Solar photo-Fenton treatment of a commercial pesticide mixture

Evaluation of the temperature as a process parameter
Including a study of toxicity and biodegradability

Degree thesis
in solar chemistry
Course of studies Geoecology
at the
Technical University of Karlsruhe

Cand. Geoök. Stephan Hilgert

First examiner: em. Prof. Dr.-Ing. E.h. Ph. Hermann H. Hahn
Second examiner: Dr.-Ing. Stephan Fuchs

This thesis was developed between 29. September 2008 till 29. March 2009

Karlsruhe, March 2009

Thesis Declaration

I hereby declare that this thesis is my own, unaided work and that recognition has been given to the references used. It has not been submitted for any degree or examination at any other university.

Karlsruhe, 27th March 2009

Abstract

The water supply situation is deteriorating globally due to economical and industrial growth. Especially in the Mediterranean basin the increase of intense agriculture caused a high consumption of fresh water and also a problematic pollution originated by pesticides and other chemical compounds. In this work the possibility of treating wastewater polluted by pesticides coming from the horticultural centre in the south of Spain, is studied. AOPs seem to be the most promising solution as a preliminary treatment of biorecalcitrant contaminants for the purpose of degrading those using an inexpensive biotreatment. AOPs are known to be the most effective way for oxidizing biorecalcitrant substances, but have the major drawback of high operation costs. The combination of a solar advanced oxidation process (AOP) and a conventional biological treatment has been reported as an attractive approach for solving this problem. This work was elaborated and carried out at the PSA (Tabernas, Spain). as a part of the FOTOBIOX project, which is focused on the optimization of a combined solar photo-Fenton/biological system for the decontamination of a pesticide mixture.

Evaluating the influence of the temperature as an important factor on the photo-Fenton degradation process was the main objective of the present study. The final aim was to find the best operating conditions for the preliminary treatment of a high concentrated commercial pesticide mixture. The operational conditions should be optimized in order to minimize the costs. In this context photo-Fenton degradation experiments at four different temperatures (25, 35, 42, 50°C) were carried out and the obtained results and effects were controlled by Fenton experiments. All experiments were processed at an iron concentration of 20 mg L^{-1} and a pH of 2.8.

Finally, selected samples from different stages of the photo-Fenton degradation process were analysed in order to determine the toxicity and biodegradability. The objective was to find the optimal point for the consequent biotreatment, and additionally prove the feasibility the proposed combined system.

Keywords: water scarcity, advanced oxidation technologies, pesticides, photocatalytic processes, Fenton, photo-Fenton, toxicity, biodegradability

Table of contents

Index of figures

List of tables

List of abbreviations

ACN	Acetonitrile
ADI	Acceptable Daily Intake
AOP	Advanced Oxidation Processes
ARfD	Acute Reference Dose
AU	Astronomic Unit
BAT	Best Available Technology
bCOD	Biodegradable fraction of COD
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas
CO	Consumed Oxygen
COD	Chemical Oxygen Demand
CPC	Compound Parabolic Collector
CR	Concentration Ratio
DOC	Dissolved Organic Carbon
ETFE	Ethylenetetrafluoroethylene
EU	European Union
FEP	Fluorinated ethylenepropylene
HPLC-UV	High Performance Liquid Chromatography with UV/Vis detector
IC	Ion Chromatography
LD	Lethal Dose
LMCT	Ligand to Metal Charge Transfer
OUR	Oxygen Uptake Rate
PCOs	Photocatalytic Oxidation Processes
pH	"potential hydrogenii" – pH value
PHS	Priority Hazardous Substances
POPs	Persistent Organic Pollutants
PS	Priority Substances
PSA	Plataforma Solar de Almería
PTC	Parabolic Trough Collector
Rs	dynamic uptake Rate
TC	Total Carbon
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
UV	Ultraviolet light
UV/Vis	ultraviolet/visible light
WHO	World Health Organisation

1 Actual context

Potable water in general is one of the most important resources, but in contrast to the real supply situation it is often taken as granted and as an unlimited resource. With economic and agricultural growth the use of drinking water increases and likewise the pollution of the present water bodies. Especially agricultural industries originate a huge demand of fresh water, which is particularly in the Mediterranean area very scarce. Since the dry regions of the Mediterranean coast have never been a highly productive part of Spain, the latest revolution in agriculture stands for an absolute change of land use in the Province of Almeria. In 1962 the first plastic greenhouses were erected in Roquetas de Mar. From these beginnings until 1985 the area covered by greenhouses grew up to 11.400 ha. [Tout D., 1990]. In the following years the missing infrastructure, which was necessary for further advancement of the economy and agricultural industry, was build and the area of greenhouses continued growing. Finally in the year 2007 the agricultural industry comprised 48.730 ha and produced nearly a value of two billion Euros. The average growth rate of the last years was about 2.7% per year.

The vast growth caused several problems and a high consumption of the local and regional resources. Although 35% of the spanish agricultural production is grown in Andalucía the covered surface amounts only 7.7% of Andalucía. A big part, 66% in the year 2006, of the produced vegetables and fruits from the Almeria region were exported. By now this region contains the biggest greenhouse concentration in the world [Costa J.M., Heuvelink E., 2000]. With reference to the mentioned worths it is obvious that the productivity of the greenhouses is clearly higher than it would be under natural circumstances. The plants grow in plastic greenhouses on applied artificial mineral soils and are droplet irrigated. Via the droplet irrigation 4 to 5 times the amount of water of the annual rainfall is used per m² in the greenhouses. In addition to that 60% of the annual rainfall falls during only six days [Costa J.M., Heuvelink E. 2000; Tout D., 1990]. The high consumption and the water scarcity over most of the year exceed the local water resources. Therefore underground water reservoirs and the water coming from the close Sierra Nevada have to be used to supply the horticulture in the Almeria region. To raise the quality and the yield of the soil, huge amounts of fertilizers have been used and are still used with increasing amounts every year. [Fenández-Soriano, 1995] The other parts of applied chemicals are the pesticides, for example fungicides, insecticides and nematicides. The whole consume of pesticides rose from 115.5 kg per hectare in the year 1995 to 142 kg in 2004, which is an equivalent to a growing rate of 28.2%. Despite the fact that the agrochemicals constitute 27.5% of the overall costs in the horticultural sector, the profits are still very high. As the figures show the use of pesticides in the horticulture in the Almeria region seems to be very high. Particular in comparison to the also well developed greenhouse sector in the Netherlands the use of biocides in Almeria is 7 to 11 times higher [Costa J.M., Heuvelink E., 2000]. Based on

different physical and chemical characteristics and due to several features of the pesticide industry these substances should be considered as a major threat to the ecosystem. The pesticide production, transport, application and finally the recycling of the containers stand for many opportunities where the environment is consciously or unconsciously exposed to these contaminants. For instance the residual water of the washing facilities of pesticide containers comprises a high concentration of pesticides and is not always well treated. General problems in this product chain are the diffuse sources of contaminants and the large amounts of pesticides being deployed in the ecosystem. A major problem is the complexity of the composition of these chemicals due to varying compounds and concentrations. Depending to the physical and chemical attributes of these compounds the aforementioned problems are even graver. A big part of these compounds exhibit a high persistence in the ecosystem and are called “persistent organic pollutants” (POPs). Further important attributes which affect the behavior of the contaminants in the environment are the solubility in water the absorption coefficient, ionization constant, stability and volatility. The characteristics of each specific location, including the type of soil, the amount of rainfall or the irrigation and also the drainage system play an important role in the behavior of the compounds. Concerning the solubility some of the pesticides represent a threat to the surface water as well as to the groundwater. The limestone- dolomite fractured rock formation allows a fast penetration of leached contaminants into the groundwater in the Almeria region. Some compounds, like Imidacloprid were investigated in regards to the leaching in the upper soil layers. The results show a transport through the upper soil layer (40 cm) in the first two years [Gonzales-Paradas E., Urena-Amate M. D. et al. 2002]. The problem dealing with POPs or similar compounds is well reflected in plenty of the directives issued by the European Union. The Water Framework Directive (2000) sets one of the most important instruments for protection and improvement of water quality in the EU, the identification of Priority Substances (PS) and Priority Hazardous Substances (PHS) [European Commission, 1999; European Commission, 2000]. These substances including some pesticides (PS) are considered of crucial impact for the European aquatic system. The 23 PS and 10 PHS which have been already disclosed are, depending to the classification, subject to strong limitations (PS) or a planned complete phase-out until the year 2020 (PHS) [European Commission, 2000] More detailed regulations are described in further (daughter) directives [European Drinking water directive, 1980; European Commission, 1991 Waste water treatment directive]. The Water Framework Directive from the year 2000 has been updated by the Commission Proposal [COM (2006) 397 final]. Regarding to the Lisbon strategy paper of the EU (2005) all water bodies should be in a good state until the year 2015. This will make a strong reduction of use, emissions and production of these contaminants necessary. The following objectives had been focused:

- Reduction to a minimum of the threads and risks caused by pesticides to the health and the environment

- Intensification of the controls of use and distribution of the pesticides
- Reduction of the active pollutants and substitution of the most dangerous and toxic pollutants by alternatives
- Building up a type of agriculture, in which the use of these pesticides is not necessary or strongly limited
- Establish a transparent system of communication and aftercare of the reached advance

To meet the objectives defined by the EU there must be a development of environmental technologies including innovative processes. Pesticides are comparatively resistant to normal oxidation or reduction processes and sometimes as well to biodegradation according to their toxicity or structure. Advanced Oxidation Processes (AOPs) have been reported as effective methods for eliminating these compounds [Zapata A., Oller I. et al., 2008; Pignatello J., Oliveros E. et al., 2006; Gernjak W., Malato S. et al., 2006; Oller, I., Malato, S. et al., 2007], but their main drawback is their relatively high operating costs. The combination of a Solar AOP as a preliminary treatment, followed by an inexpensive biotreatment, would seem to be an economically attractive option to solve this problem.

2 Project overview

This study is part of the FOTOBIOX project which is a national research project of three institutions and universities in Spain. The partners are the University of Alcoy (Valencia), the University of Almeria and the solar chemistry group of the Plataforma Solar de Almeria (PSA-CIEMAT). In this collaboration the PSA group officiates as a coordinator. The overall objective is the combination of solar photocatalysis and biological oxidation targeting to the detoxification of wastewater containing pesticides. This overall objective is divided into three sub objectives.

1. Evaluation and optimization of the photo-Fenton degradation of the mixture,
2. Investigation of the biological oxidation including biodegradability and toxicity studies
3. Design and implementation of a coupled system that integrates both processes

Within the photo-Fenton degradation process the influence of five variables is to be evaluated with the objective of finding the most suitable operational conditions. These variables are: iron concentration, H_2O_2 dosage, salinity, pH and the temperature. After the influence of salinity, the optimal concentration of H_2O_2 and iron had been elaborated the factor of temperature is to be investigated in this study. Elaborating the optimal values for these parameters should lead to the main objective of this project. This is to design a system which can be scaled up to be used in a real industrial application. Since the optimization of the photo-Fenton process is a crucial factor as the central part of the degradation process. The optimization includes minimal illumination time required for the substantial mineralization and a low hydrogen peroxide consume. The illumination time determines the size of the collector field as an important design parameter and the consume of hydrogen peroxide is to be minimized, because it is the most expensive reagent used in the process. Optimization should lead to reduced investment and operational costs, since this is the main aim in an industrial application.

3 Objectives of this work

This study has been developed in the Plataforma Solar de Almeria (Tabernas, Spain) as a part of the above explained project. Depending to this, some of the experimental and operational parameters are determined by the results of previously performed experiments.

The main objective of this work is a detailed analysis of the influence of the temperature on the reactions during the photo-Fenton degradation of a commercial pesticide mixture and the behavior of the other process parameters. Fenton experiments were carried out to obtain a close look to parts of the degradation process. The aim is to determine the optimal operational temperature for a feasible real application of the technology. Especially the influence of the temperature to the important variables hydrogen peroxide consume, dissolved iron concentration and pH value are focused to be investigated. These experimental parameters are to be connected with the process of mineralization and the required treatment time.

Finally, the obtained results (optimal operational parameters) are transferred to the degradation of the same pesticide mixture with a higher initial concentration of pollutants, since this concentration is closer to real values of contamination. The main aim of this study is an investigation of the biodegradability and toxicity during the decomposition of the compounds is carried out to provide information for the next step in the FOTOBIOX project. This information will serve as a basis for the conceptual design of a coupled photocatalytic/biological system.

4 Fundamentals

4.1 Solar resources and technology

4.1.1 Irradiance and physical Fundamentals

The emitted radiation by the sun is the incentive for many fundamental processes on earth like atmospheric circulation, photosynthesis and ocean currents. In general the earth receives about $1.7*10^{14}$kW solar radiation, which is equivalent to $1.5*10^{18}$kWh per year. The radiation which reaches the earth outside the atmosphere is called extraterrestrial radiation and has an intensity of 1367 W/m² [Fröhlich C., Brusa R. W., 1981]. The unfiltered radiation which impacts the atmosphere has a wavelength between 0.2 µm and 50 µm. When the radiation reaches the surface of the earth the remaining spectrum is between 0.28 µm and 0.4µm. This reduction of the spectrum is due to a filter effect caused by various atmospheric components like ozone, oxygen, carbon dioxide, aerosols, steam and clouds. The whole radiation hitting the surface of the earth is called global radiation and can be separated in the direct radiation and the diffuse or indirect radiation. The direct radiation gets neither nor absorbed. Indirect radiation has been diffused before reaching the surface. For most application which are using sunlight as energy source for any kind of process it is crucial to calculate the share of the diffuse and direct radiation and also the amount of solar radiation available for a corresponding site. These measurements should be estimating the radiation for the whole year and to provide a good significance they should be carried out for at least five years [Iqbal M., 1983]. Today it is possible to know all the geometric and physical fundamentals which are needed to calculate the solar irradiance for various locations on earth and different times of the year. A basic factor is the distance between the earth and the sun which is called Astronomic Unit (AU) and got a value of $1.496*10^{11}$ m. Since the earth rotates on an elliptical orbit around the sun the distance is not constant. It varies between the perihelion (3rd Jan.) and the aphelion (4th July). As the earth receives radiation proportional to the square of the distance to the sun, it receives more radiation in the perihelion when the distance is only 0.983 AU and less radiation during the aphelion 1.017 AU. In addition to this cycle the earth also revolves on its own axis with an inclination of 23.5° compared to the perpendicular of the eclipse during the whole year. The variation of the angle between the lines joining the center of the sun and the terrestrial equatorial plane is called declination. The declination varies from +23.5° to -23.5° during the year causing an annual shift of locally received radiation and so the seasons. The day angle (Γ) expresses the date of the year according to

$$\Gamma = \frac{2\pi\,(n-1)}{365} \qquad \text{(eq. 4.1)}$$

in which *n* stands for the number of the day in the year. The fact that not all the months have the same number of days causes an aberration which can be calculated in an extra formula. The zenith angle is 90° minus the local latitude and the solar declination at midday. The hour angle is 0° at midday and varies from +15° in the morning to -15° in the evening. The solar midday is referring to the true solar time, which can be calculated from the local standard time, the local longitude and the day angle. The moment when the altitude of the sun is the highest during the day is denominated as solar midday. To optimize the position of a solar plane, two more parameters have to be taken into account. The angle of the inclination with respect to a horizontal plane (ß) and the orientation depending to the azimuth angle (γ) [Iqbal M., 1983].

Furthermore the solar radiation, which incidents on a surface depends not only to the geometrical relationships but also to atmospheric conditions. In a calculation providing a precise estimation of the real solar irradiance for sun collectors it is obligatory to take both factors into account. In these calculations it is important to consider the difference of the direct and the diffuse radiation, because of the share of diffuse radiation even under cloudless sky. With regards to photochemical processes the diffuse radiation plays a particular role concerning the stronger scattering of the shorter wavelengths.

$$I_{Bn\lambda} = I_{on\lambda} * T_{R\lambda} * T_{o\lambda} * T_{n\lambda} * T_{g\lambda} * T_{w\lambda} * T_{a\lambda} \qquad \text{(eq.4.2)}$$

Equation *4.2 gives the* beam irradiance $I_{Bn\lambda}$ at wavelength λ, received at ground level by a surface normal to the sun rays, depending on $I_{on\lambda}$ the extraterrestrial irradiance corrected for the actual sun-earth distance and parameters representing the different extinction processes: Rayleigh scattering ($T_{R\lambda}$), absorption by ozone ($T_{o\lambda}$), NO_2 ($T_{n\lambda}$), uniformly mixed gases ($T_{g\lambda}$), water vapor ($T_{w\lambda}$) and aerosol extinction ($T_{a\lambda}$). Generally the calculations for the indirect irradiance are more complicated and have to be processed by computers. In a simplified way it is possible to use the formula mentioned above, since all necessary parameters are already included. As the function of transmittance predicts the scattered radiation it is possible to estimate the share of photons redirected to the surface of the earth. The four following components result in the diffuse irradiation of an arbitrarily oriented surface: diffuse radiation caused by Rayleigh scattering, aerosol scattering, sky and ground backscattering. Further the cosine decrease regarding to the angle of incidence of the beam irradiance, all corresponding geometrical considerations and the fact that a tilted surface only receives diffuse radiation from one part of the sky vault. To calculate the ground backscattering correctly the albedo has to be known.

4.1.2 Solar collectors for the photochemical application

Non-concentrating collector systems are most suitable for photochemical applications. First, because, the concentrating systems normally achieve high temperatures in the receivers which are not necessary or even disadvantageous for photochemical processes. Second, photochemical applications are often based on the use of UV- radiation which is partly irradiated diffusely, while the diffuse light cannot be used by concentrating systems. As non-concentrating systems are static they cannot track the sun. They are aimed at the sun at a specific tilt, which depends to the geographic position. Examples for a simple use of this technology are the domestic hot water systems. Regarding to the photochemical processes the design of the collectors has been changed from reflection of all wavelengths to a more specific reflection of the high energetic short wavelengths. Still the hardware for solar photochemical applications has much in common with those from conventional thermal applications like parabolic troughts (PTCs) and non-concentrating collectors [Minero C., Pelizzetti E. et al., 1993]. The main differences are the need to expose the fluid directly to the sunlight in photochemical applications and further the less important role of the temperature which makes any kind of isolation superfluous. Since the experiments on which this work is based were carried out in a reactor using compound parabolic collectors (CPCs) and due to the fact that these collectors seem to be the most promising cross between the "one sun collectors" and the PTCs, the CPCs will be explained more detailed. [Malato S., 2004]

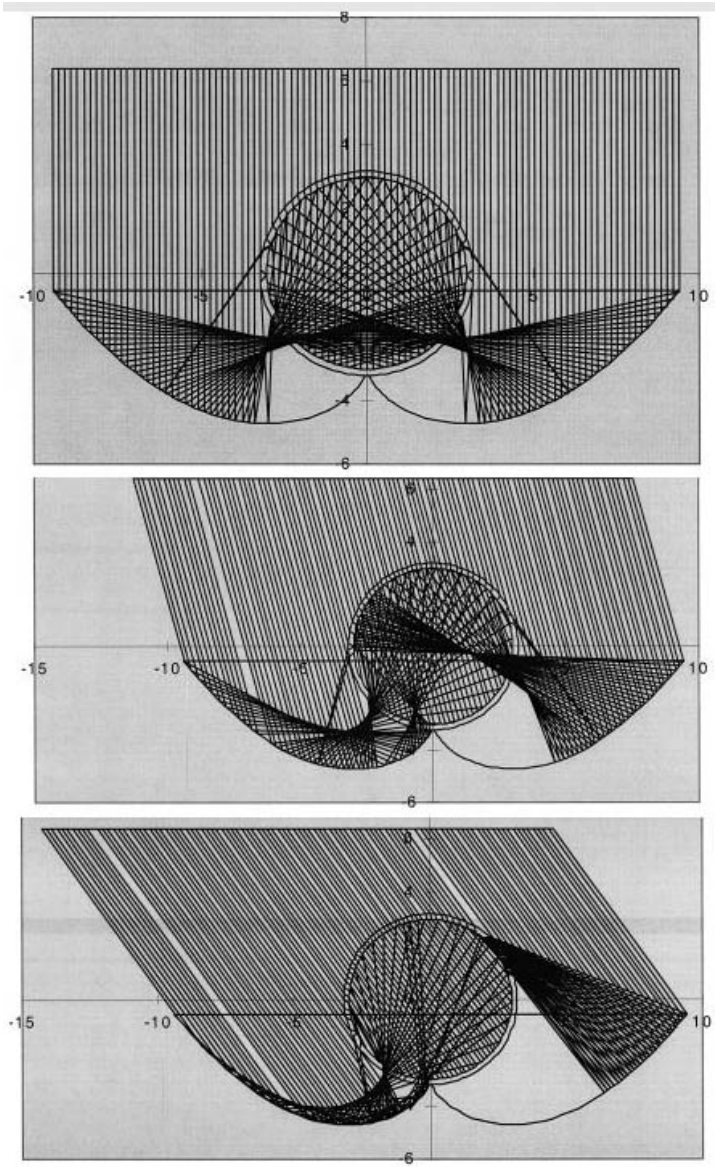


Figure 1 CPC reflector with tube [Malato S., 2004]

CPC

CPCs are static collectors with a reflector following an involute around a cylindrical reactor tube (figure 1). Combining the advantages of the PTCs and the one sun collectors they provide best optics for low concentrating systems with a concentration ratio (CR) close to one. The concentration ratio is the ratio of the collector aperture area and the absorber or reactor area. Because of the special reflector design almost the entire UV-radiation, coming from the direct irradiation as well as from the diffuse radiation, reaching the CPC aperture can be used for photochemical processes in the reactor. The form and aperture of the reflector related to the tube diameter ensures that most of the reactor tube circumference is illuminated. In this way the impinging light is similar to a one sun design, but with a clearly easier piping and fluid distributing system. The wide acceptance of irradiation angles allows the reactor not only to use the direct and diffuse irradiation, but also generates the advantage that alignment errors of the tubes are ameliorated, what is a very important factor in cost reduction. The CPC reflectors are normally made of polished aluminium and the whole reactor is built upon a simple support frame. These characteristics and the possible low construction costs make the CPC first choice for photochemical processes [Malato S., 2004; Well M., Dillert R. H. G. et al.,1994].

Some general differences between tracking and non-tracking systems should be explained to underline the advantages of non-tracking systems regarding to photochemical processes. As mentioned above the collecting of diffuse radiation is apart from thermal applications very useful. This results from the fact that the UV-radiation is more susceptible to scattering than light with a longer wavelength. Half of the UV-radiation gets scattered on the way to the earth surface. Hence the near UV-light (285-385nm) comprise only 2-3% of direct sun light but up to 4-6% of diffuse irradiation. The direct part of the sunlight gets more filtered by clouds, aerosols, haze, etc. than diffuse radiation which raises the efficiency of the non-tracking collectors. The simplicity of the construction of the non-tracking systems is the second advantage, resulting in notedly lower constructing costs and maintenance requirements. Furthermore the non-tracking collectors have significant higher potential for reduction of the manufacturing costs. In terms of efficiency the one sun (static flat plate) collector with an inclination equal to the latitude (37° in case of the PSA) achieves a maximum yearly efficiency of 70%. This value was calculated on the basis of geometric calculations based on the cosine of incident angle formed by the solar ray with the line normal to the aperture plane of the collector. With an efficiency of 70% the non-tracking collectors are less efficient than other one axis PTCs, but the variation of efficiency during the year is lower which is another advantage pertaining to photochemical processes [Malato S., 2004].

4.1.3 General characteristics of the photochemical reactor (CPC)

The reactor has to contain the work fluid inclusive the catalyst or the sensitizer and must be transmissive to UV-radiation. The lower the pressure drop within the system

the better it is. Especially for heterogeneous systems with a static part supporting the catalyst or sensitizer a good mass flow from the fluid stream to the surface of the illuminated photocatalyst is necessary. To work near the ideal-flow conditions an adequate flow distribution must be assured in the reactor. A non-uniform distribution leads to non-uniform residence times in the reactor which is decreasing the performance of the system. As a fragile part, the tubes have to be stable and hard enough to withstand the usable water pressure, while the choice of tube materials is limited due to the requested resistance and transmissibility of UV- light. All parts of the reactor have to be made of materials resisting high temperatures between 40-50°C in normal use phases and up to 70-80°C during the summer. In addition the materials have to be inert towards low and very high pH-values and to the chemicals included in the photochemical reactions especially in the detoxification. Quartz with its high transmissibility, hardness, resistance against chemical compounds and high temperatures makes a good material for the tubes. The major drawback is the very high costs which make it unfeasible for large reactors. Other materials like fluoropolymers, acrylic polymers and various types of glass have different disadvantages and advantages as well. They vary in transmission, in tensile strength, in resistance against UV- radiation and chemical inertness. Fluoropolymers are not strong enough to provide a reasonable wall thickness with a high pressure which counts particularly for large reactor systems. Acrylic compounds, ETFE (ethylenetetrafluoroethylene) and FEP (fluorinated ethylenepropylene) do not have the required stability against UV-radiation (UV-solarisation) and chemicals. The general detriment of the various glass types is the loss of UV-radiation due to the iron compounds in the crystal structure. Anyhow there are iron-reduced types which have a better performance regarding to UV-transmission. For each reactor concerning the size and function the material with the highest performance for the lowest costs has to be found. In terms of reflective surfaces in non-concentrating systems the minimum reflectance does not need to be as high as in concentrating systems. Which causes again lower construction costs because the reflector can be an expensive part of the collector. Silver, as it absorbs a big part of the UV-radiation is not recommended to be used as a reflective surface for photochemical applications. By contrast aluminium is highly reflective between 300 and 400 nm as it reflects 92.3% (280 nm) to 92.5% (385 nm) of the radiation, while silver only reflects 25.2% to 92.8% at the same wavelengths [Muschaweck J., Spirkl W. et al., 2000; Blanco J., Malato S. et al., 2000]. Since the thin oxide layer of the aluminium does not protect the reflectors from the influence of the outdoor environment like abrasion, aluminium coated mirrors seem to be a good alternative. But for this mirrors the principal negative effect of the glass layer which filters two times (incoming and outgoing) the UV-radiation is a constricting disadvantage. In order to find the optimal reflective surface for photochemical applications which promise a high reflectance in the UV-spectrum combined with an acceptable durability in outdoor conditions for a reasonable price, there are two actual approaches. Electropolished anodized aluminium (electrolytically formed aluminium oxide layer) with a thicker oxide layer protecting the reflector is one option. This layer can be 2-3 µm thick or even

up to 50 µm, but the thicker the layer the lower the reflectance. The other option is to cover the aluminium with a thin layer of acrylic lacquer [Muschaweck J., Spirkl W. et al., 2000; Blanco J., Malato S. et al., 2000].

As mentioned above all components of the reactor as well as the piping have to be resistant against corrosion by the original contaminants and their potential by-products during the destruction process. No materials which possibly interfere with the photochemical process are to be used. Every compound like pipes and the connection devices must be inert to degradation of UV-radiation and strong enough to withstand the nominal pressure of the system between 2-4 bar and maximum loads of 5 to 7 bar. They have to be stable even with high temperatures.

The last important part of the solar reactor is the intermediate element that absorbs the UV-radiation. These elements are called photocatalysts or sensitizers and they provide electrons to the medium while absorbing the UV-light which passes the fluid. The photocatalysts can be provided to the system in a heterogeneous or a homogeneous way. Heterogeneous systems consist of a two phases, for example a static part coated with the catalyst or a supporting for the catalyst. Many different forms of supports and methods have been tested in heterogeneous systems to achieve the highest efficiency. The support has to be illuminated and in the same moment in optimal contact with the medium. It should also maintain a high flow rate of the medium to ensure a good mixing. The contrary system type is the homogeneous or slurry system. This system renounces the static part because the photocatalyst is solved in the medium, creating the advantage of clearly higher throughputs and low pressure drops through the reactor combined with excellent fluid-to-catalyst mass transfer. It is important that the catalyst can be easily removed from the medium after the process or there is no need to remove the catalyst. If this is assured the homogeneous systems reduce the size of the reactor and the whole solar collector field. Making the entire system considerably more cost efficient and competitive. One relevant factor for both types of systems is the diameter of the tubular photo reactor. It must be guaranteed that all through passing photons are kept inside the reactor. The intensity of the illumination affects the relationship of the reaction rate and the concentration/density of the photocatalyst. The dispersion and absorption of light causes photon density to diminish almost exponentially over the length of the optical path. At higher light intensity the concentration of the catalyst can also be higher. If the concentration is too high the efficiency of the system is reduced, if the concentration is to low some photons can pass through the tube without being caught. Very thin tubes can be completely illuminated but cause a very strong pressure drop in the circulation. On the contrary tubes with a large diameter imply a big dark volume which also sets down the efficiency of the system [Malato S. et al., 2000; Pacheco K., Watt A. S., Turchi C. S., 1993].

4.2 Treatment of wastewater with photo-Fenton

4.2.1 AOPs

The wastewater coming from usual sources like private households can be treated in ordinary two phases wastewater treatment plants. The physical (mechanical) part combined with the activated sludge biological treatment, which is named the “best available technology” (BAT) by the EU, is sufficient to treat all biodegradable wastewater. To cope with the large and still growing number of anthropogenic pollutants which are non-biodegradable exist different technologies of treatment [Gernjak W., Krutzler T. et al., 2003; Chiron S., Fernandez-Alba A. R. et al., 2000]. Technologies like phase-transfer, air stripping, adsorption or extraction which are already established have the severe disadvantage of not destroying the contaminant. For organic pollutants in general but especially for toxic pesticides the Advanced Oxidation Processes (AOPs) seem to be a promising technology regarding to the potential of mineralizing most of the contaminants [Hincapié M., Maldonado M. I. et al., 2005]. In comparison to conventional oxidation technologies which also chemically attack the pollutant and alter the chemical structure of the specific molecule, the AOPs provide hydroxyl radicals with very high oxidation potential. The oxidation potential of hydroxyl radicals is the second highest, 2.8 V vs. NHE compared to oxidants like ozone (Eo = 2.07 V), hydrogen peroxide (Eo = 1.78 V) and chlorine dioxide (Eo = 1.57 V). [Blanco J., Malato S. et al., 2008]. As the oxidation potential of the hydroxyl radicals is high and the oxidation is unselective they are able to oxidize and finally mineralize nearly all organic compounds yielding CO_2 and inorganic ions in the end which again means a remedy of the pollution problem. Hence it is likely that the AOPs will become the most widely applied water treatment technology for organic pollutants not treatable by conventional techniques regarding to their high chemical stability and non-biodegradability due to toxicity [Hincapié M., Maldonado M. I. et al., 2005]. There are various techniques to generate hydroxyl radicals:

- Direct photolysis of oxidants [H_2O_2, O_3) or water with high energy UV radiation [Legrini O., Oliveros E. et al., 1993; Gogate P. R., Pandit A. B., 2004]
- Heterogeneous photocatalysis illuminating a semiconductor [Legrini O., Oliveros E. et al., 1993, Gogate P. R., Pandit A. B., 2004]
- Fenton and Fenton-like processes with transition metals [Gogate P. R., Pandit A. B., 2004; Safarzadeh-Amiri A., Bolton J. R. et al., 1996]
- Cavitation techniques (hydrodynamic and ultrasound) [Gogate P. R., Pandit A. B., 2004; Safarzadeh-Amiri A., Bolton J. R. et al., 1996]

Most reactions involving hydroxyl radicals in aqueous solution have rate constants in the order of 10^6 to 10^9 [Haag W. R., Yao C. D., 1992; Buxton G. U., Greenstock C. L. et al., 1988]. The Fenton and photo-assisted Fenton systems in comparison to other AOPs turn up to be favorable [Pignatello J., Oliveros E. et al., 2006]. The Fenton reaction was first reported by Henry J. Fenton in the year 1894, when he reported that H_2O_2

could be activated by Fe(II) salts to oxidize tartaric acid [Fenton 1894]. There have been some publications in the last century followed by a wave of research and publications starting from the 1990s [www.scopus.com, January 2009]. The homogeneous catalysis by the photo-Fenton reaction has several advantages compared to bulk reactions [Gernjak W., Malato S. et al., 2006]. The hydrogen peroxide is inexpensive, easy to handle, safe and since it is decomposed to water and oxygen it is no threat to the environment. The second compound used in the photo-Fenton reaction is iron, which neither is expensive nor hazardous to the environment due to the ubiquitous presents in the biosphere. Since the production of UV-radiation with lamps is expensive regarding to the consumption of energy, the application of this technology in photo-reactors using the sun light as a driving force seems to be the most promising alternative [Oller I., Fernandez-Ibánez P. et al., 2006; Pulgarin C., Intervernizzi M. et al., 1999; Pignatello J., Oliveros E. et al., 2006]. The production of hydroxyl radicals in the heterogeneous catalysis by the UV/TO_2process is not discussed in this work.

4.2.2 Characteristics of iron in aqueous solution

Iron is not only a vital element for plants and animals, it also plays a central role in the nutrition of aerobic biological decomposition processes [Henze M., Harremöes P. et al., 2000]. It is omnipresent in the nature as the fourth most abundant element in the earth crust. Naturally it occurs in oxidation numbers from –II to +VI with coordination numbers from 3 to 8 [Hawker P. N., Twigg M. V., 1994] while in aqueous solutions the oxidation number +II (ferrous iron) or +III (ferric iron) are the most stable species. As the rest of the iron species are very unstable they are not of importance for the behavior of iron in water and are not dealt with in the following. The dissolved ferric and ferrous iron is complexed by up to six ligands building up octahedral complexes. In absence of other complexing substances the ligands in water are hydroxyl ions and water molecules. The acid/base equilibrium is directly dependent to the pH of the solution which again affects the ratio of hydroxyl ions to water molecules in the aquo complex.

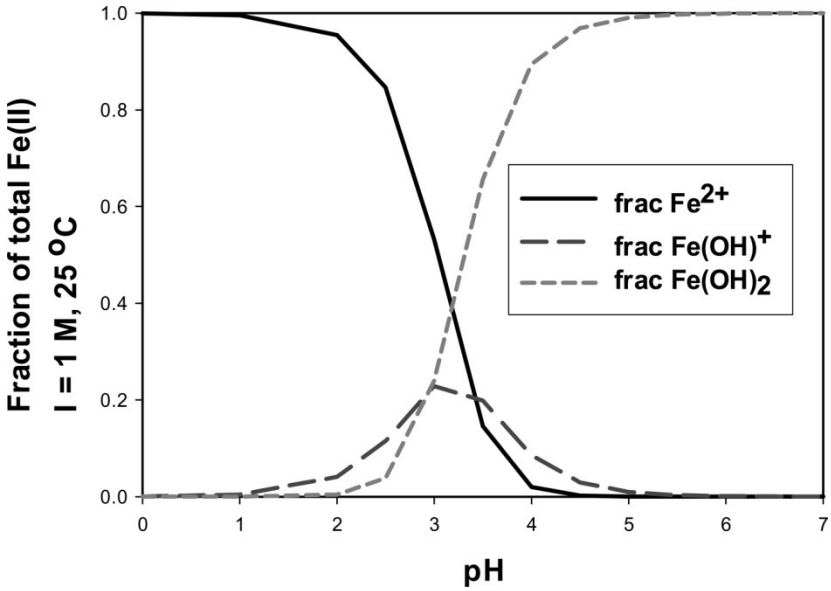


Figure 2 Speciation of Fe (II) in water as a function of pH at 1 *M* ionic strength [Pignatello J., Oliveros E. et al., 2006]

Since the pH of photo-Fenton systems is around 2.8 ferric iron plays the more critic role due to the low solubility of ferric iron hydroxide ($K_s(Fe(OH)_3) = 10^{-37}$) among a pH of 2.5 to 3.5. The solubility also depends of the temperature and the concentration. The first step of the precipitation process is the forming of dimmers and oligomeres. As the polymerization goes on the compound grows while losing water until the insoluble iron hydroxide (e.g. goethite or hematite) precipitates. The precipitation is strongly temperature dependent, the higher the temperature the faster the precipitation [Krýsová H. et al., 2003]. The resulting amorphous ferric oxyhydroxides still contain a lot of water, have a red-brown color and absorb over the whole UV/Vis spectral range. Owing to the strong cationic character of the ferric compounds, co-precipitation with other ions and organic substances can take place and therefore iron is used as a coagulant in other processes. While the majority of iron below a pH of 3 will be existent as ferrous iron (see figure 2), which is soluble up to a neutral pH there could be some loss of ferrous iron as it precipitates together with ferric iron-oxyhydroxides [Pignatello J., Oliveros E. et al., 2006]. There are two ways to re-dissolve the very stable precipitated iron. At a pH of 1-1.5 it can be re-dissolved with other complexing substances like oxalic acid [Mazellier P., Sulzberger B., 1994] or by the process of photoleaching the ferrous iron can be subsequently leached from the precipitate as ferric iron ions get reduced.

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+ \quad (4.3)$$

$$[Fe(H_2O)_5(OH)]^{2+} \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+} + H^+ \quad (4.4)$$

$$[Fe(H_2O)_4(OH)_2]^{+} \rightleftharpoons [Fe(H_2O)_3(OH)_3] + H^+ \quad (4.5)$$

$$2\,Fe_{aq}^{3+} \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ \quad (4.6)$$

4.2.3 Fenton chemistry

As a general reaction hydrogen peroxide is decomposed to water and oxygen in the presence of iron ions. Reactions between ferrous iron and hydrogen peroxide are called Fenton reactions. The following equations (eq. 4.7-4.13) show the reactions of ferrous iron, ferric iron and H_2O_2 without any interfering ions or substances [H.J.H. Fenton 1894]. The reaction pathway can be a radical chain reaction (Haber-Weiss mechanism) [Haber F., Weiss J., 1934, Barb W. G., Baxendale J. H. et al., 1951, Part I+II] or an ionic mechanism (Kremer-Stein mechanism) [Kremer M. L., Stein G., 1959, 1962 and 1977]. After [Bossmann S. H., Oliveros E. et al., 1998; Pignatello J., Oliveros E. et al., 2006; Gogate P. R., Pandit A. B., 2004] should be mentioned that probably ferrate and ferryl ions (+IV and +V) are included in the reaction at least as intermediate complexes. It was found that a good peroxide-to-iron molar ratio lies in the range of 100 to 1000 [Pignatello J., Oliveros E. et al., 2006], using iron catalytically will minimize the scavenging of $OH^\bullet$ by C and likewise the production of oxyhydroxides (eq. 4.8). The Fenton reaction in absence of light is called “thermal Fenton reaction”, which means that the necessary thermal energy is taken from the surroundings. If the ferrous iron in

the Fenton reaction is substituted by ferric iron it is called “Fenton like” reaction regarding to several authors. On the other side it was posted that there is no difference between “Fenton” and “Fenton like” reaction, because ferric and ferrous ions are present at the same time in the reaction chain and for this reason it is regardless which species is used to start the reaction. This counts especially if there is an excess of peroxide in the initial phase oxidizing all of the Fe^{2+} to Fe^{3+} which makes the system behave independently of the initial state afterwards [Pignatello J., Oliveros E. et al., 2006]. Depending to the Fe/contaminant ratio there can be a burst of hydroxyl radicals in the beginning of the reaction if it is started with Fe^{2+}. Reverse starting with Fe^{3+} can cause a lag phase in the beginning, because the regeneration of ferrous iron is the rate limiting step in the catalytic iron cycle if it is present in small doses (4.10-4.12). The equilibrium constants for the eqation 4.7 – 4.16 had been posted in [Sychev A. Y., Isaak V. G., 1995].

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\bullet \qquad k = 53 - 76\ M^{-1}s^{-1} \qquad (4.7)$$

$$Fe^{2+} + OH^\bullet \longrightarrow Fe^{3+} + OH^- \qquad k = 2.6 - 5.8 * 10^8\ M^{-1}s^{-1} \qquad (4.8)$$

$$Fe^{2+} + HO_2^\bullet \longrightarrow Fe^{3+} + HO_2^- \qquad k = 0.75 - 1.5 * 10^6\ M^{-1}s^{-1} \qquad (4.9)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + OH_2^\bullet + H^+ \qquad k = 1 - 2 * 10^{-2}\ M^{-1}s^{-1} \qquad (4.10)$$

$$Fe^{3+} + HO_2^\bullet \longrightarrow Fe^{2+} + O_2 + H^+ \qquad k = 0.33 - 2.1 * 10^6\ M^{-1}s^{-1} \qquad (4.11)$$

$$Fe^{3+} + O_2^{\bullet -} \longrightarrow Fe^{2+} + O_2 \qquad k = 0.05 - 1.9 * 10^9\ M^{-1}s^{-1} \qquad (4.12)$$

$$OH^\bullet + H_2O_2 \longrightarrow H_2O + HO_2^\bullet \qquad k = 1.7 - 4.5 * 10^7\ M^{-1}s^{-1} \qquad (4.13)$$

$$2OH^\bullet \longrightarrow H_2O_2 \qquad k = 5 - 8 * 10^9\ M^{-1}s^{-1} \qquad (4.14)$$

$$2HO_2^\bullet \longrightarrow H_2O_2 + O_2 \qquad k = 0.8 - 2.2 * 10^6\ M^{-1}s^{-1} \qquad (4.15)$$

$$HO_2^\bullet + OH^\bullet \longrightarrow H_2O + O_2 \qquad k = 1.4 * 10^{10}\ M^{-1}s^{-1} \qquad (4.16)$$

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \qquad K = 2.63 * 10^{-12}M \qquad (4.17)$$

$$[Fe]^{3+} + H_2O_2 \rightleftharpoons [Fe(HO_2)]^{2+} + H^+ \qquad K = 3.1 * 10^{-3}M \qquad (4.18)$$

$$[Fe(OH)]^{2+} + H_2O_2 \rightleftharpoons [Fe(OH)(HO_2)]^+ + H^+ \qquad K = 2 * 10^{-4}M \qquad (4.19)$$

$$HO_2^\bullet \rightleftharpoons O_2^{\bullet -} + H^+ \qquad K = 3.55 * 10^{-5}M \qquad (4.20)$$

$$OH^\bullet \rightleftharpoons O^{\bullet -} + H^+ \qquad K = 1.02 * 10^{-12}M \qquad (4.21)$$

$$HO_2^\bullet + H^+ \rightleftharpoons H_2O_2^{\bullet +} \qquad K = 3.16 - 3.98 * 10^{-12}M \qquad (4.22)$$

4.2.4 Fenton reactions in presence of organic compounds

There are many different ways for organic compounds to react with the hydroxyl radicals generated in the $Fe^{2+}/Fe^{3+}/H_2O_2$ reaction system. Since the reaction of hydroxyl radicals with organic compounds is highly unselective nearly all of them get oxidized through an electrophilic attack which follows a rate constant close to the diffusion-controlled limit [Haag W. R., Yao C. D., 1992; Buxton G. U., Greenstock C. L. et al., 1988; Pignatello J., Oliveros E. et al., 2006]. The electrophilic character is proven by the reduced rate of H-abstraction when an electron-withdrawing carbonyl group is located in the alpha position (e.g. $k_{HO} = 1 * 10^8 M^{-1}s^{-1}$ for acetone and versus $k_{HO} = 1.4 * 10^9 M^{-1}s^{-1}$ for ethane) which does not occur in the case of methyl [Pignatello J., Oliveros E. et al., 2006]. There several factors besides the electrophilic character influencing the reactions, the strength of the C-H bond, stability of the nascent organoradical, statistical factors (the number of equivalent H atoms or the position of attack) and steric effects. Some of these are influencing each other, for example the strength of the C-H bond is strongly affected by the electronegativity of substituents. The order for reactivity for alkane functional groups is *tertiary > secondary > primary* which is congruent with the order of electron density on C, but the contrary order in C-H bond strength. The following reactions can be reported [Legrini O., Oliveros E. et al., 1993; Haag W. R., Yao C. D., 1992]:

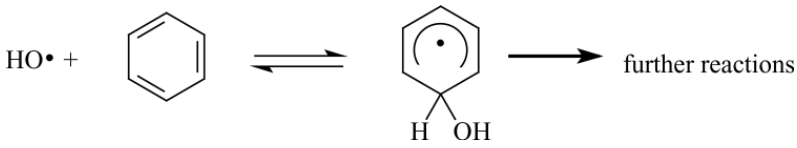
- Abstraction of hydrogen from aliphatic carbon atoms
- Electrophilic addition to double bonds or aromatic rings
- Electron transfer reactions

In these reactions organic radicals, eventually prolonging the chain reaction, can be produced. The oxidation-reduction potential of the resulting organic radical determines the reactions with ferrous and ferric iron ions. As long as the reactor system is open to the atmosphere and a turbulent flow is prevailing there is air and therefore oxygen in the solution. The oxygen can react with the organic radicals like in reaction $(4.23, 4.24)$ [Pignatello J., Oliveros E. et al., 2006].

$$R^{\bullet} + O_2 \longrightarrow R(-H^+) + HO_2^{\bullet} \quad (4.23)$$

$$R^{\bullet} + O_2 \longrightarrow R - OO^{\bullet} \longrightarrow R - O^{\bullet} \quad (4.24)$$

The reactions $(4.23, 4.24)$ are bimolecular and with a rate constant in the order of $10^9\ M^{-1}s^{-1}$ very fast. If the contaminants contain aromatic structures they get hydroxylated and build up a hydroycyclohexadienyl radical as a result from the $OH^{\bullet}$ attack on the aromatic ring.



(4.25)

Quinine and hydroquinone as well are typical intermediate degradation products which are very important due to their ability to fasten the pathway for ferrous iron regeneration through reactions which likewise accelerates the photo-Fenton process. As the catalytic cycle competes with the ring breaking reaction the reduction of ferrous iron by this process stops at the point when the ring breaks open and the mineralisation process carries on [Chen R., Pignatello J. J., 1997]. The mineralisation process often ends with the formation of carboxylic and dicarboxylic acids which form stable complexes with iron inhibiting the further degradation shown in the reaction (4.26) [Kavitha V., Palanivelu K., 2004]. In this thesis the effect of the presence of inorganic ions will not be discussed in detail, because the experiments were carried out with a strongly limited influence of those.

$$Fe^{3+} + n\,L \longrightarrow [FeL_n]^{X+} \xrightarrow{H_2O_2,dark} no\ further\ reactions \qquad (4.26)$$

L: Mono- Dicarboxylic acids

4.2.5 Photochemical reactions

The part of the AOPs which uses the power of solar photons to generate oxidant radicals is called “Photocatalytic Oxidation Processes” (PCOs). Using the energy of the sun makes the degradation of contaminants more environmental friendly like for example in solar detoxification. This is the main advantage of PCOs over the AOPs. [Blanco J., Malato S. et al., 2008]. A broad part of irradiation up to 580 nm is usable for the photo reduction of dissolved ferric iron to ferrous iron [Brauer R., Waldner G. et al., 1999]. The wavelength of the absorbed radiation depends to the ligand of the complex as well as the specific quantum yields and the following reactions (4.27). Generally the first step of the reaction is the ligand to metal charge transfer (LMCT) [Zepp R. G., Faust B. C., Hoigne J., 1992; Gernjak W., Malato S. et al., 2006] causing intermediate complexes to dissociate (4.27) [Sai Wei Lam, Ken Chiang et al., 2005]. As the ligand can be any Lewis base which is able to form a complex with ferric iron (H_2O, HO_2, Cl^-, R^-, COO^-, etc.) the result of the reaction can be a hydroxyl radical or another radical derivated from the ligand (4.28, 4.29) [Gernjak W., Malato S. et al., 2006]. It is also possible that the ligand is directly oxidized to carbon dioxide and an organic radical (4.30) [Gernjak W., Malato S. et al., 2006]. The capturing of high energetic photons mainly depends to the amount of iron complexes in the solution, while the most photoactive complex is the *[Fe(OH)$^{2+}$]*-complex. As discussed earlier the presence and stability of the iron species in aqueous solution is strongly dependent to the pH therefore the pH of 2.8 was postulated [Safarzadeh-Amiri A., Bolton J. R., et al., 1996; Pignatello J., Oliveros E. et al., 2006,] as the optimum for photo-Fenton reactions. Around this pH the above

named iron complex is mostly prevalent and the iron still does not precipitate. In this study all experiments were carried out at the pH of 2.8. A special effect caused by ferric iron-carboxylate complexes seems to play an important role in the photo-Fenton chemistry. On the one hand these complexes exist in relatively high concentrations due to the fact that carboxylic acids are common intermediates in the degradation of pesticides. On the other hand, compared to the ferric iron-water complexes, they have significantly higher quantum yields. The effect of this behavior can be noticed in the progress of a degradation of pesticides, since there are no carboxylic acids in the initial phase the progress is slower than in the subsequent phase which is accelerated by these higher quantum yields causing a higher regeneration rate of ferrous iron from ferric iron [Gernjak W., Malato S. et al., 2006]. An approach to overcome the initial lag phase is the addition of oxalate which in return raises the costs of the whole process because the oxalate is getting used in the degradation process as well [Braun A. M., Maurette M.-T., Oliveros E., 1991; Hatchard C. G., Parker C. A., 1956]

$$[Fe^{3+}L] + hv \longrightarrow [Fe^{3+}L]^* \longrightarrow Fe^{2+} + L^* \quad (4.27)$$

$$[Fe(H_2O)]^{3+} + hv \longrightarrow Fe^{2+} + OH^{\bullet} + \mathrm{H}^+ \quad (4.28)$$

$$[Fe(OH)]^{2+} + hv \longrightarrow Fe^{2+} + OH^{\bullet} \quad (4.29)$$

$$[Fe(OOC-R)]^{2+} + hv \longrightarrow Fe^{2+} + CO_2 + R^{\bullet} \quad (4.30)$$

5 Experimental

5.1 Pollutants and reagents applied in the experiments

Technical information about the Pollutants:

In the experiments carried out in relation to this work a mixture of five commonly used commercial pesticides have been degraded. Commercial formulations of Vydate® (10% w/v oxamyl, $C_7H_{13}N_3O_3S$), Metomur®, (20% w/v methomyl, $C_5H_{10}N_2O_2S$), Couraze® (20% w/v imidacloprid, $C_{16}H_{22}ClN_3O$), Ditimur-40® (40% w/v dimethoate, $C_5H_{12}NO_3PS_2$) and Scala® (40% w/v pyrimethanil, $C_{12}H_{13}N_3$) are used as received. Figure 2 shows the pesticide chemical structures of the active ingredients contained in the pesticides. Analytical standards (>98 %) for chromatographic analyses are purchased from Sigma-Aldrich.

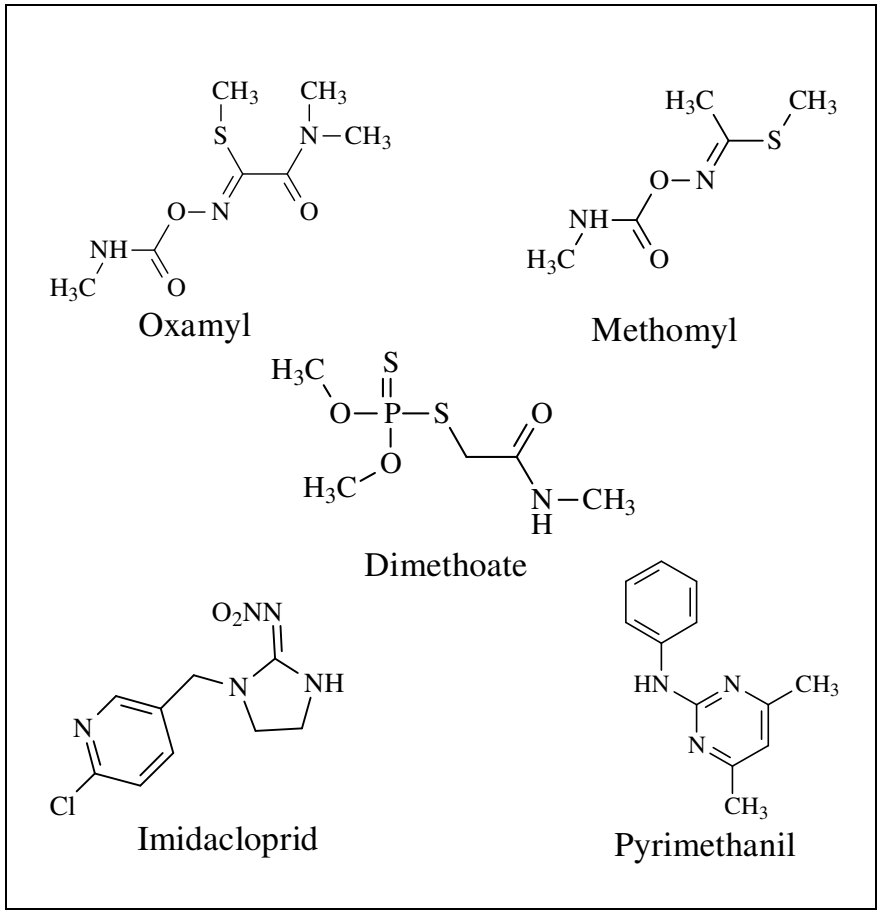


Figure 3 Chemical structure of the pesticides

Toxicity and environmental behavior of the pollutants:

The toxicity and the environmental behavior of the five pesticides used in this study depends mainly to the chemical properties of each compound, but also the method of use and the characteristics of the environment (soil, drainage, vegetation, etc.). All five compounds are at least moderately toxic to mammals and humans like Imidacloprid and Dimethoate, while Methomyl and Oxamyl are proven to be highly toxic. Methomyl can cause weakness, blurred vision, headache, muscle tremors or even death from discontinued breathing only to mention some of the symptoms [Baron R. L., 1991]. Oxamyl can cause similar symptoms, but the lethal dose (LD 50) of 5.4mg/kg (oral) in rats is even lower than the one of Methomyl. The ARfD- and ADI-value for Oxamyl is 0.001 mg/kg body weight and there with one of the most toxic pesticides in use (WHO). The persistence of both compounds in soil is limited to 14 to 20 days depending to the pH and the activity of microorganisms. In water the breakdown is faster, the half-life lies between 2 and 6 days. Since Imidacloprid has a LD 50 of 450mg/kg (oral) in rats it is less toxic to humans and mammals but then has a significantly higher half-life in soils (48-190 days) and water (greater than 31 days) [Wauchope R. D., Buttler T. M, Hornsby A. G., 1992]. All contaminants are more stable in neutral or even acidic environments. Solved in water and under the condition of fast infiltration and rapid trickling through the underground the pesticides can reach the groundwater. Especially Methomyl is highly soluble and has a low affinity for soil binding and therefore represents an extra threat to groundwater [Howard, P.H., 1991]. After reaching the groundwater the contaminants can be more persistent than in contact with the atmosphere and due to that a hazard to the quality of the local drinking water. As Imidacloprid was found frequently in comestibles and water bodies it was rated to be particular hazardous due the high factor of exposure [Krautter M., N.L., 2008]. Apart from the severe effects to humans and mammals the effects caused by these compounds to other parts of the biosphere can be even worse. If transported and dispensed outside the greenhouses the pesticides can influence further animals, insects, microorganisms or plants causing uncontrolled damage to any of these parts of the environment. For example Imidacloprid and Oxamyl are highly toxic to bees, which are an indicator for toxicity to insects in general [Kidd H., James D. R., 1991], especially during the flowering phase. Assimilated by insects the pesticides enter the food chain and can be a serious threat to birds and other animals [U.S. Environmental Protection Agency (Oxamyl, Methomyl), 1987].

Table 1 Chemical and physical information about the pesticides Source: [Kidd H., James D. R., 1991]

Property	Pyrimethanil	Imidacloprid	Oxamyl	Dimethoate	Methomyl
Activity	fungicides	insecticide	insecticide, nematicide, acarecide	insecticide, nematicide, acarecide	insecticide
CAS-Nr.	53112-28-0	13826-41-3	23135-22-0	60-51-5	16752-77-5
Formula	$C_{12}H_{13}N_3$	$C_9H_{10}ClN_5O_2$	$C_7H_{13}N_3O_3S$	$C_5H_{12}NO_3PS_2$	$C_6H_{12}N_2O_3S$
Molec. Mass ($g\ mol^{-1}$)	199.11	255.7	219.36	229.28	162.21
Solubility in water (20°C) mg l^{-1}	121	510	$280*10^3$(25° C)	25 (21°C)	57.9 (25°C)
Melting Point (°C)	96.3	143.8	100-102	43-45	79

Reagents applied in the experiments and analysis:

The distilled water which was used in the pilot plant and for all other experiments carried out in conjunction with this study was supplied by the Plataforma Solar de Almeria (PSA) distillation plant (conductivity<10 µS/cm, Cl^- = 0.2-0.3 mg/L, NO_3^-<0.2 mg/L, organic carbon <0.5 mg/L). The photo-Fenton experiments were performed using iron sulphate ($FeSO_4$ * $7H_2O$), reagent-grade hydrogen peroxide (30% w/v) and sulphuric acid (96% w/w, p.A.) and NaOH (p.A.) for pH adjustment (around 2.7-2.9, all purchased from Panreac. Ultrapure water was received from Millipore Milli-Q® system. Milli-Q® water was applied for preparation of all standards and for eluent preparation and sample dilution in chromatography. Analytical standards for chromatography analyses (solids) were purchased from Sigma-Aldrich: Oxamyl (99.6 % purity, $C_7H_{13}N_3O_3S$); Methomyl (99.9% purity, $C_5H_{10}N_2O_2S$); Imidacloprid (99.9 % purity, $C_{16}H_{22}ClN_3O$); Dimethoate (99.4 % purity, $C_5H_{12}NO_3PS_2$) and Pyrimethanil (99.9 % purity, $C_{12}H_{13}N_3$). The analytical standard used as a reference in the HPLC measurements was a mixture of the five pesticides (20 mg/L each). This mixture was prepared diluting a mother solution of 1000 mg/L of each pesticide in acetonitrile.

5.2 Analysis

5.2.1 UV radiation measurement

The most appropriate way to measure the UV radiation which is the driving force for the experiments in this study, is a broadband radiometer tilted 37° (local latitude) towards the equator in the same way like the CPCs of the solar pilot plant. As described before the CPCs are able to utilize global radiation, hence the radiometer should measure global radiation from an adequate position. The measurement of the global radiation suits better for the characterization of the power input of the collectors than measurement of direct radiation. The radiometer used to collect the radiometric data was a Kipp & Zonen CUV 3 broadband UV radiometer with a sensitivity spectrum from 285 to 400nm. To simplify the comparison of results between different studies about photo-Fenton and related disciplines the same spectral range for measurement has been chosen. A further advantage is the self-adjusting of the radiometers in their spectral range [Kipp & Zonen CUV3] which lies within the optimal spectral range for the photo-Fenton process [Bauer R., Waldner G. et al., 1999]. The radiometer is a combination of a diffuser, a filter and a photodiode. The diffuser ensures that radiation can be incident from an optimal angle and so determines a correct angular response. To make sure that the response at 90° is zero a shadow of a rim shades off the diffuser side. The filter determines the spectral response of the system to ensure that only deliberated radiation is measured. As the photodiode generates a voltage output linearly proportional to the number of incident photons, these values have to be converted including the own attenuation factor of each wavelength caused by the filter. Furthermore the system has to be calibrated using a tungsten-halogen lamp by ISO 9847 Appendix C [Kipp & Zonen CUV3] as a artificial radiation source for the calculation of the final value of global UV intensity in the spectrum between 285-400nm including the properties of the filter. Due to the fact that all photons reaching the photodiode count as one photon without considering their actual energy regarding to their wavelength distribution this calibration is obligatory.

To compare the different daytimes, days and various photocatalytic experiments it is necessary to process the measured UV-radiation of the relevant time spans with equation 5.1.

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30}\frac{V_i}{V_t} \; ; \qquad \Delta t_n = t_n - t_{n-1} \; ; \qquad t_0 = 0 \; (n = 1) \qquad (5.1)$$

Where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation (λ<400 nm) measured between t_{n-1} and t_n and t_{30W} is the “normalized illumination time”. In all experiments time refers to a constant solar UV power of 30W m^{-2} which is nearly equivalent to the UV power of a perfectly sunny day.

5.2.2 DOC

Description of the equipment and measurement theory:

To control the general degree of mineralization of the pesticides during the photo-Fenton process the DOC was measured. An analyzer, model Shimadzu TOC-5050A equipped with a Shimadzu ASI-5000A auto sampler was used. To calculate the Total Organic Carbon (TOC) as a difference between the Total Carbon (TC) and Total Inorganic Carbon (TIC) the TC and TIC were measured by the analyzer. TC measurement is based on combustion of the aqueous sample on a platinum catalyst supported on aluminium oxide spheres thereby converting all carbon into CO_2. The combustion chamber has a temperature of 680°C. After the combustion the combustion off-gas is transported by a CO_2 free carrier gas (air flow of 150 ml min^{-1}) to a common dispersive infrared detector for the analysis of CO_2 in gaseous samples. In relation to the concentration of the CO_2 the detector generates an analogue signal, whose shape depicted against time is a peak similar to a Gaussian normal distribution. Further this signal is converted by a standard D/A converter and the area of the peak is evaluated by the equipment software. For the measurement of TIC the sample is fed into 25% w/v phosphoric acid. Due to the reaction with the acid carbonate and bicarbonate are set free as CO_2 which again is stripped from the reactor by CO_2 free air (150 ml min^{-1}) as a carrier gas. The same detector and signal processing devices are used as for the TC measurement.

To quantify the concentration of carbon in the samples a linear relationship between the peak area and concentration of TC as well as TIC exists. This relation is quantified by calibration with standard solutions prepared in ultrapure water (Milli-Q® system). For the TC measurement calibration potassium hydrogen phthalate (Panreac ACS-ISO) is used as a standard solution, containing sulphuric acid in addition to avoid contamination by dissolution of atmospheric CO_2. Four linear regression curves were established for the concentration ranges 1–10, 10–50, 50–250 and 250–1000 mg L^{-1}. The TIC measurement standards contain one half of the carbon in the form of sodium carbonate and the other half in the form of sodium hydrogen carbonate (both analytical grade from Nacalai Tesque). Analogue, four linear regression curves were used for the concentration ranges 0.5–2.5, 2.5–15, 15–75 and 75–250 mg L^{-1}. The wide dynamic range of the carbon contents makes two separate control mechanisms necessary for adequate measurement. The first mechanism is the variation of the sample volume in a range from 4 to 250 µL depending to the installed syringe and injected by a precision injection system. The second mechanism is the attenuation of the electronic signal by a factor up to 30. The standard deviation of the equipment is around 1% of the measured value. The standard deviation of the equipment is around 1% of the measured value. Furthermore, the analyser has automatic statistical quality control based on standard deviation limits set prior to the analysis by the operator for measurements with multiple sample injections. If the criteria are not met, automatic sample re-injection is performed.

Procedure:

Prior to injection into the system all solids have to be removed due to the narrow capillary tubes of the equipment. This limits the measurement to Dissolved Organic Carbon (DOC). The filtering step was applied by using 0.22 µm pore size PTFE syringe-driven filters (Millipore Millex® GN). No further preparations of the sample were carried out before the sample was injected and analyzed by the Shimadzu TOC-5050A analyser as described above. In general all measurements were based on two injections with a maximum coefficient of variance of less than 2% (otherwise the measurement was repeated). Only some measurements during the photo-Fenton process were carried out injecting only one time per sample in order to receive faster results for adequate adjusting of process parameters. With regards to the presents of Fenton´s reagent (hydrogen peroxide and dissolved iron) the samples are not stable over a long time and have to be measured as soon as possible.

Quality control:

Standard solutions are injected regularly to check the correct operation of the equipment. To verify the conditions of the degradation experiment as well as the functionality of the equipment the DOC of the initial sample has to be congruent with the theoretical value. Finally, if samples are as well measured as in the HPLC-UV the concentrations of the first sample have to be in agreement to the DOC.

5.2.3 High Performance Liquid Chromatograpy

Measurement principle

To control the degradation of the pesticides during the photo-Fenton process it is indispensable to use the High Performance Liquid Chromatography (HPLC). The central compounds (Oxamyl, Methomyl, Imidacloprid, Dimethoate and Pyrimethanil) can be detected with a UV-detector as they absorb light with a wavelength greater than 200nm.

The used chromatographic system consisted of a chromatograph of the Agilent 1100 series including a vacuum solvent degassing system, a quaternary solvent pump, an auto sampler, thermostatic column oven and a UV/Vis diode array detection system. For the separation of the compounds a C18 reversed phase column (LUNA® 5 micron, 3*150mm from Phenomenex) protected by guard-column (Phenomenex Security Guard®) was used. The Agilent ChemStation software installed on a PC was the interface to control the whole system and evaluate the data. In the HPLC a mobile phase is pumped through the system under laminar conditions, to make vertical mixing negligible. Depending to the mobile phase viscosity and column properties and due to the small pore size of the chromatographic column the pressure drop along the column of 50-200 bars is high. The equilibrium solution in stationary and mobile phase dependent on the analyte properties constitutes the separation principle of the method. A function of the affinity of the organic compounds to the stationary phase defines the terms of

dissolving into the stationary and re-dissolving in the mobile phase. Hydrophobic substances are retained stronger in reversed-phase chromatography than hydrophilic substances, i.e. they move slower through the chromatographic column and hence are detected later. The ultrapure mobile phase is usually a mixture of an organic solvent (normally acetonitrile (ACN) or methanol) and water. A rise of the percentage of the organic solvent in the mobile phase causes the analytes to become more dissolved and therefore migrate faster through the chromatographic system. It is crucial that the contaminants are uncharged in the chromatographic system to provide a good separation and thus good results by the detection. Consequently, in the case of weak acids or bases, the pH of the mobile phase is adjusted accordingly (e.g. acidic to detect weak acids). There are two different elution methods which can be used regarding to the separation problem. One is the isocratic elution defined through constant mobile phase properties during the analysis which is less complex and therefore suitable for simple separation problems. The other one is the gradient elution including a change of the composition of the mobile phase along the analysis. The last one is applied for more complex problems like the separation of several contaminants simultaneously. Later in the circuit the UV/Vis detector measures the change of absorption in the flow-through cell, caused by the absorptive properties and concentrations of the contaminants generating a signal. The analogue signal is digitized and recorded against time by the software generating peaks with Gaussian form. The calibration with standard solutions of the analyte gives the linear relationship for the quantification between the peak area and the concentration of the compound in the sample.

Procedure:

To prepare the sample for the injection into the HPLC the sample has to be homogenized and diluted with ultrapure water if necessary. Further it has to be complemented with the specific organic solvent receiving the same proportion between the sample and solvent similar to the percentage in the mobile phase at the time of injection. To ensure an accurate dilution factor the procedure is carried out in a graduated flask. Previously all suspended solids have to be removed by filtering the sample through a 0.22µm pore size PTFE syringe-driven filter (Millipore Millex® GN) to protect the whole chromatography system. By now the sample can be injected in the HPLC-UV system. In this case, the preparation of the sample was performed mixing 80 % of the aqueous sample and 20 % of acetonitrile. There are several aspects which have importance as a background of the sample preparation procedure. The adding of the organic solvent to the sample before being filtered avoids the adsorption of the contaminants on the filter disk and also dissolves most likely any organic compound present as a solid. Furthermore, due to this manner of preparation the sample matrix is similar to the mobile phase which optimizes the performance of the chromatography and also avoids so-called peak fronting. Lastly the addition of comparably large amounts of organic solvents any further reaction of the contaminants with the Fenton´s reagent is quenched.

Hence the samples can be considered as stable after the preparation process is finished.

As indicated, the appropriate elution and detection conditions depend on the analytes characteristics. Table 2 shows the corresponding conditions for the model substances applied in this work. The flow of the mobile phase was 0.5mL min^{-1} in all elution programmes. Detection limits depend on the analytes properties but are usually below 100 µg L^{-1}.

Table 2 HPLC configuration for the five pesticides

Compound	Mobile phase (percentages)	Wavelength (nm)
Oxamyl		234
Methomyl		234
Imidacloprid	H_2O/ACN (85/15): 0-7 min	270
Dimethoate	H_2O/ACN (85/15 – 20/80): 7-12 min	210
Pyrimethanil	H_2O/ACN (20/80): 12-18 min	210

Quality control parameters:

A daily control of the system by injecting standard solution is necessary. In addition to that before each measurement a standard containing the five different contaminants is measured to control the chromatography parameters like retention time and the resulting peak area. The overall concentration of the compounds in the samples measured by the HPLC-UV should contribute to the detected concentration of DOC. This is to check that all analytes are dissolved and no adsorption on the filter disk has taken place.

5.2.4 Dissolved iron concentration

Measurement principle:

Ferrous (Fe^{2+}) iron forms colored chelate complexes with three 1,10-phenantroline molecules. The colour of this complex is red-orange and the concentration can be measured by the absorbance of radiation with a wavelength of 510 nm. This absorbance follows the Beer´s law and is proportional to the concentration of ferrous iron. From a pH around 3 to 9 the absorbance of these complexes is stable. To ensure that the

complexes are formed rapidly a pH between 3 and 3.5 is advantageous. Oxidizing reagents like hydrogen peroxide have an influence on the results as they oxidize ferrous iron to ferric iron. For the purposes of the measurements carried out in this work the amount of total dissolved iron was relevant so this interference could be excluded. Nevertheless other types of interference can occur. The 1,10-phenantroline eventually forms complexes with other complexing agents like cyanides, nitrites and polyphosphonates. Further interference can occur through reaction with heavy metals (Cr^{3+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}) which also tend to form complexes with the phenantroline. Other heavy metals induce precipitation of the phenantroline (Ag^{2+},Bi^{3+}, Hg^{2+}, Cd^{2+}, MoO_4^{2-}). As there are no heavy metals prevalent in the photo-Fenton experiments in this study, the interference due to the color of the sample is most common as well as the interference with peroxide. If total iron is to be measured ferric iron can be reduced to ferrous iron with ascorbic acid and likewise all other oxidants in the solution. In this way the whole dissolved iron can be measured. As a consequence the amount of ferric iron can be calculated from the difference between total iron and the concentration of ferrous iron.

Reagents:

- Solution: 1g/L 1,10-phenantroline (0.1% w/v in distilled water)
  62.5 g ammonium acetate + 175 mL acetic acid filled up to 250 mL (acetate/acetic buffer solution)
- Ascorbic acid, solid

Procedure:

For total dissolved iron measurement 4ml of the sample has to be filtered through a 0.22µm pore size PTFE syringe-driven filter (Millipore Millex® GN) and mixed with 1ml of the phenantroline solution, 1ml of the buffer solution and two spatula tips of ascorbic acid. The assay is homogenized and the suspended ascorbic acid is left to settle. If the concentration of dissolved iron is too high for precise spectrophotometric measurement the sample has to be diluted before mixing with the other compounds. The normal dilution steps were 1:2 or 1:4. It is important that the dilution factor is considered in the calculation of the concentration afterwards. After the reagents were homogenized a fix time between 1 to 5 minutes should pass for the reaction. This time span should be the same for all samples before they are measured in the spectrometer (Unicam-II spectrophotometer). To cancel the effect of the colour the samples have to be measured against a blank sample (1,10-phenantroline solution substituted by distilled water). The formula for the calculation of the real concentration is given in equation 5.2.

$$C_{Fe^{2+}}\ \left(\frac{mg}{L}\right) = (7.15 * Absorbance - 0.036) *\ factor\ of\ dilution \qquad (5.2)$$

Quality control:

A ferrous iron standard solution is measured to control the proper state of the spectrophotometer. At the beginning of the experiment the first sample after iron addition is very important to control the initial conditions of the experiment and the calculations for the theoretical iron value. The measured concentration and the theoretical iron value should correspond. This control has to be carried out before the degradation process is initiated. To obtain reliable results of the iron concentration it must be ensured that all samples have the same reaction time after homogenization.

5.2.5 H_2O_2 concentration

Measurement principle:

The detection and measurement of hydrogen peroxide in photo-Fenton degradation processes is a very important parameter which has to be evaluated. If, for example all peroxide has been used in the degradation process the process slows down significantly or even stops and it will be necessary to add more peroxide to the reaction [Nogueira R.F., Oliveira M.C. & Paterlini W.C., 2005.]. The measurement of the concentration of H_2O_2 with ammonium metavanadate in acidic medium is based on the formation of the peroxovanadium cation (eq. 5.3).

$$VO^{3-} + 4H^+ + H_2O_2 \rightarrow VO_2^{3+} + 3H_2O \qquad (5.3)$$

The reaction of hydrogen peroxide with metavanadate has been published previously [Sandel E. B. (ed), 1959]. The peroxovanadium cation causes a red-orange color of the solution with a maximum absorbance at 450 nm. Due to the fact that the absorbance peak of $H_2O_2 + VO_2^{3+}$ is clearly distinguishable from the absorbance spectrum of separate H_2O_2 or VO_2^{3+} like it is shown in figure 3 the spectrometric analysis of peroxide concentration seems to be advisable.

Especially because comparable methods have certain disadvantages, like the DPD-method (spectrometric analysis using titanium sulfate or oxalate and *N*,*N*diethyl- *p*-phenylenediamine) which uses high cost reagents or the iodometric titration which is subject to errors due to volatilization and hydrolysis of I_2 and air oxidation of I^- and also takes more time than the spectrometric analysis. The method using permanganate is discarded due to the presence of iron in the photo-Fenton degradation. As various ions are set free in the degradation of pesticides the test has to be un-

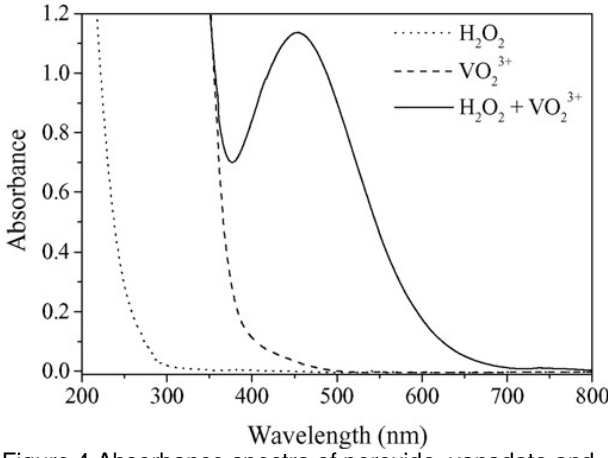


Figure 4 Absorbance spectra of peroxide, vanadate and peroxide in the presence of vanadate solution [Nogueira R.F et al.., 2005]

influenced by those. It was proven by Nogueira et al. (2005) that the spectrometric determination of H_2O_2 is not influenced by following ions, Cl^- (0.2–1.3 mmol L^{-1}), NO^{3-} (0.3–1.0 mmol L^{-1}), Fe^{3+} (0.2–1.2 mmol L^{-1}) and 2,4-dichlorophenol (DCP) (0.2–1.0 mmol L^{-1}). A further advantage of this testing method is the stability of the ready pared samples which are proven to be stable over 180h at room temperature [Nogueira R.F., Oliveira M.C. & Paterlini W.C., 2005.].

Procedure:
To prepare the vanadate solution for the later determination of peroxide sulfuric acid with a concentration of 9mol L^{-1} were added slowly to ammonium metavanadate, NH_4VO_3. This was carried out under continuous stirring and a temperature of 50°C. After complete dissolution the solution was cooled down and diluted to a concentration of 6.2mmol L^{-1} of vanadate. To analyze the peroxide concentration 1.03ml of the prepared solution were given in a 10ml graduated flask. Thereafter the sample was added to the solution and filled up to 10ml with distilled water. The amount of sample was elected after the estimated concentration of hydrogen peroxide in the sample in a range of 1 to 8ml of sample. After that the sample was homogenized and the absorbance was measured in a spectrometer (Unicam-II spectrophotometer). A 10ml flask filled with 1.03ml of the vanadate solution and distilled water was used as a blank to calibrate the absorbance. The real concentration of peroxide in the sample was later calculated using the dilution factor of each sample.

Quality control:
To control the correctness of the measurement the concentration of peroxide in the first sample can be controlled with the theoretically calculated concentration.

5.2.6 Laboratory pH measurement

As mentioned for example in chapter 4.2.2 the pH plays a crucial role for the whole Fenton and photo-Fenton reaction. Hence it is obligatory to control the alteration of the pH during and at the beginning of each experiment.

The pH is defined by the negative common logarithm of the activity of the positively charged hydrogen ions in aqueous solution. During the measurement of all samples the pH was directly corrected by convention to a fixed temperature. In this study this temperature was 25°C. The correction was done automatically using the pH-meter from Crison, model micro pH 2002. This pH-meter works, like the most pH-meters with the potentiometric measurement of the potential generated by a concentration difference on a membrane. For all measurements a standard glass electrode from Crison and as a reference electrode system a conventional Ag/AgCL/Cl was used.

Procedure and quality control:
In the laboratory the measurement was simple as the electrode was submersed in the homogenized sample. After the pH-meter reached the equilibrium the value was noted. Since a correct calibration is essential for precise measurement the pH-meter was cali-

brated using a two point calibration. Two standard buffer solutions (Panreac) were used for the calibration, one at pH 4.01 and the other one at pH 7.00. Calibration was carried out weekly.

5.2.7 IC

Description of the equipment and measurement theory:

Basically the ion chromatography works like a HPLC system, but uses a distinct separation principle. The IC can detect most of the compounds present in ionic form in aqueous solution and especially the counter ions of weak and strong acids and bases. The stationary phase inside the chromatographic column contains synthetic ion exchange resins with charged anchor groups as active sites. Depending on the nature of the ion which is to be retained there are two different types of resins. The cationic ion exchange resins contain negatively charged anchor groups, for example sulphonic or carboxylic acids (strong or weak acid). For anionic ion exchange it works reversely as the positively charged quaternary or primary amines (strong or weak base) occupy the active sites of the resins. This basic difference of the system causes that cations and anions cannot be measured in the same type of IC at the same time. Nevertheless the general set-up is common to both types of IC. Consequently a system for cation measurement can be easily re-equipped to measure anions and vice versa. In the IC the mobile phase usually consists of ions in aqueous solution which competes with the analytes for the active (counter-charged) sites. For anion detection common mobile phases contain hydrogen carbonate/ carbonate, hydroxide or boric acid/ tetraborate and for cation detection sulphuric acid, methanesulphonic acid or hydrochloric acid. As a detection system the electric conductivity detector is most common. It detects the increased electric conductivity of the mobile phase when the analytes pass the detector. Until the seventies of the last century the resolution of the IC systems was very low due to the background signal caused by the mobile phase. The eluent suppression which solved this problem is based on the principle of modern membrane suppression. The eluent is neutralized by hydronium or hydroxyl ions generated by electrolysis and supplied through an ion exchange membrane. Therefore, the background at the detector is greatly reduced and the sensitivity enhanced, so that the detection limits of modern standard IC systems are in the range of several µg L^{-1}. The detector works similar to other chromatographic systems as the signal is recorded and peaks with Gaussian shapes are generated and the area of these peaks is evaluated. Following the Kohlrausch square root law there is no linear response over a wide dynamic range of the electric conductivity detector. Hence three different calibration curves were used in this study (0.1–1, 1–10, 10–50 mg L^{-1}), characterized through partial linear sections. In the case of ammonium these partial calibration curves were second degree polynomial regression curves, because of the dissociation degree at neutral pH (after suppression) of weak acids/ bases is affected by their concentration. The standard deviation of both

systems is around 3%. Data evaluation and operation of both systems at the PSA laboratory were done by PC interface with Chromeleon ® software from Dionex.

The anion IC system at PSA is used to quantify fluoride, chloride, nitrite, nitrate, bromide, sulphate and phosphate with a fast gradient elution programme and acetic acid, formic acid, propionic acid, pyruvic acid, oxalic acid and maleic acid with a slower gradient elution programme. The anion IC system is a Dionex DX-600 system consisting of an autosampler (Dionex AS40 Automated Sampler), quaternary pump (Dionex GP50 Gradient Pump), thermostatic column oven (Dionex LC30 Chromatography Oven) and an electric conductivity detector (Dionex ED50). To guarantee the purity of the mobile phase, it passes an anion trap column (Dionex Ionpac ATC-3) before entering the injection valve. After that the eluent flows through a guard column (Dionex Ionpac AG11-HC 4x50mm), followed by the chromatographic column (Dionex Ionpac AS11-HC 4x250 mm), the suppression module (Dionex ASRS-Ultra II 4 mm) and the electric conductivity cell. Then the flow is directed into a full, closed, pressure-resistant 250 mL bottle, where the eluent is mixed to yield a composition changing only very slowly. From the full vessel at the same time the liquid displaced is supplied to the regeneration port of the suppression module. This tailor-made set-up permits working in “Auto-Suppression Recycle Mode”, while using gradient elution programmes, because it provides the suppression module with a regeneration solution of stable composition. The cation IC system at PSA is used to determine ammonium, sodium, potassium, magnesium and calcium. It is a Dionex DX-120 system consisting of an autosampler (Dionex AS40 Automated Sampler), a quaternary pump, a guard column (Dionex Ionpac CG12A 4x50 mm), the chromatographic column (Dionex Ionpac CS12A 4x250mm), the suppression module (Dionex CSRS-Ultra 4 mm) and the electric conductivity cell. The eluent is fed to the regeneration port of the suppression module after passing the conductivity cell. Thus, the IC system at the PSA is working in the standard configuration for “Auto Suppression Recycle Mode”, which is possible due to the excessive use of isocratic elution.

Procedure:

After homogenizing the samples were filtered through a 0,22 µm pore size PTFE syringe-driven filter (Milipore Millex® GN) into the sample vials provided for the Dionex autosampler. Due to the presence of Fenton´s reagent the samples are not stable and should be measured immediately. The flow rates were 1.5 and 1.3 mL min^{-1} for the anion and the cation IC system, respectively. The eluent conditions are listed in table 3.

Table 3 Configurations of the IC

Equipment	Ions	Mobile phase	Gradient	
			Start (ratio)	End (ratio)
Dionex DX-120	Na^+, NH_4^+, K^+ Mg^{2+}, Ca^{2+}	H_2SO_4, 20 mN	Isocratic	
Dionex DX-600	Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}	H_2O / NaOH 100mM	0 min (80/20) 10 min (65/35)	10 min (80/20) 15 min (65/35)

Quality control:
Standard solutions are injected daily to maintain and control a correct operation of the system. Due the fact that not all of the compounds in the pesticide mixtures are known it is difficult to use the final concentration of the ions as a control parameter.

5.2.8 Toxicity

5.2.8.1 Respirometry

Measurement principle:
The Respirometry is based on the measurement of the respiration rate (Oxygen Uptake Rate, OUR) from the microorganisms of the activated sludge. It is an important point for wastewater treatment to understand the activated sludge as living and breathing process to obtain information which cannot be provided by chemical or physical analysis methods. The BM Respirometry (manufactured by SURCIS, S.L.) analysis can provide information about the actual genuine activated sludge which can be used to optimize the management of a wastewater treatment plant. There are several advantages of the BM Respirometry like simple, fast and user friendly analysis with non-pollutant reagents. It can further be used for the measurement of toxicity and biodegradability. In this study the BM Respirometer was used for the determination of toxicity of the samples from photo-Fenton degradation process. The oxygen consumption was measured and application under the following options is possible:

- Oxygen uptake rate = Respiration rate (Rs, OUR)
- Consumed oxygen (CO) for total or partial sample
- Biodegradable fraction of COD (bCOD)

For the toxicity assay only the OUR and the Rs were applied. The activity of the aerobic biomass is influenced by

- The types of microorganisms

- The real concentration of the vivid cells which are able to respire
- Amount of biodegradable substances
- Presents of toxic or inhibitory substances
- The temperature
- Disposability of sufficient molecular oxygen

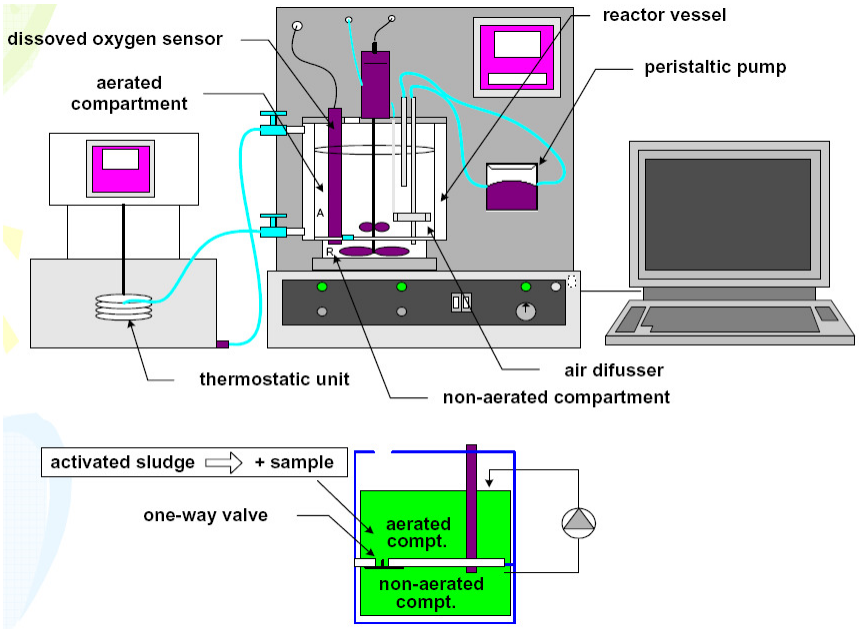


Figure 5 Experimetal set-up of the Respirometer

To measure the toxicity of a sample all other factors were kept constant. The measurements were carried out with the same activated sludge for all assays to ensure a comparable composition of microorganisms as well as a similar concentration of vivid cells. By measuring the DOC it was controlled that only little amounts of biodegradable substances were present (ca. 5 ppm). The temperature was held constant at 20.0 °C. Figure 4 shows the set-up of the Respirometer used for the assays. To obtain the oxygen uptake rate of the microorganisms the upper part of the reactor vessel is aerated continuously providing a high oxygen level to the activated sludge. It was waited until the dissolved oxygen concentration reached a constant level of around 8mg L^{-1}. This level is set as the base line for the assay. In the non-aerated compartment the oxygen sensor gets the actual dissolved oxygen measurement as the result of the microorganism's respiration. This resultant oxygen is then processed with the initial base line. The toxicity assays in this study were carried out using the dynamic mode, measuring the dynamic respiration rate (Rs; mg O_2 L/h). Important parameters of the used activated sludge were a concentration of 2.26 g $L^{-1}$and a share of 50-60% of volatiles (1.2g L^{-1}). To calculate the toxicity of the different samples the Rs of the reference was set to 100% and compared with the Rs-values of the samples, receiving percentages of inhibition or if above 100%, stimulation.

Procedure:

The Respirometer was cleaned and the thermostatic unit was filled with distilled water. Before introducing the activated sludge into the reactor vessel it has been homogenized. The assays were processed using one liter of activated sludge. The circulation of the thermostatic unit, the peristaltic pump, the stirrer and the aeration was started.

Consequently it was waited until the sludge reached the temperature of 20.0°C and a dissolved oxygen concentration a level around 8mg L^{-1}. After the stabilization phase, the reference, 30ml of a solution of distilled water containing 150mg of DOC (acetate), was added to the reactor vessel. The maximum Rs was measured and stored, using the software provided by SURCIS. For the samples from the photo-Fenton degradation reaction the procedure was carried out in the same way, however the reference was substituted by the same volume of the according sample. It is important to note, that for each assay the activated sludge was changed and replaced by new sludge from the stock.

Quality control:
To control the quality of the activated sludge the OUR was measured before the Rs measurement was processed. Only if the state of the sludge was satisfactory the sludge was used for the tests. As the state of the sludge was good the measurement of the reference was repeated and the results were compared. Only with a high conformity the obtained Rs value was used as a reference.

5.2.8.2 Vibrio fischeri

Measurement principle:
One way to control the toxicity of the compounds during the degradation process is the application of tests based on the behavior and mortality of bacteria or other organisms. *Vibrio fischeri* is a gram-negative rod-shaped bacterium found in nearly all marine environments and belongs to the family *Vibrionaceae*. Due to the bioluminescence it is suitable for toxicity tests measuring the intensity of the luminescence of the bacteria under the influence of toxic compounds. As water is used as a matrix in the photo-Fenton degradation process it is obvious to use *Vibrio fischeri* (*Photobacterium phosphoreum* NRRL- B-11177) as an indicator [Lapertot M., Ebrahimi S. et al., 2008]. Regarding to the natural marine environmental conditions of *Vibrio fischeri* the tests have to be performed within pH 6 to 8. The concentration of salt has to be adjusted as well. As the essay is based on the different intensities of the emitted luminescence correlated to the mortality of bacteria caused by toxic compounds in the samples, it is important to ensure that there are no other substances in the sample that can influence the bacteria. In terms of photo-Fenton reaction the remaining hydrogen peroxide has to be eliminated by adding catalase. In this manner at the same amount of matrix and the same concentration of bacteria in each testing tube the luminescence is measured and compared to the initial value and a blank sample. The more bacteria died or were inhibited due to the toxicity of the sample the less luminescence can be detected. The measurement is carried out after 5, 15 and 30 min. to obtain more information about the effects of the compounds related to the time. To enlarge the expressiveness of the

essay the measurement was repeated with a dilution factor of 1:20. This dilution factor permits a more detailed distinction between the different levels of toxicity of the samples. Thus the response of the *Vibrio fischeri* to the compounds can be observed more precisely, especially if the samples show a high toxicity.

Procedures:

All tests were carried out with BioFix®Lumi "Multishot" test kits for 200 Macherey-Nagel (ref.: 945007) determinations. Every single kit includes a certificate of quality after the pertinence with the UNE_EN_ISO 11348-3. The used photometer, BioFix®Lumi 10 (Macherey-Nagel) has a special design for ultra fast photon detection (Ultra Fast Single Photon Counter) with spectral range from 380 to 630nm. First the pH of the samples has to be neutralized (pH 6-8). Then the remaining H_2O_2 has to be eliminated by adding catalase which is prepared by adding 0.01g of catalase to 100ml of distilled water. To each sample should be added 500µL of the catalase solution before the samples are left to react for at least 10 minutes to ensure that the hydrogen peroxide is consumed entirely. While doing so the freeze-dried bacteria can be regenerated by adding 11ml of regeneration-solution to the flask. This regeneration solution has to be left to reclaim in the fridge for 30 minutes at 4-6C°. During this the samples can be diluted if necessary obtaining a final volume of 5ml. To acclimatize the bacteria to the needed temperature and to maintain the same temperature during the whole assay they are kept in a thermo-block maintaining 15C°. A constant temperature is essential for reliable results on account of a crucial influence of the incubation temperature to the later luminescence [Ribo J. M. et al., 2006] In order to generate a appropriate environment for the bacteria a solution of NaCl (Macherey-Nagel, ref.: 945601) has to be added to the samples before adding them to the bacteria resulting a salinity of 2% (p/v). To start the assay all empty testing tubes are labeled according to the samples and filled with 500µL of the bacteria solution. The luminescence of these is determined in the photometer and used as a reference value for the following measurements. During the whole assay the testing tubes are kept in the thermo-block to ensure a constant temperature. In the next step 500µL of the prepared samples are added to the bacteria solution. After a incubation time of 5 minutes the luminescence is measured the next time for this part of the assay the method "Biotox-B" was used. The first testing tube is filled only with bacteria and salt solution to serve as a blank sample. After a total time of 15 and 30 minutes the measurement was repeated using the method "Biotox-S". The inhibition or stimulation of the bacteria is given in percent of the original value of luminescence.

Quality control:

In order to quantify toxicity is has to be mentioned that the measurement including *Vibrio fischeri* has a limited validity. Bioluminescent bacteria are very sensible to some compounds and therefore their response in the operational conditions cannot reflect the real impact to microbial communities. If the concentration of some toxicants is too high the bacteria in the assay cannot survive and thus the reliability for monitoring

overall toxicity is very low. The toxicity measurement with *Vibrio fischeri* should always be combined with further types of tests to corroborate the results.

5.2.9 Biodegradability - Zahn-Wellens Test

Method and processing:

The Zahn-Wellens Test has the purpose to evaluate the ultimate degradability of water-soluble, non-volatile organic substances. These are exposed to a relatively high concentration of micro-organisms in a static test. The tests were run with a maximum DOC of 500 mg L^{-1} which was the initial concentration of the pollutants in photo-Fenton degradation process. To calculate the attained degradation at the end of the test equation 5.4 was used.

$$D_t = [1 - \frac{(C_T - C_B)}{(C_A - C_{BA})}] \times 100 \qquad (5.4)$$

Where D_T =biodegradation (%) at time T, C_A = DOC value in the test mixture measured three hours after the beginning of the test (mg L^{-1}), C_T = DOC value in the test mixture at time of sampling (mg L^{-1}), C_B = DOC value of the blank at time of sampling (mg L^{-1}), C_{BA} = DOC value of the blank, measured three hours after the beginning of the test. The resulting extend of degradation was rounded to the nearest full percent.

The measuring principle is based on the fact, that the sample, in this case from the photo-Fenton degradation process, is the only carbon source for the micro-organisms. Together with mineral nutrients the sample is introduced into a 1-4L glass vessel, filled with the activated sludge and equipped with aeration and an agitator. The mixture is aerated and agitated at a constant temperature of 20- 25℃ exposed to little or no light for 28 Days. The degradation process caused by the organisms is monitored in daily intervals by measuring the DOC value. The ratio of eliminated DOC between the DOC of each interval (day) to the DOC value after three hours after the beginning stands for the extend of degradation at the certain time.

During the test the concentration of dissolved oxygen has to be controlled as well as the pH value and the temperature. The oxygen concentration must not fall under 2mg L^{-1}, the pH should be kept between 7-8 and the temperature between 20-25℃. If these values pass these limits the regarding values have to be adjusted or the heating or aeration has to be controlled. Because of the duration of the test and that the process is open to the atmosphere the losses of water through evaporation have to be refilled every day with deionized water. This should be carried out before the next sample is drawn to keep the volume of the solution constant. The sludge in the drawn samples (5ml) has to be removed by using the centrifugation. Afterwards the sample can be filtered easily through a 0.22µm pore size PTFE syringe-driven filter (Millipore Millex® GN) and the DOC can be measured. The test was carried out for 28 days.

5.3 Reactors

5.3.1 CADOX

All photo-Fenton experiments were carried out in the CADOX reactor on the PSA. The reactor is designed to work in batch mode. The maximum volume, including the whole system and a full tank is 82 L, while the working volume for all experiments was 75 L. The reactor consists of the previously named, permanently stirred tank, a centrifugal re-circulation pump, the solar collector and the connecting tubing including the heating and cooling devices and the valves.

The heating and cooling played a major role for the automatic control of the temperature in the experiments. The system is equipped with several sensors for measurements, but these have not been used for the experiments in this study, since all parameters except for the temperature have been measured manually. Reaction parameters like temperature and flow rate were controlled from the instrument panel containing all electronic installations. The maximum irradiated volume in the solar collector amounts to 44.6 L, and can be covered by aluminium sheets. Furthermore the solar collector consists of four CPC modules (maximum irradiated surface of 4.16 m^2) which are installed on fixed supports with an inclination of 37° facing south. The plug flow photo-reactor is made of 20 borosilicate glass tubes with an inner diameter of 46.4 mm, an outer diameter of 50.0 mm and a length of 1.32 m. As described in chapter 4.1.2 the CPC has a concentration factor of 1 and an acceptance angle of 90°, the reflectors consist of electro polished aluminium and all tubes and collectors are connected in series. The tank is a round flask and is made of borosilicate with a volume of 20 L. The pipes and connections are made of inert polypropylene and have an inner diameter of ¾". By regulating the abnormal shaft driven pump (Bominox SIM-1051, 370W, 400V AC) the flow rate could be modulated, albeit the flow rate was stant in all experiments (1.5 m^3 h^{-1}). This flow rate ensures a turbulent flow with a Reynolds number of 13000. In order to control the temperature of the fluid the heating and cooling was coupled with the temperature probes integrated in the sensors which normally measure the system parameters. Except for the temperature these sensors were not used in the experiments of this study. All measurements during the experiments were carried out as described in chapter 5.2.

Figure 6 Photo of the CADOX plant at PSA

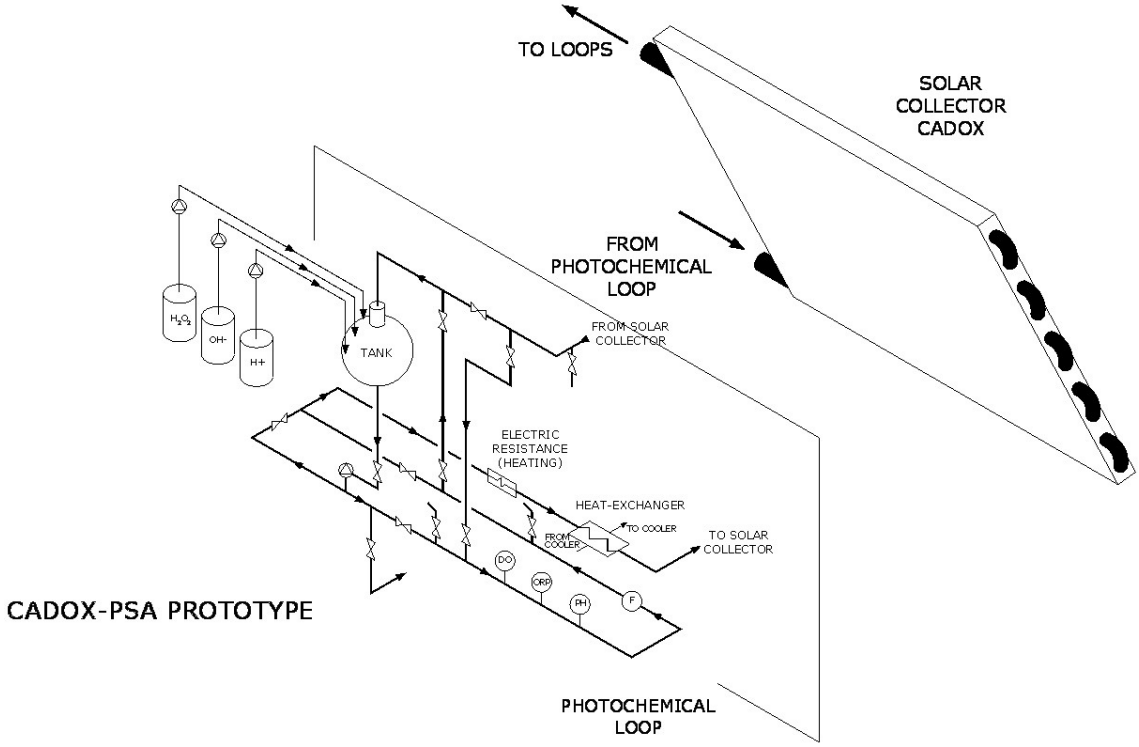


Figure 7 isometric drawing of the CADOX plant at PSA

5.3.2 Fenton reactor

The Fenton experiments were carried out in the laboratory on the PSA. A 3 L borosilicate beaker glass was used as a reaction vessel and since the experiments were dark-Fenton experiments the glass was enveloped in aluminium foil. In this way the solution was protected against light but open to the atmosphere to permit gas exchange. The temperature was measured with a thermometer and controlled with a heating plate including a magnetic stirrer which ensured the homogenization of the solution. All adjustments and sample drawings were performed manually.

5.4 Experimental set-up

5.4.1 Photo-Fenton experiments:

The preparation of the experiments in the CADOX reactor was processed in the same way for all photo-Fenton experiments with 200mg L^{-1} and for the kinetic experiments with 500mg L^{-1}. The dispensing of the hydrogen peroxide during the experiments with "controlled doses" was processed in a different way.

1. The solar reactor was cleaned and filled with distilled water to ensure that no other compounds were present in the reactor. The solar collector was covered with aluminium sheets to prevent any photochemical reactions.

2. The correct amount of pollutants was measured and diluted in distilled water. This solution was introduced into the pilot plant.
3. Perfect homogenization and dilution of the pollutants was achieved by re-circulating of the pilot-plant. The process fluid was adjusted to the different temperatures using the temperature controlling system (25, 35, 42 and 50°C) in this phase of preparation. This phase had a duration of minimum 30-60 minutes.
4. To control the initial DOC the first sample was taken and the pH value was adjusted to a value close to 2.8, immediately afterwards with a defined amount of sulphuric acid (60 ml, 2N). The next 15min. were used for further homogenization.
5. The second sample was drawn (to control the pH value) and immediately afterwards the calculated amount (7.48 g) of ferrous iron heptahydrate pre-dissolved in ca. 60ml of aqueous solution (pH 2) was added to the pilot plant, in order to achieve a concentration of 20 mg L^{-1} of iron. One more time the process fluid was re-circulated for homogenization for 15min.
6. Sample 3 was drawn to control the dissolved iron concentration and directly afterwards the calculated amount of H_2O_2 (30% w/v solution) was introduced to the system to reach a concentration of minimum 200 mg L^{-1}. Again followed by 15min. of homogenization.
7. The fourth sample was drawn to check the initial conditions for the photo-Fenton experiment. Immediately after this the aluminium sheets were removed from the collectors and the photo-Fenton degradation process started.
8. During the photo-Fenton experiments regular samples were drawn (each 15-30 minutes) to measure the main process variables. The concentration of hydrogen peroxide in the drawn samples was measured and regarding to these concentrations further adjustments were carried out by adding more peroxide to the reaction. In all kinetic experiments the concentration was kept constant in a range between 200-300mg L^{-1}. In some experiments the pH as well as the concentration of dissolved iron was adjusted by adding more base (NaOH, 2N) or more ferrous iron heptahydrate.

The experiments with “controlled doses” of hydrogen peroxide were started with a certain amount of hydrogen peroxide compared to the kinetic experiments and the following doses of H_2O_2 were added after the concentration was confirmed to be zero. Normal doses amounted between 60 and 160mg $^{-1}$. After the total consumption of each dose of H2O2 added, a sample was taken in order to evaluate the evolution of toxicity and biodegradability during the process. The taken samples were stable, since the reaction had stopped in the absence of hydrogen peroxide.

5.4.2 Fenton experiments:

The Fenton experiments which were carried out in the 3L vessel had a procedure similar to the sequence processed in the photo-Fenton experiments. However, the H_2O_2 was added at the beginning (300 mg L^{-1}) and no further additions were necessary as it was not totally consumed during the reaction, due to the slowness of the Fenton process. The initial DOC concentration was 200 mg L^{-1} (40 mg/L of each pesticide), the pH was set to 2.8 and the iron concentration was 20 mg L^{-1}.

5.4.3 Analytical controls:

To follow the kinetic degradation process (Fenton and photo-Fenton), the main parameters monitored in each sample during the reaction were the DOC and the concentration of the active ingredients contained in the commercial pesticides using the HPLC. To evaluate the efficiency of the treatment, the evolution of the mineralization grade of the pesticides and the formed intermediates is essential. In this case the relation of the DOC to the DOC_0 is used as an indicator of the extent of the photocatalytic reaction. Some other crucial measurements were the iron and the H_2O_2 concentration and the pH value. In order to compare the results of different experiments and evaluate their efficiency, the normalized illumination time (see fundamentals) was used as independent variable.

In the case of the evaluation of biodegradability and toxicity (samples without H_2O_2), the monitored parameters were: DOC, concentration of the pesticides, COD (chemical oxygen demand), total dissolved iron concentration, pH, temperature, ions and carboxylic acid concentration, toxicity (Vibrio Fischeri and Respirometry) and biodegradability (Zahn-Wellens test). As these experiments were no kinetic ones, due the limitation of H_2O_2, in this case the independent variable was the consumption of H_2O_2.

6 Results and discussion

6.1 Influence of the temperature on the degradation process

To evaluate the optimal parameters for the degradation process of a common pesticide mixture in the CADOX reactor pre-experiments were carried out. These experiments were performed in the time from 15.09.08 to 20.12.08. The experimental parameters were set referring to previously published articles and results from different sources [Zapata A., Oller I. et al., 2008; Pignatello J., Oliveros E. et al., 2006; Gernjak W., Malato S. et al., 2006; Oller, I., Malato, S. et al., 2007]. To examine the effect of different temperatures (25°C, 35°C, 42°C and 50°C) all experiments were carried out under the same circumstances. Thus, the Volume of the solution, the initial concentration of dissolved iron, the initial concentration of hydrogen peroxide the pH value and the technical parameters of the reactor system like flow rate and ground settings of the heating and cooling were ensured to be equal. Furthermore, the manners of adding reagents to the system or dissolving the iron were maintained through all experiments. In addition to that the experiments were performed on days with at most comparable conditions even if the input of UV-radiation to the system was normalized afterwards (see chapter 5.2.1) to exclude the fluctuation of irradiance as a changing parameter.

6.1.1 Photo-Fenton studies

The photo-Fenton experiments were carried out using a concentration of 200mg L^{-1} of the organic contaminants, divided to the five compounds as follows, Oxamyl 75.4, Methomyl 19.5, Imidacloprid 19.9, Dimethoate 29.6 and Pyrimethanil 56.1 mg L^{-1} as initial concentrations. The pH was adjusted to 2.8 by adding ca. 60 ml H_2SO_4 (2N). By dissolving 7.48g $FeSO_4$ *$7H_2O$ in ca. 50ml acidic solution (using H_2SO_4) and addition of this solution to the reactor an initial concentration of 20mg L^{-1} of dissolved iron was achieved. The experiment was started by adding 50 ml of hydrogen peroxide (30% w/v) obtaining a concentration of 200 mg L^{-1}. The exact procedure of preparing the system was explained in chapter 5.4. Using the same conditions the experiments were carried out at 25, 35, 42 and 50°C maintained by the heating and cooling system of the CADOX reactor and a average duration of 200 min. t_{30W}.

At all four temperatures which were tested the pesticide mixture could be successfully destroyed by photo-Fenton treatment. After ca. 100 minutes of illumination time the active pesticide compounds had been degraded entirely. Until an illumination time of 200 minutes a mineralization of 50% had been achieved and the efficiency of the process varied due to the temperature of the specific experiment. As a general result the progression of the degradation of the pesticide mixture followed a constant tendency and can be divided in three phases. The first phase is characterized by the stable DOC which is not decreasing significantly during the first 55 to 70 min t_{30W}, depending

to the temperature of the experiment. This can be explained because the reduction of the DOC is related to a complete oxidation of the organic pollutants into CO_2. During the first phase the degradation process is running, but the initial compounds are only oxidized to carbonated intermediates, which keeps the DOC stable. The mineralization (phase two) started earlier with the temperatures of 35 and 42°C (after ca. 55min t_{30W}). The second phase was a phase of relatively fast degradation of the DOC with an analogue behavior of hydrogen peroxide consume, increasing reversely to the decrease of DOC (figure 8). In this phase mainly aromatics or unsaturated hydro-carbons are formed as intermediates, which again can be easily oxidized to CO_2.

In the last phase of the degradation the mineralization slowed down, since the DOC/DOC_0 in relation to t_{30W} decreased more slowly. This can be explained by the formation of carboxylic and aliphatic compounds, which can hardly be attacked by the OH radicals. These three phases occurred in each experiment at the four different temperatures and are therefore general attributes of the photo-Fenton degradation process. Consequently the degradation to a DOC of nearly zero takes disproportionally longer than a degradation to a DOC/DOC_0 of 0,3 -0,5 and also consumes much more peroxide. As this is the case the goal was to find the optimal operation temperature to reach the point at which the intermediates and other organic compounds are least toxic and most biodegradable. Optimal operation temperature means that the reaction should be processed as fast as possible (shortest illumination time) by using the least amount of iron and peroxide and so causing the lowest costs, as explained before.

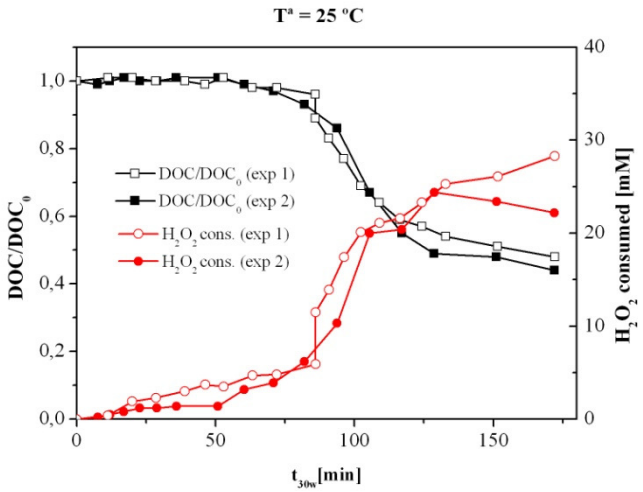


Figure 8 Mineralization of the pesticide mixture (DOC_0 = 200 mg L^{-1}, 20 mg L^{-1} Fe^{2+}) and H_2O_2 consumption at 25°C

Figure 9 summarizes the results of the experiments at all temperatures tested. As expected the photo-Fenton efficiency (fast pesticide degradation, short illumination time for substantial mineralization (50%) and low H_2O_2 consumption) rose gradually with the temperature from 25 to 42°C. The faster rate of ferrous regeneration from ferric iron is temperature dependent, since it runs faster at higher temperatures. Thus at higher temperatures more Fe^{2+} is available generating more hydroxyl radicals. This explains the higher efficiency at 42°C compared to 25 and 35°C.

Table 4 Results of the photo-Fenton experiments at four temperatures, 200 mg L^{-1} initial DOC

T°C	25	35	42	50
$DOC_{50\%}/t_{30W}$ min	130	126	85	130
H_2O_2 consumption [mM]	20	22	25	25

Table 4 and figure 9 confirm that the best degradation performance was achieved at a temperature of 42°C, while the consumption of H_2O_2 was comparable at all temperatures contrary to the elapsed illumination time (t_{30W} min.) which was significantly shorter compared to the results from the other experiments. Reaching the same point of degradation it would be logic that the same amount of hydrogen peroxide would have been consumed to oxidize the organic compounds. But as the difference of H_2O_2 consume between the reactions at 25 and 50°C after the same time (t_{30W} min.) shows, that there must be an additional factor influencing the consume of hydrogen peroxide additive to the consumption through oxidization of the organic compounds. To explain the difference in the consumption of H_2O_2 at the various temperatures additional Fenton experiments were carried out and the results are ana-

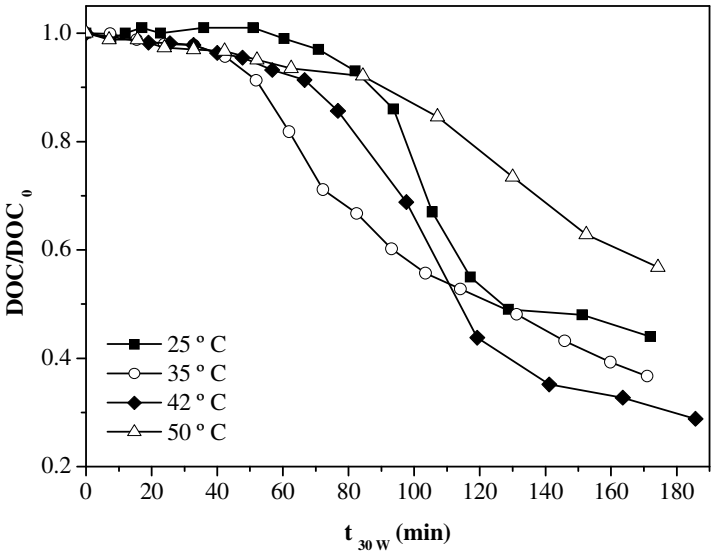


Figure 10 Mineralization depicted on illumination time for all temperatures, DOC 200mg L^{-1}

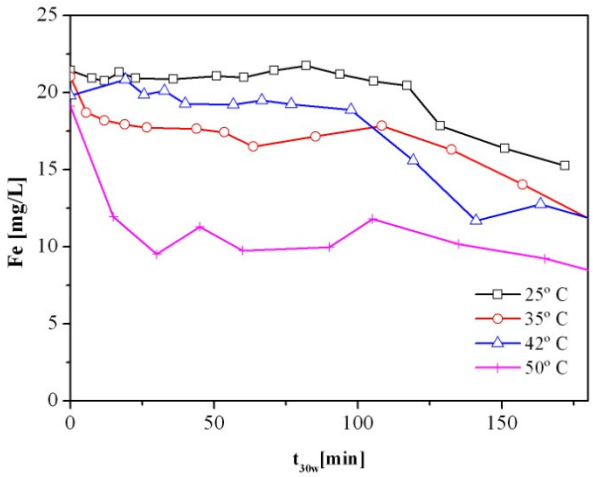


Figure 9 Behavior of dissolved iron at all temperatures in presence of the pesticide mixture (DOC 200 mg L^{-1}) depicted on illumination time (t_{30W} min.)

lyzed regarding the results of the effects obtained in the photo-Fenton experiments.
As well as the hydrogen peroxide, the concentration of dissolved iron plays a major role in the photo-Fenton degradation process. To compare the influence of the four different temperatures to the behavior of iron figure 10 shows the concentration of total dissolved iron depicted on t_{30W} [min.]. The figure shows clearly that the higher the reaction temperature was the higher were the losses of dissolved iron, even if the concentration of dissolved iron was nearly equal at the temperature of 35 and 42°C after t_{30W} ≈180 minutes, the difference between 25, 35/42 and 50°C is significant. At a temperature of 25°C the concentration of total dissolved iron was still 15 mg L^{-1} while the loss at 35/42°C had led to a remaining concentration of 12.5 mg L^{-1}. The lowest value was achieved at 50°C with a final concentration of 8.5mg L^{-1}. This caused the above explained effect, that the efficiency of the photo-Fenton degradation process is notedly lower at 50°C, because the precipitated iron did not partake in the photocatalytic reaction. This is the main factor for the decreased efficiency at 50°C. The losses of dissolved iron are due to two effects. The first is the continual loss of iron beginning after a 100 – 125 min t_{30W} until the end of the experiment. This effect was nearly independent to the temperature (figure 5). The second effect, a rapid loss of dissolved iron, is slightly notable during the initial phase of the experiment at a temperature of 35°C but none the worse significant at a temperature of 50°C. At 50°C the dissolved iron decreased from 20mg L^{-1} to less than 10mg L^{-1} within 25 min t_{30W}. From that point on the iron concentration stayed stable until the continual decrease beginning after ca. 125 min. t_{30W}. It can be stated already that one crucial point which is influencing the efficiency of the photo-Fenton degradation process is the concentration of dissolved iron in the solution [Zapata A., Oller I. et al., 2009; Gernjak W., Malato S. et al., 2006] and therefore the loss of iron at a temperature of 50°C can be assumed to be one factor causing the relatively low efficiency at this temperature. Figure 11 reveals a connection between the precipitation of iron and a change of the pH value. As 12.5mg of dissolved iron were precipitated in the first 30 min. t_{30W} the concentration went down to 6.5mg L^{-1}.

In the same phase of the experiment the pH value decreased from 2.76 to 2.31. This effect was described by Grundl T. and Delwiche J. 1993 and analogue reactions for the first three reaction steps are given in chapter 4.2.2 (eq. 4.3-4.6). By these

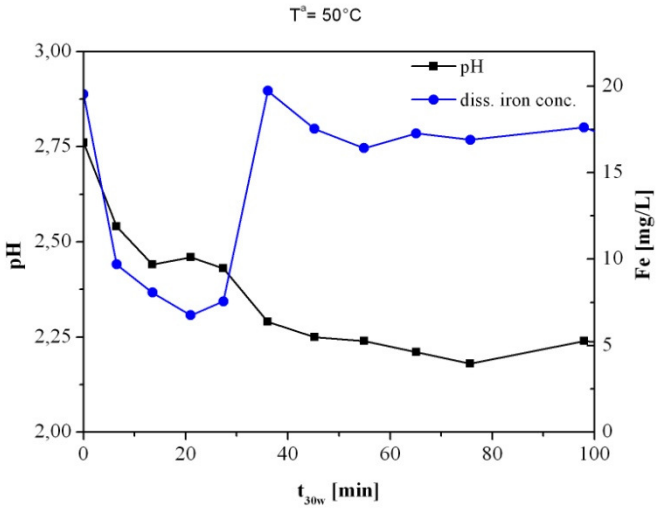


Figure 11 Behavior of the pH and total diss. Iron at 50°C and 200 mg L^{-1} DOC

reactions the decrease of the pH value can be explained due to the H^+ ions which were set free. These first steps "proceed virtually instantaneously" [Grundl T., Delwiche J., 1993] and so the rate controlling step is the precipitation of solid ferric hydroxide (eq. 6.1). Given that the obtained results express that the precipitation of ferric iron was significantly higher at 50°C it can be presumed that the precipitation step was strongly influenced by the temperature.

$$[Fe(H_2O)_3(OH)_3] \longrightarrow [Fe(H_2O)_3(OH)_3]_{(solid)} \qquad (6.1)$$

A second effect could be observed in the experiment. After adjusting the dissolved iron concentration to 20mg L^{-1} after 30min. t_{30W} the pH decreased once more (figure 11). This can be explained with the addition of Fe^{3+} to the system which has been nearly in an equilibrium state in terms of iron species and concentrations. Hence the concentration of free Fe^{3+}, $[Fe(H_2O)_5(OH)]^{2+}$ and $[Fe(H_2O)_4(OH)_2]^+$ increased and caused the pH to decrease [Grundl T., Delwiche J., 1993]. To investigate the effects mentioned above in a more detailed way and to clear the behavior of the dissolved iron including the organic compounds and the effect of H_2O_2, Fenton experiments were carried out and the results are discussed in chapter 6.1.2.

6.1.2 Fenton studies

To control the results identified during the photo-Fenton experiments those were combined and compared with the results of the Fenton experiments. As the presence of organic molecules like the contaminants and the produced intermediates seemed to have a influence to the behavior of the dissolved iron, experiments in presents and absence of organic molecules were carried out at all temperatures. Table 5 gives an overview over the obtained data relevant for the comparison between the 8 experiments.

Table 5 Results of the Fenton studies

T°C	25	35	42	50
H_2O_2 consumption Blank (after 180min.)	4mM	5.7mM	5.9mM	6.2mM
H_2O_2 consumption Pest. Mix.	0.5mM	1.6mM	2.5mM	4mM
Loss of diss. Iron Blank	12mg	13mg	13.5mg	14mg
Loss of diss. Iron Pest. Mix.	0.2mg	3mg	7mg	10mg

There are two significant trends shown in table 5. First, the higher the temperature ing the experiments was the more increased the consumption of peroxide and the loss

of dissolved iron. Second, for both parameters an explicit difference between the results of the Blank experiments and the experiments carried out in presence of the pesticides can be perceived. The consumption of H_2O_2 was significantly higher in absence of the organic compounds. Further on the difference in the consumption between Blank and Pest. Mix. was more evident at a low temperature (25°C) than at a high temperature (50°C). Coherent results were obtained for the loss of iron from the solution, since the final iron concentration went down to 6-8mg L^{-1} in the Blank experiments compared to the notedly lower loss of iron in the experiments with the pesticide mixture. Like noted for the consumption of hydrogen peroxide the difference between the results from the Blank experiments and experiments with the pesticide mixture was significantly higher at low temperature. For example at 25°C the difference of the loss of dissolved iron with and without the organic compounds amounted 11.8mg L^{-1}, while the difference at 50°C was only 4mg L^{-1}. In addition to the mentioned effects under the various conditions of the experiments a further detail can be discerned. At temperatures above 25°C the dissolved iron concentration seems to be stable at a concentration between 5 and 6mg L^{-1} as shown in figure 12. This effect could not be verified in the literature but the coherent results from various different experiments seem to be reliable as tendency.

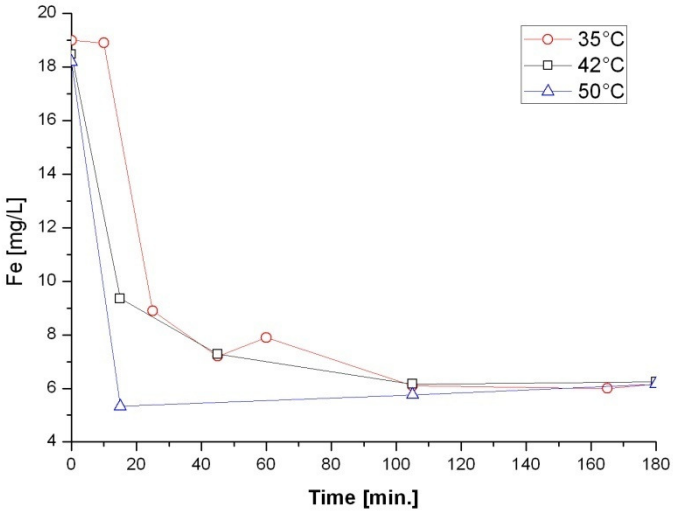


Figure 12 Behavior of dissolved iron in absence of pesticides (blank) at three different temperatures

The considerably higher concentration of dissolved iron in presence of the contaminants can be explained by complexation processes, which stabilized the iron and so averted the precipitation of iron hydroxide. [Fujii M., Ito H. et al., 2008]. These complexes seemed to be more stable at low temperatures, since the total dissolved iron concentration was stable close to the initial concentration at a temperature of 25°C and decreased with higher temperatures to a minimum at 50°C. This effect was discovered to occur mainly in the presence of none or little degraded pesticide mixture as present in the Fenton experiments. During the first 180 minutes of the Fenton experiments the decomposition of the initial compounds was lower than 5% which leads to the conclusion that this type of complexation had to take place with the initial compounds. A contrary effect which occurred during photo-Fenton experiments was mentioned in chapter

6.1.1. During the later phase of the degradation process a loss of dissolved iron could be ascertained. This effect can be also explained by the presence of organic compounds, but with the difference that the original pesticides had been decomposed already. As described in chapter 4.2.1 and proven by manners of the IC analysis (figure 15) one fraction of the intermediates formed during the degradation process are organic acids [Gernjak W., Malato S. et al., 2006]. These organic acids (acetic, formic, pyruvic, maleic and oxalic acid) are known to form complexes with ferric iron [Faust B., Hoigné J., 1990; Sulzberger B., Laubscher H. et al., 1994; Fujii M., Ito H. et al., 2008] which caused the decrease of free dissolved iron in the solution of the photo-Fenton experiments after 120min t_{30W}. Regarding to the temperature the difference between the complexes formed during the Fenton experiments and the complexes with the organic acids formed in photo-Fenton degradation are, that the stability of the iron complexes formed with the pesticide compounds is significantly more influenced by the temperature. This is shown in table 5. Contrariwise the loss of free dissolved iron due to complexation during the photo-Fenton reaction is not significantly influenced by the temperature.

In the following part the coactions of dissolved iron, hydrogen peroxide and the organic compounds will be analyzed. First as a basic reaction the ferrous iron is oxidized by the hydrogen peroxide (eq. 6.2-6.4). The formed products comprise hydroxyl radicals which again react with ferrous iron in the solution and oxidize the ferrous iron to ferric iron. A comparable reaction takes place with hydroperoxyl radicals and ferrous iron. As ferric iron is the crucial species in relation to precipitation at a pH below 3, this ferric iron forming reactions are essential for the understanding of the above mentioned conclusions.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^{\bullet} \qquad k = 53 - 76\, M^{-1}s^{-1} \qquad (6.2)$$

$$Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^- \qquad k = 2.6 - 5.8 * 10^8\, M^{-1}s^{-1} \qquad (6.3)$$

$$Fe^{2+} + HO_2^{\bullet} \longrightarrow Fe^{3+} + HO_2^- \qquad k = 0.75 - 1.5 * 10^6\, M^{-1}s^{-1} \qquad (6.4)$$

The data from the photo-Fenton experiments compared to the data from the Fenton experiments show that the difference of the consumption of hydrogen peroxide depending on the temperature is notedly higher in Fenton experiments (table 5, table 4) and especially in presence of the pesticide mixture. The higher losses of dissolved iron at higher temperatures have been explained before, but have to be extended by one more relation. Whereas in the photo-Fenton reaction the ferric iron can be regenerated to ferrous iron driven by the UV-radiation (eq. 4.27 -4.29), the regeneration step in the Fenton reaction is known to be very slow [Pignatello J., Oliveros E. et al., 2006]. Due to that the concentration of ferric iron during the Fenton reaction is permanently higher than in the photo-Fenton reaction, accelerating the precipitation process of iron hydroxide. This leads to the significantly higher influence of the temperature in terms of iron precipitation in absence of UV-radiation.

To explain the differences between the results in presence and absence of the pesticide mixture in the Fenton experiments the reactions of hydrogen peroxide with organic compounds can be noted as very important [Gernjak W., Malato S. et al., 2006]. The simple fact that the peroxide can also react with the organic compounds and not only with the dissolved iron matches the previously described effect that in presence of organic compounds the loss of iron is clearly lower. Since less ferrous iron gets oxidized to ferric iron which is more likely to precipitate. Furthermore at the given pH value the auto-decomposition of hydrogen peroxide plays a role in the amounts consumed under the various conditions of the experiments. In general compared to the reactions including iron or organic compounds the auto-decomposition of the hydrogen peroxide is a slow reaction (eq. 6.5).

$$2\,H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (6.5)$$

It is assumed that in absence of the organic contaminants one part reacts with the dissolved iron in the aqueous solution and one part reacts in the “auto-decomposition mode”. Still the auto-decomposed part is very small compared to the share reacting with ferrous iron. The auto-decomposition of peroxide is among other factors dependent to the temperature. With a higher temperature the decomposition increases.

6.2 Photo-Fenton degradation of the pesticide mixture

After the experiments with an initial concentration of 200mg L^{-1} of contaminants the concentration was elevated to 500mg L^{-1} to adapt the conditions to the later application. According to the results of the previous Fenton and photo-Fenton experiments, the temperature for the subsequent experiments was set to 35°C. This was decided considering two major reasons. On the one hand the optimum degradation results were considered and on the other hand the feasibility including the later conditions of the application. Both factors had to lead to the best degradation performance and the lowest costs.

The application for the analysed photo-Fenton processes in a pilot plant should not make an additional heating necessary regarding the costs for energy and maintenance. Hence the previously elaborated optimal temperature of 42°C during the photo-Fenton experiments was considered to be not feasible in a large scale pilot plant. Therefore the next better results were elected leading to a working temperature of 35°C which is clearly more realistic as a working temperature in a pilot plant. Once photo-Fenton degradation of the pesticide mixture had been evaluated and the main parameters optimized, reduced operating costs from combining photo-Fenton and biological treatments became possible. The next step was to investigate whether photo-Fenton is able to transform the toxic and recalcitrant pesticides into biodegradable intermediates.

6.2.1 Kinetic studies

The kinetic experiments were carried out to obtain information about the photo-Fenton process used to degrade the pesticide mixture in a high concentration (500mg L^{-1}) with abound in hydrogen peroxide. In this experiment the concentration of hydrogen peroxide was ensured to stay above 300mg L^{-1} during the whole experiment, to make sure the degradation is not slowed down due to insufficient peroxide. The results of the experiment are shown in figure 13 depicted on t_{30W} (min.). For the subsequent experiments which lead to the biodegradability assay the "point of no pesticides" related to the consumed hydrogen peroxide and the DOC is most important. At a consumption of 45.6mM of hydrogen peroxide and a remaining concentration of 66% DOC all initial

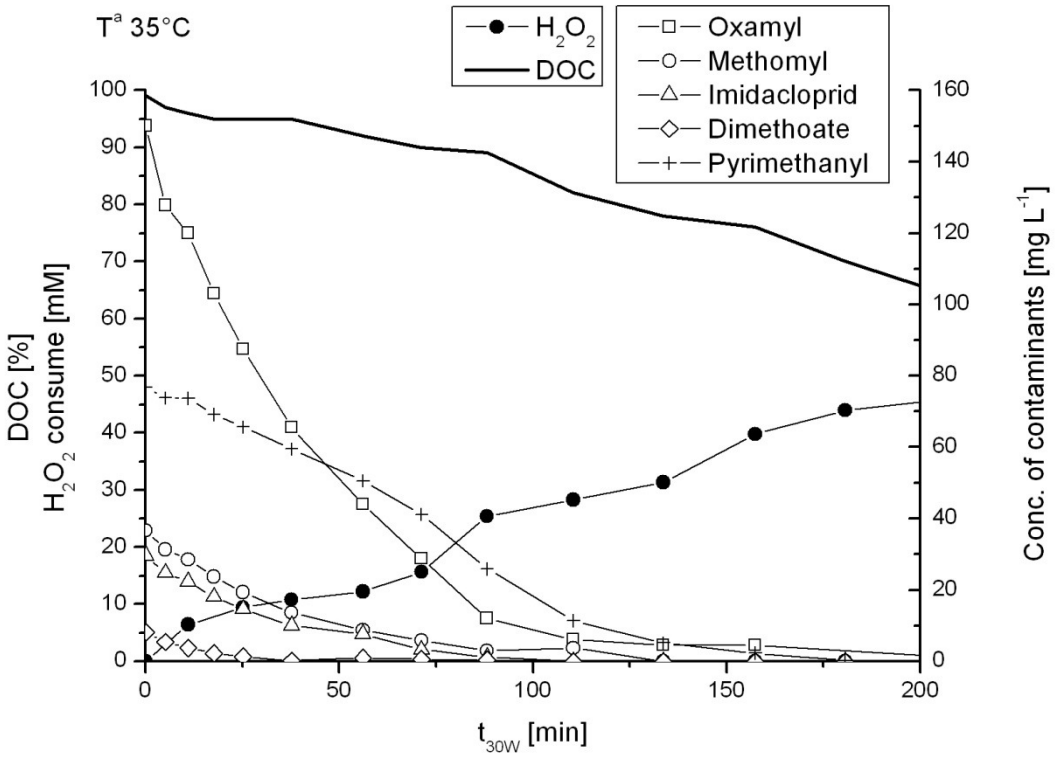


Figure 13 Mineralization, H_2O_2 consumption and decomposition of the initial compounds at 35°C, initial DOC 500 mg L^{-1}

pesticide compounds had been entirely degraded.

6.2.2 Controlled doses:

After the kinetic experiment an experiment with limited amounts of hydrogen peroxide has been carried out. One sense of the experiment with controlled doses was to obtain samples from the different parts of the degradation process without containing hydrogen peroxide. These samples are necessary for further determinations of toxicity and biodegradability. The other sense was to process a comparable reaction like the kinetic degradation experiment with limited amounts of peroxide to control the efficiency of peroxide consume in both experiments.

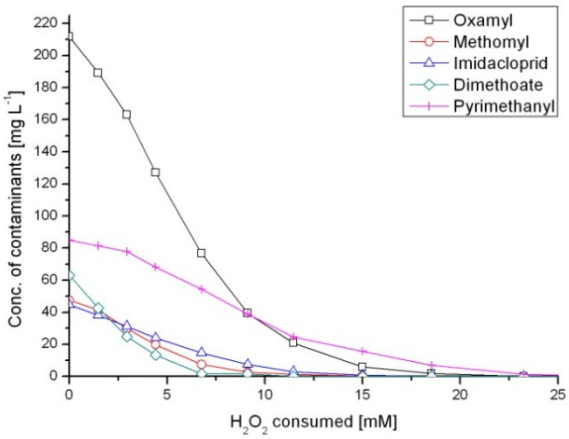


Figure 14 Decomposition of the five pesticides with controlled doses, initial DOC 500 mg L^{-1}

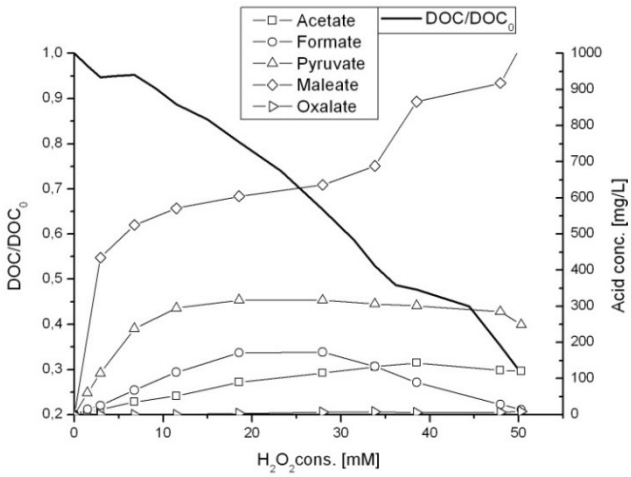


Figure 15 Results of the IC analysis, formation of organic acids and mineralization at 35°C (500 mg L^{-1} initial DOC)

The samples were taken after all H_2O_2 of the last dosage had been used entirely. At these points the next dose of hydrogen peroxide was added to the reaction. The doses amounted between 10 – 40 ml of H_2O_2 (30% w/v). In order to be available for the assays of toxicity and biodegradability one part of the taken samples was stored in a fridge to reduce the chemical reactions to a minimum. The rest of the samples were analyzed in the IC, HPLC and for DOC.

While the primary compounds were destroyed (figure14) intermediates were formed. Among others these intermediates were organic acids (figure 15). The phase of fast decomposition of the pesticides correlates with the main formation phase of the organic acids (consume till 15 mM H_2O_2).

6.3 Toxicity

6.3.1 Vibrio fischeri

The results of the toxicity assay using Vibrio fischeri are partly shown in figure 16. The results after 15 minutes are left out as they were coherent with those after 5 and 30 minutes. The difference between the inhibition caused by the diluted and non-diluted samples is most clearly in the middle part of the experiment and becomes less significant in the last part. Over the whole experiment the non-diluted samples were more toxic than the diluted ones. The primary compounds (all five pesticides) have a very strong toxic effect to the Vibrio fischeri, causing an inhibition above 90% in the initial phase of the degradation experiment, even with a dilution factor of 1:20. Along with the decomposition of the primary compounds and a consumption between 10 and 20 mM of H_2O_2, the toxicity of the samples decreased (figure 16). Especially the measurement with the diluted samples reached a good correlation with the decomposition of the contaminants as they were entirely destroyed after a consumption of 23 mM of H_2O_2 and a very low inhibition was measured at the same point. The results obtained from the non-diluted samples show the same trend, but are less sensitive to small changes of toxicity, because the higher concentration of the toxic compounds inhibits the bacteria permanently on a higher level. After the primary compounds of the pesticides were decomposed entirely the level of inhibition was increasing up to an inhibition of 30%. It can be assumed that during the decomposition of the primary compounds other intermediates were formed which are also toxic and inhibited the bacteria. These intermediated could be proven to be organic acids (figure 16). Maleate for example as an intermediate is still toxic to organisms [Mallinckrodt Chemicals, 2006] and can be assumed to be one reason for the inhibition in the final part of the degradation process.

6.3.2 Respirometry

Due to the limited expressiveness of the Vibrio fischeri the obtained data has to be controlled and compared to the results obtained by the Respirometry. A direct correlation is not possible because the activated sludge is supposed to react in a different way to the toxic impact caused by the compounds in the samples. As shown in figure 16 the inhibition of the respiration rate of the activated sludge was lower than the inhibition of the Vibrio fischeri. The combination of different bacteria forming the activated sludge makes them less sensitive for toxic effects. Nevertheless the main trend in the same, with the progressing decomposition of the primary compounds the inhibition sank, and raised again with the formation of organic acids and other intermediates. Between a consumption of 20 to 30 mM of hydrogen peroxide the activated sludge reacted with stimulation to the introduced sample. This means, that the compounds which were present during this part of the degradation process did not have a toxic impact to the sludge, on the contrary the additional DOC in the sample stimulated the sludge and

caused a higher respiration rate than in the reference. However the final inhibition of 56% correlates with the inhibition measured in the Vibrio fischeri assay. To describe the direct relation between the intermediates and the toxicity in a more detailed way further analysis has to be carried out in order to detect and describe more compounds formed during the degradation process. In addition, the fact that not the whole composition of the common pesticides which were used for the experiments is known makes it difficult to draw conclusions in terms of toxicity related to single molecules.

Anyhow the obtained results are coherent and give sufficient information regarding to the main objective of this work. It can be figured out at which stage during the degradation process the present compounds are least toxic and therefore probably biodegradable. After a consumption of ca. 23 mM of hydrogen peroxide seems to be the best stage to discharge the fluid to the biological treatment. This consume of H_2O_2 is equivalent to a DOC of 395 mg L^{-1}. It is important to state, that not all mixtures of compounds with a lower toxicity are more biodegradable, but it still gives a hint in the right direction. As mentioned before the toxicity gives only a clue to the real biodegradability.

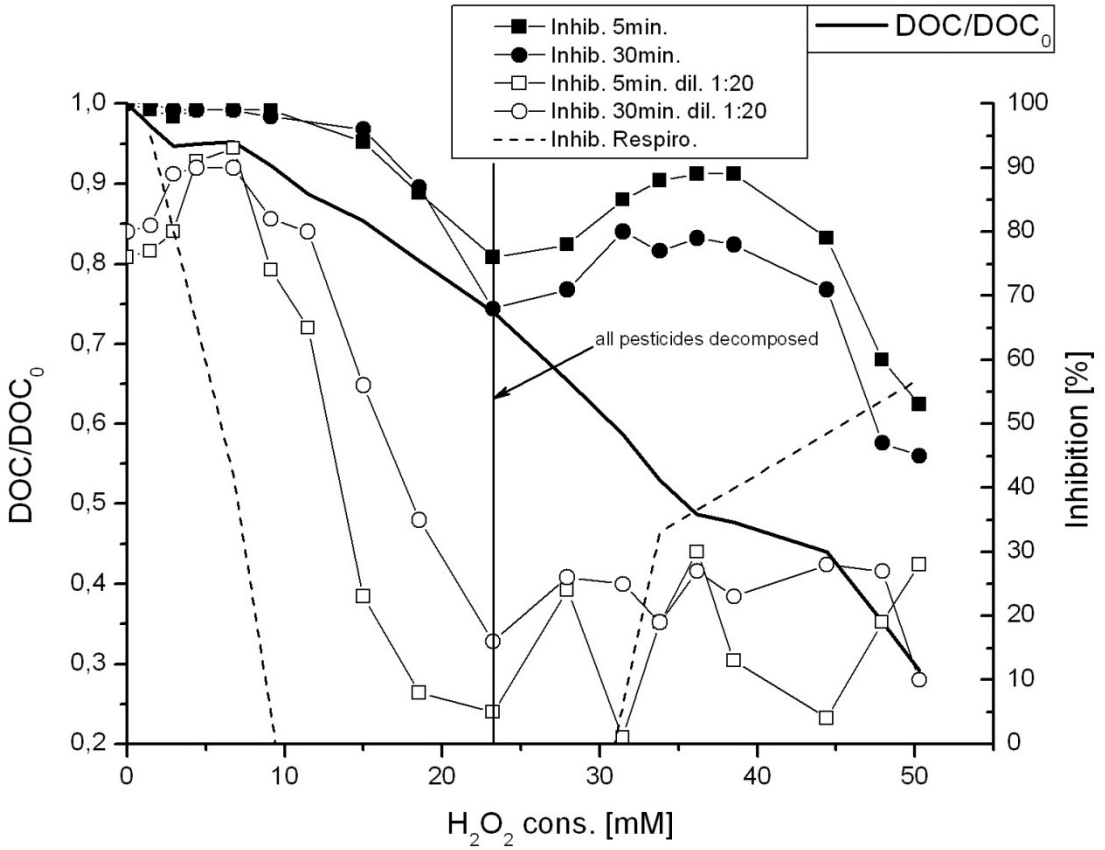


Figure 16 Results for toxicity assays with Vibrio fischeri (Inhibition after 5 + 30min., non diluted and with a dilution factor of 1:20) and Respirometry; mineralization depicted on H_2O_2 consumption

6.4 Biodegradability - Zahn-Wellens test

To denominate a sample biodegradable, the degradability has to be at least 70%. Referring to the results of the toxicity assays the first five samples were predicted to be non-biodegradable and therefore not analysed in the Zahn-Wellens test. The initial sample was analysed for reasons of comparability and was, as expected least biodegradable (48%). The aimed biodegradability of 70% was not reached until sample 7 with a DOC of 473.5 mg L^{-1}. However, the residual DOC was still high (124.5 mg/L), and the time to reach 70 % of degradation was 28 days. Moreover, the active ingredients were present also at the end of the test, as they are not biodegradable. That is the reason why this is an early stage in photo-Fenton process to couple the biological treatment. Each further sample with a lower DOC was more biodegradable, hence a relation between the DOC and the biodegradability was proven. This continual increase in biodegradability after 28 days cannot be correlated with the entire trend obtained from the toxicity assays, since the toxicity increased with the formation of intermediates during the later stage of the degradation process. But as shown in table 6 the results of the biodegradability after a shorter time (3 or 6 days) again confirmed the trend of the toxicity. The biodegradability of sample 15 after 3 days was 80% whereas the degradability of sample 16 and 18 after 6 days amounted only 70%. This validates the tendency that the final products formed through the photo-Fenton degradation process are more toxic and less biodegradable than the intermediates formed before. This is true for a short testing time, since the sludge has the capacity to adapt to the toxic impact. After the whole 28 days of the test this effect did not occur.

Considering the Zahn-Wellens test, the optimal results were observed between sample 10 and 13, just after the total elimination of all active ingredients, which agree with the toxicity analysis. This can be stated as the optimal stage for discharging the pre-treatment into the bioreactor. Consequently the photo-Fenton degradation process should be extended until a mineralization of 35-40% is reached. At this point, the active ingredients are totally degraded and 30 mM is consumed. This pre-treated mixture can be successfully treated in a conventional aerobic biological reactor.

Table 6 Results of the Zahn-Wellens test; (DOC_0: 500 mg/L)

Sample (initial DOC, mg/L)	% Biodegradability (28 days)	Residual DOC (mg/L)	BIODEGRAD
S0 (534)	**48 %**	**172.88**	**Non-biodegradable**
S6 (492.5)	**69 %**	**143.40**	**Non-biodegradable**
S7 (473.5)	**70 %**	**124.52**	**Biodegradable**
S9 (428.9)	**80 % (70 % in 9 days)**	**85.76**	**Biodegradable**
S10 (394.7)	**85 % (70 % in 6 days)**	**56.50**	**Biodegradable**
S13 (282.4)	**90 % (70 % in 3 days)**	**76.50**	**Biodegradable**
S15 (254.5)	**89 % (80 % in 3 days)**	**16.25**	**Biodegradable**
S16 (234.8)	**95 % (70 % in 6 days)**	**18.33**	**Biodegradable**
S18 (165.6)	**93 % (70 % in 6 days)**	**20.34**	**Biodegradable**

7 Conclusions and summary

To summarize the results of the carried out experiments in this study it can be stated, that at all four tested temperatures the pesticide mixture could be successfully degraded by the photo-Fenton pre-treatment. Based on the performance target to minimize the illumination time and the consumption of hydrogen peroxide resulting in minimal operating costs, a temperature of 35°C was elected for the toxicity and biodegradability assays. At this temperature the loss of iron was figured out to be acceptable compared to higher temperatures. Likewise the consumption of hydrogen peroxide was lower than in the experiments carried out at higher temperatures. As the results have shown the mineralization at 42°C was processed in less illumination time than at 35°C. However the main objective was to find the optimal parameters for a large scale application of the photo-Fenton degradation process, which makes a relatively high temperature of 42°C less efficient due to the heating and maintenance costs. The kinetic experiments and the experiments with controlled doses of hydrogen peroxide were carried out at 35°C and had the objective to find the earliest point during the photo-Fenton degradation process, at which the remaining compounds were biodegradable, also aiming to minimize the operating costs. At this point the process flow could be interrupted and it should be able to discharge the working fluid of the photo-Fenton reactor to the biological reactor without harming the bacteria due to the toxicity of the remaining pollutants. The lowest toxicity was achieved after a consumption of ca. 23 mM of hydrogen peroxide. The analysis of the HPLC showed that this was the point when all initial pesticide compounds were destroyed. Since the toxicity gives only a hint to the real biodegradability, the toxicity results were controlled processing the Zahn-Wellens test. This test validated the fact that the initial compounds were toxic and non biodegradable and likewise the tendency that the finally formed intermediates and products of the photo-Fenton degradation process again showed a higher toxicity and a lower biodegradability. Consequently the photo-Fenton degradation process should be extended until a mineralization of 35-40% is reached. To mineralize a pesticide mixture at 35°C operational temperature with an initial concentration of 500 mg L^{-1} to this point, 30 mM of hydrogen peroxide were consumed. The resulting compounds in the pre-treated mixture could be successfully degraded in a conventional aerobic biological reactor. These results confirm the election of 35°C as the optimal operating temperature. Using this temperature with a similar configuration of the system, the costs of the pre-treatment can be minimized and the used operation parameters can be suggested to be applied in a large scale pilot plant.

References:

Amat, A.M., Arques, A., Garcia-Ripoll, A., Santos-Juanes, L., Vicente, R., Oller, I., Maldonado, M.I. & Malato, S. 2009, "A reliable monitoring of the biocompatibility of an effluent along an oxidative pre-treatment by sequential bioassays and chemical analyses", *Water research,* vol. 43, no. 3, pp. 784-792.

Ballesteros Martin, M.M., Sanchez Perez, J.A., Acien Fernandez, F.G., Casas Lopez, J.L., Garcia-Ripoll, A.M., Arques, A., Oller, I. & Malato Rodriguez, S. 2008, "Combined photo-Fenton and biological oxidation for pesticide degradation: effect of photo-treated intermediates on biodegradation kinetics", *Chemosphere,* vol. 70, no. 8, pp. 1476-1483.

Ballesteros Martin, M.M., Sanchez Perez, J.A., Casas Lopez, J.L., Oller, I. & Malato Rodriguez, S. 2009, "Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation", *Water research,* vol. 43, no. 3, pp. 653-660.

Ballesteros Martin, M.M., Sanchez Perez, J.A., Garcia Sanchez, J.L., Montes de Oca, L., Casas Lopez, J.L., Oller, I. & Malato Rodriguez, S. 2008, "Degradation of alachlor and pyrimethanil by combined photo-Fenton and biological oxidation", *Journal of hazardous materials,* vol. 155, no. 1-2, pp. 342-349.

Barb W. G., Baxendale J. H., et al. 1951, "Reactions of ferrous and ferric ions with hydrogen peroxide. Part II. The ferric iron reaction", *Trans. Faraday Soc.,* vol. 47, pp. 591-616.

Barb W. G., Baxendale J. H., et al. "Reactions of ferrous and ferric ions with hydrogen peroxyde", *Trans. Faraday Soc.,* vol. 47, pp. 462-500.

Baron R. L. 1991, "Carbamate insecticides" *In Handbook of Pesticide Toxicology* Academic Press, New York, pp. 3-6.

Bauer R., Waldner G., et al. 1999, "The photo-Fenton reaction and the TiO_2/UV process for wastewater treatment- novel developments", *Catalysis Today,* vol. 53, pp. 131-144.

Blanco J., Malato S., et al. 2008, "Review of feasible solar energy applications to water processes", *Renewable and Sustainable Energy Reviews,* .

Blanco J., Malato S., et al. 2000, "Compound parabolic concentrator technology development to comercial solar detoxification applications", *Sol. Energy,* , no. 67, pp. 317-330.

Bobu, M., Wilson, S., Greibrokk, T., Lundanes, E. & Siminiceanu, I. 2006, "Comparison of advanced oxidation processes and identification of monuron photodegradation products in aqueous solution", *Chemosphere,* vol. 63, no. 10, pp. 1718-1727.

Bossmann S. H., Oliveros E., et al. 1998, "New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reactions", *J. Phys. Chem.,* vol. 102, pp. 5542-5550.

Braun A. M., Maurette M.-T., Oliveros E. 1991, *Photochemical technology,* Wiley, Chichster.

Buxton G. U., Greenstock C. L., et al. 1988, "Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution", *J. Phys. Chem. Ref. Data,* vol. 17, pp. 513-886.

Chen R., Pignatello J. J. 1997, "Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton axidations of aromatic compounds", *Environmental science & technology,* vol. 31, pp. 2399-2406.

Cooper A. T. et al. 1998, "Solar Photochemical Detoxification and Disinfection for Water Treatment in Tropical Developing Countries", .

Costa J.M., H., E. 2000, *Greenhouse horticulture in Almeria*.

European Commission 2006, *COM (2006)397 final*.

European Commission 2005, *Common Actions for Growth and Employment: The Community Lisbon Programme COM(2005) 330 final*, Lisbon.

European Commission 2000, *List of 32 Priority substances. COM(2000)47final*.

European Commission 2000, *The Water Framework Directive; EC Directive 2000/60/EC*.

European Commission 1999, *COMMPS procedure. Study of the prioritisation of substances dangerous to the aquatic environment.*, Luxembourg.

Farre, M.J., Maldonado, M.I., Gernjak, W., Oller, I., Malato, S., Domenech, X. & Peral, J. 2008, "Coupled solar photo-Fenton and biological treatment for the degradation of diuron and linuron herbicides at pilot scale", *Chemosphere,* vol. 72, no. 4, pp. 622-629.

Faust B., H.J. 1990, "Photolysis of hydroxy-complexes as sources of OH-radicals in clouds, fog and rain", *Atmos. Environ.,* vol. 24A, pp. 79-89.

Fenández-Soriano M. A. 1995, *Estudio epidemiológico y analitico sobre la exposicion ambiental a pesticides y su repercusion materno-fetal durante el embarazo y parto*.

Fernandez-Alba, A.R., Hernando, D., Aguera, A., Caceres, J. & Malato, S. 2002, "Toxicity assays: a way for evaluating AOPs efficiency", *Water research,* vol. 36, no. 17, pp. 4255-4262.

Fröhlich C., Brusa R. W. 1981, "Solar Radiation and its variation in time", *Sol. Phys.,* , no. 74, pp. 209-215.

Fujii M., Ito H., et al 2008, "Superoxide-mediated Fe(II) formation from organically complexed Fe(III) in coastal waters", *Geochimica et Cosmochimica Acta,* vol. 72, no. 24, pp. 6079-6089.

Gernjak W., Malato S., et al. 2006, *Solar photo-Fenton of EU priority Substances*.

Gernjak, W., Krutzler, T., Glaser, A., Malato, S., Caceres, J., Bauer, R. & Fernandez-Alba, A.R. 2003, "Photo-Fenton treatment of water containing natural phenolic pollutants", *Chemosphere,* vol. 50, no. 1, pp. 71-78.

Gogate P. R., Pandit A. B. 2004, "A review of imperative technologies for wastewater treatment I:
oxidation technologies at ambient conditions", *Advances in Environmental Research,* , no. 8, pp. 501-551.

Gogate P. R., Pandit A. B. 2004, "A review of imperative technologies for wastewater treatment II: hybrid methods", *Advances in Environmental Research,* vol. 8, pp. 553-597.

Gomathi Devi, L., Girish Kumar, S., Mohan Reddy, K. & Munikrishnappa, C. 2008, "Photo degradation of Methyl Orange an azo dye by Advanced Fenton Process using zero valent

metallic iron: Influence of various reaction parameters and its degradation mechanism", *Journal of hazardous materials,* .

Gonzales-Paradas E., Urena-Amate M. D. et al. 2002, *Leaching of Imidacloprid and Procymidone in a Greenhouse of southeast Spain*.

Haag W. R., Yao C. D. 1992, "Rate constant for Reaction of Hydroxyl Radicals with several Drinking Water Contaminants", *Environmental science & technology,* vol. 26, pp. 1005-1013.

Haber F., W.J. "The catalytic decomposition of hydrogen peroxide by iron salts", *Proc. Roy. Soc.,* vol. 64, pp. 1105-1129.

Hatchard C. G., Parker C. A. 1956, "A sensitive chemical actinometer II. Potassium ferrioxalate as a standard chemical actinometer", *Proc. Roy. Soc.,* .

Hawker P. N., Twigg M. V. 1994, "Iron: inorganic & coordination chemistry" in *Enceclopedia of Inorganic chemistry*, ed. King P. B.,Chichster, pp. 1698-1725.

Henze M., Harremöes P., et al. 2000, *Wastewater treatment: Biological and chemical processes,* 3rd edn, Springer Verlag, Berlin.

Hernando, M.D., Malato, O., Farre, M., Fernandez-Alba, A.R. & Barcelo, D. 2006, "Application of ring study: Water toxicity determinations by bioluminescence assay with Vibrio fischeri", *Talanta,* vol. 69, no. 2, pp. 370-376.

Hincapié M., Maldonado M. I., et al. 2005, "Solar photocatalytic degradation and detoxification
of EU priority substances", *Catalysis Today,* , no. 101, pp. 203-210.

Howard, P.H. 1991, "Handbook of Environmental Fate and Exposure Data for Organic Chemicals: Pesticides" in , ed. Lewis Publishers, Lewis Publishers, Chelsea, pp. 3-15.

Iqbal M. 1983, "An introduction to Solar Radiation", *Academic Press,* .

Kavitha V., P.K. 2004, "The role of ferrous ion in Fenton and photo-Fenton processes for degradation of phenol", *Chemosphere,* vol. 55, pp. 1235-1243.

Kidd H., James D. R. 1991, "The Agrochemicals Handbook" in , ed. Royal Society of Chemistry Information Services, 3rd edn,Cambridge, pp. 3-11.

Kositzi, M., Poulios, I., Malato, S., Caceres, J. & Campos, A. 2004, "Solar photocatalytic treatment of synthetic municipal wastewater", *Water research,* vol. 38, no. 5, pp. 1147-1154.

Krautter M., N.L. 2008, "Die Schwarze Liste der Pestizide Spritzmittel", *Greenpeace Magazin,* .

Kremer M. L., Stein G. 1977, "Kineticsof the Fe^{3+} ion- H_2O_2 reaction: steady state and terminal-state analysis", *Int. J. Chem. Kinet.,* vol. 9, pp. 179-184.

Kremer M. L., Stein G. 1962, "Nature of intermediates in the catalytic decomposition of hydrogen peroxide by ferric ions", *Trans. Faraday Soc.,* vol. 58, pp. 702-707.

Kremer M. L., Stein G. 1959, "The catalytic decomposition of hydrogen peroxide by ferric perchlorate", *Trans. Faraday Soc.,* vol. 55, pp. 959-973.

Krýsová H. et al. 2003, "Comparative kinetic study of atrazine photodegradation in aqueous Fe(CL4)3 solutions and TiO2 suspensions", *Applied Catalysis B: Environmental,* , no. 40.

Lapertot, M., Ebrahimi, S., Oller, I., Maldonado, M.I., Gernjak, W., Malato, S. & Pulgarin, C. 2008, "Evaluating Microtox as a tool for biodegradability assessment of partially treated solutions of pesticides using Fe3+ and TiO2 solar photo-assisted processes", *Ecotoxicology and environmental safety,* vol. 69, no. 3, pp. 546-555.

Lapertot, M., Pulgarin, C., Fernandez-Ibanez, P., Maldonado, M.I., Perez-Estrada, L., Oller, I., Gernjak, W. & Malato, S. 2006, "Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton", *Water research,* vol. 40, no. 5, pp. 1086-1094.

Legrini O., Oliveros E., et al. 1993, "Photochemical Processes for Water Treatment", *Chem. Rev.,* vol. 93, pp. 671-698.

Malato, S. 2004, "Photocatalytic Reactors for the Treatment of liquid Wastewater in the presence of Solar Irradiation.", [Online],

Malato, S., Blanco, J., Maldonado, M.I., Oller, I., Gernjak, W. & Perez-Estrada, L. 2007, "Coupling solar photo-Fenton and biotreatment at industrial scale: main results of a demonstration plant", *Journal of hazardous materials,* vol. 146, no. 3, pp. 440-446.

Malato, S., Caceres, J., Fernandez-Alba, A.R., Piedra, L., Hernando, M.D., Aguera, A. & Vial, J. 2003, "Photocatalytic treatment of diuron by solar photocatalysis: evaluation of main intermediates and toxicity", *Environmental science & technology,* vol. 37, no. 11, pp. 2516-2524.

Maldonado, M.I., Malato, S., Perez-Estrada, L.A., Gernjak, W., Oller, I., Domenech, X. & Peral, J. 2006, "Partial degradation of five pesticides and an industrial pollutant by ozonation in a pilot-plant scale reactor", *Journal of hazardous materials,* vol. 138, no. 2, pp. 363-369.

Mallinckrodt Chemicals 2006, *Maleic Acid*.

Mazellier P., S.B. "Diuron degradation in irradiated, heterogeneous iron/oxalate systems: The rate determining step", *Environmental science & technology,* vol. 35, pp. 3314-3320.

Minero C., Pelizzetti E., et al. 1993, "Large Solar Plant photocatalytic water decontamination: Degradation of Pentachlorophenol", *Chemosphere,* vol. 26, pp. 2103-2119.

Mosteo, R., Gumy, D. & Pulgarin, C. 2008, "Coupled photo-Fenton-biological system: effect of the Fenton parameters such as residual H2O2, Fe2+ and pH on the efficiency of biological process", *Water science and technology : a journal of the International Association on Water Pollution Research,* vol. 58, no. 8, pp. 1679-1685.

Munoz, I., Peral, J., Ayllon, J.A., Malato, S., Passarinho, P. & Domenech, X. 2006, "Life cycle assessment of a coupled solar photocatalytic-biological process for wastewater treatment", *Water research,* vol. 40, no. 19, pp. 3533-3540.

Muschaweck J., Spirkl W., et al. 2000, "Ptimized reflectors for non-tracking solar collectors with tubular absorbers", *Sol. Energy,* , no. 68, pp. 151-159.

Nogueira, R.F., Oliveira, M.C. & Paterlini, W.C. 2005, "Simple and fast spectrophotometric determination of H(2)O(2) in photo-Fenton reactions using metavanadate", *Talanta,* vol. 66, no. 1, pp. 86-91.

Oller I., Fernandez-Ibánez P., et al. 2006, "Solar heterogeneous and homogeneous photocatalysis as a pre-treatment option for biotreatment", *Res. Chem. Interm.,* .

Oller, I., Gernjak, W., Maldonado, M.I., Perez-Estrada, L.A., Sanchez-Perez, J.A. & Malato, S. 2006, "Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale", *Journal of hazardous materials,* vol. 138, no. 3, pp. 507-517.

Oller, I., Malato, S., Sanchez-Perez, J.A., Maldonado, M.I., Gernjak, W. & Perez-Estrada, L.A. 2007, "Advanced oxidation process-biological system for wastewater containing a recalcitrant pollutant", *Water science and technology : a journal of the International Association on Water Pollution Research,* vol. 55, no. 12, pp. 229-235.

Pacheco K., Watt A. S., Turchi C. S. 1993, "Solar Detoxification of Water: Outdoor Testing of Prototype Photoreactors", *ASME/ASES Joint Solar Energy Conference,* , pp. 43-49.

Pignatello J., Oliveros E., et al. 2006, "Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry", *Critical Reviews in Environmental Science and Technology,* vol. 36, pp. 1-84.

Pulgarin C., Intervernizzi M., et al. 1999, "Strategy for the coupling of photochemical and biological flor reactions useful in mineralization of biorecalcitrant industrial pollutants", *Catalysis Today,* vol. 54, pp. 341-352.

Raquel F. Pupo Nogueira & José Roberto Guimarães 2000, "Photodegradation of dichloroacetic acid and 2,4-dichlorophenol by ferrioxalate/H_2O_2 system", *Water research,* vol. 34, no. 3, pp. 895-901.

Ribo J. M. & Kaiser K. 2006, "*Photobacterium phosphoreum* toxicity bioassay. I. Test procedures and applications", *Environmental Toxicology & Water Quality,* .

Safarzadeh-Amiri A., Bolton J. R., et al. 1996, "The use of iron in Advanced Oxidation Processes", *J. Adv. Oxid. Technol.,* vol. 1, pp. 18-26.

Sai Wei Lam, Ken Chiang, et al. 2005, "The role of ferric ion in the photochemical and photocatalytic oxidation of resorcinol", *Journal of Catalysis,* , no. 234, pp. 292-299.

Sandel E.B. (ed) 1959, *Colorimetric Determination of Traces of Metals*, 3rd edn, Interscience Publishers, New York.

Sirtori, C., Zapata, A., Oller, I., Gernjak, W., Aguera, A. & Malato, S. 2009, "Decontamination industrial pharmaceutical wastewater by combining solar photo-Fenton and biological treatment", *Water research,* vol. 43, no. 3, pp. 661-668.

Sulzberger B., Laubscher H., et al. 1994, "Photoredox reactions at the surface of iron (III)(hydr-)oxides" in *Aquatic and surface photochemistry*, ed. Helz G. R., Zepp R. G., Lewis Publishers, , pp. 53-74.

Sychev A. Y., Isaak V. G. 1995, "Iron compounds and mechanisms of the homogeneous catalysis of the activation of O_2 and H_2O_2 and of the oxidation of organic substrates", *Russ. Chem. Rev.,* vol. 64, pp. 1105-1129.

Tout D. 1990, "The horticulture industry of Almeria Province", *The geographical journal,* vol. 156, no. 3, pp. 304-312.

U.S. Environmental Protection Agency 1987, *Health Advisory Summary: Methomyl*, Office of Drinking Water, Washington.

U.S. Environmental Protection Agency 1987, *Health Advisory Summary: Oxamyl*, Office of Drinking Water, Washington.

von Sonntag, C. 2008, "Advanced oxidation processes: mechanistic aspects", *Water science and technology : a journal of the International Association on Water Pollution Research,* vol. 58, no. 5, pp. 1015-1021.

Wang, Y., Liu, C.S., Li, F.B., Liu, C.P. & Liang, J.B. 2009, "Photo degradation of polycyclic aromatic hydrocarbon pyrene by iron oxide in solid phase", *Journal of hazardous materials,* vol. 162, no. 2-3, pp. 716-723.

Wauchope R. D., Buttler T. M, Hornsby A. G., 1992, "SCS/ARS/CES pesticides properties database for environmental decision making", *Rev. Environ. Contam. Toxicol.,* , no. 123, pp. 3-14.

Well M., Dillert R. H. G., et al. 1994, "A novel non-concentrating reactor for solar water detoxification", *J.Sol. Energ.-T ASME,* , no. 119, pp. 8-13.

Zapata A., Oller I. & et al. 2008, "Comparison of Photo-Fenton Treatment and Coupled Photo-Fenton and Biological Treatment for Detoxification of Pharmaceutical Industry Contaminants", *J. Adv. Oxid. Technol.,* vol. 11, no. 2.

Zaror, C., Segura, C., Mansilla, H., Mondaca, M.A. & Gonzalez, P. 2008, "Effect of temperature on Imidacloprid oxidation by homogeneous photo-Fenton processes", *Water science and technology : a journal of the International Association on Water Pollution Research,* vol. 58, no. 1, pp. 259-265.

Zepp R. G., Faust B. C., Hoigne J. 1992, "Hydroxyl radical formation in aqueous reactions (ph 3-8) of iron (II) with hydrogen peroxide: The photo-Fenton reaction", *Environmental science & technology,* vol. 26, pp. 313-319.