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DIPLOMARBEIT

Photo-Fenton treatment of olive mill wastewater – Possible use as fertiliser

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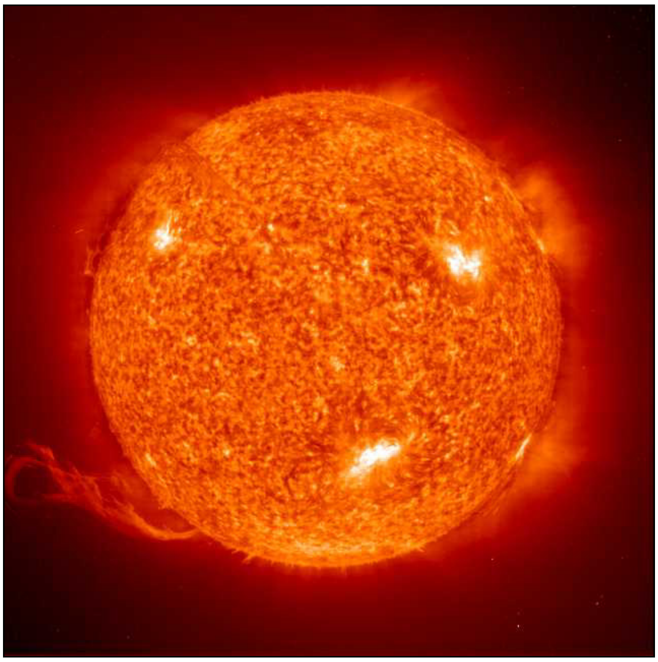
Abstract

Olive mill wastewater (OMW) contains large amounts of organic matter, potassium and phosphorus. A considerable part of the organic matter is of phenolic nature. These phenols are toxic to plants and to many bacterial species. This impedes the use of OMW for irrigation, taking advantage of the high content of plant nutrients, as well as the discharge to biological wastewater treatment.

In the present work a pretreatment involving a combination of acidification, the Fenton method and flocculation was successfully applied to remove the suspended solids. The pretreatment was followed by a photo-Fenton treatment under solar irradiation in compound parabolic collectors common in photocatalysis. A significant selectivity of the photo-Fenton method to the phenolic substances compared to other organic substances present in OMW was proved.

Decrease of phytotoxicity in the course of the treatment was monitored by germination tests. OMW treated by the photo-Fenton method was applied for irrigation in pot experiments with barley (hordeum vulgare L.). The results obtained were promising and the proposed treatment should be considered a possible solution to the existing environmental problem caused by OMW.

A cost estimation of the treatment based on assumptions was performed, taking into account the major factors. It demonstrated that the costs of the treatment would be reasonable in relation to the value of the obtained olive oil.



The sun – source of life and beauty on earth

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1.4 Index of abbreviations

AOP	advanced oxidation process
BOD_n	biological oxygen demand measured after n days
°C	degree Celsius
cf.	confer
cm	centimetre
COD	chemical oxygen demand
CPC	compound parabolic collector
conc.	concentration
EC	electric conductivity
e.g.	“exempli gratia” - for example
eq.	equation
et coll.	and collaborators
EU	European Union
g	gram
GI	germination index
h	hour
I	intensity
i.e.	“id est” – that is
IC	inorganic carbon
L	litre
m^2	square metre
mg	milligram
mL	millilitre
mM	millimolar
µm	micrometre
mS	milli Siemens
µS	micro Siemens
N	normal
n.m.	not measured
OMW	olive mill wastewater
pH	“potentia hydrogenii” – pH value
PI	phenol index
PSA	Plataforma Solar of Almería
Q	accumulated ultraviolet radiation energy in reaction solution
SHE	standard hydrogen electrode
t	reaction time
T	temperature
TOC	total organic carbon
UV	ultraviolet
V	volt
vs.	versus
W	watt

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 [WHO, 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 Joint Monitoring Programme, 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 [Directive 2000/60/EC, 2000].

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 Olive mill wastewater (OMW)

The cultivation of olives in Crete dates back to 5000 BC. By the expansion of Greek and then Roman colonies it was spread over almost all the mediterranean area. Its long history is deeply related with the mediterranean culture.

Nowadays olive oil production is an economically important branch of the mediterranean agriculture, especially in Spain, Italy and Greece. Figures of European olive oil production clearly show the dimensions of this industry (cf. Table 2.1). Olive trees cultivation manners differ largely from region to region. They reach from small, fragmented upland-holdings to big monocultures. A detailed study of the environmental impact of olive tree cultivation can be found in a study by the European Forum of Nature Conversation and Pastoralism [EFNCP, 2000].

Table 2.1: Olive oil production in EU. Figures for olive area and number of producers are from 2000, oil production is the average of the years 1991-95 [EFNCP, 2000]

	Olive area [Ha]	Oil production [tons]	Producers	Approximated % of world olive oil output
Spain	2,423,841	535,000	396,899	28%
Italy	1,430,589	467,000	998,219	24%
Greece	1,025,748	307,000	780,609	16%
Portugal	529,436	35,000	117,000	2%
France	39,421	2,000	19,271	<0.1%
EU	5,449,035	1,346,000	2,311,998	70%

During the milling of olives another environmental problem arises, the accruing wastewater, henceforward called olive mill wastewater or just OMW.

There are three kinds of press systems. The traditional system is a discontinuous press system, which generates three products: Press cake, OMW mainly originating from the water content of the fruits and olive oil. This system was widely replaced by the continuous 3-phase technology established in the 1960’s and 70’s, yielding the same products, but a higher, more diluted amount of OMW because of added process water. Its heart piece is a centrifugation decanter. The recently developed continues 2-phase system, produces just olive oil and pulp. It is the most modern and also environmentally most beneficient system, because adequate technologies exist to treat the press residue.

In regions with intense cultivation, like in Andalusia, the 2-phase technology has already replaced to a considerable extent the 3-phase technology. In less intensly cultivated regions the change to the new technology is financially not viable due to the investment costs. So the OMW production will diminish but not disappear in the future.

The traditional system produces 2-3 litres of OMW for each litre of olive oil, while the ratio in the continuous 3-phase system is about 4-6 litres of OMW per litre olive oil. The 3-phase technology is still predominant. The overall OMW generation in Spain is between 2 and 3 million tons / year [Borja et coll., 1998; Paredes et coll., 1999]. The OMW generation for the whole EU projected by using Table 2.1 is between 5 and 7 millions tons / year.

It should be pointed out that production figures vary significantly. Andalusia reports an average annual olive oil production of 707,000 tons on an area of 1,321,000 Ha in the years 1996-1999 [Junta de Andalucía, 2001] (cf. Table 2.1).

A general characterisation of OMW is difficult, because numerous factors influence its composition. The most important ones are: Annual climatic conditions, variety of olive processed, local soil conditions, press technology, amount of added process water. The analytical characteristics of OMW mentioned in literature vary by several 100 percent

[Beccari et coll., 1999; Fiestas et coll., 1991; Fiestas et coll., 1992; Paredes et coll., 1999]. This high variance also presents a problem to process. Even in the same mill effluent parameters can change significantly within an hour due to the olives processed.

However, OMW could be described as a wastewater with high organic load, high COD, high salt concentration and low pH. Part of the organic load consists of polyphenols. These polyphenols have phytotoxic effects [Maureen et coll., 1982; Paredes et coll., 1999]. They also hamper biological treatment of OMW due to their toxicity to bacteria used in common wastewater treatment plants [Beccari et coll., 1999; Borja et coll., 1996]. Application to soil affects the existing population of fungi and bacteria [Tardioli et coll., 1997]. Furthermore the low pH and the polyphenols can raise the solubility of heavy metals [Bejarano and coll., 1992; Gerke, 1997]. The high salt content of OMW also has to be taken into account when it is to be used as irrigation water.

On the other hand its high organic, potassium and phosphate content has given rise to the discussion about a possible use as fertiliser, e.g. concentrations from 2 to 11 g potassium per litre OMW are reported [Cegarra, 1997; Hamdi, 1993; Junta de Andalucía, 1995].

The dominating current treatment strategy is the storage of OMW in large evaporation ponds to dry it. The solid residue can be burned afterwards. However very large and shallow ponds are necessary to deal with the huge amounts of OMW, which often leak. Because of that again OMW is discharged into the environment. Besides, the ponds represent a strong smell molestation during the whole summer season.

The importance of the environmental problems is confirmed by the number of proposed solutions, although none of them seems really satisfying. Reviews about the general OMW situation and possible treatments can be found [Fiestas et coll., 1991; Fiestas et coll., 1992; Hamdi, 1993], as well as literature about aerobic treatment [Borja et coll., 1998; Garcia et coll., 2000], AOPs applied to model phenols present in OMW [Gernjak et coll., 2002; Herrera et coll., 1998; Miranda et coll., 2000; Miranda et coll., 2001], AOPs [Benitez et coll., 1997a], combination of AOP and anaerobic treatment [Benitez et coll., 1997b], combination of AOP and aerobic treatment [Benitez et coll., 1999] and physical pretreatments like flotation, filtration and centrifugation [Mitrakas et coll., 1996].

The quoted literature represents only a small selection of the literature relevant to the topic that can be found.

2.3 Objectives of this work

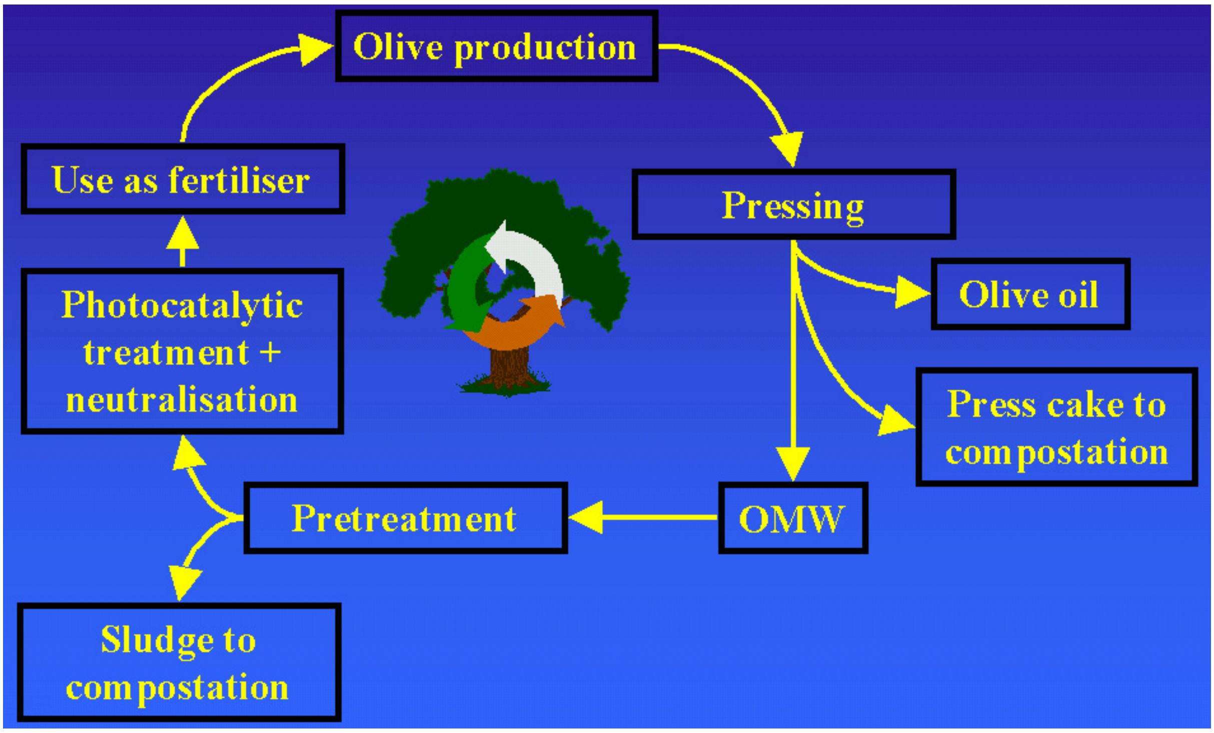
Knowing the situation of OMW, a possible solution to the problem was sought and a zero discharge process was designed. Scientific groups from Portugal, Greece, Spain (Dr. Sixto Malato, Solar Chemistry group at Plataforma Solar of Almería) and Austria (Dr. Rupert Bauer, Vienna University of Technology) applied jointly for a project funded by the EU. The proposal was accepted and funding was granted for the following project:

LAGAR: Water recovery from olive mill wastewaters after photocatalytic degradation and desinfection (contract: FAIR-CT97-3807).

The main scheme of the LAGAR project is depicted in Figure 2.1. The present work was conducted within the scope of this project. Experiments were performed at PSA in Spain.

The first task of the present work was to develop a suitable pretreatment preceding the photocatalytic treatment. In other experiments during the course of the LAGAR project a strategy combining flocculation and Fenton treatment had already been employed successfully. Due to the mentioned big differences between OMW from different sources, this pretreatment was to be adapted to the OMW used in this work. The solid residues after the pretreatment, a sludge containing large amounts of water, was not to be examined in this work. So no statement about the feasibility of this process step can be made.

Figure 2.1: The LAGAR project



The next step was to apply the photo-Fenton method to the pretreated OMW. As this is the most cost-extensive step of the process, the task was to screen the possibilities to improve reaction rates and lower hydrogen peroxide consumption. An adequate stopping point of the photocatalytic treatment was to be found, at which the OMW's conditions were favourable for a subsequent application for irrigation.

The phytotoxicity and the applicability of the treated OMW for irrigation were to be tested by determination of germination indices and plant growth experiments in pots.

2.4 A note on the assessment of the experiments

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. In the latter case it can be a difficult task to choose the relevant parameters during the treatment for the judgement of the process.

In the present work the intention was to avoid unnecessary expenses in the treatment by stopping it, when the toxicity of the OMW was sufficiently decreased to make a use as irrigation water having fertilising effects possible.

The following parameters were measured frequently to characterise the wastewater: TOC, IC, COD, phenol index, pH, EC and the iron concentration, as it was of particular interest due to the treatment method. Also the applied H_2O_2 amount was monitored as it is a primary cost factor of the process. Furthermore germination indices were performed and OMW at different treatment stages was used diluted for the fertirrigation of barley. Besides some more parameters were measured occasionally, like the amount of base necessary to neutralise the OMW.

Other useful and important parameters like the BOD_n or the toxicity to bacterial populations could not be measured due to the relation of complexity, i.e. ratio of work to available workforce (myself) in the course of this work.

Almost all of the parameters measured during the degradation experiments are sum parameters and do not give explicit information about the chemical nature and toxic behaviour of the OMW. As the high phenol content is often mentioned as one of the primary environmentally harmful properties of OMW, consequently the lowering of the phenol index was one of the main aims in the treatment. On the other hand not all phenols have inhibitory effects on plant growth and bacterial populations. As inhibitory substances like p-coumaric acid proved to be well degradable by the Photo-Fenton reaction in prior experiments in the LAGAR project, it was not considered necessary to diminish the phenol index to zero. Neither was it intended to completely eliminate the organic content of the wastewater. On the contrary the aim was to eliminate the wastewater’s toxicity as selective as possible maintaining organic carbon in solution, which can have positive effects in a following application as fertirrigation solution to plants. So also TOC and COD were just parameters to estimate how the process advances. EC and pH were monitored to be in reasonable ranges before application to plants.

3 Theoretical background

3.1 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes are chemical oxidative processes, which are applied in wastewater treatment to oxidise pollutants. A part of them generates hydroxyl radicals. After fluorine the hydroxyl radical is the second strongest known oxidant (2.8 V vs. SHE). It is therefore able to oxidise and mineralise almost every organic molecule yielding in the end CO_2 and inorganic ions. Rate constants for most reactions involving hydroxyl radicals in aqueous solution are usually in the order of 10^6 to 10^9 M^{-1} s^{-1}. The reactions by which hydroxyl radicals attack organic molecules are hydrogen abstraction, electrophilic addition, electron transfer and also radical-radical reactions [Legrini et coll., 1993]. The most common methods of hydroxyl generation in AOPs are presented in Table 3.1.

Table 3.1: Hydroxyl generation in different AOPs [Bauer et coll., 1999; Blanco et coll., 2000a; Legrini et coll., 1993]

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

The use of AOPs for wastewater treatment was studied extensively [Feng et coll., 2000; Legrini et coll., 1993; Safarzadeh-Amiri et coll., 1996]. 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/TiO_2 process, with and without addition of oxidants [Bauer et coll., 1999; Malato et coll., 2002]. Although the interest of investigation just as of companies is growing, few applications at industrial scale are known yet.

3.2 The photo-Fenton method

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 et coll., 2000; Safarzadeh-Amiri et coll., 1996; Walling, 1975; Zepp et coll., 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 (Eq. 3.11 and 3.12).

(3.11) $$[Fe(H_2O)_6]^{3+} + OH^- \rightleftarrows [Fe(H_2O)_5(OH)]^{2+} + H_2O \qquad K=6.5\cdot 10^{11}$$

(3.12) $$[Fe(H_2O)_5(OH)]^{2+} + OH^- \rightleftarrows [Fe(H_2O)_4(OH)_2]^{+} + H_2O \qquad K=3.08\cdot 10^{10}$$

Water and hydroxyl ligands of iron are normally not crucial and will be left out therefore in the rest of the equations, to improve their legibility.

Iron is almost omnipresent in small concentrations, in aquatic and surface water as well as in clouds. Equations 3.13 - 3.15 are therefore thought to be responsible for the formation of hydrogen peroxide in aquatic and surface waters.

(3.13) $$Fe^{2+} + O_2 \longrightarrow Fe^{3+} + O_2^{-\bullet}$$

(3.14) $$O_2^{-\bullet} + H^+ \longrightarrow HO_2^{\bullet}$$

(3.15) $$HO_2^{\bullet} + Fe^{2+} + H^+ \longrightarrow H_2O_2 + Fe^{3+}$$

Some important reactions occurring in an aqueous solution of iron and hydrogen peroxide are represented in the equations 3.9 and 3.16 - 3.21. If organic substances are present, the reaction scheme gets 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.

(3.16) $Fe^{3+} + H_2O_2 \rightleftarrows Fe(OOH)^{2+} + H^+$

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

(3.9) $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^-$

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

(3.19) $OH^{\bullet} + H_2O_2 \longrightarrow H_2O + HO_2 \cdot$

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

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

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. 3.17 and 3.20), 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. 3.22), with carboxylic acids decarboxylation takes place (Eq. 3.23). The reaction is a ligand-to-metal charge-transfer reaction (LMCT), where the activating energy is provided by the incident photon.

(3.22) $[Fe^{3+}L] + h\nu \longrightarrow [Fe^{3+}L]^* \longrightarrow Fe^{2+} + L^{\bullet}$

(3.23) $[Fe^{3+}(RCO_2)] + h\nu \longrightarrow [Fe^{3+}(RCO_2)]^* \longrightarrow Fe^{2+} + CO_2 + R^{\bullet}$

Equations 3.22 and 3.23 are also relevant in atmospheric chemistry and surface waters and are believed to be partly responsible for the autopurification capacity of these systems.

(3.24) $R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$

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

Another important factor is the participation of oxygen in the process (Dorfman mechanism, Eq. 3.24 and 3.25), 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 (normally below 4), because at higher pH ferric ions would begin to precipitate as hydroxide. Furthermore, the added iron has to be removed after the treatment.

4 Materials and methods

4.1 Olive mill wastewater

OMW for the experiments was collected twice from the OMW storage basin of a small olive press working with the traditional press system and located in Uleila del Campo in the Spanish province of Almería near the PSA. OMW from the first trip was applied only in Experiment 1. In all other experiments OMW from the second trip was applied. Measured characteristics are listed in Table 4.1. An absorption spectrum is not presented, because it is pH dependant. The optical density of OMW rises, if the pH is increased. For further general characteristics reported in literature confer Chapter 2.2.

Table 4.1: Characteristics measured of OMW treated in experiments

Parameter	**OMW (first trip)**	**OMW (second trip)**
TOC [mg.L^{-1}]	16400	23500
COD [mg.L^{-1}]	47100	64100
PI [mg.L^{-1}]	3950	5300
pH	5.0	4.5
EC [mS.cm^{-1}]	3.8	5.0
Iron [mM]	1.5	2
Total solid residue [g.L^{-1}]	Not measured	51

4.2 Reagents used

Reactives for photo-Fenton treatment

Formula	*Product*	*Company*	*Product Number*
H_2O_2	30% w/v PRS	Panreac	PA 141076
$FeSO_4.7H_20$	Iron(II)sulphate 7-hydrate PRS	Panreac	PA 141362

Flocculation agent

	VTA 32 from VTA Engineering und Umwelttechnik GmbH
	The formulation of VTA 32 was not provided by the producer. The label mentioned that it contained polyaluminium silicates. The TOC was 34 g/ L. A dilution 1/100 had a pH of 3.84 and a EC of 7.7 mS/ cm.

Reactives for pH adjustment

Formula	*Product*	*Company*	*Product Number*
H_2SO_4	Sulphuric acid 96 % p.a.	Panreac	PA 131058
HNO_3	Nitric acid 65 % p.a.	Merck	1.00456
NaOH	Sodium Hydroxide pellets p.a.	Panreac	PA 131687
KOH	Potassium Hydroxide pellets 85 % p.a.	Panreac	PA 121515
NH_3	Ammonia solution 25 % p.a.	Merck	5432

Reagents for wastewater analytics

	Product	*Company*	*Product Number*
	Folin-Ciocalteau's phenol reagent	Merck	1.09001
	Sodium Carbonate PRS	Panreac	PA 141648
	1,10-Phenantroliumchloride p.a.	Merck	7223
	L(+)-Ascorbic acid p.a.	Merck	127
	Sodium thiosulphate 5-hydrate p.a.	Merck	6516
	Potassium iodide p.a.	Panreac	PA 121542
	Zinc iodide starch solution p.a.	Merck	1.05445
	Catalase from bovine liver, 2390 units / mg solid	Sigma	C-9322
	COD cell test 10-150 mg / L	Merck	1.14540
	COD cell test 100-1500 mg / L	Merck	1.14541
	COD cell test 500-10000 mg / L	Merck	1.14555

Reagents applied for fertilisation in pot experiments

Formula	*Product*	*Company*	*Product Number*
NH_4NO_3	Ammonium nitrate p.a.	Panreac	PA 131135
K_2HPO_4	Di-Potassium hydrogen phosphate anhydrous p.a.	Merck	1.115071
K_2SO_4	Potassium sulphate p.a.	Panreac	PA 131532
$CaCl_2$	Calcium chloride p.a.	Merck	102378
$Mg(Cl)_2.6H_2O$	Magnesium chloride 6-hydrate PRS	Panreac	PA 131396
$Mg(NO_3)_2.6H_2O$	Magnesium Nitrate 6-hydrate p.a.	Panreac	PA 131402
$FeSO_4.7H_20$	Iron(II)sulphate 7-hydrate PRS	Panreac	PA 141362
$MnCl_2.4H_2O$	Manganese(II) chloride 4-hydrate p.a.	Merck	5927
$CuSO_4.5H_2O$	Copper(II) sulphate 5-hydrate p.a.	Panreac	PA 131270
H_3BO_3	Boric acid p.a.	Probus	10402
$ZnSO_4.7H_2O$	Zinc sulphate p.a.	Panreac	PA 131787

Reagent applied for measurement of GI of salt solution

Formula	*Product*	*Company*	*Product Number*
KCl	Potassium chloride p.a.	Merck	104936
NaCl	Sodium chloride p.a.	Merck	406404
Na_2SO_4	Sodium sulphate p.a.	Merck	106649

4.3 Analytic equipment used

Total organic carbon (TOC) and inorganic carbon (IC) were measured by means of a TOC analyser, model Shimadzu TOC 5050A. COD measurements were performed using Merck COD cell tests and the according equipment, the Merck Thermoreactor TR 300 and the photometer Spectroquant® Nova 30. 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 µS – 200 mS. Anion concentrations were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac AS14

4 mm column. Eluent was an aqueous solution of $NaHCO_3$ (1 mM) and Na_2CO_3 (3.5 mM) at a flow rate of 1.2 $mL.min^{-1}$. For photometric measurements a Unicam-2 spectrophotometer was used.

For preparation of standards Milli-Q water (EC 0.054 $\mu S.cm^{-1}$) prepared with a Millipore System was used. All filtrations were performed with filters from Millipore with a pore size of 0.2 µm, type Millex-GN, Syringe Driven Filter.

Global UV (300-400 nm) irradiance 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.

4.4 Analytical methods

4.4.1 Determination of phenol index

The phenol index is commonly measured with the 4-Aminoantipyrine reagent [Council directive, 1979], but 4-Aminoantipyrine has a poor or no response to para-substituted phenols [Box, 1983]. It was therefore measured with the Folin-Ciocalteau phenol reagent [Singleton et coll., 1965], which is also widely employed [Box, 1983]. It is based on the reduction of phosphomolybdic and phosphotungstic acids in alkali media by phenolate anions. Partly reduced heteropoly acids form molybdenium-tungsten blue, which is measured colorimetrically. Caffeic acid was used for calibration. However, different phenols respond differently to this method, depending on the number of hydroxyl moieties on the aromatic ring and several other reasons [Box, 1983].

The measurement was carried out as follows: To 1 mL of first diluted and afterwards filtered sample 5 mL of Folin-Ciocalteau reagent (10% v/v) were added. The resulting solution was shaken for 3 minutes until 4 mL of Na_2CO_3 solution (7.5 % w/v) were added to the test-tube. Afterwards the solution was shaken for further 120 minutes without protection from light until the absorption compared to distilled water was measured at a wavelength of 765 nm [Singleton et coll., 1965].

Ferrous iron and hydrogen peroxide can influence the measurement. As long as hydrogen peroxide is present in the solution, almost no ferrous iron is present. Furthermore, usually diluted solutions are applied, because the phenols represent a principal component in the solution. So separation of the disturbing ferrous iron and hydrogen peroxide was not performed, as their effects were not considered significant after comparison in preliminary experiments of directly applied and extracted samples.

4.4.2 Determination of iron concentration

The method follows ISO 6332. For measuring the Fe^{2+} concentration in the sample 4 mL of phenantroline solution (0.1% w/v) were mixed with 2 mL of diluted and then filtered sample. The absorption at 510 nm of this solution was measured against a blank containing 1 mL distilled water and 2 mL of the phenantroline solution in case of colourless samples and against a blank containing 2 mL distilled water and 1 mL sample in case of coloured samples.

To measure the total iron concentration a spatula-tip of ascorbic acid was introduced directly into the cuvette and the cuvette shaken to dissolve the solid ascorbic acid. The absorption at 510 nm was measured after exactly two minutes against the same blank used before in the Fe^{2+} measurement. Fe^{3+} concentration was obtained by calculating the difference between total and ferrous iron concentration.

4.4.3 Iodometric determination of hydrogen peroxide

1 mL of untreated sample was 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.

4.4.4 Chemical oxygen demand

Hydrogen peroxide in solution disturbs the measurement of COD. To remove it from the solution the enzyme catalase was applied like described below.

In a beaker 25 mL of diluted but not filtered sample were adjusted to pH 7 with diluted soda lye. 1 mL of catalase solution (10 mg catalase dissolved in 100 mL H_2O) was added to the sample and stirred for 10 minutes until all peroxide was destroyed. The volume was filled up to 50 mL and filtered. Then 1 mL (in range 500-10000 mg $O_2.L^{-1}$ COD) or 3 mL (lower ranges of COD) were added to the COD cell test. The COD test was put into the thermoreactor for two hours at a temperature of 148 °C. Afterwards the COD test was put into the dark for cooling down until the absorption compared to the reference cuvette provided in the test kit was measured at the corresponding wavelength following the instructions by Merck. The measurement with the cell tests for the range from 10 to 150 mg $O_2.L^{-1}$ formed an exception. Air was used as blank, because the UV spectrometer’s software impeded to measure negative absorbance lower than -0.3.

4.4.5 Total organic carbon, inorganic carbon, anions

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

4.4.6 Determination of pH value and EC

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

4.4.7 Determination of total solid residue

Total solid residue was measured by drying 50 mL of OMW in a petri dish at 90 °C until no further weight loss occurred.

4.5 Pretreatment of OMW

4.5.1 Pretreatment in test tubes

A series of tests in test tubes was performed, in which parameters like the sequence of pretreatment steps, iron concentration and flocculation agent concentration were varied. Acidification, when realised, took place at the beginning with sulphuric acid. Acidified samples had a pH of 2.6 and non-acidified samples a pH of 4.6.

The tests were carried out in 15 mL test tubes. Each test tube was filled with 10 mL OMW, afterwards further reagents (iron solution, hydrogen peroxide, flocculation agent) were added step by step. After each addition the solutions were homogenised 15 minutes by automatic shaking. Of the supernatant solutions TOC, phenol index and supernatant volume were measured and its transparency and hue verified by eye-check. If no sedimentation took place, TOC and phenol index were measured from the homogeneous solution (for details cf. Chapter 5.1).

4.5.2 Pretreatment in degradation experiments

The in Table 4.2 listed different pretreatment strategies were tried. They can be divided into two principal strategies: To combine Fenton treatment and flocculation afterwards, or without a prior Fenton treatment accepting a higher need of flocculation agent (Experiment E4-E6). The pretreatment was always performed with undiluted OMW, even in those degradation experiments where diluted OMW was used.

The pretreatment was usually performed in a open plastic ton (volume 54 L, inner diameter 33 cm, height 63 cm) with 50 L OMW. After addition of flocculation agent the OMW was stirred manually with a stick for 10-15 minutes to promote formation of flocs. Afterwards the OMW was left standing to sediment. After sedimentation OMW for the experiment was taken from the supernatant containing no suspended solids. The accruing sludge was discharged. No experiments were performed with it.

Experiments 5 and 6 were an exception in that the pretreatment was conducted directly in the 200 L barrel, in which the OMW was stored. Here flocculation agent was added in portions of 2.5 mL.L^{-1} OMW and homogenised manually some minutes by shaking the whole barrel as stirring was not possible due to too small openings at the top. Then the barrel was left standing to enable sedimentation, which did not occur until this procedure was repeated four times yielding a total added amount of 10 mL flocculation agent per litre OMW.

Table 4.2: Assay of pretreatment in experiments. E11 is not mentioned, because it was performed with the residual solution of E10 without another pretreatment

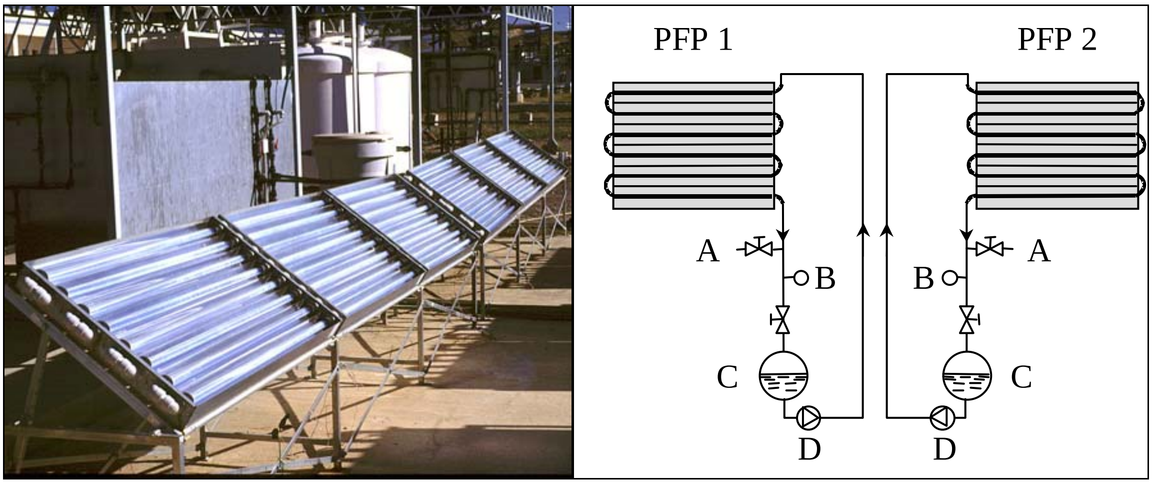
Experiment	**Applied acid**		**$FeSO_4$**	**H_2O_2**	**VTA 32**	**Remarks**
	Which	**$[mL.L^{-1}]$ ≙ [mM]**	**[mM]**	**$[mL.L^{-1}]$**	**$[mL.L^{-1}]$**	
E1	H_2SO_4	2.33 ≙ 28	1	--	--	Blind experiment without pretreatment
E2	H_2SO_4	1 ≙ 12	2	10	2.5	Flocculation in 55 L ton
E3	H_2SO_4	1 ≙ 12	2	50	2.5	Flocculation in 55 L ton
E4	H_2SO_4	--	--	--	10	Flocculation in 55 L ton
E5, E6	H_2SO_4	--	--	--	10	Flocculation in 200 L barrel
E7, E8, E9	HNO_3	6 ≙ 87	4	30	2.5	Flocculation in 55 L ton
E10, E12, E13	HNO_3	6 ≙ 87	1	10	1.5	After acidification separation of mud, then Fenton, all in 55 L ton

4.6 Degradation experiments

4.6.1 CPC reactors at PSA

The photocatalytic experiments were carried out by using CPCs installed at PSA. Two identical reactors were available to enable parallel experiments under exactly the same conditions. Normally just one of them was used at a time, the exception being the Experiments 7 and 8, which were executed in parallel.

Figure 4.1: Picture and scheme of the CPC at PSA: (A) sampling valve; (B) thermocouple; (C) not-reacting tank; (D) pump; (PFP) plug flow photoreactor



The photoreactor configuration is common in photocatalysis (cf. Figure 4.1). It consists of a plug flow reactor in a total recirculation loop with a not-reacting tank whose function is to provide aeration and samples for analyses. Each photoreactor consisted of three CPC modules in series (total irradiated surface: 3.08 m^2) placed on fixed supports inclined 37° (latitude of PSA) with respect to the horizontal plane and facing south, in order to maximise the daily absorption of solar radiation.

The plug flow photoreactor consisted of Pyrex glass tubes (inner diameter 29.2 mm). Behind each tube two parabolic electro-polished aluminium reflectors are placed to redirect incident global radiation towards the tube. All the tubes and the collectors were connected in series. The reaction solution was continuously fed to the plug flow photoreactor from the not-reacting tank by means of a centrifugal pump (PAN WORLD, Japan, Model: NH-100 PX, 100 W). The flow rate, maintained constant for all the runs, was 20 $L.min^{-1}$. The Reynolds number value was of about 17000 indicating a turbulent regime of the flow inside the tubes. Normally the total volume in the whole system was 30 L to leave room in the tank for building foam (the maximum volume of the whole system with a full tank is 39 L), the volume irradiated in the glass tubes was 22 L. A more detailed description of the CPC at PSA can be found elsewhere [Blanco et coll., 2000b].

4.6.2 Measurement of incident radiation

Global UV (300-400 nm) irradiance 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.

The accumulated incident UV-radiation can be calculated by using equation 4.1 [Malato et coll., 2000].

$$Q_{UVn} = Q_{UVn-1} + \frac{\Delta t_n * UV_{GN} * A}{1000 * V} \tag{4.1}$$

where Q_{UVn}, Q_{UVn-1} are irradiated UV-energy of samples n and (n-1) in $kJ.L^{-1}$, Δt_n is the time interval between two sampling points in s, UV_{GN} is the average incident radiation on the irradiated area in $W.m^{-2}$, A is the irradiated area in m^2 and V is the total plant volume in L.

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 coll., 1999].

4.6.3 Realisation of degradation experiments

Experiments 1-11 were conducted in the CPC described above. Experiment 12 and 13 were no photocatalytic degradation experiments. They were performed in black 25 L plastic canisters, which were placed into sunlight to heat up the reaction solution. An overview including the experiment schedule is given in Table 4.3.

Table 4.3: Degradation experiments – Overview: hours of duration are hours of irradiation, further iron was added sometimes during the experiments (cf. Table 4.5)

Experiment	Date	Wastewater	Volume	Iron conc. At beginning	Duration
	(all in year 2001)		[L]	[mM]	[days / hours]
Exp1	5., 6., 7., 9.02.	OMW, without pretreatment, only experiment with first, less polluted OMW	32	1.5	2 / 21
Exp2	21., 22., 23.2.	Pretreated OMW, undiluted	30	4.8	3 / 15.5
Exp3	8., 9., 12., 13.3.	Pretreated OMW, undiluted	30	3.7	4 / 27.6
Exp4	5., 6., 7., 8., 9., 12.3.	Pretreated OMW, undiluted	30	3.4	6 / 39.1
Exp5	30.4, 2., 3., 4., 7.5.	Pretreated OMW, undiluted	30	4.3	5 / 33.3
Exp6	13., 14. 5.	Pretreated OMW, undiluted	30	3.4	2 / 9.5
Exp7	17., 18.5.	10 L pretreated OMW diluted	32	2.2	2 / 9
Exp8	17., 18.5.	10 L pretreated OMW diluted	30	2.5	2 / 9
Exp9	21., 22.5.	10 L pretreated OMW diluted	30	2.8	2 / 10
Exp10	23., 24., 25., 28.5.	Pretreated OMW undiluted as feed solution, Experiment starting with 10 L feed solution diluted to 30 L	30	3	4 / 19.8
Exp11	29., 30.5.	Further degradation of solution of Experiment 10, after stopping of addition of feed and taking out bleed, 3 mM Fe added at start	30	6	2 / 5.3
Exp12	4.-18.6.	pretreated OMW undiluted	10	7	11 / -
Exp13	4.-12.6.	pretreated OMW undiluted	10	12	7 / -

The general procedure of an experiment usually involved the following steps in the mentioned order: Covering the CPC with black polyethylene foil to protect it from light, filling the reaction solution into the CPC, turning on the centrifugal pump, 15 minutes homogenisation period due to reactor configuration (plug flow photoreactor), initial sample taking, adjustment of pH (sulphuric or nitric acid) and addition of ferrous sulphate if not already done in the pretreatment, homogenisation period of 15 minutes, next sampling, addition of hydrogen peroxide, 15 minutes reaction without solar irradiation, sampling and uncovering of CPC, 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 starting parameters after pretreatment and filling of reactor for the degradation experiments are given in Table 4.4.

Table 4.4: Starting parameters after pretreatment and filling of reactor

Experiment	TOC	COD	Total Phenols
	[mg.L^{-1}]	[mg.L^{-1}]	[mg.L^{-1}]
Exp1	16400	47100	3950
Exp2	20100	53000	3300
Exp3	20400	55500	2400
Exp4	18700	53500	4150
Exp5	19100	59900	4100
Exp6	19500	60500	4150
Exp7	5550	20400	1100
Exp8	6800	21400	1260
Exp9	6200	20200	1100
Exp10	6400	20100	1400
Exp11	12800	35300	1450
Exp12	19600	59800	3450
Exp13	19600	59800	3450

In the degradation experiments ferrous sulphate was used to add iron. Ferrous iron and hydrogen peroxide react by the Fenton reaction without sunlight. To determine this effect separately the CPC was covered with black plastic when iron was added to measure the effect in the dark. These dark times are not considered in the reaction time, because the reaction time was defined as time under irradiation. Due to this proceeding an abrupt change can be observed partly at the beginning of the reactions in the depictions of measurements vs. time and vs. accumulated UV-radiation energy. Furthermore, in Experiment 12 and 13 no reaction time was noted down, because they were executed without solar irradiation. Further abrupt changes could be observed when ferrous iron was added by the same procedure or when an experiment was interrupted due to nightfall and continued on the subsequent workday. During such a pause the CPC was always covered with black polyethylene foil to prevent light from entering the solution.

Due to slow reaction times further iron was added during Experiment 1, 2, 3 and 4. Data on amount of iron added, reaction time, accumulated UV-radiation energy and hydrogen peroxide consumed at the moment of iron addition is given in Table 4.5.

Hydrogen peroxide concentration was tried to maintain constant around 5 g.L^{-1} (147 mM) during the Experiments 1, 2, 3, 4, 6, 7, 8 and 11. This proved difficult, because the hydrogen peroxide consumption rate varied considerably (from 0 to 15 $g.L^{-1}.h^{-1}$) and hydrogen peroxide concentration was not known until 45 minutes after the time of sample taking due to analysis duration. So estimations of the hydrogen concentration had to be made, which were not always correct. Nevertheless the hydrogen peroxide concentration seemed not to be rate limiting as long as there was oxidant in the solution.

Table 4.5: Iron addition during degradation experiments

Experiment	Amount of iron added	t	Q	H_2O_2 consumed
	[mM]	[h]	[$kJ.L^{-1}$]	[$g.L^{-1}$]
Exp1	1	9	73.7	7.2
Exp1	3	15	122.2	12.8
Exp2	1	6.5	62.7	9.3
Exp2	2	9.5	89.9	11.1
Exp3	2	6	27.4	10
Exp4	2	25.3	158.4	29.1

In Experiment 5 a concentration of less than 1 gram hydrogen peroxide per litre was maintained, to investigate if lower concentrations provoke a lower consumption of hydrogen peroxide per removed COD.

In Experiment 7 the introduction of more air into the solution was attempted to provide oxygen for the reaction on the one hand and to diminish the inorganic carbon on the other hand. To achieve this a small modification was made to the original CPC configuration (cf. Figure 4.1). An additional upward directed tube was inserted in the horizontal tube leading back to the tank. This tube was open to the ambient air on its upper end and thereby air was sucked into the solution by Bernoulli’s law.

In Experiment 9 just one hydrogen peroxide supplement was made (6.7 $g.L^{-1}$), because the intention was to produce OMW with a definite hydrogen peroxide consumption for irrigation.

In Experiment 12 and 13 hydrogen peroxide was added in portions of 15 $g.L^{-1}$. A new portion was added always when the former portion had reacted completely.

The particularities of Experiment 10 will be described here in detail as its execution differed stronger from the others experiments. While the other experiments were performed in batch-mode, in Experiment 10 a semi-continuous experiment was tried. This was done to investigate how the phenol concentration of the bleed solution developed applying a fixed amount of 20 grams hydrogen peroxide per litre undiluted pretreated OMW. Information about the selectivity of the process towards phenols was expected.

First sufficient pretreated OMW was provided with a definite iron concentration of 3 mM and pH of 2.6. The experiment was started by diluting 10 L of pretreated OMW to 30 L in the

CPC and the iron concentration of the diluted solution was adjusted to 3 mM to keep the iron concentration constant throughout the experiment. Then a definite amount of hydrogen peroxide was added (20 grams hydrogen peroxide per litre pretreated OMW).

After the consumption of this portion hydrogen peroxide the pump was turned off and the CPC was covered and thereby protected from light. Five litres of the reaction solution were taken out of the reactor and discarded (the bleed solution) and five litres of pretreated OMW were added. Then the pump was turned on. Besides OMW also between 20 and 50 mL of NH_3 solution (25% w/v) were added to maintain the pH constant during the experiment. After 20 minutes of homogenisation again 20 grams hydrogen peroxide per litre pretreated OMW added were supplied to the solution and the CPC was uncovered again.

By this procedure seven times a quantity of five litres OMW feed solution was added.

4.7 Determination of germination index

The determination of the GI is a rapid bio-assay performed in petri dishes, which measures phytotoxic effects. Usually extracts of soils or composts are applied to measure its phytotoxicity and influence on radical growth [Moreno et coll., 1998; Zucchoni et coll., 1981]. The method has also been applied to OMW or composts containing OMW [Murillo et coll., 1995; Riffaldi et coll., 1993; Zucchoni et coll., 1985] and other wastes containing phenols as main toxic components [Maureen et coll., 1982; Ortega et coll. 1996]. Barley (Hordeum vulgare L.) was chosen as plant species used in this work, because high sensitivity to phenols has been reported [Maureen et coll., 1982]. Also it proved to be more sensitive than the widely applied cress (Lepidium sativum L.) in a preliminary experiment. The comparably rapid determination of the germination index was also used to estimate the toxic potential and the applicability of the OMW for the pot experiment.

The measurement was conducted as follows. In a PVC petri dish (85 mm diameter) 15 barley seeds were placed on a filter paper disk moisted with 2.5 mL liquid (with NaOH or KOH neutralised OMW for sample, samples were not filtered, distilled water for blank). The seeds were covered with another filter paper disk and the petri dish was shut with its fitting cover. To prevent desiccation and thereby concentration variations, the petri dish was wrapped up in Parafilm® leaving only a small open space to enable some necessary gas exchange. Then the petri dish was incubated for 72 hours at 20 °C in the dark. Afterwards the percentage of seeds germinated and the average length of the principal roots were determined. This procedure was executed with three petri dishes for each sample to increase the number of seeds applied to 45 to improve the quality of the results. Three petri dishes with distilled water as a blank were also always prepared. The GI was then calculated with Equation 4.2 [Moreno et coll., 1998].

(4.2) $$\mathrm{GI} = \frac{\%\mathrm{germinated}_{Sample} \cdot AvgRootlength_{Sample}}{\%\mathrm{germinated}_{Blank} \cdot AvgRootlength_{Blank}} \cdot 100\%$$

4.8 Pot experiments

Pot experiments can be applied to determine nutrient deficiencies and nutrient reserves in soil, to investigate plant physiological consequences of substance deficiencies or abundance of potentially harmful substances and to test new fertilising or soil improving products [Kühn, 1972; Schilling, 2000]. It therefore seemed to be an adequate tool to measure the applicability of OMW for irrigation of plants, before and after treatment.

Of the many possibilities of principal set-ups two were chosen due to their comparably easy implementation and the few materials needed: The cultivation in natural soil and the cultivation in an inert substrate, in this case perlite, which will be described below.

4.8.1 Materials

4.8.1.1 Plant

As mentioned above barley (Hordeum vulgare L.) was chosen as plant species used in this work, because high sensitivity to phenols had been reported [Maureen et coll., 1982].

Further advantages of using cereals in pot experiments are, that they grow rather fast and above all that a considerably high number of plants can be sown in a single pot, which increases the total number of plants and thereby the statistic reliability [Kühn, 1972; Schilling, 2000].

4.8.1.2 Greenhouse

To provide good control of a pot experiment it has to be conducted in a protected environment. Thereby the pots can be protected from wind, rain, harsh temperature changes, animals and insects, and the irrigation can be controlled.

The greenhouse used in this experiment was provisional but suitable for this pot experiment (cf. Figure 4.2). It consisted of a plastic tunnel approximately 18 m long, 2.3 m high and 4 m wide. The plastic foil was made of polyethylene. The orientation of the greenhouse was north-south. The floor was not covered. Inside 6 tables (total length 8.5 m) were placed in a row as support for the 32 pots on them. They were covered with white paper to prevent them from heating up. On the north end was a door and two windows placed on western and eastern side of the greenhouse. The south end was covered by black polyethylene, which did not influence homogenous irradiation, as the tables with the pots on them were put close to the centre of the tunnel. Of the above mentioned functions this greenhouse clearly did not fulfil the task to prevent insects from entering, but the rest of them was accomplished.

Figure 4.2: Total view of greenhouse facing west and inside view of greenhouse facing south

4.8.1.3 Substrate

Two different substrates were chosen for the pot experiments: Earth and perlite.

The earth was collected from land from Cabo de Gata, a zone near the PSA. Earth was chosen because it was supposed to possess microbiological activity which could possibly interact with the organic carbon supplied by irrigation with OMW. Thereby possible positive fertilisation effects were expected by the organic carbon. Disadvantages of earth as substrate were that the earth's composition, texture and content of nutrients was unknown and could not be determined within the scope of this work. So according to these factors the utilisation of earth resembled a black box.

To rule out the above mentioned uncertainties considering content of nutrients also the inert substrate perlite was used. Perlite is an aluminium silicate taken from volcanic rock formed by rapid cooling under the sea and containing 2-5% water. This volcanic rock is furnaced at 1000 °C. The obtained perlite particles are 10 – 20 times its original size, white in colour and have a porosity exceeding 95%. It is chemically inert, contains no mineral nutrients and has no biological activity. Perlite is available in various particle sizes. In this work perlite from the Spanish company Marjal, type B6 (this means an average particle size of about 2-3 mm) was used.

4.8.1.4 Pots

The pots were made of polyvinylchloride and were of a fair grey colour. Their volume was 12 L. Their bottom diameter was about 18 cm, their top diameter 29 cm and their height 26 cm.

They were supplied with saucers which could contain around 0.7 L with the pot inside. They had three holes in the bottom to permit aeration and furthermore in this case irrigation by capillarity.

4.8.2 Realisation

Two pot experiments were conducted. Each of the pot experiments contained 8 series with different irrigation and fertilising strategies. Each series was conducted with 4 pots receiving the same treatment for statistical reasons. That means that in total in each experiment 32 pots were used.

The first sowing was done on 30th of March 2001. This experiment was harvested 28 days later on 27th of April of 2001. The second sowing was performed on 11th of June of 2001 and the plants were harvested again 28 days later on 8th of July 2001. After harvesting the plants a weight analysis was conducted to compare the growth.

The first pot experiment will henceforward be called PotA and the second PotB. The single series will be called PotA1 - PotA8 and PotB1 - PotB8.

4.8.2.1 Filling of pots and sowing of barley

Each pot was filled first with 0.5 kg of washed gravel to favour aeration of the actual substrate. By filling the pots with gravel also through each of the three holes in the bottom a cord (0.5 cm, length 25 cm) was fixed, so that about 15 cm of the cord were inside and 10 cm outside of the pot. Than the actual substrate was filled into the pot taking care that the cord was embedded in a rather vertical position to connect also the upper part of the pot by capillary force with the liquid reservoir (cf. Figure 4.3).

Figure 4.3: Filling of pots and sowing of barley with sowing template

Then during some days the filled pots were irrigated by capillarity via the saucer to saturate the Perlite with liquid and to humidify the earth. During these days also first fertilisation and supply with trace elements took place to provide a substrate ready for cultivation for the sowing.

For the sowing of the barley a template was used to sow 31 seeds of barley into each pot, that means that in an experiment in total 124 (4*31) seeds were treated equally. The depth of the hole was around 1.5 – 2 cm, into which the seed was placed (cf. Figure 4.3).

4.8.2.2 Fertilisation

No example could be found in literature, where an experiment equal in terms of chosen plant, pot volume, used substrate and experimental goals was described. So considering descriptions and examples in literature [Finck, 1982; Kühn, 1972; Schilling, 2000] an new fertilisation strategy was worked out for this experiment.

All mineral fertilisation was donated by addition of dissolved salts of the minerals to the irrigation water.

In all pots with perlite micronutrients were added before the experiment started. The amounts per pot were 50 mg iron, 20 mg manganese, 10 mg zinc and copper and finally 2 mg boron. In pots with perlite also 500 mg calcium and 100 mg magnesium were added before the sowing took place. These amounts were equal in each pot with perlite as substrate. Pots with earth as substrate were not provided with these elements, because it was supposed that they should be sufficiently available in normal soil. The salts used were iron(II) sulphate, manganese chloride, zinc sulphate, copper(II) sulphate, boric acid, calcium chloride and magnesium chloride.

The main plant nutrients nitrogen, phosphorus and potassium were added as solutions of ammonium nitrate, di-potassium hydrogen phosphate and potassium sulphate. A total donation throughout the whole experiment of 1.6 g nitrogen, 0.65 phosphorus and 1.6 g potassium was considered a fertilisation of 100% as well in experiments with earth as substrate as in experiments with perlite as substrate. That means that a fertilisation of 25% in a pot meant that just 25% of the three main plant nutrients were supplied to this pot during the experiment (cf. Table 4.7).

To prevent too high salt concentrations in the pots and thereby salt damages to the recently germinated plants these main nutrients were added in three equal donations. The first donation was given before the sowing took place. The second donation was given 10 days after sowing and the third donation was given 17 days after sowing.

4.8.2.3 OMW applied, Fertilisation strategy and irrigation procedure

In different series OMW from different experiments in different dilutions was used. All dilutions were prepared with distilled water. Also in blank series distilled water was used. Furthermore the applied fertilisation strategies were different.

Data about the OMW applied to prepare the irrigation solutions can be found in Table 4.6. Exp4, Exp9 and Exp11 were used as taken out of the CPC after the end of the corresponding experiments. OMW untreated obviously was taken as brought from the mill. Before dilution for irrigation took place, the OMW was neutralised with KOH and the parameters represented in Table 4.6 were determined. Note that iron did not precipitate at pH 7, although it was mainly present as ferric iron. Nitrate and phosphate in Exp4 were not measured, but are most probably in the range of the untreated OMW.

Furthermore it has to be kept in mind that Exp4 and OMW untreated were not diluted before these measurements were conducted. Exp9 and Exp11 origin from experiments in which diluted solutions were used, namely diluted 1/3 in Exp9 and 4/5 in Exp11. The latter value was calculated by making a mass balance for the preceding semi-continuous Experiment 10. The calculated value was confirmed by conformity of calculated and measured nitrate concentration (knowing feed concentration and assuming that nitrate did neither form nor disappear during the experiment). Applying the same mass balance for ammonia yields a calculated ammonia concentration of about 0.5 g.L^{-1}, again assuming that the ammonia concentration was unaffected by the reactions taking place in the solution.

Potassium was never measured in the OMW due to lack of a readily available analytical method at PSA where the experiments were performed. Literature reports values of 2 g.L^{-1} or more. For calculations of donations of potassium in the pot experiments a value of 2 g.L^{-1} was presumed, being aware of the uncertainties produced by this presumption.

Table 4.6: Parameters of OMW used for preparation of irrigation solutions after neutralisation with KOH, cf. text for further details

		Exp4	OMW untreated	Exp9	Exp11
TOC	**[mg.L^{-1}]**	4800	21500	5700	4350
COD	**[mg.L^{-1}]**	14000	60300	14700	8600
PI	**[mg.L^{-1}]**	210	4800	680	190
K^+ added by neutralisation	**[mg.L^{-1}]**	6500	5200	3800	4600
Fe	**[mg.L^{-1}]**	160	150	135	320
SO_4^{2-}	**[mg.L^{-1}]**	n.m.	100	310	950
NO_3^-	**[mg.L^{-1}]**	n.m.	-	1600	3100
PO_4^{3-}	**[mg.L^{-1}]**	n.m.	750	250	540

In Table 4.7 the single series of PotA and PotB are described considering substrate, fertilisation and application of OMW.

Table 4.7: Irrigation strategies in pot experiments

Series	Substrate	Fertilisation		Irrigation solution		
		Nitrogen / phosphorus	Potassium	Origin of OMW	Dilution	EC [mS.cm^{-1}]
PotA1	Earth	100%	100%	Dist. H_2O	-	-
PotA2	Earth	0%	0%	Dist. H_2O	-	-
PotA3	Earth	0%	0%	Exp4	1/40	2.3
PotA4	Earth	0%	0%	Exp4	1/20	4.5
PotA5	Perlite	100%	100%	Dist. H_2O	-	-
PotA6	Perlite	25%	25%	Dist. H_2O	-	-
PotA7	Perlite	25%	25%	Exp4	1/40	2.3
PotA8	Perlite	0%	0%	Exp4	1/40	2.3
PotB1	Perlite	150%	150%	Dist. H_2O	-	-
PotB2	Perlite	100%	100%	Dist. H_2O	-	-
PotB3	Perlite	100%	100%	Untreated	1/50	1.04
PotB4	Perlite	100%	0%	Untreated	1/50	1.04
PotB5	Perlite	100%	100%	Exp9	1/33	1.03
PotB6	Perlite	100%	0%	Exp9	1/33	1.03
PotB7	Perlite	100%	100%	Exp11	1/50	1.09
PotB8	Perlite	100%	0%	Exp11	1/50	1.09

Irrigation by capillarity was applied. Irrigation took place once per day between 8:30 and 10 a.m. in the morning. The irrigation solution was poured into the saucer of the pot and was then sucked in via the cords reaching from the saucer into the substrate.

Table 4.8: Carbon, phenols and plant nutrients added to each pot

Series	Organic carbon	Phenols	N	P	K
	[mg]	[mg]	[g]	[g]	[g]
PotA1	0	0	1.6	0.65	1.6
PotA2	0	0	0	0	0
PotA3	1440	63	0	0.07	2.5
PotA4	2880	126	0	0.14	5.1
PotA5	0	0	1.6	0.65	1.6
PotA6	0	0	0.4	0.16	0.4
PotA7	1440	63	0.4	0.07	2.9
PotA8	1440	63	0	0.07	2.5
PotB1	0	0	2.4	0.98	2.4
PotB2	0	0	1.6	0.65	1.6
PotB3	5200	1150	1.6	0.70	3.3
PotB4	5200	1150	1.6	0.70	1.6
PotB5	2100	250	1.73	0.67	3.2
PotB6	2100	250	1.73	0.67	1.6
PotB7	1050	45	1.77	0.69	3.1
PotB8	1050	45	1.77	0.69	1.6

By this way during the 28 days of the pot experiments between 10 and 14 litres of irrigation solution were added to each pot, mainly depending on growth and thereby need of liquid of each pot.

The total amounts of organic carbon, phenols (as caffeic acid) and plant nutrients added in PotA and PotB are depicted in Table 4.8. The values presented include fertilisation and supply by OMW in irrigation solution, calculating with 12 L of applied irrigation solution and estimated values for potassium in OMW (2 $g.L^{-1}$) and nitrate (0 $g.L^{-1}$) and phosphate (0.75 $g.L^{-1}$) for OMW applied in PotA.

4.8.3 Analysis of pot experiments

As mentioned many possibilities of analysis and interpretation of pot experiments exist, among others for example leaf colour analysis, analysis of fresh weight, dry weight, ash weight, elemental analysis after chemical pulping of ash. Realisation of detailed plant analysis was not within the scope of this work. Therefore just a simple weight analysis was conducted apart from very general observations of the plant’s leaf colouring.

On the 28th day after sowing the plant parts above the surface were harvested. Before harvesting the number of germinated and grown plants in each pot was noted down. Then all the plants of each single pot were harvested and weighed together to determine the yield of fresh plant weight of each pot. Then the plants were dried at 60 °C until there weight was constant and they were weighed to determine the yield of dry weight of each pot.

5 Results

5.1 Pretreatment

The solid content of OMW varies between 40 and 160 g/L [Paredes et coll., 1999]. A varying part of it is suspended, which is mainly residual plant material. During a photocatalytic treatment particles in solution hinder photons to enter and hence diminish the process efficiency. They precipitate on the walls of the photoreactor's tubes and form opaque mud layers, thus decreasing the amount of light entering the reactor. This also causes long, unavoidable cleaning times between two runs in batch mode.

Finally, adsorption and desorption processes seemed to take place at the particles in preliminary experiments, which provoked irreproducible analysis results, e.g. sometimes parameters like TOC or PI rose during these experiments when the solution heated up.

Flocculation was chosen of the available methods to remove solids out of solution, as it can be performed with low investment costs, is cheap and apt for the problem. The high amount of solids presents a problem for filtration procedures, because filter cakes and pressure loss increase fast [Mitrakas et coll., 1996].

In prior still unpublished experiments [Krutzler, 2002] lime flocculation and various flocculation reagents from VTA Engineering und Umwelttechnik GmbH, an Austrian company were tested. In these tests the flocculation reagent VTA 32 performed best. Therefore it was the reagent of choice in the present work.

5.1.1 Pretreatment in test tubes

Preliminary still unpublished tests [Krutzler, 2002] showed that a combination of Fenton treatment, pH adjustment and flocculation led to a more complete separation of solids than just flocculation. Therefore a series of tests in test tubes was performed (cf. Table 5.1).

The measured contents of the blind sample were: TOC 21900 mg.L^{-1} and phenol index 4920 mg.L^{-1}. Looking at the values in Table 5.1 it has to be taken into account that TOC and phenol index measurement are preceded by a filtration step, so to judge the pretreatment, transparency of the supernatant is an essential factor.

The first observation was the big difference between acidified and non-acidified samples. In all acidified solutions a lot of solids were already sedimented after acidification. The reason might be that colloid substances in water usually are charged negatively. By the addition of hydronium ions their negative charge is neutralised, thereby lowering their zeta potential and the repulsive electrostatic forces [Hernández Muñoz, 1998].

Table 5.1: Assay of pretreatment in test tubes

Sample	OMW	Fe^{2+} (100 mM)	H_2O_2 (290 $g.L^{-1}$)	Flocculent (10%)	Sequence of steps
	[mL]	[mL]	[mL]	[mL]	
1	10	0	0	0	Blind sample
2	10	0	0	0	1) acidify
3	10	0.2	0.5	0	1) acidify 2) Fenton
4	10	0	0	0.25	1) acidify, 2) flocculation
5	10	0	0	1	1) acidify, 2) flocculation
6	10	0.2	1	0.25	1) acidify, 2) flocculation, 3) Fenton
7	10	0.2	0.5	0.25	1) acidify, 2) Fenton, 3) flocculation
8	10	0.6	0.5	0.25	1) acidify, 2) Fenton, 3) flocculation
9	10	1	0.5	0.25	1) acidify, 2) Fenton, 3) flocculation
10	10	0	0	0.25	1) flocculation
11	10	0	0	1	1) flocculation
12	10	0	0	0.25	1) flocculation, less homogenising
13	10	0.2	0.5	0.25	1) Fenton, 2) flocculation
14	10	0.6	0.5	0.25	1) Fenton, 2) flocculation
15	10	1	0.5	0.25	1) Fenton, 2) flocculation

Sedimentation without acidification was achieved only in sample 10, in which a fourfold amount of flocculation reagent was applied. In later degradation experiments preceded by a similar pretreatment it turned out, that foam formation was increased significantly by applying higher flocculation reagent amounts. This is an undesirable side-effect, as foam in the tubes can impede light to enter and the reactor tanks can overflow.

Transparent supernatants were only achieved by applying a final flocculation step. Changing the sequence of flocculation and Fenton reaction like in sample 6 yields turbid supernatants, because in the first vivid oxidation phase solids are formed again by the Fenton reaction. As solids form mainly in the first phase of degradation, it does make sense to apply flocculation at this point. That way the solution stays almost transparent in the further course of degradation.

Comparing samples 2, 3 and 7 it can be seen, how acidification, Fenton reaction and flocculation each improve the result obtained step by step. Increasing the iron concentration (performed in samples 7, 8 and 9) did not show the expected differences. The results depicted in Table 5.2 are very similar. In the experimental procedure time did not play a role, as measurements were performed 48 hours after the assay to ensure that all hydrogen peroxide was consumed and sedimentation was completed. It has to be remarked though, that sedimentation was accelerated by increasing the iron concentration.

As the duration of the pretreatment was not considered a key factor in the experiments, a pretreatment similar to sample 7 was chosen to be suitable to precede the photocatalytic degradation. Furthermore it was convenient to begin the degradation experiment after the pretreatment with an iron concentration as low as possible. For various reasons also other pretreatments were tried for the degradation experiments (cf. Chapter 5.2).

Table 5.2: Result of pretreatment in test tubes

Sample	Supernatant volume	Phenol index	TOC	Supernatant
	[%]	[% of blind sample]	[% of blind sample]	
1	0%	100.0%	100.0%	no supernatant
2	81%	85.0%	86.2%	not transparent
3	79%	40.8%	85.4%	not transparent
4	85%	83.9%	95.0%	transparent
5	86%	87.1%	93.7%	transparent
6	89%	43.0%	89.2%	not transparent
7	77%	35.4%	85.5%	transparent
8	75%	32.8%	85.9%	transparent
9	77%	38.5%	86.7%	transparent
10	0%	90.3%	95.4%	no supernatant
11	62%	80.6%	90.7%	transparent
12	0%	93.9%	86.4%	no supernatant
13	0%	53.8%	98.7%	no supernatant
14	0%	42.8%	94.4%	no supernatant
15	0%	43.5%	93.4%	no supernatant

5.1.2 Pretreatment in degradation experiments

In the pretreatment of the experiments a wider view of the whole process and its cost efficiency was applied, whereas in the pretreatment experiments in the test tubes primarily a method to fulfil the task to achieve transparent supernatants was sought. This evoked to take into account the further following aims.

- To attain an effective photocatalytic treatment, long-lasting transparency of the OMW and prerequisites for a controllable reaction should be given.
- Thinking of the subsequent use as fertirrigation solution using plant nourishing ions in necessary pH-value adjustments is of advantage.
- To avoid unnecessary use of chemicals, on one hand to minimise their costs and on the other hand to keep electrical conductivity of the solution low and apt for application to plants.
- To achieve good separableness of mud and supernatant.

Naturally such a list of requirements concerning a single process step can just partially be fulfilled, depending on which aspect emphasis is laid.

Comparing the results in the pretreatment in the experiments (cf. Table 5.3) to the results achieved in the pretreatment in the test tubes (cf. Table 5.2) it is striking how much more decrease of PI and TOC could be accomplished in the test tubes. This is explained by the proportionally higher amount of added peroxide. In the test tubes around 100 mL H_2O_2 solution were added per litre (if added, cf. Table 5.1), whereas in the pretreatment for the degradation experiments this value varied from 10 to 50. Obviously H_2O_2 can react without light in OMW, but it is uncertain which oxidising intermediates are involved, what they oxidise exactly and how efficient is the use of H_2O_2 this way (cf. Chapter 5.2 for the latter point).

Comparing Sample 11 of the test tube pretreatments and the pretreatments of the experiments E4 - E6, the difference between the three treatments is remarkable and beyond analytical errors. The explanation is likely to be the following: The efficiency of flocculation also depends highly on process parameters like sedimentation height or duration and vehemence of the homogenisation step preceding the sedimentation phase. In these three cases completely different treatments according to these conditions were applied, in the test tube automatic shaking at 150 rpm, in the usual ton (E4) around 10 minutes manual stirring with a stick and in the barrel (E5 and E6) slow manual shaking (try it yourself with a 200 L barrel). The worsened homogenisation with increasing vessel size negatively affected the formation of flakes. This hints at the unexploited potential through optimisation of the flocculation (cf. Chapter 6.1), which in the course of this work was not possible to exhaust with the available equipment.

Table 5.3: Result of pretreatment of experiments

Experiment	Phenol index	TOC	pH
	[% decrease]	[% decrease]	
E1	0.0%	0.0%	5.02
E2	23.4%	9.3%	3.23
E3	53.0%	14.2%	3.50
E4	25.7%	16.6%	4.21
E5, E6	18.6%	8.7%	4.01
E7, E8, E9	33.2%	10.0%	2.84
E10, E12, E13	17.7%	12.0%	2.54

Applying the pretreatment of E4-E6 had the side-effect that the foam-formation during the photocatalytic treatment increased strongly. Foam in the tubes impeded therefore light from entering. Besides the tank can overflow. Furthermore the flocculation agent contributed significantly to the EC in the solution (EC of flocculation agent diluted 1/100 as applied in these experiments was 7.7 mS/cm, compare EC of untreated OMW was 5.0 mS/cm in E7-E9). It is of advantage, that few additional chemicals had to be added to adjust the pH-value.

The other strategy needed less flocculation agent. After acidification to pH 3 suspended solids were coagulating and sedimenting. Only in the experiments E10, E12 and E13 the solids were separated before the pretreatment was proceeded with Fenton treatment and flocculation. By the introduction of this additional separation step, the necessary amount of flocculation agent could be reduced by 40% compared to the preceding experiments.

On the other hand acid before and additional base after the pretreatment is needed to adjust the pH. This disadvantage can be partly overcome, if the added chemical reagents are chosen well according to their fertilising effects in a subsequent application to plants and to their price. Nitrogen can be introduced by this way of which OMW lacks, whereas it contains potassium and phosphate.

Another rarely measured but important parameter was the total solid residue. By the pretreatment of Experiment 7, 8 and 9 the total solid residue of the OMW decreased from 51 to 31 g / L.

Both types of pretreatment produced a mud with a high water content. After dewatering this mud could possibly be fed to compostation, while the wastewater out of the dewatering could be returned to the pretreatment step. Another possibility would be the incineration of the dried mud to gain energy. Research referring to this mud was not undertaken.

5.2 Degradation experiments

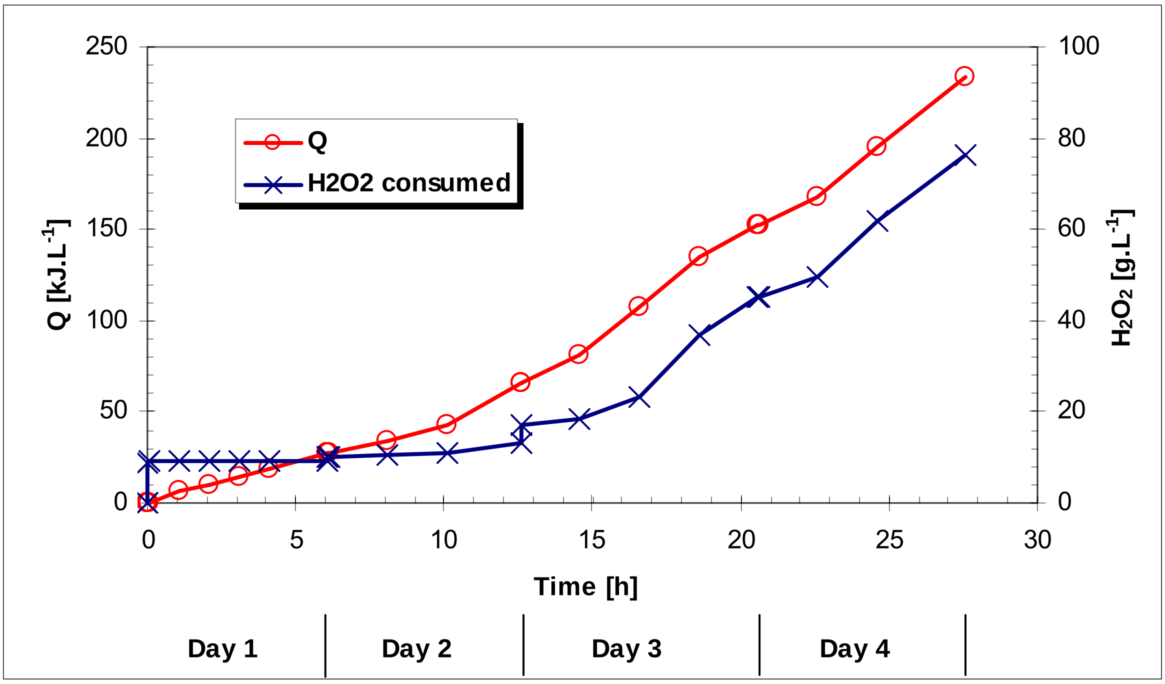
5.2.1 Experiment 3 – Example for a degradation experiment

This Chapter will give a general idea about the course of events and the influencing parameters as well as the chosen way of assessment of a degradation experiment.

In Figure 5.1 the relations between the different used abscissa and in Figure xxx.2 the most important reaction parameters of Experiment 3 are depicted. It can be seen that a degradation experiment can last several days. This experiment was performed on four days in the first half of March 2001. The necessary nightly pauses and the change of daytime during the experiments cause some notable particularities considering reaction parameters and realisation of the experiments (cf. also Chapter 4.6).

Figure 5.1 shows that the slope of the accumulated UV-radiation per litre (Q) as well as the slope of the consumed H_2O_2 vary during the experiment. The slope of Q is nothing else than the UV solar radiation intensity depicted in Figure 5.2. The radiation intensity depends on the cloud coverage, the daytime, the season and of course also the geographical location. In this particular experiment the sky was cloudy nearly until the end of the second day of the experiment. From hour 10 onward the slope increased due to the change to sunny weather. The noticeable changes on the third day were due to the advancement in daytime.

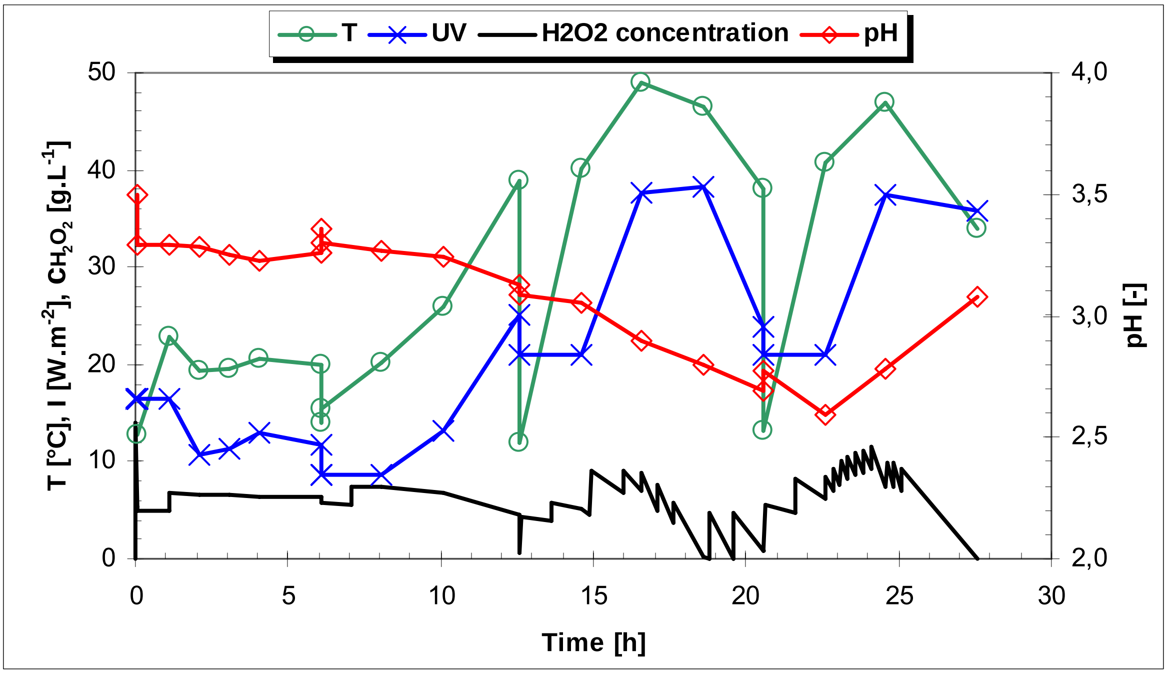
Figure 5.1: H_2O_2 consumed and accumulated radiation vs. time in Experiment 3



The H_2O_2 consumed started with already 8.5 g/L. This was the amount of H_2O_2 consumed in the pretreatment, which had to be taken into account, as different amounts of H_2O_2 were applied in the pretreatment, if the H_2O_2 consume is to be balanced for the whole process. Until hour 10 almost no H_2O_2 was consumed in the photocatalytic treatment. Afterwards the rate of peroxide consumtion increased until about between hour 15 and 17, when the solution colour turned from a dark to a light brown. The higher transparency caused the reaction rate to increase once more.

The use of each of these three abscissas (t, Q, H_2O_2 consumed) has its particular use. Although time does not imply a lot of changing factors like radiation, it is useful considering engineering parameters like the hourly throughput with the used experimental set-up. The use of the accumulated radiation energy takes into account the varying solar radiation, and is therefore a more correct way to depict experiments. The use of the consumed H_2O_2 is useful as H_2O_2 is one of the main cost factors of the photochemical treatment. Furthermore, according to reaction time and accumulated radiation very different seeming experiments turned out to be quite similar when depicted against the H_2O_2 consume. Therefore monitoring the H_2O_2 already consumed can help to estimate the process advancement. Consumed hydrogen peroxide is always depicted on a 100 % basis.

Figure 5.2: Reaction parameters vs. time in Experiment 3



The main parameters of the photocatalytic treatment are depicted in Figure 5.2. They include the solar radiation intensity, the temperature and the pH of the solution and the H_2O_2 concentration. Another important parameter is the iron concentration, which is not depicted as it remains almost constant throughout the experiment.

The solar radiation intensity varies considerably as was already pointed out before. The temperature of the solution naturally correlates with the solar radiation intensity. As it takes time to warm up and cool down the solution the temperature reacts not immediately on changes in radiation. Temperature is an important parameter considering reaction rate. In a complex wastewater matrix many reactions take place at the same time, of which part are thermally activated. Below 30° they seem to be very slow. As a consequence almost no H_2O_2 was consumed during the first 10 hours of the experiment until the weather changed. Due to the dark colour of OMW temperature rises fast under sunny conditions, e.g. on day 4 of Experiment 3 from 13 to 41 °C from 9 to 11 a.m..

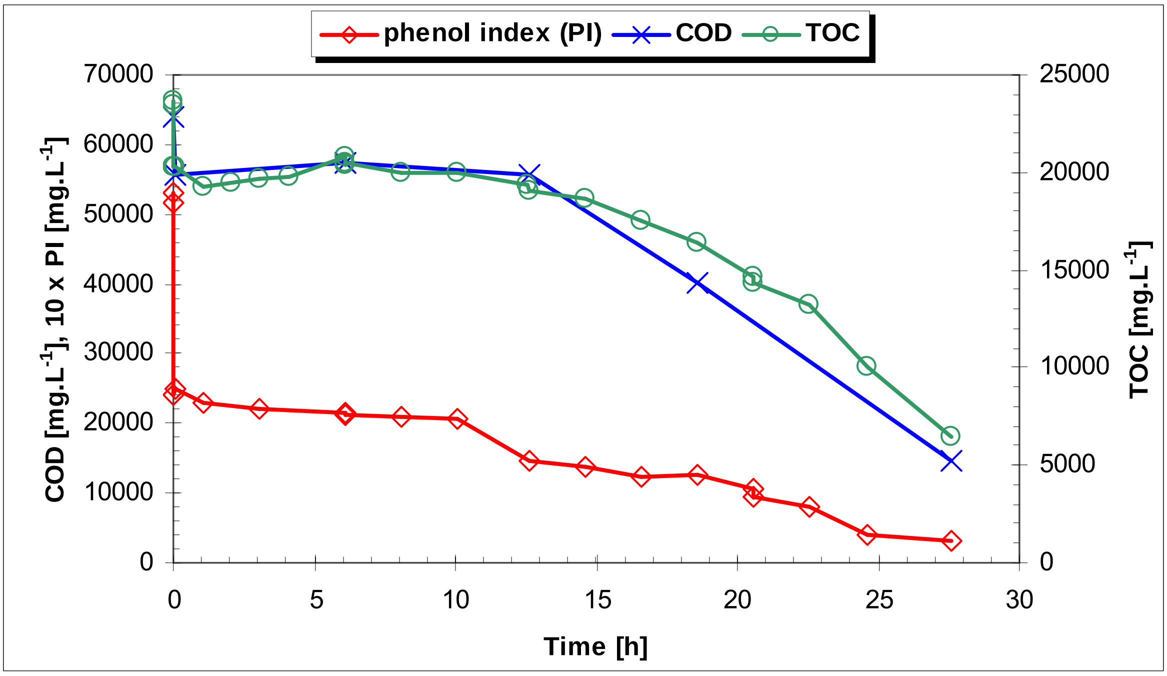
For high quantum yields and avoidance of precipitation of ferric oxide normally a pH around 2.8 is considered to be optimal according to the iron aquo complexes dominant at this pH and their extinction coefficients [Safarzadeh-Amiri et coll., 1996]. In the case of the OMW the pH was adjusted due to the pretreatment. As a lot of complexing substances can maintain the iron in solution [Sun et coll., 1993], the pH was not that critical. Interesting is that there was a first phase during which the pH declined steadily due to the reactions taking place and a second phase when it rose again. In the first phase more and more carboxylic acids were formed by addition of the OH-radical. In the second phase the decarboxylation processes outweighed the newly formation of carboxylic acids, whereby the TOC also declined fast (cf. Figure 5.3).

In Figure 5.2 the H_2O_2 concentrations were not all measured. The points after addition were calculated. The H_2O_2 concentration varied from 0 to 10 g.L^{-1}. Theoretically it was intended to be kept constant at 5 g.L^{-1}, but reaction rate was not always easy to judge and measurement by iodometric titration takes 45 minutes.

Another crucial parameter especially according to the reaction rate is the iron concentration. In Experiment 3 two millimolar iron was added in the pretreatment. Together with the iron content of the OMW this yielded 3.7 mM iron after the pretreatment. After 6 hours of reaction measurement showed 3.2 mM iron. Because of the slow reaction another 2 mM iron were added, but did not evoke a considerably higher reaction rate immediately. At the end of Experiment 3 an iron content of 4.2 mM was measured.

As can be seen during the photocatalytic treatment iron was lost, which also happened in other experiments. Probably this is not due to precipitation of ferric oxide but due to adsorption processes on residual colloidal solids. This is sustained by the fact, that the phenomenon occurred stronger in preliminary experiments without pretreatment, namely with solids inside.

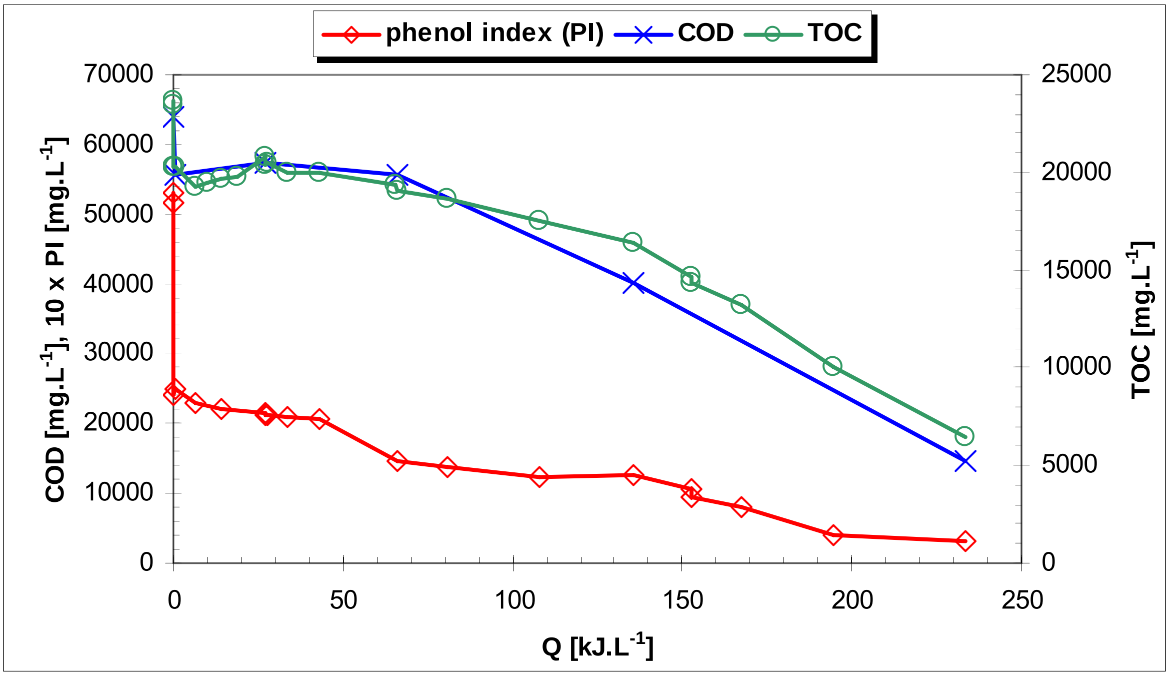
Figure 5.3: PI, COD and TOC vs. reaction time in Experiment 3



As can be seen in Figure 5.3 in the first 10 hours of the photocatalytic treatment none of the three sum parameters changed significantly. This corresponds with the negligible H_2O_2 consume during this period. With the weather change at this hour also the degradation began. The COD began to decrease earlier than the TOC, as substances are first converted into more oxidised forms, which affects the COD, before finally also the TOC decreases by decarboxylation of acids. For this reason the TOC curve is slightly more concave than the COD, i.e. its degradation rate increases more towards the end of the treatment.

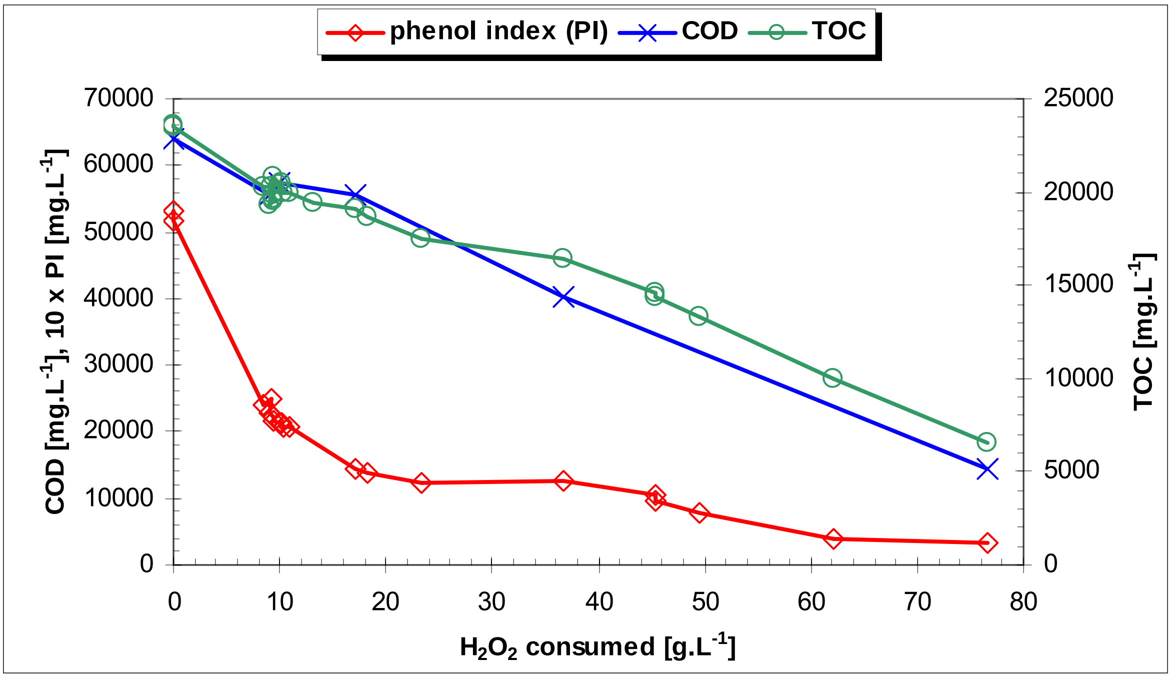
If the same degradation curves are depicted vs. the accumulated UV-radiation (cf. Figure 5.4), the initial phase without significant degradation is compressed, but still progressing on the abscissa does not imply necessarily a progression of the degradation. This is due additional factors, above all the influence of the solution temperature, which did not rise over 25 °C in this period.

Figure 5.4: PI, COD and TOC vs. accumulated radiation in Experiment 3



If TOC and COD are depicted vs. the altogether consumed amount of H_2O_2, almost linear dependence of the abscissa results for both parameters (cf. Figure 5.5). This can help to estimate the reaction progression if measurement is not possible. Also the pretreatment fits into this linear trend and its effect on the measured parameters can be judged better by this way of representation of results.

Figure 5.5: PI, COD and TOC vs. consumed H_2O_2 in Experiment 3



The phenol index (PI) was already halved by the pretreatment. Including the pretreatment the development of the PI can be divided into three phases: A first phase in which the PI was lowered to around 30% (1.5 $g.L^{-1}$ in E3). This phase took longer (12 hours) in E3 than in other experiments as the reaction almost did not proceed until hour 10. A second phase in which the PI diminished very slowly (in E3 not that obvious) although H_2O_2 was consumed and a third phase after the always observed colour change in which the PI decreases again. The depiction of PI vs. the consumed H_2O_2 points out these phases distinctively. The first phase ends at about 20 $g.L^{-1}$ and the second at about 45 $g.L^{-1}$.

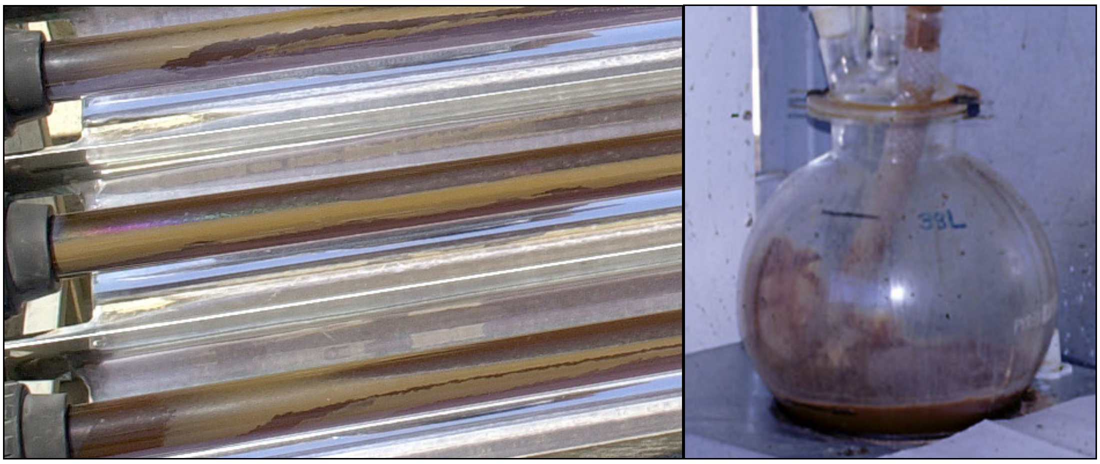
5.2.2 Effect of pretreatment

Without pretreatment the measured values proved to fluctuate stronger than in experiments, in which the solids were removed out of the OMW prior to the photocatalytic treatment. The problem could be explained by adsorption and desorption processes on the particles. This led to fluctuating measurements, because in all analysis procedures the solids were removed by filtration. Special problems occurred considering the iron concentration. Ferric iron itself is applied as flocculation agent as it is able to neutralise negative electric charges by adsorption on particles [Hernández Muñoz, 1998]. The same process seemed to happen in the OMW in an unpredictable manner. E.g. in Experiment 1 after 15 hours 3 mM iron were added to accelerate the reaction, but the measured concentration increased just from 2.6 to 3.8 mM.

Besides more solids were formed which precipitated in the tank, where less turbulent flow conditions were present.

Another advantage was that by applying the same pretreatment as in Experiment 7, 8 and 9 the total solid residue of the OMW decreased from 51 to 31 g.L^{-1}. This means that 20 g of solid plant material were quit out of the OMW, which instead would also consume hydrogen peroxide if oxidised.

Figure 5.6: Solids in the reactor in Experiment 1



As shown in Figure 5.6 on the walls of the reactor tubes films of unknown composition were forming which impeded light from entering. This was particularly disturbing as they tended to form on the downward side of the tubes, where due to reactor geometry a high share of the radiation enters the tubes. Besides these films provoked long cleaning times after the experiment.

5.2.3 Reaction rate – Influencing parameters

Reaction rate is a crucial parameter thinking of necessary reactor size and thereby plant investment costs to achieve a desired daily throughput determined by the amount of wastewater to be treated. Reaction parameters like temperature of solution or light intensity could not be controlled in the performed experiments, i.e. changes in different parameters happened usually simultaneously. This impeded quantitative considerations, nevertheless qualitative trends could be ascertained.

5.2.3.1 Iron concentration

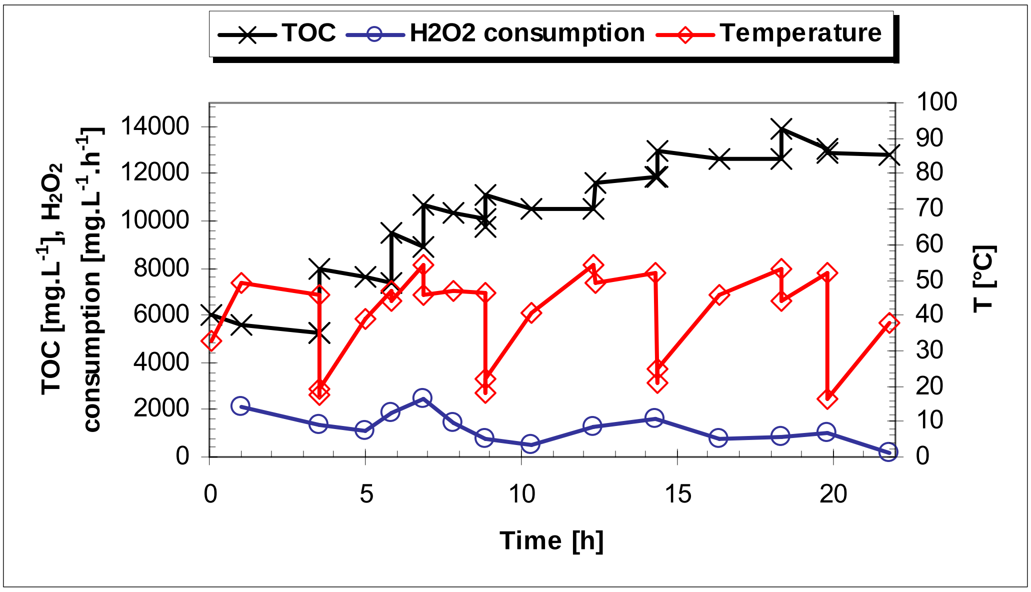
At low iron concentrations further addition of iron increases the rate of generation of hydroxyl radicals and thereby the degradation rate, but it does not increase indefinitely but reaches a maximum at an optimum iron concentration, because ferrous and ferric ions can also scavenge radicals and thus diminish the degradation rate. The optimum concentration depends on the type of wastewater and the reactor geometry. The iron concentrations used in the reaction solutions were between 2 and 6 mM. Never a negative effect of further addition of iron could be observed in the experiments described in this work.

In wastewater with high optical density like OMW ferric ions compete with organic substances for the incident photons. Furthermore ferric ions form complexes, which might not be all photo-reactive.

During a degradation experiment the solution characteristics changed significantly, while oxidation took place. Among others also decolourisation occurred at a certain stage, after which peroxide consumption and degradation rate increased considerably. For instance the absorption in a 1 cm cuvette at wavelength of 350 nm decreased from 0.136 (dilution 1:50) to 0.022 (dilution 1:25) from the start until the end of Experiment 5. This means a decrease of optical density by more than factor 10.

The effects of the competition of iron with organic matter for photons could also be measured in Experiment 10, where the implementation of an experiment in semi-continuous mode was tried (cf. Chapter 4.6 for description of implementation). The iron concentration was constant, while TOC augmented due to the different concentrations of inflow (OMW after pretreatment) and discharge.

Figure 5.7: Peroxide consumption rate in Experiment 10



In Figure 5.7 TOC, solution temperature and peroxide consumption rate are depicted versus time. TOC and solution temperature are the measured values at sampling time. The stepwise increases of TOC mark the additional amendments of OMW and the large stepwise decreases of solution temperature the end of an experiment day. Peroxide consumption rate was calculated out of two subsequently measured values. This calculated values were depicted according to the sampling time of the later value, thereby the rise in peroxide consumption rate seems to lack behind the rise in solution temperature, which obviously also influences greatly.

It can be seen, that at constant iron concentration (3 mM) the peroxide consumption rate diminished from day to day as the TOC increased. Due to the experimental procedure (addition of OMW in portions) the chemical nature of the TOC should have been quite similar throughout the experiment, so changes affected mainly the amount of TOC.

5.2.3.2 Temperature of solution, light intensity and peroxide concentration

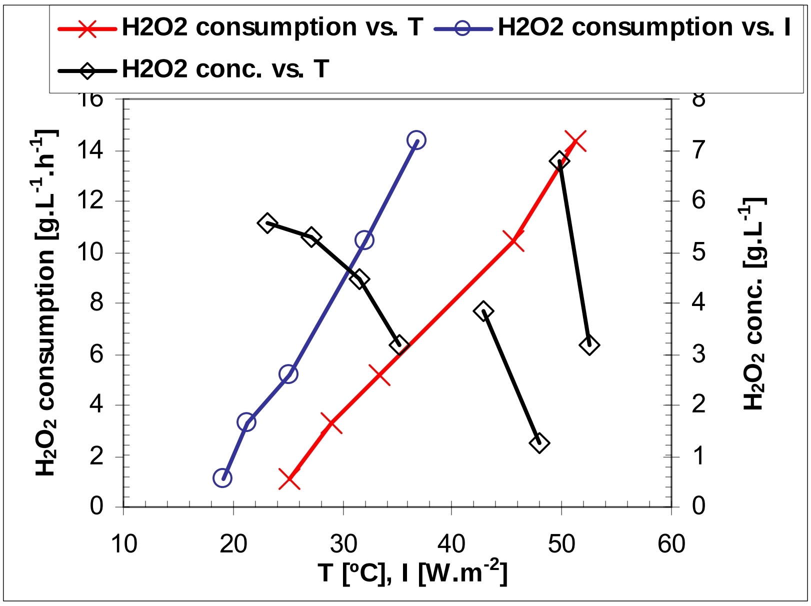
A lot of different thermal reactions take place apart from photo-induced reactions, which are mainly independent of temperature. These are accelerated by temperature rise according to the Arrhenius law. Especially mentioned should be the Fenton reaction, the thermal decomposition of hydrogen peroxide, the oxidation of organic substrate by hydrogen peroxide and the thermal reaction of ferric iron with hydrogen peroxide to ferrous iron and hydrogen peroxyl radical (cf. Chapter 3.2). All these reactions cause degradation and consumption of hydrogen peroxide.

As well in the Figure 5.7 as in the Figure 5.8 the effects of temperature rise can clearly be seen. However it has to be kept in mind, that this temperature rise is provoked by warming up by the absorption of radiation, whose intensity rises also during the morning.

At constant temperature increasing radiation intensity increases also the reaction rate. To try to assess the two parallel effects towards the end of Experiment 4 samples were taken in shorter 15 minutes intervals, peroxide concentration, solution temperature and radiation were noted. The measurements were performed after the colour change, when the solution was readily degradable. TOC during the measurements was between 10 $g.L^{-1}$ and 12.5 $g.L^{-1}$.

In Figure 5.8 the results of these measurements are presented. The peroxide consumption rate during the interval of 15 minutes between two samples is depicted vs. the average temperature and the average UV radiation intensity between the two corresponding sample points. The peroxide concentration is depicted vs. the temperature at time of sample taking, so variation during the measurement intervals can be seen. Peroxide concentration is separated in three parts, because addition of peroxide took place twice to prevent running out of peroxide.

Figure 5.8: H_2O_2 consumption towards end of Experiment 4



Depicting the peroxide consumption rates this way linear dependence can be observed for both curves. If photo-induced reactions were the rate determining step, doubling the radiation intensity, like in the measurements, would result in a doubled peroxide consumption rate. As it can be seen the rise was much higher (from 1 to 14 $g.L^{-1}.h^{-1}$). So the acceleration must be effectuated by the temperature rise. Uncertain is to which extent peroxide consumption was caused by photo-induced reactions or by alternative reaction pathways. Laboratory experiments in the dark at different temperatures did not yield satisfying results, which could give an answer to this question.

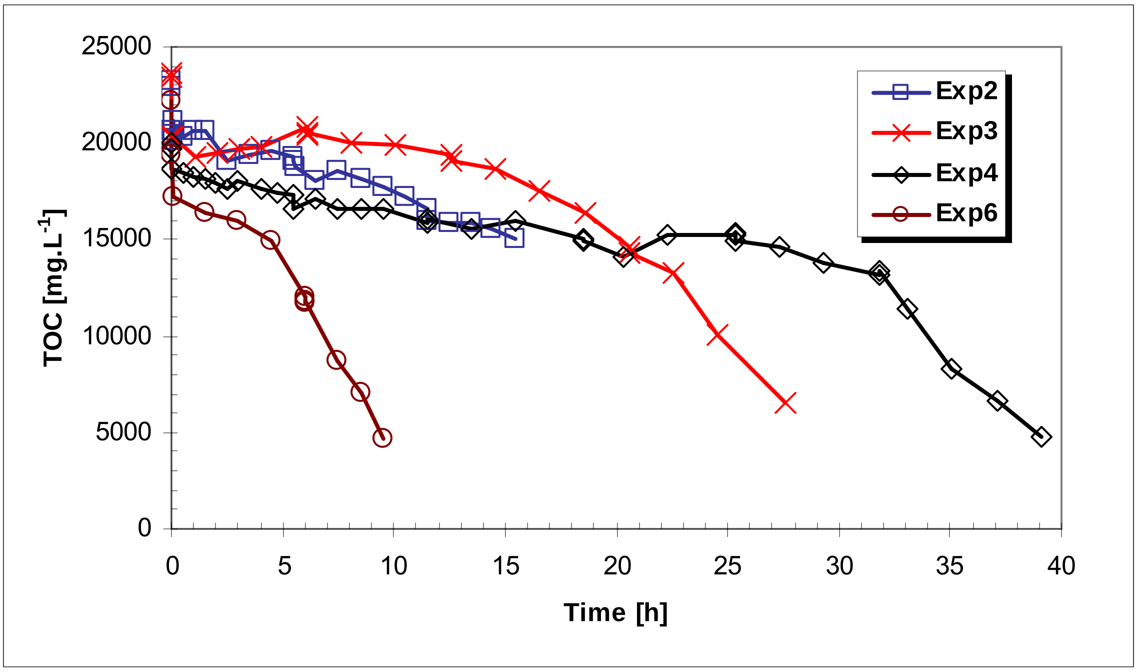
As it can be seen the linear trend was not affected by the measurement at different peroxide concentrations. It can be concluded, that the peroxide concentration does not affect the peroxide consumption rate. But this would rule out any of the thermal reactions mentioned at the beginning of this Chapter, because their rate laws all imply the hydrogen peroxide concentration. While the reason of the phenomenon lacks an explanation, the measurements showed, that to prevent limitation of the peroxide consumption rate, it is sufficient to keep peroxide from running out.

TOC degradation during the measurements kept ongoing like in the other experiments. This means that peroxide consumption signified also degradation of organic matter.

5.2.3.3 Pretreatment

Considering the aim of high reaction rates an effective pretreatment mainly is to be supposed to quit the solids out of the OMW. The pretreatment of Experiment 6 for example produced a perfectly solid free solution. Furthermore the application of higher flocculation agent amounts seemed to have a lasting preventive effect on solid formation in the first phase of the photocatalytic treatment. The absence of particles, high radiation intensity and higher ambient temperatures due to the advanced spring season compared to former experiments let the solution temperature rise higher than in former experiments (most time from 55 to 60 °C while in Experiments 2-4 50 °C were rarely reached). Thereby Experiment 6 was by far the fastest experiments performed with undiluted OMW (cf. Figure 5.9).

Figure 5.9: TOC degradation in Experiments 2, 3, 4 and 6 vs. time



5.2.4 Residence time in photocatalytic reactor

High reaction rate is one decisive factor to achieve low residence times. The main influencing parameters have been described in the former Chapter. Another possibility is to take advantage of formation of precursors in the dark before exposition to radiation [Herrera et coll., 1998]. Besides, residence times can also be kept low by stopping the photocatalytic treatment at the moment when toxicity has vanished. The wastewater can be discharged to conventional and cheaper biological wastewater treatment or used for fertirrigation of plants as intended in this case.

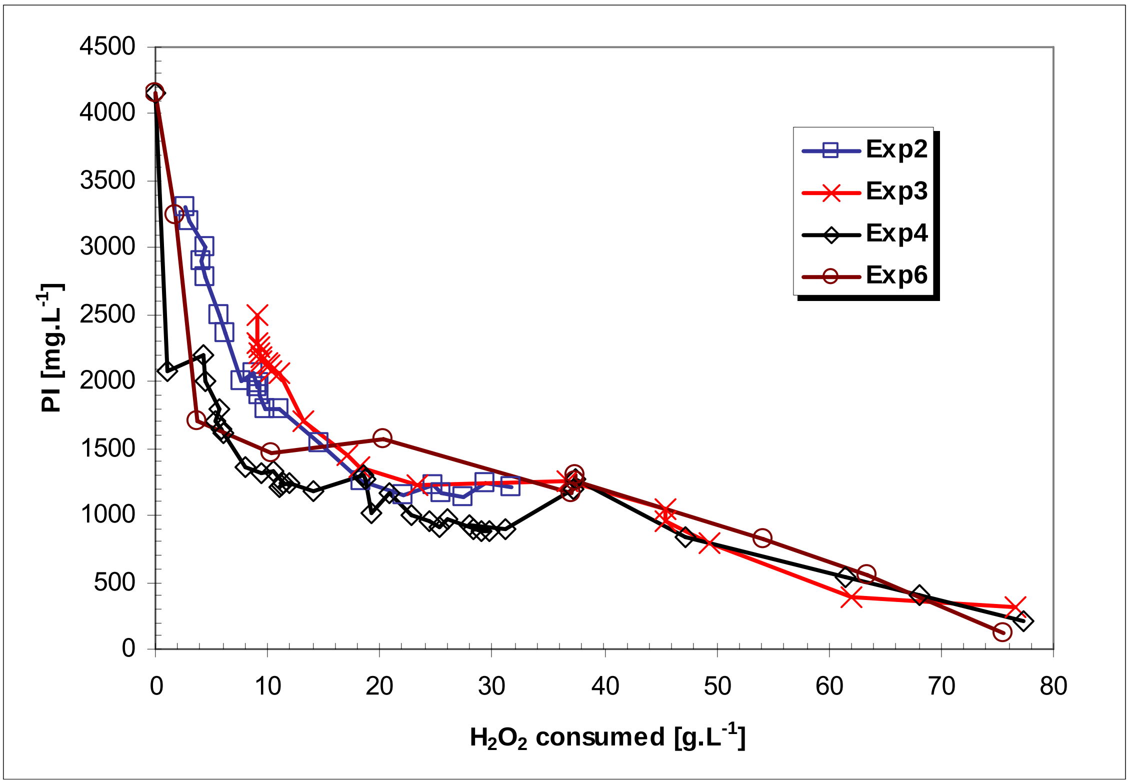
5.2.4.1 Stopping point of photocatalytic treatment

Phenols are considered the chief factor for toxicity. As mentioned before the progression of the phenol index during the photocatalytic treatment can be separated in three different stages:

A first rapid decrease, a steady phase around 1500 mg.L^{-1} and a third stage in which further slow decrease takes place.

In Figure 5.10 the progression of the phenol index for the four degradation experiments performed with undiluted OMW after different pretreatments is represented. Thus it appears that all experiments show a similar progression depending on the amount of oxidant used. Just during the first stage Experiment 4 and Experiment 6 enter sooner in the steady phase. In these experiments no Fenton treatment was applied, but higher amounts of flocculation agent were used.

Figure 5.10: Phenol index vs. consumed hydrogen peroxide



Peroxide consumption and reactor investment would be two of the prime cost factors of an application. Both could be cut down, if toxicity had decreased sufficiently already after the first stage and the photocatalytic treatment could be stopped at this point. At least a decrease of about 70 % of the initial phenol index has already taken place at this point. This topic will be discussed more in detail later, when the application in germination tests and a pot experiment will be presented (cf. Chapters 5.3 and 5.4).

5.2.4.2 Reactions in the dark

In Experiment 12 and Experiment 13 Fenton treatment was performed on pretreated OMW. Higher iron concentrations were used in this experiments, namely 7 mM in Experiment 12 and 12 mM in Experiment 13. Ten litres of OMW were put into a black 25 L plastic canister and placed into sunlight to heat the reaction solution. Peroxide was added in portions of 15 g.L^{-1} reaction solution.

Temperature reached 40 to 50 degrees. The pH dropped down to 1.4 whereas in comparable experiments under irradiation a pH of 2.2 was the minimum measured. The TOC and PI progression is represented in Figure 5.11. For reasons of comparison also the data of Experiment 6 is depicted.

Figure 5.11: Experiment 13 – TOC and PI vs. H_2O_2 consumed

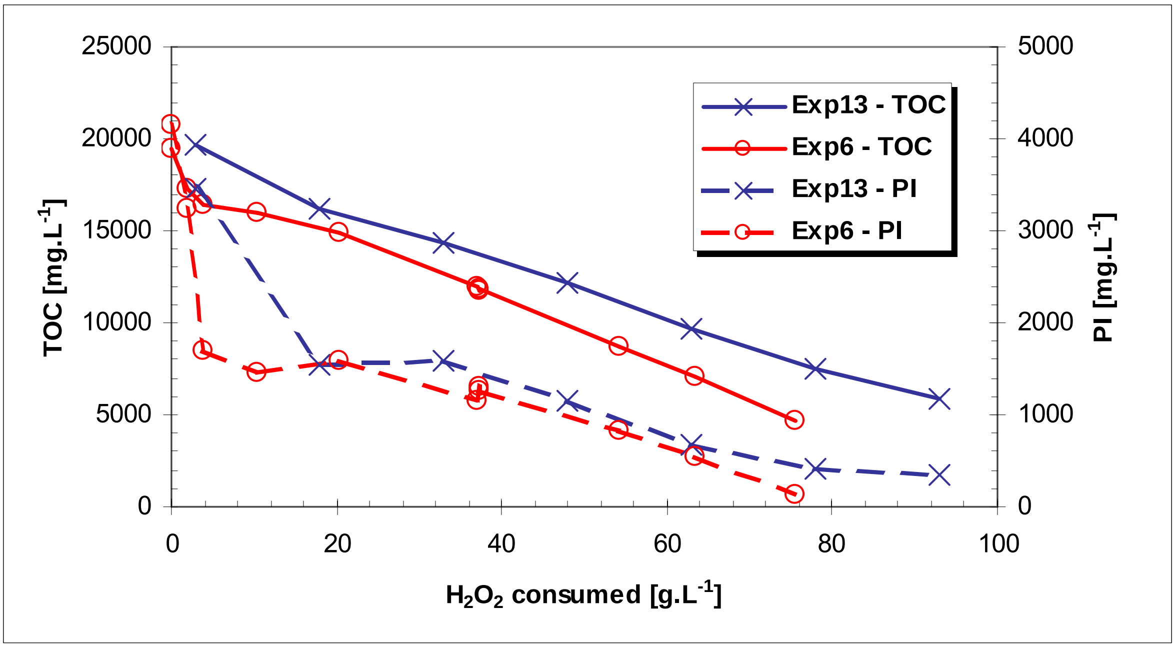


Figure 5.11 shows that degradation took also place completely without light, as far as the complete exclusion of light can be guaranteed by the reaction vessel. Furthermore, it shows that compared to Experiment 6 more hydrogen peroxide was necessary to achieve the same degradation level.

As mentioned the pH had lower values in Experiment 13. Seemingly more carboxylic acids were formed in this experiment. This could be due to the lack of the photo-induced ligand to metal charge transfer decarboxylation reaction of ferric ion - carboxylic acid complexes (cf. Eq. 3.23).

Also the TOC progression behaved differently compared to experiments under solar irradiation. In Experiment 13 the TOC degradation efficiency sunk towards the end considering the exploitation of hydrogen peroxide. In contrast in Experiment 6 the TOC degradation efficiency increased slightly towards the end. It seemed that in Experiment 13 readily degradable substances reacted at the beginning and later on intermediates were formed, which were more difficult to degrade. This is also sustained by the fact, that it took a lot more time to consume the last two portions of hydrogen peroxide than the first ones.

Experiment 12 showed very similar results as Experiment 13. The only notable difference was, that the hydrogen peroxide consumption rate was much lower in Experiment 12. This leads to the conclusion that iron ions play a significant role in the consumption of hydrogen peroxide, as the higher iron concentration in Experiment 13 was the only different reaction parameter.

According to the residence time of the OMW in the more expensive photo-reactor can be stated, that it is possible to make use of the obvious fact, that part of the reaction can also take place without light. How residence time in the dark and under solar irradiation have to be combined to yield the best results is a question of optimisation, which has not been tackled in this work.

5.2.5 Consumption of hydrogen peroxide

Consumption of hydrogen peroxide is a chief cost factor in the treatment. Therefore lowering it is of great interest. One possibility is to stop the oxidation process as soon as sufficient detoxification has been achieved. This was discussed formerly briefly and will be discussed later (cf. this Chapter and Chapter 5.5). Another possibility to exploit is to make efficient use of the oxidant, i.e. to achieve as much degradation as possible with as few hydrogen peroxide as possible. This Chapter will show results obtained related to that.

5.2.5.1 Hydrogen peroxide consumption and COD degradation

The COD is a parameter to estimate the oxidant necessary to completely mineralise a wastewater to CO_2 and inorganic ions. If hydrogen peroxide is the only reacting oxidant and if it reacts stoichiometrically with the organic matter, a stoichiometric demand of hydrogen peroxide can be calculated for a measured COD. One mole hydrogen peroxide can set free half a mole of oxygen which in turn can oxidise substrate. Then a COD of 16 000 mg $O_2.L^{-1}$ has a stoichiometric hydrogen peroxide demand of one mole or 34 grams per litre.

In the degradation experiments less than the stoichiometric hydrogen peroxide demand was consumed, namely just around two thirds (cf. Table 5.4). An explanation based on experimental results cannot be given, but hydrogen peroxide can be formed out of oxygen in aqueous solutions containing iron ions [Safarzadeh-Amiri, 1996; Utset et coll., 2000; Zepp et coll., 1992].

Table 5.4: COD degradation and H_2O_2 consumption, COD_0 is the COD before pretreatment, except Exp 7-9 where measured values after dilution are shown, COD_f is the COD at the end of the experiment

Experi-ment	COD_0	COD_f	ΔCOD	H_2O_2 stoichio-metric for ΔCOD	H_2O_2 consumed	% of stoichio-metric demand	COD degraded per g H_2O_2 consumed
	[mg $O_2 . L^{-1}$]	[mg $O_2 . L^{-1}$]	[mg $O_2 . L^{-1}$]	[g $H_2O_2 . L^{-1}$]	[g $H_2O_2 . L^{-1}$]		[mg $O_2 . g^{-1} H_2O_2$]
Exp1	47100	25500	21600	45.9	25.8	56%	837
Exp2	60000	35000	25000	53.1	31.6	59%	791
Exp3	64100	14600	49500	105.2	76.5	73%	647
Exp4	64100	15500	48600	103.3	77.4	75%	628
Exp5	64100	9900	54200	115.2	71.2	62%	761
Exp6	64100	9200	54900	116.7	75.5	65%	727
Exp7	20400	4600	15800	33.6	22.7	68%	696
Exp8	21400	3700	17700	37.6	27.8	74%	637
Exp9	20200	14700	5500	11.7	6.7	57%	821
Exp12	64100	15800	48300	102.6	78	76%	619
Exp13	64100	17300	46800	99.5	78	78%	600

The results presented in Table 5.4 are to be considered with care due to the experimental set-up of the reactors, with which it was not possible to work with the same precision as with laboratory equipment. Also the COD tests had a limited accuracy. Nevertheless two general trends seem to be true. First that in experiments with low solar irradiation intensity less COD is degraded per gram hydrogen peroxide. This was the case in Experiment 3 and 4, when the weather was rather cloudy and of course especially in Experiment 12 and 13, which were performed without irradiation. Second that these Experiments perform better, which were not carried out down to low COD values.

5.2.5.2 Degradation without hydrogen peroxide added

Many authors report photocatalytic degradation in iron containing aqueous solutions without addition of hydrogen peroxide [e.g. Utset et coll., 2000; Zepp et coll., 1992]. Therefore in Experiment 6 on the morning of the second experiment day no peroxide was added during three hours and the reaction solution was circulated in the reactor. As can be seen in Table 5.5 no measurable degradation took place.

Table 5.5: Solar irradiation in Experiment 6 without H_2O_2

	TOC	COD	PI	T
	[mg . L^{-1}]	[mg . L^{-1}]	[mg . L^{-1}]	[°C]
Before irradiation	11770	27750	1300	19
After 3 h of irradiation	11800	28300	1250	46.5

5.2.5.3 Experiment 5 – Low hydrogen peroxide concentration

In Experiment 5 it was tried to keep the hydrogen peroxide concentration constantly below one gram per litre to prevent large excess of hydrogen peroxide from decomposing fast. The performance of the experiment considering COD degraded per gram hydrogen peroxide applied was good, but the difference to Experiment 6 for example, which was conducted with OMW from the same pretreatment, was not big enough to draw reliable conclusions.

5.2.5.4 Parallel experiment – Experiment 7 and 8

In these experiments it was tried to introduce more oxygen in the solution in Experiment 7 to see if it was possible to obtain a more efficient exploitation of hydrogen peroxide. Experiments 8 was conducted in parallel with normal reactor set-up and the same iron concentration for reasons of comparison. Furthermore it was hoped to remove the carbon dioxide forming during degradation faster out of the solution, because carbonate ions are known to scavenge hydroxyl radicals. The latter goal was not really achieved, which was proved by IC measurements. Oxygen concentration was not measured in the reaction solution. In Experiment 7 heavy foaming was produced by the alteration of the reactor, while Experiment 8 was easy to control. Apart from this no significant differences considering TOC and PI progression were measured. Also the reaction rates and the COD degraded per gram hydrogen peroxide were quite similar.

5.3 Germination Tests

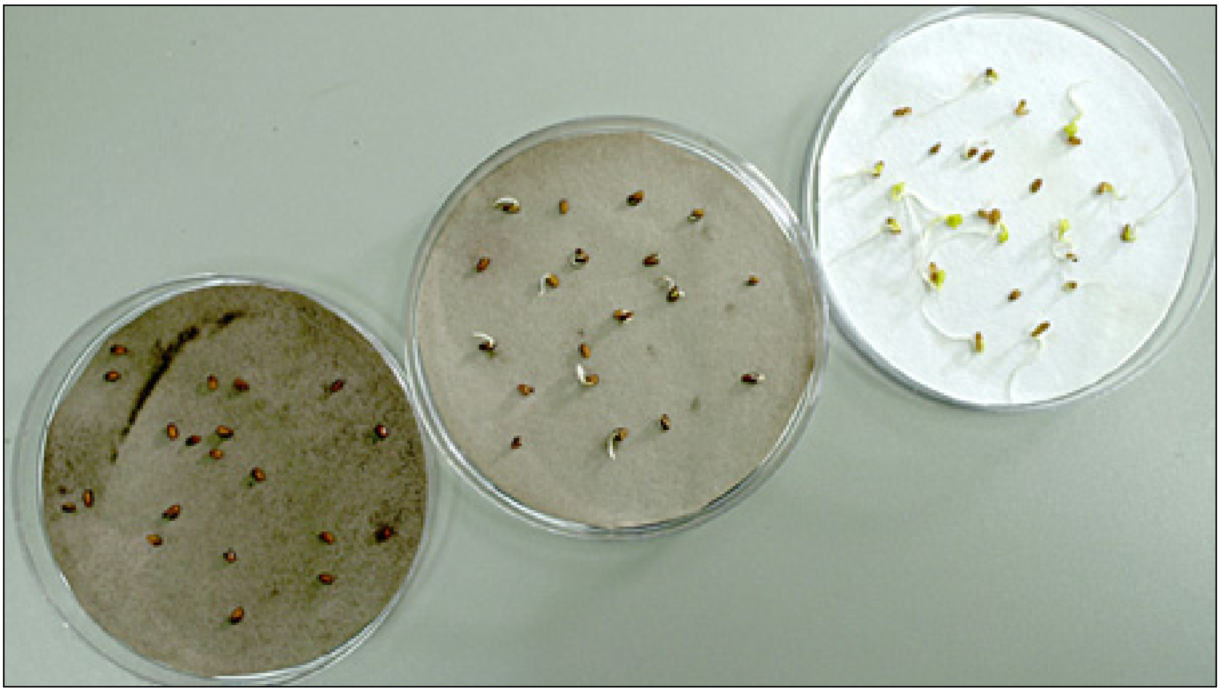
The determination of the germination index is a rapid bio-assay to determine phytotoxic effects on germinating and therefore highly sensible plants.

First determinations of the germination index were conducted with cress (Lepidium sativum L.) and untreated OMW originating from the first trip to the olive mill. The results are represented in Table 5.6 and Figure 5.12. With cress the incubation phase was 48 hours at 20 °C. As formerly stated barley proved to be a little bit more sensitive to the OMW. Germination tests conducted with the same OMW samples as in Table 5.6 yielded germination indices of 12 % (diluted 1:1) and 0 %. The germination index was also used to estimate the necessary dilution of the OMW for the irrigation in the subsequent pot experiments. So the use of barley in the germination tests was thought to allow more correct conclusions considering the preparation of the pot experiments.

Table 5.6: Germination index of cress seed with untreated OMW as tested solution, neutralised with NaOH, incubation 48 hours at 20 °C

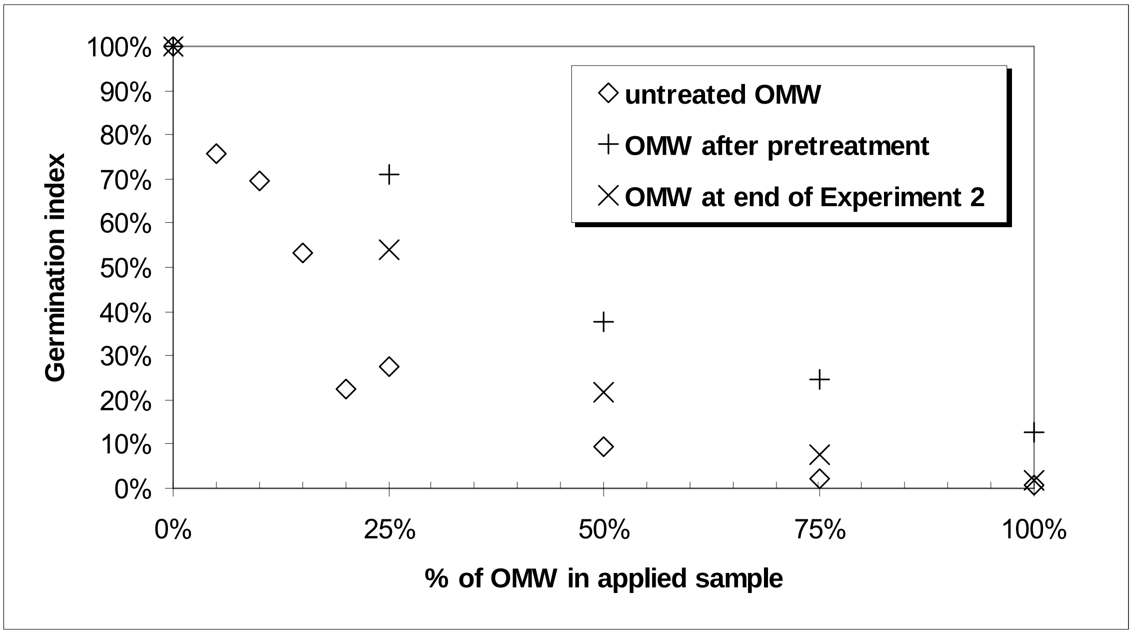
Sample	TOC	PI	Mean length of root	% germinated	GI
	[mg.L^{-1}]	[mg.L^{-1}]	[mm]	[%]	[%]
Blank, distilled water	0	0	18.4	85	100
Untreated OMW from first trip, diluted 1:1	8200	1975	3.8	85	21
Untreated OMW from first trip, undiluted	16400	3950	1	10	1

Figure 5.12: Germinated cress seeds, incubated 48 hours at 20 °C with untreated OMW



The germination index was also determined of the untreated OMW used in Experiment 2 (neutralised with KOH, OMW used in all experiments from there on), after the pretreatment in Experiment 2 and at the end of Experiment 2 (both neutralised with NaOH). The determined germination indices of various dilutions of these samples are depicted in Figure 5.13. The untreated OMW had a TOC of 23500 mg.L^{-1} and a PI of 5300 mg.L^{-1}, after pretreatment the TOC was 21000 mg.L^{-1} and the PI 3500 mg.L^{-1}. In the final sample of Experiment 2 a TOC of 15000 mg.L^{-1} and a PI of 1200 mg.L^{-1} were determined.

Figure 5.13: Germination index in Experiment 2



It can be seen that the untreated OMW had clearly the strongest toxic effects, i.e. the lowest germination indices. The effect of detoxification by the pretreatment was stronger than could be expected by considering just the parameters TOC and PI. E.g. the germination index of a solution containing 75 % of pretreated OMW (i.e. TOC of 15750 mg.L^{-1}, PI of 2675 mg.L^{-1}) was approximately the same as the germination index of a solution containing 25 % of untreated OMW (i.e. TOC of 5875 mg.L^{-1}, PI of 1325 mg.L^{-1}). This shows that the effect of removing the suspended solids in the pretreatment must not be underestimated. As described the measurements of TOC, COD and PI were conducted with filtered solutions, whereas the germination index was performed with unfiltered solutions. This is always to be taken into account when interpreting results.

At first sight it was surprising that also the final sample of Experiment 2 yielded lower germination indices as the pretreated OMW. This could be explained by the formation of carboxylic acids during the oxidation process. On the one hand they could possess adverse effects on the germination by themselves, but on the other hand they also increased the amount of necessary base to neutralise the OMW before the determination of the germination index. In Figure 5.14 the progression of TOC, PI and concentration of Na^+ ions introduced by neutralisation with NaOH vs. the hydrogen peroxide consumption is depicted. In the untreated OMW 2.4 g Na^+.L^{-1} were introduced by neutralisation. This amount rose only to 2.6 g Na^+.L^{-1} after the pretreatment, but to 6.6 g Na^+.L^{-1} in the final sample.

Figure 5.14: TOC, PI and base necessary to neutralise vs. hydrogen peroxide consumption in Experiment 2

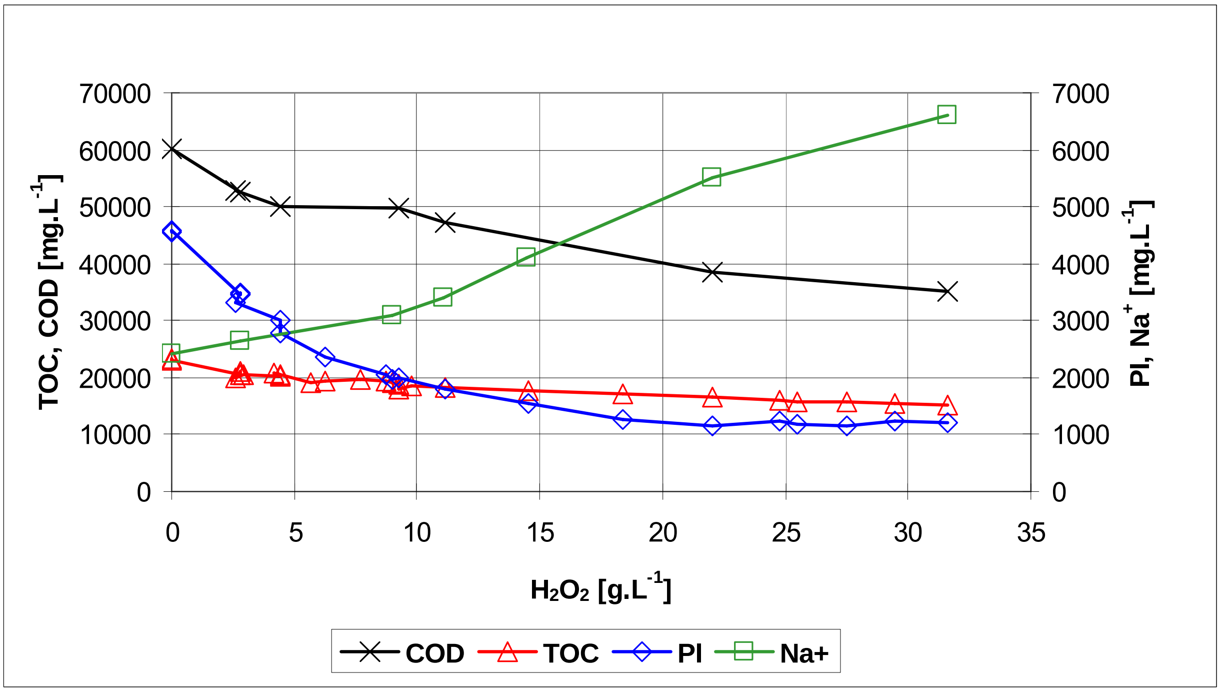


Table 5.7: Germination index of salt solution, weight of KCl : NaCl : Na_2SO_4 = 2 : 2 : 1

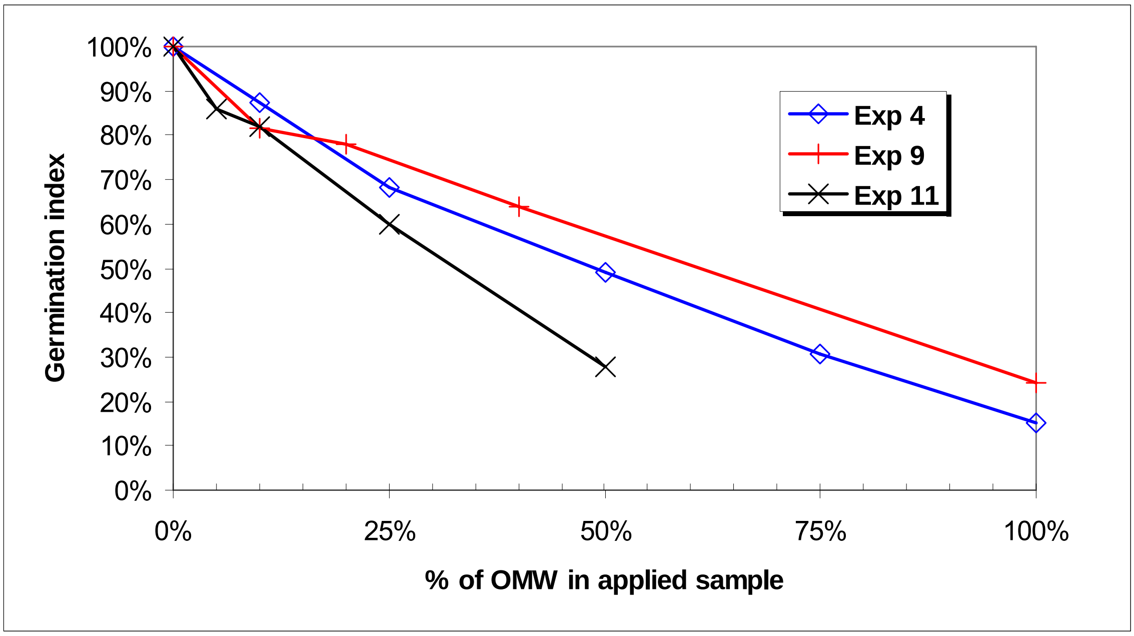
Salt concentration [g.L^{-1}]	0	2.5	5	7.5	10
Germination index [%]	100	88	72	67	52

Experiment 2 was not proceeded until high TOC degradation grades were achieved. When the experiments were conducted until higher degradation grades, the amount of base necessary for neutralisation began to decrease when the turning point of the pH value was reached.

To estimate the effect of salts on the germination also germination indices of salt solutions were determined. The results are presented in Table 5.7. KCl, NaCl and Na_2SO_4 were chosen, because these ions are also present in OMW and their dissolution does not affect the pH value.

As a consequence of these obtained results it was decided to take into account strongly the avoidance of excessive use of chemicals. If chemical consumption was unavoidable, chemicals were used, which provide plant nutrients, if possible. Therefore from Experiment 7 on always nitric acid was used to acidify OMW. OMW from Experiment 4 was not acidified during the pretreatment (cf. Chapter 4.5). Neutralisation for preparation of irrigation solutions was always undertaken with potassium hydroxide.

Figure 5.15: Germination indices for final samples of Experiment 4, 9 and 11 after neutralisation with KOH, applied for irrigation in pot experiments



In Experiment 10 pH control was performed during the degradation experiment, which was carried out by addition of ammonia. After the end of Experiment 10 the solution of this experiment was employed in Experiment 11, which provided OMW for preparation of irrigation solution. This OMW thereby contained about 0.5 g/L ammonia. The determined germination indices for the OMW neutralised with KOH which was employed for irrigation can be found in Figure 5.15.

It was decided to employ OMW from Experiment 4 in PotA diluted 1:40 and 1:20, based on the condition to have a germination index higher than 90 %. The dilution factors in PotB were chosen to achieve a desired electric conductivity of around 1 mS/cm after the occurrence of salt damages in PotA.

5.4 Pot experiments

5.4.1 General observations and photos of plants

Germination in the pot experiments took place faster than in the germination experiments in the petri dishes due to higher temperatures in the greenhouse. In the 28 days lasting pot experiments plants grew differently according to growth speed and also to leaf colouring.

Figure 5.16: Pot of series PotA5 on day 13, 20 and 27 after sowing

In Figure 5.16 a pot from series PotA5 is depicted after 13, 20 and 27 days. PotA5 was fully fertilised and no OMW was applied.

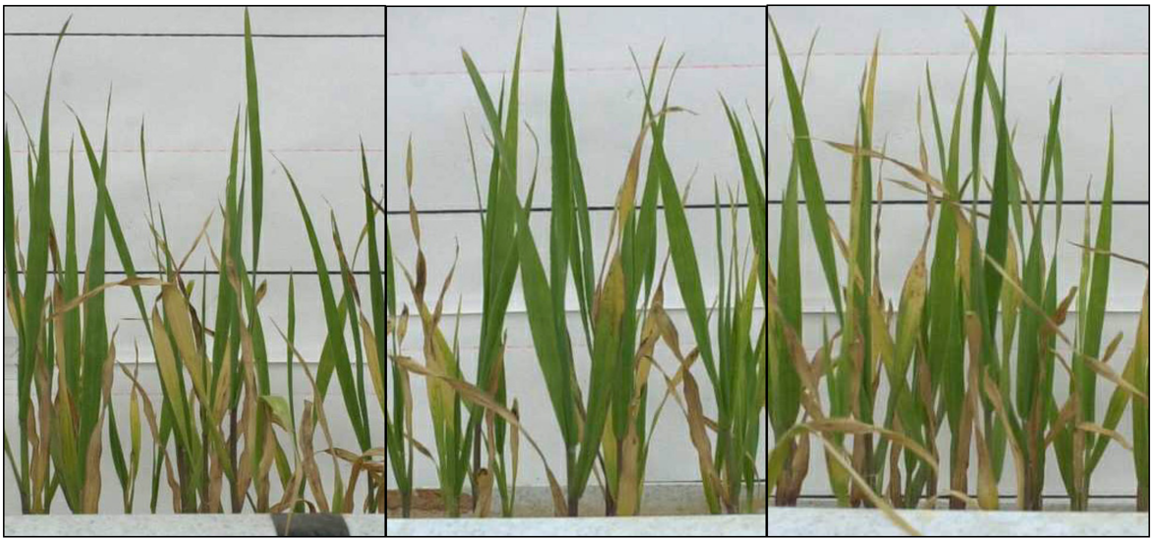
The series PotA5 grew strongest of all series. For comparison in Figure 5.17 average pots from all the series of PotA are depicted on the 27th day after sowing.

Apart from different heights and plant mass also the leaf colouring was partly different. In Figure 5.18 amplified clippings of the pictures of PotA2, PotA3 and PotA4 in Figure 5.17 are depicted. These pots grew similar in height, but by increasing applied amounts of OMW the plants were damaged stronger, i.e. more leaves suffered yellow and brown colouring (PotA2 without OMW, PotA3 OMW diluted 1/40, PotA4 OMW diluted 1/20). It has to be stated that this trend cannot be seen in Figure 5.18 as clearly as it was in fact.

Due to colouring and occurrence mainly on older leafs it was presumed, that these damages occurred because of too high salt concentration in the soil solution. Therefore it was decided to choose the necessary dilution for application of OMW in PotB based on a desired EC of the irrigation solution clearly lower than in PotA, namely 1 mS/cm.

Figure 5.17: Pots of series PotA1 – PotA8 on day 27 after sowing

Figure 5.18: Leaf colouring in pots of series PotA2, PotA3, PotA4 (from left to right) on day 27 after sowing



5.4.2 Weight analysis of PotA

PotA1, PotA2, PotA3 and PotA4 are the four series performed with earth as substrate. The results displayed in Table 5.8 and Table 5.9 show that weight analysis did only yield significant differences for the series PotA1. This was the only series in earth in which fertilisation was applied. The other three irrigation strategies produced nearly the same amount of plant material. It can be seen that the healthier plants in PotA1 have a lower share of dry weight of the fresh weight, whereas the other three treatments have very similar results. Comparing PotA1 and PotA2 (none with OMW) shows that fertilisation clearly did positively affect the growth. The similar results of PotA2, PotA3 and PotA4 show that the addition of by the photo-Fenton method treated OMW did not affect significantly the production of plant material. Potassium was sufficiently added in PotA3 and PotA4 (12 L of irrigation solution containing OMW of Experiment 4 as described, diluted 1:20 contain around 5 g K^+) with the irrigation solution. This testifies again the lack of nitrogen and phosphorus (only around 0.15 g added originating from OMW), which seemed to limit growth according to Liebig's minimum law. Nevertheless it has to be kept in mind that although growth of plant material was not affected, leaf colouring was influenced.

Table 5.8: PotA – Weight analysis on base of pot

Series	Fresh weight per pot	Dry weight per pot	Dry weight share of fresh weight
	[g]	[g]	[%]
PotA1	54.6	10.27	18.8%
PotA2	27.7	5.82	21.0%
PotA3	23.6	5.47	23.2%
PotA4	27.5	6.14	22.3%
PotA5	441.1	68.7	15.6%
PotA6	140.3	30.7	21.9%
PotA7	68.1	14.9	21.9%
PotA8	n.m.	n.m.	n.m.

In PotA5, PotA6, PotA7 and PotA8 barley was cultivated in perlite. Comparing the results of PotA5 and PotA1 (both fully fertilised, no OMW) it can be seen, that the plant growth was stronger in perlite. This was attributed to the light and porous, artificial substrate, which seemed to favour radical growth. During the disposal of the pots after the harvest it was observed that the radical system of plants cultivated in perlite was developed much stronger than of plants cultivated in earth. Also PotA6 and PotA7 produced more plant mass than the pots in earth. On the other hand the share of seeds germinated was lower in perlite, because the outer regions of the substrate surface seemed to be less humid than the centre inhibiting germination there. Due to these facts the dry weight per grown plant was considered the key figure to rule out these differences.

Table 5.9: PotA – Weight analysis on base of grown plants

Series	Plants germinated / pot	Died during growth period per pot	Plants grown per pot	Fresh weight / grown plant	Dry weight / grown plant
				[mg]	[mg]
PotA1	28	3	25	718	135
PotA2	29	2	27	342	72
PotA3	29	3	26	306	71
PotA4	29	3	26	353	79
PotA5	22	1	21	5129	799
PotA6	23	1	22	1542	337
PotA7	23	1	22	783	171
PotA8	n.m.	n.m.	n.m.	n.m.	n.m.

PotA5 (fully fertilised, no OMW) clearly grew stronger than PotA6 (25% fertilised, no OMW), showing that the given plant nutrient donations decided were well chosen and not beyond the critical plant nutrient concentration. Also PotA6 yielded more weight per pot as PotA7 (25% fertilised, with OMW). The reason could be too high salt concentrations as stated before. Weight analysis of PotA8 (no fertilisation, with OMW) was not conducted, as none of the plants made a really lively impression.

In perlite the application of OMW seemed to affect stronger the plant growth than in earth.

5.4.3 Weight analysis of PotB

The second pot experiment was performed keeping in mind a lower intended EC in the irrigation solution and the low concentrations of nitrogen and phosphorus in OMW used for preparation of the irrigation solutions. Another aim was to test irrigation solutions with OMW from different stages of the treatment, namely without treatment (PotB3, PotB4), second after application of pretreatment and the phase in the photocatalytic treatment, in which the rapid decrease of the PI takes place (PotB5, PotB6) and third similar to PotA OMW after strong TOC degradation had happened (PotB7, PotB8). All series of PotB received nitrogen and phosphorus donations, while potassium was only added in PotB3, PotB5 and PotB7. In PotB4, PotB6 and PotB8 potassium was supplied just by the addition of OMW. For a detailed overview confer to Table 4.7 and Table 4.8.

Table 5.10: PotB – Weight analysis on base of pot

Series	Fresh weight per pot	Dry weight per pot	Dry weight share of fresh weight
	[g]	[g]	[%]
PotB1	46.8	8.73	19.1%
PotB2	33.4	6.59	20.1%
PotB3	19.6	5.14	26.5%
PotB4	3.5	1.35	40.5%
PotB5	31.6	6.52	21.7%
PotB6	13.8	3.32	24.7%
PotB7	9.0	2.69	31.0%
PotB8	10.3	2.90	28.5%

PotB1 (150% fertilised, no OMW) grew stronger than PotB2 (100% fertilised, no OMW), meaning that increasing fertiliser donations still exhibited an effect (cf. Table 5.10). Comparing PotB2 and PotA5 showed, that although the two series were conducted equally, PotA5 yielded higher results. This was attributed to excessive heat in the greenhouse due to the seasonal differences in the realisation of the two experiments. Whereas PotA was realised mainly in April, PotB was realised almost in midsummer in June and July. Therefore any comparison between PotA and PotB has to be regarded with care.

Table 5.11: PotB – Weight analysis on base of grown plants

Series	Plants germinated / pot	Died in 4 weeks per pot	Plants grown per pot	Fresh weight / grown plant	Dry weight / grown plant
				[mg]	[mg]
PotB1	21	1	21	2327	432
PotB2	22	1	21	1629	317
PotB3	25	2	23	838	221
PotB4	23	5	18	194	76
PotB5	23	1	22	1421	295
PotB6	21	2	19	750	180
PotB7	22	4	18	494	149
PotB8	21	3	18	561	160

Table 5.11 shows that the additional potassium fertilisation produced the biggest differences in the result of PotB3 and PotB4. Also between PotB5 and PotB6 still a remarkable difference existed. In these series more organic carbon but above all more phenols were added, especially in the first two series mentioned. Almost no difference was determined between PotB7 and PotB8 where practically no phenols were added.

It seemed to yield bad results to apply the irrigation solution prepared with OMW, which was treated until TOC was diminished considerably (PotB7 and PotB8). More favourable was to prepare the irrigation solution with OMW after the pretreatment and few hydrogen peroxide consumption (PotB5 and PotB6). PotB5 almost yielded the same result as PotB2. Also the costs of the photo-Fenton treatment thereby incurred would be lower in a possible large-scale application.

5.5 Cost estimation

The intention of the following cost estimation shall serve as an approximate comparison between the different factors which have to be taken into account. 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 coll., 1997].

Prices used for calculation are listed in Table 5.12. The price of the flocculent agent was received from the producing company. The prices for the chemicals originate from the internet [ChemEXPO, 2002] and are market prices of the United States. Prices were calculated assuming an exchange rate of 0.88 US$ per Euro. Prices for electricity, reactor surface and workforce were estimated.

Table 5.12: Prices used for calculations

Product	**Price**	**Source**
VTA 32	2.180 Euro.L^{-1}	Producing company
HNO_3	0.263 Euro.kg^{-1} HNO_3 in 67.2% solution	US market price
H_2O_2	1.200 Euro.kg^{-1} H_2O_2 in 35% solution	US market price
$FeSO_4$.7H2O	0.170 Euro.kg^{-1}	US market price
K_2CO_3	0.092 Euro.kg^{-1}	US market price
Electricity	0.100 Euro.kWh^{-1}	Assumption
CPC + necessary tubes and pumps	60 Euro.m^{-2}	Assumption
Human resource	30 Euro.h^{-1}	Assumption

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. Treatment plants could be small or big, could be located directly beside the olive mill to treat the effluents of the mill or be provided by several mills. OMW treatment could be performed during a few weeks or continuously over 12 months.

In the following calculations treatment in a plant beside the mill during an eight months period following the press season was assumed. This seems reasonable because more solar irradiation is available in these months than in the months of the press season. Furthermore a working place would be maintained for an operator outside the press season, who could be an employee during the press season. Calculations were performed with 1000 annual operating hours of the photocatalytic plant.

Considering the hourly throughput as volume per area of CPC and hour a rough assumption was to be made. The throughput actually implies all the thoughts about reaction rate and residence time mentioned before. The hypothesis was that an optimised treatment would at least have the best throughput achieved in the own experiments (1 L.m^{-2}.h^{-1} in Experiment 6) and at best have a throughput 10 times higher. The factor is at such a large scale because higher throughput could also be achieved by stopping the treatment earlier than done in Experiment 6.

Table 5.13: Reactor investment costs per cubic metre OMW

Throughput	[m^3.m^{-2}.h^{-1}]	0.001 – 0.01
Annual operating time	[h.year^{-1}]	1000
Annual throughput	[m^3.m^{-2}.year^{-1}]	1 – 10
CPC area needed	[m^2.m^{-3}]	0.1 – 1
Purchase price of CPC	[Euro.m^{-2}]	60
Depreciation period	[year]	5
Finance price of CPC	[Euro.m^{-2}.year^{-1}]	12
Investment costs	**[Euro.m^{-3}]**	**1.2 – 12**

Multiplying throughput and annual operating time the amount of OMW treated per CPC area, respectively the necessary CPC area per cubic metre OMW, was calculated. The CPC reactor investment costs were divided by 5 years, which should be the minimum lifetime for the reactor. The calculation of the reactor costs is depicted in Table 5.13.

Electricity costs for the pump were calculated by upscaling the pump and the CPC used the experiment. In the CPC a 100 W pump was used to circulate the volume according to 3 square metres, furthermore the CPC area needed per cubic metre OMW, the operating hours per year and the electricity price were factored in the calculation, which can be looked up in Table 5.14.

Table 5.14: Electricity consumption by pumps

Power needed per CPC area	[kW.m^{-2}]	0.033
Operating time	[h]	1000
CPC area needed	[m^{2}.m^{-3}]	0.1 – 1
Annual electricity consumption	[kWh.m^{-3}]	3.3 – 33
Electricity costs	**[Euro.m^{-3}]**	**0.33 – 3.3**

Chemicals consumption was set according to the pretreatment of Experiment 10-13. For acidification 5.5 kg nitric acid, for flocculation 1.5 litres flocculation agent and an iron concentration of 5 mM, which means 1.5 kg $FeSO_4.7H_2O$ per cubic metre OMW were assumed. Like in the experiments two different amounts of hydrogen peroxide consumptions were assumed: 20 g.L^{-1} to reach the steady phase in the phenol degradation and 80 g.L^{-1}, respectively 20 and 80 kg per cubic metre OMW.

Table 5.15: Total reagent costs per cubic metre OMW for A) endpoint after consumption of 80 kg H_2O_2 and B) endpoint after consumption of 20 kg H_2O_2 per cubic metre OMW

		Quantity	Price per unit	Price
	Nitric acid	5.5 kg.m^{-3}	0.26 Euro.kg^{-1}	1.43 Euro.m^{-3}
	VTA 32	1.5 L.m^{-3}	2.18 Euro.L^{-1}	3.27 Euro.m^{-3}
	$FeSO_4$.7H2O	1.5 kg.m^{-3}	0.17 Euro.kg^{-1}	0.26 Euro.m^{-3}
A)	H_2O_2	80 kg.m^{-3}	1.2 Euro.kg^{-1}	96 Euro.m^{-3}
	K_2CO_3	11 kg.m^{-3}	0.09 Euro.kg^{-1}	0.99 Euro.m^{-3}
	Total reagent cost			**~102 Euro.m^{-3}**
B)	H_2O_2	20 kg.m^{-3}	1.2 Euro.kg^{-1}	24 Euro.m^{-3}
	K_2CO_3	18 kg.m^{-3}	0.09 Euro.kg^{-1}	1.62 Euro.m^{-3}
	Total reagent cost			**~31 Euro.m^{-3}**

Potash needed for neutralisation was estimated to be 11 kg in case of 80 kg hydrogen peroxide consumption per cubic metre consumption and 18 kg in case of 20 kg hydrogen peroxide consumption per cubic metre OMW. The resulting reagent costs are listed in Table 5.15.

So far it can be seen that be seen that the reagent costs would be the major cost factor. Reactor investment costs and electricity costs for the pump would be 15.3 Euro per cubic metre OMW in the worst case and a tenth part of it in the best case.

By contrast the reagent costs were approximately 102 Euro per cubic metre in case of that the treatment was ended after the consumption of 80 kg hydrogen peroxide per cubic metre and 31 Euro if the treatment was carried out until a consumption of 80 kg.

Furthermore it could be seen that hydrogen peroxide consumption is the main cost factor.

Olive mills produce between 800 and 8000 cubic metres of OMW each year dependent on the size of the mill and the harvest. Cost for human resource were assumed to be unaffected by plant size, as it can be supposed that one operator is needed for plant operation independently from the plant size. 1200 necessary annual working hours of human resource producing a total annual cost of 36000 Euro were assumed.

The total costs of the treatment for one cubic metre OMW including reactor investment, electricity, reagents and human resource are depicted in the Figures 5.19 and 5.20 for the two different scenarios; end of treatment after consumption of 80 kg or 20 kg hydrogen peroxide per cubic metre OMW.

Figure 5.19: Total costs of treatment – Endpoint after 80 kg hydrogen peroxide consumption per cubic metre OMW

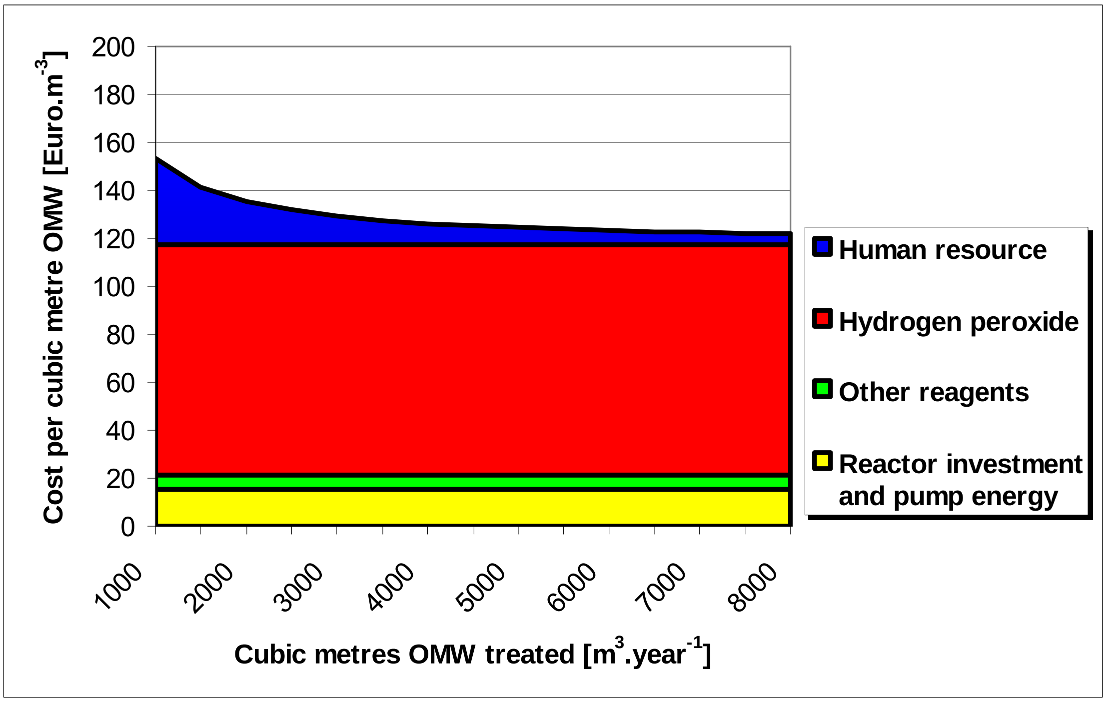
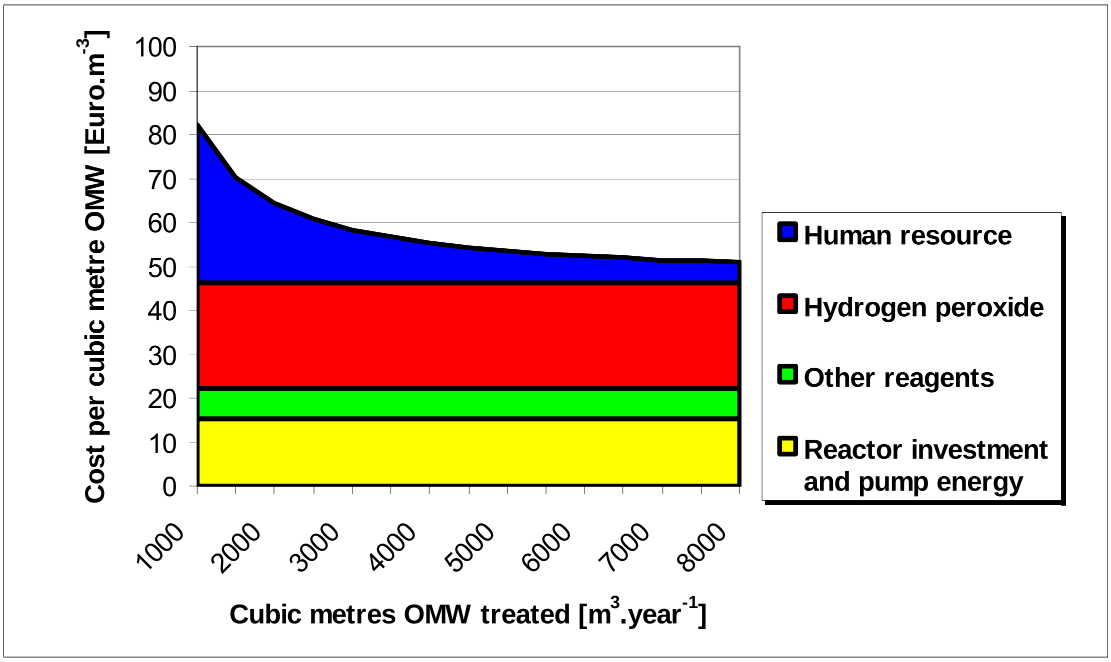


Figure 5.20: Total costs of treatment – Endpoint after 20 kg hydrogen peroxide consumption per cubic metre OMW



It can be seen that the relative costs of the human resource diminish significantly when the plant size increases.

Reactor investment costs and electricity consumption were depicted according to the worst case assumption. It has to be kept in mind that the best case assumption would provoke only a tenth part of the 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 coll., 1997; Wyness et coll., 1994a, Wyness et coll., 1994b; Yi-zhong, 1998].

Nevertheless the figures stated have to be regarded with care. As mentioned before no logistic, no maintenance and no investment costs for the pretreatment or other machinery were included (e.g. a forklift truck). Therefore the real costs would be higher. Another uncertainty is to which degree these figures can be generalised. As mentioned before the composition of OMW varies very much due to a multitude of factors.

On the other hand due to the reasons stated above all the high potassium content the treated OMW also possesses a certain value as fertiliser and irrigation water, but it is difficult to estimate.

6 Summary and perspectives

6.1 Pretreatment

The main aim of the pretreatment was to remove the suspended solids out of the OMW. Two different pretreatment strategies were performed and both could fulfil this task, but both had its advantages and disadvantages.

Renouncing acidification e.g. had the advantages that less chemicals were needed for pH adjustment and that it had a very long lasting effect, i.e. no suspended solids formed in the photocatalytic treatment. On the other hand this pretreatment needed more flocculent agent. This produces extra costs, EC rose considerably and foam formation in the photocatalytic treatment was promoted.

The strategy combining acidification, Fenton method and flocculation needed less flocculation agent. The drawback of additional chemical consumption for pH adjustment could be compensated by using plant nutrients. Nitrogen and potassium could be added by adjusting the pH with nitric acid and potassium hydroxide. The neutralisation step could also be performed with potash, which is cheaper than potassium hydroxide. It proved to be advantageous to separate the formed sludge after acidification. By this way less flocculent was necessary to obtain transparent supernatants.

Another aim was to diminish the relevant parameters like TOC and PI already in the pretreatment. Optimisation according to the execution of the flocculation step was not performed in this work. Many factors influence the performance of the flocculation, e.g. duration and vehemence of homogenisation and the sedimentation height. Considerable differences occurred when performing the flocculation with the same flocculation agent concentration in different vessels with different possibilities of homogenisation (test tube, 50 L ton, 200 L barrel).

No tests were performed according to the sludge produced in the pretreatment. In a comprehensive optimisation of the pretreatment it would be necessary to include as well studies on separableness of mud and supernatant, floc size and possible treatment of the sludge.

6.2 Photocatalytic treatment

In all the experiments it was shown that extensive degradation of TOC and COD is possible. Also the PI could be diminished significantly. In the most progressed experiment the degradation of TOC was carried out until a decrease down to 20 % of the original TOC was accomplished, PI was degraded to around 2 % of the original value. Further decrease of both parameters probably would have been possible, but this was not the goal of this work, as reagent consumption was to be kept low and the organic carbon in OMW was intended to apply to the plants by irrigation.

The decrease of TOC and COD was almost linear dependent on the applied amount of hydrogen peroxide. Although some parameters were varied during the experiments (hydrogen peroxide concentration, iron concentration, improved aeration, irradiation intensity, temperature of solution), deliberately or not, no big influences on the COD decrease per gram hydrogen peroxide applied could be determined.

In contrast the PI was degraded with few oxidant consumption down to around 30 % of its original value. A steady phase followed, until in a third phase the PI was lowered again slowly.

A possible explanation would be, that in the first phase the original phenol content of the OMW is degraded rapidly. During the steady phase a steady-state is achieved, because at the same time phenols are formed due to addition of hydroxyl radicals to aromatic compounds while simultaneously degradation of phenols takes place. The third phase begins, when all aromatic substances are already converted to phenols or degraded. At that time a colour change to a lighter colour occurred in the experiments. Interference to the phenol measurement due to reaction intermediates would also be a possible explanation.

The iron concentration proved to be a key factor to achieve high reaction rates. The applied concentrations (around 5 mM or 280 $mg.L^{-1}$) top the legal boundary limits for discharge into natural waterbodies (between 2 and 20 $mg.L^{-1}$ depending on country inside EU) significantly. No legal boundary limits could be found for irrigation water, but iron normally presents no problem due to its low solubility at neutral pH. It normally also is abundant in soils. On the other hand complexing watersoluble substances can mobilise heavy metals in soils.

Elevated temperature was another key factor to accomplish high reaction rates. Temperatures measured in the reaction solution reached from 15 to 60 °C. Based on the results obtained, it cannot be judged, if working in dilution raises or lowers the throughput of the photocatalytic reactor. On the one hand it could raise the throughput, because iron ions (same concentration supposed) would be favoured competing for the photons. On the other hand the efficiency of the radical interactions should decrease in diluted solutions.

Degradation experiments in the dark were also performed. They showed that degradation could also be accomplished in the dark. Apparently the mechanisms differed somehow, because the pH sunk down to 1.5 in these experiments. Compared to photocatalytic degradation experiments probably higher concentrations of organic acids were formed, which are known to form stable complexes with iron in the dark. Maybe thereby reaction rates sunk during the experiments performed completely without light. A combination of dark times and irradiated times could prevent accumulation of acids.

In the photocatalytic degradation experiments performed in this work a fixed ratio between total volume and irradiated volume was predetermined by the reactor configuration. Thereby also the residence time under irradiation and the residence time in the not-reacting tank were fixed. Raising this ratio by enlarging the tank could possibly help to increase the throughput per square metre photoreactor.

Not only high reaction rates and good reactor configuration have to be provided to achieve a high throughput. Another decisive point is the endpoint of the treatment. This endpoint should be as soon as sufficient detoxification for the subsequent step has been accomplished. Besides increasing the throughput through the reactor, this lowers also the reagent consumption per amount of wastewater. In the experiments hydrogen peroxide consumption between 20 and 80 grams per litre OMW were applied.

Studies on optimisation of the photocatalytic treatment should take all the mentioned factors into account.

6.3 Application of OMW to plants after photo-Fenton treatment

Application of untreated OMW to plants has negative impact due to its high phenol content, high salinity and low pH. The organic matter and above all its high potassium content could be beneficial. The absence of nitrogen presents a problem, because high applied C/N ratios promote nitrogen immobilisation in soil.

So the task was to degrade the mainpart of the phenols, to raise the C/N ratio and to adjust the pH to neutral values. The salinity problem could not be solved by the applied methods. Harmful effects were tried to prevent by controlling the EC of the applied irrigation solution by dilution. This is no contradiction to the principle that wastewater usually is not diluted for treatment. The important thing is, that no additional clean water is wasted for the treatment and that no additional logistic costs would be incurred, because dilution would take place on the location of application. Furthermore the quantities of applied OMW would be negligible compared to the amounts of irrigation water.

As mentioned nitric acid and potassium hydroxide were used for necessary pH adjustments. In germination tests performed with OMW samples taken from the photocatalytic experiments a first considerable detoxification was determined after the pre-treatment. This showed that the suspended solids also had phytotoxic effects. In the course of the experiment the toxicity rose slowly. This was due to the higher salt content produced by the increasing amount of potassium hydroxide necessary to neutralise the oxidised reaction intermediates (carboxylic acids). When TOC degradation progressed the amount of potassium hydroxide to neutralise the OMW decreased too and the toxicity sunk again.

Different strategies according to the amount of fertiliser and OMW and the progress of treatment of OMW were pursued in pot experiments performed in perlite and earth with barley.

The experiments showed the beneficial effect of phenol degradation on the plant growth. Furthermore it was proven that the potassium contained in the diluted OMW used for irrigation solution could replace an otherwise necessary extra donation of potassium.

The natural potassium concentration in OMW is reported between 2 and 11 grams per litre OMW. Around 5 grams per litre were added in the experiments by neutralisation.

The barley plants suffered severe damage in the pot experiments, but it has to be taken into account, that they were still exposed to high amounts of OMW in pots. The situation would be different in an application on natural soil. In the pot experiments the barley showed higher tolerance to phenols in natural soil. Furthermore in the pot experiments young seedlings were exposed to high amounts of OMW. In an agricultural application the time of spreading could be chosen according to the crop’s needs.

6.4 Overall treatment costs

An example of a cost estimation including investment of photocatalytic reactor, electricity, reagents and human resource costs was presented for a OMW treatment plant (confer Chapter 5.5). In the example the overall treatment costs were around 130 Euro per cubic metre OMW in case A), where 80 kg hydrogen peroxide were applied to each cubic metre OMW and around 60 Euro in case B), where the treatment was ended after 20 kg. The numbers are given for a medium sized mill, which generates around 3000 cubic metres OMW annually. In both numbers the worst case assumption considering throughput through the reactor was applied. A real treatment would be a little more expensive, because some factors could not be estimated exactly and were ignored hence.

In case A) more than 70% of the costs can be attributed to hydrogen consumption, in case B) still 40% are mainly determined by the hydrogen peroxide consumption under the condition that the mill.

Although being rough estimations these numbers should be compared to the value of the olive oil gained in the process. Therefore a last assumption has to be made, the ratio between the amount of OMW generated per olive oil gained. Presuming that four litres OMW are generated for each litre olive oil obtained would mean that in case A) 52 cents have to be spent on the treatment of the wastewater brought into existence by the production of each litre olive oil. In case B) 24 cents must be spent on the treatment of the OMW accruing in the production of each litre olive oil.

As it is always the case with environmental problems society has to decide how high it esteems the value of a clean environment. If society is willing to pay the price, it is up to European Community legislation to provide the regulating general framework.

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