Effects of the Parameters Temperature, Iron Concentration and Irradiation on the Reaction Rate of the Photo-Fenton Process using Alachlor as a Model Compound

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Effects of the Parameters Temperature, Iron Concentration and Irradiation on the Reaction Rate of the Photo-Fenton Process using Alachlor as a Model Compound

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Abstract

Pesticide waste waters contain organic compounds which are recalcitrant to biological treatment and furthermore toxic in most cases. So they usually are not treated sufficiently. The CADOX project is developing a treatment for these waste waters by Advanced Oxidation Processes (AOP) to diminish their toxicity and make them applicable for biological treatment. In the present work the effects of iron concentration, temperature and illuminated reactor area on the reaction rate of the photo-Fenton process, an AOP applied to the waste waters within the CADOX project, were investigated.

In experiments made previously to determine the ideal pH for the degradation experiments it was found out that most of the added iron precipitates at a pH higher than 2.8 so that photo-Fenton experiments had to be performed at a lower pH. In experiments using Alachlor as a model compound the reaction rate varied from a necessary equivalent illumination time at 30W (t_{30W}) of less than 5 minutes in the fastest experiments to t_{30W} of 190 minutes in the slowest one for degrading 50% of the total organic carbon (TOC). Alachlor was degraded completely in all cases. Further experiments with a mixture of five different pesticides in distilled water and simulated tap water were carried out. These proved that the added salts did not have significant effects on the reaction rate. All pesticides could be degraded completely. A cost estimation of the treatment based on assumptions was performed, taking into account the major factors. The costs were estimated below 5 Euro per m³ waste water at realistic pesticide concentrations and so reasonable in relation to pesticide prices.

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1.4 Index of Abbreviations

A	area – reactor surface
AOP	advanced oxidation process
С	concentration
°C	degree Celsius
cm	centimetre
CPC	compound parabolic collector
conc.	concentration
e.g.	"exempli gratia" - for example
eq.	equation
et al.	"et alteri"- and collaborators
EU	European Union
g	gram
h	hour
HPLC	high performance liquid chromatograph
I	intensity
i.e.	"id est" – that is
IC	inorganic carbon
IPPC	Integrated Pollution Prevention and Control
L	litre
mAU	milli absorption unit
m²	square meter
mg	milligram
mL	millilitre
mM	millimolar
μm	micrometer
mS	milli Siemens
μS	micro Siemens
Ν	normal
ORP	oxidation reduction potential
рН	"potentia hydrogenii" – pH value
PSA	Plataforma Solar of Almería
SHE	standard hydrogen electrode
t	reaction time
Т	temperature
t _{30W}	standardised reaction time
TOC	total organic carbon
UV	ultraviolet
V	Volt
VS.	versus
VV	Watt
WFD	Water Framework Directive

2 Introduction

2.1 Water

Water is a pre-requisite for life and a key resource of humanity. Of the abundant water on earth 97.5 % are salt water. Of the remaining 2.5 % of fresh water 70 % are frozen in the polar caps, the rest is mainly present as soil moisture or in inaccessible sub-terraneous aquifers. The remaining 1 % of the world's fresh water resources, which is available for use, is very unevenly distributed [University of Michigan, 2002].

On the "blue planet" nearly 1.1 billion people still remain without access to improved sources of water, and about 2.4 billion have no access to any form of improved sanitation. As a consequence, 2.2 million people in developing countries, most of them children, die every year from diseases associated with lack of safe drinking-water, inadequate sanitation and poor hygiene [WHO and UNICEF, 2000].

Compared to less rich regions water supply and sanitation in the EU are fairly well developed. Nevertheless varying contamination and regional problems exist. Furthermore, health and other malevolent effects of many substances present in water are still uncertain and lack investigation. EU legislation takes into account increasing knowledge and adapts EU law in force to protect and improve the quality of Europe's fresh water resources. The most recent adaptation was the European Water Framework Directive (WFD) [European Comission, 2000a].

To fulfil its goals pollutant sources have to be identified and appropriate treatment strategies have to be applied to diminish contamination and thereby environmental risks throughout the EU.

2.2 Pesticides

The increase in production and use of chemical products in the last century led to a growing preoccupation about the effect which these products might have on terrestrial and aquatic ecosystems. Due to their chemical characteristics the pesticides in most cases are persistent pollutants that resist in variable degree the photochemical, chemical and bio-chemical degradation, so they can have a high life time in the environment. [Albert, 1998; Hayo and van der Werf, 1996; Tomlin, 1994]. Synthetic pesticides have been applied routinely in agriculture during the last 50 years. Due to the

indifferent use of these substances in the past residues of them can be found in the environment, which possibly can be a danger for public health [Bandala et al., 1998]. Actually, residues of pesticides have been found in all environmental mediums (air, water and soil) and in all geographic regions, including those, that are very remote from their original place of disposal, such as oceans, deserts and polar zones. They can be bio-accumulated and bio-magnified through the food chain. Due to that they could be found in different tissues and secretions of humans, including inhabitants of very isolated regions.

Reports of the United Nations estimate that of all the pesticides used in agriculture less than 1% enters the cultivated plants. The rest of them enters the soil, the air, or principally the water. Most of these pollutants have very long half-life times in the soil. This results in a great problem of accumulation with non-predicable consequences in the near future. Despite all those problems the sale of these substances keeps rising, especially in the developing countries. In 1996 pesticides for 33 billion dollars were sold, of which more than 70 % are consumed in development countries. [AEPLA, 2001].

The main sources of water contamination by pesticides are listed in Table 2-1. To avoid impact on human health and the environment these wastewaters need to be treated by adequate technologies. [Chiron et al., 1997 and 2000]

Source	resulting concentration
Agricultural application of pesticides	10µg/L
Waste waters from washing pesticide containers or application equipment	10-100µg/L
Waste waters from agricultural industries	10-100µg/l
Waste waters from pesticide producing industries	1-1000µg/L

Table 2-1: Main Sources of water contamination by pesticides [Chiron et al. 1997 and 2000]

2.3 Legal Framework of the EU

Water pollution is not only a problem of developing countries. In the EU the environmental damage caused by chemical substances are still far from being under control, although much progress has been made since the first European directive in 1975. An estimated 20% of all surface water in the EU is seriously threatened with

pollution. Besides, groundwater supplies around 65% of all European drinking water. Consequently, human health is threatened by high concentrations of pesticides, chlorinated hydrocarbons (i.e. NBCS), nitrates, heavy metals and hydrocarbons [EEA, 1998].

The Water Framework Directive (WFD), adopted in October 2000 [European Comission, 2000a] Article 16 contains a legal framework and methodological basis for the prioritisation of substances. According to the WFD, the Commission `shall submit a proposal setting out a list of priority substances selected amongst those which present a significant risk to or via the aquatic environment`. Following expert discussions, the Commission has proposed [European Commission, 2000b, p.74] a list of 32 Priority Substances (PS) of special importance. The proposed substances should be subject to emission controls at the Community level in order to achieve a `progressive reduction of discharges, emissions and losses`.

2.4 Objectives of this Work

This work was carried out as a part of the CADOX project at Plataforma Solar de Almería (PSA). The aim of this project is to make waste water containing biorecalcitrant compounds suitable for biological treatment by treatment with Advanced Oxidation Processes (AOP). The task of the present work was to analyse how the reaction rate of the photo-Fenton process depends on varying parameters such as concentration of reactants and solar irradiation using Alachlor as a model compound. These data are important for process optimisation and thereby cost reduction. A series of experiments on precipitation of iron was performed in the laboratory to determine the ideal pH for the experiments to be realised in the reactor. To choose the process parameters to be varied a series of experiments with 4-Chlorophenol, a well investigated model compound, has been carried out. Based on these preliminary results photo-Fenton process parameters on different target parameters (such as total irradiation time or equivalent irradiation time at 30 W (t_{30W}) needed to decrease 50% or 90% of the initial Total Organic Carbon).

3 Theoretical Background

3.1 Advanced Oxidation Processes (AOP)

Wastewater treatment usually has one of the two following objectives. First to make wastewater fulfil the demands of legal boundary limits concerning its disposal to a stretch of running water or to another wastewater treatment plant, or second to make it suitable for its use in a following revalorization process.

The main causes of surface water and groundwater contamination are industrial discharges (even in low quantities), excess use of pesticides, fertilisers (agrochemicals) and landfilling domestic wastes. The wastewater treatment is based upon various mechanical, biological, physical and chemical processes. In fact, this is a combination of many operations like filtration, flocculation, sterilisation or chemical oxidation of organic pollutants. After filtration and elimination of particles in suspension, the biological treatment is the ideal process (natural decontamination). Unfortunately, not all organic pollutants are biodegradable. Effort has been put in the decontamination of water concerning the treatment of these compounds with Advanced Oxidation Processes (AOP) [Peñuela and Barceló; 1998; Chiron et al. 2000]. Above methods rely on the formation of highly reactive chemical species, which degrade the more recalcitrant molecules into biodegradable compounds. These processes although making use of different reacting systems [Legrini et al. 1993, Venkatadri and Peters 1993, Rajeshwar 1996, Prousek 1996, Andreozzi et al. 1999] are all characterised by the same chemical feature: production of OH radicals (OH) with an oxidation potential of 2.8 V vs. SHE. They attack most of the organic molecules with rate constants usually in the order of 10⁶ to $10^9 \text{ M}^{-1} \text{ s}^{-1}$ yielding in the end CO₂ and inorganic ions. They are also characterised by a little selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOPs is also enhanced by the fact that they offer different possible ways for hydroxyl radicals production, thus allowing a better compliance with the specific treatment requirements. The reactions by which hydroxyl radicals attack organic molecules are hydrogen abstraction, electrophilic addition, electron transfer and also radical-radical reactions [Legrini et al., 1993]. The most common methods of hydroxyl generation in AOPs are presented in Table 3.1.

	Method	Key reaction	Light
			necessary
(3.1)	UV/ H ₂ O ₂	$H_2O_2 + hv \rightarrow 2 \text{ OH}^*$	<u>λ</u> < 310 nm
(3.2)	UV/ O ₃	$O_3 + h\nu \rightarrow O_2 + O(^1D)$	<u>λ</u> < 310 nm
(3.3)		$O(^{1}D) + H_{2}O \rightarrow 2 OH^{-1}$	
(3.4)	UV/ H ₂ O ₂ / O ₃	$O_3 + H_2O_2 + hv \rightarrow O_2 + OH + OH_2$	<u>λ</u> < 310 nm
(3.5)	UV/TiO ₂	$TiO_2 + hv \rightarrow TiO_2 (e^- + h^+)$	<u>λ</u> < 380 nm
(3.6)		$TiO_2(h^+) + OH_{ad} \rightarrow TiO_2 + OH_{ad}$	
(3.5)	UV/H ₂ O ₂ /TiO ₂	$TiO_2 + hy \rightarrow TiO_2 (e^- + h^+)$	<u>λ</u> < 380 nm
(3.6)		$TiO_2(h^+) + OH_{ad}^- \rightarrow TiO_2 + OH_{ad}^-$	
(3.7)		$H_2O_2 + e^- \rightarrow OH^- + OH^-$	
(3.5)	UV/S ₂ O ₈ ²⁻ /TiO ₂	$TiO_2 + hy \rightarrow TiO_2 (e^- + h^+)$	<u>λ</u> < 380 nm
(3.6)		$TiO_2(h^+) + OH_{ad} \rightarrow TiO_2 + OH_{ad}$	
(3.8)		$S_2O_8^{2-}$ + $e^- \rightarrow SO_4^{}$ + SO_4^{2-}	
(3.9)	H_2O_2/Fe^{2+}	$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^-$	
	Fenton-Reaction		
(3.9)	UV/ H ₂ O ₂ / Fe ²⁺	$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^-$	
(3.10)	photo-Fenton	$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + H^+ + OH^-$	<u>λ</u> < 580 nm
	reaction		

Table 3-1: Hydroxyl generation in different AOPs [Bauer et al., 1999; Blanco et al., 2000;Legrini et al., 1993]

The use of AOPs for wastewater treatment was studied extensively [Feng and Nansheng, 2000; Legrini et al., 1993; Safarzadeh-Amiri et al., 1996]. As can be seen from Table 3-1 for all reactions apart from the Fenton-Reaction irradiation is needed. Production of UV radiation by lamps is expensive. Therefore investigation is focusing more and more on the two AOPs, which can be powered by solar irradiation, i.e. light with a wavelength greater than 300 nm, homogeneous catalysis by the photo-Fenton reaction and heterogeneous catalysis by the UV/TiO₂ process, with and without addition of oxidants [Bauer et al., 1999; Malato et al., 2002]. Although the interest of

investigation just as of companies is growing, few applications at industrial scale are known yet.

3.1.1 Photo-Fenton

The oxidising effect of Fenton's reagent was already known at the end of the 19th century [Fenton, 1894], but its application for wastewater treatment was not reported until the sixties of the 20th century. In the meantime many authors have reviewed the Fenton method and the photo-Fenton method [e.g. Feng and Nansheng., 2000; Safarzadeh-Amiri et al., 1996; Walling, 1975; Zepp et al., 1992]. The following introduction is based mainly on the review from Safarzadeh-Amiri.

Iron is the second most abundant metal and the fourth most abundant element on earth. In water it is present as ferric or ferrous ions, which are complexed by water and hydroxyl ions, depending on pH. Iron is almost omnipresent in small concentrations, in aquatic and surface water as well as in clouds. Equations 3.11 - 3.13 are therefore thought to be responsible for the formation of hydrogen peroxide in aquatic and surface waters, which plays an important role in the auto purification of those water bodies.

- $(3.11) \qquad Fe^{2+} + O_2 \longrightarrow Fe^{3+} + O_2^{-\bullet}$
- $(3.12) O_2^{-\bullet} + H^+ \longrightarrow HO_2^{\bullet}$
- $(3.13) \qquad HO_2^{\bullet} + Fe^{2+} + H^+ \longrightarrow H_2O_2 + Fe^{3+}$

Some essential reactions occurring in an aqueous solution of iron and hydrogen peroxide are represented in the equations 3.9 and 3.14 - 3.19. If organic substances are present, the reaction scheme becomes more complex as they can react in a manifold way yielding organic radicals, which participate further in the reactions. Applying hydrogen peroxide and iron to oxidise organic matter is referred to as the Fenton's method in wastewater treatment.

 $(3.14) Fe^{3+} + H_2O_2 \iff Fe(OOH)^{2+} + H^+$

$$(3.15) \qquad Fe(OOH)^{2+} \longrightarrow Fe^{2+} + HO_2^{\bullet}$$

- (3.9) $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$
- $(3.16) Fe^{2+} + HO_2^{\bullet} \longrightarrow Fe^{3+} + HO_2^{-}$
- $(3.17) \qquad OH^{\bullet} + H_2O_2 \longrightarrow H_2O + HO_2 \cdot$

 $(3.18) Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + O_2 + H^+$

 $(3.19) Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^{-}$

Nevertheless applying Fenton's method has some drawbacks. The regeneration of ferric iron is slow. By applying irradiation the photo-Fenton reaction takes place (Eq. 3.10), which accelerates the overall reaction rate by closing the catalytic cycle of Fenton and photo-Fenton reaction faster (Eq. 3.9 and 3.10). This results in the advantage that another highly reactive hydroxyl radical is produced without consumption of hydrogen peroxide. Equation 3.10 has the highest reaction rates with $Fe(OH)^{2+}$, which is the predominant ferric ion species at pH from 2.5 to 3. This pH region is therefore the most effective one for the photo-Fenton method.

Although above reactions are reported, in which ferric iron is transformed again into ferrous iron (Eq. 3.15 and 3.18), ferric iron is known to form in the dark stable complexes especially with carboxylic acids. This can completely stop the reaction in the dark. Under irradiation these complexes are able to photolyse yielding organic radicals (Eq. 3.20), with carboxylic acids decarboxylation takes place (Eq. 3.21). The reaction is a ligand-to-metal charge-transfer reaction (LMCT) where the activating energy is provided by the incident photon.

$$(3.20) \qquad [Fe^{3+}L] + hv \longrightarrow [Fe^{3+}L]^* \longrightarrow Fe^{2+} + L^\bullet$$

$$(3.21) \qquad [Fe^{3+}(RCO_2)] + hv \longrightarrow [Fe^{3+}(RCO_2)]^* \longrightarrow Fe^{2+} + CO_2 + R^\bullet$$

Equations 3.20 and 3.21 are also relevant in atmospheric chemistry and surface waters and are believed to be partly responsible for the auto-purification capacity of these systems.

 $(3.22) R^{\bullet} + O_2 \to RO_2^{\bullet}$

 $(3.23) \qquad RO_2^{\bullet} + H_2O \rightarrow ROH + HO_2^{\bullet}$

Another important factor is the participation of oxygen in the process (Dorfman mechanism, Eq. 3.22 and 3.23), which can lead to formation of hydrogen peroxide. As already mentioned, AOPs and therefore also the photo-Fenton reaction can mineralise almost all organic pollutants completely. The photo-Fenton method has the advantage that it has high reaction rates and can be powered by sunlight. Furthermore hydrogen peroxide is a cheap oxidant compared for example to persulphate. The commonly mentioned disadvantage of the photo-Fenton method is the necessity to work at low pH (in literature normally a pH below 4 is considered to be necessary), because at higher

pH ferric ions would begin to precipitate as hydroxide. Furthermore, the added iron has to be removed after the treatment.

3.2 The CADOX project at the Plataforma Solar de Almería (PSA)

PSA (a large European scientific installation and the largest European laboratory for solar energy applications) is actively participating in demonstrative applications, both at national and international level, of solar technology [Plataforma Solar de Almería, 2003]. PSA is exploring innovative uses of our oldest renewable source of energy, solar energy, to drive photochemical processes since early 1990s. One of the applications in which PSA has been deeply involved is solar detoxification with the use of solar photons to degrade hazardous toxic compounds in water by photocatalytic processes. Although scientific research on these processes has been conducted for at least the last three decades [Blake, 1994,1995, 1996, 1999 and 2001], industrial/commercial applications, engineering systems and engineering design methodologies have only been developed recently [Blanco et al. 2000]. The experience acquired on solar detoxification systems at engineering level, particularly through EU projects, led to the development and installation of different pilot plants with different collector fields [Plataforma Solar de Almería, 2003] at PSA, which have been used successfully by many European Research Institutions.

One of the projects being carried out at the PSA is CADOX (A Coupled Advanced Oxidation-Biological Process for Recycling of Industrial Wastewater Containing Persistent Organic Contaminants, EU 5th Framework Programme, Contract No EVK1-CT2002-00122). Between the above mentioned 32 Priority Substances, CADOX Project will focus on decontaminating wastewaters containing pesticides (Alachlor, Atrazine, Chlorfenvinphos, Diuron, Isoproturon, Lindane and Pentachlorophenol) and non-biodegradable chlorinated solvents (NBCS) (Dichlorethane, Dichlormethane and Chloroform). The source of these substances is usually industrial wastewater containing them at low-medium concentration [Plataforma Solar de Almería, 2003]. Due to the lack of available on site treatment technologies, a large quantity of the industrial activities included in Annex I of the Integrated Pollution Prevention and Control (IPPC) Directive are not treating these wastewaters appropriately. As a consequence, simple, low cost and at hand technologies are needed [European Commission, 1998a].

Advanced Oxidation Processes are characterised by the generation of highly oxidative radicals that can oxidise almost any organic substance. But although everybody recognises the strong potential of AOP for PS-containing wastewater treatment, it is also well known that operational costs of these AOP for the total oxidation of hazardous organic compound remains relatively high compared to those of biological treatment. However, their use as a pre-treatment step for the enhancement of the biodegradability of wastewater containing recalcitrant compounds can be justified if micro-organisms in a biological treatment readily degrade the intermediates resulting from the reaction. Therefore, the coupling of AOPs and biodegradation has a great advantage over either treatment alone in the remediation of organic contaminants. This project will create and demonstrate a new technology (CADOX technology) that could reduce substantially the treatment costs of wastewater containing PS.

4 Materials and Methods

4.1 Analytics

4.1.1 Reagents used

Table 4-1: Reagents used for experiments on iron precipitation and photo-Fenton treatment

Product	Company
H ₂ O ₂ 30% w/v PRS	Panreac
Iron(II)sulphate 7-hydrate PRS	Panreac
Iron(III)nitrate 9-hydrate PRS	Panreac

Table 4-2: Chemicals used for pH adjustment

Product	Company
Nitric acid 65 % p.a.	Merck
Sulphuric acid 96% p.a.	Panreac

Table 4-3: Chemicals used for waste water analytics

Product	Company
1,10-Phenantroliumchloride p.a.	Merck
L(+)-Ascorbic acid p.a.	Merck
Sodium thiosulphate 5-hydrate p.a.	Merck
Potassium iodide p.a.	Panreac
Zinc iodide starch solution p.a.	Merck
Ammoniumacetate p.a.	Panreac
Acetic acid 96% p.a.	Merck

Product	CAS number	purity	company	grade
4-Chlorophenol	106-48-9	98%	Merck	PRS
Alachlor	15972-60-8	95%	Aragonesas Agro S.A.	technical
Atrazine	1912-24-9	95%	Ciba-Geigy	technical
Clorfenvinphos	470-90-6	93.2%	Aragonesas Agro S.A.	technical
Diuron	330-54-1	98.5%	Aragonesas Agro S.A.	technical
Isoproturon	34123-59-6	98%	Aragonesas Agro S.A.	technical

Table 4-4: Pollutants used for degradation experiments

4.1.2 Analytic Equipment used

Total organic carbon (TOC) and inorganic carbon (IC) were measured by means of a TOC analyser, model Shimadzu TOC 5050A. pH measurements were carried out with a pH-meter from Crison, model micro pH 2002 and conductivity was measured by a conductometer from Crison, model 525, range of measurement 20 μ S – 200 mS. Cation concentrations were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex lonpac CS12A 4*250 mm column. Isocratic elution was done with H₂SO₄ (10mM) at a flow rate of 1.2 mL*min⁻¹. Anion concentrations were measured with a Dionex DX-600 ion chromatograph using a Dionex lonpac AS11-HC 4*250 mm column. The gradient programme was pre-run 5 minutes with 20 mM NaOH, injection, 8 minutes 20mM NaOH and 7 minutes NaOH 35mM. For photometric measurements an Unicam-2 spectrophotometer was used.

For preparation of standards Milli-Q water (EC 0.054 μ S.cm⁻¹) prepared with a Millipore System was used. All filtrations were performed with filters from Millipore with a pore size of 0.2 μ m, type Millex-GN, Syringe Driven Filter.

Global UV (300-400 nm) irradiation in the solar plant was recorded by a Kipp&Zonen CUV3 detector with the same 37° inclination as the reactor modules. That way incident UV-radiation could be evaluated as a function of time of day, cloudiness and other environmental variations [Malato et al., 2003].

Pesticide concentration was analysed using reverse-phase liquid chromatography (flow 0.5 ml/min) with UV detector in a HPLC-UV (Agilent Technologies, series 1100) with C-18 column (LUNA 5 micron, 3x150 mm, from Phenomenex). 4-chlorophenol was determined by isocratic elution with 70% water at pH=3 / 30% methanol, Alachlor was analysed with isocratic elution 40 % water/ 60 % acetonitrile. For the separation of the

mixture of five pesticides the eluent composition during 5 minutes pre-run and the first 12 minutes of the analysis was 35% water / 65% acetonitrile and then 65% water / 35% acetonitrile for 13 minutes.

4.1.3 Analytical Methods

Iron Concentration

Iron concentration was measured according to the two following methods, based on American Standard Methods for the Examination of Water and Wastewater [APHA et al., 1998]. In both cases the absorption was measured in a 1 cm cuvette against distilled water. The sample was diluted according to the expected iron concentration. The buffer solution was prepared with 75 g ammoniumacetate and 175 mL acetic acid diluted to 250 mL. The phenantroline solution was prepared with 1% of phenantroline in distilled water.

Method A (without buffer, 0.6 mg/L< iron concentration < 15 mg/L)

- 2 mL sample
- mL 1 g/L phenantroline solution
- 3 spatula ascorbic acid

Method B (0.3mg/L<iron concentration<7 mg/L)

- mL sample
- 1 mL 1 g/L phenantroline solution
- 1 mL buffer solution
- 3 spatula ascorbic acid

Iodometric Determination of Hydrogen Peroxide

X mL of untreated sample (according to expected concentration) were diluted to 25 mL, then 20 mL of 2 N H_2SO_4 , 25 mL of 0.2 N KI solution and 10 drops of commercial available ready for use zinc iodide starch solution were added. The whole solution was homogenised and stored in the dark for 30 minutes. Afterwards the solution was titrated with 0.1 N $Na_2S_2O_3$ solution until it became colourless.

Total Organic Carbon, Inorganic Carbon, Anions and Cations

The sample was first diluted if necessary, afterwards filtered and then analysed with the TOC analyser and the ion chromatographs respectively.

Determination of pH Value

The samples were measured undiluted at ambient temperature with the according equipment.

4.2 Experiments

4.2.1 Precipitation of Iron

Iron as a catalyst is an essential reactive of the Photo-Fenton method. Precipitation of iron during the process can affect negatively the efficiency. The following experiment shall demonstrate the effect of pH, temperature and phosphate on the precipitation of iron. Initial iron dose was varied from 2 (lowest concentration for direct discharge into waterbodies in the EU) to 56 mg/L (high concentration) as ferric nitrate, pH varied from 2 to 4 and temperature from 20 to 60 °C. In some experiments 100 mg/L phosphate as KH_2PO_4 were added. The experimental set-up can be seen from Table 4-5.

initial iron concentration	рН	temperature	phosphate concentration
[mg/L]		[°C]	[mg/L]
29	4.8	40	0
29	2.3	40	0
29	3.1	40	0
29	2.8	20	0
29	3.4	60	0
2	3.4	40	0
56	3.0	40	0
29	3.1	40	0
29	2.7	40	0
29	2.8	40	100
29	2.2	40	100
29	1.9	40	100

Table 4-5 : Setu	p of experime	ents for preci	pitation of iron
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The according amount of iron was diluted in 200 mL of distilled water at pH 2. The solution was protected from light, agitated magnetically and heated to the corresponding temperature, and then pH was adjusted. Temperature varied about +/- 1°C around set point during experiments. As the pH-meter does not have temperature compensation, pH was adjusted to the value measured at the according temperature +/- 0.1 and later the temperature compensation was made by calculation. Iron concentration was measured at pH adjustment, at 1 h, 2 h, 4 h and 24 h according to measurement methods A and B respectively. The samples containing phosphate were filtered before adding them to the reagents.

4.2.2 General Set-up for Degradation Experiments

All of the following experiments were carried out in the CADOX-reactor that was erected at the beginning of 2004. The CADOX reactor is a compound parabolic collector (CPC). This collector has been especially designed for solar chemical applications that do not need concentration of solar radiation. Unlike the parabolic trough collectors it is able to use as well direct as diffuse solar radiation so that it can be used also on cloudy days. The general design of a CPC can be seen from Figure 4-1. In contrast to the reactor in Figure 4-1 in CADOX the tubes are in horizontal position. A flow diagram of the CADOX reactor is displayed in Figure 4-2.



Figure 4-1:Schematic drawing of a CPC [Malato et al., 2002]

The CADOX reactor has a total volume of 75 L of which 50 L are irradiated in Pyrex glass tubes. The total reactor area is 4 m², consisting of 4 modules of 1m² CPC surface and 5 horizontal absorber tubes with a length of 132 cm and a diameter of 50 mm each. It disposes of a dosage pump for H_2O_2 , acid and base additions, but these were not employed in the following experiments. Furthermore, it possesses an online measurement system for pH, ORP, oxygen concentration and temperature as well as a cooling and heating system for temperature regulation. The CADOX reactor is a plug flow reactor, i.e. the current in the tubes is laminar and there is no homogenisation taking place in the circulating solution but only in the tank.



Figure 4-2: Flow diagram of CADOX reactor



Figure 4-3: The CADOX reactor with its complete surface uncovered

Experiment Preparation

The general procedure of the experiments was the following:

- Reactor covered to protect it from light
- Reactor filled with distilled water and set heating to corresponding temperature
- Sample 0 taken
- Pollutant added, let homogenise 45 minutes
- Sample 1 taken
- Acid added, let homogenise 15 minutes
- Sample 2 taken
- Iron added, let homogenise 15 minutes
- Sample 3 taken
- H₂O₂ addition, leave recirculating in the dark 30 minutes
- Sample 4 taken
- Uncover corresponding reactor area
- After 15 minutes sample 5 taken; proceed taking samples first every 15, when TOC falls slower every 30 minutes

4.2.3 Preliminary Experiments with 4-Chlorophenol

The experiments with 4-chlorophenol were made to determine the parameters to be varied in the Alachlor experiments. Possible parameters were temperature, iron concentration, hydrogen peroxide concentration, irradiation/collector area (by partly covering the collector) and pH. The experimental set-up can be seen from Table 4-6. The added concentration of 4-Clorophenol was 150 mg/L in all experiments and all experiments were performed uncovering the complete reactor area.

Table 4-6: Experimental Set-up for 4-Chlorophenol: irradiation intensity, temperature,

initial concentration of 4-Chlorphenol and iron concentration

 Irradiation
 T
 4-CP0
 CFe

 N°
 intensity
 I'radiation
 I'rad

N° Irradiation		Т	4-0	C _{Fe}	
	intensity	[°C]	[mM]	[mg/L]	[mg/L]
1	medium	30	1	128.5	2
2	poor	20	1	128.5	2
3	poor	40	1	128.5	2
4	good	20	1	128.5	2

4.2.4 Alachlor

The varied factors in the experiment were selected according to the Central Composite Design without star points (Wu and Hamada, 2000, pp. 412-417). The general points of this design can be seen from Table 4-7 and from Figure 4-4. The coordinate -1 will be be the minimum for the according parameter as negative values for concentrations do not exist and the coordinate 1 will be the maximum.



Figure 4-4: Points for Central Composite Design

Table 4-7: Experim	enta	al Se	t-up	for
Alachlor according	to	the	Cen	tral
Composite design				

8 cube points					
X 1	X ₂	X 3			
-1	-1	-1			
-1	-1	1			
-1	1	-1			
-1	1	1			
1	-1	-1			
1	-1	1			
1	1	-1			
1	1	1			
3 centre points					
x ₁	X 2	X ₃			
0	0	0			

Table 4-8: Central Composite Designapplied to Parameters in AlachlorExperiments

8 cube points					
C _{Fe} [mg/L] T [°C] A [m ²]					
2	20	0.8			
2	20	4			
2	50	0.8			
2	50	4			
20	20	0.8			
20	20	4			
20	50	0.8			
20	50	4			
3 centre points					
c _{Fe} [mg/L]	T [°C]	A [m ²]			
11	35	2.4			

The varied parameters within the experiment were iron concentration (x_1) , temperature (x_2) and collector area (x_3) . Collector area was varied by partly covering the reactor surface. Applying the design from Table 4-7 to these parameters the following values presented in Table 4-8 were chosen. A minimum of 20 °C for the temperature has been selected to make the experiments comparable to literature data. The upper limit of 50°C was chosen due to sensor limits. The minimum value for the iron concentration is the lowest limit for direct discharge in waters in Europe, for example in Austria. The maximum value of 20 mg was chosen because with higher iron concentration little changes in reaction rate are expected due to experiments performed before at PSA. Considering the collector surface it was considered easiest to cover always whole tubes, which means multiples of 0.2 m^2 .

The concentration of Alachlor was always 100 mg/L added as one dose at the beginning of the experiment. H_2O_2 was kept constantly at a value between 200 and 500 mg/L adding about 40-100 mL after sampling according to last measured concentration. The pH was 2.6 in all experiments, adjusted by adding 75 mL of 1 M H_2SO_4 . The total volume was always 75 L and the flow set to 1500 L/h.

4.2.5 Pesticides Mixture

In most cases wastewaters do not contain only one component but different substances. Furthermore the medium in which the pollutants are dissolved is not distilled water but tap water or other type of water with certain salt contents. Salts dissolved in the water can have a negative effect on the Photo-Fenton process. Especially $HPO_4^{2^-}$, HCO_3^{-} , CI^- and $SO_4^{2^-}$ can form complexes with the iron, and thereby make it precipitate or slow down the overall reaction rate by a factor between 4 and 20 depending on their concentration in the water. NO_3^- and CIO_4^- do not have significant effects on the reaction rate. [Lipczynska-Kochany, 1995]

Pesticides added to the reactor for the degradation experiments were Alachlor, Atrazine, Chlorfenvinphos, Isoproturon and Diuron. In all cases reactor temperature was 30° C, iron concentration 10 mg/L, flow 1500 L/h. To adjust pH 100mL or in case of simulated tap water 150 mL respectively HNO₃ (1M) were added. Varied values were pesticide concentration, amount of H₂O₂ added and the medium in which the experiment was performed (see Table 4-9).

The "tap water" used in the experiment was prepared by adding certain amounts of salts to distilled water (see Table 4-10) to imitate "real" tap water but also have the same defined conditions at all times.

Experiment	pesticides concentration	total pesticides concentration	medium	H_2O_2 added
Mixture 1	10 mg/L each	50 mg	H ₂ O dist.	115 mL
Mixture 2	30 mg/L each	150 mg	H ₂ O dist.	3*115 mL
Mixture 3	10 mg/L each	50 mg	tap water	115 mL
Mixture 4	30 mg/L each	150 mg	tap water	3*115 mL

Table 4-9: Set-u	p for ex	periments	Pesticides	Mixture
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Table 4-10: Preparation of "tap water"

Substance	quantity
KCI	4 mg/L
NaHCO ₃	96 mg/L
CaSO₄*2H₂O	60 mg/L
MgSO ₄	60 mg/L

Before adding the pesticides to the reactor they were pre-dissolved in bottles of 5 L (c=10 mg/L) and 10 L (c=30 mg/L) respectively of distilled water. This solution was light protected, heated to 60 °C, agitated magnetically and left over night. Despite this preparation the pesticides did not dissolve completely in the bottles and there was still some solid pesticide suspended when they were added to the reactor.

The general procedure of an experiment involved the following steps in the mentioned order:

- CPC covered to protect it from light
- CPC filled with distilled water and pesticides
- centrifugal pump turned on and temperature adjusted
- 45 minutes for dissolving and homogenisation
- salts added in case of tap water as medium
- 15 minutes homogenisation period due to reactor configuration (plug flow photoreactor)
- sample 0 taken
- adjustment of pH (nitric acid), 15 minutes of homogenisation
- addition of ferrous sulphate, homogenisation period of 15 minutes
- sample 1 taken
- addition of first dose of hydrogen peroxide, 15 minutes reaction without solar irradiation
- sample 2 taken
- CPC uncovered, start of photocatalytic degradation experiment.

Further hydrogen peroxide was supplied afterwards in portions. To ensure homogeneity in the solution at the moment of sampling, supplements of any sort were never added in the last 15 minutes before sampling but usually directly afterwards. The experiments were stopped when the pesticides were completely degraded and no further significant TOC reduction was observed.

5 <u>Results</u>

5.1 Iron

At a pH higher of 2.8 and higher without phosphate and in all measurements with phosphate once the reactants were added the absorption of the sample rose during measuring. For this values at 1 min, 2 min, 3 min, 4 min and 5 after adding the sample to the reagents were measured. Using these values the iron concentration at the moment of adding the sample to the reagents was extrapolated. For the measurements without phosphate the values shown as results are the mean values between measurement according to method A and measurement according to method B as both values always were close together and there was no reason to consider one method more reliable than the other one. At the experiments with phosphate measurements were made only according to method C, once with filtering the sample and once without filtering it. With the filtered samples the problem of rising absorption during measurement occurred less so this method was considered more reliable and values shown in the results base on concentrations measured this way.

As can be seen from Table 5-1 and Figure 5-1 at a pH of 2.8 and higher without phosphate the major part of the iron precipitates. Elevated temperature accelerates the precipitation, low temperature slows it down. When phosphate was added iron even precipitated almost completely at pH of 1.9. Due to these results the following photo-Fenton experiments in the pilot-plant were carried out at a pH of 2.6 to avoid problems with iron precipitation. For the treatment in commercial plants phosphate will have to be removed from wastewater before photo-Fenton treatment as a treatment at pH below 2 will not be possible as precipitating phosphate in the reactor would result in turbidity and by this impede the light from entering the solution and slow down the photo-Fenton reaction. Apart from that the solution would cause corrosion problems at the metal and plastic parts of the reactor (e.g. pumps). Furthermore elevated salt freights would occur after neutralising.

initial iron concentration	рН	phosphate	т	iron precipitation as % c initial value	
[mg/L]		[mg/L]	[°C]	at 4 hours	at 24 hours
29	4.8	0	40	83%	88%
29	2.3	0	40	18%	0%
29	3.1	0	40	88%	88%
29	2.8	0	20	59%	72%
29	3.4	0	60	93%	93%
2	3.4	0	40	82%	84%
56	3.0	0	40	89%	90%
29	3.1	0	40	88%	87%
29	2.7	0	40	14%	3%
29	2.8	100	40	100%	100%
29	2.2	100	40	99%	98%
29	1.9	100	40	91%	91%

Table 5-1: Iron precipitation observed in the experiments





Without phosphate iron could be kept in solution at pH below 3; with 100 mg phosphate even at pH 1.9 iron precipitated

5.2 General Procedures for Evaluation of the Degradation Experiments

5.2.1 Evaluation of Radiation

As radiation conditions vary from day to day as well as during the experiments depicting reactions against time does not provide all information of interest. For that global UV (300-400 nm) irradiation in the solar plant was recorded by a Kipp&Zonen CUV3 detector with the same 37° inclination as the reactor modules. That way incident UV-radiation could be evaluated as a function of time during the experiments. To make experiments at different light conditions comparable the TOC was depicted against t_{30W} , which means that irradiation time is standardised to the equivalent time at a radiation of 30 W applied to the total reactor volume according to Equation 5.1 and 5.2 An UV irradiation intensity of 30 W/m² is typical for a perfectly sunny day around noon. [Malato et al., 2003].

(5.1)
$$t_{30W,n} = t_{30W,n-1} + \Delta t_n * \frac{UV}{30} * \frac{V_{ill}}{V_t}$$

$$(5.2) \quad \Delta t_n = t_n - t_{n-1}$$

UV= Intensity of UV Radiation in W/m² V_{ill} = Illuminated Volume V_t = total Reactor volume n = sample

The reactor area does not provide all information about irradiation as its intensity changes during the day. Furthermore, the relation between reactor area and total reactor volume is not taken into account. To evaluate these parameters an so make the data easier transferable to other reactors the irradiation power per reactor volume is calculated (Equation 5.3). Due to the mentioned changing irradiation intensity PI/V has to be calculated separately for a TOC degradation of 50% and of 90% as the reaction times are different and thereby also the average irradiation intensity will vary.

(5.3)
$$P_I / V = \frac{A * \overline{I_{\Delta t}}}{V_t}$$

 $A = CPC \text{ area}$
 $\overline{I_{\Delta t}} = \text{average irradiation intensity during the time } \Delta t$
 $V_t = \text{total reactor volume}$
It should be noted that the PSA radiometer measures only the UV bandwidth of the solar spectrum, while the photo-Fenton reaction also takes place with the visible spectrum up to 580 nm [Bauer et al., 1999].

5.2.2 Evaluation of Reaction Rate

The expression 'reaction rate' used in the following evaluations was defined as TOC (or referred parameter in the context respectively) reduction per time. The criteria to quantify the reaction rate were:

 $t_{30W 50\%}$ = t_{30W} after which 50% of TOC have been degraded $t_{30W 90\%}$ = t_{30W} after which 90% of TOC have been degraded

5.3 4-Chlorophenol

With 4-chlorophenol various experiments were carried out at different temperatures and radiation conditions to prove the feasibility of these parameters to be varied in the Alachlor experiments. All these experiments were made with a total volume of 75L, an illuminated volume of 50L and a CPC surface of 4 m². In Figure 5-2 the TOC is depicted against the reaction time. As can be seen the reaction is slowest at poor radiation conditions and low temperature. Reaction at 30°C and medium radiation is almost the same as at 40°C and poor radiation. The difference between the reaction rates at various temperatures is obvious so that temperature will be used as one parameter to be varied in the Alachlor experiments.



Figure 5-2: TOC degradation depicted against irradiation time



Figure 5-3: TOC degradation depicted against t_{30W}

In Figure 5-3 TOC degradation is depicted against t_{30W} to consider the different radiation intensity. Here as well reaction rate varies as function of temperature: Reaction is slowest at 20°C and fastest at 40°C. Furthermore, it can be seen that at same temperature (20°C) at poor radiation less radiation energy per amount of waste water is needed (i.e. t_{30W} is shorter) to reach the same state of degradation than at good radiation and same temperature. This can be explained by the Fenton-reaction in the dark which always and in all experiments occurs apart from the photo-Fenton reaction. At poor radiation total reaction time is longer so that a greater amount of the substance is degraded by the dark Fenton reaction and less substance remains to be degraded by the photo-Fenton reaction. As the results usually are depicted against t_{30W} and the shape of TOC against t_{30W} varies with the intensity of solar radiation, radiation intensity is an interesting parameter to be varied. Because weather conditions are not exactly predicable (experiments cannot be made for example on a cloudy day with a radiation of constantly 20W/m²) experiments will be made at good radiation partly covering the reactor surface. By this the incoming radiation can be set to sufficiently determined values. On the contrary to that the concentration of H₂O₂ is difficult to control as the consumption is difficulty predicable and concentration can not be measured online. Using it as a process parameter to be varied would be possible if the values to compare differed from each other with a factor of about 10. But this would not provide information of interest as change in reaction rate is only expected from H₂O₂ concentrations close to

a limiting value. So the third parameter to be varied will be reactor surface or radiation per volume respectively.

5.4 Alachlor

A summary of the results from the experiments with Alachlor is given in Table 5-2 and Table 5-3. In some of the slow experiments TOC could not be degraded to 10% of the initial value due to time problems (It has to be taken into account that in the afternoon illumination quality drops drastically) so that estimation had to be made. The iron value and the temperature given in this table are always the mean values of the measurements during the experiment. It has to be remarked that despite of the low pH (experiments were performed at a pH of 2.6) iron precipitated at high temperatures. So the average iron concentration is lower than the initial iron concentration according to the experimental design. The parameter P_I/V represents the uncovered reactor surface. It was calculated according to Equation 5.3. It includes the varying illumination intensity and the relation of illuminated surface to total reactor volume to make the model feasible to other reactors.

Table 5-2: Resu	lting irradiation	power per v	olume (P _I /V),	t _{30W} and	hydrogen	peroxide
consumption for	50% TOC reduc	tion in the Ala	achlor experim	ents (H ₂ O ₂	, 50%)	

experiment	Fe	т	Α	P _I /V _{50%}	t _{30W,50%}	H ₂ O _{2, 50%}
•	[mg/L]	[°C]	[m²]	[W/L]	[min]	[m M]
Centre 1	11.3	34.9	2.4	1.14	17	14
Centre 2	11.5	35.0	2.4	1.15	21	15
Centre 3	10.0	35.2	2.4	1.04	18	25
Cube 1	2.2	20.4	4.0	1.59	26	11
Cube 2	20.8	20.1	4.0	1.46	191	8
Cube 3	2.2	50.4	0.8	0.36	14	9
Cube 4	14.3	50.0	4.0	1.22	34	17
Cube 5	15.1	49.9	4.0	1.50	3.8	11
Cube 6	2.3	50.4	0.8	0.32	1.4	14
Cube 7	2.0	20.5	0.8	0.35	18	18
Cube 8	10.0	35.2	0.8	0.32	52	8

experiment	Fe	Т	Α	P _I /V _{50%}	t _{30W,90%}	H ₂ O _{2 ,90%}
experiment	[mg/L]	[°C]	[m²]	[W/L]	[min]	[mM]
Centre 1	11.3	34.9	2.4	1.24	45	44
Centre 2	11.5	35.0	2.4	1.26	52	50
Centre 3	10.0	35.2	2.4	1.12	49	65
Cube 1	2.2	20.4	4.0	1.96	78	46
Cube 2	20.8	20.1	4.0	1.42	286	28
Cube 3	2.2	50.4	0.8	0.39	30	35
Cube 4	14.3	50.0	4.0	1.45	68	29
Cube 5	15.1	49.9	4.0	1.57	21	52
Cube 6	2.3	50.4	0.8	0.34	7.0	63
Cube 7	2.0	20.5	0.8	0.32	45	37
Cube 8	10.0	35.2	0.8	0.32	90	50

Table 5-3: Resulting irradiation power per volume (P_I/V), t_{30W} and hydrogen peroxide consumption for 90% TOC reduction in the Alachlor experiments ($H_2O_{2,90\%}$)

In Figure 5-4 and Figure 5-5 TOC degradation in all experiments is depicted against irradiation time and in Figure 5-6 and Figure 5-7 against t_{30W} . Same reactor area is indicated by same colour, same temperature by same shape of data point symbols and same iron concentration by same type of lines. As the three centre points are very similar only one of them is depicted to improve the legibility of the charts. For the same reason the depiction of TOC against irradiation time is split into two charts and different scalings are used.



Figure 5-4: TOC degradation depicted against irradiation time, experiments at 50°C and experiment Centre 1



Figure 5-5: TOC degradation depicted against irradiation time, experiments at 20°C and experiment Centre 1



Figure 5-6: TOC degradation depicted against t_{30W} , experiments at 20°C and experiment Centre 1



Figure 5-7: TOC degradation depicted against t_{30W} , experiments at 50°C and experiment Centre 1

From Figure 5-4 to Figure 5-7 can be seen that only in the experiments Cube 5 (iron concentration 20 mg/L, temperature 50°C, reactor surface 4 m²) and Cube 6 (iron concentration 20 mg/L, temperature 50°C, reactor surface 0.8 m²) TOC diminishes

significantly before uncovering the reactor. As can be seen from Figure 5-4 and Figure 5-5 degradation is fastest at Cube 5 with iron concentration of 20 mg/L, temperature 50°C and reactor surface of 4m² and slowest at Cube 8 with iron concentration of 2 mg/L, temperature 20°C and reactor surface 0.8m². Referring to the total illumination time the experiments carried out with a reactor surface of 4m² are always faster then the according experiments with 0.8m². Depicted against t_{30W} (see Figure 5-6 and Figure 5-7) this order is just the contrary, t_{30W} is shorter for experiments carried out at $0.8m^2$ then for the ones at 4m² with equal conditions. This confirms the theory made up in the 4- Chlorophenol experiments that beside the photo-Fenton reaction the Fenton reaction in the dark plays always a role in the degradation process which becomes more important at low irradiation as in this circumstances the photo-Fenton reaction is slower. The by far slowest experiments are the ones with low iron and low temperature (Cubes 2 and 8) and the fastest ones the ones with high iron and high temperature (Cubes 5 and 6). So these two parameters seem to be the most crucial ones for the reaction rate. In the graphs of Cube 2 and Cube 8 it can bee seen that for some time the TOC hardly diminishes. This was due to heavy clouds and very low irradiation. Depicting TOC against t_{30W} these horizontal parts almost disappear.

5.4.1 Development of UV-Absorbance

In Figure 5-8 the different spectra recorded during experiment Cube 8 (iron concentration 2mg/L, temperature 20°C, reactor surface 0.8m²) are depicted. As spectra 1, 2 and 3 (the ones after addition of Alachlor, iron and acid respectively) are practically identical spectra 1 and 2 were left out to improve the legibility of the chart. For the same reason only every fourth sample is depicted. Sample 0 is just distilled water so that the absorption is zero at all wavelengths. It was measured to control remaining substances in the reactor. The solution with Alachlor has an absorption maximum at 272 nm. It can be seen that with proceeding degradation this maximum is shifted to longer wavelengths and the absorbance rises generally. By that also the absorbance at 254 nm, which is called the aromat index, rises. Even at the end of the degradation process it is hardly below the initial value.



Figure 5-8: Development of the UV absorption spectrum

Figure 5-9 and Figure 5-10 show the development of the aromat index during the different experiments. The depiction of the absorbance against t_{30W} has been split up into two charts using different scaling for t_{30W} and same scaling for absorbance to improve their legibility. Depicting the absorbance at 254 nm (see Figure 5-9 and Figure 5-10) against t_{30W} various things can be observed: The reaction rate is analogue as it was for the development of the TOC: Experiments with quick TOC degradation also show a quick development of the absorption. In all cases absorption rises to a value that is a lot higher than the initial value. In experiments Cube 1 and Cube 3 (Figure 5-9) it even reaches 13 times the absorbance of the solution with Alachlor only. This can be explained by the relatively low absorption of Alachlor at 254 nm (see Figure 5-8) and the formation of various intermediate phenolic substances with a higher absorbance at this wavelength during the degradation process. In the experiments with an iron concentration of 20 mg/L always a high absorbance at the end of the degradation processes remained. This is because iron, especially ferric iron, also has a high absorbance at this wavelength and so a high remaining aromats concentration is pretended erroneously. Same combinations of temperature and iron concentration lead to the same height of the absorption maximum. The highest peak appears in the experiments Cube 1 and Cube 3 with an iron concentration of 20 mg/L and a

temperature of 20°C. The lowest absorption maximum has the experiment with 20°C and 2 mg/L iron. So it cannot be said that at lower temperature always a higher maximum has to be expected but the dependence has to be on a combination of the factors iron concentration and temperature. The experiments Cube 5 and Cube 6 do not fit into this theory. But as mentioned before the maximum in experiments with an area of 0.8 m² always occurs before the maximum for experiments at 4m², so that the maximum in experiment Cube 6 has to be expected shortly before t_{30W}=0, supposing that for Cube 5 the correct maximum was measured. At this time no measurement was made, so it is probable that the maximum of Cube 6 is just as high as the one of Cube 5 and was simply missed.



Figure 5-9: Absorbance at 254 nm depicted against t_{30W} , experiments at 20°C and experiment Centre 1



Figure 5-10: Absorbance at 254 nm depicted against t_{30W} , experiments at 50°C and experiment Centre 1

5.4.2 Data from High Performance Liquid Chromatograph



Figure 5-11: HPLC data of experiment Cube 3 (c_{Fe} 20 mg/L, temperature 20°C, reactor area 0.8m²).

Absorbance in milli Absorption Unit depicted against retention time in the HPLC and t_{30W} of the according samples, experiment Cube 8. The peak at a retention time of 6.4 minutes is Alachlor. The area of the peak (absorbance*retention time) is proportional to the concentration of Alachlor

In Figure 5-11 the HPLC chromatograms measured in experiment Cube 3 (iron concentration 20 mg/L, temperature 20°C, reactor area 0.8m²) at 225 nm in milli Absorption Unit is depicted against retention time and t_{30W} of the corresponding sample. I.e. each of the lines with same t_{30W} represents one sample. The area retention time*absorption is proportional to the concentration of the measured substance. The high peak at a retention time of 6.4 minutes is the peak that corresponds to the Alachlor concentration. At t_{30W} =-15min the initial concentration of Alachlor of 100 ppm can be seen. At the time of uncovering the reactor ($t_{30W}=0$) the concentration has already diminished significantly and other peaks with shorter retention time appear. These are more polar degradation products of Alachlor. At less than 9 minutes there is no detectable quantity of Alachlor remaining and degradation products start to diminish (compare also TOC degradation in figure 5-7). After 14 minutes the degradation products are reduced significantly. Table 5-4 gives an overview over the standardised irradiation time t_{30W} needed for complete degradation of Alachlor. It has to be remarked that this times only give a rough idea as samples were only taken every 15 minutes but the degradation process was very fast in most of the experiments. In experiments Cube 5 and 6 Alachlor was completely degraded by the Fenton reaction in the dark before uncovering the reactor so that the necessary standardised irradiation time t_{30W} in these cases is <0.

experiment	Fe	Т	area	t _{30W}
	mg/L	°C	m²	min
Centre 1	11	35	2.4	<14
Centre 2	11	35	2.4	<14
Centre 3	11	35	2.4	<13
Cube 1	20	20	4	<9
Cube 2	2	20	4	<89
Cube 3	20	20	0.8	<9
Cube 4	2	50	4	<22
Cube 5	20	50	4	<0
Cube 6	20	50	0.8	<0
Cube 7	2	50	0.8	<8
Cube 8	2	20	0.8	<55

 Table 5-4: Necessary t_{30W} for total degradation of Alachlor

5.4.3 Development of pH

The depiction of the pH against t_{30W} has been split up into two charts using the same scaling to improve their legibility. The pH dropped in all experiments about 0.04 units and reaches its minimum at a degradation state of approximately 40% and later raised to its initial value. There is no significant difference in the development of the pH according to the experiment parameters temperature, irradiation power per volume or iron concentration. The development of pH is depicted against TOC degradation in Figure 5-12 and Figure 5-13. The little differences in the initial values can be explained by small errors in addition of acid or in total water volume in the reactor.



Figure 5-12: Development of the pH depicted against TOC degradation, experiments at 20°C and experiment Centre 1



Figure 5-13: Development of the pH depicted against TOC degradation, experiments at 50°C and experiment Centre 1

5.4.4 Development of Oxygen Concentration



Figure 5-14: Oxygen concentration depicted against TOC degradation, experiments at 20°C and experiment Centre 1



Figure 5-15: Oxygen concentration depicted against TOC degradation, experiments at 50°C and experiment Centre 1



Figure 5-16: Oxygen concentration depicted against t_{30W} , experiments at 20°C and experiment Centre 1



Figure 5-17: Oxygen concentration depicted against t_{30W} , experiments at 50°C and experiment Centre 1

The oxygen concentration seems to rise almost linearly with the TOC degradation (see Figure 5-14 and Figure 5-15). It may be interesting to investigate this relation more closely as oxygen concentration can be measured online (on the contrary to TOC) and so might serve as an indicator for the degradation state. The oxygen concentration rises slowest in the experiment Cube 8 (iron concentration 2 mg/L, temperature 20°C, reactor area $0.8m^2$) which also took the longest illumination time for TOC degradation. The development of oxygen concentration is depicted against t_{30W} in figure Figure 5-16 and Figure 5-17. From these figures can be seen that the oxygen concentration drops little at beginning of the reaction (after adding H_2O_2) but rises significantly and rapidly when degradation accelerates as well. It reaches a maximum when most of the organic substance is degraded and then starts falling again (see e.g. experiment Cube 1).



5.4.5 Development of Oxidation Reduction Potential (ORP)

Figure 5-18: Development of ORP against t_{30W} , experiments at 20°C and experiment Centre 1



Figure 5-19: Development of ORP against t_{30W} , experiments at 50°C and experiment Centre 1

5. Results

From Figure 5-18 and Figure 5-19 can be seen that the biggest changes in oxidation reduction potential (ORP) occur before uncovering the reactor. They are caused by the addition of the various reagents. Adding the pesticide to the reactor causes ORP to decrease, the acid makes it rise, after the iron addition ORP falls again and rises again at the addition of H_2O_2 . In the experiments Cube 1, Cube 2 and Cube 4 this development differs from the other experiments. Cube 2 and 4 show a slightly risen ORP after iron addition instead of a falling one and at experiment Cube 1 the ORP rises after addition of Alachlor. Furthermore the initial ORP at t_{30W} =-60 min (distilled water) is already different in the experiments. This may be due to residues remaining in the reactor from experiments carried out the day before despite cleaning.

The ORP remains almost stable during the experiments as can be seen from Figure 5-20 and Figure 5-21. Depiction was split up into two charts displaying only one centre point to improve their legibility. Furthermore depiction starts at t_{30W} =0 (i.e. after addition of all reagents), so that for experiments Cube 4, 5 and 6 there are no data points displayed for a TOC degradation of zero. At most experiments ORP slightly falls at the end, starting at a TOC degradation of about 70%. It is remarkable that the centre point is not situated in the middle but has the highest ORP of all experiments. Furthermore experiment Cube 7 (iron concentration 2mg/L, temperature 50°C, reactor surface 0.8m²) has a lower ORP than the others and Cube 3 (iron concentration 20mg/L, temperature 20°C, reactor surface 0.8 m²) has an ORP slightly higher. All other experiments are very similar and have an ORP around 520 mV.



Figure 5-20: Development of ORP against TOC degradation, experiments at 20°C and experiment Centre 1



Figure 5-21: Development of ORP against TOC degradation, experiments at 50°C and experiment Centre 1

5.4.6 Hydrogen Peroxide Consumption

In Figure 5-22 and Figure 5-23 hydrogen peroxide consumption is depicted against t_{30W} . Like in the charts above depiction was split up into two charts displaying only one centre point and different scalings were used to improve their legibility. As can be seen it has an almost perfectly linear development. The inclination depends basically on the reaction rate. The highest inclination is observed in experiments Cube 6 and 5, which have a high iron concentration and a high temperature, lowest inclination at Cubes 2 and 8 with low iron and low temperature. Just as the TOC reduction the H₂O₂ consumption depicted against t_{30W} is slower with experiments Cube 5 and Cube 6 a H₂O₂ consumption before t_{30W} =0 can be observed. In these experiments the H₂O₂ consumption rises significantly with uncovering the reactor.



Figure 5-22: H_2O_2 consumption as function of t_{30W} , experiments at 20°C and experiment Centre 1



Figure 5-23: $\rm H_2O_2$ consumption as function of $t_{30W,}$ experiments at 50°C and experiment Centre 1

As can be seen from Figure 5-24 and Figure 5-25 hydrogen peroxide consumption depicted against TOC degradation rises drastically.. The depiction has been split into two charts using same scalings to improve its legibility. Relatively few hydrogen peroxide is needed to degrade 50% of the TOC but the amount rises immensely (factor 3 to 6) when more than 90% of the TOC is to be degraded. Furthermore it can be seen that the H_2O_2 consumption needed to degrade a certain amount of organic substance is similar (factor 2) for all experiments i.e. it does not depend as much on the reaction parameters temperature, iron concentration and irradiation as the reaction rate does.



Figure 5-24: H₂O₂ consumption as function of TOC degradation, experiments at 20°C



Figure 5-25: H₂O₂ consumption as function of TOC degradation, experiments at 50°C

5.5 Pesticides Mixture

On Figure 5-26 the degradation of TOC is depicted against t_{30W} . As can be seen there is no significant difference between the degradation using distilled water and using

simulated "tap water". Detailed experimental set-up can be looked up in Table 4-5 and Table 4-6.



Figure 5-26: TOC degradation in the Pesticides Mixture experiments as function of t_{30W}



Figure 5-27: TOC degradation as relation to initial TOC as function of t_{30W}

In all cases TOC start to diminish significantly with exposition to light. All pesticides are degraded in all experiments within 30 minutes of illumination. In the Figure 5-27 the relation of measured TOC to initial TOC is depicted against t_{30W} . As can be seen 50% TOC has been diminished to 50% of its initial value after 6 minutes in case of an initial concentration of 10 ppm and after 12 minutes in case of an initial concentration of 30 ppm. It can be seen that at a concentration of 10 ppm the TOC degradation as percentage of initial value is faster than at an initial concentration of 30 ppm. So

reaction rate does not only depend on the remaining organic carbon but also on the exact structure of the organic substance as some substances are degraded easier than others. There is a certain almost stable amount of TOC remaining in each of the experiments. Great part of that are probably substances produced at the degradation of Atrazine which are very recalcitrant to treatment with AOP but can be degraded by biological treatment [Pelizetti et al., 1993]. Further substances remaining may be aliphatic derivates of urea coming from Isoproturon and Diuron [Maletzky et al., 1999].

5.6 Cost estimation

The intention of the following cost estimation shall serve as an approximate comparison between the different factors, which have to be considered. The figures are partly based on rough estimations. Not all relevant factors could be taken into account.

According to Goswami cost analysis of a photocatalytic process should be based on a calculation of operational and maintenance costs and necessary collector area [Goswami et al., 1997].

Prices used for calculation are listed in Table 5-5 and were received on request from DICSA, the main supplier for chemical reagents of Plataforma Solar de Almería. Prices for electricity, reactor cost and workforce were estimated.

Product	Price	Source
HNO ₃	0.82 Euro.kg ⁻¹ HNO ₃ in 65% solution	DICSA
H ₂ O ₂	1.18 Euro.kg ⁻¹ H_2O_2 in 30% solution	DICSA
FeSO ₄ .7H ₂ O	0.30 Euro.kg ⁻¹	DICSA
КОН	2.2 Euro.kg ⁻¹	DICSA
Electricity	0.10 Euro.kWh ⁻¹	Assumption
CPC + necessary	1000 Euro.m ⁻²	Assumption
tubes and pumps		
Human resource	30 Euro.h ⁻¹	Assumption

Table 5-5: Prices used for calculations

Maintenance and logistic costs were not estimated due to lack of information on the topic. Logistic costs would depend heavily on the general strategic set-up of a treatment, such as scale and location of the plant or annual operation hours.

In the following calculations it was assumed that the plant will be operated during working hours, which means 8 hours a day 5 days a week and that its availability due to weather conditions and necessary maintenance will be 80%.

Considering the hourly throughput as volume per area of CPC and hour a rough assumption was to be made. The hypothesis was that an optimised treatment would at least have the best throughput achieved in the own experiments. The time used in calculation was the time needed to degrade the TOC to 50% of the initial value, supposing that the Photo-Fenton treatment would be followed by a biological treatment. In the experiments Pesticides Mixture this time basically depended on the initial TOC and hardly on the medium used (distilled water or simulated tap water). As can be seen from Figure 5-28 for initial concentrations of the five pesticides of 30mg/L each an illumination time of about 35 minutes is needed to reduce the TOC to 50% of its initial value and at pesticide concentrations of 10 mg/L only 15 minutes are needed. Only the time under illumination was estimated as treatment time as the adding of the reagents can be done in a tank apart from the CPC plant.



Figure 5-28: TOC degradation as relation to initial TOC as function of illumination time

For the calculation of the annual throughput per area CPC the treated volume is divided by the occupied surface and the needed time. The results can be seen from Table 5-6 and Table 5-7.

Table 5-6: Treatment time and annual throughput, 10 ppmCASE 1: pesticide concentration = 10ppm each

Treatment time for TOC 50% in CADOX	15	min
CPC surface CADOX	4	m²
Treated volume CADOX	75	L
Throughput per m ² and hour	75	L
Annual operation hours	1664	h
Annual throughput per m ² CPC	124.8	m³

Table 5-7: Treatment time and annual throughput, 30 ppm

CASE 2: pesticide concentration = 30 ppm each

Annual throughput per m ² CPC	53	m ³
Appual operation hours	1664	h
Throughput per m ² and hour	32	L
Treated volume CADOX	75	
CPC surface CADOX	4	m³
Treatment time for TOC 50% in CADOX	35	h

Multiplying throughput and annual operating time the amount of waste water treated per CPC area was calculated. The CPC reactor investment costs were divided by 10 years, which should be the minimum lifetime for the reactor. Dividing annual investment costs by treated waste water volume the investment costs per m³ waste water were calculated. The calculation of the investment costs for the reactor is depicted in Table 5-8 and Table 5-9.

Table 5-8: Investment costs for CPC reactor per m³ waste water, 10 ppm CASE 1: pesticide concentration = 10ppm each

Investment CPC per m ² surface	1000	€/m²
Depreciation period	10	а
Throughput per m ² CPC	125	m³/(a*m²)
Investment costs per m ³ waste water	0.80	€/m³

Table 5-9: Investment costs for CPC reactor per m³ waste water CASE 2: pesticide concentration = 30 ppm each

Investment CPC per m ² surface	1000	€
Depreciation period	10	а
Throughput per m ² CPC	53	m³/(a*m²)
Investment costs per m ³ waste water	1.87	€

For electricity costs up-scaling the pump and the CPC used in the experiments does not provide valid data as in this reactor the heat exchanger causes a raised pressure loss. In a different plant at bigger scale in cooperation with the PSA a 750 W pump is used to recirculate the volume according to a CPC surface of 150m². According to this relation a pump power of 5 W per m² reactor area is estimated. Furthermore the CPC area needed per cubic metre waste water, the operating hours per year and the electricity price were factored in the calculation, which can be looked up in Table 5-10 and Table 5-11.

Table 5-10: Electricity consumption by pumps, 10 ppm

CASE 1: pesticide concentration = 10ppm each

Electricity consumption per m ² CPC	5	W
Annual operation hours	1664	h
Electricity costs per kWh	0.10	Euro
Annual electricity costs per m ² surface	0.83	Euro
Annual throughput per m ² CPC	124.8	m³/m²*a
Electricity costs per m ³ waste water	0.01	Euro

Table 5-11: Electricity consumption by pumps, 30 ppm

CASE 2: pesticide concentration = 30 ppm each

Electricity consumption per m ² CPC	5	W
Annual operation hours	1664	h
Electricity costs per kWh	0.10	Euro
Annual electricity costs per m ² surface	0.83	Euro
Annual throughput per m ² CPC	53	m³
Electricity costs per m ³ waste water	0.02	Euro

Chemicals consumption was set according to the quantities used in experiments Pesticides Mixture1-4. As H_2O_2 consumption the quantity necessary to degrade 50% of the initial TOC was assumed. It was supposed that at that point the waste water has lost most of its toxicity and is feasible to biological treatment. The amount of H_2O_2 consumed up to this point can be seen from Figure 5-29. The quantity of nitric acid is 0.125 kg/m³ which is needed to adjust pH to 2.6 to assure that no precipitation of iron occurs. The amount of iron is 50g/L FeSO₄*7H₂O, corresponding to a concentration of 10 mg/L Fe²⁺.



Figure 5-29: TOC in relation to initial TOC depicted against H₂O₂ consumption per m³ waste water in experiments Pesticides Mixture

Potassium hydroxide needed for neutralisation was estimated to be 0.14 kg per cubic metre waste water, which is the necessary quantity for neutralising from pH 2.6 to pH 7. The resulting reagent costs for cases 1 and 2 are listed in Table 5-12 and Table 5-13.

Total reagent costs	1.49	€/m³
KOH costs per m ³ waste water	0.31	€
KOH price	2.2	€/kg
KOH consumption per m ³ waste water	0.14	Kg
FeSO ₄ *7H ₂ O costs per m ³ waste water	0.01	€
FeSO ₄ *7H ₂ O price	0.30	€/kg
FeSO ₄ *7H ₂ O consumption per m ³ waste water	50	g/m³
HNO ₃ costs per m ³ waste water	0.11	€
HNO ₃ price	0.82	€/kg
metre waste water ³ waste water	0.13	Kg
HNO ₃ 65% consumption per m Total reagent costs per cubic		
HNO ₃ 1M consumption per m ³ waste water	1.3	Mol
H ₂ O ₂ costs per m ³ waste water	1.06	€/m³
H ₂ O ₂ price	1.32	€/L
H ₂ O ₂ consumption (30%) per m ³ waste water	0.8	L/m³

CASE 1: pesticide concentration = 10ppm each

Table 5-13: Total reagent costs per cubic metre waste water, 30 ppm

CASE 2: pesticide concentration = 30 ppm each

H ₂ O ₂ consumption (30%) per m ³ waste water	1.0	L/m³
H ₂ O ₂ price	1.32	€/kg
H ₂ O ₂ costs per m ³ waste water	1.32	€/m³
HNO ₃ 1M consumption per m ³ waste water	1.3	L
HNO_3 65% consumption per m Total reagent costs per cubic	0.13	Kg
HNO ₃ price	0.82	€/kg
HNO ₃ costs per m ³ waste water	0.11	€
FeSO ₄ *7H ₂ O consumption per m ³ waste water	50	g/m³
FeSO ₄ *7H ₂ O price	0.30	€/kg
FeSO₄*7H₂O costs per m³ waste water	0.01	€
KOH consumption per m ³ waste water	0.14	Kg
KOH price	2.2	€/kg
KOH costs per m³ waste water	0.31	€
Total reagent costs	1.75	€/m³

For the calculation of the costs of human resources it was assumed that always one person is needed to take care of all tasks considering the plant five days a week, eight hours per day and 52 weeks per year no matter which size it is. So costs for human resources diminish significantly with plant size. This is of great importance because for small plants human resources are by far the most important cost factor. Costs for human resources can be seen from Table 5-14, Table 5-15 and Table 5-16.

Table 5-14: Costs for human resources per year

Human Resources

Working hours per year	2,080	h/a
Price per working hour	30	€/h
Annual costs for human resource	62,400	€/a

Table 5-15: Costs for human resources considering the plant size, 10 ppm

Throughput			125	m³/(m²a)
Plant size (CPC surface)	100	500	1000	m²
Treated waste water	12,480	26,743	53,486	m³/a
Costs human resources	5.00	1.00	0.50	€/m³

CASE 1: pesticide concentration = 10ppm each

Table 5-16: Costs for human resources considering the plant size, 30 ppm

CASE 2: pesticide concentration = 30ppm each

Throughput			53	m³/(m²a)
Plant size (CPC surface)	100	500	1000	m²
Treated waste water	5,349	26,743	53,486	m³/a
Costs human resources	11.67	2.33	1.17	€/m³

For plants smaller than 200 m² human resources cause more than 50% of the total treatment costs. As they diminish significantly with plant size it is recommendable use big scale plants in order to reduce the treatment costs. A further important factor is the investment cost of the reactor per m² or the waste water to be treated per reactor area respectively. Reactor investment costs and electricity consumption were depicted according to up-scaling pilot plant values. It has to be kept in mind that a plant at bigger scale probably will cause lower costs. Furthermore, CPC reactors are very reliable, high

quality reactors. A cheaper reactor concept than the CPC reactor could be imagined. Different concepts for reactor configurations were proposed and evaluated by various authors [Van Well et al., 1997; Wyness et al., 1994a, Wyness et al., 1994b; Yi-zhong et al., 1998].

Considering the chemicals hydrogen peroxide is the main cost factor. The H2O2 consumption depends on the initial pollutant concentration as can be seen from Figure 5-29 but mainly on the state of TOC degradation (see Figure 5-24 and Figure 5-25). So possibly a cheaper treatment could be achieved if the photo-Fenton treatment was stopped earlier and a biological treatment was applied. Therefore more investigation on the intermediate products and their biodegradability is necessary. Of the other chemicals only KOH causes considerable costs. It would be possible to replace it by other substances, but as it also provide potassium as a nutrient for the bacteria employed in the later biological treatment this would not contribute to reduction of total treatment costs as potassium would have to be added separately causing in the end higher costs.

The total costs of the treatment for one cubic metre waste water including reactor investment, electricity, reagents and human resource are depicted in Figure 5-30 and Figure 5-31. For a plant size of 1000 m³ CPC area treatment costs of less than 3 Euro per m³ waste water with a total pesticide concentration of 50 ppm is expected and less than 5 Euro for a total pesticide concentration of 150 ppm. A plant at this scale would be able to treat around 50,000-100,000 m³ of pesticide waste water per year, depending on the concentration of the pollutants.



Figure 5-30: Total treatment costs for case 1: 10ppm each pesticide



Figure 5-31: Total costs of treatment for case 2: 30 ppm each pesticide

The following example shall give an idea of treatment costs in relation to pesticide costs. A pilot plant for photo-Fenton treatment has been erected in the municipality of El Ejido close to Almería where 50% of the regions 35,000 ha of greenhouses are situated. According to data from 1995 5200 t of pesticides per year are applied in this region. Until now there is no organised disposal for the empty pesticide containers so they

usually are disposed with other agricultural waste contaminating soil and groundwater. A recycling process for these containers was designed which includes a washing of the plastic material. The waste waters from this washing can be treated by AOP [Fallmann et al., 1999]. Assuming that pesticides are sold as a 30% w/v concentrated solution and 0.5% of the solution remains in the empty bottle, per 5L-bottle of pesticides 50 L of waste water with a pesticide concentration of 150 ppm (as in Pesticide Mixture experiments) has to be treated. This would result in treatment costs of 0.20 Euro per 5 L concentrated pesticide solution as displayed in Table 5-17. Considering the pesticide price of 20-40 Euros per bottle, the treatment would result in additional costs of about 1%.

Bottle volume	5	L
Pesticide concentration in containers	300	g/L
Remaining rest in bottle	0.5	%
Remaining rest in bottle	7.5	g
Resulting wastewater with 150 ppm pesticides	0.05	m³
Resulting treatment costs per bottle	0.24	€
Price per bottle of pesticides	20-40	€
Treatment costs in relation to pestcide costs	0.6-1.2	%

Table 5-17: Treatment costs in relation to consumed pesticides

Nevertheless, the figures stated have to be regarded with care. As mentioned before no logistic, no maintenance, no costs for the following biological treatment or other machinery were included. Therefore this would be additional costs. On the other hand a plant operator probably will not have to attend 100% of his working time to the plant and could be employed with other skills reducing the effective costs for human resources. Another uncertainty is to which degree these figures can be generalised as the composition of pesticide waste waters varies due to a multitude of factors.

6 Summary and Perspectives

6.1 Precipitation of Iron

In the experiments without phosphate addition iron precipitated at 40°C above pH 2.8, but only 3% of the iron precipitated at pH 2.7 at the same temperature. So it will be necessary for photo-Fenton treatment to remain a pH below 2.8 to keep iron in solution. Iron precipitation is faster at higher temperatures: At a pH of 3.4 and a temperature of 60°C 93% of the iron precipitate after 24 hours whilst at a lower temperature of 40°C and an even higher pH of 4.8 only 88% of the iron precipitate.

With the addition of 100 mg/L phosphate even at a pH of 1.9 and a temperature of 40°C more than 90% of the iron precipitated. As it is not possible to realise a photo-Fenton treatment below this pH phosphate in the waste water will have to be removed before the treatment.

6.2 Preliminary Experiments with 4-Chlorophenol

The dependence of reaction rate on the temperature can be clearly seen from the experiments so that temperature was chosen as a parameter to be varied in the Alachlor experiments. Irradiation intensity has an influence on the necessary reaction time for a certain TOC reduction and on the necessary t_{30W} . As irradiation can not be controlled it was decided to vary it by partly covering the reactor and so varying the illuminated surface. The importance of the iron concentration has been demonstrated before, so iron concentration was the third reaction parameter to be varied.

6.3 Alachlor

The influence of the chosen parameters on the TOC degradation was high. The shortest t_{30W} for a TOC reduction of 50% was lower than 5 minutes in experiments Cube 6 and Cube 5 (initial iron concentration 20mg/L, temperature 50°C, reactor surface 0.8 m² or 4m² respectively) the longest one was 190 minutes in experiment Cube 2 (iron concentration 2mg/L, temperature 20°C, reactor surface 4m²).

The UV absorbance of the solution rises during the degradation process but falls towards the end. By that also the aromat index which is a parameter for waste waters

strongly rises value and even at the end of treatment hardly falls below its initial value due to the absorption at the same wavelength caused by the iron.

As can be seen from the samples analysed by HPLC Alachlor in all experiments was degraded mostly even before significant TOC reduction. In all cases it could be degraded completely.

The oxygen concentration in the solution rises strongly when significant TOC reduction starts. As there seems to be some dependence of the oxygen concentration on the state of the TOC reduction it might be worth investigating this relation more closely to be able to estimate TOC from oxygen concentration which can be measured online.

The pH falls slightly during the experiments and rises at the end to its initial value. Oxidation reduction potential stay fairly stable during the experiments.

The H_2O_2 consumption hardly depends on the investigated reaction parameters. It rises almost linearly with t_{30W} . It rises immensely with the TOC degradation so that it needs about 3 to 6 times as much to degrade 90% of the TOC then just 50%. This favours the application of biological treatment as soon as toxicity is reduced significantly by the photo-Fenton treatment and remaining substances are expected to be bio-degradable.

6.4 Pesticides Mixture

The degradation of a mixture of the pesticides Diuron, Alachlor, Chlorfenvinphos Isoproturon and Atrazine was tested at concentrations of 10ppm and 30 ppm each using distilled water and artificial "tap water" to simulate real conditions. No significant difference could be observed using distilled water and tap water. There was always a certain TOC remaining that could not be degraded, due to under AOP conditions stable final degradation products.

These experiments were used to estimate treatment times for cost estimation. For a TOC reduction of 50% in case of 10ppm each pesticide an illumination time of 15 min was needed, in case of 30 ppm 35 min.

6.5 Cost estimation

A cost estimation has been made based on the experience made with pilot plants. By that rough estimation treatment cost of less than 3 Euro/m³ in case of a waste water with the pesticides Diuron, Alachlor, Chlorfenvinphos Isoproturon and Atrazine at a concentration of 10 ppm each and of less than 5 Euro/m³ at a concentration of 30 ppm

each could be achieved with a treatment plant of at least 1000 m² reactor surface area. A plant at this scale would be able to treat around 50,000-100,000 m³ of pesticide waste water per year. In relation to the turnover made with the pesticides the treatment costs seem to be reasonable

7 Literature

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Hiermit versichere ich, dass ich die vorliegende Arbeit selbständig angefertigt und alle verwendeten Hilfsmittel angegeben habe.

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