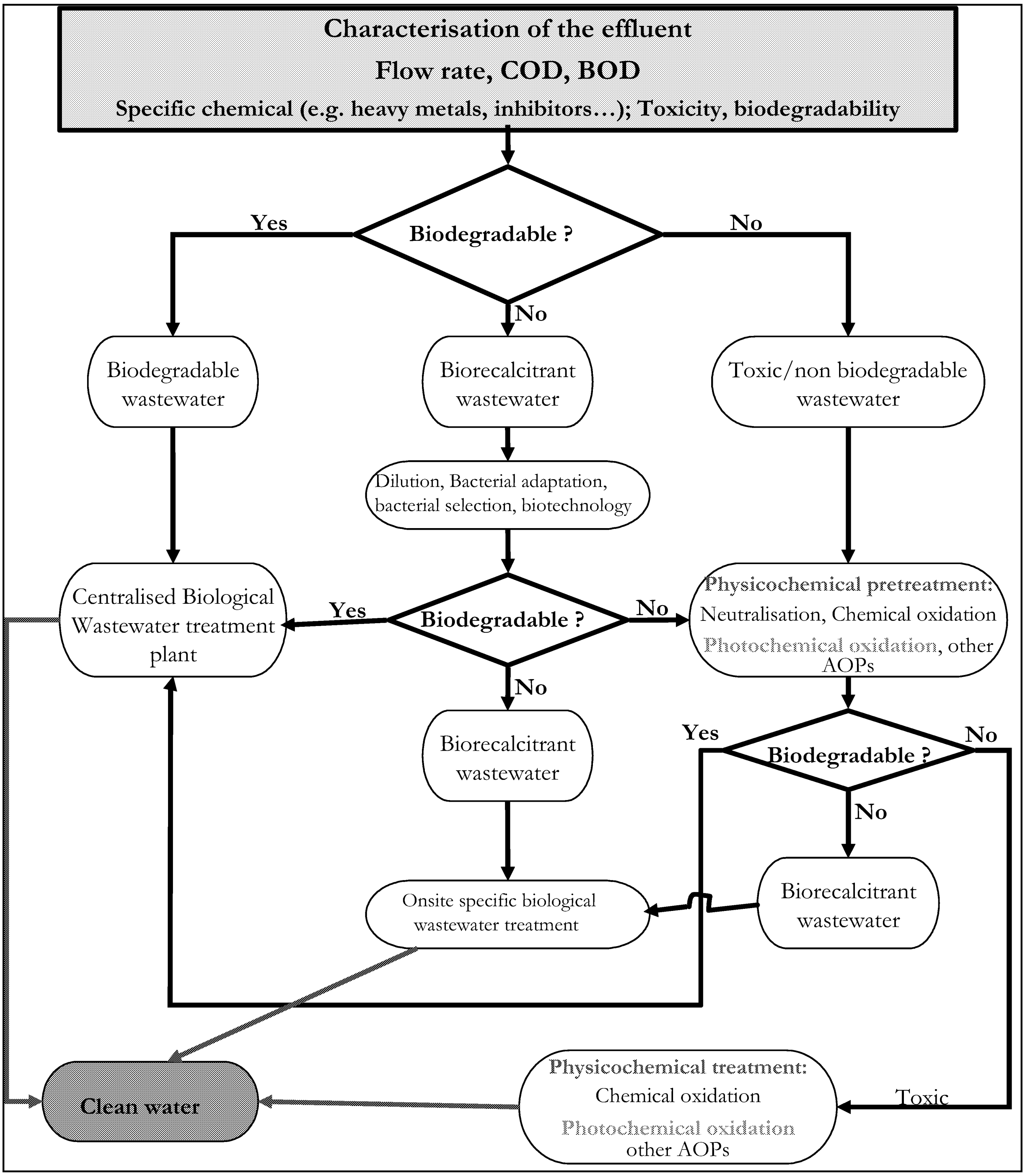

Figure 6.1: *Schematic diagram of the state of art in the field of wastewater treatment including innovative photochemical processes.*

Through the onsite characterisation of the solar radiation at Ouagadougou done over one year of measurements, it was noticed that the December - February period is the less sunny in

Ouagadougou and this less favourable solar photo-processing period should be considered when planning an helio-dependant processes there.

Basing on these solar data collected, three novel models are proposed in this study:

a) A solar UVA radiation statistical model upon which: Rad_{UVA} (t) = $a*t^2 + b*t + c$ where Rad_{UVA} (t) is the radiation at time t in the given site, a, b and c are scalar number depending on the locality and the month.

b) A solar UVA energy statistical model: $E_{UVA}(t) = A*t^3 + B*t^2 + C*t + D$ where E_{UVA} (t) is the accumulated UVA energy per meter square from an initial time (t_0) to a final time (t). The coefficients A, B, C and D have been statistically determined by the day's energy (from 08.00 am to 04.00 pm) at Ouagadougou, for all the months in a year.

c) An adjustment model linking the solar UVA radiation statistical and the solar UVA energy: $E_{UVA}(t) = \int Rad_{UVA}(t)\, dt$.

From these models, the evaluation of the average daily solar UVA energy per month could easily be made for a specific locality in the world when its solar database is available (e.g. where meteorological stations are available). The accuracy of the adjustment solar UVA energy model could be admitted with a 5% coefficient of variation on monthly average daily; but since the database of the solar radiation was only made of 22% of days over one year, further investigations are recommended in order to collect more solar data of Ouagadougou (for five to ten years more) and this would enable it to improve the robustness of these models. Thus, the modelling approach proposed in this study would be of a great importance when dimensioning photo-reactors and planning helio-photo applications in a specific site. These fast and easier ways for estimating solar data would also be beneficial to other scientific solar dependant applications.

Finally the feasibility study to carry out the helio-photo-Fenton process in a large scale CPC plant (300 m^2) in Burkina Faso in order to destroy an important stock of 4 m^3 commercial obsolete stock of Endosulfan (350 g.L^{-1}) was simulated and showed that the operation could be hold in 3 years with an average cost of 39 US$.L^{-1}. The treatment cost and the duration of such operation could be lowed down by constructing larger photo-reactors (c.a. 500 m^2) since the land cost is relatively null in Burkina.

Curriculum Vitae

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Education

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Professional Experience

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Languages

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Computer Skills

Microsoft Office (Word, Excel, PowerPoint), Adobe Illustrator and PhotoShop. Loop, sewer, branch and regress for calculations on potable and waste water sewers. Good usage skills of Epi Info for investigation data treatment.

Licence

1. Pulgarín C, Sarria V, **Kenfack S.**, Malato S, Blanco J. Hybrid Photocatalytic/Photovoltaic Hybrid System for Simultaneous Water Decontamination and Solar Energy Conversion. Centro de Investigaciones Energeticas, Medioambientales Y Tecnologicas (CIEMAT) & Ecole Polytechnique Fédérale de Lausanne (EPFL), *Licence n° P200401376, 06th July 2004 in Spain.*

Referee Papers

2. **Kenfack S.**, Sarria V.; Cissé G. Maïga A. H. and Pulgarin C.: Helio-photochemical degradation of an Endocrine Disrupting Chemical: The diethyl phthalate *(accepted in the J. of Photochemical and photobiology).*

3. **Kenfack S.**, Rincón A.G., Kampara M., Maïga A.H., Cissé G. and Pulgarin C. Traitement de la pollution microbienne de l'eau par le rayonnement solaire: cette technologie pourrait-elle être adaptée à la potabilisation de l'eau de boisson pour les communautés rurales dans les pays à fort taux d'ensolaillement? *Info CREPA n° 50, décembre 2005.*

4. Sarria V, **Kenfack S.**, Malato S, Blanco J, Pulgarín C. (2005) New helio-photocatalytic/photovoltaic hybrid system for the simultaneously photodegradation and energy production. *Solar Energy 79, 353-359.*

5. Sarria V., **Kenfack S.**, Guillod O. and Pulgarin C., 2003. An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants. *J of Photochemical and photobiology. A: chemistry 159, 89-99.*

Conferences

6. **Kenfack S., Sarria V. and Pulgarin C.:** Helio-photo-Fenton degradation of an Endocrine Disrupting Chemical: The diethyl phthalate; *1st European conference on the Environmental Applications of the Advanced Oxidation Processes (EAAOP), 7-9 September 2006, Chania, Greece.*

7. **Kenfack S.**, Kientga M, Yonkeu S, A. H. Maïga, Cissé G. et Pulgarin César: Problématique de la gestion des eaux usées industrielles au Burkina Faso: Analyse des risques environnementaux majeurs pour les villes de Ouagadougou et de Bobo Dioulasso; *3è journée Scientifique le l'EIER, 06-07.12.04, Ouagadougou, Burkina Faso*

8. Yonkeu S., Denyigba K.G, Djotsa A.B.S, Maïga A.H., Yacouba H., Wéthé J., Roche M., **Kenfack S.,** Mampouya M., Compaoré P. Parasitoses intestinales et maladies diarrhées chez les enfants de 0 à 7 ans vivant dans six villages riverains du barrage de Yitenga au Burkina Faso. *Actes des 3è journées Scientifiques le l'EIER, 06-07.12.04, Ouagadougou, Burkina Faso.*

9. Sarria V., **Kenfack S.**, Malato S., Blanco J. and Pulgarín C.. Solar Hybrid Photocatalytic Photovoltaic system. *12th Solar Paces International Symposium: concentrated solar power and chemical energy technologies. Oaxaca, Mexico, October 6-8, 2004.*

10. Sarria V., **Kenfack S.**, Malato S., Blanco J. and Pulgarín C. New Helio-Photocatalytic Photovoltaic system hybrid system for simultaneous water decontamination and solar energy conversion. *3rd European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications. Barcelona, Spain, June 28 – July 1, 2004.*

11. Sarria V., **Kenfack S.** and Pulgarín C.. Solar-biological field pilot system scale for the iron(III) photo-assisted treatment of biorecalcitrant pollutants. *The 9th international conference on advanced oxidation technologies for water and air remediation. Montreal, Canada, October 26-29, 2003.*

12. **Kenfack S.**, Sarria V., Rincón A., Becker K., de Alencastro F., Cissé G., Maïga A.H., and Pulgarín C.. Utilisation du rayonnement solaire pour le traitement de la pollution chimique et microbienne dans l'eau: Etat de l'art et Perspectives de recherche en Afrique tropicale. *Colloque International EREC 2002 "Energies renouvelables et cogénération pour le développement durable en Afrique", Ecole Nationale Supérieure Polytechnique, Université de Yaoundé I, Yaoundé, Rép. Cameroun, 16-20 décembre 2002.*

13. Sarria V., **Kenfack S.**, Péringer P. and Pulgarín C.. Coupling solar and biological processes for the degradation of a dye biorecalcitrant pollutant. European Meeting on Environmental Chemistry (EMEC3), *European Association of Chemistry and the Environment, December 11-14, Geneva, pp.104, 2002.*

14. Mampouya, M., **Kenfack S.** and Cissé, G., 2000: Wastewater- Environment and Health. *International colloquium Water and Health-Ouaga 2000, 21-24th november 2000, Ouagadougou, Burkina Faso.*