# PHOTOCATALYTIC OXIDATION OF GLYMES IN AN AQUEOUS SUSPENSION OF TITANIUM DIOXIDE

By

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#### ABSTRACT

Lower members of the glyme family CH3-(-O-CH2-CH2-)<sub>n</sub>-O-CH3 are refractory to the usual biological and physicochemical treatments, do not get retained on biofilters and are hardly sorbed to activated sludge or carbon. An alternate form of elimination is hence to be devised. TiO<sub>2</sub> particles have been utilized in the photocatalytic degradation of organic compounds often found in contaminated waste streams. When they are exposed to UV light, an electron is excited from the TiO<sub>2</sub> valence band into the conduction band. The photogenerated electron vacancy ("hole") can initiate the oxidation of the organic, while the photogenerated electron must be removed from the particle by transfer to a suitable electron acceptor (scavenger).

The photocatalytic oxidation of triglyme in an aqueous suspension of TiO<sub>2</sub> has been studied, proving the concept to be feasible. Characterization of the light distribution in the reactor has been carried out and related to the influence of catalyst load. The rate of the reaction was considerably enhanced by introducing  $Cu^{2+}$  as cocatalyst and by controlling the pH, with the existence of an optimum co-catalyst concentration ([triglyme]/[ $Cu^{2+}$ ] = 2) and an optimum pH at 3.5. The influence of both parameters is explained and the pathway of the interfacial charge-transfer reaction is proven to be of the Fenton type (indirect oxidation through activation of water) and not of the Photo-Kolbe type (direct attack of the holes).

### RÉSUMÉ

Les membres à faible point moléculaire de la famille des glymes CH3-(-O-CH2-CH2-)<sub>n</sub>-O-CH3 sont réfractaires aux traitements biologiques et physicochimiques habituels, ne sont pas retenus sur biofiltres et ne sont quasiment pas absorbés ni sur boue activée, ni sur charbon. Un autre procédé d'élimination doit donc être conçu. Des particules de TiO<sub>2</sub> ont été utilisées pour la dégradation photocatalytique de composés organiques communément trouvés dans les flux aqueux de refus contaminés. Lors d'exposition aux UV, un électron de la bande de valence du TiO<sub>2</sub> est excité vers la bande de conduction. Cette vacance électronique photogénérée ("trou") peut initier l'oxydation du composé organique, alors que l'électron célibataire doit être éliminé de la particule en le transférant vers un accepteur ("éboueur").

L'oxydation photocatalytique du triglyme dans une suspension aqueuse de TiO<sub>2</sub> a été étudiée, prouvant le concept faisable. La distribution de la lumière dans le réacteur a été réalisée et un rapport avec l'influence de la charge du catalyseur établi. La cinétique de la réaction est considérablement améliorée en introduisant Cu<sup>2+</sup> comme co-catalyseur et en contrôlant le pH. Il existe une concentration de co-catalyseur optimale ([triglyme]/[Cu<sup>2+</sup>] = 2) et un pH optimal à 3.5. L'influence complexe des deux paramètres est expliquée. Le chemin réactionnel du transfert de charge interfacial est déterminé être de type Fenton (oxydation indirecte par l'intermédiaire de l'activation de l'eau), et non du type photo-Kolbe (attaque directe des trous).

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# NOMENCLATURE

AOP	Advanced oxidation process
CAS	Chemical Abstracts Service
D	Diameter
df	Film thickness
EDTA	Ethylenediaminetetraacetic acid
FID	Flame Ionization Detector
GC	Gas chromatography
HPLC	High pressure (or performance) liquid chromatography
ID	Internal diameter
IR	Infra-red
MCLG	Maximum contamination level goal
MS	Mass spectrometry
OD	Outer diameter
PCO	Photocatalytic oxidation
PEG	Polyethylene glycol
ppb	part per billion (µg/L)
ppm	part per million (mg/L)
PVC	Polyvinyl chloride
RP-HPLC	Reverse phase HPLC
SPME	Solid phase microextraction
SVOC	Semi-volatile organic compounds
TIC	Total inorganic carbon
TOC	Total organic carbon
UV	Ultra-violet
VOC	Volatile organic compounds

## **CHAPTER 1: INTRODUCTION**

#### **1.1 General Introduction**

Public awareness regarding environmental matters has been steadily on the rise over the last few decades, with a remarkable increase since the early 1960s. This translated into a proliferation of environmental laws and regulations (see Figure 1.1). It is hence now vital for the marketability of a consumer and industrial product to be *"green"*, or at the very least recyclable and/or degradable. Possession of a single environmental-friendly process can reshape large portions of the industrial landscape, as can be seen by Solvay's acquisition of B.A.S.F.'s PVC production facilities, made after the former developed the Vinyloop<sup>®</sup> recycling process. This helped Solvay to jump overnight into a position of PVC production leader. New European regulations on the maximum chloride content allowed in solid waste would have made PVC noneconomical compared to the halogen-free polyurethane (which has similar physical properties).



Figure 1.1: Cumulative growth in federal environmental laws and amendments in the United States [1]

1

Next to recycling – which, contrary to common public opinion is not necessarily the ultimate environmentally friendly waste treatment method – oxidative destruction is an excellent solution. It can be attained either by biological, physico-chemical or thermal (incineration) means. While large scale thermo-treatment plants are commonly in use today, they are not readily accepted by the public. They are also not thoroughly adapted to the treatment of aqueous waste as it takes considerable energy to heat and vaporize the water. The excessive energy consumption is further exacerbated by the very high temperature required to destroy the organic pollutants (usually greater than 850°C [2]). Large attention has been given in the past to the biological oxidation processes, in part thanks to its cost effectiveness and its versatility in handling a wide variety of organic pollutants. It does, however, suffer from quite large start-up and retention times. Another handicap is that despite the global biological process being non-discriminatory, the right cultures have to be found and grown specifically for each pollutant, or at least for each class thereof. This makes the process sluggish to adapt to those pollutants that are either toxic or simply refractive to the biological system, causing potential operational difficulties. Such a pollutant class is the glyme family [3-6], the lower member of which are being examined in the present thesis. Glymes are commonly used as solvents in the fine chemical industry and can also be found in lithium batteries and brake fluids amongst other things.

A promising physico-chemical method for the degradation of biologically refractive chemicals in aqueous solutions involves the use of an advanced oxidation process (AOP), a destructive oxidation process involving the generation of hydroxyl radicals. In this dissertation, a heterogeneous photocatalytic oxidation (PCO) process was utilized, using fine particles of suspended semi-conductor as primary catalyst (*e.g.* titanium dioxide) and ultra-violet light as the activation source. This method has the potential of totally mineralizing the pollutant – *i.e.* eventually to degrade completely a complex organic molecule to simple and harmless carbon dioxide, water and/or elementar hydrogen – although this is not needed. The degradation just needs to be partial: eliminating the refractive moiety is enough to allow the subsequent biological

treatment to take over unhindered. Applying the photocatalytic oxidation technique to the degradation of glymes has not been tried before the present study. More so, surprisingly few articles dedicated to the study of the degradation of glymes by any means can be found in the literature.



Figure 1.2: Position of the PCO treatment in the global waste water treatment scheme

#### **1.2 Research Objectives**

The overall objective of the research conducted was to study the UV-activated photocatalytic oxidation of the lower members of the glyme family, specifically of triglyme (triethylene glycol dimethyl ether), in an aqueous suspension of titanium dioxide (a.k.a "titania").

The feasibility of the process was determined and the reactor characterized. The interfacial mechanism involved in the charge-transfer reaction was elucidated (Fenton chemistry *vs.* Photo-Kolbe process). The impacts of parameters, such as the pH and the concentration of the different chemicals involved were studied. Inroads into the reaction kinetics were also made. A cornerstone of this work was the aim to improve the degradation of glymes as much as possible.

#### **1.3 Thesis Outline**

This thesis is divided into 5 chapters and a concise description of each chapter is as follows:

#### Chapter 1 - Introduction

This chapter opens the thesis with an introduction to the field of study and gives a brief statement of objectives.

#### Chapter 2 - Background & Theory

The literature review covers the glymes' properties, application and toxicology and shows that alternative waste water treatments are not applicable to their elimination. The mechanism behind the photocatalytic oxidation and the influence of metal cations thereupon is shown here and the properties of the main catalyst ( $TiO_2$ ) reviewed

#### Chapter 3 - Experimental Setup & Analytical Methods

The reactor is described and characterized and the experimental protocol clarified. The different analytical methods used are explained.

#### Chapter 4 - Results & Discussion

The results of various experiments on the effect of various parameters such as initial pH, effect of cupric ion as co-catalyst and concentrations of the involved chemicals are presented and discussed. This leads to the optimization of the process and the determination of the photocatalytic mechanism. A brief study of the recyclability is also included.

#### Chapter 5 - Conclusions & Recommendations

The major conclusions arrived upon this study are summarized in this chapter, followed by recommendations for future work to be carried out.

# **CHAPTER 2: BACKGROUND & THEORY**

#### 2.1 Glyme Properties & Toxicology

Glymes are classified as ethylene glycol dimethyl ethers, a subcategory of ethylene glycol ethers. They have been chosen as the pollutant in this study because they are present in industrial waste water and apparently cannot be eliminated using classical treatments [5].

#### 2.1.1 Chemical Characteristics

The chemical identifying features of the ethylene glycol dimethyl ethers are their two terminal methyl groups, which impart their characteristic properties to this subgroup of ethylene glycol ethers. Ethylene glycol dimethyl ethers are generally clear, colorless to pale yellow liquids with a very faint odor: only monothylene glycol dimethyl ether possesses a characteristic odor which is reminiscent of diethyl ether. They retain their low viscosities even at low temperature.

The general chemical formula of glymes is shown below:

H<sub>3</sub>C-[-0]nO-CH<sub>3</sub>

Table 2.1 shows the nomenclature used to denominate glymes and Table 2.2 the characteristics of triglyme, which is the chemical studied in the thesis.

n	Usual name	Name	C.A.S. #
1	Monoglyme	1,2-dimethoxyethane	[110-71-4]
2	Diglyme	bis(2-methoxy ethyl)ether	[111-96-6]
3	Triglyme	triethylene glycol dimethyl ether	[112-49-2]
4	Tetraglyme	tetraethylene glycol dimethyl ether	[143-24-8]

#### Table 2.1: Nomenclature of the glyme family

#### Table 2.2: Triglyme properties

Formula	$C_8H_{18}O_4$
CAS #	112-49-2
Molecular Weight	178.2278 g/mol
Density	0.986
Melting Point	228 K
Boiling Point	489.2 K
Flash Point	386 K
Water Solubility	Soluble
Vapor Pressure	0.210 Torr at 298 K
Ср	368 J/mol/K at 298.15 K
$\Delta_{\rm fus} { m H}$	23.715 kJ/mol
$\Delta_{\rm fus} S$	103.4 J/mol/K

#### 2.1.2 Industrial use of Glymes

Glymes are some of the most powerful solvents available today. According to one of the manufacturers (Clariant GmbH [7]), they have the following principal properties:

- very good miscibility with water
- very good miscibility with aliphatic/aromatic hydrocarbons
- solubilizer (linear crown ethers property)
- phase transfer catalyst (linear crown ethers property)
- high dissolving power for organic and inorganic compounds and for natural substances and polymers
- inert reaction medium, used *e.g.* for organometallic (Grignard, *etc...*) reactions and polymerizations (SciFinder<sup>™</sup> has an inventory of over 150,000 reactions involving any of the four first glymes as a solvent!)

- absorption medium for gases and VOCs, particularly tetraglyme for gases such as sulphur dioxide, carbon dioxide and hydrogen sulphide
- aprotic solvent, *i.e.* they solvate cations well and anions poorly so that the latter gain in reactivity
- ability to lower the viscosity and increase the ion mobility, used in the formulation of electrolyte systems for lithium batteries (monoglyme)

Another possible large-scale future application for glymes is in reformulated fuels [6], as currently developed by Air Products And Chemicals Inc [8] in their CETANER<sup>TM</sup> fuel which is a blend of diesel fuel and different oxygenated compounds, glymes included. Finally, even if they do not seem to be widely used for this property, the higher molecular weight glymes are also non-ionic surfactants.

Hence the causes of pollution by glymes are from industrial waste waters on the one hand (mainly from their use as inert special solvent and teflon etching), and domestic waste on the other from sources such as: fuel leaks, battery disposal, paint, delacquer, brakefluids, etc...

#### 2.1.3 Toxicology

Not much definitive data regarding the toxicity of glymes are available; however the literature [9, 10] implies that glymes are teratogens and reproductive toxins. Ferro Corporation, the sole known U.S. manufacturer of glymes, states in its product literature [11] that the glymes exhibit only low to moderate toxicity. However, it is further stated that concern regarding chronic exposure and reproductive effects indicate that glymes be used only in industrial applications. However, Clariant [7], basing its data on more stringent German regulations on dangerous substances (*BAuA GefStoffV*), classifies mono- and diglyme as poisonous (relevant hazard and warning symbol "T") and triglyme as harmful to one's health (symbol "Xn"). In that same report all glymes are classified as slightly hazardous to water (water hazard class No. 1). According to Air Products And Chemicals' Corporate Toxicology Department [8], it appears that the adverse effects of the glyme family are related to its metabolism to 2-methoxyethanol  $CH_3OCH_2CH_2OH$  and ultimately to methoxyacetic acid,  $CH_3OCH_2COOH$ , for which adverse health effects are well established. This was proven for diglyme and deemed as likely to be the same for the mono- and triglyme.

Finally, according to INSERM [12], the amphiphilic characteristic of glymes makes them especially prone to very easy cutaneous adsorption; hence the user always has to be very careful to wear gloves while handling.

#### 2.2 Alternative Waste Water Treatment

Waste water treatments can be broadly separated into two classes: separation processes and destructive processes. The following is a discussion giving us an insight on how difficult the proper treatment of glyme-contaminated material can be.

#### 2.2.1 Separation Processes

Examples of separation processes are air stripping, soil vapor extraction, activated carbon adsorption and thermal desorption. As the name points out, those methods only allow the separation of the pollutant from its solid or liquid support while the problem of what is to be done with that pollutant remains unsolved.

In the process of air stripping, the volatile organic compounds (VOC) are removed from the contaminated material, such as ground water, by forcing an airstream through the material and causing the compounds to evaporate (mass transfer from water to air). Commonly the water is pumped into a stripping tower and runs over packing material or trays inside an enclosed chamber to increase its surface area. In in-well stripping technology, air is introduced into a water column within an extraction well. Typically, organic compounds with Henry's constants greater than 0.01 atm.m<sup>3</sup>.mol<sup>-1</sup> are amenable to air stripping. Since triglyme has a low volatility at low temperatures (vapor pressure of 0.210 Torr at 298 K [13]), this method is not suitable for our purpose.

For the *in situ* soil vapor extraction, a vacuum is applied to the soil so as to induce a flow of clean air from the atmosphere into the subsurface. Compounds with a Henry's law constant higher than 0.01 or with a vapor pressure greater than 0.5 Torr can be successfully treated in this way. Thus, this route is not appropriate for triglyme.

In the activated carbon adsorption process waste water is pumped through a series of canisters or columns containing activated carbon. Commonly, either fixed bed or moving bed reactor configurations are used. The technique is useful for the separation of hydrocarbons, semi-volatile organic compounds (SVOC), non-volatile organic compounds and anions. Liquid-phase carbon adsorption is effective for removing contaminants at low concentrations (<10 ppm) from water at nearly any flow rate. However a study showed [4, 14] that glymes are hardly sorbed onto activated carbon apparently because of their polarity.

In thermal desorption, water and organic pollutants are volatilized through heating and swept away by a carrier gas or vacuum system. Commonly, either a rotary dryer or a thermal screw design is employed. It is not known how effective this type of separation is with regards to triglyme separation, albeit its high boiling point 489 K [15], and low vapor pressure would, once again, point against it. However, since thermal desorption is known to be effective for a large range of organic contaminants, it might be practical to use this technique as part of the recycling treatment needed to regenerate the solid catalyst used in the present work. For example, if a reaction by-product happened to foul the titanium dioxide particles, this ought to take care of it.

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#### 2.2.2 Destructive Processes

Destructive treatments of pollutants in waste water can be achieved either through incineration, biological treatment, or by using an advanced oxidation process (AOP) such as ozone treatment, Fenton reagent, supercritical water oxidation, sonolysis, high-energy electron beam, zero-valent iron or photocatalytic oxidation. A combination of various AOPs can, of course, be used as well.

#### 2.2.2.1 Classical Oxidation Processes

Incineration is the sledgehammer method for waste treatment. Used as a modern industrial application for hazardous waste treatment as far back as 1874 in the UK (1885 in the US), it has a destruction and removal efficiency greater than 99.99 % [1]. Incinerators come in all types and shapes, with temperatures reaching 1,500 K: We can have incineration via various routes such as: liquid injection, rotary kiln, infrared, fluid-bed, or bubbling fluid-bed. No studies dedicated to the incineration of glyme-waste have been made, but since glyme is being used as a fuel additive, it can be reasonably well assumed that its removal through this method is feasible. However, as has been pointed out in the introduction, the handicap of having to heat up and vaporize so much water makes this method not very energy-efficient. This method is also not available for the post-process recycling treatment of the TiO<sub>2</sub> catalyst, as high temperature will affect its crystalline structure: anatase heated up to 800 °C forms rutile [1].

There are very few hard data available regarding the specific degradation of glymes by biological means. However, the consensus [16-18] is that ethylene glycol ethers are very refractive to biological treatment. Given that the *methyl* functionality is chemically less reactive than the *alcohol* functionality, the previous assessment can be considered all the more true for ethylene glycol dimethyl ethers. This is also in accordance with the fact that, generally, nonionic (*e.g.* glymes) and cationic surfactants exhibit poor biodegradability. In a classification of 14 such nonionic and cationic

surfactants, glymes appears in the third-worst position [19]. The biodegradation rate increases in the order:

# (ether linkage) < (ester linkage) < (peptide linkage)

We can easily see that glymes fall into the worst case group. However, no article give any specific data regarding the actual consumption rates of glymes by microorganisms. Moreover, glymes are not retained on biofilters and are hardly sorbed to activated sludge, apparently because of their polarity [20]. An encouraging study for this thesis has been highlighted in an article [21] about the combination of  $\gamma$ -irradiation and biological oxidation: a 27 % TOC (Total Organic Carbon) reduction has been achieved for monoglyme. This implies that the bio-refractive moiety can indeed be broken down by physico-chemical means and the waste water effectively treated by the typical subsequent biological oxidations.

#### 2.2.2.2 Advanced Oxidation Processes (AOP)

Destructive oxidation processes involving the generation of hydroxyl radical are called Advanced Oxidation Processes (AOP). They usually require the presence of a catalyst such as metals or metal oxides and/or energy-activators such as photons or ultrasound. A combination of catalysts can also be used.

The only articles [18, 20] found specifically on the degradation of glymes by OAPs were about the elimination of triglyme by a combination of ozonation and UV irradiation (without catalyst) or hydrogen peroxide addition. Ozone alone has a negligible impact on the degradation, and combining it with UV irradiation is not much better. However, in the additional presence of humic acids (the authors do not give more specifications), the total organic carbon (TOC) goes down 30 % within one hour. This is explained by the enhanced formation of hydroxyl radicals. However, the data is dubious and some graphs even show an apparent *increase* in triglyme concentration with time for some experiments! According to the authors, combining ozonation with hydrogen peroxide at 7 % is a good method for triglyme degradation, with an 80 % reduction in TOC after 100 minutes (down from a rather initially low 22 ppm).

Encouraging data can also be found in a study [17, 19, 22] about the photodegradation, in an aqueous titanium dioxide suspension, of  $C_9H_{19}-C_6H_4$ -O- $(CH_2CH_2O)_n$ -H, *i.e.* a nonionic surfactant that contains a glyme-like moiety. They find an 85 % decrease in concentration after an irradiation time of one hour (down from 0.10 mM). The proposed mechanism for the photodegradation of the ethoxylate moiety is of interest for the present work: it occurs first through an  $\alpha$ -oxidation that gives an intermediate of the acetic acid type via hydroperoxide. On C-C fission, a formic ester forms; on C-O fission, glyoxal and formic acid are formed, which subsequently degrade to give carbonate ions. These eventually escape the system due to the acidic condition used.

Photocatalytic oxidation is, *stricto sensus*, not necessarily an AOP as the mechanism does not unconditionally involve the formation of hydroxyl radicals. It is one of the aims of this study to find out which interfacial charge-transfer reaction occurs in our system.

#### 2.3 Photocatalytic Oxidation

The process of photocatalytic oxidation in aqueous  $TiO_2$  suspensions has the big advantage of yielding rapid, non-selective degradation of a broad range of organic compounds. Being a heterogeneous reaction, the catalyst can easily be eliminated from the system and recovered through simple filtration. Hence, it is ideal for the treatment of large quantities of waste water. The inexpensiveness, photostability, availability and non-toxicity of titania [1, 23] gives it an edge compared to other potential semiconductors such as CdS,  $MoS_2$  or ZnO.

The first step in photocatalytic oxidation [24, 25] is the absorbance by the semiconductor of ultra violet light which is more energetic than the  $TiO_2$  band gap, resulting in the transition of electrons from the valence to the conductive band and generation of electron / electron hole pairs ( $e^-$  /  $h^+$ ), as can be seen in Figure 2.1. The "hole" is simply a free electron space in the valence band. Both the electron and the hole can migrate to the surface of the particle to react subsequently with adsorbed species in oxidative (hole) or reductive (electron) reactions. The band gap is 3.2 eV for anatase and 3.0 eV for rutile, so the whole UV-spectrum below 390 nm is available to the process. The time needed for the electron and hole to migrate from their point of creation to the surface has been computed to be about 2 ps only [26] for the particle size used in this study.

The electron / electron hole pairs can very easily recombine, returning the semiconductor to its initial non-excited stage by releasing the excess energy through heat. To prevent this undesirable electron-hole recombination, the electrons must be scavenged by adding an oxidizing agent such as  $O_2$ ,  $O_3$  or  $H_2O_2$ . In our case, oxygen from air is used, forming a super oxide radical. In the absence of electron donors and/or acceptors on or near the surface of the excited particle, relaxation occurs within a few nanoseconds. [27]



Figure 2.1: Photo-activation and thermal relaxation of the catalyst

As this takes place in an aqueous solution, the predominant reaction is the oxidation of adsorbed water by holes to produce hydroxyl radicals, widely believed to be the most important oxidizing species in  $TiO_2$  photocatalytic systems (Fenton chemistry). However, some direct oxidation of adsorbed organic compounds is also believed to take

place (Photo-Kolbe process) [28]: as has been stated in Section 1.2, it will be one of the aims of this study to determine which path is being used in the PCO of glymes. For both situations – considering the extremely short lifespan of the active species involved – we can notice how important it is for the targeted pollutant to be completely soluble in water, which, fortunately, is the case for glymes. Figure 2.2 shows the possible interfacial charge transfer reaction in the photocatalytic oxidation of glymes.



Figure 2.2: e<sup>-</sup>/hole migration and interfacial charge-transfer reactions ("G" stands for "Glyme")

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The general proposed mechanism for such a photocatalytic process can be visualized by the following steps [29]:

(i) Absorption of efficient photons  $h\nu \ge E_G = 3.2 eV$  by titania.

 $TiO_2 + hv \rightarrow TiO_2\left(e_{CB}^- + h_{VB}^+\right)$ 

The electron/holes pair can be lost by spontaneous recombination within a few nanoseconds [27].

$$TiO_2\left(\bar{e_{CB}} + h_{VB}^+\right) \rightarrow TiO_2 + heat$$

(ii) Electron scavenging by the adsorbed  $O_2$ .

$$\left(O_2\right)_{ads} + e_{CB} \to O_2^{\bullet-}$$

(iii) Neutralization of HO<sup>-</sup> groups into HO<sup>-</sup> by valence band photoholes.

$$\left( H_2 O \Leftrightarrow H^+ + HO^- \right)_{ads} + h_{VB}^+ \to H^+ + HO^{\bullet}$$

(iv) Neutralization of super oxide radicals by protons.

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet-}$$

(v) Transient hydrogen peroxide formation.

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$

(vi) Decomposition of hydrogen peroxide (hydrogen peroxide is only found in traces[30]).

$$H_2O_2 \xrightarrow{h\nu} 2HO^{\bullet}$$

(vii) Oxidation of the organic reactant via successive attacks by HO' radicals (Fenton).

$$(R)_{aq} + HO^{\bullet} \rightarrow (R^{\bullet})_{aq} + H_2O$$

or by direct reaction with the valence band holes (Photo-Kolbe). followed by the hydrolysis of the intermediate radical cation [26]:

$$(R)_{ads} + h_{VB}^{+} \rightarrow (R^{+\bullet})_{ads}^{\neq} \xrightarrow{H_2O} degradation products$$

Strictly speaking, the name "Fenton reaction" is only applicable to the Fenton Reagent [31, 32] (mixture of  $H_2O_2$  and  $Fe^{2+}$ ), but since it involves hydroxyl radicals as an active species [33], it is, by extension, used for any oxidation mechanism due to HO<sup>•</sup>.

Similarly, the Photo-Kolbe process is actually just the last step of the mineralization, but the name is commonly used for all direct oxidation of an adsorbed organic species by the holes.

The Fenton reaction on unsaturated organic compounds involves a C-H bond break by hydroxyl radicals with the following selectivity [34-38]: primary < secondary < tertiary, but it is also clear that reactivity is significantly enhanced by potentially electron-donating groups ( $\alpha$ -OH,  $\alpha$ -OR, and amide N) and decreased by electronegative substituents ( $\alpha$ -carboxylic acids,  $\alpha$ -ketones, halogens). The subsequent C-O homolysis is much faster than the C-C homolysis [39]. Glymes with their ether chains are, hence, a very good candidate for Fenton-type chemistry.

In contrast to most other oxidants, reactions involving hydroxyl radicals proceed with rate constants approaching the diffusion-controlled limit  $(10^{10} \text{ M}^{-1}.\text{s}^{-1})$ ; therefore, oxidation rates are usually limited by the rates of HO<sup>•</sup> generation and competition by other HO<sup>•</sup> scavengers in solution rather than by inherent reactivity of the radical [1, 40-42].

Next to hydrogen abstraction, hydroxyl radicals can also interact with organic compounds either by hydroxyl addition or by electron transfer [43, 44]. However, the former usually applies to organic  $\pi$  systems, while the latter typically involves inorganic ions. Out of the three major reaction types involving hydroxyl radicals, only the hydrogen abstraction is taking place in the studied system.

Involving hydroxyl radicals has the advantage of using a "clean" oxidant, *i.e.* an oxidant made out of hydrogen and oxygen: no non-organic elements (fluor, manganese or others...), that will eventually have to be removed for environmental reasons, are introduced to the system. As can be seen in the Table 2.3 below, hydroxyl radical is the second-best oxidizing agent after fluorine.

Redox reaction	E°(NHE)
	Volts at 25°C
$F_2 + 2 e^- = 2 F^-$	2.87
$HO' + H^+ + e^- = H2O$	2.33
$O_3 + 2 H^+ + 2 e^- = H_2O$	2.07
$H_2O_2 + 2 H^+ + 2 e^- = O_2 + H_2O$	1.76
$MnO_4 + 4 H^+ + 3 e^- = MnO_2 + 2 H_2O$	1.68
$MnO_4^{-} + 8 H^{+} + 5 e^{-} = Mn^{2+} + 4 H_2O_{-}$	1.49
$HOC1 + H^+ + 2 e^- = C1^- + H_2O$	1.49
$Cl_2 + 2 e^- = 2 Cl^-$	1.36
$HBrO + H^{+} + 2 e^{-} = Br^{-} + H_2O$	1.33
$O_3 + H_2O + 2 e^- = O_2 + 2 HO^-$	1.24
$Br_2 + 2 e^- = 2 Br^-$	1.07
$HIO + H^+ + 2 e^- = I^- + H_2O$	0.99
$ClO_2(aq) + e^- = ClO_2^-$	0.95
$ClO^{-} + 2 H_2O + 4 e^{-} = Cl^{-} + 4 HO^{-}$	0.90
$H_2O_2 + 2 H^+ + 2 e^- = 2 H_2O$	0.87
$ClO^{2-} + 2 H_2O + 4 e^{-} = Cl^{-} + 4 HO^{-}$	0.78
$BrO^{-} + H_2O + 2e^{-} = Br^{-} + 4HO^{-}$	0.70
$IO^{-} + H_2O + 2 e^{-} = I - + 2 HO^{-}$	0.49

Table 2.3: Red/Ox Potentials of oxidation agents [2]

The influence of pH is highly dependant on the nature of the organic molecules involved in the reaction. Since the hole is an abstract electronic concept, it cannot "jump" into the aqueous solution. The direct oxidation through the Photo-Kolbe process necessitates the pollutant to be adsorbed onto the solid catalyst. However, the extremely short half-life of hydroxyl radicals in water assumes that in the case of Fenton-type chemistry the pollutant be also, if not adsorbed, then at least extremely close to the surface of the titania. In both cases the interaction between the surface chemistry of the catalyst and the organic species plays the determining role in the influence of the hydrogen potential. As can be seen in Figure 3.2, the photodegradation of electron-rich molecules should be enhanced at low pH, whereas basic conditions are better for electrophilic pollutants.

It can be noted that in the Fenton-Chemistry, the crucial hydroxyl radical formation step (step iii) is enhanced at a higher pH. The water-to-hydroxyl radical conversion decreases with the lowering of the pH due to the abundance of hydronium

groups on the surface which interfere with the transfer of holes to the adsorbed water. In acidic medium, the chemisorption of the electron scavenger  $O_2$  is lowered with respect to the alkaline medium, yet again indicating that extreme acidity is not favorable to the PCO process [45, 46].

For dissolved dioxygen concentration higher than 3 ppm, the oxidation rates are zero order with regards to  $[O_2]$  [47]. The study uses concentrations of about 7-8 ppm, hence the exact oxygen level will not affect the rates. The influence of the light intensity is not directly studied here, but the degradation is either showing a linear increase of the reaction rate with light [48], or there is a square-root relationship between the two [27]. Neither is the influence of temperature studied, however the typically low activation energies of the photoreactions and high reactivity of hydroxyl radicals should make the PCO relatively temperature-insensitive [49, 50] and hence the study unnecessary.

#### 2.4 Influence of Metal Cations on the PCO

As will be shown in Chapter 4, cupric ions have been identified as being a very good co-catalyst to this process. In the past studies on the influence of metal ions on the photocatalytic oxidation on titanium dioxide, conflicting results were reported as can be seen in the Table 2.4 below, which focuses on the influence of  $Cu^{2+}$ . More on the subject can be found in Section 4.3.2.

Pollutant	Metal ion	Effect	Ref.
Formic acid	Cu <sup>2+</sup>	Beneficial	[52]
Acetic acid	Cu <sup>2+</sup>	Beneficial (optimum)	[48]
Propionic acid	Cu <sup>2+</sup>	Beneficial	[53]
Toluene	Cu <sup>2+</sup>	Beneficial	[54]
PhMe	Cu <sup>2+</sup>	Beneficial	[55]
Bacteria	Cu <sup>2+</sup>	Beneficial	[56]

*Table 2.4:* Review of metal ion effect on the PCO of various organic pollutants (in part from [51])

Sucrose	Cu <sup>2+</sup>	Beneficial (optimum)	[57]
Phenol	Cu <sup>2+</sup>	Beneficial / Detrimental	[58]
Toluene &	Cu <sup>2+</sup>	Beneficial at low conc.	
Clorobenzne	Fe <sup>3+</sup>	detrimental at high conc.	[59]
	Ni <sup>2+</sup>	(optimum)	
Pyrimidines	Cu <sup>2+</sup>	Detrimental	[60]
4-nitrophenol	Cu <sup>2+</sup>	Detrimental	[61]
AO-7 & 3-NBSA	Cu <sup>2+</sup>	Detrimental	[62]
Phenol	Cu <sup>2+</sup>	Detrimental	[63, 64]
Azo dyes	Cu <sup>2+</sup>	Detrimental in alkaline conditions	[65]
	Ni <sup>2+</sup>	Neutral in acidic conditions	

# **CHAPTER 3: EXPERIMENTAL SETUP & ANALYTICAL METHODS**

#### 3.1 Experimental Setup

#### 3.1.1 Reactor

The reaction takes place in a well mixed 4 liter, pyrex glass, cylindrical batch reactor (D = 127 mm, L = 330 mm) depicted in the schematic below (Figure 3.1). The PVC cover has the following features:

- A 6-bladed Rushton turbine with its shaft, propelled by an electrical motor.
- 4 quartz sleeves (22 mm OD, 20 mm ID, 294 mm from top) in which 4 UV Hg-Ar lamps (Altlantic Ultraviolet Corp. GPH212T5L) can be inserted. Contrary to glass, quartz is reputed to being UV-transparent, but measurement done in the course of this study showed that 49 % of the emitted light is still lost through the sleeves. The sleeves do not just serve as protection of the lamps against the water, but also act as antivortex baffles. Each lamp delivers 1.67 µEinstein/min (unit of irradiance equal to one mole of photons, regardless of theur frequency) into the solution, with 80 % of the energy output at 254 nm (Hg-ray). The emission spectrum of the lamp can be found in the Appendices.
- A stainless steel air inlet reaching under the turbine (air sparger). The required air is supplied by the building's air compressor and regulated by an online rotameter. The maximal air flow is 2.31 L.min<sup>-1</sup> and that flow was always used.
- Two holes that can either be used to insert probes (pH, temperature, etc...) or to take samples with a syringe.

The reactor is wrapped in aluminum foil to protect the user from the light, which is fully in the visible/IR spectrum since the glass wall of the reactor filters out 100 % of the UV-light. It also hinders any possible interference of external light sources, which would be negligible anyway. The reactor is submerged to the rim in a temperaturecontrolled water bath at 20 °C in order to have an isothermal reaction.



Figure 3.1: Reactor design (water bath not shown)

#### 3.1.2 Experimental Protocol

Typically, the experiments were conducted in the following fashion: All solid components (*i.e.* the TiO<sub>2</sub> from Degussa and CuSO<sub>4</sub>.5H<sub>2</sub>O from Fisher Scientific) are measured out on an electronic precision scale ( $\pm$  0.1 mg, Mettler<sup>TM</sup> AE240). Since the minimal buyable quantity of titania is in 10 kg bags, Degussa graciously provided 500 g samples free of charge. 2.5 liters freshly deionized (Easypure<sup>TM</sup> RF 18 MΩ) distilled water are measured out using a large graduated cylinder and about 50 mL set aside to

pre-dissolve the cupric sulfate. All the above are put into the reactor, which is then sealed and the lamps, electric motor and air-feed connected. The lamps are quickly tested for faulty electric connection. The pH is modified using concentrated 85 % HCl acid (Fisher Scientific), using a frequently calibrated pH-meter (AR-50 pH meter from Accumet Research<sup>®</sup>). Usually, less than 0.2 mL of acid is necessary, hence no variation in volume takes place. Adding only negligible amounts of Cl<sup>-</sup> is important because at higher doses it may act as a poison on the co-catalytic activity of Cu<sup>2+</sup> [45, 54]. Then, 0.51 mL of triglyme (for a typical 200 ppm load) is introduced through the reactor top using a 1 mL syringe and the system is left to equilibrate under constant agitation and air bubbling for about 15 min. The concentration of O<sub>2</sub> quickly reaches a constant 7-8 ppm. In alkaline solutions, negligible amounts of triglyme are lost to the solution in foam, but most of the reactions take place in acidic conditions, where no foam is being formed.

At the start of the experiment, the light is turned on and a first sample immediately taken using a 20 mL syringe through a plastic tubing. Each sample is filtered through Fisherbrand 0.8  $\mu$ m filters (D = 25 mm) to remove the solid catalyst particles and eliminate any possible solid impurities that could damage the analytical material. Subsequent sampling is then done at predetermined reaction times, up to 3 hours. Samples are stored in the dark at 4°C, but the analyses are always done within 48 hours.

#### 3.1.3 Primary Catalyst Properties

The primary catalyst used is ultra-pure titanium dioxide P25S manufactured by Degussa.  $TiO_2$  has been chosen over any other wide-bandgap semiconductor that could potentially be used in a PCO process because it is the catalyst commonly used successfully [29]. It can also reach a much larger surface area than most of the others and is very cheap. Its characteristics can be found in the table below.

Appearance	Fluffy white powder
Behaviour towards water	Hydrophilic
CAS Reg. number	13463-67-7
BET surface area	$50 \pm 15 \text{ m}^2/\text{g}$
Total pore volume	$0.063 \text{ cm}^{3}/\text{g}$
pH-value (4% aqueous dispersion)	3.5 - 4.5
Average primary particle size	~ 21 nm
Tapped density	~ 130 g/L
Loss on drying (2 h at 105°C)	< 1.5 %
Loss on ignition (2 h at 1000°C)	< 2.0 %

Table 3.1: Catalyst properties (titanium dioxide P25S) [66, 67]

TiO<sub>2</sub> is typically prepared through flame-hydrolysis of TiCl<sub>4</sub> [68] and exists in three crystalline configuration: anatase, rutile and brookite. Only the first two are used as pigments: since pigments *per se* interact with light and the catalyst used in the PCO process needs to be activated by light, it is safe to assume that the non-pigment brookite cannot be used in PCO (it also does not show up in literature in that capacity). The catalyst used here is 80 % anatase and 20 % rutile. In all three cases, the crystal mesh is composed of a Ti<sup>4+</sup> ion surrounded by a slightly distorted octahedra with only six O<sup>2-</sup> ions. Oxygen has a coordination number of 3 with regards to the titanium and the bond type is in-between pure ionic and covalent bond, the ionic character being prevalent [69].

From the thermodynamical point of view, photooxidation should occur with the same efficiency for both anatase and rutile, but it has been reported that – despite the greater free-carrier mobility in anatase – the surface recombination of photoexcited electrons and positive holes is higher in rutile [45, 70, 71].

The isoelectric point for pure anatase is close to pH 6.4, but it seems to be lowered somewhat by the presence of impurities [65, 72], the value for this catalyst being pI = 5.3 [19]. This means that the electric surface properties of the main catalyst can be seen in Figure 3.2:


Figure 3.2: Electrical surface structure of TiO<sub>2</sub> with pH

Note that since the values of  $pK_A$  are respectively 2.4 and 8.0 for the  $Ti - OH_2^+/Ti - OH$  and  $Ti - OH/Ti - O^-$  pairs [27], the main structural component between those two pHs are actually Ti - OH. The Figure 3.2 above only takes the electrically active species into consideration.

An actual picture of the catalyst in use can be seen below. As in every system containing nanoparticles, there is a certain amount of aggregation which, in this case, is dependent upon the pH of the solution: the maximum particle size is about 13  $\mu$ m at pH 8 [73] and drops to about 2-3  $\mu$ m in acidic or basic conditions.



Figure 3.3: Picture of Degussa TiO<sub>2</sub> P25 [66]

### **3.2 Analytical Methods**

## 3.2.1 Gas Chromatography (GC) and GC / Mass Spectrometry

The quantitative measurement of glyme concentration is done using gas chromatography (GC) on a Hewlett Packard 5890 in no-split mode. The chosen column is a Stabilwax (crossbonded carbowax-PEG, 30 m, 0.32 mm ID, 0.25  $\mu$ m df) from Chromatographic Specialities Inc., the carrier is helium at 30 cm<sup>3</sup>.sec<sup>-1</sup>, and the detector a FID at 275 °C. Injections are carried out manually using a Supelco SGE 0.5  $\mu$ l syringe, introducing a 0.4  $\mu$ l sample at 225 °C. The oven starts at 80 °C on a one minute isotherm and then heats up to 210 °C at a constant rate of 10 °C.min<sup>-1</sup>.

The best internal standard found is acetic acid at 1000 ppm in deionized water, diluted approximately at a 1-to-5 ratio with the sample (1 mL + 5 mL). This allows having a standard-signal of about the same intensity as a triglyme-signal at an initial load of 200 ppm (*i.e.* standard experimental conditions). Raw data corrections with regards to the internal standard are not made using volume, deemed too imprecise, but mass of sample preparations as measured on the electronic precision scale. This allows an exceptional reproducibility of less than 2 % on a new injection liner. However, the wear-and-tear on the liner quickly interferes with the results and worsens the reproducibility to up to 5 %. The retention times of the internal standard and of triglyme are respectively 5.7 and 9.1 minutes in the given conditions.

It was hoped to determine qualitatively the nature of the degradation products by using a mass-spectrometer as detector (GC/MS), but unfortunately the results were extremely non-conclusive and unusable. The GC column used in the Finnigan Polaris GC/MS and the initial MS vaporization filament do not support the aqueous phase, so the reaction mixture had to be extracted using either SPME (solid phase microextraction) [74] or chloroform.

## 3.2.2 Total Organic Carbon (TOC)

Measurements of the total organic carbon in the reactor over time allow the quantification of the mineralization. The analyzer indiscriminately mineralizes all organic molecules into carbon dioxide using persulphate/UV oxidation and measures the produced CO<sub>2</sub> through a nondispersed infrared analyzer. The latter is calibrated using a standard 400 ppm TOC hydrogen phthalate solution prior to each usage and after every 5 to 6 injections. The injection volume per sample is a uniform 200  $\mu$ l.

The material used was a Rosemount Dohrmann Total Organic Carbon DC80 and allowed a reproducibility of about 1 ppm TOC. However, an inherent instability due to poor evacuation of the heat generated by the lamp renders the results less precise when the machine is used over a longer period of time (over one hour).

The total inorganic carbon content (TIC) is also accessible by using the same settings in dark mode (lamp off), but since the typical reaction conditions are at low pH, the TIC is always negligible (below 1 ppm) due to the insolubility of CO<sub>2</sub>.

### 3.2.3 High Pressure Liquid Chromatography (HPLC)

The Agilent 1100 series high pressure (or performance) liquid chromatograph available offers a tremendous gain in time thanks to its autosampler. Bar the transparence of glyme with regards to the UV used in the machine's detector, it would have been the analytical method of choice. Unfortunately the detector cannot detect glyme and hence it cannot be used to study the evolution of glyme concentration over irradiation time.

Nevertheless, a method has been devised allowing it to quantitively study the cupric ion content in the reactor without having to resort to the cumbersome ICP method, which would here again involve lengthy manual sample injections. Adding a known excess of EDTA will chelate it to the only polyvalent metal cation present in the

system:  $Cu^{2+}$ . Typically, 150 % of the theoretical maximal equimolarity with regards to copper is used. The excess EDTA and the EDTA-Cu complex have separate retention times of respectively 4.9 and 5.4 minutes, allowing a very precise (reproducibility within 1 ppm) determination of the copper content after calibration of the EDTA-Cu peak (*cf.* Appendices). Here again, all raw data corrections are made with regards to the precise weight of the components, and not their volumes.

The column used is the Zorbax SB-C18 (5  $\mu$ m, 4.6 x 250 mm) from Agilent. It is a reversed-phase column with a non-polar stationary phase requiring a polar mobile phase, hence separating the entities involved according to their hydrophobicity. The mobile phase is made up of freshly prepared aqueous (deionized) solution of 20 mM monobasic ammonium phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) adjusted to pH 2 using 85 % phosphoric acid and filtered. The pH might seem to be a bit extreme for usual RP-HPLC, risking the breaking of the alkyl grafts on the silica, but according to the manufacturer, this column can go down to pH 0.8. It is maintained at a constant 15 °C, the flow rate is 1 mL.min<sup>-1</sup> and the injection volume 20  $\mu$ l.

#### 3.2.4 UV Transmission Measurement

The UV light availability is of great importance to this study and was determined using two different methods. The first one is the standard *ex-situ* use of a CARY 1E UV-Visible Spectrometer. The samples are placed in a little Suprasil<sup>®</sup> quartz-basin with an optical path length of 10 mm and the transmittance measured against pure deionized water by sweeping a pre-determined wavelength-range.

The second method allows a real-time, *in-situ* measurement of the light availability for the whole UV-visible range by using the USB 2000 solid-state spectrometer from Ocean Optics Inc. The light is collected through a cosine-corrected irradiance probe and dispatched out of the reactor through a fiber-optic cable. The light emission being radial, the collector is placed perpendicularly to a lamp, facing it head-on.

# **CHAPTER 4: RESULTS & DISCUSSION**

In this Chapter, the results and discussion of the experimental work are presented. Experiments were done showing the impact of initial pH, the influence of metal cations (in particular cupric ions) and catalyst load. Various experiments were done to corroborate our hypotheses.

#### **4.1 Reactor Characterization (Light Distribution)**

Photocatalytic reactions *per se* require UV light to reach the surface of the catalyst. So the reactor may be well mixed and the catalyst uniformly distributed throughout, but the light has to be available to generate the  $e^{-}/h^{+}$  pairs. The purpose of these experiments was to determine what portion of the catalyst was activated by the lamps. The measures were carried out *in situ* as described in section 3.2.4.

As can be seen in the vertical light distribution on Figure 4.1, there are quite significant variations depending on the vertical position in the reactor, with the maximal emission being close to either end of the lamps. However, as soon as the probe is placed either immediately above or below the lamp, the UV light intensity decreases drastically: this means that the light emission is mostly radial and the zones above and below the lamps can be considered as dead zones. These dead zones accounts for about 25 % of the reactor and cannot be reduced because of space constraints in the lower part of the reactor. The subsequent light distribution measurements were done at a constant distance of 200 mm from the top of the reactor.



Figure 4.1: Vertical light distribution (254 nm ray, 10 mm from lamp)

As can be seen in Figure 4.2, the UV-light availability decreases exponentially with the main catalyst concentration. The measurements below were done specifically for the 254 nm ray, but  $TiO_2$  acts as a very effective filter throughout the whole UV range. There is, however, hardly any noticeable absorption in the visible range.

A point of concern can clearly be seen in Figure 4.3, which uses the same points as Figure 4.2, but interpolates them using the cubical interpolation method and presents them in a more usable way. The catalyst load is on the abscissa and the distance from the lamp ion the ordinate: for any given (x,y) coordinates, the light intensity can be read using the grayscale. *E.g.* at a titania load of 0.04 g/L and at a distance of 5 mm from the lamp,



Figure 4.2: Radial light distribution, log-scale, as a function of catalyst load and at various distances from the lamp

the available 254 nm UV-light will be 3000 units, hence half as much as if there is no catalyst present in the solution. Considering that the scale used in the grey color map is non-linear (cubical variation in grayscale), it is very clear that the overwhelming majority of the reactor is, in fact, in the UV-dark. This is especially true since the typical catalyst load is 2 g/L. As will be shown later, the reaction is dependent on hydroxyl radicals, which have a half-life in water of only 200 ps to 3 ns [75]: so no matter how good the agitation, the reactions will always take place at the surface of the lamps as the catalyst lacks its activator (UV light) anywhere else. Since it was technically not possible to bring the UV-probe any closer than 2 mm to the lamps, the amount of catalyst actually involved in the reaction is not calculable. Hence, the intrinsic reaction rates and the catalyst activity cannot be determined and all rates found in this reactor are specific to this reactor. Nevertheless, as will be seen later, useful mechanistic aspects of the photodegradation can still be deduced from them.



Figure 4.3: Radial light distribution with distance from the lamp and catalyst load (254 nm)

## 4.2 Photocatalytic Oxidation in the Absence of Copper(II)

#### 4.2.1 Feasibility Study

Since the photocatalytic oxidation of glymes in an aqueous suspension of titanium dioxide had never been studied before, the feasibility of the process had to be determined.

To do so, the evolution of the concentrations and total organic carbon contents of diglyme, triglyme and tetraglyme was studied using the default settings of the reactor,

*i.e.* without controlling the initial pH (pH  $\approx$  4.4), nor adding any metal ions to the solution and using a catalyst load of 2 g/L. The results are depicted in Figure 4.4 below, where the full lines are the averages of the 3 experiments. All three started at an initial concentration of 200 mg/L and the TOC is represented in percentage of the initial value, which is slightly different for each glyme as the carbon mass-ratio varies with *n* (where *n* is the number of ethoxy-groups as defined in the generic chemical formula of the glyme family, see Section 2.1). Blank experiments conducted in the dark or by UV irradiation only (no TiO<sub>2</sub>) are not depicted here as nothing happens. Since glymes are completely UV transparent entities, their total inactivity with regards to UV irradiation does not come as a surprise.







It can immediately be seen that this process works, but is not very good, as the reaction is slow (with a half-life of slightly below one hour). Also, the complete mineralization far from being achieved (only about 25% after 3 hours).

### 4.2.2 Mechanism

The fact that there is no difference with the chain length suggests that the initial attack preferentially occurs at a chain-end. If it did not, the following would be observed:

- a faster decrease in concentration with *n*, as more attack-sites would be available (no matter how long the linear chain, there are always only two ends to it)
- a slower decrease in TOC with *n*, as mid-chain breaks would results in bigger first-degree sub-products requiring more steps to reach full mineralization than smaller end-of-chain sub-products would.

Since there is no difference between the three glymes, it can be assumed that focusing on triglyme will give the right insight into the degradation of the lower members of the glyme family from waste waters.

Note also interesting that the TOC starts decreasing as soon as the glymes are being degraded. This implies that the by-products of the degradation are immediately attacked by the PCO as soon as they are formed, confirming the non-selectivity of the process. Later on, in Section 4.3.2.2, it will be shown how correlating this to the TOC evolution found when adding a co-catalyst ( $Cu^{2+}$ ) allows for the deduction of the role of the latter in the mechanism.

#### 4.3 Co-Catalytic Activity of the Cupric Ion

From the literature (Section 2.4) and from previous experiences of the author with the process, it is known that metal ions can have an influence on the degradation rates. They can act either as accelerators or as inhibitors, and hence they offer a potential way to easily accelerate the degradation of triglyme.

# 4.3.1 Identification of $Cu^{2+}$ as Best Reaction Rate Accelerator

Different experiments have been carried out by adding various metal salts ( $Ni^{2+}$ ,  $Co^{2+}$ ,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ) in equimolar quantities with regards to triglyme. In each case, the associated anion is sulfate and the only variable is the nature of the cation. The raw data for those experiments are depicted in Figure 4.5A, where the variation in triglyme concentration is plotted versus irradiation time for the different metal ions. Figure 4.5B allows a better comparison of the impact, by normalizing the initial rates with respect to the reference (no metal ion addition) at 2.4 ppm/min. The data have been obtained by measuring the initial slope in Figure 4.5A.



Figure 4.5A: Identification of  $Cu^{2+}$  as best accelerator (raw data)



**Figure 4.5B:** Identification of  $Cu^{2+}$  as best accelerator (normalized initial kinetics)

Cupric ion clearly stands out as the best accelerator in this category. These results can be related to the influence of ion-metal addition to the PCO of EDTA-Ni as seen in Figure 4.6, where here, once again,  $Cu^{2+}$  was the best possible option. In all the subsequent experiments, cupric ions are added to the studied solution in the form of pentahydrated copper(II) sulfate (CuSO<sub>4</sub>.5H<sub>2</sub>O).



Figure 4.6: Comparison with PCO of EDTA-Ni (metal variation)

4.3.2 Catalytic Properties of  $Cu^{2+}$  (Synergy with PCO)

4.3.2.1 Synergistic Effect

Cupric ion is a known oxidizing agent and a catalyst in liquid phase oxidation reactions [76-84]. As can be seen in the experimental data shown in Figure 4.7, copper(II) alone with UV-light is enough to degrade some of the triglyme. However, the mathematically added effect (curve "c") of the independent reactions due to Cu<sup>2+</sup>/UV (curve "a") and TiO<sub>2</sub>/UV (curve "b") is much less than the degradation found in the TiO<sub>2</sub>/Cu<sup>2+</sup>/UV system (curve "d"). Hence, the acceleration generated by copper is not due to the additive effect of two parallel reactions feeding on the same reactant. Instead, the cupric ions are acting on the PCO itself in a synergistic way. Not shown on the figure for, obvious reasons, is that UV light alone has no effect and that both TiO<sub>2</sub> and Cu<sup>2+</sup> absolutely need to be activated by UV light in order to degrade any triglyme.



Figure 4.7: Identification of the intrinsic effect of  $Cu^{2+}$  on the PCO (no pH control, catalyst load of 2 g/L)

4.3.2.2 Discussion on the Catalytic Effect of the Cupric Ions

There could be four different hypotheses that could potentially explain how cupric ions affect the photocatalytic reaction are proposed.

Firstly, the copper ion could be reduced to its metallic state and partially impregnate the  $TiO_2$  particles [65, 85-88]. This would enhance the photocatalytic activity of the main catalyst by trapping the conductive-band electron [89, 90], reducing the likelihood of electron-hole recombination and making them more readily available to the electron scavenger. However, this would result in a decrease in cupric ion concentration in the bulk solution. This stands in contradiction with the experimental data presented in Figure 4.8, showing the concentration of copper(II) in solution at different contact times with  $TiO_2$ , with or without triglyme added to the system. As the results show, there is no measurable adsorption since the changes are less than 1 %. Note

that the exact same maximum variation of 1 % is found at higher  $Cu^{2+}$  concentrations. Therefore, this hypothesis is discarded.



Figure 4.8: Conservation and non-adsorption of  $Cu^{2+}$  in the active reactor (TiO<sub>2</sub> load of 2 g/L)

Cupric ions could also accelerate the reaction by acting as electron scavenger in parallel to the dissolved oxygen. Since it is now known that there is no decrease in  $Cu^{2+}$  concentration over time, the co-catalyst would need to be regenerated *e.g.* according to the following reactions [59-61, 63, 81]:

$$Cu^{2+} + e_{CB}^{-} \rightarrow Cu^{+}$$
$$Cu^{+} + \frac{1}{2}O_{2} + e^{-} + 2H^{+} \rightarrow H_{2}O + Cu^{2+}$$

However, scavenging implies that adsorption onto the catalyst particle [91-93] has to occur first. Hence the bulk concentration would be lower than what is calculated from the known addition of hydrated cupric sulfate in the known reactor volume: the material balance would show a deficit in copper. As can be seen again in Figure 4.8, this is not the case: the material balance on  $Cu^{2+}$  is respected as it is. Therefore, this hypothesis is discarded [57, 59]. Since the pH also systematically decreases by about 0.1 units over reaction time, the hydronium ion consumption needed for the regeneration is also not very likely.

A third possible hypothesis would be if copper(II) acted through a homogeneous catalysis pathway according to the following reactions [53, 57]:

$$Cu^{2+} + e_{RA}^{-} \xrightarrow{h\nu} Cu^{+}$$
$$Cu^{+} + H_{2}O_{2} \rightarrow Cu^{2+} + HO^{-} + HO^{-}$$

where the electron is not provided by the activated  $TiO_2$ , but by a reducing agent that gets oxidized (triglyme or its degradation sub-products). The hydrogen peroxide required for the cupric ion regeneration would come from the product of the electron-scavenging by oxygen, as was shown in step (v) in Section 2.3. The additional advantage in this is that the regeneration step would also create hydroxyl radicals, which, in turn, would actively degrade the organic pollutants. It is known from Figure 4.7 that the first step definitively happens, but it is also known that UV-light is a pre-requisite for this reaction. Unfortunately, the light-distribution study in the reactor showed that the primary catalyst acts as a filter and the UV-light is only available to the co-catalyst in the first 1-2 mm (or less) away from the lamps. Hence, even if this pathway were to occur, it would have a negligible impact on the overall rates.

Finally, the fourth and last hypothesis will be adopted. It is known that triglyme is an aprotic solvent with linear crown ether properties, *i.e.* it can readily interact with cations and act as a chelating agent. It is also known that, according to the Williams classification [94, 95], for bivalent ions of the first transition series, the stability of OO, NO and NN coordination pattern complexes is

Mn < Fe < Co < Ni < Cu > Zn

irrespective of the nature of the coordinated ligand or the number of ligand molecules involved. This is justified by the cupric ion's large potential for ligand field stabilization, which itself is due to the high energy d orbitals of copper. Consequently, Cu<sup>2+</sup> would be prone to form a stable complex with triglyme. This metal-triglyme complex [34, 59] could be much more favorable to PCO, either for steric reasons by presenting its hydrogen to the attacking oxidizing agent (*cf.* next figure), or by having a lower potential. A possible such Cu<sup>2+</sup>-triglyme is depicted in Figure 4.9, but it has to be stressed here that the exact structure of the complex is not known to the author.



Figure 4.9: Possible Cu<sup>2+</sup>-triglyme complex

This would explain why cupric ion is the best co-catalyst that could be found in Figure 4.5. It also fits neatly with the results from Figure 4.10, where it can be seen that the TOC only starts decreasing once there is very little triglyme is present in the solution. Indeed, in the experiments conducted in the absence of copper as presented in Figure 4.4, there is a simultaneous decrease of the TOC with triglyme. Yet here, the TOC remains constant as long as substantial amounts of triglyme remain in the solution. This means that the Cu<sup>2+</sup>-triglyme complex is so much more prone to be oxidized that its degradation sub-products have to "wait their turn". If Cu<sup>2+</sup> were to influence the PCO in any other way than through the complex formation, then it would affect the rate of the reaction with triglyme as well as the rate of all the other reaction with its products. This would eventually lead to immediate mineralization. Only the complex formation is specific to triglyme.



**Figure 4.10:** Triglyme and TOC evolution with reaction time  $([TiO_2] = 2 \text{ g/L}, [Triglyme]_0 = 200 \text{ ppm}, \text{ pH}_0 = 3.5, [Cu^{2+}]/[Triglyme]_0 = 0.5 \text{ molar})$ 

The above hypothesis of a triglyme- $Cu^{2+}$  complex formation indicates a homogeneous reaction pathway and hence the PCO mechanism involves Fenton-type chemistry and no Photo-Kolbe process (*cf.* Figure 2.2).

## 4.3.3 Optimum Cupric Ion Concentration

Experiments conducted at various  $Cu^{2+}$  concentrations showed that the effect of the cupric ions on the photocatalytic degradation of triglyme is not equally beneficial throughout the concentration range. As can be seen in Figures 4.11 A&B (concentration evolution) and Figure 4.12 (TOC evolution), there is an optimum concentration at half-equimolarity with respect to triglyme.



Figure 4.11A: Influence of Cu<sup>2+</sup> concentration (raw experimental data)

Figure 4.11B is a 2D projection of the interpolated data from Figure 4.11A. Reaction time is found on the abscissa and the cupric ion concentration on the ordinate. The remaining quantity of triglyme after  $\mathcal{T}$  minutes reaction time when  $\mathcal{U}$  Cu<sup>2+</sup> is present in the reactor can be read by relating the color found at the ( $\mathcal{T}$ ,  $\mathcal{U}$ ) coordinates to the provided linear grayscale colormap. For example, after 20 minutes irradiation time at equimolar [Cu<sup>2+</sup>] and triglyme concentration (*i.e.* 100 %), only 25 % of the initial triglyme remains in the solution.



Figure 4.11B: Optimum Cu<sup>2+</sup>/triglyme ratio (concentration)

This allows a clear separation of the  $[Cu^{2+}]$  domain into two zones: Zone A, where the triglyme degradation rate increases with the increase of cupric ions; and Zone B, where the opposite happens. The optimum cupric ion concentration is where the kinetics are at their fastest, at the threshold between the two zones. The same zones can of course be found in Figure 4.12 as well.



Figure 4.12: Optimum Cu<sup>2+</sup>/triglyme ratio in terms of TOC

The effect in Zone A can be easily explained: the more co-catalyst is added to the system, the faster the reactions occur. The decreased co-catalytic activity at higher concentration in Zone B has been reported in the literature (Table 2.4) but not explained to satisfaction. In this study, this decrease can be explained by the absorption of UV light by the cupric ions. As can be seen in Figure 4.13, every 10 ppm increment in Cu<sup>2+</sup> results in a decrease of available UV light by 4.5 % (linear Beer-Lambert absorption). These data were obtained using the method described in Section 3.2.4. This only affects the 254 nm ray, which is the driving force behind the main catalyst's activation. All the other wavelengths are hardly affected: their transmittance decreases by only 4.5 % after addition of 120 ppm of cupric ions. At the optimum concentration of 36 ppm, there is already a decrease in available light by 16 % at the point of measurement. Since the Beer-Lambert law binds the transmittance not only linearly to the concentration, but also to the distance traveled by the light, the results in Figure 4.13 do not imply that no light is available at [Cu<sup>2+</sup>] = 220 ppm and that the PCO stops! It just implies that, in fact, the

more co-catalyst is introduced to the system, the less primary catalyst participates in the photodegradation.



Figure 4.13: Influence of  $[Cu^{2+}]$  on light availability (*in situ* measurements in proximity of the lamps)

This explanation would allow reconciling the apparently contradictory reports found in the literature: as has been shown in Chapter 2 (Table 2.4), some research groups report the beneficial impact of cupric ions (Zone A), while other groups find it to have an inhibiting effect on the photocatalytic oxidation (Zone B and beyond). Data obtained from work previously done by the author regarding the PCO of EDTA are in accord with the above as well: as can be seen in Figure 4.14,  $Cu^{2+}$  initially has a very great impact on the degradation kinetics, but the effect is dampened when higher concentrations of the co-catalyst are used. This shows that the decrease in co-catalytic activity is due to the interaction of  $Cu^{2+}$  with light alone, and not to some other possible auto-inhibiting effect of *e.g.* the  $Cu^{2+}$ /triglyme complex.



*Figure 4.14:* Comparison with PCO of EDTA-Ni ([Cu<sup>2+</sup>] variation)

#### 4.4 Influence of the pH

As can be seen in Figures 4.15 A&B (triglyme concentration evolution) and Figure 4.16 (TOC at 120 min reaction time), there is also an optimum initial pH at 3.5. Figure 4.15B is to be read exactly like the previous figures of the same type. In point of fact, there is a plateau between 3 and 3.5. Even so, since the overall process (PCO, preand post-treatments) is dedicated to waste water treatment, the higher value is chosen as optimum operational condition. It would be counter-productive to lower the pH by more than absolutely necessary: the more acid is added pre-PCO, the more base will be necessary to neutralize it post-PCO.



Figure 4.15A: Influence of the initial pH on [triglyme] evolution: raw experimental data ( $[TiO_2] = 2 \text{ g/L}$ )



Figure 4.15B: Influence of the initial pH on [triglyme] evolution: interpolated data



Figure 4.16: Influence of the initial pH on TOC evolution at 120 min

No degradation takes place at pH 5 and above for two reasons. Firstly the surface of the catalyst is negatively charged; hence an electrostatic repulsion of the electron-rich triglyme takes place and blocks the initial oxidation. Also hindering the PCO is a decrease in UV light (254 nm) transmission by the cupric ion co-catalyst, lowering the photo-activation of the main catalyst (*confer* Figure 4.17). In very alkaline conditions,  $Cu^{2+}$  precipitates out. This results in an increase of the opacity of the solution even more and the decrease of the co-catalytic effect.

The low PCO rates at very low pH also have two separate explanations. In those conditions, the UV-transmission of cupric ion is decreased as well, as can been seen in Figure 4.17. Secondly, as has been pointed out earlier in Chapter 2, the water-to-hydroxyl radical conversion decreases with the lowering of the pH due to the abundance of hydronium groups on the surface which interfere with the transfer of holes to the adsorbed water.



Figure 4.17: Cu<sup>2+</sup> light absorption as a function of pH

However despite what could be deduced at first glance, the above reasoning, which involves non-adsorption of triglyme onto titania at higher pHs, is not in accordance with the Photo-Kolbe process. As can be seen in the Figure 4.18, no actual adsorption takes place at any triglyme concentration and exposure time: the material balance is within experimental error (less than 1 %) and respected throughout, no matter what triglyme concentrations are being tested. Both potential mechanisms necessitate an extreme closeness of the triglyme to the  $TiO_2$  and Figure 4.18 shows that the photocatalytic oxidation, in this case, involves Fenton-chemistry and no Photo-Kolbe process.



Figure 4.18: Non-adsorption of triglyme onto TiO<sub>2</sub>

### **4.5 Kinetic Measurements**

## 4.5.1 Effect of TiO<sub>2</sub> Concentration

As has been pointed out previously, the measured kinetics cannot be used to design a reactor. This is due to the huge dark zones (*i.e.* dead zones) in the reactor, as shown in Figure 4.3, making it impossible to calculate any proper catalyst activity. The Figures 4.19 A&B below, representing the observed initial oxidation rates as a function of the catalyst load, confirms the finding from Figure 4.3: above 0.2 g/L of TiO<sub>2</sub>, the reaction is surface-bound to the quartz sleeves because of the UV-light availability restriction and, hence, increasing the load in the bulk does not affect the kinetics.



Figure 4.19A: Influence of the [TiO<sub>2</sub>] load



Figure 4.19B: Global rates as a function of TiO<sub>2</sub> (based on Figure A)

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#### 4.5.2 Rate Laws

It is however possible to derive the interfacial charge-transfer mechanism from the observed kinetics. To do so, it is feasible to draw on the fact that the compulsory adsorption of triglyme onto the catalyst in the case of the Photo-Kolbe process would induce a Langmuir-Hinshelwood-type kinetic law:

$$r = \frac{Kk_1C(t)}{1+k_1C(t)} \quad \text{where } C(t) = [Triglyme]$$

This integrates and simplifies by using the boundary conditions into the function given below:

$$C(t) = \frac{1}{k_1} LambertW\left\{k_1 e^{\left[Kk_1 t + \ln(C_0) + k_1 C_0\right]}\right\}$$

Where *LambertW* is the principal branch of the solution to Lambert's transcendental equation  $x = ye^{y}$  [96], the Excel-macro of which can be found in the appendices.

Now, this adsorption is not necessarily a pre-requisite for the charge-transfer based on Fenton-Chemistry (Section 2.3). Thus, if the experimental kinetic law can be related to a simple kinetic law as stated below, then the interfacial charge-transfer reaction cannot be of the Photo-Kolbe type and hence is by default of the Fenton-Chemistry type.

 $r = kC^{\alpha}$ 

This integrates into:

$$C(t) = \left[C_0^{(1-\alpha)} - k(1-\alpha)t\right]^{\left(\frac{1}{1-\alpha}\right)}$$

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:	Langmuir-Hinselwood	Simple law
-	K = 11.381	k = 2.326
	$k_1 = 2.60 \text{E-}2$	$\alpha = 0.260$
Average		
model/experimental	2.8 %	2.2 %
data difference over	-	
10 min		
Median		
model/experimental	1.6 %	0.9 %
data difference over		
10 min		

Table 4.1:Kinetic law determination and constantsdetermination (Concentration in ppm, time in minutes)

Using the two parameters for each kinetic law as variables, MS-Excel's built-in Solver minimizes the difference between experimental data and estimated results for experiments at optimum conditions with an initial triglyme concentration ranging from 100 to 600 ppm.

As can be seen from the results in the Table 4.1 above, both laws give good quality results: if anything, the simple law seems to be a better fit than the Langmuir-Hinshelwood law. Nevertheless, the  $k_1$  coefficient in the latter is very small, hence, minimizing the impact of the auto-inhibition due to the adsorption constraint. Note that after 10 min or so, the kinetic fit breaks down completely. This is to be expected in a system with multiple reactions feeding off a common reagent (HO').

The kinetic measurements show that, yet again, the interfacial charge-transfer mechanism is using a Fenton-Chemistry pathway involving hydroxyl radicals and not a Photo-Kolbe process involving direct oxidation of the organic pollutant by the holes.

#### 4.6 Catalyst and Co-Catalyst Recycling

According to the maxim that everything added to the system has to be taken out of it eventually so as to not simply eliminate one type of water pollution by replacing it by another, both catalysts used in the present PCO process have to be easily removable. Making them recyclable would even add more value to the process.

Titanium dioxide is not affected by the reaction and is a solid in form of particles whereas all other components are in the aqueous phase. Adding an organic polymer as a binder would not be the preferential method chosen here to enhance the solid-liquid separation because it would involve yet another polymer-titania separation step before the catalyst can be recycled. It is, at any rate, extremely easy to filter it out of the system and/or let it sediment and then separate it by using a filtrating hydrocyclone [97] or by cross-flow microfiltration [73].

Removing the co-catalyst from the system involves an additional step since it is soluble in the process conditions. According to the national primary drinking water standards (U.S. EPA), the maximum contaminant level goal (MCLG) for copper in the US is 1 ppm.

Cupric cations combine with hydroxide anions and precipitate out in alkaline conditions, which is quite fortunate as it allows for an easy separation:

$$Cu^{2+}_{(aq)} + 2HO^{-} \rightarrow Cu(OH)_{2}$$
 (solid)

The solubility of copper hydroxide between pH 8 and 11 is 400 ppb [98]. Quantitative HPLC measurements have been taken on a solution containing 100 ppm of  $Cu^{2+}$  at pH 3.5. When the pH was set to 8, the bulk concentration of cupric ions after filtration was below the 1 ppm detection limit and could be fully regenerated to its initial value after acidifying the solution again.

This implies that the catalyst (TiO<sub>2</sub>) and the co-catalyst (Cu<sup>2+</sup>) can both be added and removed from the system using a single-step separation: post-degradation the pH is set to 8 and the solution filtered, the solid TiO<sub>2</sub> and Cu(OH)<sub>2</sub> being then reused by adding them to the new waste water feed. Setting the pH to the optimum value of 3.5 liberates the cupric ions again. pH 8 is optimum for the recycling procedure because that is the pH value where the copper solubility is as its lowest and the particle size at its highest [73].

# **CHAPTER 5: CONCLUSIONS & RECOMMENDATIONS**

Photocatalytic oxidation using a suspension of titanium dioxide can be used to clean glyme-contaminated waste waters, at the very least, as a preliminary process (break-up of the refractory moiety) followed by, *e.g.*, bio-treatments. It is the only known process for large-scale glyme decontamination.

Cupric ion has been found to act as a very good co-catalyst by forming a more reactive complex with triglyme. Similar to titanium dioxide, it is a *true* catalyst, *i.e.* it remains completely unaffected by the process. The interfacial charge-transfer goes through the activation of adsorbed water by photogenerated migrating valence-band holes, thereby creating hydroxyl radicals. The oxidation of the pollutant is due to the attack – according to Fenton chemistry – of the latter at the triglyme end-of-chain in its complex with  $Cu^{2+}$ . Non-adsorption of the players and non-Langmuir-Hinshelwood kinetic laws point towards the non-implication of the Photo-Kolbe process involving direct triglyme oxidation.

The optimal pH should be set to 3.5 and the optimal cupric ion concentration is the  $\frac{1}{2}$ -equimolar quantity with respect to triglyme. This results in an 84 % decrease in triglyme half-life to 7.5 minutes, down from 55 minutes in control conditions (no copper, no pH control, 2 g/L catalyst load, and initial triglyme concentration of 200 ppm). The lowering of the degradation at higher pH is due to the adverse electronic surface properties of titania and to the lowering of the UV-light transmittance by the cocatalyst. In very acidic conditions, the opacity of cupric ions with regards to the 254 nm wavelength is on the rise again, while the interfacial charge-transfer is hindered as well. The detrimental effect of high Cu<sup>2+</sup> concentrations is due to its classic Beer-Lambert absorption of the titania-activating UV-light. The degradation products were not readily determinable in this study. Nevertheless, at high enough residence time, a high degree of mineralization can be reached: 62 % after 2 hours. The exact nature of those degradation products needs to be determined and biodegradability ascertained.

Recycling of  $Cu^{2+}$  and  $TiO_2$  is straightforward. It involves the post-process precipitation of copper by increasing the pH to an optimum of 8, followed by a single-step solid/liquid separation process. Both catalysts can then be reused by adding them to the waste water feed and lowering the pH to 3.5 again.

The important UV-light absorbance by the catalyst clearly makes the reactor design inappropriate for the process. Alternative methods need to be studied, such as immobilization of  $TiO_2$ . This would however bring up the problem of getting the pollutant into contact with the catalyst. Another option would be an array of annular reactors design of just a few millimeters thickness, with a UV source at their cores and a cooling system on their outer edges. Static mixers either within the annular space or at discrete intervals would assure the mixing. The main hurdle for this type of reactor would be the pressure loss due to the very narrow space in which the water needs to be pumped.

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## **APPENDIX A:** HPLC





Typical result graph:





## **APPENDIX B:** Light emission spectrum of the UV lamps.



APPENDIX C: Optical fiber transmission.

## APPENDIX D: LambertW macro.

Public Function LambertW R(ByVal X As Double, ByVal Digt As Integer)

```
' computation of an inital guess
  If X < -1 / Exp(1) Then
  LambertW R = Error(1)
   Exit Function
   ElseIf X < -0.26 Then
   p = Sqr(2\# * (Exp(1\#) * X + 1))
   Wx = -1\# + p - p^{2}/3\# + 11\#/72\# * p^{3}
  ElseIf X < 0.37 Then
   Wx = X - X^{2} + 3\# * X^{3} / 2\# - 8\# / 3\# * X^{4}
  ElseIf X < 2 Then
   Wx = 0.0979767105 + 0.5764369031 * X - 0.1072703232 * X ^ 2
  Else
   sigma = 1\# / Log(X)
   tau = Log(Log(X)) * sigma
   Ltau = -Log(1\# - tau)
   Wx = (1\# - tau) / sigma + Ltau - Ltau * sigma / (1\# - tau + sigma)
  End If
'iterative solver
  Ewx = Exp(Wx)
  Residu = Wx * Ewx - X
  Precis = 1\# / (10\# ^ Digt)
  I = 0
  Do While Abs(Residu) > Precis
    I = I + 1
    Wx = Wx - \text{Residu} / ((Wx + 1\#) * Ewx - 0.5 * (Wx + 2\#) * \text{Residu} / (Wx + 1\#))
    Ewx = Exp(Wx)
    Residu = Wx * Ewx - X
    If I > 1000000 Then
    LambertW R = Error(1)
```

End If

Loop

' final value LambertW\_R = Wx End Function

**Exit Function** 

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