UNIVERSITY OF ALMERÍA
Department of Hydrogeology & Analytical Chemistry

in collaboration with

PLATAFORMA SOLAR DE ALMERIA
"Environmental Applications of Solar Energy" group

APPLICATION OF A SOLAR PHOTO-FENTON FOR THE TREATMENT OF CONTAMINANTS IN MUNICIPAL WASTEWATER EFFLUENTS

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APLICACIÓN DE FOTO-FENTON SOLAR PARA EL TRATAMIENTO DE CONTAMINANTES EN EFLUENTES DE EDAR

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We wish to pursue the truth no matter where it leads, but to find the
truth we need imagination and scepticism both.
We will not be afraid to speculate, but we will be careful to
distinguish speculation from fact.

Carl Sagan

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TABLE OF CONTENTS

INDEX OF TABLES

INDEX OF FIGURES

Abstract

This work investigated the application of a solar driven advanced oxidation process, (photo-Fenton) for the degradation of micro and emerging contaminants in municipal wastewater treatment plant effluents. As normal municipal wastewater treatment plants are not able to entirely degrade xenobiotic substances like pesticides, pharmaceuticals, fragrances, personal care products etc., it is necessary to treat the effluents to eliminate them. It is a well known fact that photo-Fenton is capable of degrading almost any organic contaminant, but the main drawback of this process is that it only works well at pH 3 for keeping iron dissolved and promoting light-absorbing Fe-water complexes. Besides, the main operational costs of photo-Fenton are related with hydrogen peroxide consumption. This research was conducted whether a modified photo-Fenton at neutral pH using low iron concentration and a low hydrogen peroxide dose was efficient enough for the removal of micro and emerging contaminants, jointly with attaining water disinfection.

To achieve this, 15 compounds were selected as model contaminants out of more than 80 contaminants present in MWTP effluents and treated at low initial concentrations (100 and 5 µg L^{-1}) in different water matrices. As municipal wastewater treatment plant effluents are a complex mixture, a step by step approach from deionised water to real municipal wastewater treatment plant effluent water was applied to clarify the possible negative impacts of the water matrix, like organic content, carbonates etc. onto the degradation behaviour of the selected contaminants. The experiments were performed in compound parabolic collector (CPC) solar pilot plants designed for solar photocatalytic applications at the Plataforma Solar de Almería, in southern Spain. The process was mainly evaluated by a fast and robust analytical method based on Solid Phase Extraction and a UPLC-UV/DAD system. It was validated by using a HPLC-Qtrap-MS applied for the analysis of the evolution of contaminants in real wastewater treatment plant effluents.

Although it was possible to degrade contaminants in some real effluent waters at neutral pH, the complete degradation below LOD was not achieved, and as a general rule the neutral pH was not adequate for the process due to iron precipitation and/or inhibition of the formation of suitable Fe-water complexes. To circumnavigate the negative effect of the neutral pH, several complexing compounds were investigated. These compounds (oxalic acid, humic acid and EDDS) had the purpose to form complexes with the iron, thus making it available for the photo-Fenton process. The use of oxalic acid had a positive impact onto the degradation of the contaminants, but the residual pH after the process was quite low (pH 4). Humic acids too had a beneficial impact onto the degradation, but none of the tested concentrations delivered satisfactory results. Experiments conducted with both oxalic acid and humic acid in effluent waters containing carbonates/bicarbonates showed that the contaminants could not be degraded sufficiently, due to the scavenging effects of the carbonates/bicarbonates on hydroxyl radicals formed during the process. EDDS delivered in both water containing natural carbonates/bicarbonates and in water without carbonates/bicarbonates (stripped with acid) satisfactory results. One drawback though was the increased DOC of the treated waters, as EDDS has to be added in at least the same molar concentration as iron to deliver good results.

Another part of this work was the evaluation of the disinfection power of the process taking into account total bacteria and total coliforms. Typical photo-Fenton was sufficient to disinfect the water (colony forming units < 1 mL^{-1}). In all other processes, the CFU declined at least 2-log degrees reaching in most cases a CFU lower than 10^2 CFU mL^{-1}, but did not reach LOD of 1 CFU mL^{-1}.

Resumen

En este trabajo se ha investigado la aplicación de un proceso avanzado de oxidación (foto-Fenton) para la degradación de microcontaminantes y contaminantes emergentes en efluentes de depuradoras municipales (EDAR). Como las EDARs no son capaces de eliminar completamente estos compuestos (plaguicidas, fármacos, fragancias, productos de higiene personal, etc) es necesario tratar sus efluentes. Es conocido que el proceso de foto-Fenton es capaz de degradar casi cualquier contaminante, pero su principal inconveniente es que debe operarse a pH cercano a 3 para mantener el hiero en disolución y poder formar complejos fotoactivos. Además, el peróxido de hidrógeno necesario para ello es el principal coste de operación. Por tanto, esta investigación se ha dirigido hacia el desarrollo de un proceso de foto-Fenton modificado para operar a pH cercano a la neutralidad, a baja concentración de hierro y con la menor cantidad de peróxido de hidrógeno posible. Todo ello para eliminar microcontaminantes y contaminantes emergentes, además de alcanzar la desinfección del agua.

Para conseguir esto, se seleccionaron 15 compuestos como modelo para entre 80 encontrados habitualmente en efluentes de EDAR y se trataron a baja concentración (100 y 5 µg L^{-1}) en diferentes matrices acuosas. Como los efluentes de EDAR son complejos y variados, se procedió por pasos desde agua desionizada hasta efluente real para aclarar en la medida de lo posible el impacto de la composición del agua (contenido orgánico, carbonatos, etc) sobre el proceso. Los experimentos se realizaron en una planta piloto solar con captadores parabólicos compuestos (CPC) diseñados APRA aplicaciones fotocatalíticas en la Plataforma Solar de Almería. El proceso se evaluó principalmente mediante un método robusto y rápido basado en Extracción en Fase Sólida y Cromatografía Líquida (UPLC/DAD). Y se validó mediante HPLC-Qtrap-MS aplicado a la evolución de los contaminantes presentes en efluente s reales.

Aunque se consiguió eliminar contaminantes en algunos efluentes reales a pH neutro, la degradación completa por debajo del LOD no se alcanzó y, como regla general, el pH neutro no fue adecuado debido a la precipitación del hierro y/o inhibición de la formación de aquocomplejos adecuados. Para solventar el efecto negativo del pH neutro se ensayaron diferentes agentes complejantes. Estos compuestos (ácido oxálico, ácidos húmicos y EDDS) tenían como propósito formar complejos con el hierro para que estuviera disponible para el proceso de foto-Fenton. El uso de ácido oxálico tuvo un impacto positivo en la degradación de los contaminantes pero el pH final resulto muy bajo (pH = 4). Los ácidos húmicos también tuvieron un efecto beneficioso en la degradación, pero ninguna de las concentraciones ensayadas llevó a un resultado satisfactorio. En cualquiera de los casos, los experimentos mostraron que si el agua contenía carbonatos/bicarbonatos los contaminantes no se degradaban lo suficiente debido a la captura de los radicales hidroxilo formados. El EDDS mostró eficacia tanto en agua con carbonatos/bicarbonatos como en ausencia de ellos después de haber tratado el agua con ácido para su eliminación. Un inconveniente fue el aumento de COD en el agua tratada, ya que el EDDS debe ser añadido en una concentración equimolar con el hierro.

Otra sección de este trabajo se dedicó a la evaluación de la desinfección durante el proceso mediante la medición de bacterias totales y coliformes totales. Un tratamiento de foto-Fenton convencional es capaz de desinfectar el agua (por debajo de 1 CFU mL^{-1}). En todos los demás casos, CFU disminuyeron al menos dos órdenes de magnitud alcanzando en muchos de los casos menos de 10^2 CFU mL^{-1}, pero no el límite de detección (1 CFU mL^{-1}).

Objectives

In the last decade due to the increasing sensitivity of analytical instrumentals, an ever increasing number of contaminants have been found in waste water, surface water and even ground water. Special attention has recently been given to what are called emerging contaminants. These are mostly unregulated compounds which may be candidates for future regulations and consist of a wide range of substances and include pharmaceuticals, personal care products, synthetic fragrances etc. These contaminants are present in waters in increasing concentrations up to µg L^{-1}. The presence of these contaminants in water bodies can have huge impacts onto aquatic life and as a consequence onto human health in the long run. It may have even more impact onto humans, if waters, which contain these contaminants, are used for irrigation, as water scarcity becomes an ever increasing problem. These contaminants are hardly biodegradable and resist treatment by conventional sewage treatment plants. And even if these substances are biodegradable, their constant release into wastewater battles the degradation process. Possible ecological problems are microbiological resistance, accumulation in soils, bioaccumulation in plants and animals, feminization of higher organisms, as many of these substances have endocrine disrupting abilities, etc. It is therefore important to degrade these contaminants prior to their release into the environment, and even more so it the water is reused for irrigation. If waters are subject to reuse, they also have to be disinfected. For these reasons, the application of more thorough wastewater treatment protocols, including the use of new and improved technologies, is a necessary task.

Among the treatment technologies for the degradation of waters, advanced oxidation processes (AOPs) present a particularly attractive option. In the area of advanced oxidation processes and their applications for the treatment of contaminated waters, the photo-Fenton process has been proven to be an effective treatment for a large number of organic substances like phenols, halogenated compounds, pesticides, antibiotics, dyes, etc. The usual drawbacks for the AOPs are high electricity demand for devices such as UV-lamps, ozonators, large amounts of oxidants and catalysts, as well as the low pH operating conditions for Fenton and photo-Fenton. Photo-Fenton efficiency for the removal of contaminants in water has been usually studied in demineralised water at initial concentrations in the milligram-to-gram range, which is not realistic compared to the concentrations detected in real water and wastewater. In this context, the principal objectives of this work were to develop a mild solar powered photo-Fenton process which can operate at neutral pH, low iron concentrations and low initial peroxide concentration, which is capable of degrading contaminants in water and disinfect it.

To achieve this, several sub objectives had to be evaluated:

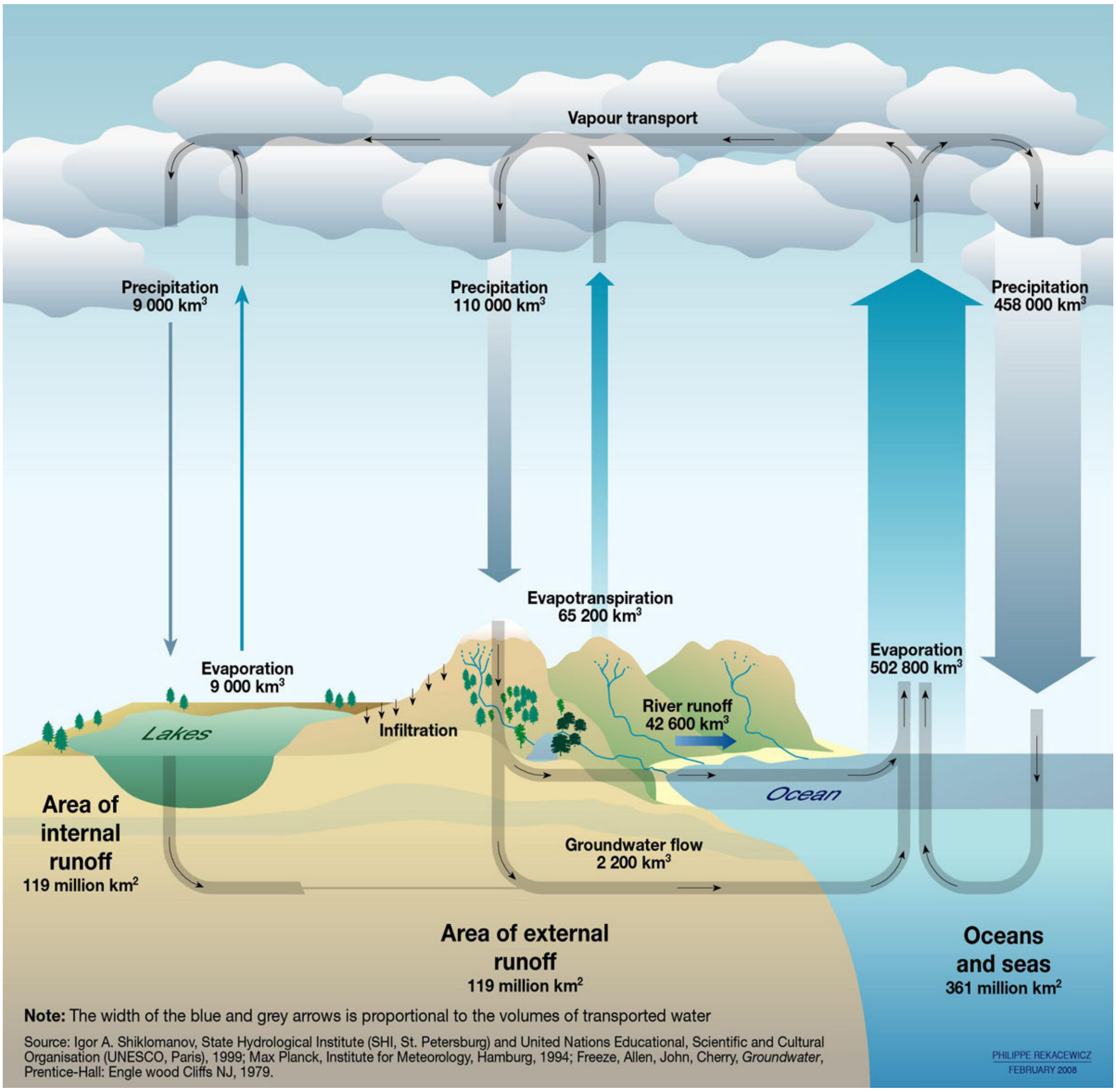
- The selection of a number of contaminants as model compounds frequently present in municipal wastewater treatment plants.
- Development of a fast and reliable method for their determination at very low concentration levels with a HPLC/UV system.
- Degradation of these model compounds by solar photo-Fenton in different water matrices (deionised water, simulated fresh water, simulated effluent water and real effluent water) and the evaluation of the impact of the composition of water onto the degradation behaviour (organic matter, carbonates etc.).
- Evaluation of the degradation behaviour of contaminants at neutral pH by solar photo-Fenton.
- Evaluation of the use of biodegradable, nontoxic compounds which are capable of complexing iron and improving the photo-Fenton process at neutral pH.
- Evaluation of disinfection efficiency of the abovementioned processes.
- Evaluation of possible toxic side effects of the treated waters.

1 Introduction

1.1 Water and the environment

Through the water cycle (see Figure 1.1), which consists of precipitation, vapour transport, evaporation, evapo-transpiration, infiltration, groundwater flow and runoff, water is transported from the oceans back to land and precipitates as rain, which in turn fills up lakes, rivers and groundwater basins, making it available as freshwater for plants, animals and humans [UNEP, 2010]. Nearly 577,000 km^3 of water circulates through the cycle each year. The availability of this freshwater is the driving force in the development of human culture and the access to water has been declared a fundamental human right, but clean water supplies and sanitation is still a major problem. Although the United Nations General Assembly declared on 28 July 2010 that safe and clean drinking water and sanitation is a human right essential to the full enjoyment of life and all other human rights, 2.5 billion People are without improved sanitation, more than 20% of the world's population lack access to safe drinking water. As a consequence polluted waters affect the health of more than 1.2 billion people, and 1.5 million children die every year from diseases related to and associated with inadequate sanitation and poor hygiene. [WHO, 2008]

On the other hand, water seems to be the one resource which is infinite in this world. But on the blue planet, most of the water is saltwater (see **Figure 1.2**). Various estimates [Shiklomanov and Gleick, 1999] have calculated that the total volume of water on Earth is ~1.4 billion km^3, 2.5 % of this volume, or ~35 million km^3 is fresh water. Of these freshwater resources, 24 million km^3 or 68.9% is in the form of ice and permanent snow cover in mountainous regions, the Arctic and Antarctic regions. Some 8 million km^3 or 30.8% is stored underground in the form of groundwater (shallow and deep groundwater basins up to 2000 meters, soil moisture, swamp and permafrost water). This constitutes about 99.7% about of all the freshwater potentially available for human use.



Note: The width of the blue and grey arrows is proportional to the volumes of transported water

Source: Igor A. Shiklomanov, State Hydrological Institute (SHI, St. Petersburg) and United Nations Educational, Scientific and Cultural Organisation (UNESCO, Paris), 1999; Max Planck, Institute for Meteorology, Hamburg, 1994; Freeze, Allen, John, Cherry, *Groundwater*, Prentice-Hall: Engle wood Cliffs NJ, 1979.

Figure 1.1 The global water cycle

Freshwater lakes and rivers contain an estimated 0.3% of the worlds freshwater resources, the total usable freshwater supply for ecosystems and humans is $2 \cdot 10^5$ km^3 of water, which is <1% of all freshwater resources, and only 0.01% of all the water on earth.

So the seemingly infinite abundant resource is not so abundant at all, and in some places it is becoming increasingly scarce.

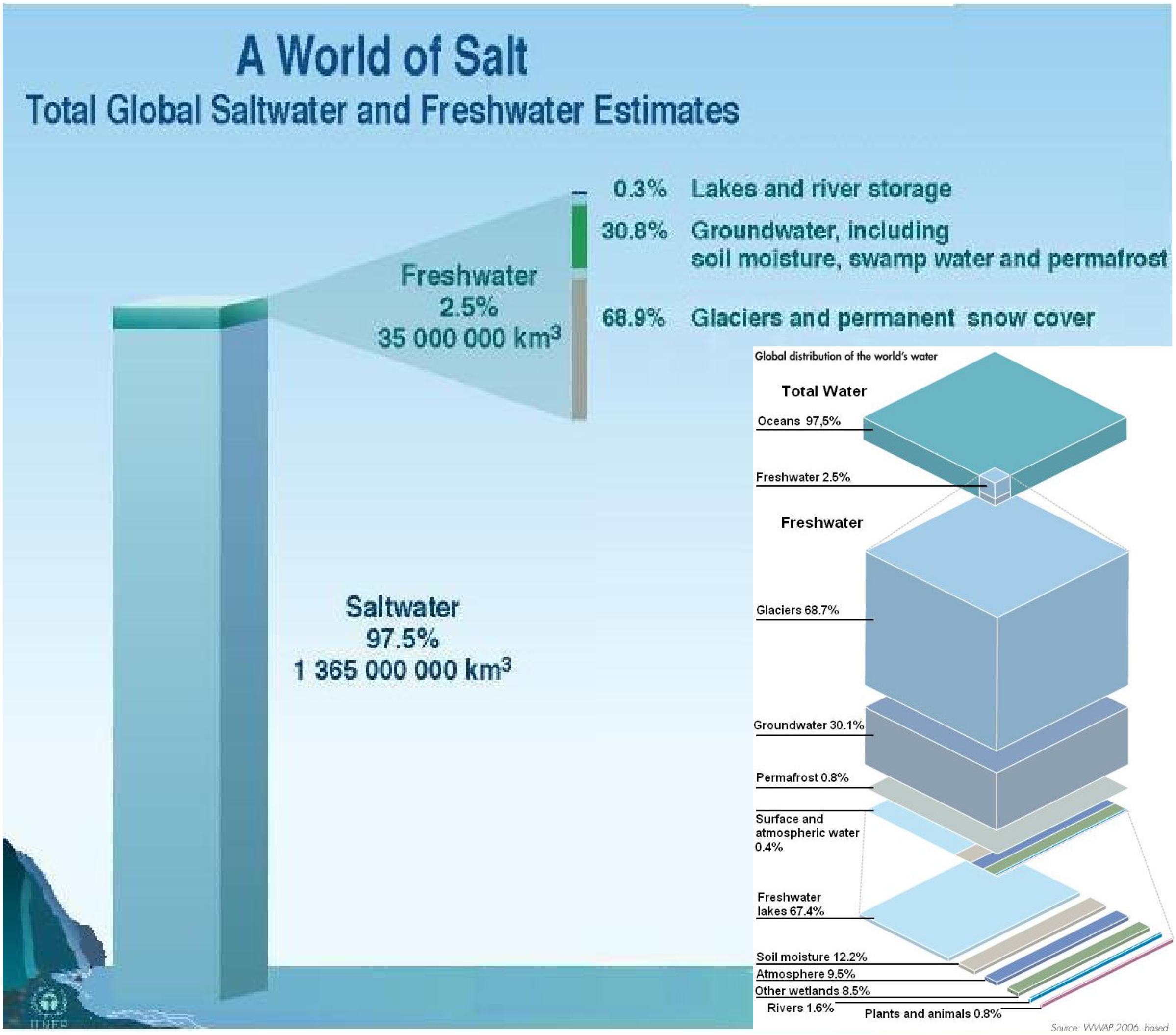


Figure 1.2 A world of salt. Total global Saltwater and Freshwater estimates

And the human race does everything in its power, or so it seems, to even reduce the scarce resource some more, by polluting water, by deforestation and surface sealing which leads to rain runoffs, excessive water abstractions and old fashioned irrigation, which leads to loss of more than 80% of the applied water, salinisation of soils and following desertification, which even enhances the problem of water scarcity and stress, as it changes the microclimate and rainfall in the affected regions. A good, or one might say bad example, is the shrinking of the Aral Sea in the former Soviet Union, now between Uzbekistan and Kazakhstan. It is one of the biggest environmental disasters caused by man in this world. Between 1960 and 2009 the

Aral Sea lost more than 90% of its original surface. Prior to 1960 an average of 55.000 million m^3 of water flowed into the Aral Sea per year.

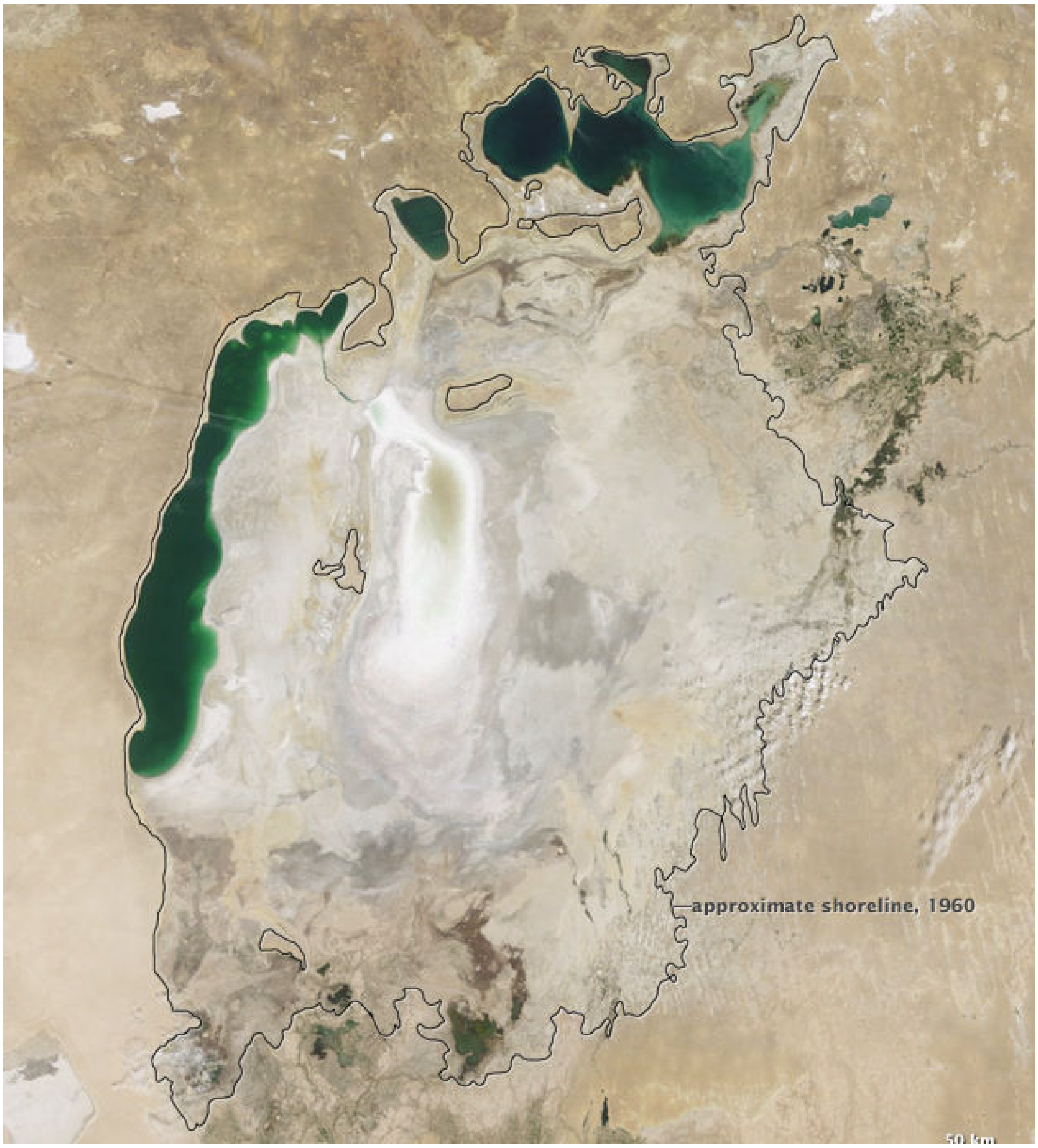


Figure 1.3 The shrinking of the Aral Sea.

Irrigation for the cotton fields and the construction of storage dams resulted in an average 7.000 million m^3 annual flow. The result was a sea level drop of 16 meters between 1962 and 1994 and the desertification of the whole area [NASA, 2010].

Since 1900, world population has doubled yet the amount of fresh water used has increased more than six-fold. Agriculture is by far the largest consumer of water, mostly because of the spread of irrigation.

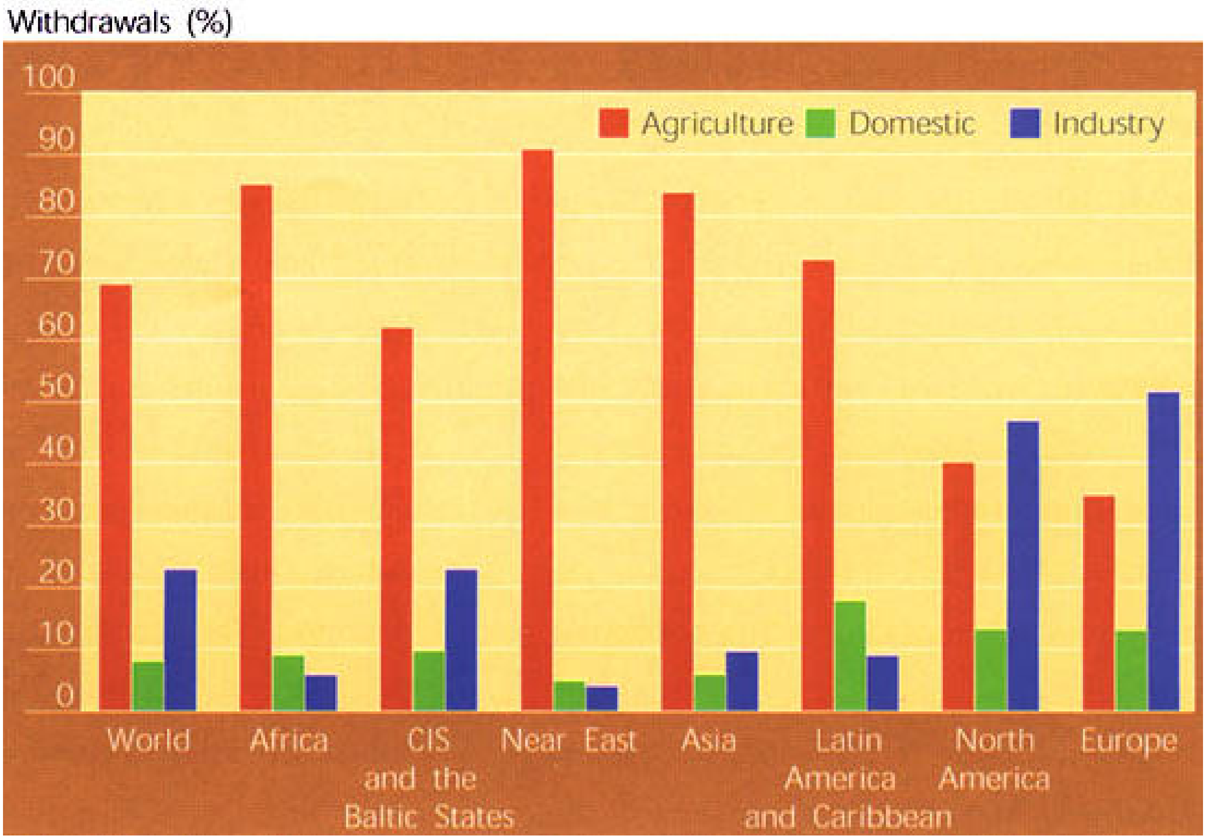


Figure 1.4 Water withdrawals for agriculture, industry and domestic use.

More than two-thirds of all the water consumed in the world is used in the agricultural sector (70-75%), a share expected to shrink only slightly by 2025. More efficient irrigation techniques are clearly the first and crucial step to reducing water use. 20-25% of the water is used by the industry, while the rest (5-10%) is used for direct domestic use. Of the water withdrawn for industry, about 5 percent is consumed; of the water withdrawn for municipal use, about 10 percent is consumed; of the water withdrawn for agriculture, consumption varies between 30 and 90 percent depending on the technology used [FAO, 2010].

Actually the relationship between the use and consumption and the extraction and exploitation of water shows a great gap. The use of fresh water in each continent depends on various socioeconomic factors like development, geographical characteristics, climate and demographic factors. The world's annual water exploitation has risen between 1995 and 2000 from 3790 km^3 to 4430 km^3 and is expected to raise 10-12% every 10 years to approximately 5240 km^3 in 2025. It is estimated, that water efficiency in the EU could be improved by nearly 40% through technological improvements alone and that changes in human behaviour or production patterns could further increase such savings.

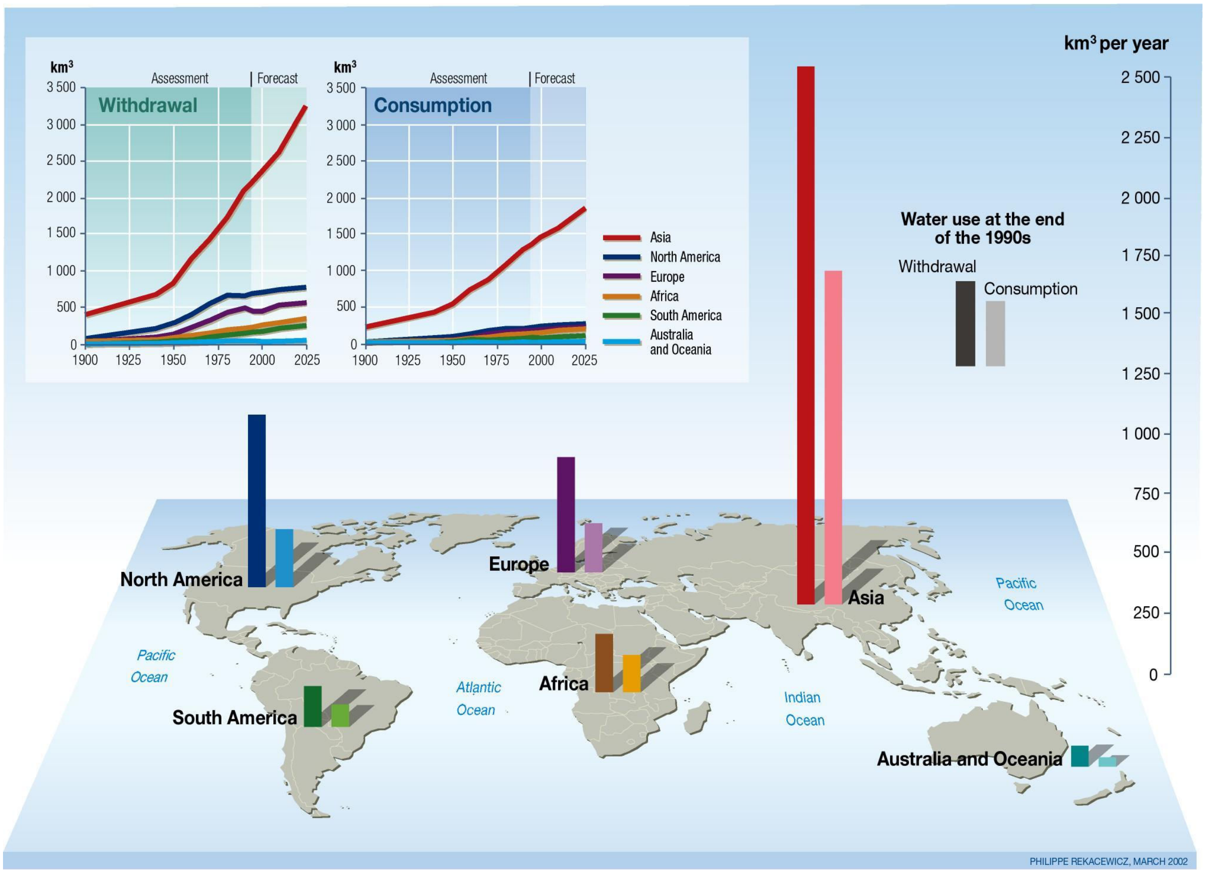


Figure 1.5 Worldwide water withdrawal and consumption.

In a business as usual scenario the study estimates that water consumption by the public, industry and agriculture would increase by 16% by 2030. Conversely, the use of water-saving technologies and irrigation management in the industrial and agricultural sectors could reduce excesses by as much as 43% [European Commission, Environment 2010].

The concept of water stress is based on the minimal necessities of water per capita which permits to maintain the quality of life in moderately developed regions. This definition considers 100 L per day and capita as a reference number for the minimal daily consumption for a region not to suffer from water stress. This number varies considerably depending on the climate, hydrological conditions, economic development and so forth and can be influenced by environmental programs and the use of efficient technologies for water reuse. It is estimated that by 2025 every one in two people will live in water stressed areas, in Africa alone it is estimated that 25 countries experiencing water stress (below 1.7 m^3 per capita per year) by 2025 [UNEP, 2008] As of 2002, 450 million people in 29 countries suffer from water shortages. Today, 2.3 billion people live in water-stressed areas. If current trends continue, water stress will affect 3.5 billion - or 48 percent of the world's projected population in 2025 [World Resources Institute; UNEP, 2010].

The raising demand of water, its association with the decline in river flows and the overexploitations of aquifers as well as the decline in water quality and contamination are problems which need to be addressed and solved urgently. Nowadays, there are numerous regions in the world where the abundant water bodies (rivers, lakes and aquifers) are contaminated and thus are unsuitable for human use. The main part of the pollution in these waters comes from human wastes (more than 2 million tons per day), followed by industrial wastes, chemical products and finally pesticides [UNESCO, 2003]. An example of this can be seen in the Yamuna River in India, which flows through New Delhi. Through the high population growth in recent years, the absence of almost any kind of waste water treatment and the rapid industrialization, the Yamuna River has become one of the most polluted rivers on earth. New Delhi dumps around 60% of its waste directly into the river, making it an "open sewer" [Rahul Upadhyay et al, 2010].

1.2 The European Water Framework Directive and its amendments

To battle water stress and water contamination and to maintain good water quality in the river basins, the European Union implemented the first Water Framework Directive (WFD) in 2000 [Directive 2000/60/EC] and amended it in 2008 [2008/32/EC Amendment of the Directive 2000/06/EC]. The WFD establishes a legal and binding directive for the protection of subterranean, superficial, coastal and estuary waters. The purpose of this Directive is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater which:

(a) prevents further deterioration and protects and enhances the status of aquatic ecosystems and, with regard to their water needs, terrestrial ecosystems and wetlands directly depending on the aquatic ecosystems;

(b) promotes sustainable water use based on a long-term protection of available water resources;

(c) aims at enhanced protection and improvement of the aquatic environment, through specific measures for the progressive reduction of discharges, emissions and losses of priority substances (PS) and the cessation or phasing-out of discharges, emissions and losses of the priority hazardous substances (PHS);

(d) ensures the progressive reduction of pollution of groundwater and prevents its further pollution, and

(e) contributes to mitigating the effects of floods and droughts and thereby contributes to: -the provision of the sufficient supply of good quality surface water and groundwater as needed for sustainable, balanced and equitable water use,

-a significant reduction in pollution of groundwater,

-the protection of territorial and marine waters, and

-achieving the objectives of relevant international agreements, including those which aim to prevent and eliminate pollution of the marine environment, by Community action under Article 16(3) to cease or phase out discharges, emissions and losses of priority hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances.

It is the hope that all targets are reached as proposed in the self implemented timetable by 2015, yielding the maintenance and/or enhancement of the water quality in all EU member states, and after 2015 that the plans are reviewed on a 6 year basis.

In addition to the WFD, the directive 2455/2001/EC [Directive 2455/2001/EC] identifies and lists 33 priority substances (PS) or groups of substances which are of major concern to the aquatic environment (see **Table 1.1**). Within this list, 20 substances have been identified as priority hazardous substances (PHS) which are of particular concern for the inland, transitional, coastal and territorial waters. These substances will be subject to cessation or phasing out of discharges, emissions and losses within an appropriate timetable that shall not exceed 20 years. A further 13 substances were identified as being subject to review for identification as possible "priority hazardous substances" (see **Table 1.2**). This list is kept under revision and is readapted every four years. The original list of the priority substances includes various pesticides, polycyclic aromatic hydrocarbons (PAH), benzenes, halogenated solvents, flame retardants, plasticizers (phthalates), surfactants, antifouling products and some heavy metals [Directive 2000/60/EC; Directive 2001/2455/EC,].

Recently, at the end of 2008, the European Commission approved a new Directive [Directive 2008/105/EC] on Priority Substances and Certain Other Pollutants (According to Annex II of the Directive 2008/105/EC) on environmental quality standards in the field of water policy which amends and subsequently repeals the Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amends Directive 2000/60/EC of the European Parliament and of the Council. This Directive lays down environmental quality standards (EQS) for priority substances and certain other pollutants as provided for in Article 16 of

Directive 2000/60/EC. The aim is to achieve good surface water, in accordance with the objectives specified in article 4 of the Directive.

-According to Annex V, point 1.4.3 of the WFD and Article 1 of the Priority Substances Directive, good chemical status is reached for a water body when compliance with all environmental quality standards for the priority substances and other pollutants listed in Annex I of this directive is achieved. The main provisions laid down by this directive are the following:

-Settlement of the limits on concentrations in surface waters of 33 PS and 8 other pollutants;

-Annex II listing the 33 PS will become Annex X of the Water Framework Directive;

-Environmental quality standards for sediment and biota could be used instead of those for water;

-Necessity to designate mixing zones adjacent to discharge point where concentrations of the substances, mentioned above at the first bullet, may exceed;

-Necessity to establish an inventory of emissions, discharges and losses of the substances, mentioned above at the first bullet, may exceed the agreed concentration limit;

-Next review of the list of PS together with the environmental quality standards for the new substances was achieved by 13 January 2011, results are still pending and it has not been updated until now.

Table 1.1 List of the priority Substances and other pollutants

Number	CAS Number (i)	EU number (ii)	Name of priority substance (iii)	Identified as PHS
(1)	15972-60-8	240-110-8	Alachlor	
(2)	120-12-7	204-371-1	Anthracene	X
(3)	1912-24-9	217-617-8	Atrazine	
(4)	71-43-2	200-753-7	Benzene	
(5)	not applicable	not applicable	Brominated diphenylether (iv)	X
	32534-81-9	not applicable	Pentabromodiphenylether (v) (congener numbers 28, 47, 99, 100, 153 and 154)	
(6)	7440-43-9	231-152-8	Cadmium and its compounds	X
(7)	85535-84-8	287-476-5	Chloroalkanes, C10-13 (iv)	X
(8)	470-90-6	207-432-0	Chlorfenvinphos	
(9)	2921-88-2	220-864-4	Chlorpyrifos (Chlorpyrifos-ethyl)	

(10)	107-06-2	203-458-1	1,2-Dichloroethane	
(11)	75-09-2	200-838-9	Dichloromethane	
(12)	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)	
(13)	330-54-1	206-354-4	Diuron	
(14)	115-29-7	204-079-4	Endosulfan	X
(15)	206-44-0	205-912-4	Fluoranthene (vi)	
(16)	118-74-1	204-273-9	Hexachlorobenzene	X
(17)	87-68-3	201-765-5	Hexachlorobutadiene	X
(18)	608-73-1	210-158-9	Hexachlorocyclohexane	X
(19)	34123-59-6	251-835-4	Isoproturon	
(20)	7439-92-1	231-100-4	Lead and its compounds	
(21)	7439-97-6	231-106-7	Mercury and its compounds	X
(22)	91-20-3	202-049-5	Naphthalene	
(23)	7440-02-0	231-111-4	Nickel and its compounds	
(24)	25154-52-3	246-672-0	Nonylphenols	X
	104-40-5	203-199-4	(4-nonylphenol)	X
(25)	1806-26-4	217-302-5	Octylphenols	
	140-66-9	not applicable	(4-(1,1',3,3'-tetramethylbutyl)-phenol)	
(26)	608-93-5	210-172-5	Pentachlorobenzene	X
(27)	87-86-5	201-778-6	Pentachlorophenol	
(28)	not applicable	not applicable	Polyaromatic hydrocarbons	X
	50-32-8	200-028-5	(Benzo(a)pyrene)	X
	205-99-2	205-911-9	(Benzo(b)fluoranthene)	X
	191-24-2	205-883-8	(Benzo(g,h,i)perylene)	X
	207-08-9	205-916-6	(Benzo(k)fluoranthene)	X
	193-39-5	205-893-2	(Indeno(1,2,3-cd)pyrene)	X
(29)	122-34-9	204-535-2	Simazine	
(30)	not applicable	not applicable	Tributyltin compounds	X
	36643-28-4	not applicable	(Tributyltin-cation)	X
(31)	12002-48-1	234-413-4	Trichlorobenzenes	
(32)	67-66-3	200-663-8	Trichloromethane (Chloroform)	
(33)	1582-09-8	216-428-8	Trifluralin	

(i) CAS: Chemical Abstracts Service.

(ii) EU number: European Inventory of Existing Commercial Substances (EINECS) or European List of Notified Chemical Substances (ELINCS).

(iii) Where groups of substances have been selected, typical individual representatives are listed as indicative parameters (in brackets and without number). For these groups of substances, the indicative parameter must be defined through the analytical method.

(iv) These groups of substances normally include a considerable number of individual compounds. At present, appropriate indicative parameters cannot be given.

(v) Only Pentabromobiphenylether (CAS number 32534 81 9).

(vi) Fluoranthene is on the list as an indicator of other, more dangerous polyaromatic hydrocarbons.

Table 1.2 Substances in revision for their possible identification as PS or PHS

CAS number	EU Number	Name of Substance
1066-51-9	-	Aminomethylphosphonicacid AMPA
25057-89-0	246-585-8	Bentazon
80-05-7	201-245-8	Bisphenol A
115-32-2	04-082-0	p,p'-Kelthane
60-00-4	200-449-4	EDTA
57-12-5	200-821-6	HCN
1071-83-6	213-997-4	Glycophosphate
7085-19-0	230-386-8	Mecoprop
81-15-2	201-329-4	Musk xylol
1763-23-1	217-179-8	Heptadecafluorooctanesulfonicacid PFOS
124495-18-7	-	Quinoxyfen
-	-	Dioxin
-	-	PCB

Table 1.3 Substances listed under the Annex to Directive 76/464/EEC

Number	CAS Number	EU Number	Name of substance
(6a)	56-23-5	200-262-8	Carbon-tetrachloride (1)
(9b)	not applicable	-	DDT total (1)(2)
	50-29-3	200-024-3	para-para-DDT (1)
(9a)			Cyclodiene pesticides
	309-00-2	206-215-8	Aldrin (1)
	60-57-1	200-484-5	Dieldrin (1)
	72-20-8	200-775-7	Endrin (1)
	465-73-6	207-366-2	Isodrin (1)
(29a)	127-18-4	204-825-9	Tetrachloro-ethylene (1)
(29b)	79-01-6	201-167-4	Trichloro-ethylene (1)

(1) This substance is not a priority substance but one of the other pollutants for which the EQS are identical to those laid down in the legislation that applied prior to 13 January 2009

(2) DDT total comprises the sum of the isomers 1,1,1-trichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 50-29-3; EU number 200-024-3); 1,1,1-trichloro-2 (o-chlorophenyl)-2-(p-chlorophenyl) ethane (CAS number 789-02-6; EU Number 212-332-5); 1,1-dichloro-2,2 bis (p-chlorophenyl) ethylene (CAS number 72-55-9; EU Number 200-784-6); and 1,1-dichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 72-54-8; EU Number 200-783-0).

Ten pollutants (see **Table 1.3**), which fall under the scope of Directive 86/280/EEC and are amended by Directive 88/347/EEC and Directive 90/415/EEC and which are included in List I of the Annex to Directive 76/464/EEC, are not in the priority substances list. Environmental quality standards for these substances are included in the Commission proposal to maintain the regulation of the substances at Community level.

Outside of the EU, there are several international juridical instruments, which have been adapted in the last 30 years with the goal to eliminate or limit the use of Persistent Organic Pollutants (POPs). The main initiatives were:

-The protocol to the 1979 convention on long-range trans-boundary air pollution (Air Pollution or LRTAP) [UNECE, LRTAP, 1979], adapted in 1998 in Aarhus (Denmark) as the Aarhus Protocol on Persistent Organic Pollutants [UNECE, Aarhus Protocol, 1998].

-The Rotterdam Convention on the prior informed consent procedure for certain hazardous chemicals and pesticides in international trade [EC, Rotterdam Convention, 1997].

-The Barcelona Convention for the Protection of the Mediterranean Sea against Pollution [UNEP, Barcelona Convention, 1976] which was signed 1976, enforced in 1978 and was revised in Barcelona, Spain, in 1995 as the Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean.

-The OSPAR convention, which started in 1972 with the Oslo Convention against dumping. It was broadened to cover land-based sources and the offshore industry by the Paris Convention of 1974. These two conventions were unified, up-dated and extended by the 1992 OSPAR Convention. The new annex on biodiversity and ecosystems was adopted in 1998 to cover non-polluting human activities that can adversely affect the sea [OSPAR commission, 1992].

-The London Convention (1972) and Protocol (1996), which is a Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter [International Maritime Organisation, 1996].

-The IFCS (Intergovernmental Forum on Chemical Safety) [WHO, 2006] which is a broad consensus-building mechanism that serves as a facilitator and advocate aiming to bring order to global actions taken in the interest of global chemical safety.

-And finally, the Stockholm Convention on Persistent Organic Pollutants [UNEP, Stockholm Convention, 2001] which was implemented 2001 and is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. It listed 12 POPs ("The Dirty Dozen") see **Table 1.4**, which have been recognized as causing adverse effects on humans and the ecosystem.

Table 1.4 List of the Persistent Organic Pollutants according to the Stockholm Convention

CAS Number	Name	Category(1)	Annex(2)
309-00-2	Aldrin	P	A
57-74-9	Chlordane	P	A
50-29-3	DDT	P	B
60-57-1	Dieldrin	P	A
72-20-8	Endrin	P	A
76-44-8	Heptachlor	P	A
118-74-1	Hexachlorobenzene (HCB)	P, I, B	C
2385-85-5	Mirex	P	A
800135-3	Toxaphene	P	A
-	Polychlorinated biphenyls (PCBs)	I, B	C
-	Polychlorinated dibenzo-p-dioxins (PCDD)	B	C
-	Polychlorinated dibenzofurans (PCDF)	B	C
143-50-5	Chlordecone	P	A
319-84-6	α-Hexachlorocyclohexane	P, B	A
319-85-7	β-Hexachlorocyclohexane	P, B	A
58-89-9	Lindane	P	A
608-93-5	Pentachlorobenzene	P	C
36355-01-8	Hexabromobiphenyl	I	A
36483-60-0	Hexabromodiphenyl ether	I	A
189084-68-2	Heptabromodiphenyl ether	I	A
608-93-5	Pentachlorobenzene (PeCB)	I	A
1763-23-1	Perfluorooctane sulfonic acid (PFOS)	I	B
307-35-7	Perfluorooctane sulfonyl fluoride	I	B
40088-47-9	Tetrabromodiphenyl ether	I	A
182346-21-0	Pentabromodiphenyl ether	I	A

(1) Category: P: Pesticide; I: Industrial chemicals; B: By-Products
(2) Annex: A: elimination; B: Restriction; C: Unintentional Production

The Stockholm Convention was amended and the Conference of the Parties (COP), by decisions SC-4/10 to SC-4/18, adopted amendments to Annexes A (elimination), B (restriction) and C (unintentional production) of the Stockholm Convention to list nine additional chemicals as persistent organic pollutants.

Any committee member may submit proposals for listing a new chemical in Annex A, B, or C of the Convention. The POPs Review Committee evaluates the proposals

and makes recommendations to the Conference of the Parties on such listing. The chemicals currently under review for the proposed listing are:
-Short-chained chlorinated paraffins
-Endosulfan
-Hexabromocyclododecane

As of 2010, of the 185 countries, 13 countries (Brunei, Haiti, Italy, Israel, Malaysia, Malta, Montenegro, Palau, Russian Union, Saudi Arabia, Suriname, USA and Zimbabwe) did not sign or ratify the treaty. The overall goal of this treaty is:
-the implementation scientific committee consisting of government designated experts to review new chemicals proposed for addition under the convention;
-the collection of national reports and regional monitoring data to facilitate the evaluation of its implementation as an effective tool to protect human health and the environment from POPs;
-the facilitation of providing technical and financial assistance for eligible parties to assist them in implementing the convention;
-the support of parties in establishing, implementing and strengthening their national capacities to address POPs contaminated wastes (including PCBs). The Convention provides guidance and facilitates the exchange of information on environmental sound management of wastes, equipments and oils containing PCBs.

In general, all those conventions and international treaties have the goal to implement political instruments for the preservation and conservation of water resources. However, many political, economical and sociological decisions which are made are actually contradict the effort of water conservation and lead to the low number of regulated contaminants.

1.3 Contaminants in the environment

Humankind has been changing, contaminating, and polluting their environment since the Palaeolithic era. This first type of pollution was air pollution through the use of fire [Spengler and Sexton, 1983]. Later, in the Bronze Age and Iron Age, the forging of metals produced significant air and soil pollution as can be seen in glacial core samples in Greenland [Sungmin et al, 1996]. And as early as the 9th century, Arab and Persian scientists have written about pollution and waste handlings [Gari, 2002]. The industrial revolution in the 19th century led to the environmental pollution as we know it today with its new industries and the enormous consumption of coal and oil, which lead to air pollution and the discharge of chemicals and industrial wastes into waterways (streams and rivers). After WWII, the matter of pollution came into public focus not only through the matter of atomic fallout (atomic warfare and testing), but as well as through the great smog event in 1952 in London, which killed between 4000 and 12000 people [Davis et al, 2002; De Angelo and Black, 2008], and several environmental disasters such as the Mercury poisoning of Minamata Bay (Japan) 1956, the Dioxin disaster in Seveso (Italy) 1976, the Love Canal chemical waste dump (USA) 1978, Three Mile Island core meltdown (USA) 1979, the Union Carbide gas leak in Bhopal (India) 1984, Thermonuclear Meltdown in Chernobyl (Ukraine) 1986 and Fukushima (Japan) 2011, numerous events of oil leaks and spills (Torrey Canyon 1967, Piper Alpha 1988, Exxon Valdez 1989, the Gulf War 1991, Deepwater Horizon 2010, etc.), the use of more than 75000 m^3 of Agent Orange in Vietnam during 1962-1971 and the destructive impact of acid rain on limestone, plants and lakes, which was discovered as early as 1852 by Robert Angus Smith [Seinfeld et al, 1998], but was not studied widely until the late 1960 [Likens et al, 1996].

All these events raised public awareness on pollution and resulted in various laws and legislations to prevent future disasters and clean up polluted sites. In contrast to those big environmental disasters, the impact of continuous discharge of industrial wastes, pesticides, fertilizers and food industry pharmaceuticals were considered to be nearly non existent or without any possible negative consequences, due to the wide spread thought “the solution to pollution is dilution”, and no thought was lost on the impact of unregulated substances like hormones, pharmaceuticals for human use etc. But as early as the 1940s, there was awareness in the scientific community that certain chemicals can act as endocrine disrupting substances, or can mimic hormones [Schueler, 1946; Sluczewski and Roth, 1948], and the first report of pharmaceuticals in wastewater treatment plant effluents was published 1977 [Hignite and Azarnoff, 1977]. During the last 30 or so years, the analytical and environmental chemistry has focused more or less exclusively on the “conventional contaminants” (CC), mainly pesticides, industrial chemicals, heavy metals etc. Although these contaminants pose a great threat to the environment when released, they only represent a small percentage of chemicals which can be detected nowadays in the environment. [Daughton and Ternes, 1999]. The types of potentially hazardous substances and their range of concentration in the environment may vary considerably. In the EU approximately 100000 different organic substances are registered, although this number rises constantly as new ones are developed and registered. Apart from the priority contaminants, whose environmental risks are well documented, for the majority of these organic compounds there does not exist any environmental quality data.

The development of new analytical techniques like gas chromatography coupled with mass spectrometry (GC-MS and GC-MS/MS), liquid chromatography coupled with mass spectrometry (LC-MS, LC-TOF/MS, LC-MS/MS), which push the limit of quantification/detection further into the low nano-gram range, permitted the detection and analysis of those new organic substances and its metabolites in environmental samples, in extremely low concentrations [Petrovic and Barceló, 2006; Hogenboom et al, 2009; Gómez et al, 2009; Robles-Molina et al, 2010; Pietrogrande and Basaglia, 2007].

The so called “emerging contaminants” (ECs) are defined as a group of organic substances which are not subject to restrictions of any kind, but may be candidates for future regulations, depending on the investigative results on the effects on human health, aquatic life forms and their presence in the environment. A wide range of compounds are considered to be relevant emerging compound such as: detergents, pharmaceutical products and its metabolites, personal care products, flame retardants, antiseptics, fragrances, industrial additives, steroids and hormones. The principal characteristic of these contaminants is that they do not have to be persistent in the environment to cause negative effects on life forms, as their possible high degradation and/or elimination are compensated through the constant release into the environment.

Table 1.5 Types of contaminants found in the environment

Emerging Contaminants and other contaminants	
Types	**Example**
Pharmaceuticals	
Veterinary and human antibiotics	Trimetoprim, Erythromycin, Lincomycin, Sulfamethoxazol
Analgesics and anti-inflammatory drugs	Codeine, Ibuprofen, Acetaminophen, Acetylsalicylic acid, Diclofenac, Fenoprofen
Psychiatric drugs	Diazepam
Anticonvulsant drugs	Carbamazepine
Lipid regulators	Benzafibrate, Clofibric acid, Fenofibric acid
β-blockers	Metoprolol, Propanolol, Timolol
X-Rey contrast agents	Iodopromide, Iopamidol, Diatrizoate,
Steroids and Hormones (contraceptives)	Estradiol, Estrone, Estriol, Diethylstilbestrol
Personal Care Products	
synthetic musk fragrances	Musk xylene, Galaxolide, Tonalide
Sun-screen agents	Benzophenone, Methylbenzylidene camphor
Insect repellents	N,N-diethyltoluamide
Surfactants and metabolites	Alkylphenol ethoxylates, Alkylphenoles (Octylphenol, Nonylphenol), Alkylphenol carboxylates
Flame retardants	Polybrominated diphenylethers (PBDEs), Tetrabromo bisphenol A, Tris-(2-chloroethyl)phosphate
Industrial additives and agents	Chelating agents (EDTA), aromatic sulfonates, benzotriazole, bisphenoles, phthalates
Gasoline additives	Dialkylethers, Methyl-t-butylether (MTBE)
Disinfection by-products	Bromoacids, Iodo-THMs, Bromoacetonitriles, Cyanoformaldehyde, NDMA,
Pesticides	Carbaryl, Metolachlor, Alachlor, 2,4-D, Dieldrin, Lindane, Esfenvalerate, Simazine, Atrazine, Isoproturon

For the majority of these "ECs" there is no available data on the ecological impact, risk assessment and eco toxicological behaviour. Therefore it is difficult if not impossible to predict which effects these contaminants have on the human health and on aquatic organisms [Barceló, 2003]. The most relevant micro contaminants and emerging contaminants which are found in the environment in low concentrations are listed in **Table 1.5** with their most relevant examples. Many of them are omnipresent and persistent and they have been detected in effluents of municipal wastewater treatment plants, rivers, aquifers and even in drinking water [Kasprzyk-Hordern et al, 2009; Kim et al, 2007; Mitch et al, 2003].

Contaminants enter the environment through different routes as can be seen in **Figure 1.6**. The two main ones are untreated urban wastewaters and MWTP effluents, as most of the MWTP are not designed to treat compounds like these. Another big contributor is the agricultural sector with its use of veterinary drugs and pesticides. These substances are released directly into surface waters, and may even seep through the soil to contaminate ground water.

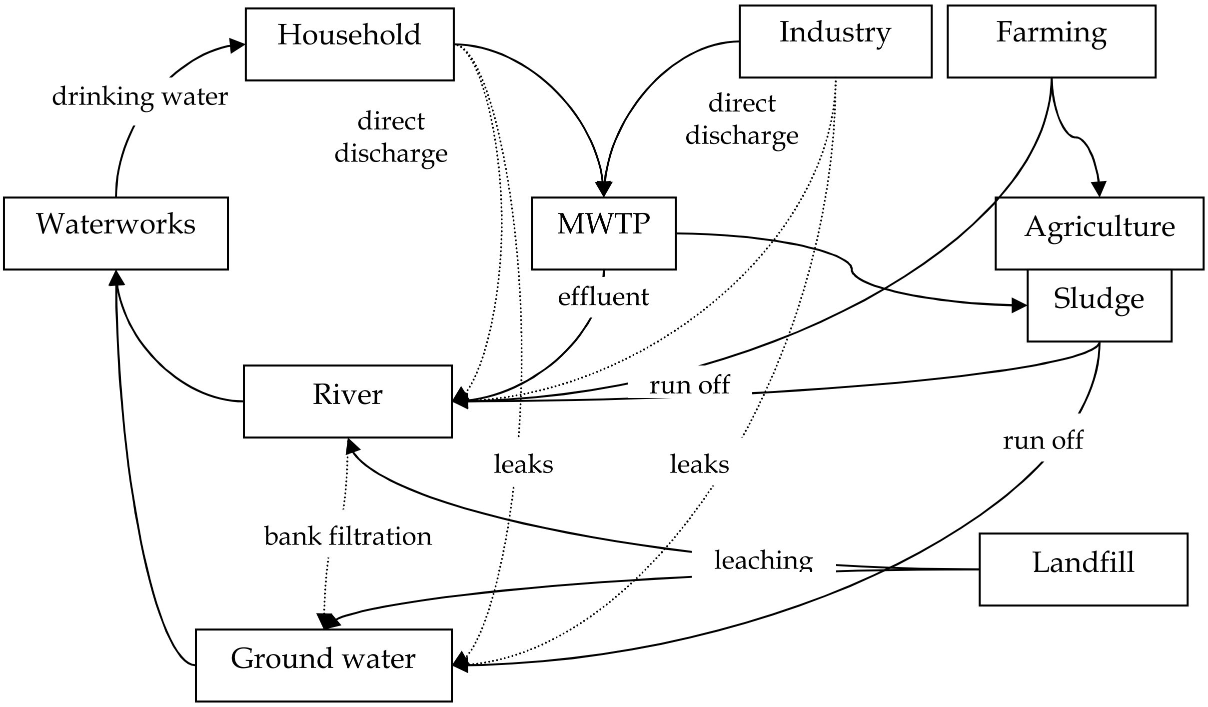


Figure 1.6 Routes of contamination

Another way of entering is through the application of sewage sludge onto fields and subsequent leaching and run offs into surface and ground water, as well as the leaching of land fills into the aquifer.

1.3.1 Pharmaceuticals

Pharmaceuticals are chemical substances intended to be used for medical treatment, cure or prevention of diseases [Directive 2004/27/EC]. They are complex organic molecules with diverse physical, biological and chemical properties, have a molecular weight between 100 and 1000 Da and an elevated polarity. Some of those pharmaceuticals are defined as "micro contaminants", because they are present in the aquatic environment in variable concentrations between ng L^{-1} and µg L^{-1} [Kümmerer, 2009; Pal et al, 2010]. Pharmaceuticals can be biopharmaceuticals or conventional chemical pharmaceuticals. Biopharmaceuticals have an active pharmaceutical ingredient which is produced either by microorganisms, plants or other animals. Examples are Adalimumab and Infliximab for the treatment of rheumatoid arthritis and Crohn's disease, vaccines against a multitude of viral infections like hepatitis A and B, and recombinant DNA for insulin production. Conventional pharmaceuticals are organic molecules which are designed for a specific task, like for example acetylsalicylic acid, or ibuprofen.

The pharmaceuticals represent the most important group of emerging contaminants due to their ever increasing use. Those which are detected in the highest concentrations in the environment are over the counter medications, like Paracetamol (Acetaminophen) and Aspirin (Acetylsalicylic acid). More than 80 pharmaceutical compounds were detected in recent studies in superficial waters in the ng L^{-1} - µg L^{-1} range (see **Table 1.6**), with the highest encountered levels close to waste water discharges and waste water treatment plants.

This list is gives a fairly good overview of the recent publications and the number of encountered pharmaceuticals in the environment. It is far from complete and does not include the metabolites which can be present in high concentrations as well.

Table 1.6 Examples of pharmaceutical concentrations detected in different countries and different sites.

Pharmaceutical	Mean conc. min-max [ng L^{-1}]	Country	Reference
non-steroidal anti-inflammatory drugs			
Acetylsalicylic acid	30-37	Somes river, Romania	Moldovan, 2006
	470-19400	MWTP influent, Japan	Nakada, 2006
Salicylic acid	38-2178	MWTP effluent, Canada	Verenitch, 2006
	130-371	River water, Canada	Verenitch, 2006
	2820-12700	MWTP influent, Canada	Lee, 2005
Diclofenac	200-3600	MWTP influent, Spain	Gómez, 2007
	140-2200	MWTP effluent, Switzerland	Tauxe-Wuersch, 2005
	70-156	MWTP influent, Spain	Unceta, 2010
	70-97	MWTP effluent, Spain	Unceta, 2010
	32-2400	MWTP effluent, Canada	Verenitch, 2006
	70-250	MWTP effluent, Greece	Koutsouba, 2003
	10-365	MWTP effluent, Sweden	Bendz, 2005
	20-60	Paraiba do Sul river, Brazil	Stumpf, 1999
	10-50	Drinking water, Brazil	Stumpf, 1999
	590	Groundwater, Germany	Sacher, 2001
	0.25	Drinking water, USA	Benotti, 2009
	328	Hospital effluent, Taiwan	Lin, 2009
	32-1420	MWTP effluent, Belgium	Hernando, 2006
	100-200	MWTP effluent, Netherlands	Hogenboom, 2009
	350-460	MWTP effluent, U.K.	Hilton, 2003
Fenoprofen	20-91	Surface water, Japan	Nakada, 2006
	9.68-80.6	MWTP effluent, Japan	Nakada, 2006
	1.59-9.22	MWTP influent, Japan	Nakada, 2006
Ibuprofen	34000-168000	MWTP influent, Spain	Gómez, 2007
	1750-4500	MWTP influent, Switzerland	Tauxe-Wuersch, 2005
	240-28000	MWTP effluent, Switzerland	Tauxe-Wuersch, 2005
	110-2170	MWTP effluent, Romania	Moldovan, 2006
	30-115.2	Somes river, Romania	Moldovan, 2006
	3-359	MWTP effluent, Luxembourg	Pailler, 2009
	78.5	Lambro river, Italy	Calamari, 2003
	3110	Groundwater, USA	Barnes, 2008
	781	MWTP effluent, Spain	Klamerth, 2010b
	1500-151000	Hospital effluent, Spain	Gómez, 2006
	11-38	Surface water, South Korea	Kim, 2007
Carboxy-Ibuprofen	10750	MWTP influent, Sweden	Bendz, 2005
	430	MWTP effluent, Sweden	Bendz, 2005
	230-680	Höje river, Sweden	Bendz, 2005
	11-32	Elbe river, Germany	Weigel, 2004
	9.5	Alster river, Germany	Weigel, 2004
Indomethacin	160-390	MWTP effluent, Spain	Bueno, 2009
	40-490	MWTP effluent, Canada	Lee, 2005
Ketoprofen	8-351	MWTP effluent, Canada	Verenitch, 2006
	40-90	MWTP effluent, Canada	Lee, 2005
	330	MWTP effluent, Sweden	Bendz, 2005
	10-70	Höje river, Sweden	Bendz, 2005
	313	MWTP influent, Spain	Hernando, 2006
	23	MWTP effluent, USA	Thomas, 2004

Ketoprofen	68.1-219	MWTP effluent, Japan	Nakada, 2006
Ketorolac	200-59500	Hospital effluent, Spain	Gómez, 2007
Mefenamic acid	136-363	MWTP influent, U.K.	Roberts, 2006
	290-396	MWTP effluent, U.K.	Roberts, 2006
	4.45-396	MWTP effluent, Japan	Nakada, 2006
	< 2.2-22.4	Pearl River, China	Zhao, 2009
	40-60	MWTP effluent, Spain	Bueno, 2009
	720-1100	MWTP effluent, U.K.	Hilton, 2003
	50-65	Surface water, U.K.	Hilton, 2003
Naproxen	271.4-7962.3	MWTP effluent, Canada	Verenitch, 2006
	1730-6030	MWTP influent, Canada	Lee, 2005
	360-2540	MWTP effluent, Canada	Lee, 2005
	< 0.5	Drinking water, USA	Benotti, 2009
	1.3-118	Pearl river, China	Zhao, 2009
	199-299	MWTP influent, Spain	Unceta, 2010
	1.8-18	Surface water, South Korea	Kim, 2007
Paracetamol	29000-246000	MWTP influent, Spain	Gómez, 2007
	32-4300	MWTP effluent, Spain	Gómez, 2007
	380	Groundwater, USA	Barnes, 2008
	62250	Hospital effluent, Taiwan	Lin, 2009
	78170	Danube river, Serbia	Grujić, 2009
	4.1-73	Surface water, South Korea	Kim, 2007
	13046-56944	MWTP influent, Korea	Choi, 2008
	5-9	MWTP effluent, Korea	Choi, 2008
	5-127	Han river, Korea	Choi, 2008
Codeine	17-123	Surface waters, USA	Nakada, 2007
	0.022	MWTP effluent, Germany	Wick, 2009
Hydrocodone	6-13	Surface waters, USA	Snyder, 2001
	1-2	Surface water, South Korea	Kim, 2007
blood lipid lowering agents			
Benzafibrate	< 25	Paraida do Sul river, Brazil	Stumpf, 1999
	0.79-2.75	Po river, Italy	Calamari, 2003
	57.15	Lambro river, Italy	Calamari, 2003
	40-130	MWTP effluent, Spain	Bueno, 2009
	0.3-46	Surface water, Spain	Fernández, 2010
Clofibric acid	2-40	Groundwater, Germany	Reddersen, 2003
	36-51	MWTP effluent, Spain	Bueno, 2009
	47-487	MWTP influent, Spain	Bueno, 2009
	36-2593	MWTP influent, Taiwan	Lin, 2009
	20-651	MWTP influent, U.K.	Roberts, 2006
	< 0.36-82	MWTP influent, Italy	Castiglioni, 2005
Gemfibrozil	80.1-478.2	MWTP effluent, Canada	Verenitch, 2006
	1.8-9.1	Surface waters, South Korea	Kim, 2007
	2968	MWTP effluent, Spain	Klamerth, 2010b
	470-3550	MWTP effluent, Spain	Bueno, 2009
	0.43	Drinking water, USA	Benotti, 2009
Atorvastatin	< 0.25	Drinking water, USA	Benotti, 2009
	76	MWTP influent, Canada	Miao, 2003
	37	MWTP effluent, Canada	Miao, 2003
	1	Otonabee river, Canada	Miao, 2003
Lovastatin	49	MWTP influent, Canada	Miao, 2003
	14	MWTP effluent, Canada	Miao, 2003
Pravastatin	117	MWTP influent, Canada	Miao, 2003

Pravastatin	59	MWTP effluent, Canada	Miao, 2003
	38-505	MWTP effluent, Spain	Gómez, 2010
Simvastatin	4	MWTP influent, Canada	Miao, 2003
	antibiotics		
Flourquinolones			
Ciprofloxacin	< 20	Surface water, USA	Kolpin, 2002
	<LOD-2000	Hospital effluent, USA	Brown, 2006
	100.8-309.2	MWTP effluent, Portugal	Seiftrová, 2008
	< 6-60	MWTP effluent, Sweden	Lindberg, 2005
	79.6-119.2	Mondego river, Portugal	Pena, 2007
	<LOD-1260	MWTP effluent, Spain	Gómez, 2010
Enrofolxacin	53.7-211.5	MWTP effluent, Portugal	Seiftrová, 2008
	270	MWTP effluent, USA	Karthikeyan, 2006
	67-102.5	Mondego river, Portugal	Pena, 2007
Levofloxacin	<LOD-87.4	Mankyung river, South Korea	Kim, 2009
Nalidixic acid	26-372	MWTP influent, Taiwan	Lin, 2009
	40-200	MWTP effluent, Taiwan	Lin, 2009
Norofloxacin	120	Surface water, USA	Kolpin, 2002
	29.6-35	MWTP effluent, Portugal	Seiftrová, 2008
	< 6-37	MWTP effluent, Sweden	Lindberg, 2005
	25	Mondego river, Portugal	Pena, 2007
	< 13-80	Surface seawater, China	Gulkowaka, 2007
	9.4-12.3	Victoria Harbour water, China	Xu, 2007
Ofloxacin	53-991	MWTP effluent, Taiwan	Lin, 2009
	110	MWTP effluent, USA	Brown, 2006
	1139	MWTP effluent, Spain	Klamerth, 2010b
	600	MWTP effluent, Italy	Zuccato, 2005
	306.1	Lambro river, Italy	Zuccato, 2005
	37.0	Po river, Italy	Zuccato, 2005
	<LOD-10675	Hospital effluent, Portugal	Seiftrová, 2008
β-Lactams			
Ampicillin	21	Hospital effluent, Taiwan	Lin, 2009
Penicillin G	1680	MWTP effluent, China	Li, 2008
	153000	MWTP influent, China	Li, 2008
Cephalosporins			
Cephalexin	1563-4367	MWTP influent, Taiwan	Lin, 2009
	10-994	MWTP effluent, Taiwan	Lin, 2009
	< 13-182	Surface seawater, China	Gulkowska, 2007
Lincosamide			
Lincomycin	60	Surface water, USA	Kolpin, 2002
	3.13-248.9	Po river, Italy	Calamari, 2003
	24.4	Lambro river, Italy	Calamari, 2003
	320	Groundwater, USA	Barnes, 2008
	n.d.-2000	Hospital effluent, USA	Brown, 2006
	n.d.-6600	Livestock effluent, USA	Brown, 2006
Macrolides			
Clarithromycin	0.49-20.3	Po river, Italy	Calamari, 2003
	8.31	Lambro river, Italy	Calamari, 2003
	59-1433	MWTP influent, Taiwan	Lin, 2009
	12-232	MWTP effluent, Taiwan	Lin, 2009
	<LOD-443	Mankyung river, South Korea	Kim, 2009
Erithromycin	1.4-15.9	Po river, Italy	Calamari, 2003
	4.5	Lambro river, Italy	Calamari, 2003
	47.4	MWTP effluent, Italy	Zuccato, 2005

Erithromycin	4.5	Lambro river, Italy	Zuccato, 2005
	15.9	Po river, Italy	Zuccato, 2005
	8.9-294	MWTP effluent, South Korea	Kim, 2007
	1.8-4.8	Surface water, South Korea	Kim, 2007
	<LOD -137	Mankyung river, South Korea	Kim, 2009
Roxithromycin	50	Surface water, USA	Kolpin, 2002
	5.1-6.1	Victoria Harbour water, China	Xu, 2007
	16-66	Pearl river, China	Xu, 2007
Spiramycin	<LOD-43.8	Po river, Italy	Calamari, 2003
	74.2	Lambro river, Italy	Calamari, 2003
Tylosin	40	Surface water, USA	Kolpin, 2002
	<LOD-0.30	Po river, Italy	Calamari, 2003
	2.77	Lambro river, Italy	Calamari, 2003
Sulfonamides			
Sulfachloropyridazine	< 30-476	MWTP influent, Korea	Choi, 2008
	< 30-149	MWTP effluent, Korea	Choi, 2008
Sulfadiazine	236	Tevere river, Italy	Perret, 2006
	38-209	Pearl river, China	Xu, 2007
Sulfadimethoxine	60	Surface water, USA	Kolpin, 2002
	46-68	Groundwater, USA	Batt, 2006
	0.3-26	MWTP influent, Luxembourg	Pailler, 2009
	0.3-9	MWTP effluent, Luxembourg	Pailler, 2009
	0.3-3	Alzette river, Luxembourg	Pailler, 2009
	28	Tevere river, Italy	Perret, 2006
	74	Trigno river, Italy	Perret, 2006
	11	Drinking water, Italy	Perret, 2006
Sulfamethazine	76-215	Groundwater, USA	Batt, 2006
	360	Groundwater, USA	Barnes, 2008
	160	MWTP influent, USA	Karthikeyan, 2006
Sulfamethoxazole	150	Surface water, USA	Kolpin, 2002
	1110	Groundwater, USA	Barnes, 2008
	0.32	Drinking water, USA	Benotti, 2009
	< 8-1510	Surface waters, Spain	Camacho-Muñoz, 2010
	127.2	MWTP effluent, Italy	Zuccato, 2005
	1335	Hospital effluent, Taiwan	Lin, 2009
	179-1760	MWTP influent, Taiwan	Lin, 2009
	47-964	MWTP effluent, Taiwan	Lin, 2009
	400-1100	MWTP effluent, Netherlands	Hogenboom, 2009
	1-22	Alzette river, Luxembourg	Pailler, 2009
	<LOD -300	Rio Grande river, USA	Brown, 2006
	402	Tevere river, Italy	Perret, 2006
	13-80	Drinking water, Italy	Perret, 2006
Sulfapyridine	< 12-121	Tevere river, Italy	Perret, 2006
	66	Trigno river, Italy	Perret, 2006
Sulfathiazole	0.3-2	Mess river, Luxembourg	Pailler, 2009
	< 30-531	MWTP influent, Korea	Choi, 2008
	< 30	MWTP effluent, Korea	Choi, 2008
Tertacyclines			
Chlortetracycline	420	Surface water, USA	Kolpin, 2002
Oxytetracycline	340	Surface water, USA	Kolpin, 2002
	14.35	Lambro river, Italy	Calamari, 2003
	23	Pharm. plant effluent, Taiwan	Lin, 2009
	0.3-7	Mess river, Luxembourg	Pailler, 2009

Tetracycline	110	Surface water, USA	Kolpin, 2002
	46-234	MWTP influent, Taiwan	Lin, 2009
	16-38	MWTP effluent, Taiwan	Lin, 2009
	520	MWTP influent, USA	Karthikeyan, 2006
	170	MWTP effluent, USA	Karthikeyan, 2006
	< 13-122	Surface seawater, China	Gulkowska, 2007
others			
Chloroamphenicol	41-127	Pearl river, China	Xu, 2007
Metronidazole	10-126	MWTP effluent, Taiwan	Lin, 2009
Miconazole	<LOD-35.7	MWTP effluent, Belgium	Van de Steene, 2010
Trimethoprim	150	Surface water, USA	Kolpin, 2002
	25	Danube river, Serbia	Grujić, 2009
	100	Groundwater	Grujić, 2009
	<LOD-1400	MWTP influent, USA	Brown, 2006
	180	MWTP effluent, USA	Brown, 2006
	< 13-21.8	Surface seawater, China	Gulkowska, 2007
		sex hormones	
Diethylstilbestrol	20	River water, China	Yang, 2006
17-α-Estradiol	30	Surface water, USA	Kolpin, 2002
	0.8-3.5	Groundwater, France	Vulliet, 2008
17-β-Estradiol	< 0.5	Drinking water, USA	Benotti, 2009
	0.49-12.4	MWTP effluent, Japan	Nakada, 2006
	1.0-85	MWTP effluent, Luxembourg	Pailler, 2009
	< 0.2	Berlin surface water, Germany	Zuehlke, 2005
	2-6	Tibre river, Italy	Lagana, 2004
	0.3-1.3	Groundwater, France	Vulliet, 2008
Estriol	19	Surface water, USA	Kolpin, 2002
	2-5	Tibre river, Italy	Lagana, 2004
Estrone	27	Surface water, USA	Kolpin, 2002
	2.80-110	MWTP effluent, Japan	Nakada, 2006
	<LOD-75	Pearl river, China	Zhao, 2009
	2.5-34	MWTP effluent, Japan	Isobe, 2003
	3.4-6.6	Tamagawa river, Japan	Isobe, 2003
	180±20	River water, China	Yang, 2006
17-α-Ethinylestradiol	73	Surface water, USA	Kolpin, 2002
	1.3	MWTP effluent, South Korea	Kim, 2007
	1.7	MWTP effluent, Germany	Zuehlke, 2005
	0.5-3.0	Groundwater, France	Vulliet, 2008
Mestranol	74	Surface water, USA	Kolpin, 2002
		antiepileptic drugs	
Carbamazepine	120-310	MWTP influent, Spain	Gómez, 2007
	110-230	MWTP effluent, Spain	Gómez, 2007
	290-400	MWTP influent, Finland	Vieno, 2006
	16-36	MWTP influent, Spain	Unceta, 2010
	10-51	MWTP effluent, Spain	Unceta, 2010
	380-470	MWTP effluent, Finland	Vieno, 2006
	< 8-17300	Surface water, Spain	Camacho-Muñoz, 2010
	< 1.4-66	Vantaa river, Finland	Vieno, 2006
	< 30-75.1	Somes river, Romania	Moldovan, 2006
	400-600	MWTP effluent, Netherlands	Hogenboom, 2009
	900	Groundwater, Germany	Sacher, 2001
	2100	MWTP effluent, Germany	Ternes, 1998
	193-420	MWTP influent, France	Leclercq, 2009
	86-258	MWTP effluent, France	Leclercq, 2009

Carbamazepine	<LOD -595	Mankyung river, South Korea	Kim, 2009
	108	MWTP effluent, China	Sui, 2010
	2.1	MWTP effluent, Germany	Ternes, 2007
β-blocking agents			
Acebutolol	390-510	MWTP influent, Finland	Vieno, 2006
	80-230	MWTP effluent, Finland	Vieno, 2006
	< 0.8-8	Vantaa river, Finland	Vieno, 2006
Atenolol	510-800	MWTP influent, Finland	Vieno, 2006
	40-440	MWTP effluent, Finland	Vieno, 2006
	< 11.8-25	Vantaa river, Finland	Vieno, 2006
	627	MWTP effluent, Spain	Klamerth, 2010
	30	MWTP influent, Sweden	Bendz, 2005
	200-1500	MWTP effluent, Netherlands	Hogenboom, 2009
	160	MWTP effluent, Sweden	Bendz, 2005
	10-60	Höre river, Sweden	Bendz, 2005
	100-122000	Hospital effluent, Spain	Gómez, 2006
	210-681	MWTP effluent, Taiwan	Lin, 2009
	27-1168	MWTP effluent, Italy	Castiglioni, 2005
Metoprolol	980-1350	MWTP influent, Finland	Vieno, 2006
	910-1070	MWTP effluent, Finland	Vieno, 2006
	< 3.8-116	Vantaa river, Finland	Vieno, 2006
	190	MWTP effluent, Sweden	Bendz, 2005
	30-70	Höre river, Sweden	Bendz, 2005
	14-597	MWTP influent, Taiwan	Lin, 2009
	1800-2700	MWTP effluent, Netherlands	Hogenboom, 2009
	50	MWTP effluent, Taiwan	Lin, 2009
Propanolol	50	MWTP influent, Sweden	Bendz, 2005
	30	MWTP effluent, Sweden	Bendz, 2005
	< 1-10	Höre river, Sweden	Bendz, 2005
	< 1-640	Surface water, Spain	Camacho-Muñoz, 2010
	62-119	MWTP influent, UK	Roberts, 2006
	195-373	MWTP effluent, UK	Roberts, 2006
	35-107	Tyne river, UK	Roberts, 2006
	20	MWTP effluent, Spain	Klamerth, 2010
	< 10-37	Surface water, UK	Hilton, 2003
	200-6500	Hospital effluent, Spain	Gómez, 2006
Sotalol	640-830	MWTP influent, Finland	Vieno, 2006
	160-300	MWTP effluent, Finland	Vieno, 2006
	< 3.9-52	Vantaa river, Finland	Vieno, 2006
	700-2600	MWTP effluent, Netherlands	Hogenboom, 2009
	560	Groundwater, Germany	Sacher, 2001
diuretics			
Furosemide	<LOD -21	Rivers water, Japan	Nakada, 2007
	<LOD -67	River water, Italy	Zuccato, 2005
	429	MWTP effluent, Spain	Klamerth, 2010
gastrointestinal drugs			
Ranitinide	3-39	Surface waters, UK	Kasprzyk-Hordern, 2008
	77-175	River water, Spain	Rodríguez-Gil. 2010
antidepressants / antipsychotics			
Amitriptyline	17.6-20.8	MWTP influent, Canada	Lajeunesse, 2008
	15.6-21.0	MWTP effluent, Canada	Lajeunesse, 2008
	0.87-3.7	St. Laurence river, Canada	Lajeunesse, 2008
Nortriptyline	3.1-4.5	MWTP influent, Canada	Lajeunesse, 2008
	1.5-3.8	MWTP effluent, Canada	Lajeunesse, 2008

Nortriptyline	0.41-0.73	St. Laurence river, Canada	Lajeunesse, 2008
Citalopram	13-612	MWTP influent, Norway	Vasskog, 2006
	9.2-382	MWTP effluent, Norway	Vasskog, 2006
	62.9-303.6	MWTP influent, Norway	Vasskog, 2008
	21.9-238.4	MWTP effluent, Norway	Vasskog, 2008
	52.2-52.7	MWTP influent, Canada	Lajeunesse, 2008
	46.8-57.8	MWTP effluent, Canada	Lajeunesse, 2008
	3.4-11.5	St. Laurence river, Canada	Lajeunesse, 2008
Flouxetine	12	Surface water, USA	Kolpin, 2002
	56	Groundwater, USA	Barnes, 2008
	0.64	Drinking water, USA	Benotti, 2009
	1.1-18.7	MWTP influent, Norway	Vasskog, 2008
	0.6-8.4	MWTP effluent, Norway	Vasskog, 2008
	3.1-3.5	MWTP influent, Canada	Lajeunesse, 2008
	2.0-3.7	MWTP effluent, Canada	Lajeunesse, 2008
	0.42-1.3	St. Laurence river, Canada	Lajeunesse, 2008
Fluvoxamine	0.4-3.9	MWTP influent, Norway	Vasskog, 2006
	< 0.15-0.8	MWTP effluent, Norway	Vasskog, 2006
	0.8-1.7	MWTP influent, Norway	Vasskog, 2008
	< 0.379-0.8	MWTP effluent, Norway	Vasskog, 2008
	0.5-0.8	Seawater, Norway	Vasskog, 2008
Paroxetine	0.6-12.3	MWTP influent, Norway	Vasskog, 2006
	0.5-1.6	MWTP effluent, Norway	Vasskog, 2006
	2.9-12.9	MWTP influent, Norway	Vasskog, 2008
	1.0-11.7	MWTP effluent, Norway	Vasskog, 2008
	0.6-1.4	Seawater, Norway	Vasskog, 2008
	4.6-5.3	MWTP influent, Canada	Lajeunesse, 2008
	4.3-5.2	MWTP effluent, Canada	Lajeunesse, 2008
	1.3-3.0	St. Laurence river, Canada	Lajeunesse, 2008
Sertraline	1.8-2.5	MWTP influent, Norway	Vasskog, 2006
	0.9-2.0	MWTP effluent, Norway	Vasskog, 2006
	8.4-19.8	MWTP influent, Norway	Vasskog, 2008
	3.7-14.6	MWTP effluent, Norway	Vasskog, 2008
	< 0.52	Seawater, Norway	Vasskog, 2008
	6.0-6.1	MWTP influent, Canada	Lajeunesse, 2008
	5.1-5.8	MWTP effluent, Canada	Lajeunesse, 2008
	0.84-2.4	St. Laurence river, Canada	Lajeunesse, 2008
Venlafaxine	195.7-213.0	MWTP influent, Canada	Lajeunesse, 2008
	175.9-214.6	MWTP effluent, Canada	Lajeunesse, 2008
	12.9-45.9	St. Laurence river, Canada	Lajeunesse, 2008
Diazepam	3-62	Surface waters, USA	Snyder, 2001
	0.38	River water, South Korea	Yoon, 2010
	9	MWTP effluent, Spain	Klamerth, 2010
	4.6-59	River waters, Spain	Rodríguez-Gil. 2010
Pipamperone	n.d.-961.3	Surface waters, Belgium	Van De Steene, 2010
anti-neoplastic drugs			
Cyclophosphamide	< 30-64.8	Somes river, Romania	Moldovan, 2006
	< 1.9-9.0	MWTP effluent, Italy	Castiglioni, 2005
	2.0-6.0	MWTP influent, Switzerland	Buerge, 2006
	2.1-4.0	MWTP effluent, Switzerland	Buerge, 2006
Ifosamide	< 0.3-5	MWTP influent, Switzerland	Buerge, 2006
	1.7-6.0	MWTP effluent, Switzerland	Buerge, 2006
Methotrexate	< 0.83-12.6	MWTP effluent, Italy	Castiglioni, 2005

Tamoxifen	143-215	MWTP influent, UK	Roberts, 2006
	146-369	MWTP effluent, UK	Roberts, 2006
	24-212	Tyne river, UK	Roberts, 2006
	0.2-15	MWTP influent, UK	Zhou, 2009
	0.2-0.7	MWTP effluent, UK	Zhou, 2009
X-ray contrast media			
Diatrizoate	250	MWTP effluent, Germany	Ternes, 2000
	< 10-8700	Surface water, Germany	Ternes, 2000
	30	Ground water, Germany	Ternes, 2000
	1600-9600	Ground water, Germany	Ternes, 2007
	2000	Surface water, Germany	Putschew, 2000
	1200	Drinking water, Germany	Hirsch, 2000
	110-140	Rhine river, Germany	Hirsch, 2000
Iohexol	2800-4760	MWTP influent, Australia	Busetti, 2008
	40-86	Danube river, Germany	Seitz, 2006
Iomeprol	370	MWTP effluent, Germany	Ternes, 2000
	10-890	Surface water, Germany	Ternes, 2000
	100-160	Danube river, Germany	Seitz, 2006
Iopamidol	300	Groundwater, Germany	Sacher, 2001
	400-620	MWTP influent, Australia	Busetti, 2008
	<220	MWTP effluent, Australia	Busetti, 2008
	590	MWTP effluent, Germany	Hirsch, 2000
	180-300	Rhine river, Germany	Hirsch, 2000
Iopromide	1170-4030	MWTP effluent, South Korea	Kim, 2007
	20-361	Surface water, South Korea	Kim, 2007
	6600	MWTP influent, Spain	Carballa, 2004
	9300	MWTP effluent, Spain	Carballa, 2004
	4400	MWTP effluent, Germany	Ternes, 2000
	4.6	MWTP effluent, USA	Trenholm, 2006
	2.2	Ohio river, USA	Trenholm, 2006
	4.6	Drinking water, USA	Trenholm, 2006
	152-2670	MWTP effluent, South Korea	Trenholm, 2006
	7.0	MWTP effluent, Switzerland	Morasch, 2010
	150	Rhine river, Germany	Hirsch, 2000
others			
Nicotine	31-117	River water, Spain	Rodríguez-Gil. 2010
	166	MWTP effluent, Spain	Klamerth, 2010
Caffeine	21-1308	River water, Spain	Rodríguez-Gil. 2010
	150-2720	Surface water, Spain	Camacho-Muñoz, 2010
	15	MWTP influent, China	Sui, 2010
	3782	MWTP effluent, Spain	Klamerth, 2010
Methadone	0.087	MWTP effluent, Germany	Wick, 2009
Cocaine	9-683	MWTP influent, Belgium	van Nuijs, 2009
THC-COOH	159	MWTP influent, UK	Zuccato, 2008
THC	11-18	MWTP influent, Spain	Postigo, 2008
Methamphetamine	<LOD-541.7	Surface water, USA	Bartelt-Hunt, 2009

1.3.2 Personal Care Products

Personal Care Products (PCPs) is a group of emerging contaminants widely used in daily life. They are products used for personal hygiene and include soaps, shampoos, toothpaste, mouthwash, insect repellents, sun creams, deodorants, lubricants, balms, etc. (see **Table 1.7**) and are introduced through the MWTP or directly via release from the skin during swimming and bathing [Giokas et al, 2007]. Some of these products' ingredients are persistent and some of them have endocrine disrupting properties [Soliman et al 2004; Witorsch and Thomas, 2010; Rodil and Moeder, 2008]. Apart from that, most of the PCPs are very lipophilic and tend to accumulate in the environment [Andresen et al, 2007; Plagellat et al 2006]. UV filters have been found in river and lake fish at levels ranging from 50 to 1800 ng g^{-1} lipid weight for 4-methylbenzylidene camphor (4-MBC) and 40 to 1700 ng g^{-1} lipid weight for octocrylene.

Table 1.7 PCPs found in the aquatic environment

Compound	Mean conc., min-max [ng L^{-1}]	Country	Reference
	synthetic fragrances		
Celestolide	23, 11-30	MWTP effluent, Spain	Gómez, 2009
Phantolide	14, 13-16	MWTP effluent, Spain	Gómez, 2009
Traseolide	20-22	MWTP effluent, Spain	Gómez, 2009
Galaxolide	1259-8697	MWTP effluent, Spain	Gómez, 2009
	440, 44-1861	Surface water, Spain	Gómez, 2009
	3.95-25.1	Surface water, USA	Reiner, 2010
	2.10-3.18	MWTP influent, Spain	Carballa, 2004
	0.49-0.6	MWTP effluent, Spain	Carballa, 2004
	<LOD-9.24	Nakdong river, South Korea	Lee, 2010
	1840-3430	MWTP influent, China	Zhang, 2008
	233-336	MWTP effluent, China	Zhang, 2008
	790-4443	MWTP influent, various	Miège, 2009
	451-1080	MWTP effluent, various	Miège, 2009
	65	Raw drinking water, USA	Snyder, 2008
Musk Xylene	104, 59-203	MWTP effluent, Spain	Gómez, 2009
	13, 10-23	Surface water, Spain	Gómez, 2009
Tonalide	365, 56-981	MWTP effluent, Spain	Gómez, 2009
	58, 12-194	Surface water, Spain	Gómez, 2009
	5.09-21.4	Surface water, USA	Reiner, 2010
	0.9-1.69	MWTP influent, Spain	Carballa, 2004
	0.15-0.20	MWTP effluent, Spain	Carballa, 2004
	<LOD -2.80	Nakdong river, South Korea	Lee, 2010
	435-1043	MWTP influent, China	Zhang, 2008
	74-93	MWTP effluent, China	Zhang, 2008

Tonalide	210-1690 144-200	MWTP influent, various MWTP effluent, various	Miège, 2009 Miège, 2009
Musk Ketone	107, 34-218 29, 15-40 <LOD -0.42	MWTP effluent, Spain Surface water, Spain Nakdong river, South Korea	Gómez, 2009 Gómez, 2009 Lee, 2010
Cashmeran	238-533	Ter river, Spain	Calderón-Preciado, 2011
sun-screen agents			
Benzophenone	720-7800	MWTP influent, Switzerland	Balmer, 2004
Benzophenone-3	5-125	Lake water, Switzerland	Poiger, 2004
4-MBC	9-82 420 ng g^{-1} lipid	Lake water, Switzerland Fish, Rivers Switzerland	Poiger, 2004 Buser, 2006
Octocrylene	3-27 630 ng g^{-1} lipid	Lake water, Switzerland Fish, Rivers Switzerland	Poiger, 2004 Buser, 2006
disinfectant			
Triclosan	380 70-430 60-719 24-157 22	MWTP influent, various MWTP effluent, various MWTP effluent, Spain River water, Spain Ter river, Spain	Miège, 2009 Miège, 2009 Gómez, 2009 Gómez, 2009 Calderón-Preciado, 2011
anti-oxidants			
Butylated hydroxytoluene	100	Surface waters, USA	Kolpin, 2002
Butylated hydroxyanisole	50	Surface waters, USA	Snyder, 2008
Insect repellent			
N.N-diethyl-metatolumide	60	Surface waters, USA	Kolpin, 2002

1.3.3 Pesticides

Pesticides are substances to control and kill pests, hence the name. They are not emerging contaminants but normal conventional contaminants which are regulated. They are divided into various sub-classes: herbicides, insecticides and fungicides. Chemically they are classified by chemical makeup as organochlorines, organophosphates, pyrethroids, triazines, carbamates, chlorophenoxy acids and chloroacetanildes.

Carbamates like Carbaryl have been detected in groundwater in the USA due to extensive use [Lindsey et al, 2006] and Carbendazim has been found in MWTP influents [Kupper et al, 2006].

Chloroacetanilides are generally used as herbicides to control broadleaf and grassy weeds. Metolachlor has been detected in ground and surface water in the US [Kolpin et al, 2002; Penetra et al, 2010] and Alachlor has been detected in surface and groundwater in agricultural regions in the US and the EU, although it shows decreasing trends due to the increasing use of Acetochlor [Kolpin et al, 1997; Gilliom et al, 2006; Loos et al, 2010].

Chlorophenoxy acids, like 2,4-D (2,4-Dichlorophenoxy acid), Bentazone and Triclopyr are commonly used as herbicides for agricultural and weed control activity [Luque-García and Luque de Castro, 2002]. Triclopyr and 2,4-D were detected in surface waters in the US [Battaglin et al, 2009].

Organochlorines like DDT, Dieldrin, Lindane, Endosulfan and Methoxychlor are used as agricultural insecticides. They are highly persistent in the environment, are hydrophobic and have a high toxicity and low solubility. They have a high occurrence in the freshwater environment [Lohmann et al, 2009; Leong et al, 2007; Abrantes et al, 2010].

Organophosphates like Chlorfenvinphos, Methylparathion, Chlorpyrifos, and Diazinon are commonly used as insecticides, as they act as neurotoxins. They have a more toxic potential than carbamates or organochlorines [McKinlay et al, 2008], but have a lower persistency and are less bioaccumulative than most other classes of pesticides. Chlorfenvinphos for example has been detected in MWTP effluents in Spain [Klamerth et al, 2010b], in MWTP effluents and river water in Greece and Chlorpyrifos has been detected in MWTP effluents and river water in Greece [Stamatis et al, 2010].

Pyrethroids are compounds used as insecticides. They have a lower toxicity than other pesticides, they are hydrophobic and some of them can be persistent in the environment. The most widely used pyrethroids are Biphenthrin, Cypermethrin and Esfenvalerate, which is detected in surface water runoff [Brady et al, 2006].

Triazines are compounds heavily used in agricultural areas as herbicides. Examples are Atrazine, Cyanazine and Simazine. Atrazine and simazine are both water soluble and persistent [Wauchope et al, 1992]. They were detected in MWTP effluents and surface waters in Europe [Loos et al, 2009; Klamerth et al, 2010b; Singer et al, 2010], and groundwater in the US [Kolpin et al, 2000].

Several other pesticides like Diuron, Isoproturon, and Mecoprop are not classified in the abovementioned groups. Nevertheless they are widely used and occur in the aquatic environment [Singer et al, 2010; Stamatis et al, 2010; Meyer et al, 2010]. **Table 1.8** lists the above-mentioned pesticides and where they were found.

Table 1.8 Pesticides in the aquatic environment

Compound	Mean concentration, min-max [ng L^{-1}]	Country	Reference
Carbendazim	4000-25000	MWTP effluents, USA	Kupper, 2006
Metolachlor	19	Surface water, USA	Penetra, 2010
Alachlor	2130-2870	Ground water, USA	Abrantes, 2010
Triclopyr	9830	Surface water, USA	Battaglin, 2009
Dieldrin	1980-10120	Surface water, USA	Abrantes, 2010
Chlorfenvinphos	651	MWTP effluent, Spain	Klamerth, 2010b
	<LOD-29.5	River water, Greece	Stamatis, 2010
Esfenvalerate	56600-166000	Surface water, USA	Brady, 2006
Simazine	<LOD-160	Surface water, Spain	Benvenuto, 2010
Atrazine	15 30	MWTP effluent, Spain MWTP effluent, Switzerland	Klamerth, 2010 Singer, 2010
Diuron	40	MWTP effluent, Switzerland	Singer, 2010
Isoproturon	20 22	MWTP effluent, Spain Ground water, EU	Klamerth, 2010 Loos, 2010

1.3.4 Other Substances (Surfactants, Flame retardants, Additives)

Other types of micro contaminants are:

- **Surfactants** like perfluorinated compounds (PFCs) include: perfluorooctane sulfonate (PFOS), perfluorooctanonic acid (PFOA), perfluoro carboxylic acid (PFCA) and polytetrafluoroethylene (PTFE, Teflon)) and the possible precursor compounds for PFCA and PFOS which are fluorotelomer alcohols (FTOHs). The FTOHs are more volatile and therefore more likely to undergo long range atmospheric transport with sufficient atmospheric lifetimes to reach remote locations. These substances are used as stain repellents in fabrics and carpets; they are used in adhesives, waxes, electronics, textiles, grease proof coatings for food packaging etc. They have been manufactured for more than 50 years and have subsequently been released into the environment. Due to their strong chemical C-F bond, they have unusual chemical properties. They are hydrophobic and lipophobic at the same time, they are extremely stable in the environment and in living organisms. Since 2002 PFOS is no longer produced due to concerns about widespread global distribution in the blood of the general population. PFOA is still manufactured and like PFOS appears to have spread all over the world and seems to be ubiquitous at low levels in humans [Richardson, 2007] as well as in water, soils, sediments air and other biota samples [Vieira, 2005]. The US based EPA assumes that most Americans have about 5 ppb of PFOA in their blood [EPA, 2005], and potential health concerns include cancer, bioaccumulation and developmental toxicity [Henderson and Smith, 2007; Lau at al, 2007]. In the EU, there are currently no regulations regarding PFOA and other PFCs, although there are legislations which may be relevant to the release of PFOS [EC, IPPC Directive 96/61/EC], while US EPA has listed PFOA on the new proposed CCL-3 [EPA, 2011].

PFCs reach the aquatic environment through direct discharge into rivers or through wastewater discharge, as these compounds pass almost unaffected through MWTPs as well as through the atmospheric deposition of rain water [Scott at al, 2006a; Scott et al, 2006b].

- **Flame retardants** are a group of chemicals used in a wide range of products like construction materials, electronic appliances, computer cases, and textiles. Through activities like washing, cleaning, construction/demolition and disturbance of contaminated dusts, these chemicals can be mobilised and enter waterways. Brominated flame retardants (BFRs) which include polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), hexabromebenzene (HBB), hexabromocyclodecanes (HBCDs) and tetrabromobisphenol A (TBBPA) and chlorinated flame retardants like Mirex (which was banned in the late 1970s), Dechlorane Plus, Dechlorane 602, 603 and 604, have been used in the past in Europe and some of these substances are still in wide use. These substances are lipophilic and absorb to sewage sludge in MWTPs [La Guardia et al, 2010], which lead to low residual concentrations (< 1 ng L^{-1}) in waste water effluents. But because of their lipophilic properties they bio accumulate if released into the environment [Hoh et al, 2006; Shen et al, 2010; Ueno et al, 2010]. In general, halogenated organic chemicals are some of the most persistent and bioaccumulative pollutants. They are responsible for adverse environmental and human health effects. The polybrominated diphenyl ethers (PBDEs) for example have been in production since the 1970s and have been used in textiles, polyurethane foam, circuit boards and plastics. Through evidence of their bioaccumulation [De Wit, 2002; Hale et al, 2003; Chen et al, 2008], endocrine disrupting ability [Meerts et al, 1998; Meerts et al, 2000] and global dispersion, the production of penta- and octa- BDEs were discontinued in 2003 in the EU, and in 2004 in the USA [Directive 2003/11/EC; 76/769/EEC; Stockholm Convention]. Deca-BDE is currently being phased out in the USA until 2013 [EPA, 2004] and has been banned in the EU for electrical and electronic applications since July 2008 [European Court of Justice, 2008; Commission Decision, 2005/717/EC]. The ban on the old formulations has paved a way for the new or novel BFRs as replacements. Important representatives of this group are decabromodiphenyl ethane (DBDPE) or 1,2-bis(pentabromodiphenyl)ethane (BTBPE). But there is evidence regarding the environmental occurrence of these novel BFRs as these are as well bioaccumulative [Harju at al, 2009; De Wit et al, 2010]. Contrary to these lipophilic flame retardants, organophosphate flame retardants (OPFRs) which are used as additives in thermal insulating hard foams and construction foams are rather hydrophilic and are found in elevated concentrations in waste waters, MWTPs effluents, wastewater impacted surface waters [Andresen et al, 2004; Weigel et al, 2005] and the marine environment [Andresen et al, 2007]. Chlorinated alkyl-phosphate esters for example are included as flame retardants in PU-foams, additives in unsaturated PE resins, acrylic resins, adhesives and coatings. They are not bonded in the polymer matrix and therefore can migrate to the surface and are released into the environment, in which they have an elevated persistence [Bester, 2006]. Due to their physicochemical properties, chlorinated flame retardants can be classified as semi-volatile organic compounds (sVOCs), with water being their main mode of distribution in the environment. Three of these compounds in particular, namely TCEP (Tris(2-chloroethyl)phosphate), TCPP (Tris(2-chloro-1-methylethyl)phosphate) and TDCP (Tris(1,3-dichloro-2-propyl)phosphate) have a low biodegradability during conventional wastewater treatment [Meyer and Bester, 2004], therefore treated and untreated wastewater discharges are the main entry pathways for OPFRs into surface and groundwater and even drinking water [LeBel et al, 1981].

- **Industrial chemicals** include corrosion inhibitors, plasticizers, Phenols and Dioxane.

Corrosion inhibitors like benzotriazole (BT) and tolyltriazole (TT) are complexing agents which are widely used as anticorrosive (in aircraft de-icers, engine coolants, antifreeze liquids and dishwasher detergents [Giger et al, 2006]. They are soluble in water, resistant to biodegradation and therefore only partly removed in wastewater treatment. BT and TT are ubiquitous in European surface waters [Reemtsma et al, 2006; Loos et al, 2009].

Plasticisers are chemical compounds added to plastics, paints and fibres to improve flexibility. They are not chemically bonded into the resin and therefore can leach out and consequently are found in the aquatic environment [Clark et al, 2003]. Phthalates are mainly used in PVC resins, adhesives and cellulose film coatings. There are approximately 60 different phthalates produced, of these, diethyl phthalate (DEP), dibutyl phthalate (DBP), dimethyl phthalate (DMP) and di(2-ethylhexyl)phthalate (DEHP) are the most important [Gültekin and Ince, 2007]. The most predominant PAE in waters is DEHP due to its high production (90% of European plasticiser use). Another group of plasticisers are bisphenoles. Bisphenol A (BPA) and Bisphenol F (BPF) are constituents of some epoxy resins and plastics. BPA is used extensively in the production of polycarbonate and high concentrations of BPA were found in MWTP effluents.

1,4-Dioxane is a high production chemical which is used as a solvent stabilizer in the manufacture and processing of textile products, cotton, paper, car coolants, cosmetics, shampoos, and 1,1,1-trichloroethane (TCA). It is highly water soluble and has been discovered in groundwater [Isaacson et al, 2006], often exceeding water quality criteria and the U.S.

Table 1.9 Other Contaminants found in the environment

Compound	Mean conc., min-max [ng L^{-1}]	Country	Reference
perfluorinated compounds			
PFOS	4.5-20	MWTP effluent, Austria	Gonzáles-Barreiro, 2006
	3-68	MWTP effluent, USA	Sinclair, 2006
	8-993	MWTP effluent, USA	Schultz, 2006
	5-26	Rhine river, Germany	Skutlarek, 2006
	193	Moehe river, Germany	Skutlarek, 2006
	4.7	Tenjin river, Japan	Senthilkumar, 2007
	89.11	Shihwa lake, Korea	Rostkowski, 2006
	7.8	Maggiore lake, Italy	Rostkowski, 2006
	4.2	Huron lake, Canada	Furdui, 2007
	71-749	Harbour water, Norway	Tanabe, 1997
	33-1790	Black sea	Inneke, 2007
PFOA	10-21	MWTP effluent, Austria	Gonzáles-Barreiro, 2006
	58-1050	MWTP effluent, USA	Sinclair, 2006
	8.3-334	MWTP effluent, USA	Sinclair, 2006
	7.6	Elbe river, Germany	McLachlan, 2007
	200	Po river, Italy	McLachlan, 2007
	23	Thames river, UK	McLachlan, 2007
	177	Ruhr river, Germany	Skutlarek, 2006
	19.22	Shihwa lake, Korea	Rostkowski, 2006
	2.4	Maggiore lake, Italy	Rostkowski, 2006
	39	Tenjin river, Japan	Senthilkumar, 2007
	3.6	Huron lake, Canada	Furdui, 2007
Flame retardants			
HBCDs	43 ng g^{-1} lipid	Oyster, Hokkaido coast, Japan	Ueno, 2010
	5200 ng g^{-1} lipid	Oyster, Osaka coast, Japan	Ueno, 2010
	0.0018-0.0108	Surface water, Russian arctic	de Wit, 2010
PBDEs	22 ng g^{-1} lipid	Oyster, Iwate coast, Japan	Ueno, 2010
	86 ng g^{-1} lipid	Oyster, Osaka coast, Japan	Ueno, 2010
DEC 602	4.7-34 ng g^{-1} lipid	Fish, Lake Ontario, Canada	Shen, 2010
TCEP	41-488	Rain Samples, Germany	Regnery, 2009
	<LOQ-184	Surface waters, Germany	Regnery, 2010
	350-370	MWTP effluent, Germany	Meyer, 2004
TCPP	77-2659	Rain Samples, Germany	Regnery, 2009
	<LOQ-379	Surface waters, Germany	Regnery, 2010
	820-3000	MWTP effluent, Germany	Meyer, 2004
TDCP	2-53	Rain Samples, Germany	Regnery, 2009
	130-150	MWTP effluent, Germany	Meyer, 2004
Industrial chemicals			
Benzotriazole	7300	MWTP effluents, Europe	Reemtsma, 2006
	6300	Glatt river, Switzerland	Giger, 2006
	7997	Surface water, Europe	Loos, 2009
Tolyltriazole	2200	MWTP effluents, Europe	Reemtsma, 2006
Bis(2-ethylhexyl) phthalate	98000-122000	MWTP influent, Finland	Marttineen, 2003
	300-98000	Surface water, Germany	Fromme, 2002
	420	Surface water, USA	Kolpin, 2002
Bisphenol A	18-702	MWTP effluent,	Staples, 1998
	0.5-410	Surface waters,	Staples, 1998
	12000	Surface water, USA	Kolpin, 2002
1,4-Dioxane	n.d-2800000	Groundwater	Isaacson, 2006

EPA has listed it on the new proposed CCL-3 [EPA, 2007]. **Table 1.9** gives an overview of the occurrence of these contaminants in different water bodies and countries.

1.4 Impact of contaminants in the environment

Once released into the environment, contaminants are subject to elimination processes (biodegradation, chemical degradation, photochemical degradation, and sorption), see **Figure 1.7**. Elimination only means that the parent compound of interest is below the limit of detection in this particular compartment of interest (water phase, sludge phase, solid phase, soil, air, etc.) with a specific analytical method. If the compound is fully converted into CO_2 and inorganic salts, full mineralisation took place. If not fully mineralised, there are a number of transformation and degradation products of the parent compound, again depending on the compartment in which the degradation takes place.

These transformation and degradation products can exhibit higher persistence and/or greater toxicity than their parent compound [Adelsbach and Tjeerdema, 2003; Boxall et al, 2004; Jiao et al, 2008]. For example, a degradation product of the sunscreen agent benzophenone-3 (BP3), 2,2′-dihydroxy-4-mthoxy-benzophenone is known to be a bacterial mutagen [Mortelmans et al, 1986].

Substances which are not degraded in MWPT will reach surface waters where they can affect organisms of different trophic levels. The sensitivity of algae towards antibiotics varies widely. Blue-green algae (cyan bacteria) for example, seem to be sensitive to many antibiotics (amoxicillin, benzyl penicillin, sarafloxacin, tetracycline, etc.) [Boxall et al, 2003], and seem to be the most sensitive algae to antibiotic compounds in general [Brain et al, 2008].

Exposure to antibiotics may have adverse reproductive effects in the early life stages of different organisms like *Artemis sp.* cysts, *nauplii* and *Daphnia magna* [Macrì et al, 1988; Migliore et al, 1993; Wollenberger et al, 2000].

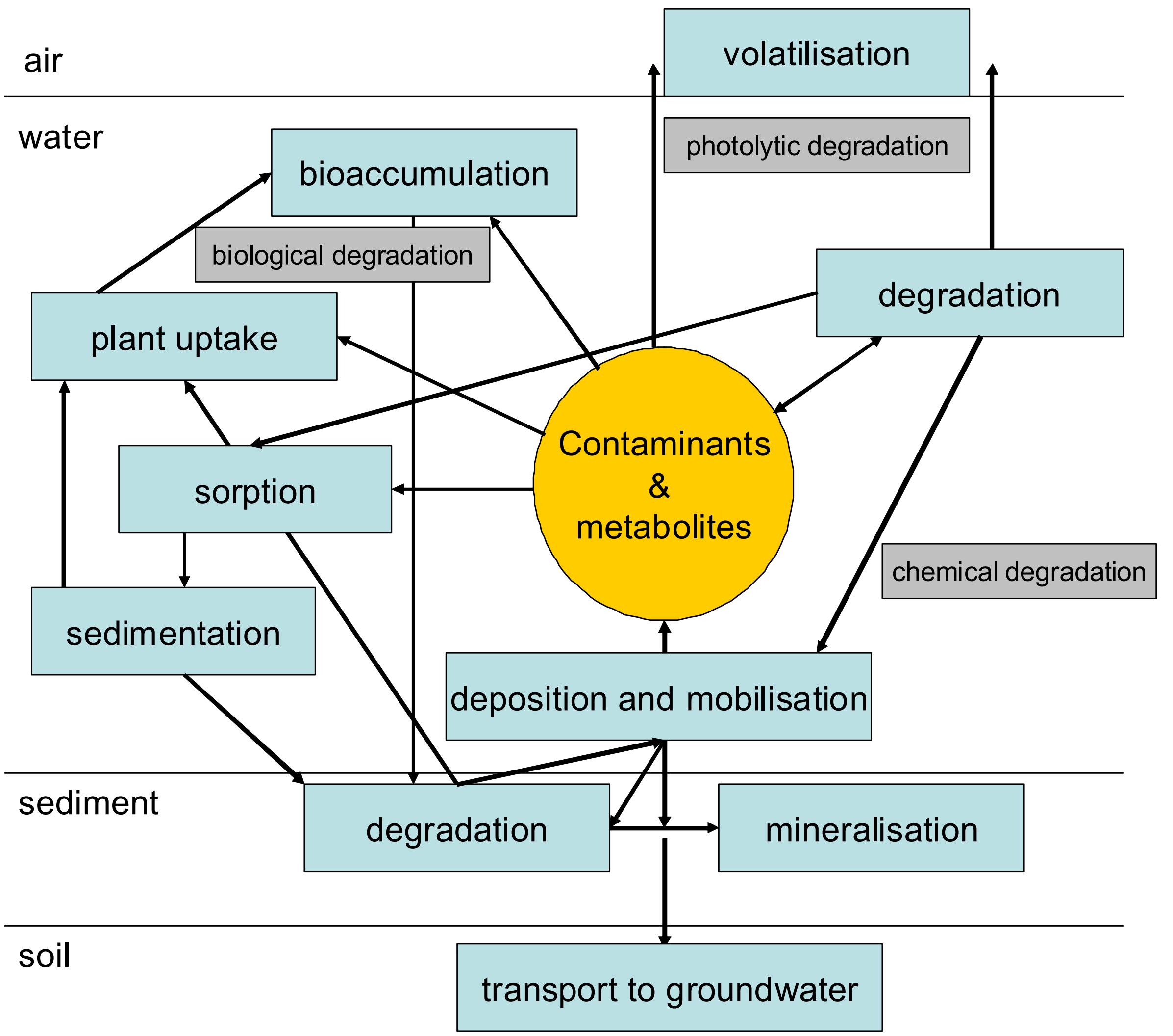


Figure 1.7 Pathways of Contaminants in the aquatic environment

It can be seen from the EC_{50} values of pharmaceuticals that acute toxicity is unlikely to occur in the environment, as acute effect concentrations are 100-1000 times higher than residues found in the aquatic environment. Therefore with the exception of chemotherapy and mutagenic antibiotics, the biological impacts will likely occur at chronically low concentrations and only if the drugs interact with cellular receptors [Trudeau et al, 2005]. It has been shown that Ethinylestradiol can alter gonadal development of fish at concentrations below 10 ng L^{-1} [Metcalfe et al, 2001]. A study conducted by Pomati et al. [Pomati et al, 2006] indicated that a mixture of 13 drugs at low concentrations (ng L^{-1}) showed inhibited cell proliferation of human embryonic cells and affected their physiology and morphology, which suggested that pharmaceuticals in water can have potential effects on aquatic life. Another study conducted by Caminada et al. [Caminda et al, 2006] evaluated the in vitro cytotoxicity of 34 pharmaceuticals in fish cells. However, these compounds are normally found in complex mixtures (various different pharmaceuticals, personal care products, plasticisers, other emerging contaminants), where different synergistic or antagonistic effects can be produced. An interesting research project has been done on that topic by Schnell et al. [Schnell et al, 2009] where the combined toxicity of pharmaceuticals and personal care products on rainbow trout liver cells was investigated. More relevant effects are the chronic ones, as many aquatic species are continually exposed over long periods (entire life cycle). There is to date, little information on these chronic and chronic synergistic effects of those micro and emerging contaminants on aquatic life forms and humans [Smital, 2008].

Apart from elevated acute and chronic toxicity, many of those emerging contaminants and their degradation/transformation products have endocrine disrupting properties. Endocrine disruption is the ability of a chemical substance to interfere with the performance of the endocrine system. The disruption may be produced by a variety of mechanisms such as interacting with target tissue (via hormone receptor or non-receptor pathway) [Simmons et al, 2010], affecting biological half-life or hormone secretion, or changing the feedback relationships in the target organs. The effects of endocrine disruptors on wildlife and humans can be severe. Such effects include neurological effects, adverse reproductive effects (infertility, sexual underdevelopment, altered or reduced sexual behaviour) [Sarcinelli et al, 2003; Stanko et al, 2010; Michael, 2001], attention deficit or hyperactivity [Bouchard et al, 2010], altered thyroid or adrenal cortical function, increased incidents of certain cancers, birth defects, abnormal behaviour [Guler and Ford, 2010], growth [Alvarez and Fuiman, 2005], etc. some effects are shown in **Table 1.10**. Since the endocrine system is complex, it is not surprising that substances which cause endocrine disruption are diverse and manifold. Among the emerging contaminants found in surface waters and MWTP effluents, estrogenic hormones have the highest endocrine disrupting potential, which can be several thousand times higher than other chemicals such as nonylphenol [Nghim et al, 2004], which implies that natural and synthetic estrogens can be biologically reactive in low ng L^{-1} levels.

Table 1.10 Environmental effects of contaminants

Compound	Use	Effect	Reference
Bisphenol A	epoxy resins, polycarbonate plastics	estrogenic effects in rats increased breast cancer in humans anti-androgen effects	Dodds, 1938 Krishnan, 1993 Sohoni, 1998
Butylated Hydroxyanisole	food antioxidant	estrogenic to breast cancer cells, rainbow trout estrogen receptor, stimulates human estrogen receptor	Jobling, 1995
Phthalates	plasticisers	miscarriage and pregnancy complication at high levels	Institute of Environmental Health, 1995
DDT	insecticide	hormonal effects, thinning of eggshells, damaged male reproductively, behavioural changes	Colborn, 1995
Prochloraz	fungicide	affects pituitary weight	McKinney, 1994
Propiconazole	fungicide	affects steroid metabolism	McKinney, 1994
PCBs	electrical equipment	metabolites mimic estradiol, exposure can cause delayed brain development	Jacobson, 1997 Routledge, 1998
Estrone, 17-β-estradiol, 17-β-ethynylestradiol	steroidal estrogens, contraceptives	feminization of fish	Witte, 1998
Penicillin, sulfonamides, tetracycline	antibiotics	resistance of pathogens affects the food chain	Witte, 1998 Daughton, 1999
Parabens	preservatives	weak estrogenic activity	Routledge, 1998
Triclosan	disinfectant	toxic to bacteria, can cause resistance	McMurry, 1998
Benzophenone-3	sunscreen agent	antiandrogenic activity in fish	Kunz, 2006
Atrazine	herbicide	feminization of male leopard frogs	Hayes, 2002

Another impact of emerging contaminants, especially in the case of pharmaceuticals, is the occurrence of antibiotic resistance of pathogens and the occurrence of antibiotic resistance genes (ARGs). Sulfonamide resistance genes (sul1, sul2 and sul3) were detected in shrimp ponds, fish ponds and a canal in Vietnam [Hoa et al, 2008], *Escherichia coli* from a poultry slaughterhouse in Portugal had multidrug resistance [Martins da Costa et al, 2008]. A study from Angenent et al., [Angenent et al, 2008] showed the increasing resistance of macrolide-lincosamide-streptogramin B (MLSB) bacteria to tylosin. Although there are indications, it is to date unclear whether the presence of antibiotics in natural waters contributes to the spread of antibiotic resistance in microorganisms [Kümmerer and Henninger, 2003; Kümmerer, 2004], apart from that, antibiotics have the potential to affect the microbial community in sewage systems, leading to inhibition of waste water bacteria which seriously affects organic matter degradation in waste waters [Kümmerer et al, 2002].

1.5 Water treatment

1.5.1 Conventional wastewater treatment plants

Conventional Municipal Wastewater Treatment Plants (MWTPs) consist of various treatment steps. Its aim is to produce an environmental friendly (in terms of biological oxygen demand, NH_4^+ load, nutrient removal, suspended solids, etc.) stream of water, which can be either subject to a tertiary treatment or can be safely discarded into the environment. The pre-treatment step removes coarse solids, grit and sand, grease and fat. The primary treatment step removes 30-35% of biological oxygen demand (BOD) and 60-65% suspended solids. The secondary step is designed to remove and degrade the organic and biological content (human faeces, food wastes, soaps, detergents, etc.) in the water with the help of aerobic biological processes. The water is then either released into the environment or subject to a third cleaning step, which normally consists of either ozonisation, UV, chlorination, etc to disinfect and clean the water further to make it available for water reuse. A schematic of a typical wastewater treatment plant can be seen in **Figure 1.8**.

As early as 1965 Stumm-Zollinger and Fair published a report, indicating that steroid hormones are not completely eliminated by conventional wastewater treatment [Stumm-Zollinger and Fair, 1965], and nowadays, the presence of a high amount of pharmaceuticals and other emerging contaminants in the ng L^{-1} to µg L^{-1} range in MWTP effluents in various countries, confirm that the conventional treatment for these micro contaminants is ineffective.

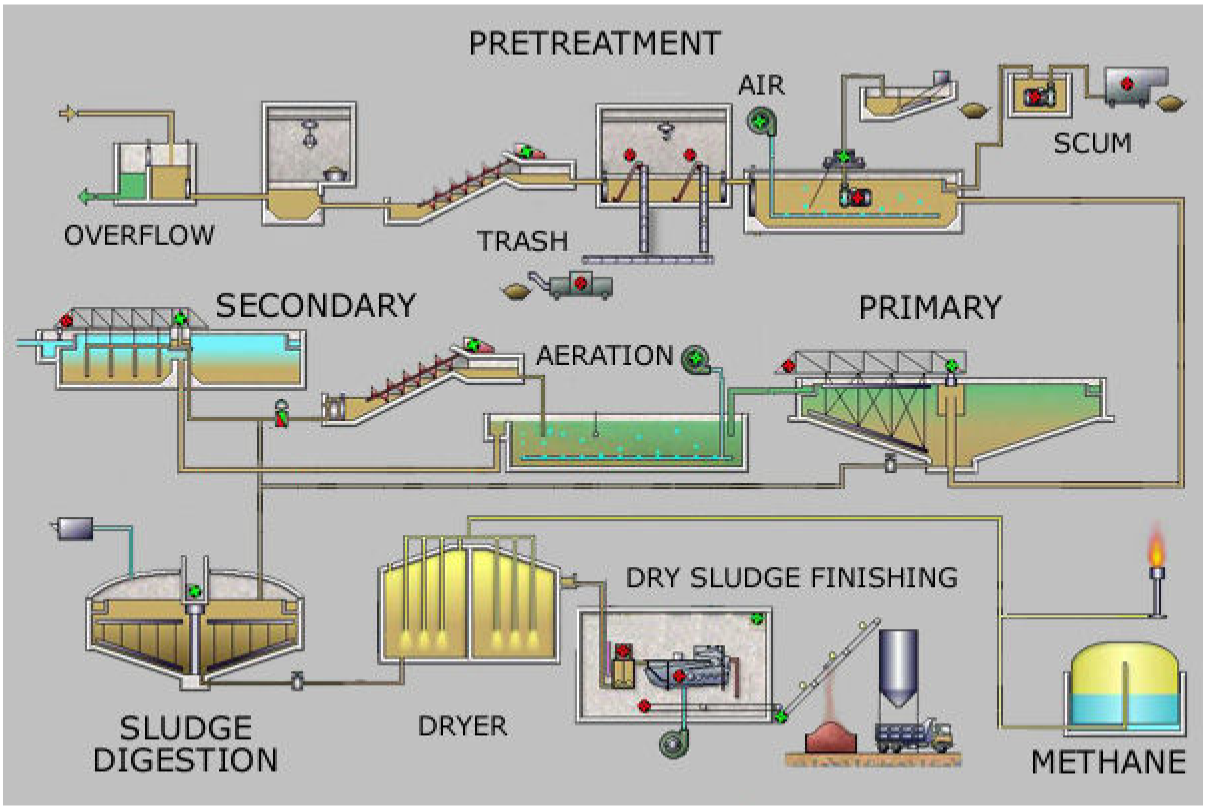


Figure 1.8 Schematics of a wastewater treatment plant

The reduction grade of contaminants in a MWTP depends on the physical and chemical properties of each compound and the applied treatment in the treatment plant. As listed in **Table 1.11**, reduction rates can vary between 100% and <0% in respect of concentrations in influent versus concentrations in effluent. One possible explanation of the increase (reduction <0%) of some compounds in the effluent is the conversion of metabolites to the initial drug through bacteria present in the MWTP [Ternes, 2001; Miao et al, 2002; Wick et al, 2009]. Other researchers support the theory that the increased concentration of pharmaceuticals in the effluents can be explained through the matrix effects (high organic content in influent vs. low organic content in effluent which affects the analytical protocol) and the ionic suppression in the LC-MS system [Antignac et al, 2005; Roberts and Thomas, 2006].

Table 1.11 Concentrations and elimination percentages of contaminants in MWTP

compound	MWTP effluent conc. [ng L^{-1}]	Elimination [%]	Country	Reference
pharmaceuticals				
analgesics / anti-inflammatory				
Diclofenac	900-2200 194-748 318 530	59 < 0 - < 0	Spain Canada China Switzerland	Gómez, 2007 Lishman, 2006 Sui, 2010 Morasch, 2010
Ibuprofen	7100-28000 6200 90 348-773	95 9 91 95	Spain Switzerland Spain Canada	Gómez, 2007 Morasch, 2010 Gros, 2010 Lishman, 2006
Naproxen	1840-420 128 300-3200 452-1189	64 - - 92	Spain Korea USA Canada	Bueno, 2007 Sim, 2010 Sedlak, 2005 Lishman, 2006
Acetaminophen	59-164 10-19	99.8 99.9	Spain South Korea	Bueno, 2007 Kim, 2007
Ketoprofen	900 340-1070 318-620 38	- 37 29 -	Switzerland Spain Croatia Korea	Morasch, 2010 Santos, 2005 Gros, 2006 Sim, 2010
Codeine	900-8100	46	Spain	Gómez, 2007
Mefenamic acid	342-396 34	< 0 -	UK Korea	Roberts, 2006 Sim, 2010
Acetylsalicylic acid	200-1500 18	- -	Germany Korea	Ternes, 2001 Sim, 2010
antibiotics				
Trimethoprim	331-1264 271-322 550-1900 400	20 < 0 - -	Spain UK USA China	Bueno, 2007 Roberts, 2006 Sedlak, 2005 Sui, 2010
Ofloxacin	4422-13426 652-1081	30 -	Spain Italy	Bueno, 2007 Castiglioni, 2005
Sulfamethoxazole	275-794 136-407 166-553 141	64 30 - -	Spain South Korea Ireland USA	Bueno, 2007 Kim, 2007 Lacey, 2008 Bartelt-Hunt, 2009
Clarithromycin	140-260 90-540	- -	Germany Canada	Ternes, 2001 Metcalfe, 2004
β- blocker				
Metoprolol	730-2200 60-160	- -	Germany USA	Ternes, 2001 Sedlak, 2005
Propanolol	44-100 20-50	< 0 -	Spain USA	Bueno, 2007 Sedlak, 2005
Atenolol	400-1150 1720-4850	< 0 38	Croatia Spain	Gros, 2006 Bueno, 2007
Sotalol	185-210	< 0	Croatia	Gros, 2006
blood lipid lowering agents				
Benzafibrate	233-484	41	Spain	Bueno, 2007
	2200-4600	-	Germany	Ternes, 2001

Gemfibrozil	2337-5428 246-436	< 0 46	Spain Canada	Bueno, 2007 Lishman, 2006
antidepressants				
Diazepam	16-87 30-40	4 -	Spain Germany	Bueno, 2007 Ternes, 2001
Flouxetine	398-929 50-140	90 -	Spain Canada	Bueno, 2007 Metcalfe, 2004
antiepileptic				
Carbamazepine	130-230 2100-6300 119 33.7-111.2	20 - - -	Spain Germany USA USA	Gómez, 2007 Ternes, 2001 Bartelt-Hunt, 2009 Spongeberg, 2008
X-ray contrast media				
Iopamidol	660-15000	-	Germany	Ternes, 2001
Iopromide	2630-4030 750-11000	- -	South Korea Germany	Kim, 2007 Ternes, 2001
Iomeprol	370-3800	-	Germany	Ternes, 2001
hormones				
Estrone	30-80 14-36 13-38	75 - 57	Spain South Korea Canada	Gómez, 2006 Kim, 2007 Lishman, 2006
Diethylstilboestrol	9-30	82	Spain	Gómez, 2006
diuretics				
Furosemide	1050-2957 749-2102	2 -	Spain Italy	Bueno, 2007 Castiglioni, 2005
Hydrochlorothiazide	3683-14857 598-1253	< 0 0	Spain Italy	Bueno, 2007 Castiglioni, 2005
Other contaminants				
Galaxolide	109-636 451-1080	<0 43-75	Spain France	Calderon-Preciado, 2011 Miège, 2009
Cashmeran	176-416	<0-20	Spain	Calderon-Preciado, 2011
Tributylphosphate	139-167	5-28	Spain	Calderon-Preciado, 2011
Atrazine	250	-	Switzerland	Morasch, 2010
Diuron	190	-	Switzerland	Morasch, 2010
Triclosan	410 250 150	- 69 60	Switzerland USA France	Morasch, 2010 Yu, 2006 Miège, 2009
Nonylphenol	426-4926	33-94		Drewes, 2005
Octylphenol	37.5-180	55-98		Drewes, 2005
BHT	79-499	0-5	Spain	Calderon-Preciado, 2011
Estrone	0-147	<0		Fernandez, 2007
Progesterone	0.31-0.37	90-96.3		Chang, 2008
Bisphenol A	16-1840 560	10-99 53	 Switzerland	Clara, 2005 Morasch, 2010
Polyaromatic hydrocarbons	5636-9085	18-50	Greece	Manoli, 2008

As can be seen in **Table 1.11** there is a large number of encountered micro, emerging and other contaminants which do have a very low degradation rate in conventional MWTPs. To degrade these contaminants other treatment steps, which either remove the compounds through membranes [Xu et al, 2005; Yoon et al, 2006], or through the use of an oxidising agents like chlorine or ozone are necessary. Several wastewater treatment oxidizers can be used to remove these contaminants. The strength order of their redox potential decreases from FeO_4^{2-} > O_3 > $S_2O_8^{2-}$ > H_2O_2, Cl_2 > ClO_2, as can be seen in **Table 1.12** (**Eq. 1.1 - Eq. 1.7**) according to House and Jiang et al, [House, 1962; Jiang and Lloyd, 2002]. To increase the removal effect, combinations such as UV/O_3, UV/H_2O_2, UV/Fenton, or UV/TiO_2 can be applied. Theses reactions are advanced oxidation processes, and will be commented on in the following section.

Table 1.12 Redox potentials of some oxidizers used in wastewater treatment

Oxidizer	Reaction	E° [V]	
FeO_4^{2-}	$FeO_4^{2-} + 8H^+ + 3e^- \Leftrightarrow Fe^{3+} + 4H_2O$	2.200	**Eq. 1.1**
O_3	$O_3 + 2H^+ + 2e^- \Leftrightarrow O_2 + H_2O$	2.076	**Eq. 1.2**
$S_2O_4^{2-}$	$S_2O_8^{2-}(aq) + 2e^- \Leftrightarrow 2SO_4^{2-}$	2.010	**Eq. 1.3**
H_2O_2	$H_2O_2 + 2H^+ \Leftrightarrow 2H_2O$	1.776	**Eq. 1.4**
Cl_2	$Cl_2(g) + 2e^- \Leftrightarrow 2Cl^-$	1.358	**Eq. 1.5**
	$ClO^- + H_2O + 2e^- \Leftrightarrow Cl^- + 2OH^-$	0.841	**Eq. 1.6**
ClO_2	$ClO_2(aq) + e^- \Leftrightarrow ClO_2^-$	0.954	**Eq. 1.7**

1.5.2 Advanced oxidation processes

Advanced oxidation processes (AOPs) are processes which are characterised by the production of hydroxyl radicals ($HO^{\bullet}$). Second to fluorine (3.03 V vs. SHE) the hydroxyl radical is the strongest known oxidant with a potential of 2.8 V versus standard hydrogen electrode (SHE). These radicals are able to oxidize almost any organic molecule yielding CO_2 and inorganic ions, rate constants for most reactions in aqueous solutions are usually in the range of 10^6 to 10^9 M^{-1} s^{-1} [Buxton et al, 1988; Haag and Yao, 1992]. The techniques to generate hydroxyl radicals are through direct photolysis of oxidants like H_2O_2, O_3 or water with high energy UV radiation, Fenton and photo-Fenton techniques, heterogeneous photocatalysis with semiconductors, electrochemical techniques and cavitation techniques [Legrini et al, 1993; Safarzadeh-Amiri et al, 1996; Herrmann, 1999; Gogate and Pandit, 2004a; Gogate and Pandit, 2004b]. The most common AOPs (listed in **Table 1.13**) used are the ones using irradiation and because the production of UV irradiation with lamps is expensive, the investigative focus lies on the two AOPs which can be powered by solar radiation (λ > 300 nm), which are heterogeneous catalysis with UV/TiO_2 and homogeneous catalysis with Fe^{2+}/H_2O_2/UV, the photo-Fenton process. An overview of the principal AOPs and their application can be found in **Table 1.14**.

Table 1.13 AOPs using radiation for the generation of hydroxyl radicals

AOP	key reaction	wavelength	
UV/H_2O_2	$H_2O_2 + h\nu \rightarrow 2HO^\bullet$	$\lambda < 300$ nm	**Eq. 1.8**
UV/O_3	$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2HO^\bullet$	$\lambda < 310$ nm	**Eq. 1.9** **Eq. 1.10**
UV/H_2O_2/O_3	$O_3 + H_2O_2 + h\nu \rightarrow O_2 + HO^\bullet + HO_2^\bullet$	$\lambda < 310$ nm	**Eq. 1.11**
UV/TiO_2	$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+)$ $TiO_2(h^+) + HO_{ad}^- \rightarrow TiO_2 + HO_{ad}^\bullet$	$\lambda < 390$ nm	**Eq. 1.12** **Eq. 1.13**
Fenton	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^-$	$\lambda < 580$ nm	**Eq. 1.14**
Photo-Fenton	$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + HO^\bullet$		**Eq. 1.15**

Table 1.14 Principal AOPs and their applications

homogeneous processes			
Chemical Process	**Characteristics**	**Applications**	**References**
Ozone in alkaline medium (O3/OH-)	O_3: potent oxidizing agent (E^o=2.07 V), unstable. Attacks through electrophilic mechanisms rings and double bounds, weak against C-C, C-O and O-H bounds. Two reaction mechanisms: direct via dissolved O_3 and indirect via $HO^\bullet$. Elevated $HO^\bullet$ production at higher pH. Disadvantages: low solubility of O_3 in water, possible formation of by products (bromates), selective, elevated costs, presence of bi- and carbonates scavenge radicals.	Elimination of organic contaminants in water. Disinfection of effluent waters. Disinfection and treatment of potable water. Taste and odour elimination. Treatment of industrial waste waters: textiles, agriculture, pharmaceuticals, leachate, etc. Industrial applications.	Rice, 1997 Wojtenko, 2001 Von Gunten, 2003 Esplugas, 2007

Ozone and hydrogen peroxide (O_3/H_2O_2) ($O_3/H_2O_2/OH^-$)	Additional generation of $HO^\bullet$ Indirect degradation through radicals is more efficient $H_2O_2 \Leftrightarrow HO_2^- + H^+$ $HO_2^- + O_3 \rightarrow HO^\bullet + O_2^{\bullet -} + O_2$ Disadvantage: additional cost of H_2O_2	Elimination of organic contaminants in water. Disinfection of effluent waters. Disinfection and treatment of potable water. Taste and odour elimination. Test runs at pilot plant scale.	Beltrán, 1998 Balcioglu, 2003
Catalytic homogeneous Ozonisation (O_3/ cat.)	Increased decomposition of O_3 in water (higher production of $HO^\bullet$) through the presence of transition metals in the water (Fe(II), Mn(II), Ni(II), Co(II), Cd(II), Cu(II), Ag(I), Cr(III), Zn(II))	Elimination of organic contaminants in water. Technology in development (laboratory scale.	Kasprzyk-Hordern, 2003
Fenton: H_2O_2 / Fe^{2+}	Catalytic system, production of $HO^\bullet$ radicals. $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^-$ Limiting factors are the regeneration of Fe^{2+}, and the concentration of Fe Disadvantages: low pH (2.8-3) and subsequent elimination of Fe necessary	Elimination of organic contaminants in water. Treatment of industrial waste waters: textiles, agriculture, pharmaceuticals, leachate, etc. Industrial applications.	Neyens, 2003 Pignatello, 2006 Bautista, 2008
Photochemical Process	**Characteristics**	**Applications**	**References**
Ozone and UV radiation (O_3/UV)	Generation of $HO^\bullet$ radicals through photolysis of O_3 by singlet oxygen ($\lambda <$ 310 nm) $O_3 + h\nu \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2HO^\bullet$ Molar extinction coefficient of O_3 at 254 nm: 3300 mol^{-1} cm^{-1} Disadvantages: high operating costs	Elimination of organic contaminants in water. Disinfection of effluent waters. Disinfection and treatment of potable water.	Beltrán, 1997 Esplugas, 2002
Hydrogen peroxide and UV radiation (H_2O_2/UV)	Generation of $HO^\bullet$ radicals through photolysis of H_2O_2 ($\lambda <$ 300 nm) $H_2O_2 + h\nu \rightarrow 2HO^\bullet$ Elevated photolysis at higher pH Disadvantages: elevated costs, low radical formation velocity through low molar extinction coefficient of H_2O_2: 18.7 mol^{-1} cm^{-1} at 254 nm	Elimination of organic contaminants in water. Disinfection of effluent waters. Disinfection and treatment of potable water. Taste and odour elimination. Treatment of industrial waste waters: textiles, agriculture, pharmaceuticals, leachate. Industrial applications.	Galindo, 1999 Neamtu, 2002 Lopez, 2003

Ozone, hydrogen peroxide and UV radiation ($O_3/H_2O_2/UV$)	Generation of $HO^\bullet$ radicals through photolysis of H_2O_2 ($\lambda < 310$ nm) $O_3 + H_2O_2 + h\nu \rightarrow O_2 + HO^\bullet + HO_2^\bullet$ Disadvantages: elevated costs	Elimination of organic contaminants in water. Disinfection of effluent waters. Disinfection and treatment of potable water. Taste and odour elimination Treatment of industrial waste waters: textiles, agriculture, pharmaceuticals, leachate, etc. Industrial applications.	Azbar, 2004 Ikehata, 2005
Photo-Fenton ($Fe^{2+}/H_2O_2/UV$)	Photocatalytic system. Generation of $HO^\bullet$ radicals, photocatalytic regeneration of Fe^{2+} $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^-$ $Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^\bullet + H^+$ Disadvantages: low pH (2.8-3) and elimination of Fe necessary	Elimination of organic contaminants in water. Treatment of industrial waste waters: textiles, agriculture, pharmaceuticals, leachate, etc. Industrial applications	Neyens, 2003 Pignatello, 2006 Malato, 2009
Electro-Fenton and photo-electro-Fenton	Augmentation of the oxidative capacity of H_2O_2 in presence of Fe^{2+} in acidic medium. Regeneration of Fe^{2+} through direct cathode reduction: $Fe^{3+} + e^- \rightarrow Fe^{2+}$ The anode has to be Pb/PbO_2 or Pt. Combination with UV radiation is possible (photo-electro-Fenton) Disadvantages: elevated costs, needs high ion concentration (g L^{-1}) in solution for conductivity	Elimination of organic contaminants in water. Technology in its first developmental steps	Brillas, 2009
Thermochemical processes	**Characteristics**	**Applications**	**References**
Wet advanced oxidation (WAO)	Formation of $HO^\bullet$ radicals through dissolved oxygen at high temperatures and pressures (200-300 °C; 20 – 200 bar). Classic process to treat elevated COD (0.5 - 15 g L^{-1}). Disadvantages: elevated costs and operating conditions (P, T).	Elimination of organic contaminants in water. Low effective for nitrogenated compounds. Treatment of wastewaters with high organic content.	Imamura, 1999 Bhargava, 2006
Supercritical wet advanced oxidation (SWAO)	Supercritical conditions (400-650 °C, >250 bar) Highly efficient through the generation of only one phase, Treatable organic load > 50 g L^{-1}. Disadvantages: elevated costs and extreme operating conditions (P, T), corrosive medium and salt deposition.	Elimination of organic contaminants in water. Low effective for nitrogenated compounds. Treatment of wastewaters with high organic content.	Mishra, 1995

Catalytic wet advanced oxidation (CWAO)	Moderate conditions in the presence of catalysts (150-250 ºC; 5 – 25 bar). Treatable organic load: > 10 g L^{-1}. Disadvantages: extreme operating conditions, need of a stable catalyst.	Elimination of organic contaminants in water. Low effective for nitrogenated compounds. Treatment of wastewaters with high organic content.	Levec, 2007
heterogeneous process			
Chemical process	**Characteristics**	**Applications**	**References**
Heterogeneous catalytic ozonisation (O_3/cat.)	Accelerated decomposition of O_3 in water (higher generation of $HO^\bullet$ radicals) in the presence of a catalyst. Principal catalysts are transition metal oxides (MnO_2, TiO_2, Al_2O_3), immobilized metals or oxides (Cu/Al_2O_3, TiO_2/Al_2O_3), granular activated carbon (GAC) and porous systems (silicates). The efficiency of the process depends on the surface properties of the catalyst and the pH of the medium.	Elimination of organic contaminants in water. Treatment and disinfection of potable water. Technology under investigation and first developmental steps (laboratory scale).	Kasprzyk-Hordern, 2003
Photochemical process	**Characteristics**	**Applications**	**References**
Heterogeneous photocatalysis (TiO_2/UV), (TiO_2/UV/H_2O_2) and (O_3/TiO_2/UV)	Excitement of a solid semiconductor in water which absorbs light (λ < 390 nm), resulting in the formation of an electron/hole pair. Generation of $HO^\bullet$ radicals through oxidation of water in the valence band and generation of $O^{\bullet}_2{}^-$ radicals through reduction of dissolved O_2 in the conduction band. TiO_2 (λ < 390 nm) $TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+)$ $TiO_2(h^+) + H_2O \rightarrow TiO_2 + H^+ + HO^\bullet$ $TiO_2(e^-) + O_2 \rightarrow O_2^{\bullet-}$ Augmented production of radicals in presence of O_3 and H_2O_2. Disadvantages: low quantum yield, the adsorbance of contaminants onto the surface of the catalyst limits the velocity of the reaction.	Elimination of organic contaminants in residual water. Disinfection of waters. Treatment of industrial waste waters: textiles, agriculture, pharmaceuticals, leachate, etc. Industrial applications	Fujishima, 2000 Vinod, 2002 Malato, 2009

1.5.2.1 *Removal of emerging contaminants by AOPs*

Applied as a process in wastewater treatment and drinking water treatment AOPs are a quite potent way of removing contaminants from these waters. One remarkable advantage of AOPs is that they are environmentally friendly, which means that they do not transfer pollutants from one phase to another like extraction, activated carbon adsorption, filtration or reverse osmosis, nor do they produce big amounts of hazardous sludge and waste. If AOPs are applied to water treatment, it is possible that they produce harmful degradation by-products [Fernandez-Alba et al, 2002], and therefore it is necessary that these applications are optimized not only in the economic viewpoint but also in the safety viewpoint. AOPs can be employed either alone or coupled with other physicochemical and biological processes. The coupling of those processes leads to improved treatment efficiencies [Malato et al, 2007].

The two main oxidation methods for these contaminants are dark oxidation, e.g. methods like ozonation without radiation, and oxidation methods with radiation, e.g. methods like UV/H_2O_2, UV/TiO_2 or photo-Fenton. Ozonation is the dark oxidation method most used in the removal of ECs, with ozone doses between 0.1 and 30 mg L^{-1} [Esplugas et al, 2007] and removal rates higher than 90% for several compounds although X-ray contrast media and Clofibric acid seem to be more recalcitrant to oxidation than other contaminants [Ternes et al, 2003]. The Fenton treatment is an important option for industrial wastewaters [Bidga, 1955], but up to date no application for the removal of micro pollutants is available. Photocatalysis with TiO_2 and UV/H_2O_2 are the oxidation methods most used to degrade ECs with removal rates higher than 98% for Carbamazepine, hormones and Bisphenoles, but to achieve these high removal rates, large irradiation times were required. **Table 1.15** shows some applications of AOPs for the removal of ECs.

It can be stated that AOPs are generally capable of degrading the compound in question or even a complex mixture of several compounds, but is not clear whether there is a total mineralization of the degradation products (when using a complex mixture of several different ECs in real wastewater matrixes), as dissolved total organic carbon (DOC) does not decline significantly.

Although AOPs seem to be a costly but simple application for the removal of pollutants from waste and freshwater sources, the growing water scarcity and water shortage in many parts of the world seems to be a good reason to apply these techniques and to use MWTP effluents as a source for different purposes.

Table 1.15 Removal of ECs by oxidation processes

Compound	Water type	Treatment	Results	Reference
Pesticides	Groundwater	O_3 / H_2O_2	80% removal of atrazine and Phenylurea herbicides	Ijeplaar, 2000
Pharmaceuticals	Distilled and drinking water	Ozonation	High doses of ozone necessary to remove all pharmaceuticals	Ternes, 2002
Pesticides	Destilled water	Ozonation	Large amounts of ozone were spent to remove pesticides	Maldonado, 2006
Pharmaceuticals and personal care products	Groundwater	Ozonation	No significant influence on PPCP elimination except for carbamazepine	Carballa, 2007
Sulfonylurea herbicide	MilliQ water	Photocatalysis	Strong affect of TiO_2 amount and light flux	Sleiman, 2007
Bisphenol A	MilliQ water	UV/H_2O_2	Better removal of Bisphenol A with UV/H_2O_2 than only UV	Chen, 2006
Metronidazole	Deionised water	Photo-Fenton	Higher removal than Fenton alone	Shemer, 2006
Trace contaminants	MWTP effluent	Ozonation, O_3 / H_2O_2	Removal of ECs with ozone efficient.	Wert, 2009
Estrone Caffeine	MWTP effluent	O_3 / UV	100% removal of target ECs, O_3 conc. 5-15 mg L^{-1}	Huber, 2003
24 different ECs	MWTP effluent	O_3 with sand filtration	> 80% removal following filtration and 27 min ozonisation	Nakada, 2007
17β-Estradiol and Estrone	Deionized water, MWTP effluents	Immobilized TiO_2 /UV	Fast degradation of compounds.	Nakashima, 2003
15 different contaminants	Deionized and simulated fresh water	Photo-Fenton, TiO_2 / UV	Fast degradation of the selected ECs	Klamerth, 2009a
15 different contaminants	Simulated effluent water, MWTP effluent	Modified photo-Fenton	Dependency on carbonates, relatively independent of water	Klamerth, 2010a
contaminants in MWTP effluent	MWTP effluent	Photo-Fenton	Fast and complete degradation	Klamerth, 2010b
15 different contaminants	MWTP effluent	Modified photo-Fenton	Dependent on complexing agent at neutral pH	Klamerth, 2010c
15 different contaminants	MWTP effluent	Immobilized TiO_2	Stable layer of immobilized TiO_2, good degradation	Miranda-Garcia, 2011
15 different contaminants	Deionized water	Immobilized TiO_2	Stable layer of immobilized TiO_2, good degradation	Miranda-Garcia, 2010
Trace contaminants	MWTP effluent	Ozonation, O_3 / H_2O_2	>99% removal of trace contaminants	Rosal, 2008
Trace contaminants	MWTP effluent	Ozonation	Good removal for contaminants	Rosal, 2010

1.5.3 The photo-Fenton process

1.5.3.1 Aquatic iron chemistry

Iron is the fourth most abundant element in the earth's crust. It occurs in oxidation states from +VI to –II, with coordination numbers from 3 to 8 [Hawker and Twigg, 1994]. Iron is omnipresent in the environment through sands, dust and ash, and practically all natural water contains iron at least in traces. Its concentration in fog, clouds and surface water is around 10^{-5} mol L^{-1} [Faust and Hoigné, 1990]. Its omnipresence in small concentrations in surface water and clouds is thought to be responsible for the formation of hydrogen peroxide (**Eq. 1.16 - Eq. 1.18**) and therefore for the self purification of these waters [Hammerschmidt and Fitzgerald, 2010].

$$Fe^{2+} + O_2 \longrightarrow Fe^{3+} + O_2^{\bullet -} \qquad \textbf{Eq. 1.16}$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet} \qquad \textbf{Eq. 1.17}$$

$$HO_2^{\bullet} + Fe^{2+} + H^+ \longrightarrow H_2O_2 + Fe^{3+} \qquad \textbf{Eq. 1.18}$$

In aqueous solutions, the most abundant iron species have oxidation numbers of +II (ferrous iron) and +III (ferric iron). Iron is complexed by water and hydroxyl ligands, provided that no other complexing substances are present. How many of these ligands are hydroxyl ions depend on the pH of the solution, which influences directly the acid / base equilibrium of the complex.

The critical ion species for the Fenton reaction is the ferric ion, because its hydroxides precipitate at lower pH than those of ferrous iron. The ferric ion hydroxide $Fe(OH)_3$ has a very low solubility product $K_s \approx 2.79 * 10^{-39}$, precipitation starts at pH 2.5 - 3.5, depending on temperature and iron concentration. Figure 1.9 shows the equilibrium concentrations of the most important ferric ion aqua complexes in water in the absence of other complexing substances for a ferric ion concentration of 20 mg L^{-1} at different pH. The most dominant species in the pH range from 2.5 - 3 is $[Fe(H_2O)_5(OH)]^{2+}$. Equilibrium constants were provided by Flynn [Flynn, 1984]. At lower pH (< 2) the ferric ions form $[Fe(H_2O)_6]^{3+}$ complexes and with rising pH this complex undergoes hydrolysis and subsequent precipitation as shown in **Eq. 1.19**. The precipitation process starts with the formation of dimers and oligomers, and then the iron hydroxyl molecule polymerises further and loses water until forming finally insoluble iron hydroxides (e.g. goethite or hematite).

$$\left[Fe(H_2O)_6\right]^{3+} \longrightarrow \left[Fe(H_2O)_5(OH)\right]^{2+} \longrightarrow \left[Fe(H_2O)_4(OH)_2\right]^{+} \longrightarrow$$
$$\left[Fe_2(H_2O)_8(OH)_2\right]^{4+} \xrightarrow{\to\to} Fe_2O_3 \cdot nH_2O$$

Eq. 1.19

The precipitation is of red brown colour, not stoichiometric, contains a lot of water, and has strong cationic character, thus co-precipitates other ions and organic substances and is therefore often used as a coagulant. This precipitate is difficult to dissolve (insoluble above pH 1-1.5), but can be dissolved by complexing compounds such as oxalic acid.

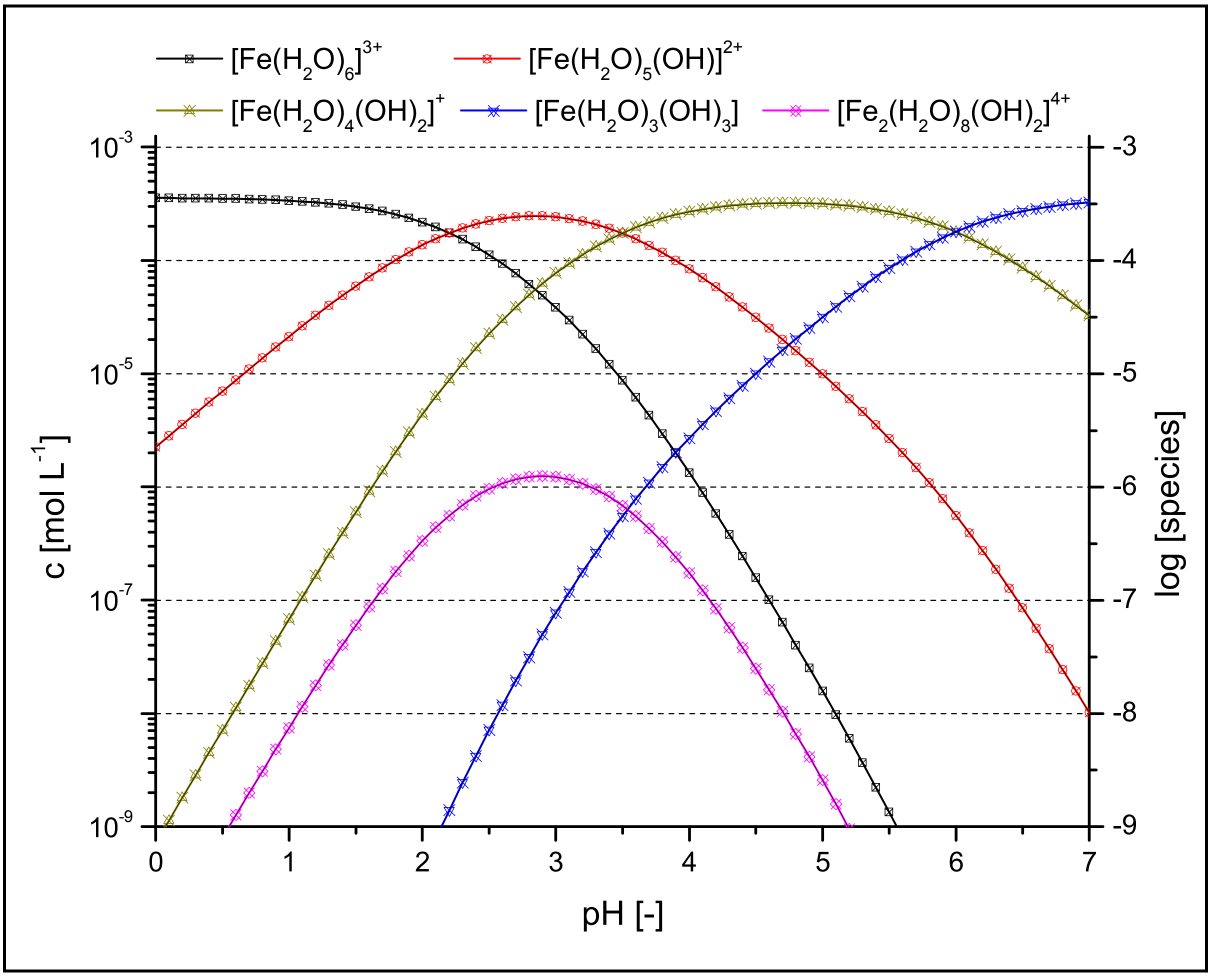


Figure 1.9 Ferric iron species present in aqueous solution at different pH

1.5.3.2 Fenton reactions in aqueous solutions

The Fenton process was described for the first time by Henry Fenton in 1894 in a study where Fenton investigated the degradation of tartaric acid with H_2O_2 in the presence of Fe^{2+} salts [Fenton, 1894], in 1934 Haber and Weiss [Haber and Weiss, 1934] proposed that the $HO^\bullet$ radical is the active oxidising species produced "in situ" by the Fenton reaction. Between 1949 and 1951 Barb et al [Barb et al, 1949; Barb et al, 1951a; Barb et al, 1951b] investigated the mechanism proposed by Haber and Weiss, and after the work of Walling [Walling, 1975] the radical mechanism has been accepted as a classical chain reaction via free radicals.

In the 1960s first applications of the Fenton method for the destruction and degradation of toxic organic substances were developed [Brown et al, 1964], and since then the Fenton method has been applied for the efficient elimination of pharmaceuticals, the treatment of hospital effluents and the treatment of veterinary effluents as a stand alone process [Shemer et al, 2006; Ben et al, 2009; Berto et al, 2009], or as a combined method with other processes for the degradation of industrial effluents [Martínez et al, 2003; Badawy et al, 2009].

The Fenton reaction which takes place between Fe^{2+} and H_2O_2 in aqueous medium at an acidic pH and in the absence of other organic substances can be seen in **Eq. 1.20 - Eq. 1.26**. The rate limiting step in the catalytic cycle is the regeneration of ferrous iron from ferric iron, see **Eq. 1.23 - Eq. 1.25**. The rate constants were published by Sychev and Isaak in 1995 [Sychev and Isaak, 1995].

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + HO^\bullet$ k = 53 - 76 $M^{-1}s^{-1}$ **Eq. 1.20**

$Fe^{2+} + HO^\bullet \longrightarrow Fe^{3+} + HO^-$ k = 2.6 - 5.8 · 10^8 $M^{-1}s^{-1}$ **Eq. 1.21**

$Fe^{2+} + HO_2^\bullet \longrightarrow Fe^{3+} + HO_2^-$ k = 0.75 – 1.5 · 10^6 $M^{-1}s^{-1}$ **Eq. 1.22**

$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HO_2^\bullet$ k = 1 - 2 · 10^{-2} $M^{-1}s^{-1}$ **Eq. 1.23**

$Fe^{3+} + HO_2^\bullet \longrightarrow Fe^{2+} + O_2 + H^+$ k = 0.33 – 2.1 · 10^6 $M^{-1}s^{-1}$ **Eq. 1.24**

$Fe^{3+} + O_2^{-\bullet} \longrightarrow Fe^{2+} + O_2$ k = 0.05 – 1.9 · 10^9 $M^{-1}s^{-1}$ **Eq. 1.25**

$Fe^{2+} + O_2^{-\bullet} + H^+ \longrightarrow Fe^{3+} + HO_2^-$ k = 1 · 10^7 $M^{-1}s^{-1}$ **Eq. 1.26**

$H_2O_2 + HO^{\bullet} \longrightarrow H_2O + HO_2^{\bullet}$ k = $1.7 - 4.5 \cdot 10^7$ $M^{-1}s^{-1}$ **Eq. 1.27**

The complexes formed between ferric iron and H_2O_2 (see **Eq. 1.28 - Eq. 1.31**) are the first step for the reaction in **Eq. 1.23** which dissociate to form ferrous iron.

$[\mathrm{Fe}]^{3+} + \mathrm{H_2O_2} \Leftrightarrow [Fe(HO_2)]^{2+} + H^+$ K = $3.1 \cdot 10^{-3}$ M **Eq. 1.28**

$[Fe(OH)]^{2+} + \mathrm{H_2O_2} \Leftrightarrow [Fe(OH)(HO_2)]^{+} + H^+$ K = $2.0 \cdot 10^{-4}$ M **Eq. 1.29**

$[\mathrm{Fe(HO_2)}]^{2+} \longrightarrow \mathrm{Fe^{2+}} + \mathrm{HO_2^{\bullet}}$ **Eq. 1.30**

$[\mathrm{Fe(OH)(HO_2)}]^{+} \longrightarrow \mathrm{Fe^{2+}} + \mathrm{HO_2^{\bullet}} + \mathrm{OH^-}$ **Eq. 1.31**

Additionally there are radical-radical reactions (**Eq. 1.32 - Eq. 1.34**) and equilibrium reactions **(Eq. 1.35 - Eq. 1.38**) which have to be taken into account:

$2\ HO^{\bullet} \longrightarrow H_2O_2$ k = $5 - 8 \cdot 10^9$ $M^{-1}s^{-1}$ **Eq. 1.32**

$2\ HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$ k = $0.8 - 2.2 \cdot 10^6$ $M^{-1}s^{-1}$ **Eq. 1.33**

$HO_2^{\bullet} + HO^{\bullet} \longrightarrow H_2O + O_2$ k = $1.4 \cdot 10^{10}$ $M^{-1}s^{-1}$ **Eq. 1.34**

$H_2O_2 \Leftrightarrow HO_2^- + H^+$ K = $2.63 \cdot 10^{-12}$ M **Eq. 1.35**

$HO_2^{\bullet} \Leftrightarrow O_2^{-\bullet} + H^+$ K = $3.55 \cdot 10^{-5}$ M **Eq. 1.36**

$HO^{\bullet} \Leftrightarrow O^{-\bullet} + H^+$ K = $1.02 \cdot 10^{-12}$ M **Eq. 1.37**

$HO_2^{\bullet} + H^+ \Leftrightarrow H_2O_2$ K = $3.16 - 3.98 \cdot 10^{-12}$ M **Eq. 1.38**

In the presence of inorganic and organic substances (quenchers, scavengers like HCO_3^- and CO_3^{2-} or organic pollutants), the reaction pathways are manifold and more complicated as the organic substances react in many ways with the generated $HO^{\bullet}$ radicals. The oxidative attack is in all cases electrophilic with rate constants close to the diffusion-controlled limit. Typical reactions with organic molecules are:

- hydrogen abstraction form aliphatic carbons (**Eq. 1.39**),
- electrophilic addition to double bonds or rings (**Eq. 1.40**),
- electron transfer reactions (**Eq. 1.41**)

$HO^{\bullet} + RH \longrightarrow R^{\bullet} + H_2O$ **Eq. 1.39**

$R - CH = CH_2 + HO^{\bullet} \longrightarrow R - C^{\bullet}H - CH_2OH$ **Eq. 1.40**

$HO^{\bullet} + RX \longrightarrow RX^{\bullet +} + HO^-$ **Eq. 1.41**

The generated organic radicals continue to react and prolong the chain reaction. Several reactions can take place (**Eq. 1.42 - Eq. 1.45**), depending on the oxidation-reduction potential of the generated species. Organic peroxides generated (**Eq. 1.45**) can react further with ferrous iron to ferric iron and organic oxyl radicals (**Eq. 1.46**).

$$R^\bullet + Fe^{3+} \longrightarrow R^+ + Fe^{2+}$$ **Eq. 1.42**

$$R^\bullet + Fe^{2+} \longrightarrow R^- + Fe^{3+}$$ **Eq. 1.43**

$$R^\bullet + R^\bullet \longrightarrow R - R$$ **Eq. 1.44**

$$R^\bullet + HO_2^\bullet \longrightarrow RO_2H$$ **Eq. 1.45**

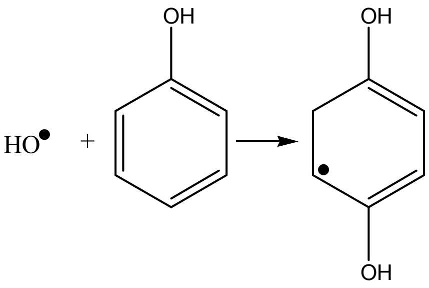
$$Fe^{2+} + RO_2H \longrightarrow Fe^{3+} + HO^- + RO^\bullet$$ **Eq. 1.46**

$$R^\bullet + O_2 \longrightarrow RO_2^\bullet$$ **Eq. 1.47**

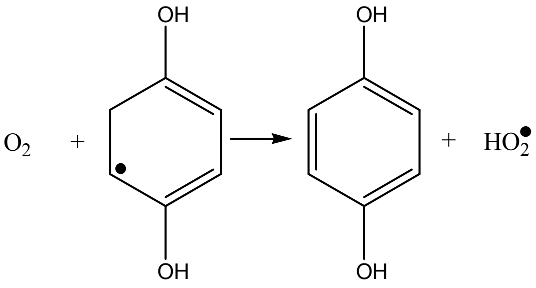
$$RO_2^\bullet + H_2O \longrightarrow ROH + HO_2^\bullet$$ **Eq. 1.48**

The reaction of organic radicals ($R^\bullet$) with dissolved oxygen (**Eq. 1.47** and **Eq. 1.48**), the so called Dorfman-mechanism, is of special interest because the peroxyl radical can regenerate hydrogen peroxide.

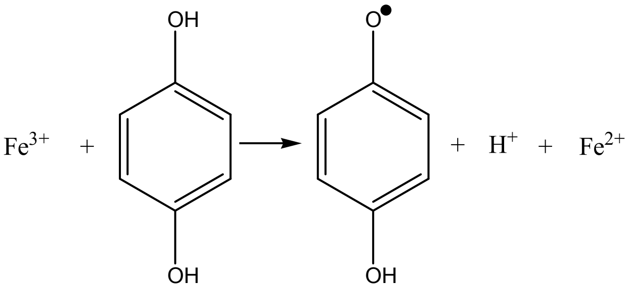
If aromatic pollutants are present, the ring system(s) are attacked via electrophilic addition and hydroxylated before the ring is opened during the oxidation process. Typical degradation products of aromatic rings are quinones and hydroquinones (**Eq. 1.49** and **Eq. 1.50**) which have the ability to regenerate Fe^{2+}. The resulting benzoquinone structures can also contribute to the reduction of Fe^{3+} to Fe^{2+}, so that each molecule can reduce several ferric iron ions in a catalytic cycle (**Eq. 1.51 - Eq. 1.53)**. This catalytic cycle is interrupted by the ring opening of mentioned quinones. Once organic pollutants are degraded down to carboxylic and dicarboxylic acids, the degradation stops, because these acids are known to form stable complexes with iron, which then inhibit reactions with peroxide (**Eq. 1.54**) [Kavitha and Palanivelu, 2004].



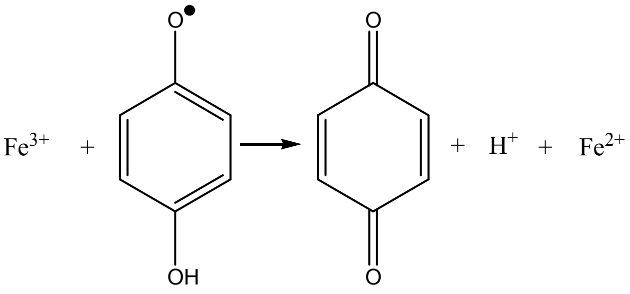
$k = 7.3 \cdot 10^{9}\,M^{-1}s^{-1}$ **Eq. 1.49**



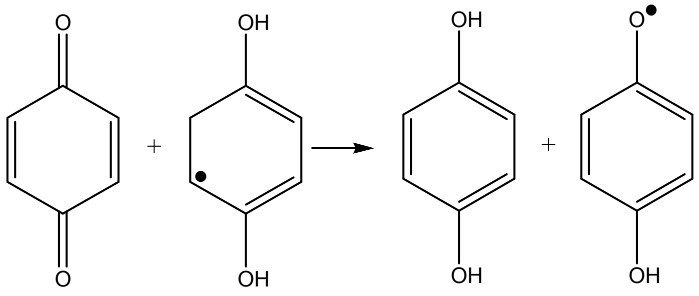
$k = 1.5 \cdot 10^{9}\,M^{-1}s^{-1}$ **Eq. 1.50**



$k = 4.4 \cdot 10^{2}\,M^{-1}s^{-1}$ **Eq. 1.51**



$k = 4.4 \cdot 10^{4}\,M^{-1}s^{-1}$ **Eq. 1.52**



$k = 3.7 \cdot 10^{9}\,M^{-1}s^{-1}$ **Eq. 1.53**

$$Fe^{3+} + nL \rightarrow \left[FeL_n\right]^{x+} \xrightarrow{H_2O_2,dark} no\ \ further\ reaction$$ **Eq. 1.54**

1.5.3.3 Photochemical reactions of the photo-Fenton process

In the end the Fenton reaction comes to a quasi standstill either through the slow regeneration of Fe^{2+} (**Eq. 1.23 - Eq. 1.25**), or through the formation of stable iron complexes (**Eq. 1.54**). If light with a wavelength shorter than 580 nm is used, the formed iron complexes suffer photoreduction. The first step in this photoreduction is a ligand-to-metal charge-transfer (LMCT) reaction and as a consequence the intermediate complexes dissociate [Zepp et al, 1992]. The ligands in these complexes can be any kind of Lewis base, able to form complexes with ferric iron ($HO^-, H_2O, HO_2^-, Cl^-, R-COO^-, R-OH, R-NH_2, etc.$). The product is either a $HO^\bullet$, or another organic radical (**Eq. 1.55 - Eq. 1.58**).

$$\left[Fe^{3+}L\right] + h\nu \longrightarrow \left[Fe^{3+}L\right]^* \longrightarrow Fe^{2+} + L^* \qquad \textbf{Eq. 1.55}$$

$$\left[Fe(H_2O)\right]^{3+} + h\nu \longrightarrow Fe^{2+} + HO^\bullet + H^+ \qquad \textbf{Eq. 1.56}$$

$$\left[Fe(OH)\right]^{2+} + h\nu \longrightarrow Fe^{2+} + HO^\bullet \qquad \textbf{Eq. 1.57}$$

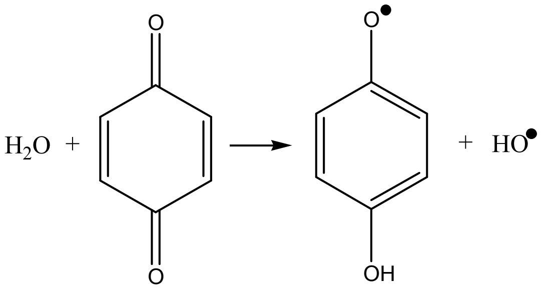
$$\left[Fe(OOC-R)\right]^{2+} + h\nu \longrightarrow Fe^{2+} + CO_2 + R^\bullet \qquad \textbf{Eq. 1.58}$$

The absorption properties of the complex depend on the ligand and reaction (**Eq. 1.55**) takes place with different quantum yields and at different wavelengths. Another crucial impact on the efficiency of the photo-Fenton reaction is the pH, as it strongly influences which complexes are formed. pH 2.8 was postulated as the optimum pH for the photo-Fenton treatment [Pignatello, 1992; Safarzadeh-Amiri et al, 1996] because at this pH precipitation does not take place and the predominant iron species in solution is $[Fe(OH)]^{2+}$, which is the most photoactive ferric iron-water complex. In contrast to the reactions in the dark, the complexes of carboxylic and dicarboxylic acids are not stable under irradiation (**Eq. 1.58**) and can have much higher quantum yields than the ferric iron-water complexes. There is actually an enhanced photo-Fenton process, which uses oxalate salts or oxalic acid to raise the efficiency of the process (**Eq. 1.59** and **Eq. 1.60**). The drawback is that oxalate is not a catalyst and it is consumed during the process, thus raising the cost of maintaining the process. Other chelating agents have been proposed as well with the additional aim of working at neutral pH [Sun and Pignatello, 1992; Sun and Pignatello, 1993].

$$[Fe(C_2O_4)_3]^{3-} + h\nu \longrightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{\bullet-}$$ **Eq. 1.59**

$$C_2O_4^{\bullet-} + Fe^{3+} \longrightarrow CO_2 + Fe^{2+}$$ **Eq. 1.60**

Another photochemical reaction, which contributes to the degradation of aromatic pollutants in the water, is the photoreduction of quinones to semiquinones. The quinones produced as intermediates can be further reduced by light, and contribute not only to the reduction of ferric iron (**Eq. 1.52**), but also produce a hydroxyl radical (**Eq. 1.61**).



Eq. 1.61

1.5.3.4 *Influence of other parameters*

Due to the high oxidation potential of the hydroxyl radical, it can also react with inorganic ions present in the solution. It is well known that sulphate, chloride and phosphate have a negative effect on the photo-Fenton reaction rate [Pignatello et al, 2006], but the negative effects of carbonates and bicarbonate ions are even worse, as they compete with organic compounds and significantly decrease the degradation efficiencies of organics through reactions **Eq. 1.62** and **Eq. 1.63** [Buxton and Elliot, 1986]. But usually at pH 2.8 there are no carbonates left in the water to influence the reaction.

$$HO^\bullet + CO_3^{2-} \longrightarrow HO^- + CO_3^{\bullet-}$$ $k = 3.9 \cdot 10^8 M^{-1}s^{-1}$ **Eq. 1.62**

$$HO^\bullet + HCO_3^- \longrightarrow H_2O + CO_3^{\bullet-}$$ $k = 8.5 \cdot 10^6 M^{-1}s^{-1}$ **Eq. 1.63**

In high concentrations, both chlorine and sulphate are capable of complexing both ferric and ferrous iron and can hinder reactions or open new reactions for the decomposition of hydrogen peroxide in the presence of iron, as well as react with hydroxyl radicals creating chlorine and sulphate radicals (**Eq. 1.64 - Eq. 1.67**).

$HO^{\bullet} + Cl^{-} \longrightarrow [ClOH]^{\bullet -}$ k = 4.3 · 10^9 $M^{-1}s^{-1}$ **Eq. 1.64**

$[ClOH]^{\bullet -} + H^{+} \longrightarrow [HClOH]^{\bullet}$ k = 3.0 · 10^{10} $M^{-1}s^{-1}$ **Eq. 1.65**

$[HClOH]^{\bullet} + Cl^{-} \longrightarrow Cl_2^{\bullet} + H_2O$ k = 8.0 · 10^9 $M^{-1}s^{-1}$ **Eq. 1.66**

$HO^{\bullet} + HSO_4^{-} \longrightarrow H_2O + SO_4^{\bullet -}$ k = 3.5 · 10^5 $M^{-1}s^{-1}$ **Eq. 1.67**

Below pH 4 practically all hydroxyl radicals end up in chlorine radicals (calculations done for 100 mM NaCl solutions by De Laat) [De Laat et al, 2004; Zapata et al, 2009a]. There are two negative effects: the chlorine and sulphate radicals are potentially weaker in their oxidants than the hydroxyl radical and chlorine radical can be added to double bonds and can create chlorinated products [Kiwi et al, 2000].

Phosphate ions have a double diametral effect, as it precipitates iron and scavenges hydroxyl radicals. Normal waste waters do not have high phosphate content, but if industrial wastes or organophosphates are treated with the photo-Fenton process, the precipitation of iron-phosphate has to be taken into account.

Investigations showed that increased temperature always had a beneficial effect on the reaction kinetics [Krutzler et al, 1999; Sagawe et al, 2001; Sarria et al, 2003; Lee and Yoon 2004]. The reaction rate increased about five times by raising the temperature from 20 to 40°C. At higher temperatures the rate declines again due to iron precipitation [Zapata et al, 2009a; Zapata et al, 2009b]. It has as well to be taken into account, that at higher temperatures more hydrogen peroxide is consumed.

1.5.4 Photo-reactors for the treatment of waste waters

There is a whole lot of literature on the design and layout of different kinds of solar powered photo-reactors [Blanco et al, 2000; Blanco et al 2009; Malato et al, 2009], so this short chapter will give only a brief overview on the topic. The photo-reactors used in this work are compound parabolic collectors (CPC) reactors. They are an interesting cross between Parabolic Trough Collectors (PTCs) and Non-Concentrating Collectors. The engineering concept for the PTCs comes from the solar thermal applications. The system supports turbulent flow with good homogenisation; it is a closed system, preventing vaporisation of volatile compounds. Its main disadvantage though, is that through their geometry the collectors can only use direct beam radiation, making them practically useless for cloudy days. Non-Concentration Collectors (NCCs) on the other hand are much cheaper than the PTCs, they have no tracking system, and not only do they harvest direct beam radiation, but they also harvest diffuse radiation. The disadvantages are the problems caused by mass transfer through laminar flow, possible vaporisation of contaminants and difficult scale up properties.

The CPCs combine the advantages of the two abovementioned reactor types without their disadvantages. They are static reactors without tracking system, and have been found to be the most efficient harvesting optics for non concentrating systems [Muschaweck et al, 2000]. They support turbulent flow, have a closed system, are cheap and easy to maintain and as temperature does not play any significant role, there is no need of insulation.

The photochemical reactor consists of various parts: the tank, where mixing of the wastewater with various chemicals (acids, photocatalyst, H_2O_2) can take place, resistant pipes, to bring the reactive mixture to the actual CPC reactor and pumps to provide a steady mass flow with minimal pressure drops.

The pipes can be made of high density polyethylene (HDPE) or polypropylene (PP), avoiding the use of metallic or composite material which could be degraded by the oxidant conditions of the process. All materials used must be inert to UV degradation in order to be compatible with the minimum lifetime requirements of the system (usually 10 years), the piping, valves and reactor must be strong enough to resist the necessary water flow pressure, which has typical parameters of 2-4 bar (nominal system pressure drop) and a maximum of 5-7 bar.

The reflective material should be cheap, weather resistant, and should have a high UV reflectivity in the desired range. The reflectivity between 300 and 400 nm of traditional silver-coated mirrors is very low (25.2% at 280 nm to 92.8% at 385 nm) and aluminium is the only metal surface which is highly reflective throughout the UV-spectrum with reflectivity ranges from 92.3% at 280 nm to 92.5% at 385 nm. The aluminium surface has to be treated, because a fresh deposited aluminium surface is fragile. Using a conventional glass cover lowers the reflectivity and filters UV light.

The thin oxide layer that forms naturally on aluminium is insufficient to protect the surface under outdoor conditions and the oxide layer continues to grow, which results in a dramatic UV reflectance drop. The best material available at the moment is electropolished aluminium or organic plastic films with aluminium coating [Blanco et al, 2000].

A uniform flow distribution inside the reactor must be assured, as non-uniform flow distribution leads to non-uniform residence times inside the reactor, resulting in decreased performance compared to ideal flow situations. Turbulent flow inside the reactor should be turbulent to ensure good mixing and to ensure that there is no settlement of suspended solids (even more important when using catalyst in suspension).

The tubing in the reactor must be UV and visible light transparent and resistant to UV, low or high pH and chemicals present in the reactor (oxidant, pollutants and their degradation products), high temperatures in the summer (60ºC). The material for the actual reactor therefore is limited to fluoropolymers, quartz glass and borosilicate glass. Quartz has excellent properties (chemical and thermal stability, mechanical resistance and excellent UV transmission), but its high production cost makes it completely feasible for photocatalytic applications. Fluoropolymers have a good thermal stability, good UV transmittance, excellent UV stability and chemical inertness. One disadvantage though is that the wall thickness of flouroploymer tubes has to be increased to achieve the desired minimum pressure rating, which in turn will lower its UV transmittance. Borosilicate glass has a good transmittance with a UV cut-off of about 285 nm. It is chemically, mechanically and UV stable, and cheaper than quartz glass.

The system consists of a tube above a reflector consisting of two truncated parables with a concentration factor (R_C) (ratio of tube perimeter to aperture) of around one (see **Figure 1.10**). The concentration factor (R_C) of a two dimensional CPC is given by **Eq. 1.68**.

$$R_{C,CPC} = \frac{1}{\sin \Theta_a} = \frac{A}{2r\pi} \quad \textbf{Eq. 1.68}$$

The normal values for the semi-angle of acceptance (Θ_a), for photocatalytic applications are between 60° and 90°. This wide angle allows the receiver to collect both direct and a large part of the diffuse light ($1/R_C$ of it). A special case is the one in which the acceptance angle is $\Theta_a=90°$, $1/R_C=1$ (non-concentrating system). When this happens, all the UV radiation (direct and diffuse) can be collected and redirected to the reactor.

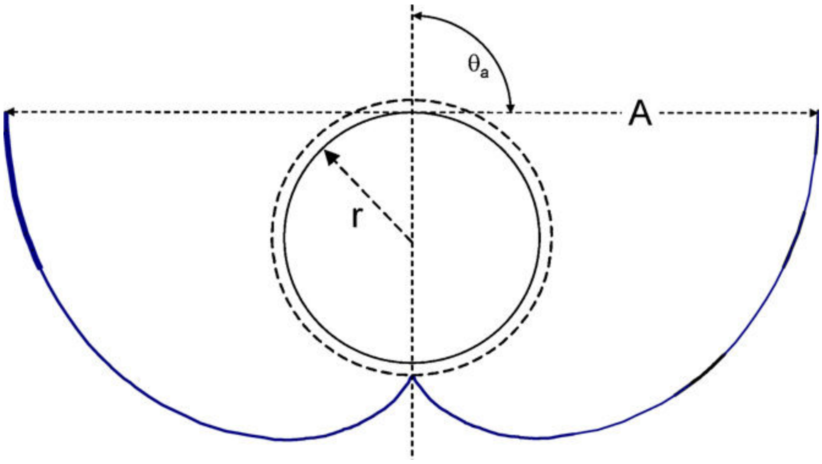


Figure 1.10 Design of a CPC-reactor

If the CPC is designed for an acceptance angle of +90° to -90°, all incident diffuse radiation can be collected and the reflected light is distributed all around the tubular receiver, so that almost the entire circumference of the receiver tube is illuminated (see **Figure 1.11**).

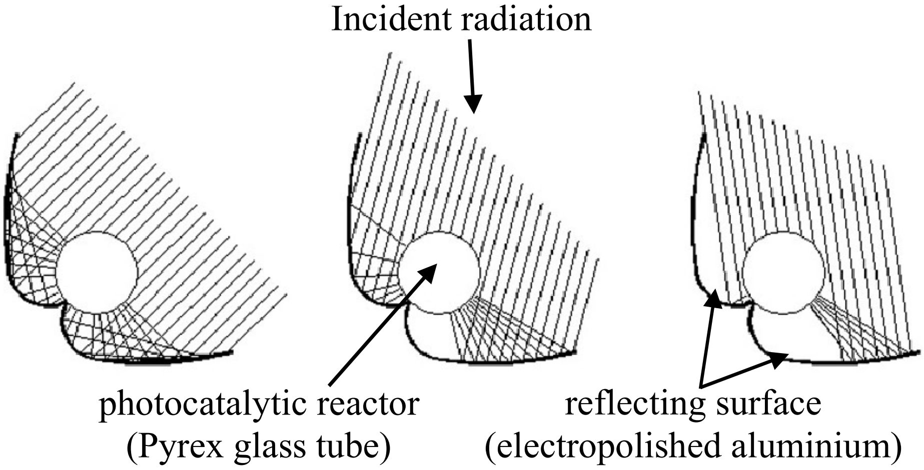


Figure 1.11 Light path of different radiation angles onto the reactor tube.

Figure 1.12 shows a typical CPC photo-reactor plant, which has been installed in 2004 for the treatment of contaminated waters. The project focuses on the problem that originates in the intensive greenhouse agriculture with its use of pesticides, as this kind of agriculture requires 200 times more pesticides than the conventional one. The related problem is the dumping of plastic containers, which usually contain pesticide residues, which, in turn, end up contaminating soil and ground water.

Figure 1.12 Photo of a CPC-solar reactor for the treatment of contaminated waters in southern Spain in El Ejido in the province of Almeria (Albaida S.A).

In the area of El Ejido in the province of Almería in southern Spain there are currently 400 km^2 of greenhouses, which use approximately 2 million plastic containers per year. Although the individual residue in each container may be small, the sheer amount of containers masses up to an environmentally dangerous volume of pesticides. The solution to that problem is the collection of those containers to recycle the plastic. But before the plastic can be recycled, it must be washed, thus leaving highly contaminated water, which in itself is unsuitable for discharge. This water is treated in the CPC plant with a conventional photo-Fenton. The plant is designed to treat 1.6 m^3 of contaminated water with 150 m^2 of collector surface in four rows of collectors.

1.6 The TRAGUA project

Spain has the highest water deficit in Europe, with water exploitation rates (annual consumption/resources) of over 20%. High water abstraction (320 L per day and capita), a lack of renewable resources and the fact that about 22% of freshwater is lost in the distribution network from leaking, leads to severe water stress [UNEP 2002; UNEP, 2003; UNDP, 2006; EEA, 2010] which is generating serious social concern. Approximately 65% of this consumption is for agriculture, 20% for industry and 15% is domestic. Although possible methods for mitigating the scarcity of water are widely discussed in the media (e.g. desalination and inter-basin water transfer), and although they may be cost-effective, they are not the best options due to high environmental costs, energy consumption and/or specific infrastructures. Therefore, economically competitive reuse of water is a necessary environmental alternative to avoid the aforementioned energy consumption and direct environmental impact. At the same moment, Spain is also one of the countries with the highest water reuse, but still in small quantities; only 5% of wastewater is reused, whilst its potential for water reuse is 1300 Mm^3, one order of magnitude more than at present [Hochstrat et al, 2005].

The reasons for this are lack of water treatment protocols, commonly accepted water quality indicators, clear criteria for choosing technologies, and tools identifying economic and social advantages. One of the main sources of water for potential reuse comes from municipal wastewater treatment plants (MWTPs). However, quality demands for reusable water [Rose, 2007; Díaz-Cruz and Barceló, 2008; Wintgens et al, 2008] are that it does not contain any toxic, endocrine-disrupting compounds or non biodegradable substances, such as pesticides, pharmaceuticals, hormones, synthetic fragrances, and others which escape conventional wastewater treatment.

The purpose of the “TRAGUA” project is to relieve this stress and promote the use of tertiary treatments as that included in this work. The research presented in this PhD thesis has been carried out in the framework of this project.

The CONSOLIDER project "Treatment and Reuse of Wastewaters for a Sustainable Management" (TRAGUA) was selected by the Spanish Ministry of Education and Science in the 2006 call for CONSOLIDER-INGENIO 2010 programs (http://www.consolider-tragua.com), which ends in October 2011.

Its main objective is to take advantage of the experience of 24 research groups in different areas to study in an integrated way the reuse of treated urban wastewaters. To achieve this objective a solid multi-disciplinary team has been formed with authorized experience in the application of water treatments coming from waste water treatment plants based on advanced technologies, the establishment of the chemical and biological quality criteria and the determination of its impact on the environment. As any other activity aimed to achieve sustainability, economical issues are also considered, and all the proposals include a socioeconomic validation.

The project will achieve its global objective by reaching the following milestones:

-A survey of the present state of the wastewater treatment in Spain.

- A methodology for the determination of the impact of the contaminants in the physical and biotic environment.

- Criteria for selecting the treatment technology most suitable for each type of water coming from WWTP.

- Criteria of use of reclaimed water.

- Training of professionals to deal with sustainable water management.

- Creation of favourable social atmosphere to use reclaimed water.

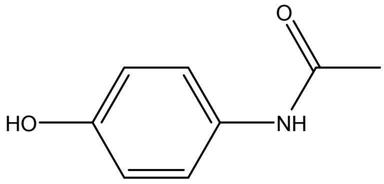
2 Experimental

2.1 Selected compounds

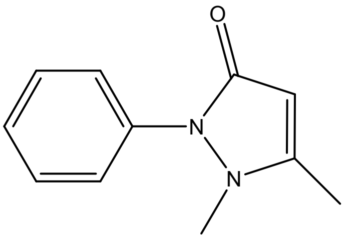
As real treated waste water from MWTPs contains a number of different compounds at different concentration levels, 15 compounds were selected to act as model compounds. These 15 compounds were selected due to their solubility, stability, polarity and separability in the HPLC system as well as detectability in a UV diode array detector (DAD). This means that substances like synthetic musks (Galaxolide, Tonalide and musk xylene) were excluded due to their low solubility, Nicotine and Atenolol were excluded due to their short retention time in the HPLC system and substances like erythromycin were excluded because they do not have sufficient UV-light absorption qualities to be detected in the HPLC-UV/DAD.

Another criteria for selecting these substances was that they should present a great variety of substances such as pharmaceuticals, pesticides, hormones and stimulants. The selected compounds with their physiochemical properties, retention time and absorption maximum can be seen in **Table 2.1**.

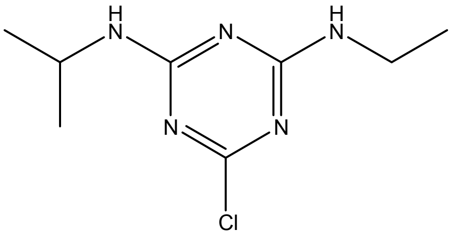
Table 2.1 Description of the selected 15 compounds

Name:	Acetaminophen		
N-(4-hydroxyphenyl) acetamide			
CAS:	103-90-2		
Formula:	$C_8H_9NO_2$		
Mol weight [g mol^{-1}]:	151.2		
log P [hydrophobicity]:	0.4		
Solubility [mg L^{-1}]:	$1.4*10^4$		
Type:	analgesic antipyretic		
Retention time [min]:	1.186 ± 0.028	Absorption max [nm]	245

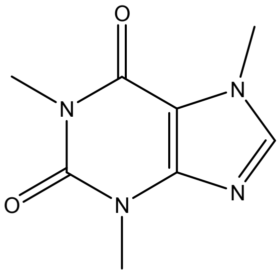
Name:	Antipyrine
1,5-dimethyl-2-phenylpyrazol-3-one	
CAS:	60-80-0
Formula:	$C_{11}H_{12}N_2O$
Mol weight [g mol^{-1}]:	188.2
log P [hydrophobicity]:	0.38
Solubility [mg L^{-1}]:	$4.2*10^4$
Type:	analgesic antipyretic
Retention time [min]:	3.221 ± 0.014
Absorption max [nm]	243



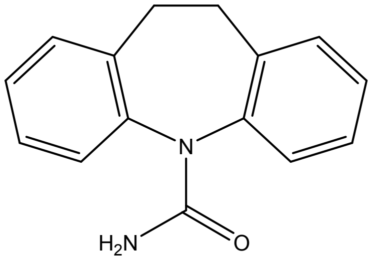
Name:	Atrazine
6-chloro-N'-ethyl-N-isopropyl-1,3,5-triazine-2,4-diamine	
CAS:	1912-24-9
Formula:	$C_8H_{14}ClN_5$
Mol weight [g mol^{-1}]:	215.7
log P [hydrophobicity]:	2.63
Solubility [mg L^{-1}]:	$2.1*10^2$
Type:	triazines herbicide
Retention time [min]:	6.811 ± 0.034
Absorption max [nm]	223



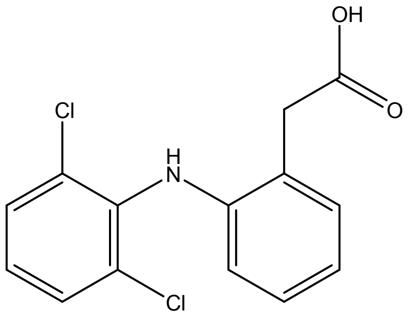
Name:	Caffeine
1,3,7-trimethylpurine-2,6-dione	
CAS:	58-08-2
Formula:	$C_8H_{10}N_4O_2$
Mol weight [g mol^{-1}]:	194.2
log P [hydrophobicity]:	-0.5
Solubility [mg L^{-1}]:	$2.2*10^4$
Type:	stimulant
Retention time [min]:	2.141 ± 0.030
Absorption max [nm]	205



Name:	Carbamazepine
benzo[b][1]benzazepine-11-carboxamide	
CAS:	298-46-4
Formula:	$C_{15}H_{12}N_2O$
Mol weight [g mol^{-1}]:	236.3
log P [hydrophobicity]:	2.3
Solubility [mg L^{-1}]:	$1.8*10^4$
Type:	anticonvulsant
Retention time [min]:	5.975 ± 0.021
Absorption max [nm]	211

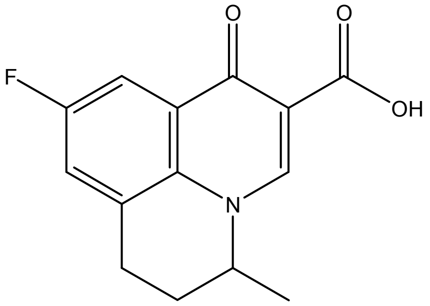


Name: Diclofenac
2-[2-[(2,6-dichlorophenyl) amino]phenyl]acetic acid
CAS: 15307-86-5
Formula: $C_{14}H_{11}Cl_2NO_2$
Mol weight [g mol^{-1}]: 296.2
log P [hydrophobicity]: 3.9
Solubility [mg L^{-1}]: 5.0*10^{4}
Type: anti-inflammatory



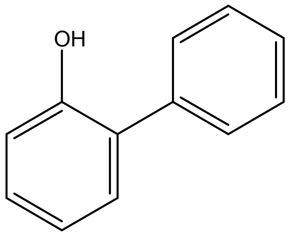
Retention time [min]: 9.238 ± 0.107 Absorption max [nm] 277

Name: Flumequine
7-fluoro-12-methyl-4-oxo-1-azatri cyclo [7.3.1.05,13] trideca 2,5,7,9 (13)-tetraene-3-carboxylic acid
CAS: 42835-25-6
Formula: $C_{14}H_{12}FNO_3$
Mol weight [g mol^{-1}]: 261.25
log P [hydrophobicity]: 2.9
Solubility [mg L^{-1}]: 5.3*10^{3}
Type: quinoline antibiotic



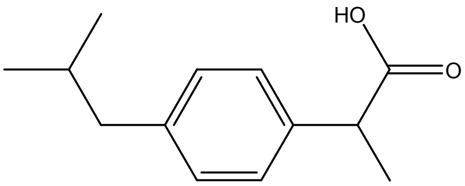
Retention time [min]: 6.266 ± 0.021 Absorption max [nm] 248

Name: Hydroxybiphenyl
2-phenylphenol
CAS: 90-43-7
Formula: $C_{12}H_{10}O$
Mol weight [g mol^{-1}]: 170.21
log P [hydrophobicity]: 2.94
Solubility [mg L^{-1}]: 5.4*10^{2}
Type: biocide



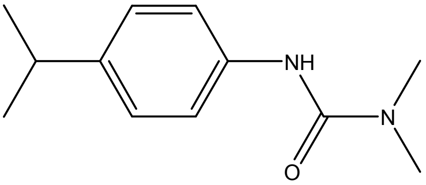
Retention time [min]: 8.305 ± 0.042 Absorption max [nm] 243

Name: Ibuprofen
2-[4-(2-methylpropyl)phenyl] propanoic acid
CAS: 15687-27-1
Formula: $C_{13}H_{18}O_2$
Mol weight [g mol^{-1}]: 206.3
log P [hydrophobicity]: 3.6
Solubility [mg L^{-1}]: 4.9*10^{1}
Type: anti-inflammatory

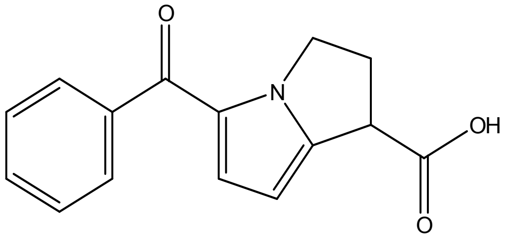


Retention time [min]: 9.467 ± 0.048 Absorption max [nm] 222

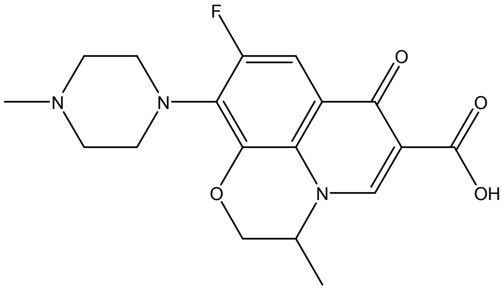
Name:	Isoproturon		
3-(4-isopropylphenyl)-1,1-dimethyl-urea			
CAS:	34123-59-6		
Formula:	$C_{12}H_{18}N_2O$		
Mol weight [g mol^{-1}]:	206.3		
log P [hydrophobicity]:	2.3		
Solubility [mg L^{-1}]:	$1.44*10^2$		
Type:	Phenylurea herbicide		
Retention time [min]:	7.056 ± 0.027	Absorption max [nm]	205



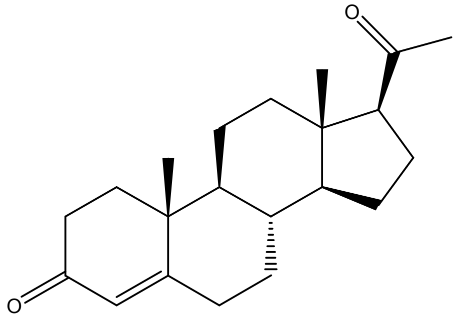
Name:	Ketorolac		
5-(benzoyl)-2,3-dihydro-1H-pyrrolizine-1-carboxylic acid			
CAS:	66635-83-4		
Formula:	$C_{15}H_{13}NO_3$		
Mol weight [g mol^{-1}]:	255.3		
log P [hydrophobicity]:	2.1		
Solubility [mg L^{-1}]:	$2.5*10^4$		
Type:	analgesic		
Retention time [min]:	6.525 ± 0.021	Absorption max [nm]	321



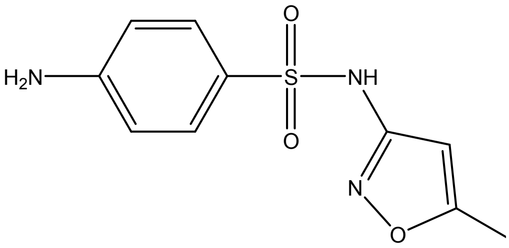
Name:	Ofloxacin		
9-fluoro-3,7-dihydro-3-methyl-10-(4-methylpiperazin-1-yl)-7-oxo-2H-[1,4]oxazino[2,3,4-ij]quinoline-6-carboxylic acid			
CAS:	82419-36-1		
Formula:	$C_{18}H_{20}FN_3O_4$		
Mol weight [g mol^{-1}]:	361.4		
log P [hydrophobicity]:	2.1		
Solubility [mg L^{-1}]:	$2.8*10^4$		
Type:	quinoline antibiotic		
Retention time [min]:	2.770 ± 0.044	Absorption max [nm]	295



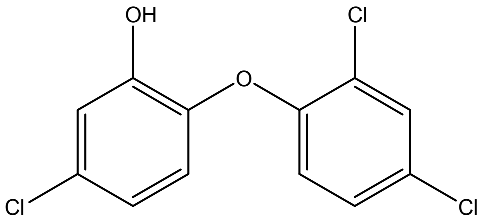
Name:	Progesterone		
(8S,9S,10R,13S,14S,17S)-17-acetyl-1,7,8,10,11,12,13,15,16,17-decahydro-10,13-dimethyl-2H-cyclopenta[a]phenanthren-3(6H,9H,14H)-one			
CAS:	57-83-0		
Formula:	$C_{21}H_{30}O_2$		
Mol weight [g mol^{-1}]:	314.5		
log P [hydrophobicity]:	3.5		
Solubility [mg L^{-1}]:	$8.8*10^0$		
Type:	hormone		
Retention time [min]:	10.162 ± 0.033	Absorption max [nm]	248



Name:	Sulfamethoxazole		
4-amino-N-(5-methyl-1,2-oxazol-3-yl) benzenesulfonamide			
CAS:	723-46-6		
Formula:	$C_{10}H_{11}N_3O_3S$		
Mol weight [g mol^{-1}]:	253.3		
log P [hydrophobicity]:	0.7		
Solubility [mg L^{-1}]:	$6.1*10^2$		
Type:	bacteriostatic		
Retention time [min]:	4.306 ± 0.027	Absorption max [nm]	267



Name:	Triclosan		
5-chloro-2-(2,4-dichlorophenoxy)phenol			
CAS:	3380-34-5		
Formula:	$C_{12}H_7Cl_3O_2$		
Mol weight [g mol^{-1}]:	289.5		
log P [hydrophobicity]:	5.17		
Solubility [mg L^{-1}]:	$4.6*10^0$		
Type:	bacteriostatic		
Retention time [min]:	11.170 ± 0.050	Absorption max [nm]	280



All these compounds were analytical grade and provided by Sigma-Aldrich. Taking into consideration that typical concentration of ECs in MWTP effluents are between 0.1 and 20.0 μg L^{-1}, it was decided to work with initial concentrations of 100 μg L^{-1} of each compound (later lowered to 5 μg L^{-1}), which is a compromise between a high enough concentration for the fast determination and characterization using conventional HPLC-(DAD)UV analytical equipment, and low enough to simulate real conditions.

Two mother solutions were prepared: mother solution I (MS I) was a solution of 2.5 g L^{-1} of each compound not including Flumequine and Ofloxacin in Methanol (HPLC grade). The high concentration of these 13 compounds in the mother solution made it possible to spike model and real waters at low concentrations (100 and 5 g L^{-1}) without raising the DOC significantly. Flumequine and Ofloxacin have a low solubility in Methanol, and therefore mother solution II (MS II) was prepared which was a solution of 100 mg L^{-1} of each compound in MilliQ® water.

2.2 Model and real waste waters

To treat real waste waters containing very low concentrations of contaminants, one has to get enough experience of the process under different conditions. Therefore the first step was to treat deionised water which was obtained directly from the PSA distillation plant ($\Lambda < 10$ μS cm^{-1}, Cl^- and SO_4^{2-} between 0.2 – 0.3 mg L^{-1}, DOC < 0.5 mg L^{-1}), and complicate the matrix step by step by using model tap water [Standard Methods for the Examination of water and Wastewater], in this case moderately hard water, as this kind of water is typical in this region of Spain (province of Almeria). The next step was to simulate waste water. This poses a problem as in the literature there is no recipe for a model effluent water (effluent of a MWTP) to be found. So the recipe for standard municipal waste water [Standard Methods for the Examination of water and Wastewater] was taken and the organic content was reduced to 20% (a supposed 80% removal in the MWTP, which is a usual efficiency in these installations). The composition of these two waters can be seen in **Table 2.2.**

Table 2.2 Simulated water composition

Simulated tap water		**Simulated effluent waste water simulated tap water +**	
Salt	Amount [mg L^{-1}]	Salt	Amount [mg L^{-1}]
$NaHCO_3$	96	Peptone	32
$CaSO_4 \bullet 2H_2O$	60	Meat extract	22
$MgSO_4$	60	Urea	6
KCl	4	K_2HPO_4	28
Simulated tap water without bicarbonates		$CaCl_2 \bullet 2H_2O$	4
Na_2SO_4 instead of $NaHCO_3$		$MgSO_4 \bullet 7\ H_2O$	2
Na_2SO_4	81	NaCl	7
		DOC	

Real waste waters were taken downstream of the MWTP in El Ejido (Province of Almeria, Andalucia, Spain) and used within 3 days. The water was kept in a tank and recirculated during the time stored. The main chemical characteristics of the waste water used can be seen in **Table 2.3**.

Table 2.3 Main characteristics of the used waste water treatment plant effluents

		Average	**Min**	**Max**
COD	[mg L^{-1}]	59	17	114
TC	[mg L^{-1}]	120	43	167
DOC	[mg L^{-1}]	16	3	38
pH	[-]	7.8	7.3	8.4
Λ	[mS cm^{-1}]	1.45	0.43	2.21
Cl^-	[mg L^{-1}]	358	292	405
SO_4^{2-}	[mg L^{-1}]	177	106	290
Na^+	[mg L^{-1}]	270	167	392
Ca^{2+}	[mg L^{-1}]	102	64	159
NH_4^+	[mg L^{-1}]	32	6	68
K^+	[mg L^{-1}]	27	19	35
Mg^{2+}	[mg L^{-1}]	49	9	72

This MWPT treats water of a medium sized community (68000 inhabitants), and it consists of a principal clarification step (sand and grit removal, grease removal), and a biological treatment with activated sludge with a mean sludge age of 7.5 days and a nitrification - denitrification step and a subsequent anaerobic sludge digestion. The MWTP is designed to treat up to 12500 m^3 d^{-1} (actual: 7000 m^3 d^{-1}) with a maximum flow of 1765 m^3 h^{-1}, the treatable load is a biological oxygen demand (BOD_5) of 350 mg L^{-1} (4360 kg d^{-1}), total suspended solids (TSS) 375 mg L^{-1} (4672 kg d^{-1}) and a total Kjeldahl nitrogen (TKN) of 60 mg L^{-1} (748 kg d^{-1}). The effluent has a final BOD_5 concentration of 25 mg L^{-1}, a final TSS of 35 mg L^{-1} and a final TKN of 15 mg L^{-1}.

2.3 Reagents applied in experiments and analysis

Ultra pure water obtained from a Millipore Milli-Q® system, HPLC grade Acetonitrile (ACN) and Methanol (MeOH) were applied for the preparation of all analytical standards, eluents and sample dilutions in chromatography and were purchased from Sigma-Aldrich. Iron(II)sulphate ($FeSO_4$•7 H_2O), Iron(III)sulphate ($Fe_2(SO4)_3$•x H_2O 75%), reagent grade hydrogen peroxide (30% w/v), humic acid sodium salt, (S,S′)-Ethylenediamine-(N,N′)-disuccine acid trisodium salt solution (35% w/v) (EDDS), oxalic acid ($C_2H_2O_4$•2 H_2O), sulphuric acid (H_2SO_4 98%), sodium hydroxide pellets (NaOH) were provided as all other reagents by Panreac.

Luri Agar for total bacteria count, Endo Agar for coliforme bacteria count and phosphate buffer solution (PBS) was provided by Fluka.

2.4 Analytical techniques

2.4.1 *Dissolved organic carbon (DOC)*

The measurement and determination of dissolved organic carbon permits the evaluation of the mineralization of organic contaminants in water. The impact of the low level concentrations of the contaminants in the water onto the DOC is negligible when treating simulated and real effluents of MWTP.

So the DOC measurements were just used to get information on the behaviour of the applied process on this parameter and not on the mineralization of contaminants.

The analysis of DOC is achieved via the analysis of total carbon (TC) and inorganic carbon (IC), the difference between TC and IC results in DOC. The DOC analysis is done in a Shimadzu Total Organic Carbon analyser model TOC-5050A (see **Figure 2.1**), equipped with an auto sampler ASI-5000A.

Figure 2.1 Picture of the Shimadzu TOC (right) with Auto sampler (left).

TC analysis is based on the combustion of the aqueous sample in a tube filled with platinum catalyst on an aluminium spheres support at a temperature of 680ºC. The carbon in the sample is oxidized to CO_2, swept by a CO_2 free carrier gas (flow of 150 mL min^{-1}) onto a dehumifier where it is cooled down and dried and then brought onto the non dispersive infrared (NDIR) detector where it is analyzed. The absorbance of the CO_2 generates a signal which is evaluated by the equipment's software and which is proportional to the quantity of carbon in the sample.

For the measurement of inorganic carbon, the sample is mixed in a reaction chamber with a 25% w/V phosphoric acid. The decomposition of the carbonates and bicarbonates generate CO_2, which is analyzed in the same way as the CO_2 for TC.

The quantification is done via a linear relationship between peak area and carbon concentration (for TC and TIC) by standard solutions prepared in ultra pure water (Milli-Q® system). The TC measurement is calibrated using potassium hydrogen phthalate standard solutions, containing sulphuric acid to avoid contamination by atmospheric CO_2. 5 linear regression curves were established for concentration ranges of 1 – 10, 10 – 50, 50 – 250, 250 – 1000 and 1000 – 4000 mg L^{-1}. TIC measurement is calibrated by sodium carbonate/sodium hydrogen carbonate (50:50) standards. Three linear regression curves were established for concentration ranges of 0.5 – 5, 5 – 20, 20 – 200 mg L^{-1}. The linear regression coefficients are close to 1 and the standard deviation of the equipment lies by 1%. Calibration and quality maintenance were performed regularly to ensure the correct operation of the equipment.

Samples (usually between 15 and 25 mL) are filtered through 0.22 µm pore size syringe driven filters (Millipore Millex® GN) prior to injection into the TOC system, as suspended solids in the sample could lead to clogging of the capillary tubes. Each measurement was based on two injections with a maximum coefficient variance of less than 2% (re injection in the case of higher values). Measurements were performed immediately after samples were taken.

2.4.2 *Ionic chromatography (IC)*

The separation principle of ion chromatography (IC) is similar to any other type of liquid chromatography; in this case compounds present in their ionic form (i.e. counter ions of weak and strong acids and bases) in aqueous solutions can be detected. The resin in the chromatographic column is a synthetic ion exchange resin with charged anchor groups as active sites. In the case of cationic exchange resins the resin contains negatively charged anchor groups such as carboxylic acids or sulphonic acids and the anionic exchange resins usually contain positively charged quaternary or primary amines. The general setup consists of a mobile phase which contains ions that compete with the analytes for the active sites on the stationary phase. In the case of anion IC the most common mobile phases contain carbonate/hydrogen carbonate, hydroxide or tetraborate/boric acid, while the cation IC mobile phases usually contain sulphuric acid, hydrochloric acid or methanesulphonic acid. The detector is a membrane suppression electric conductivity detector. The membrane suppressor neutralizes the eluent by supplying hydronium or hydroxyl ions generated by electrolysis via ion exchange membranes.

This reduces the background at the detector and enhances the sensitivity, so that modern standard IC systems have detection limits in the range of several µg L^{-1}. The response of the electric conductivity detector does not have a linear response over a wide dynamic range, therefore there are three linear calibration curves applied (0.1 – 1, 1 – 10, 10 – 50 mg L^{-1}). Operation and data analysis were done using the Dionex Chromelon® software. The used IC system can be seen in **Figure 2.2**.

The anionic IC system used is a Dionex DX-600 IC system equipped with an auto sampler (Dionex AS40), a quarterny gradient pump (Dionex GP50), a thermostatic column oven (Dionex LC30) and a conductivity detector (Dionex ED50). The eluent passes an anion trap column (Dionex Ionpac ATC-3) which ensures a pure mobile phase, then passes a precolumn (Dionex Ionpac AG11-HC 4x50mm), the chromatographic column (Dionex Ionpac AG11-HC 4x250mm), the suppressor (Dionex ASRS-Ultra II 4mm) and the electric conductivity detector. The cation IC system used is the Dionex-120 IC system. It is equipped with the same auto sampler (Dionex AS40) and quarterny gradient pump (Dionex GP50), and thermostatic column oven (Dionex LC30). The eluent passes a guard column (Dionex CG12A 4x50mm), the chromatographic column (Dionex Ionpac CS12A 4x250mm), the suppression module (Dionex CSRS-Ultra 4mm) and the electric conductivity detector.

The homogenised sample was filtered into the sample vials using a 0.22 µm pore size syringe driven filters (Millipore Millex® GN). Flow rates were 1.5 mL min^{-1} for the anion system and 1.2 mL min^{-1} for the cation system. The eluent conditions are listed in **Table 2.4**. Standard solutions were injected with every run to check the correct operation of the equipment. The standard deviation for both systems is around 3%.

Figure 2.2 Picture of the IC Dionex systems (DX120 and DX600)

Table 2.4 Mobile phase and conditions for the IC system

equipment	ions	flow / mobile phase	Gradient
Dionex DX-120	Na^+,NH_4^+,K^+, Ca^{2+}, Mg^{2+}	1.2 mL min^{-1} H_2SO_4 20 mN	Isocratic
Dionex DX-600	Cl^-, NO_2^-, NO_3^-, F^-, SO_4^{2-}, PO_4^{3-}	1.5 mL min^{-1} H_2O/NaOH 100 mM	80/20: 0-8 min 65/35: 8-15 min
Dionex DX-600	acetate, formiate, propionate, pyruvate, oxalate, maleate	1.5 mL min^{-1} H_2O/ NaOH 5 mM H_2O/ NaOH 100 mM	80/20: 0-18 min 85/15: 18-28 min 70/30: 28-38 min

2.4.3 *Ultra Performance Liquid Chromatography with Diode Array Detector (UPLC/DAD)*

In HPLC and UPLC a mobile phase is pumped through a system under laminar conditions with negligible vertical mixing. The pressure drop along the chromatographic column is high, due to the small pore size in the chromatographic column. Pressure drops are higher in UPLC systems due to different packings in the column and column size.

The type of chromatography used was a reversed phase chromatography. In this kind of chromatography, the stationary phase is non polar, while the mobile phase is moderately polar. The stationary phase commonly used is silica (RMe_2SiCl) with a side chain alkyl group (R) such as $C_{18}H_{37}$ or C_8H_{17}, hence the name C18 or C8 column. Less polar molecules have longer retention times in these columns while polar molecules elute more rapidly. By changing the mobile phase (adding more water or adding more organic solvent), the affinity of the analyte to the stationary phase is changed, and the retention time (t_R) changes and analytes can be separated. The reverse phase chromatography operates on the principles of hydrophobic forces and the hydrophobic binding interactions between the analyte in the mobile phase and the immobilized hydrophobic ligand, i.e. the stationary phase. The actual nature of the hydrophobic binding interaction itself is a matter of heated debate [Dorsey and Cooper, 1994] but the conventional wisdom assumes the binding interaction to be the result of a favourable entropy effect. Reversed phase chromatography is an adsorptive process, which relies on a partitioning mechanism to effect separation. The solute molecules partition (i.e. an equilibrium is established) between the mobile phase and the stationary phase. The distribution of the solute between the two phases depends on the binding properties of the medium, the hydrophobicity of the solute and the composition of the mobile phase.

The mobile phase usually consists of a mixture of ultra pure solvents (Milli-Q® water and organic solvents like MeOH or ACN) either isocratic or with a gradient program. The isocratic methods are preferred for simple separation problems, while gradient programmes are usually used in complex mixtures with several analytes. In the case of a gradient program, the percentage of the organic solvent in the mobile phase increases and the analytes become increasingly desorbed in the mobile phase and migrate faster through the chromatographic system. To improve the separation and peak resolution the pH of the mobile aquatic phase can be adjusted accordingly (acidic to detect weak acids). After passing through the chromatographic column, the analytes generate a signal in the UV/VIS detector passing the flow-through cell (see **Figure 2.3**). The signal is digitized and recorded with the software. There is a linear relation between peak area and concentration, which is obtained by calibration with standards solutions of each analyte.

The method used in this work was developed initially by Bueno et al [Bueno et al, 2007] for the determination of emerging contaminants and micro pollutants in MWTP effluents by HPLC-MS. This method was adapted for the determination of 15 contaminants by UPLC-UV/DAD. As the LOD and LOQ of the typical UV/DAD system lies in the µg L^{-1} range and not in the ng L^{-1} range (as in typical LC-MS systems) this method had to be modified regarding the injection volume and flow rate. The injection volume was the maximum injection volume possible for this equipment (100 µL), the flow rate was set to 1 mL min^{-1}. The flow rate for a typical UPLC it is around 4 mL min^{-1}. The reason for the low flow rate is a compromise between analysis time and LOD/LOQ, as faster flow rates lower the LOD. The absorption wavelength of each compound which was used was the maximum absorption wavelength. Although the maximum absorption wavelength chosen gives a good response for the particular contaminant, there are some possible problems, like baseline shift (different absorption of the eluent at 205 nm at 90% water and 10% ACN than 50% H_2O and 50% ACN), and interferences of other substances in the water, as nearly all substances have high absorbance lower than 200 nm.

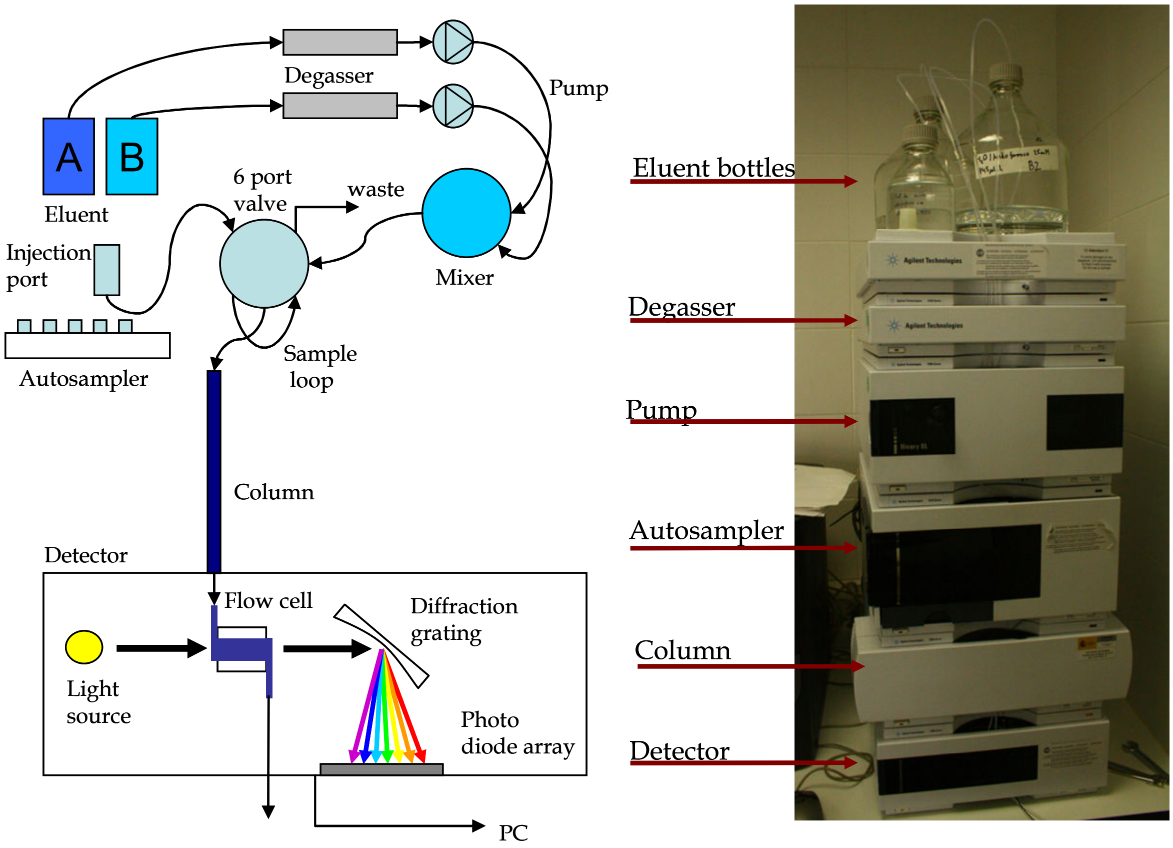


Figure 2.3 Picture and description of the UPLC – UV (Agilent 1200) system.

25 mL of sample was taken and filtered through a 0.22 µm pore size syringe driven filters (Millipore Millex® GN). The filters were washed with 3 mL of acetonitrile to desorb any organic compounds which might be absorbed on the filter. The two solutions were mixed and an aliquot was injected into the UPLC system.

The 15 selected model compounds were separated with an UPLC-UV system (Series 1200, Agilent Technologies, Palo Alto, CA) using a reverse-phased C-18 analytical column (Agilent XDB-C18, 1.8 µm, 4.6x50 mm) acetonitrile (mobile phase A) and ultra pure water (Milli-Q® system) with 25 mM formic acid (pH 3) (mobile phase B) at a flow rate of 1 mL min^{-1} and an injection volume of 100 µL. A linear gradient progressed from 10% A to 82% A in 12 minutes with a subsequent re-equilibrium time of 3 minutes.

Table 2.5 Method used for the model compounds with corresponding LOD and LOQ.

Method 1				
compound	**t_R [min]**	**abs max [nm]**	**LOD [µg L^{-1}]**	**LOQ [µg L^{-1}]**
Acetaminophen	1.187±0.027	245	1.0	2.5
Caffeine	2.143±0.030	205	0.9	2.0
Antipyrine	3.223±0.015	243	2.1	5.0
Carbamazepine	5.979±0.022	211	0.8	2.4
Atrazine	6.812±0.032	223	0.6	1.5
Isoproturon	7.057±0.027	205	0.9	2.5
Hydroxybiphenyl	8.305±0.039	243	1.2	4.5
Ibuprofen	9.468±0.046	222	2.0	5.0
Method 2				
compound	**t_R [min]**	**abs max [nm]**	**LOD [µg L^{-1}]**	**LOQ [µg L^{-1}]**
Ofloxacin	2.775±0.043	295	1.2	3.6
Sulfamethoxazole	4.306±0.026	267	1.5	4.4
Flumequine	6.268±0.020	248	1.3	3.9
Ketorolac	6.527±0.020	321	2.0	5.0
Diclofenac	9.249±0.031	277	2.5	5.0
Progesterone	10.162±0.031	248	1.5	5.0
Triclosan	11.168±0.047	280	5.0	10

The UV/VIS detector is a photodiode array with 7 wavelength slots, meaning that 7 different wavelengths can be recoded at the same time. To measure the 15 compounds it was necessary to inject the sample with two different methods, which are only distinguished by their detection of wavelengths.

The concentrations measured were calculated using a 5 point calibration curve with standard concentrations of 100, 50, 25, 10 and 5 µg L^{-1}. Standards were prepared from mothersolutions (500 mg L^{-1} of each compound in MeOH) in Milli-Q® water ACN (90:10) mixture and the matrix which was used for the experiment. The calibration curves (see **Figure 2.4**) had a correlation factor between R^2 = 0.9998 (Sulfamethoxazole) and R^2 = 0.9653 (Triclosan). Limit of detection (LOD) can be seen in **Table 2.5** were between 5.4 µg L^{-1} (Triclosan) and 0.61 µg L^{-1} (Atrazine) with their corresponding limit of quantification (LOQ) of 10 µg L^{-1} (Triclosan) and 1.8 µg L^{-1} (Atrazine).

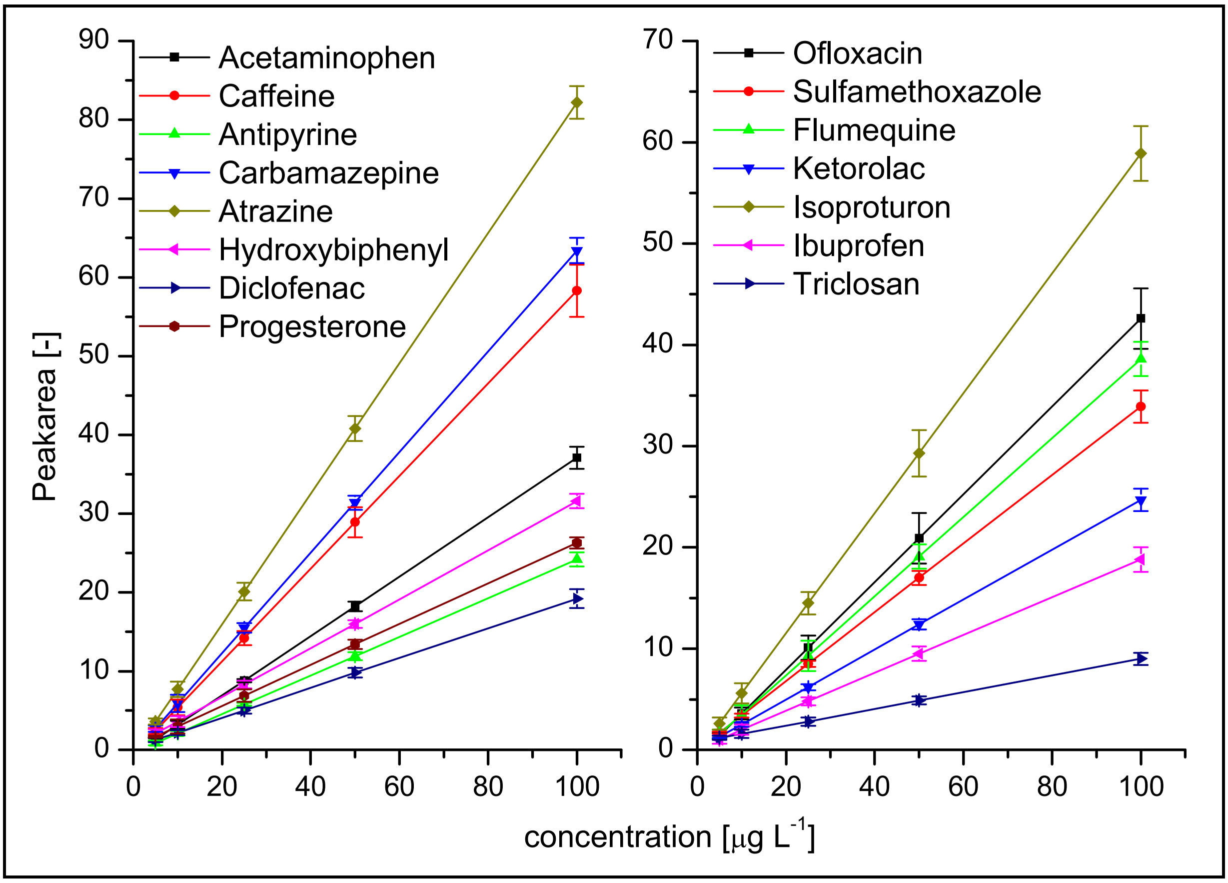


Figure 2.4 Calibration curves for the quantification of the 15 used model compounds

2.4.4 Liquid Chromatography – triple quadrupol linear ion trap Mass Spectrometry (LC-QqQLIT-MS)

Mass spectroscopy is an analytical method which uses the mass/charge ratio of ions to determine the sample molecules. The principle is to ionize the analytes to generate charged molecules (ions) which then can be separated according to their m/z by an electromagnetic field, and analyzed in a detector. A sample is introduced via an interface from the chromatographic system (either GC or LC) into the MS and evaporates. After evaporation, the samples are ionized. Ionization can be achieved through various methods like chemical ionization, electron ionization, electrospray or matrix assisted laser ionization. The analyzer can be a simple sector field (SF) mass analyzer, which uses a magnetic and/or electric field to influence the flight path of the charged ions; it can be a time of flight (TOF) analyzer, which accelerates the ions with the same potential and measures the time they take to reach the detector or it can be a quadrupole analyzer, which uses oscillating electric fields to influence ions passing through a radiofrequency quadruple field.

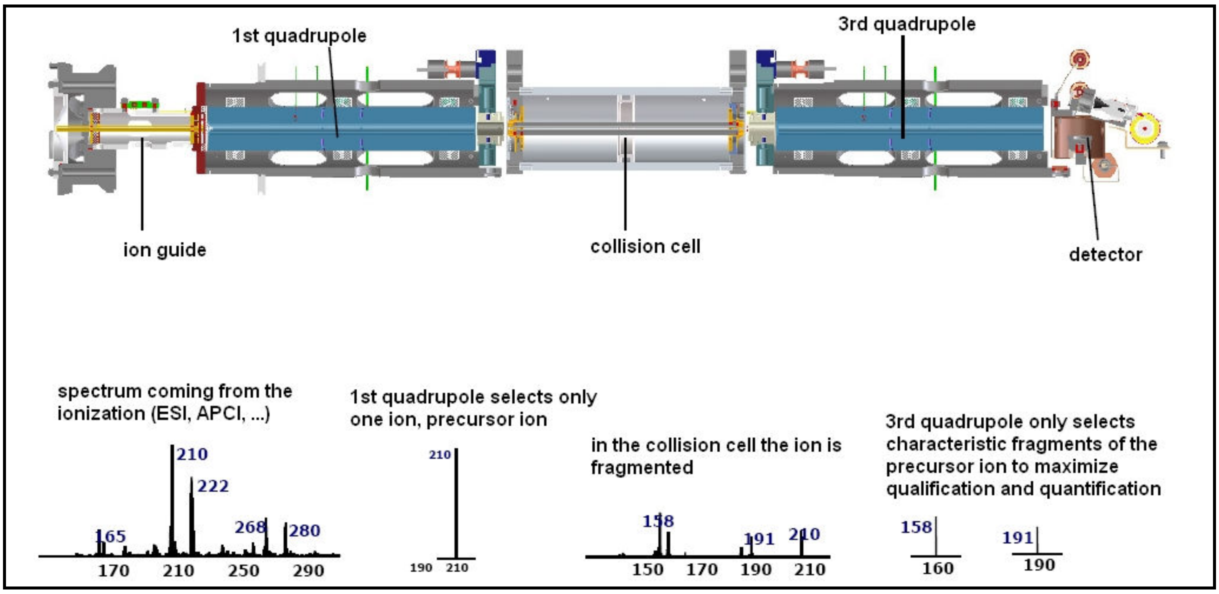


Figure 2.5 Schematics of a triple quadrupole MS

The analyzer used in this work is the triple quadrupol linear ion trap mass spectrometer. The triple quadrupol consists of two quadrupole MS in series, first and third (Q1 and Q3) quadrupoles which act ass mass filters with a non resolving quadrupole (q) in the middle, which acts as collision cell for collision-induced dissociation (see **Figure 2.5**).

The triple quadrupol linear ion trap MS used is a hybrid system in which the final quadrupole can act as a conventional selective mass filter or as an actual linear ion trap which can create a potential well for the ions along the axis of the electrodes [March, 2000].

The method for the analysis of target compounds was developed with a 3200 QLIT-MS/MS system (Applied Biosystem, Concord, Ontario, Canada) equipped with an electrospray ionisation source (ESI). Chromatographic separation of the analytes was carried out using an HPLC system (Agilent Series 1100) equipped with a reversed phase C-18 analytical column (250mm x 3.0mm, 5 µm particle size (ZORBAX SB, Agilent Technologies). The analyses were performed using a turbo ion spray source operating in both positive and negative modes; the parameters are shown in **Table 2.6**.

Table 2.6 HPLC and MS conditions

HPLC - conditions					
Positive mode	Gradient	t = 0	t = 40	t = 50	Flow rate
	ACN	10%	100%	100%	0.2 ml min^{-1}
	H_2O 0.1% formic acid	90%	0%	0%	
Negative mode	Gradient	t = 0	t = 10	t = 20	0.3 ml min^{-1}
	ACN	10%	100%	100%	
	H_2O	90%	0%	0%	
Re-equilibrium time for both modes: 15 minutes, injection volume 20 µL					
MS – conditions					
	Ion spray voltage [V]	Curtain gas [AU]	GS1 [psi]	GS2 [psi]	Probe temperature [°C]
Positive mode	5000	10	50	40	500
Negative mode	-3500	10	50	50	500
Nitrogen served as nebuliser gas and collision gas in both modes					

The GS1 parameter controls the nebuliser gas for the Turbo Ion Spray, which helps to generate small droplets of sample flow and affects spray stability and sensitivity. The GS2 parameter controls the auxiliary gas for the Turbo Ion Spray probe. It is used to help evaporate the spray droplets. GS2 works in conjunction with the temperature parameter.

The mass spectrometer was calibrated manually with a solution of poly-propylene glycol which was in accordance with the manufacturer's instructions introduced via a syringe pump to the interface. The MS operated in selected reaction monitoring mode (SMR) with a resolution set to Low and Unit for Q1 and Q3, respectively.

The instrumental detection limits (IDLs) were in the range of 0.1-100 pg, as absolute amount injected, methodogical detection limits (MDLs) were between 0.04 - 50 ng L^{-1} and methodogical quantification limits (MQLs) were between 0.1 – 160 ng L^{-1}. Relative standard deviations for the samples were lower than 20% in all cases [Bueno et al, 2007]

2.4.5 *Spectrophotometric methods for the determination of Fe, H_2O_2 and COD*

2.4.5.1 *Iron measurement*

Iron is the driving catalyst of the homogeneous photo-Fenton reaction. At a pH above 3 and/or at the presence of phosphates iron it is precipitated once oxidized to Fe^{3+} as iron hydroxide or iron phosphate. To ensure the correct working of the process iron has to be measured with a fast, simple and robust method. One of these methods is the spectrophotometric method (ISO 6332) with 1,10-phenantroline. Dissolved ferrous iron forms a stable orange-red coloured chelate complex with 1,10-phenantroline, which does not change colour between pH 3 and 9 and has a molar extinction coefficient of 11720 ± 60 L mol^{-1} cm^{-1} at 510 nm. A pH between 3 and 3.5 ensures a rapid a quantitative development of the colour, and as a consequence the measurement should be conducted in a buffered solution. H_2O_2 and other oxidizing agents interfere with the test, as they oxidize Fe^{2+} to Fe^{3+} which does not form complexes with phentrantroline. There are several heavy metals which form complexes (Co^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) or precipitate phenantroline (Ag^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+}, MoO_4^{2-}) and thus cause interferences in the sample. There are several procedures to avoid these interferences [Standard Methods for the Examination of water and Wastewater]. The interference of these heavy metals can be excluded as urban waste water normally does not and should not have any significant levels of heavy metals and H_2O_2 interference is avoided as described below.

The procedure for measuring dissolved and total iron is to mix 4 mL of sample with 1 mL of 1,10-Penantroline (0.1% w/v in deionised water), 1 mL of acetate buffer solution (250 g L^{-1} ammonium acetate and 700 mL L^{-1} acetic acid in deionised water), and a spatula tip of ascorbic acid. After some 5 minutes the absorbance is measured at 510 nm in a spectrophotometer (Unicam-II spectrophotometer) against a blank (sample where the phenantroline is replaced be deionised water) to reset any colour interference. The ascorbic acid reduces any Fe^{3+} to Fe^{2+}, and destroys H_2O_2, so that the iron measured is the total iron present in the sample. The concentration was calculated against a calibration curve which is linear between 0.2 and 7 mg L^{-1} of iron. If samples had a higher iron concentration they were diluted prior to mixing.

The concentration was calculated by **Eq. 2.1**.

Fe [mg L^{-1}] =– 0.0369 + (7.4219 x A) $R^2 = 0.9999$ **Eq. 2.1**

2.4.5.2 *H_2O_2 measurement*

Peroxide is the reagent consumed by the photo-Fenton reaction during the experiments. It is essential to determine the quantity of peroxide present in the sample and its consumption throughout the experiments to evaluate the efficiency of the chemical oxidation and to know if it is necessary to add peroxide to the reaction, otherwise it comes to a standstill. The determination of H_2O_2 during the experiments was achieved by photo spectrophotometry using titanium(IV)oxysulfate in accordance with the DIN 38402H15 method. It is a fast, rapid and robust method and is based on the formation of a stable yellow complex which is formed between H_2O_2 and $TiOSO_4$ as can be seen in **Eq. 2.2** and **Eq. 2.3**. This complex has its maximum absorption at 410 nm [Muñoz et al, 1990].

$$TiOSO_{4,(s)} + 5H_2O \longrightarrow [Ti(OH)_3(H_2O)_3]^+_{(aq)} + HSO^-_{4,(aq)}$$ **Eq. 2.2**

$$[Ti(OH)_3(H_2O)_3]^+_{(aq)} + H_2O_2 \longrightarrow [Ti(O_2)(OH)(H_2O)_3]^+_{(aq)} + 2H_2O$$ **Eq. 2.3**

The method has a detection limit of 0.1 mg L^{-1} and a linear range ranging at least from 0.1 mg L^{-1} to 100 mg L^{-1}.

The procedure for measuring H_2O_2 is as follows: 5 mL of filtered sample (0.22 µm PTFE syringe driven filters Millipore Millex® GN) is mixed with 0.5 mL of titanium(IV)oxysulfate solution. This titanium(IV)oxysulfate solution is used as received from Riedel de Haën, Germany. The reaction is instant and the colour does not change within 10 hours. The absorbance was measured at 410 nm in a spectrophotometer (Unicam-II) against a blank sample (the filtered sample without titanium(IV)oxysulfate). From the data obtained it is possible to calculate the concentration of H_2O_2 in the sample with **Eq. 2.4**.

H_2O_2 [mg L^{-1}] = -0.024 + (51.731 x A) $R^2 = 0.9998$ **Eq. 2.4**

2.4.5.3 Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand determines the quantity of oxygen which is required to oxidize the organic matter present in a sample under specific conditions (temperature, time and oxidizing agent) as described in the ISO method 15705. The organic substances in the sample are oxidized in an acidic solution of potassium dichromate in presence of silver sulphate which acts as a catalyst. Under these conditions dichromate is converted into Cr^{3+}. After 2 hours at 148°C the concentration of Cr^{3+}, which generate a green colour, is measured by spectrophotometry.

The measurement of COD is done via Merck Spectroquant® kit. The measurement range for the samples analyzed is between 10 and 150 mg O_2 L^{-1} (ref.nr. 1.14540.0001). 3 mL of a sample, which was filtered with 0.22 µm PTFE syringe driven filters (Millipore Millex® GN), is mixed with the reaction solution in the test tube (which was shaken before use), and heated for two hours at 148°C in a thermo block. After cooling down to room temperature the test tube is introduced into the Spectroquant® NOVA 30 from Merck and measured at 445 nm.

The calibration curve that related absorbance at 445 nm and COD concentration for the range 10 - 150 mg O_2 L^{-1} was done with known concentrations of potassium phthalate solutions which correspond to known COD and has the correlation as seen in **Eq. 2.5**

COD [mg L^{-1}] = 317.83 –(209.66 x A) $R^2 = 0.9989$ **Eq. 2.5**

2.4.6 Elimination of H_2O_2 by Catalase

Hydrogen peroxide present in the samples can influence some measurements like COD, can continue reacting after sampling and can influence biological measurements (bacterial count and bio toxicity) and therefore has to be eliminated. The elimination of peroxide is done with bovine liver catalase (purchased from Sigma-Aldrich, 2300 units mg^{-1}), which is an enzyme capable of neutralizing oxygen species like H_2O_2, which are formed in aqueous phases containing dissolved oxygen like the cytoplasm of cells. The catalase converts peroxide into water and dissolved molecular oxygen. One unit of catalase can approximately convert 1 µM of peroxide per minute at pH 7 and 25ºC.

The catalase solution is prepared fresh for each experiment, as it is not stable for more than 24h. It is prepared at a concentration of 100 mg L^{-1} in ultra pure water (Milli-Q® water). The enzyme is deactivated at pH lower than 5 and higher than 8, so samples have to be neutralized usually between pH 6 and pH 7 prior to adding the catalase. Catalase is added in surplus to guarantee a fast and complete destruction of peroxide.

2.4.7 Solid Phase Extraction (SPE) and Automated Solid Phase Extraction (ASPEC)

2.4.7.1 Solid Phase Extraction (SPE)

The analysis of compounds in real waste water with LC-Qtrap-MS and of the 15 model compounds in water spiked at 5 µg L^{-1} is not possible without any pre-concentration. The method of choice was the Solid Phase Extraction (SPE). The Solid Phase Extraction is a selective, efficient technique with good recuperation percentages for the analytes in question. It is a good alternative method to the classical liquid-liquid extraction (LLE), requires less time and less chemicals, produces less waste and is capable of extracting many polar substances which are very difficult to concentrate otherwise. SPE can use a lot of different solid phases like carbon, HLB, MAX, WAX resins which can be conditioned in various different ways to serve the purpose in question. Apart from the concentration of analytes, SPE has the benefit of purifying the sample as well, leading to less interference of the matrix in the analytical system and has the possibility of changing the mobile phase (e.g. water to less polar liquids). SPE can be applied on-line e.g. directly integrated into the analytical system, or off-line, in which the treatment of the sample is completely separated from the analytical step. The off-line procedure is typically done via adsorption of the analytes in cartridges (micro-columns) (see **Figure 2.6**) and subsequent elution.

Figure 2.6 Picture of a cartridge used in SPE (6 cm^3 HLB)

The sequence of a SPE extraction consists of typically of several steps:

- conditioning of the cartridge and sample (same pH)
- charging of the cartridge with the sample at low flows (10 – 20 mL min^{-1})
- washing of the cartridge with water
- drying with N_2 to evaporate water
- elution and recuperation of the analytes with an organic solvent
- evaporation to dryness or near dryness of the organic eluent using N_2
- recuperation into an appropriate solvent for the analysis

The retention mechanism of analytes in the adsorbent of the cartridge depends on the characteristics of the analyte as well as on the characteristics of the adsorbent, and is based on interactions like dipole-dipole, ion-dipole, hydrophobic and ion exchange interactions. The diversity of those interactions as well as the diversity of the materials at hand permits the adjustment of the SPE method to serve for the analytes in question. If one develops a SPE method it is necessary to know what kind of analytes one is dealing with, and how they behave in terms of polarity, hydrophobity, etc. One parameter which serves as good criteria for polarity is the octanol-water partition coefficient (K_{OW}). It is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. The solubility of an organic compound depends on the temperature and the pH, which as welll aides developing the SPE method. But in any case it might be difficult to predict the affinity of one specific analyte towards the adsorbent in the cartridge, as there are some compounds which are very water soluble, but do not retain on the adsorbent of the SPE and are better extracted through conventional LLE.

The cartridges used in this work are Oasis® HLB (Waters, Milliford, USA) and are the most common used to retain a wide amount of pharmaceuticals, pesticides and other substances with polar and apolar properties. Although there are many advantages, there exist certain limitations and disadvantages:

- Very polar compounds can be lost during the adsorption in the cartridge due to low affinity with the solid phase.
- Polar compounds with low solubility in water can deliver low recuperations through adsorption in the connections and tubing, or through incomplete desorption
- Ionic compounds need a pH adjustment to augment their retention in the adsorbent. One has to be aware that certain pharmaceuticals are only stable in certain pH ranges.
- Certain volatile compounds may evaporate during the drying steps.

The samples were extracted and pre concentrated using a Supelco Visiprep™ extraction chamber with a vacuum pump (see **Figure 2.7**). Cartridges used were Oasis® HLB (divenylbenzene/N-vinylpyrolidine) 6 cm^3 with 200 mg absorbent from Waters (Waters, Miliford, USA). The procedure for extracting samples can be seen in **Table 2.7**. This method initially was developed by Bueno et al [Bueno et al, 2007]] for a complex mixture of more than 60 contaminants (pharmaceuticals, personal care products, pesticides, etc.) present in water samples. The recuperated sample was injected into the analytical system (LC-MS or UPLC-UV) and analyzed.

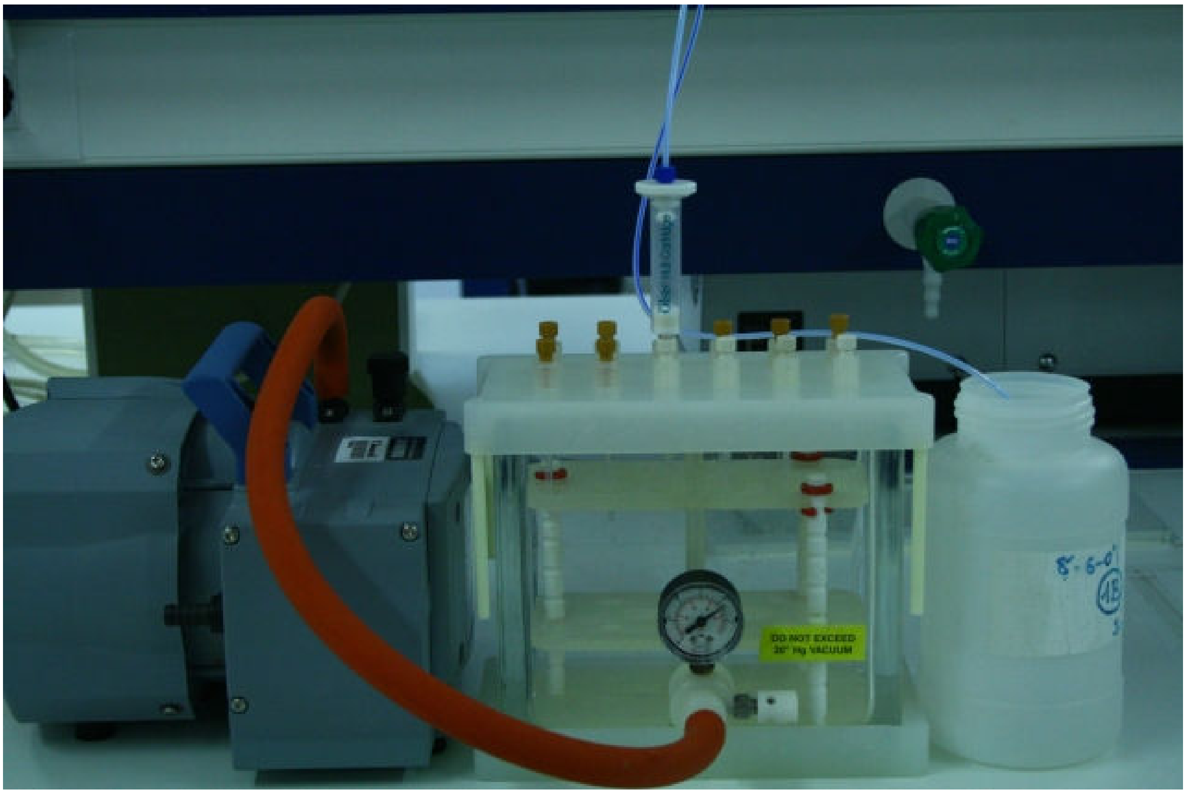


Figure 2.7 Picture of Supelco Visiprep™ manual extraction chamber.

Table 2.7 Extraction protocol for samples

conditioning	5 mL MeOH, 5 mL Milli-Q water at pH 8
extraction	100 - 200 mL sample at pH 8 (volume depends on concentration factor)
washing	2 x 2 mL Milli-Q water at pH 8 (NH_4OH)
drying	15 min in N_2 stream
elution	2 x 4 mL MeOH
evaporation	to dryness with N_2
recuperation	2 mL of ACN:H2O (1:9)
filter	0.22 µm PTFE syringe driven filters

2.4.7.2 Automated Solid Phase Extraction (ASPEC)

The Automated Sample Processor ASPEC GX-271 from Gilson was used to extract samples automatically. The advantage of this equipment is that it is, after being given the start command, capable of extracting an amount of samples without supervision and during a longer period of time (night, weekend). It is slower than conventional manual SPE, but due to its automatisation more repetive. The ASPEC GX-271 is connected to a 406 Single Syringe Pump (Gilson) and a VALVEMATE® II (Gilson) valve actuator with 8 inlets and one outlet, which permits to extract 7 samples at the same time (the 8th inlet is for washing purposes for the system) with extraction volumes bigger than 50 mL. The pressure throughout the system was controlled through the syringe pump, and the whole equipment was controlled by the TRILUTION®LH software from Gilson. Sample handling could be either sample after sample (each sample was handled from conditioning of the cartridges to extraction to elution) or step by step configuration of all samples (conditioning of all cartridges, extraction of all samples, and elution of all samples). The method used for sample extraction is the same used as in SPE.

2.5 Photocatalytic Experiments

2.5.1 CPC-solar pilot plants

Three different CPC-Reactors (A, B, C) were used in this work. The reason why different pilot plants were used lies in the objectives of each specific experiment. All photo-Fenton experiments were performed at the Plataforma Solar de Almería (lat. 37ºN, long. 2.4ºW) with natural sunlight.

All CPC reactors are mounted on a static platform tilted at the same angle as the local latitude (37º) facing south. The reflecting surface is made of resistant and highly reflecting electropolished aluminium. The hydraulic circuit of the reactor consists of a continuously stirred tank, a centrifugal recirculation pump, a solar CPC reactor, connection tubing made from highly resistant black HDPE and valves. The specifics of each reactor used can be seen in **Table 2.8**. The sample point in all systems was after the solar reactor. A temperature probe, a flowmeter and a pH meter is inserted into the system to allow online measurements of these parameters.

Table 2.8 Characteristics of the used photo-Reactors

Reactor	A	B	C
modules	2	4	3
total volume (min-max) [L]	30-40	70-84	250-450
illuminated Volume [L]	22	44.6	108
illuminated surface [m^2]	3.02	4.16	9
number of tubes	24	20	48
tube material	Borosilicate	Borosilicate	Teflon
tube length [mm]	1502	1320	1000
exterior tube diameter [mm]	32	50	48
interior tube diameter [mm]	28	46.4	46
flow [L min^{-1}]	22	25	58

Reactor A was used for standard experiments where the initial concentration of the selected contaminants was 100 µg L^{-1}. The total volume used was 35 L. The sample volume of each sample did not exceed 120 mL. Reactor B was used for experiments, where the initial concentration of the selected contaminants was 5 µg L^{-1}. As SPE was used for evaluation of the degradation, larger samples were necessary. Therefore, the total treated volume was larger. The total volume used was 80 L. The sample volume of each sample was 500 mL. Experiments conducted in the reactor C were used to treat large quantities of real MWTP effluents for providing irrigation water to be used in reuse experiments performed at CIESOL (University of Almeria) with specific crops. These experiments were done in close collaboration with the research group of the University of Almeria in the framework of the TRAGUA project. The reuse experiments were part of other research activities not included in this document. Only results selected with the treatment of MWTP effluents by photo-Fenton are included here. **Figure 2.8** shows the three CPC reactors with their mixing tanks.

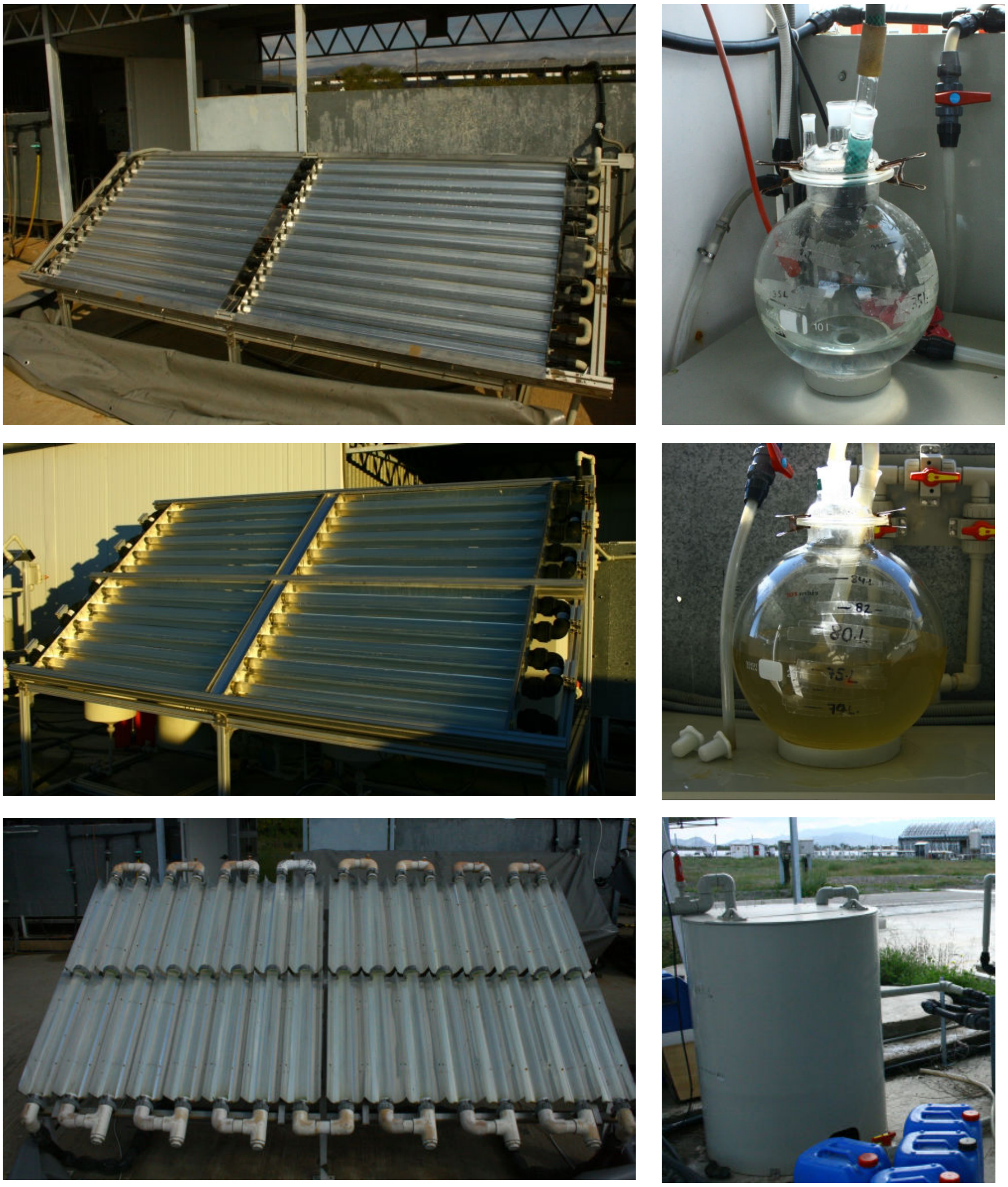


Figure 2.8 Picture of the three CPC reactors with their tanks. A (top), B (middle) and C (bottom).

Usually samples were taken every 15 minutes for the first hour, every 30 minutes for the next two hours and every 60 minutes for the next samples. Due to the design of the photo reactor it was not possible to take samples in intervals smaller than 15 minutes since the pilot plant is a dynamic system in which the outlet concentration (C_1) is not exactly the same as the mixing tank concentration (C_2). Thus, unless properly accounted for, the presence of the tank can alter the perceived photo reactor performance. There are two solutions available to solve this problem. The first is to use a very high flow rate to achieve low conversions for each pass. The high flow rate must avoid conversions higher than 1% in one pass through the reactor ($C_1(t) \approx C_2(t)$). Therefore both C_1 and C_2 could be considered the same. The second solution is a long enough sampling time (at least 5 times longer than one loop), which allows the mixing of the plug flow in the non reactive mixing tank. The more this happens, the more homogeneous the solution becomes. [Wolfrum and Turchi, 1992; Malato et al, 2000]. For all the experiments conducted in the photoreactors A, B and C, these considerations have been taken into account.

2.5.2 Experimental setup

The experiments followed a specific protocol, which was slightly adapted depending on each experimental setup. First the treated water was filled into the reactor and circulated with the CPC covered. In the case of spiking, aliquots were added into the tank and a sample was taken after 15 minutes to ensure total homogenisation. After that, peroxide was added into the tank, again with a 15 minute homogenisation time, after which iron (and in the case of complexing agents, iron and the agents together) was added into the reactor. After another 15 minutes, in which the dark Fenton reaction took place, the CPC was uncovered. In the first hour samples were taken every 15 minutes, in the second two hours samples were taken every 30 minutes, and every subsequent hour samples were taken every hour.

2.5.3 UV-measurement

The radiation reaching the earth has a wavelength between 200 nm and 50 µm, which is reduced to a wavelength between 280 nm and 4.0 µm when reaching the earth's surface, see [American Society for Testing and Materials (ASTM)]. The reduction in the UV radiation is due to different atmospheric components and conditions (O_3, CO_2, H_2O, aerosols, clouds, dusts, etc.). The radiation which reaches the ground without being absorbed or scattered is called direct radiation and radiation which has been dispersed but reaches the ground is called diffuse radiation. The sum of these two components is called global radiation (see **Figure 2.9**).

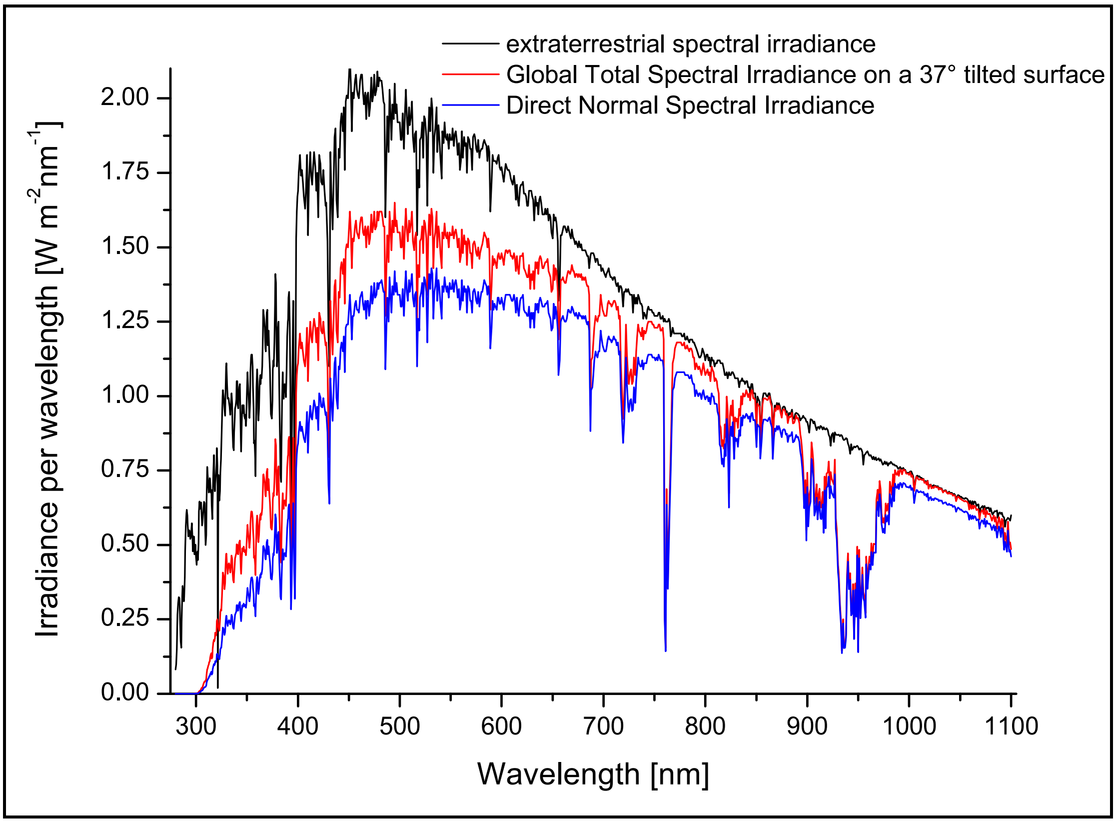


Figure 2.9 Global Irradiance standard Spectrum up to a wavelength of 1100 nm, normalized to 1000 W m^{-2} for the whole spectrum (4000nm).

The effective radiation, which reaches the ground, varies strongly due to several factors such as geographic latitude, time of year, time of day, atmospheric conditions (aerosols, humidity, dust, etc) and cloud cover (**Figure 2.11**). The equipment to measure the global UV radiation is a radiometer KIPP&ZONEN, model CUV3, with a sensitivity of 264 mV W^{-1} m^{-2} which is mounted on a platform at an angle of 37^{o} (same angle as the CPC reactors). This radiometer records data of incident radiation for wavelengths below 400 nm in W$_{UV}$ m^{-2}. The equipment can be seen in **Figure 2.10**.

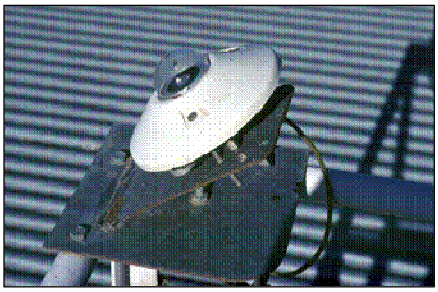


Figure 2.10 Radiometer for the measurement of global UV radiation.

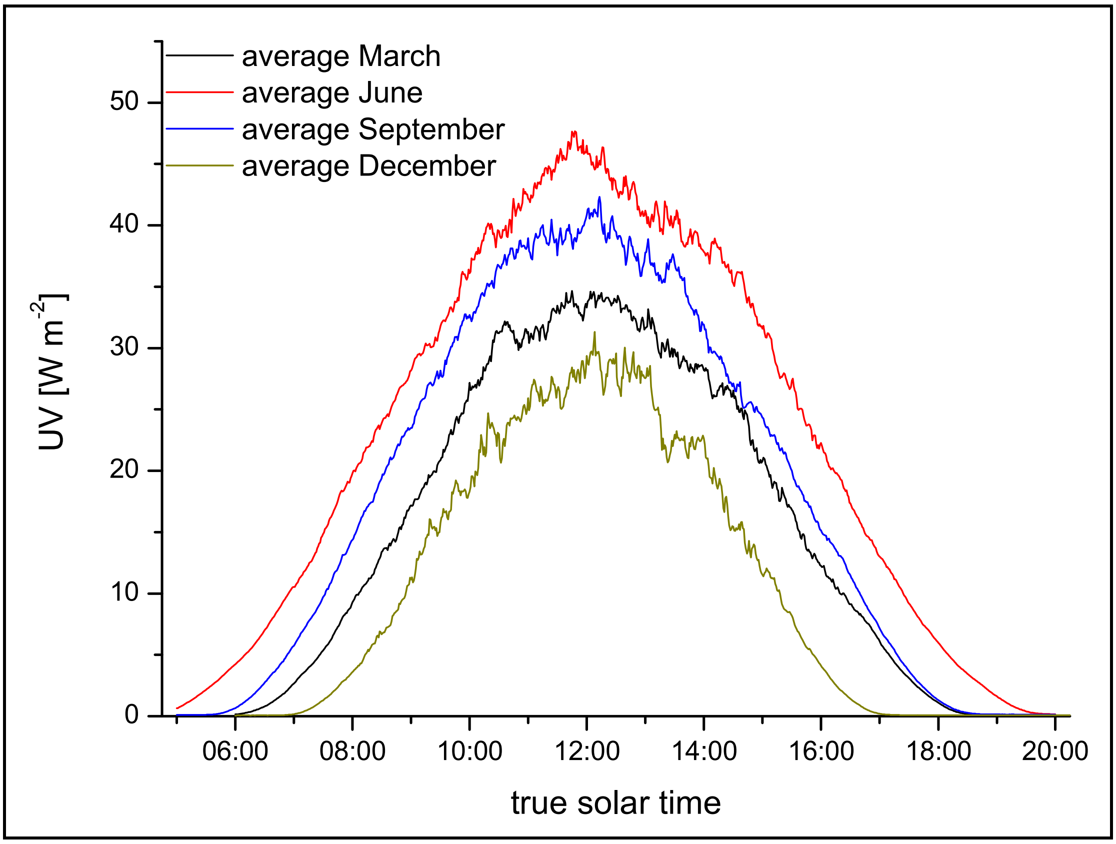


Figure 2.11 Variation of the global UV radiation measured at PSA in different months (displayed monthly average value) for the year 2010.

The measurement of the UV radiation which reaches the reactor permits to compare experiments conducted on different days and under different meteorological conditions. This mathematical relation includes the experimental time (t), the total volume (V_t), the irradiated volume (V_i), the collector surface (A_r) and the radiation ($UV_G = W_{UV}\ m^{-2}$). As the UV data is recorded continuously, it is possible to calculate the average UV radiation which reaches the collector surface ($\overline{UV}_{G,n}$), for each time interval (t). With theses parameters it is possible to calculate the accumulated energy per unit of volume for each sample taken from the beginning of the experiment until the sample time. This relation is given in **Eq. 2.6**.

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \cdot \overline{UV}_{G,n} \cdot \frac{A_r}{V_t}; \quad \Delta t_n = t_n - t_{n-1} \qquad \textbf{Eq. 2.6}$$

The results of photocatalytic experiments can be represented in terms of illumination time (t_{30W}), instead of accumulated energy ($Q_{UV,n}$). The illumination time is a normalized time, which refers to a constant solar UV power of 30 W m^{-2}, which is the average solar radiation on a perfectly sunny day around noon (see **Figure 2.11**). The illumination time is calculated by **Eq. 2.7**, in which t_n is the experimental time of each sample, UV the average radiation measured between Δt, t_{30W} the normalized illumination time, V_i the illuminated volume and V_t the total volume of the photo reactor.

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \cdot \frac{UV}{30} \cdot \frac{V_i}{V_t}; \quad \Delta t_n = t_n - t_{n-1} \qquad \textbf{Eq. 2.7}$$

All experiments in this work used t_{30W}.

2.6 Bioassays

2.6.1 Disinfection evaluation based on the heterotrophic plate count

Water, if it is being reused should be free of faecal bacteria like *Escherichia coli*. According to the Spanish legislation for the reuse of water [Spanish legislation], the total bacterial count as Colony Forming Units per millilitre (CFU mL^{-1}) should not exceed certain limits, depending on the form of reuse, for example < 100 CFU mL^{-1} for industrial reuse and irrigation of trees, < 10 CFU mL^{-1} for the irrigation of pastures and the recharge of aquifers, < 2 CFU mL^{-1} for gardens and recreative use. Effluents of wastewater treatment plants do usually have a very high load of bacteria > 10^5 CFU mL^{-1} and a high load of total coliforms > 10^3 CFU mL^{-1}.

Part of this work was the evaluation of the disinfection efficiency of the processes. The evaluation was done by the simple plate counting method with two different culture media on standard Petri dishes called the heterotrophic plate count [Standard methods for the Examination of water and wastewater]. The media, Luri Agar for total bacteria count, and Endo Agar for total coliforms was rehydrated, dispensed and sterilized in an autoclave at 121°C for 15 minutes after the temperature has reached 121°C. After the agar suspension was cooled down, it was dispersed into Petri dishes, which were stored afterwards in the refrigerator at 4° until further use.

Samples from the photo-Fenton experiments were neutralized if necessary, mixed with catalase to destroy excess peroxide and filled into sterile sample vials. These sample vials were stored in the refrigerator in the dark if rapid sample analysis was not possible, otherwise the samples were serially diluted 10 (D_1), 100 (D_2), 1000 (D_3) and 10000 (D_4) fold with PBS (phosphate buffer solution). The solutions were inoculated with a specific volume onto the agar Petri dished (total and coliforme), incubated at 37° for 24h. After incubation the colonies were counted and the CFU number was calculated by **Eq. 2.8**.

$$CFU / mL = \frac{colonies\ counted}{actual\ volume\ of\ sample\ in\ dish\ [mL]} \qquad \textbf{Eq. 2.8}$$

There are two ways to perform the heterogenic plate count. Either (usually) 3 droplets of sample solution with a volume of usually 20 µL are applied onto the dish which is subdivided into four sectors to apply all 4 dilutions (D1 – D4), or one drop of 50 µL of sample is applied and spread onto the whole dish (see **Figure 2.12**).

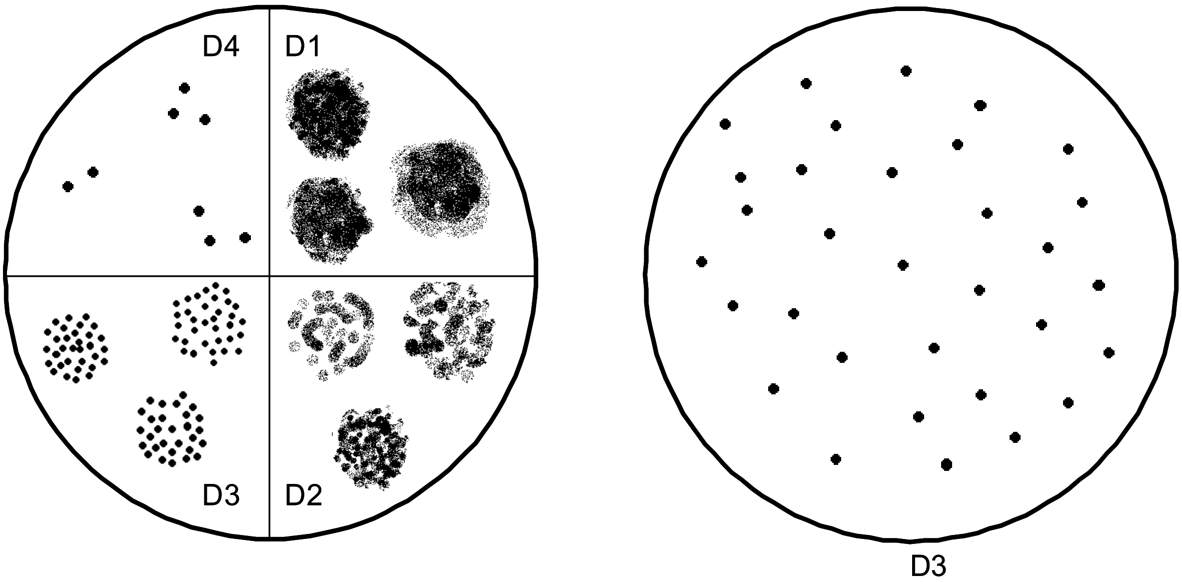


Figure 2.12 Graphic of heterotrophic plate count. Left dish, droplet count: all 4 dilutions are incubated on the same dish. Right dish, spread count: defined volume of one dilution is spread onto the dish.

Samples in this work were treated in both ways. In the case of spreading, at least three dishes were used to get a good average value with standard deviation. The total coliforms were only measured via spreading, as the Endo Agar is not suitable for droplet count. Usually samples with counts of 20 to 200 are preferred, but if not possible otherwise, counts below 20 were taken into consideration.

2.6.2 Toxicity evaluation based on the bioluminescence of Vibrio fischeri

There are various laboratory tests to determine the toxicity of water. The response of aquatic organisms to the presence of chemicals can help to evaluate the chronic or acute toxicity of these chemicals or mixtures of chemicals in waters and allows making declarations over some quality parameters of contaminated waters in the environment. Although the toxicity evaluation gives an overview over the quality of the water, it is not an absolute value, as the response of the bacteria can be different to the response of vertebrae and in particular higher mammals and humans to the same chemical.

Different responses and correlations of toxicity in different species have been described before, but it is difficult to extrapolate results gained for one species to another species or to use them to predict dangerous effects of treated waters or effluents on humans and the environment [Hodson, 1985].

The toxicity test used in the doctoral thesis was the inhibition of the bioluminescence of the marine bacteria *Vibrio fischeri* (see **Figure 2.13**). This test is reliable, representative, rapid and relatively cheap.

This bioassay determines the toxicity of a water sample based on the reduction of the natural bioluminescence of the marine bacteria *Vibrio fischeri* (*Photobacterium phosphoreum*, NRRL B-11177) in the presence of contaminants. The toxicity is expressed as the concentration of a compound (EC_{50}) which produces a 50% reduction in the initial bioluminescence or the percentage of inhibition in the case of a mixture of contaminants.

The *Vibrio fischeri* bacterium is a heterotrophic gram negative bacterium of the *Vibrionaceae* family which foremost characteristic is bioluminescence (light emitting of some living organisms). It is important to emphasise the stability of the bioluminescence of this bacterium in its natural environment (seawater without any toxic substances), as it is the basis for the measurement of toxic compounds, or a mixture of toxic substances.

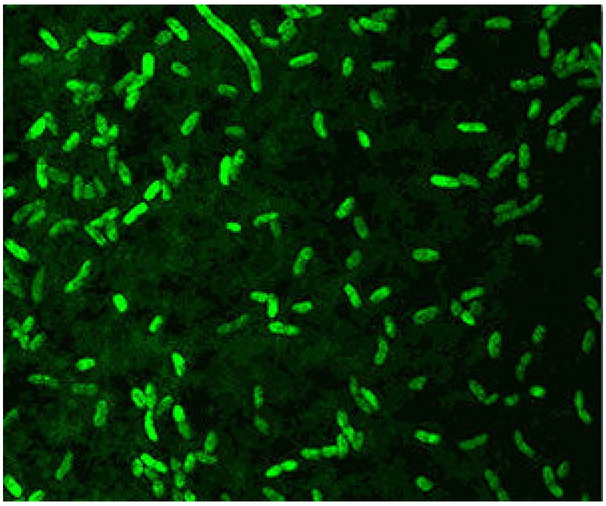


Figure 2.13 Images of *Vibrio fischeri* bacteria

Vibrio fischeri's bioluminescence has been found to be caused by five genes, luxCDABE, that are regulated by luxR and luxI. The emission of light happens from the oxidation of organic compounds. Differences in the amount of light produced can therefore be correlated to the organisms metabolism. The reduction of light emitted is proportional to the toxicity of the aquatic sample, as chemical and other contaminants influence the cell respiration, thus changing the amount of emitted light.

Possible interferences when measuring aquatic toxicity with this method can be:

- using insoluble, low soluble or volatile substances
- using substances which interfere with NaCl
- measuring waters with a high turbidity, adsorbance property of light, or colour
- using waters with a high salt concentration (> 20 g L^{-1}), which have hyper osmotic effects on the bacteria

The measurement of bioluminescence was carried out with commercially available kits. BioFix®Lumi Multi-shot luminescent bacteria for 200 samples from Macherey-Nagel (ref.: 945007), which included the restorative solution. Each kit was quality certified in conformation with the DIN EN ISO 11348-3.

The Luminometer used for the measurement of bioluminescence was the BioFix®-Lumi-10 from Macherey-Nagel which has an Ultra Fast Single Photon Counter with a spectral range of 380 to 630 nm.

Before measuring, the samples were filtered through a 0.22µm PTFE filter (Millipore Millex® GN) to remove suspended solids, peroxide was removed by catalase as described in chapter 2.4.6, the pH was adjusted to neutral (between pH 6 and pH 8), and the salinity was adjusted to 2% (w/v) by adding solid NaCl.

The freeze dried bacteria were reconstituted in 11 mL restorative solution, stored at 4ºC for 30 minutes and then temperated at 15ºC. After that, 500 µL of bacterial suspension was transferred into a test vial, which contained 5 mL of sample and 500 µL of saline solution (2% w/v). The change in bioluminescence (inhibition) was measured after 5, 15 and 30 minutes against a blank.

3 Results

3.1 Purpose of this work

The purpose of this work is to investigate and study a tertiary treatment method for municipal wastewater based on solar photo-Fenton at neutral pH. It is well known that the Fenton and photo-Fenton process is a potent application for the treatment of industrial waste waters with high organic load. Usually these processes have iron concentrations between 20 and 50 mg L^{-1}, a high initial peroxide concentration (> 200 mg L^{-1}) and the usual pH of around 2.8.

One of the main sources of water for potential reuse comes from municipal wastewater treatment plants (MWTPs). Quality demands for reusable water [Rose 2007; Díaz-Cruz and Barceló, 2008; Wintgens et al, 2008] are that they do not contain any toxic, endocrine-disrupting compounds, bio accumulative or non-biodegradable substances. But due to their growing and unregulated use, pharmaceuticals, pesticides, hormones, synthetic fragrances, illicit drugs and others which escape conventional wastewater treatment are found in increasing quantities in waste, surface and even drinking waters [Esplugas et al, 2007; Kasprzyk-Hordern et al, 2009]. As a consequence, the application of more exhaustive wastewater treatment protocols, including the use of new and improved technologies, is a necessary task. As mentioned above, photo-Fenton treatment have been reported as effective methods for the elimination of contaminants [Dalrymple et al, 2007], usually at initial concentrations of the contaminants in the mg L^{-1} to g L^{-1} range, but to apply these brute force methods to waters, which only contain contaminants as a sum in the low µg L^{-1} range would be unnecessary and too costly. So the goal is to find a mild solar photo-Fenton (low iron concentration 5 mg L^{-1} and low initial H_2O_2 concentration of 50 mg L^{-1}) which is able to degrade the micro contaminants present in treated waste water. Another goal is the application of this mild solar photo-Fenton at neutral pH.

This has the background that it would be

i) cost effective due to the fact that sulphuric acid for the lowering of pH to 3 and sodium hydroxide for subsequent neutralization after the process could be saved

ii) it would be time effective, as there would be no need of pH change, and

iii) that the salinity of the treated waters would not be raised. This is an important fact as some plants are not capable of coping with high salinity.

Another part of this work is the evaluation of disinfection of the treated waters, as water for reuse has certain limits of bacterial load (fields, gardens, agricultural use, aquifer recharge…)

3.2 Experimental design

As the concentration of micro pollutants and emerging contaminants in MWTP effluents is usually quite low, [Bueno et al, 2007; Gómez et al, 2007] it was decided to work in the range of 100 µg L^{-1} of each contaminant used as model compound. This concentration, although far from real concentrations in effluents, is considered to be low enough to simulate the real concentration level quite accurately, and is at the same time high enough to be detected without great difficulty in the UPLC-System down to a concentration of 5 - 10 µg L^{-1} (see **Table 2.5**), depending on the particular compound.

As the composition and matrix of real effluents change daily, and the behaviour of theses waters with the intended treatment is unknown, it was decided to start with deionized water and stepwise change the water from deionized water, to simulated fresh water, to simulated waste water effluents (**Table 2.2**) and finally to real waste water effluents from a MWTP using the gained experience to which was obtained along the line of work. **Figure 3.1** shows the pathway followed during this research. The red arrows show the main course followed. Experiments conducted with typical photo-Fenton at pH 3 were used as baseline experiments to compare the efficiency of the developed modified photo-Fenton processes. When not indicated otherwise, the iron concentration was 5 mg L^{-1} and the initial H_2O_2 concentration 50 mg L^{-1}.

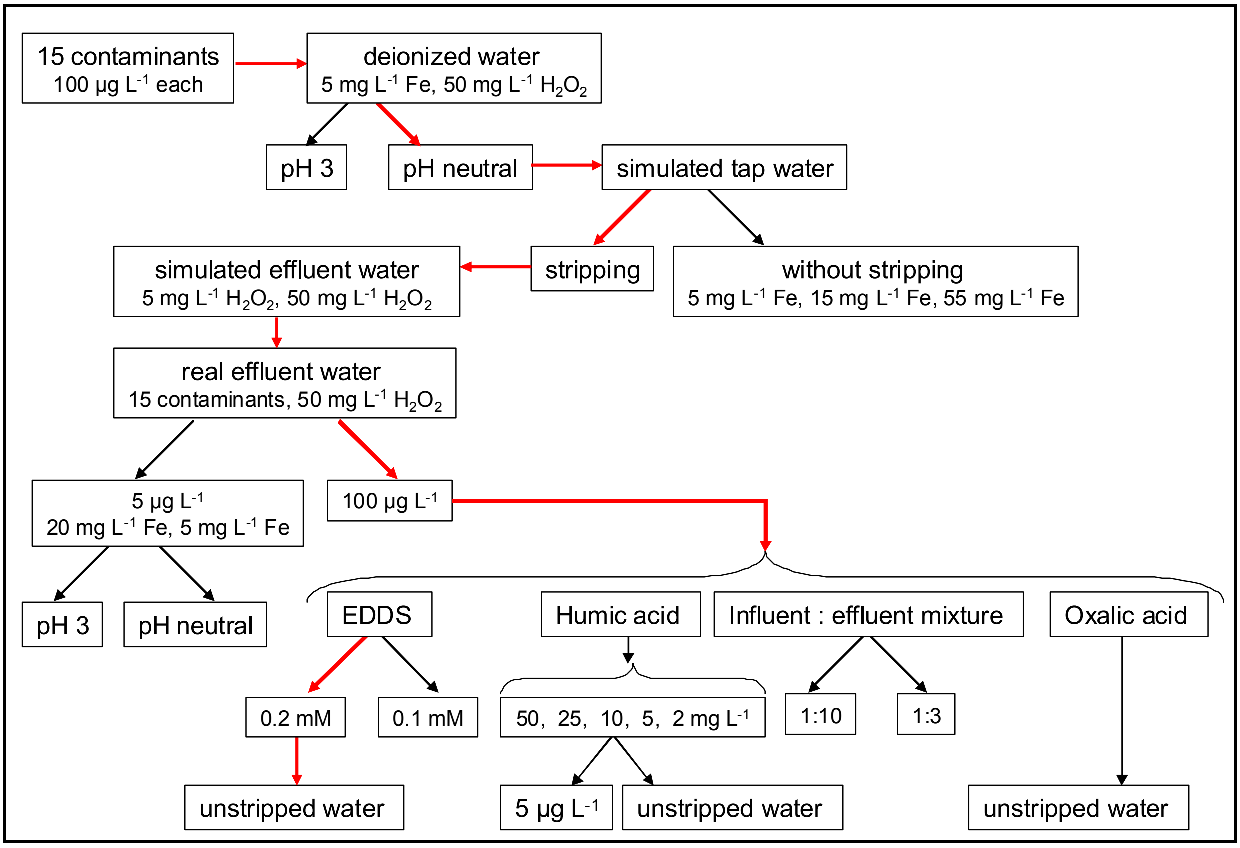


Figure 3.1 The different steps developed during this work

The experiments were conducted in the CPC reactors filled with the water in question and as a general rule lasted up to 8 hours. The water was circulated, the compounds were added and after 15 minutes of homogenization the first sample was taken (t_0, t_{30W} = -30 minutes). With the exception of the first experiment, the order of adding iron and peroxide was like this: t_0: adding of H_2O_2; t_1: t_{30W} = -15 minutes: adding of iron; t_2, t_{30W} = 0 minutes: illumination of the reactor. The reason for this order is the idea, that under neutral conditions the iron is going to be precipitated, and therefore not longer available for the reaction and through this order, it is possible to exploit the dark Fenton process. All experiments were conducted with a Fe concentration of 5 mg L^{-1} if not mentioned otherwise.

Samples were filtered through a 0.22 µm PTFE syringe driven filters (Millipore Millex® GN) for the determination of peroxide, iron, COD and IC. Samples for UPLC were filtered and the filter was washed with acetonitrile, and the two solutions mixed and an aliquot was injected into the UPLC system. As a general rule, experiments were at least repeated once to confirm the degradation behaviour.

3.3 Preliminary experiments

The stability of the used compounds was tested to rule out any degradation in water (hydrolysis), and in water with sunlight (photolysis). All compounds proved to be stable at least for more than one week in water and more than five light cycles (illumination during working hours from 9:00 to16:00 during five days). Apart from that, tests were performed which confirmed that the presence of Fe(II) salts in water did not affect the stability nor the light absorbance of these compounds due to formation of compound-Fe complexes, which could lead to misleading results in terms of concentration.

3.4 Degradation of micro contaminants in water

3.4.1 Degradation of 9 contaminants in deionized water

The first experiments were conducted with only 9 contaminants (Acetaminophen, Antipyrine, Atrazine, Caffeine, Diclofenac, Isoproturon Progesterone, Sulfamethoxazole and Triclosan) at a concentration level of 100 µg L^{-1} in deionized water in reactor A (see **Table 2.8**). The reason only 9 compounds were used in these experiments lies in the fact that the other 6 compounds (Atenolol, Endosulfan, Galaxolide, Nicotine, Oxybenzone and Tonalide) primarily selected were problematic due to low solubility, interference, etc., and the results were not consistent and therefore not included here.

Figure 3.2 shows a typical photo-Fenton experiment in deionized water at pH 2.8. This experiment delivered no new exceptional insights into the degradation behaviour of contaminants in water. Due to the fact that iron was added at t_{30W} = -15 minutes and peroxide was added at t_{30W} = 0 minutes, no Fenton reaction in the dark took place (see **Eq. 1.22**) and no degradation was detected before illuminating the reactor. Within t_{30W} = 10 minutes, the degradation below the LOQ of Acetaminophen, Caffeine, and Diclofenac was achieved. The compounds Antipyrine, Sulfamethoxazole, Atrazine, Progesterone and Triclosan were degraded below their LOQ after t_{30W} = 20 minutes and Isoproturon after t_{30W} = 32 minutes.

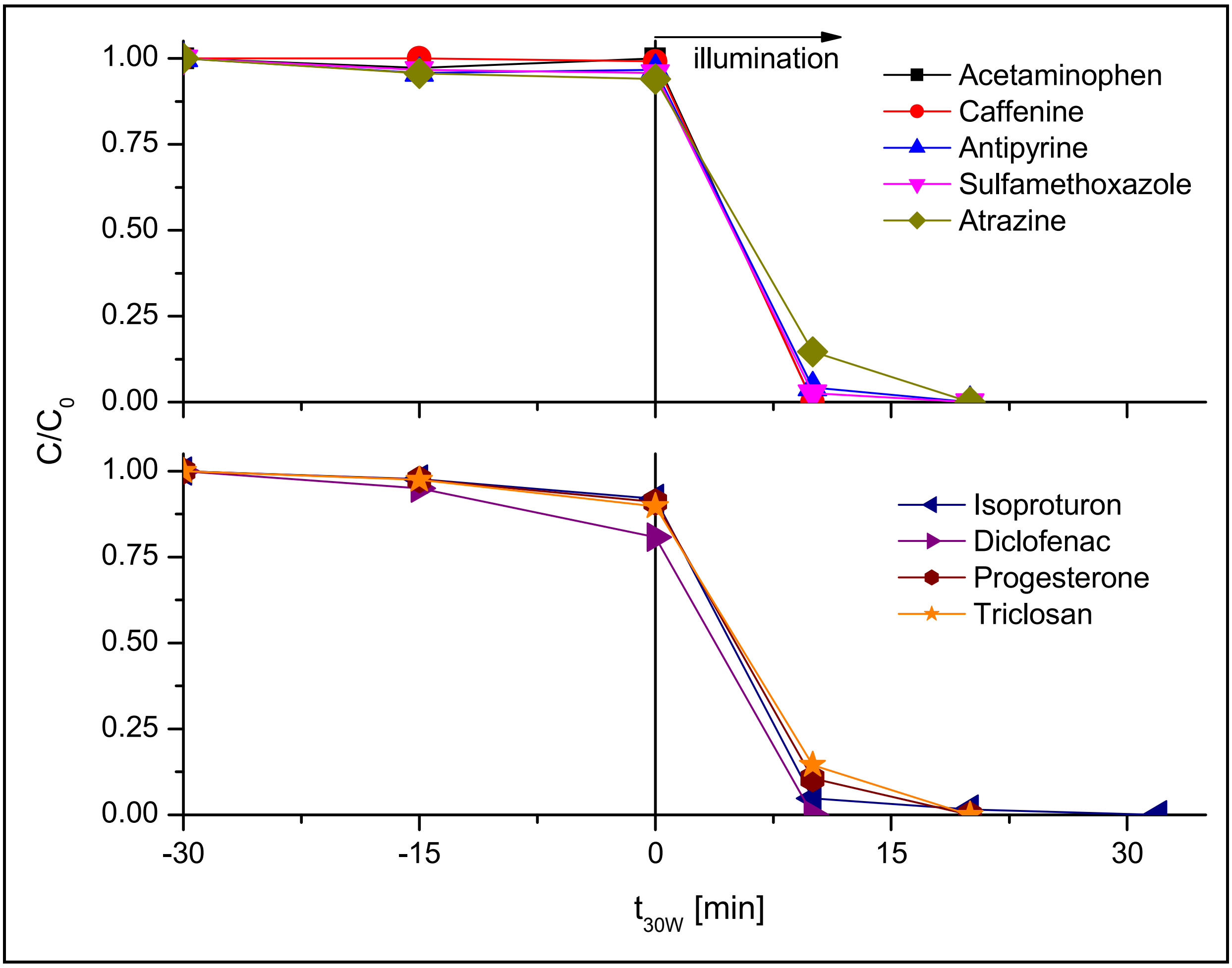


Figure 3.2 Degradation of 9 contaminants at initial concentrations of 100 µg L^{-1} each by photo-Fenton with 5 mg L^{-1} Fe and pH = 2.8 in demineralised water.

The initial DOC in this experiment was 8 mg L^{-1}, at t_{30W} = 32 minutes the DOC was 4 mg L^{-1}, and the amount of used H_2O_2 was 54 mg L^{-1}, Fe concentration was constant at 5 mg L^{-1}.

The next step was the testing of a solar photo-Fenton in deionized water without pH adjustment. As described above (**section 3.2**), this and the following experiments were conducted in the way to exploit the Fenton process. To do this the order of adding the reactives into the water was changed to t_{30W} = -30 minutes adding of peroxide and t_{30W} = -15 minutes adding of Fe^{2+}. The Fenton reaction is much faster than the slow oxidation and precipitation of Fe^{2+} to Fe^{3+} in water and helps to degrade the present contaminants in water before illumination.

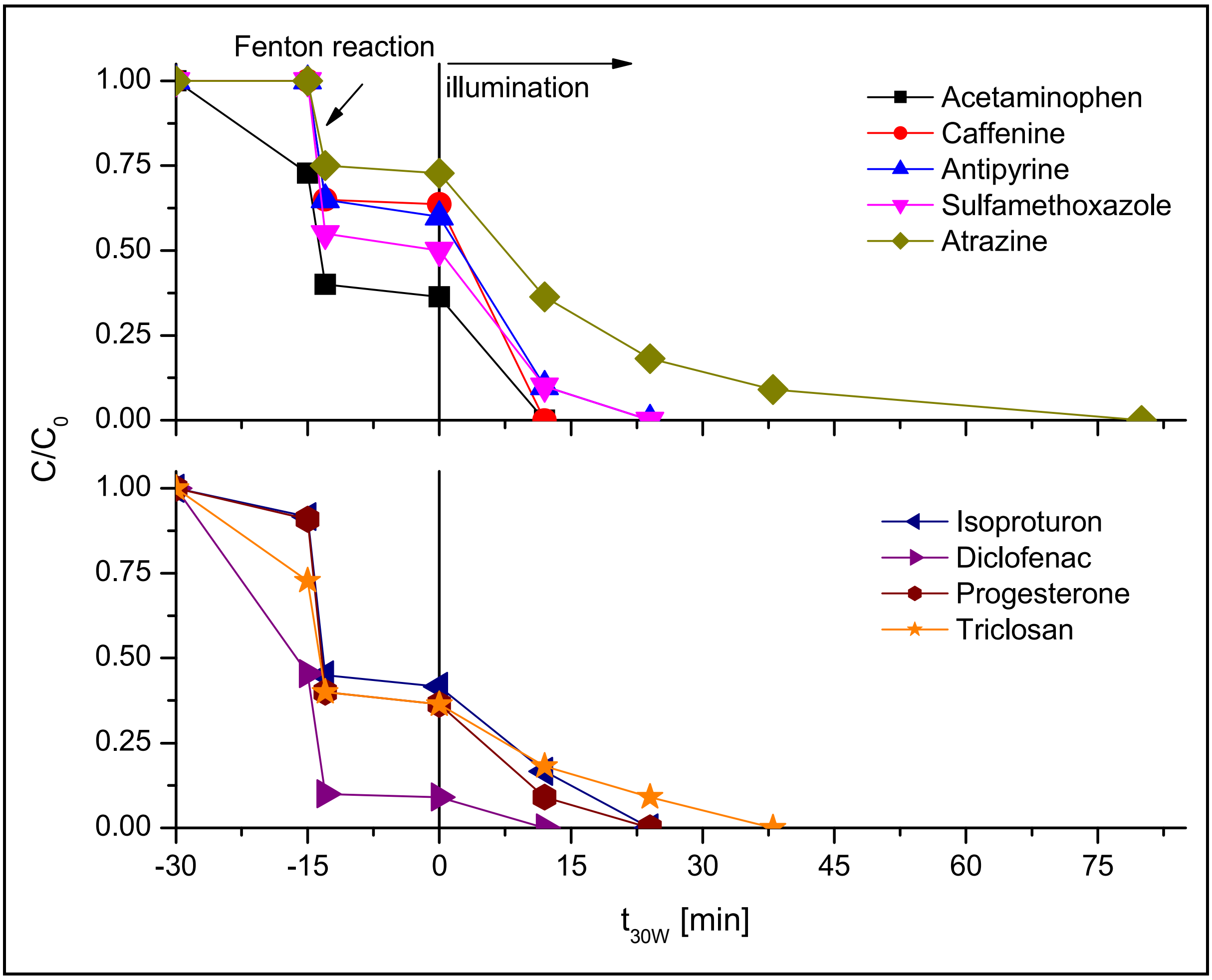


Figure 3.3 Degradation of 9 contaminants at initial concentrations of 100 µg L^{-1} each by photo-Fenton with 5 mg L^{-1} Fe in deionized water without pH adjustment.

Although the pH was not adjusted (initial pH = 6.8), it changed to pH 3.8 at the end of the experiment due to adding of the $FeSO_4$ solution (which in itself was in acidic aqueous solution), due to the photo-Fenton process (which produces organic acids) and the total lack of any buffer capacity of the deionized water.

Two effects can be seen in this experiment:

i) the impact of the presence of H_2O_2 on the direct degradation of Triclosan and Acetaminophen

ii) more important the degradation of the contaminants in the Fenton phase. The Fenton phase leads to a degradation of the compounds between 28 - 65%.

The erratic behaviour of Diclofenac (degradation of 55% in the first 15 minutes and another 35% during the Fenton phase) is explained through the low solubility of the compound at acidic pH. In neutral and alkaline medium, Diclofenac is highly soluble (50 g L^{-1}), but has a pK_a of 4.15 and at pH 4 it is almost insoluble and at pH < 4 it precipitates [Packer et al 2003]. The degradation below the LOD of all contaminants but Atrazine was achieved within t_{30W} = 20 minutes, Atrazine was degraded below the LOD at t_{30W} = 80 minutes. DOC declined from 9 mg L^{-1} to 3.6 mg L^{-1}, and the amount of H_2O_2 used was 90 mg L^{-1}. Again there was no big surprise in the degradation behaviour, although the degradation time for all of the compounds was slightly longer due to the fact that the pH is far from the optimum pH.

Table 3.1 Direct comparison of the experiments in deionized water

experiment	pH 2.8		pH without adjustment	
consumed H_2O_2 [mg L^{-1}]	55		81	
DOC initial – final [mg L^{-1}]	8	4	9	3.6
pH initial – final	2.8	2.8	6.5	3.5
time t_{30W} [min]	32		80	

3.4.2 *Degradation of 9 contaminants in standard fresh water*

The next step in complicating the matrix was the degradation of the model compounds in moderately hard simulated fresh water [Standard methods for the Examination of water and wastewater] without pH adjustment (see **Figure 3.4**). Although some of the compounds (Acetaminophen, Sulfamethoxazole, Triclosan and Diclofenac) are degraded in the dark by Fenton, the other compounds were still present after t_{30W} = 266 minutes in significant high concentrations (Atrazine 64%, Caffeine 47%, Antipyrine 45%, Isoproturon 17% and Progesterone 25% of the initial concentration). The pH changed insignificantly from pH = 8.2 to pH = 7.9, H_2O_2 consumption was 218 mg L^{-1}, total iron concentration changed from 5 mg L^{-1} to 3.2 mg L^{-1} and DOC declined from 9 mg L^{-1} to 6 mg L^{-1}. The rapid degradation of

Acetaminophen, Sulfamethoxazole, Triclosan and Diclofenac may be due to the aromatic substituted structure (HO^-, Cl^-, H_2N^-) and therefore $HO^\bullet$ radicals oxidise them so rapidly.

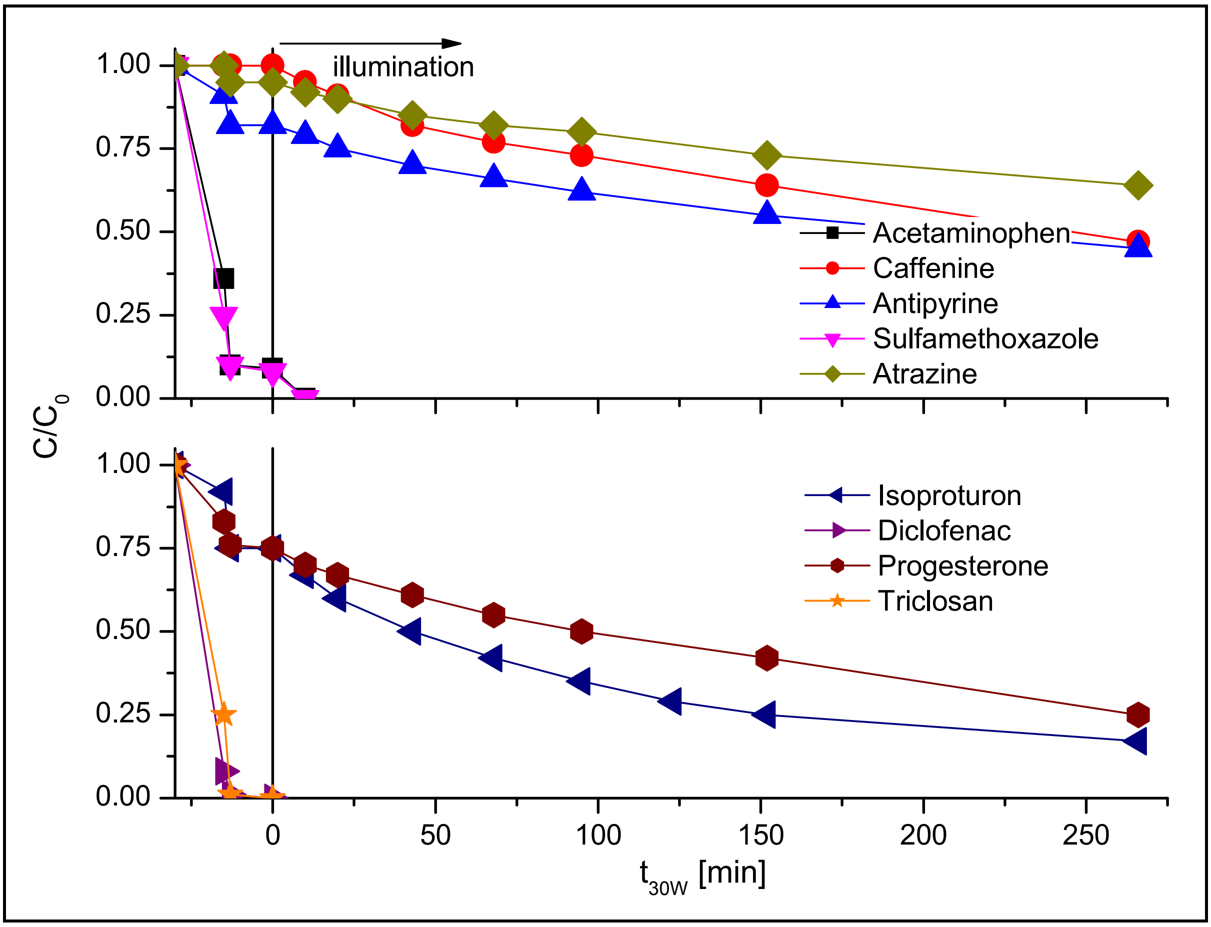


Figure 3.4 Degradation of 9 contaminants at initial concentrations of 100 µg L^{-1} each by photo-Fenton with 5 mg L^{-1} Fe in simulated moderately hard fresh water without pH adjustment.

It's a well known fact that inorganic species (chlorine, sulphate, phosphate, carbonates, etc.) which are present in water, have a dramatic negative effect on the photo-Fenton reaction rate [Pignatello et al, 2006], but radical scavengers such as carbonate species (CO_3^{2-} and HCO_3^-) especially compete with organic contaminants for hydroxyl radicals reactions, and significantly decrease the degradation efficiencies of organics through reaction **Eq. 3.1** and **Eq. 3.2** [Buxton and Elliot, 1986].

$$HO^{\bullet} + HCO_3^{-} \longrightarrow H_2O + CO_3^{\bullet -}$$ **Eq. 3.1**

$$HO^{\bullet} + CO_3^{2-} \longrightarrow HO^{-} + CO_3^{\bullet -}$$ **Eq. 3.2**

The reaction rate constants for hydroxyl radical for the carbonate ion ($k_{HO^{\bullet}CO_3^{2-}} = 3.9x10^8 M^{-1}s^{-1}$) is over 40 times higher than for the bicarbonate ion ($k_{HO^{\bullet}HCO_3} = 8.5x10^6 M^{-1}s^{-1}$). Bicarbonate species were predominant in this water as its pH was around 8. Therefore, being less detrimental than carbonates, bicarbonate ions would be the main responsible species for the low efficiency of the photo-Fenton process. One possible way of overcoming the problem of the bad degradation behaviour is to elevate of the iron concentration, in this case to 15 and 55 mg L^{-1} Fe, a dose which is three times and respectively 11 times higher than the concentration used before.

When using 55 mg L^{-1} Fe, (**Figure 3.5)** it can be seen that the initial Fenton phase degrades the contaminants below 30%, and after illumination the degradation is quite slow, it takes up to t_{30W} = 42 minutes to degrade all present contaminants below their LOD.

The slow degradation of the contaminants after illumination shows the high scavenging potential of the carbonate/bicarbonates, as high amounts of Fe are necessary to produce an excess amount of $HO^{\bullet}$ radicals to degrade the present contaminants. The high amount of Fe in the water is not suitable for MWTP effluent treatment with subsequent reuse, as this reused water would have iron concentrations which exceed the quality limit for reusable water. The DOC in this experiment declined from 16 mg L^{-1} to 10 mg L^{-1}, Fe concentration from 54 mg L^{-1} to 48 mg L^{-1}, the pH declined from pH 8.2 to pH 4 and the H_2O_2 consumption was 94 mg L^{-1}.

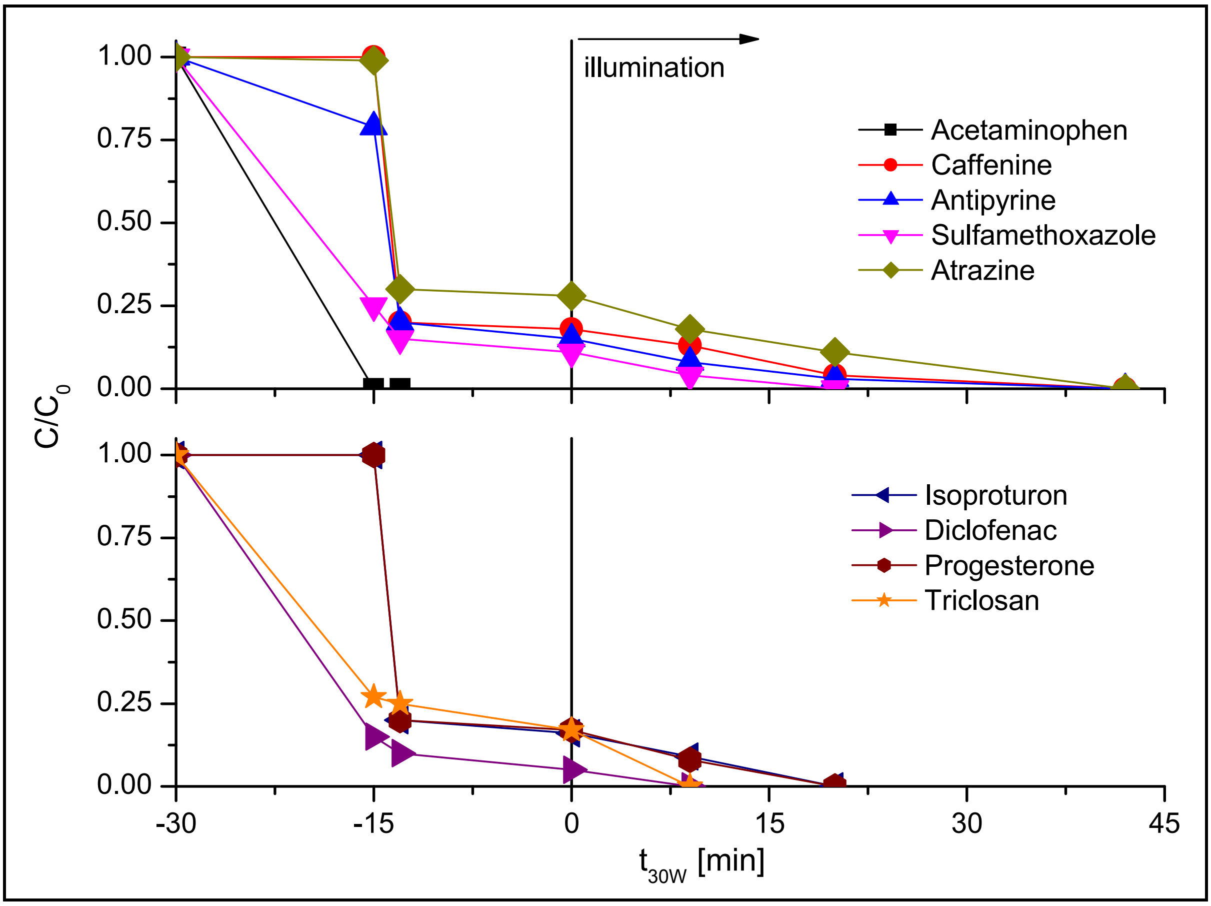


Figure 3.5 Degradation of 9 contaminants at initial concentrations of 100 µg L^{-1} each by photo-Fenton with 55 mg L^{-1} Fe in simulated moderately hard fresh water without pH adjustment.

Figure 3.6 shows the behaviour of the 9 used contaminants when treated with an initial iron concentration of 15 mg L^{-1}.

The initial Fenton phase was capable of degrading some of the compounds down to 50 % of the initial concentration (Sulfamethoxazole 50%, Acetaminophen 55%), the rest of the compounds were degraded only by 10 – 18%, and Atrazine suffered only a 2% loss. After a t_{30W} = 289 minutes, five of the 9 compounds are still present in high concentrations (Atrazine 80%, Antipyrine 50%, Caffeine 48%, Progesterone 40% and Isoproturon 31%), DOC changed from 11 mg L^{-1} to 8 mg L^{-1}, Fe from an initial 15 mg L^{-1} to a final 8 mg L^{-1}, pH changed from pH 7.8 to pH 6.2 and the H_2O_2 consumption was 200 mg L^{-1}. This experiment showed that an elevated iron concentration in the range of the quality limit for reusing water was not capable of degrading the contaminants within a reasonable time and with a reasonable consumption of H_2O_2.

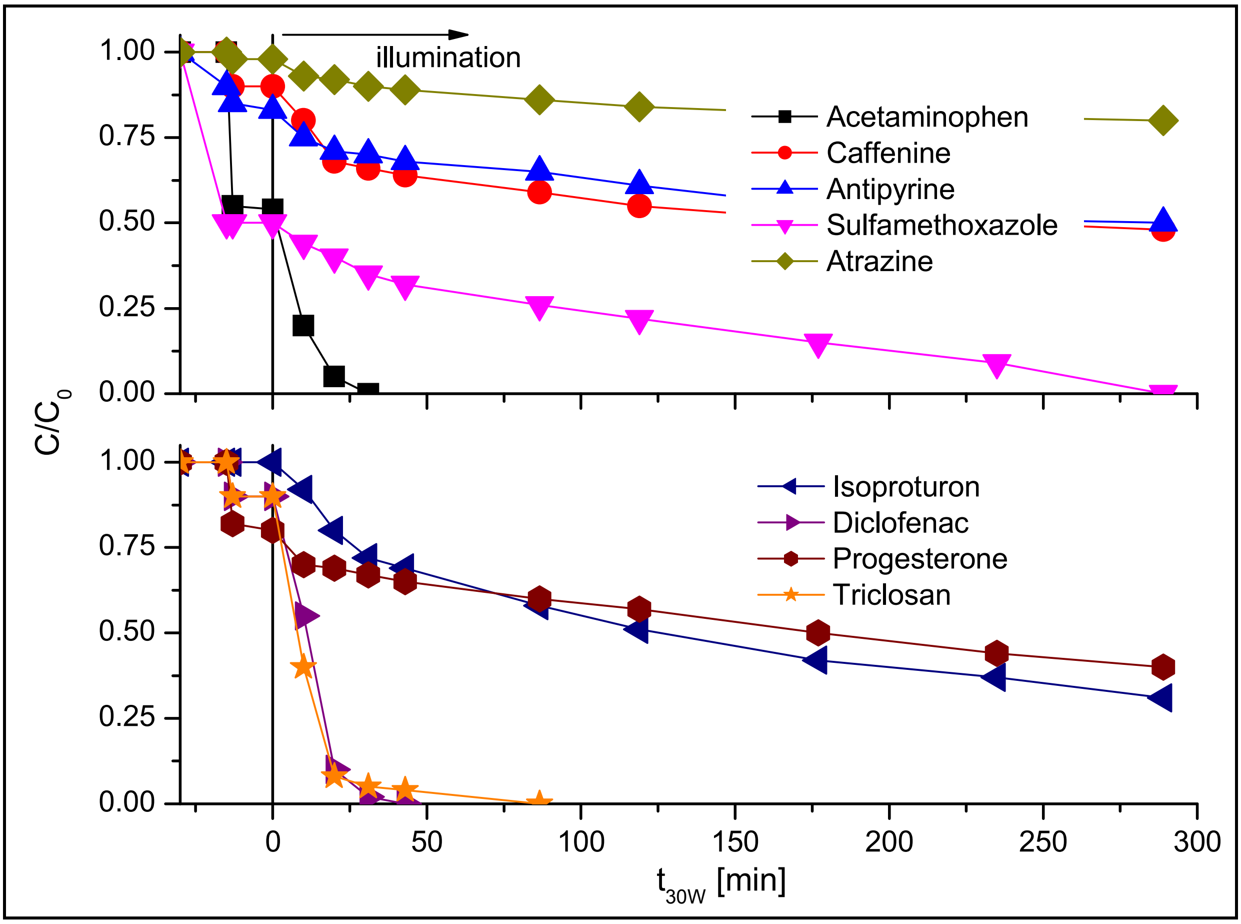


Figure 3.6 Degradation of 9 contaminants at initial concentrations of 100 µg L^{-1} each by photo-Fenton with 15 mg L^{-1} Fe in simulated moderately hard fresh water without pH adjustment.

Another possible way to augment the degradation of contaminants present in water, and to confirm the effect of bicarbonates, is the so called stripping of bicarbonates with a strong acid. In this case the composition of the moderately hard standard fresh water was changed to contain Na_2SO_4 instead of $NaHCO_3$ in order to maintain salinity, and to simulate adding of sulphuric acid for bicarbonate stripping.

The degradation of the 9 contaminants can be seen in **Figure 3.7.** Although degradation is slower than in demineralised water, it is faster than with 5 and 15 mg L^{-1} Fe in water with bicarbonates. All compounds with the exception of Atrazine and Progesterone were degraded below their LOD within t_{30W} = 80 minutes, the two before mentioned contaminants were degraded below their LOD at t_{30W} = 136 minutes. The quantity of H_2O_2 consumed at this time was 91 mg L^{-1}, DOC declined from 15 to 10 mg L^{-1}, pH changed from pH 7.6 to pH 4 due to the lack of buffer capacity of the water and Fe concentration changed from an initial 5 mg L^{-1} to 3 mg L^{-1}.

Table 3.2 Direct comparison of the experiments conducted in simulated fresh water with different Fe concentrations and without bicarbonates

	experiments with bicarbonates			**without bicarbonates**
Fe [mg L^{-1}]	55	15	5	5
consumed H_2O_2 [mg L^{-1}]	148	289	220	92
t_{30W} [min]	42	200	266	136
residual conc. $\Sigma Cs/ \Sigma Cs_0$ [%]	<LOD	50	40	<LOD
final DOC [mg L^{-1}]	8	11	10	10

The comparison of the experiments conducted with different Fe concentrations (55, 15 and 5 mg L^{-1}) in simulated fresh water with bicarbonates and with 5 mg L^{-1} Fe in water without bicarbonates shows clearly the advantage when working without bicarbonates (see **Table 3.2**). It is not clear why the experiment conducted with 5 mg L^{-1} Fe and bicarbonates present show a better behaviour in terms of residual concentration of the contaminants (% of the sum of all contaminants) and H_2O_2 consumption, than the experiment conducted with 15 mg L^{-1} Fe.

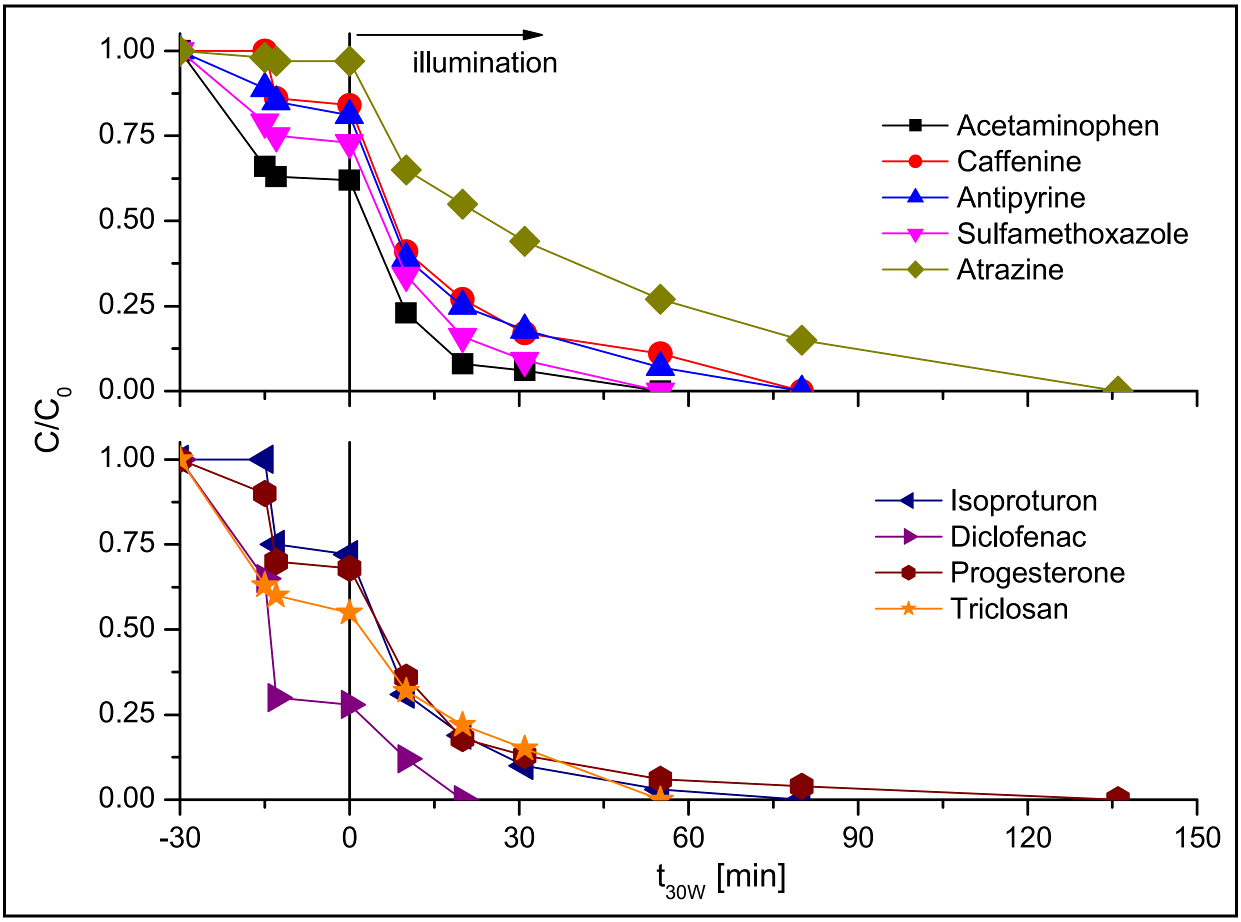


Figure 3.7 Degradation of 9 contaminants at initial concentrations of 100 µg L^{-1} each by photo-Fenton with 5 mg L^{-1} Fe in simulated moderately hard fresh water without bicarbonates and without pH adjustment

When looking at the mineralisation (see **Figure 3.8**) it can be seen that the more efficient the degradation and elimination of the 9 contaminants was, the more efficient the overall mineralisation. Photo-Fenton in demineralised water at pH 2.8 and at unadjusted pH was able to substantially mineralise the organic content of the water (down to 6% with typical photo-Fenton and down to 14% with unadjusted pH). This is important as it can be stated that not only the contaminants suffer degradation but also that their degradation products were degraded further. In the case of simulated fresh water, the mineralisation was inefficient using both 5 and 15 mg L^{-1} Fe. Using 55 mg L^{-1}, the mineralisation reached 75%, and mineralisation reached 50% when using 5 mg L^{-1} Fe in simulated fresh water without bicarbonates/carbonates.

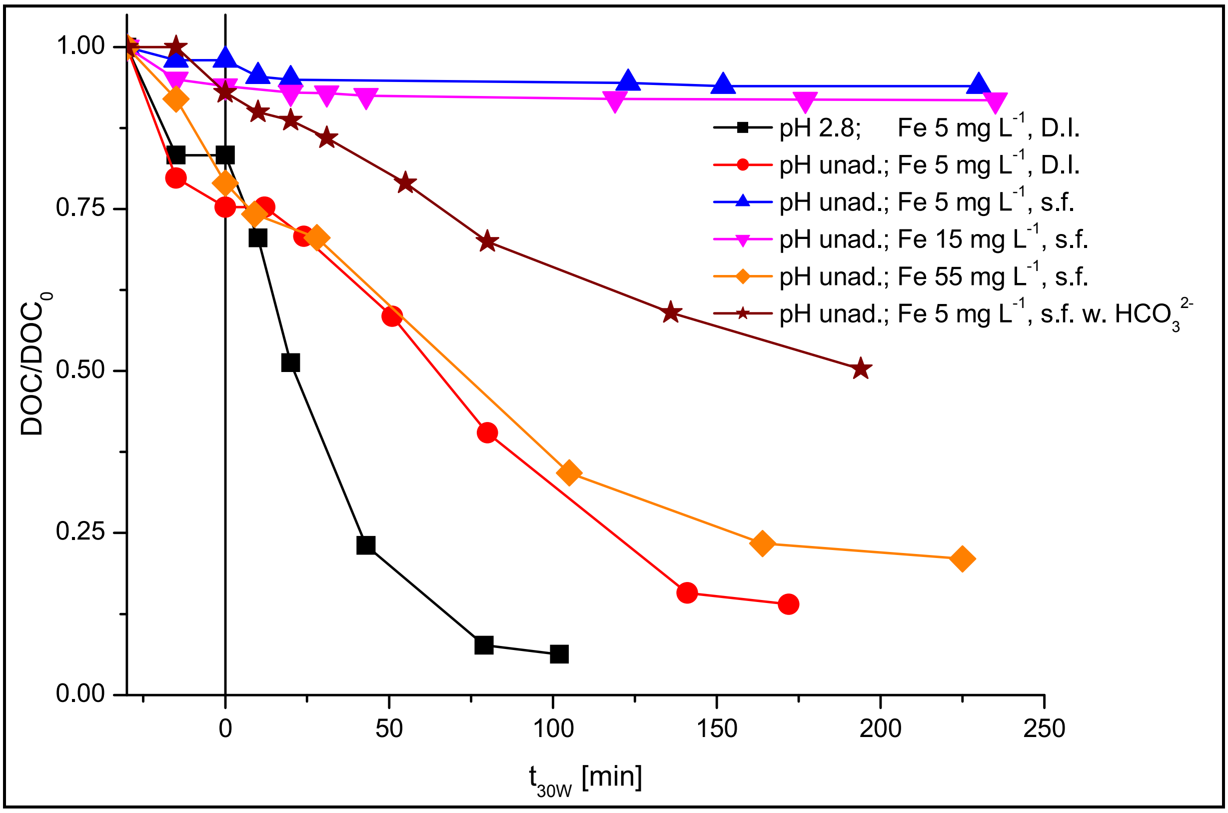


Figure 3.8 DOC mineralization during the experiments conducted with different waters (D.I.: deionized water; s.f.: simulated fresh water), and different Fe concentrations.

The H_2O_2 consumption for attaining complete degradation of the 9 contaminants below their LOQ was higher when the pH was not at the optimum. 55 mg L^{-1} H_2O_2 was consumed in photo-Fenton at pH 2.8 compared to 81 mg L^{-1} consumption at photo-Fenton with unadjusted pH. Very high consumption of H_2O_2 (> 220 mg L^{-1}) was measured in the experiments using simulated fresh water with carbonates at Fe concentrations of 5 and 15 mg L^{-1}, and in these experiments LOQ of all contaminants was not reached. 148 mg L^{-1} H_2O_2 was consumed with 55 mg L^{-1} Fe and only 92 mg L^{-1} when photo-Fenton was run with 5 mg L^{-1} Fe but without bicarbonates.

This shows again the impact of bicarbonates as radical scavengers, and the importance of removing them when applying the photo-Fenton process in these waters, but it should be emphasised, that mineralisation of DOC was not the goal of this treatment.

3.4.3 *Degradation of 15 selected contaminants in simulated effluents*

The next step in this work was to use the information gathered from the previous experiments to improve the process. The 15 selected contaminants tested were the previous nine plus 6 new ones, which have proven to be suitable for these experiments because of their solubility, stability and detectability in the analytical equipment. The list can be seen in (**Table 2.1**). As the previous experiments have confirmed the negative impact of the carbonate/bicarbonate species present in water on the degradation behaviour, simulated fresh waters were treated prior to the photo-Fenton process with sulphuric acid or hydrochloric acid to strip the water of its carbonate/bicarbonate content. The idea behind the stripping with different acids is that they have certain advantages and disadvantages as certain ions have a higher negative impact to the photo-Fenton reaction rate [Pignatello et al, 2006] due to complexation of these ions with Fe^{2+} or Fe^{3+}or the scavenging of hydroxyl radicals and formation of less reactive inorganic radicals [De Laat et al, 2004]. It has also been observed that they only reduce the reaction rate significantly if they occur in concentrations over 10 mM, usually far from the concentrations found in natural waters [Bacardit et al, 2007; Zapata et al, 2009a].

41 mg L^{-1} hydrochloric acid was added to the simulated fresh water and circulated for one hour in the reactor under turbulent conditions until the TIC was below 5 mg L^{-1}, while pH was maintained between pH 5.5 and pH 7. After the stripping step, the photo-Fenton process was tested following the normal procedure shown in previous experiments. It started with the Fenton phase, in which the removal of the compounds was between 30% for Caffeine and 60% for Ibuprofen. Only Atrazine suffered a lower degradation of 18%. The photo-Fenton process was able to degrade all contaminants but Atrazine (23% residual concentration) and Triclosan (13% residual concentration) within t_{30W} = 90 minutes (see **Figure 3.9**).

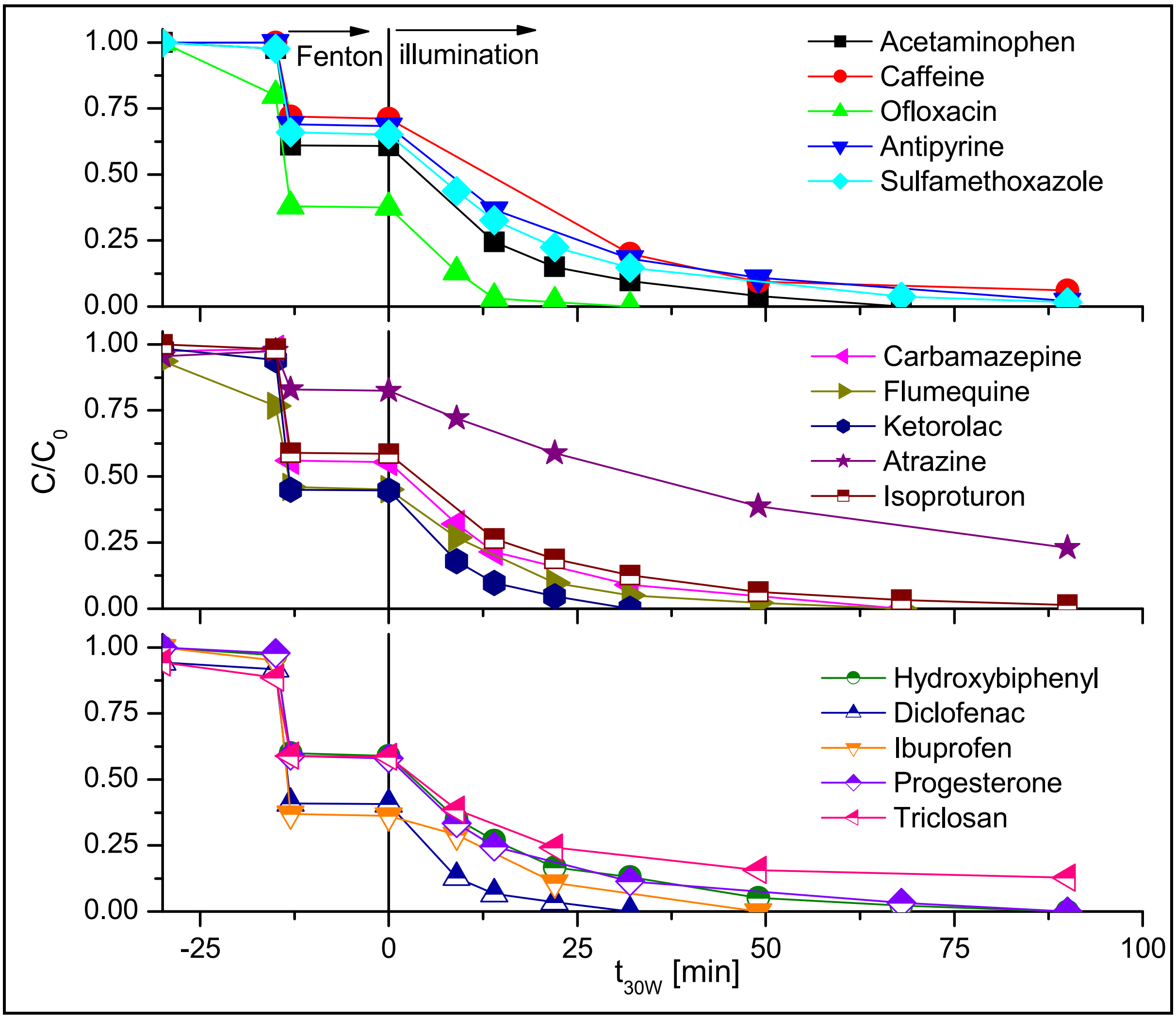


Figure 3.9 Degradation of 15 contaminants at initial concentrations of 100 µg L^{-1} each in simulated freshwater stripped from its carbonate/bicarbonate content with hydrochloric acid.

Some of the contaminants (Ofloxacin and Diclofenac) were degraded below their LOD as early as t_{30W} = 32 minutes. The Fe concentration decreased from 5 mg L^{-1} to 3 mg L^{-1}, the total amount of H_2O_2 consumed was 37 mg L^{-1}, while pH changed from initial pH 7.6 to pH 5.3 (after $FeSO_4$ mixing) to a final pH 3.8 at t_{30W} = 90 minutes. Similar results were found by adding H_2SO_4 instead of HCl. The experiments did not show any significant differences in the degradation behaviour of the 15 selected model compounds. Due to the easier handling of the sulphuric acid, this acid was selected for carbonate/bicarbonate stripping for the rest of the work.

Simulated effluent water (**Table 2.2**) was treated in the same way as all the other waters before. Carbonates/bicarbonates were stripped with sulphuric acid (56 mg L^{-1}) and the water was circulated until TIC concentration was below 5 mg L^{-1}. The degradation of the 15 contaminants in simulated effluent water was much slower both in the Fenton phase and in the photo-Fenton phase, than in simulated fresh water, as the presence of the organic fraction of the effluent water reacts as well with the hydroxyl radicals.

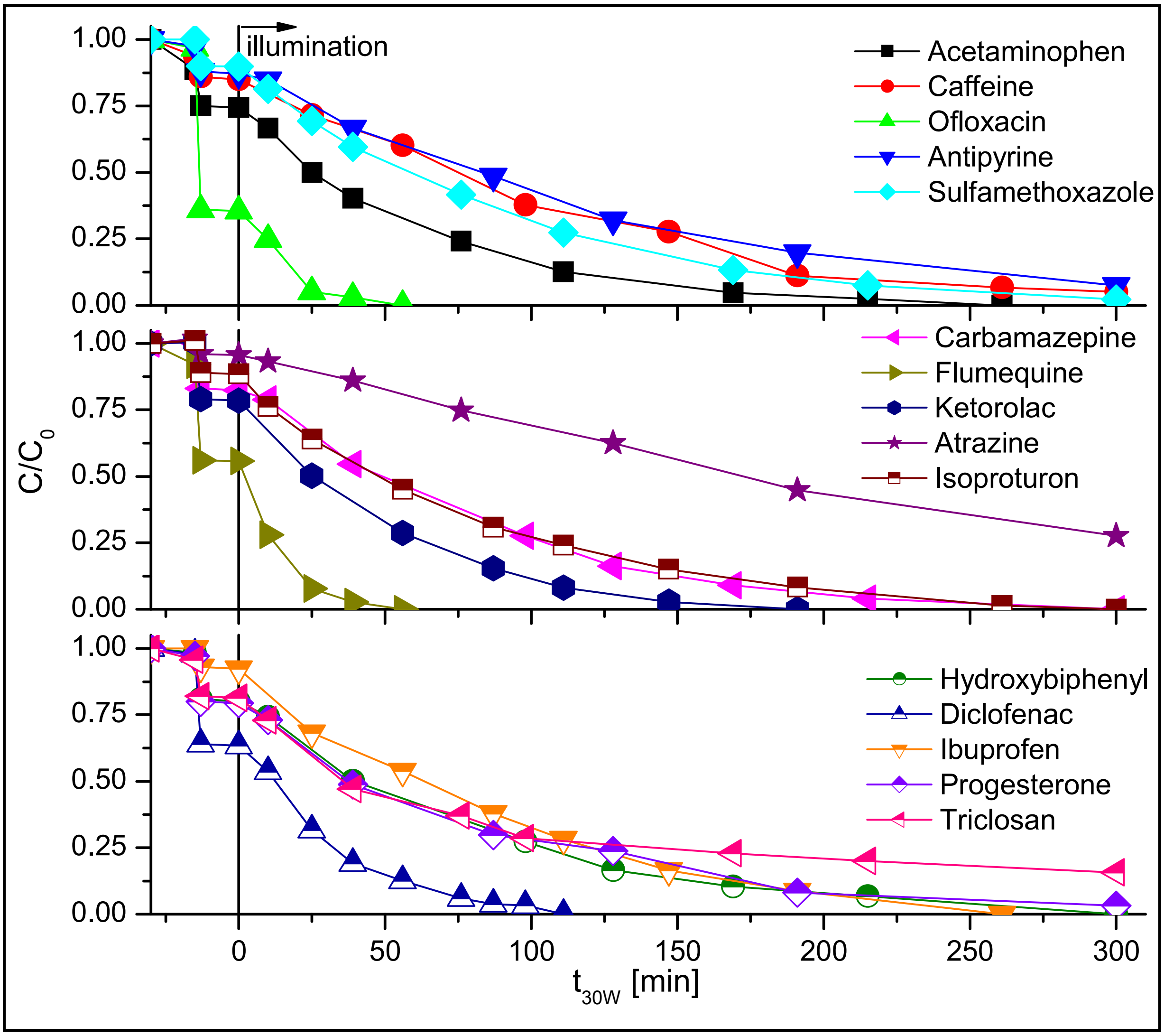


Figure 3.10 Degradation of 15 contaminants at initial concentrations of 100 µg L^{-1} each in simulated effluent water stripped from its carbonate/bicarbonate content with sulphuric acid, Fe concentration 5 mg L^{-1}, initial H_2O_2 concentration 50 mg L^{-1}.

As can be seen in **Figure 3.10** the residual concentrations at the end of the experiment (t_{30W} = 300 minutes) were between 2% (Sulfamethoxazole) and 15% (Triclosan). Atrazine however had an elevated residual concentration of 28% as can be seen in **Table 3.3**. The initial dose of H_2O_2 in this and in all previous experiments was 50 mg L^{-1}. Once the peroxide dose was almost consumed, an additional peroxide dose of 50 mg L^{-1} was added into the reactor.

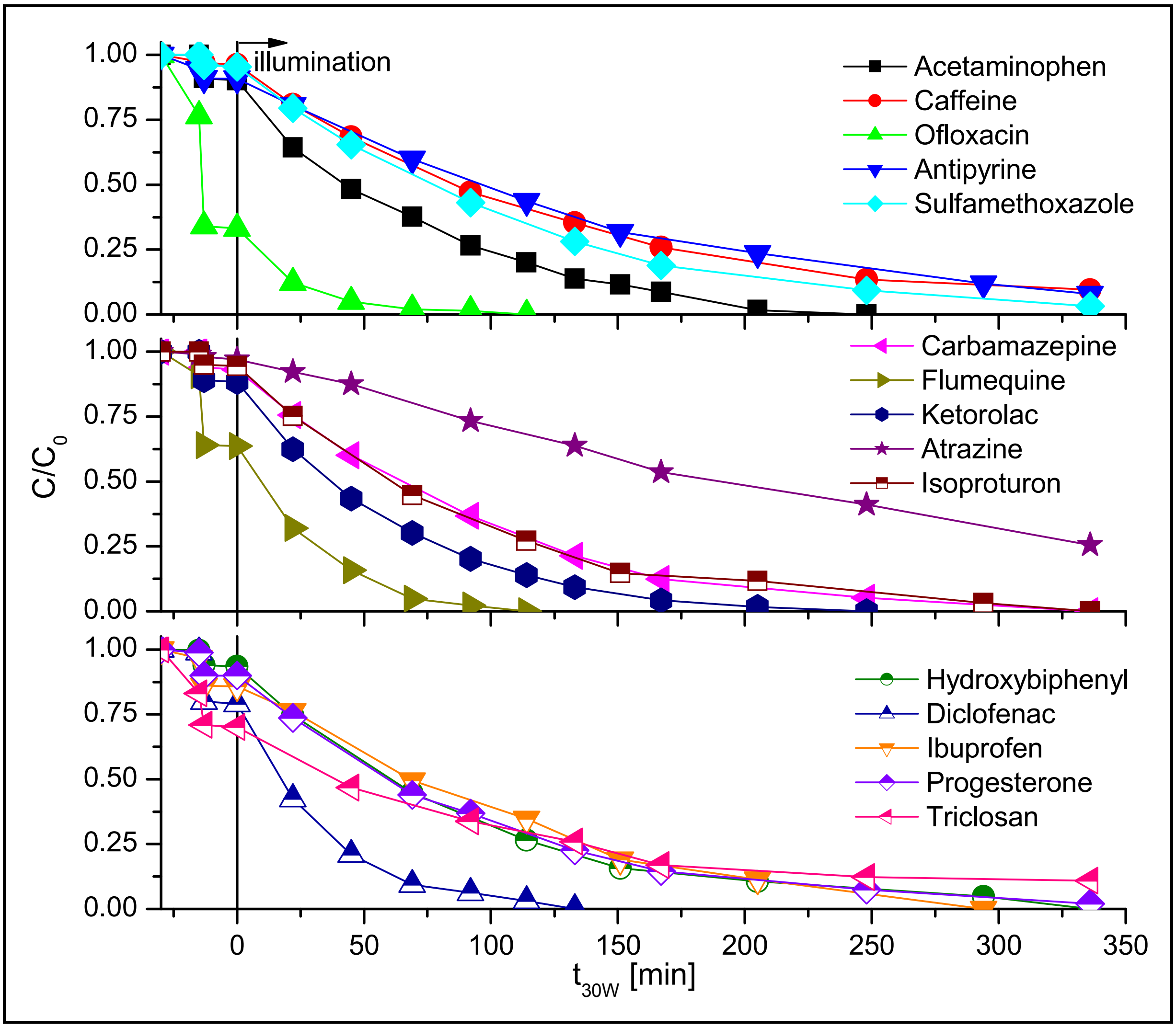


Figure 3.11 Degradation of 15 contaminants at initial concentrations of 100 µg L^{-1} each in stripped simulated effluent water, Fe concentration 5 mg L^{-1}, initial H_2O_2 concentration 5 mg L^{-1}.

Another approach for improving the degradation of the contaminants can be the continuous dosing of low quantities of peroxide into the reactor to lower the overall consumption of H_2O_2 and thus the costs. For this reason experiments were conducted with stripped simulated effluent water in which H_2O_2 was added every 30 minutes in quantities of 5 mg L^{-1} H_2O_2. The results can be seen in **Figure 3.11** and **Table 3.3**. Degradation behaviour of the 15 contaminants is quite similar to the degradation with initial higher peroxide concentrations with a slightly longer t_{30W} to reach the same residual concentrations, but clearly a peroxide consumption which is the half (52 mg L^{-1} compared to 110 mg L^{-1}). This result shows that it is possible to degrade the contaminants present in water with lower peroxide consumption if it is carefully dosed.

Table 3.3 Final concentration of contaminants in two different experiments with simulated effluent water, similar irradiation times, 5 mg L^{-1} Fe, but different H_2O_2 dosage.

compound	**$[H_2O_2]_0$ = 50 mg L^{-1}**				**$[H_2O_2]_0$ = 5 mg L^{-1}**			
	t_{30W} [min]	**C/C_0**	**Fenton deg [%]**	**k [min^{-1}]**	**t_{30W} [min]**	**C/C_0**	**Fenton deg [%]**	**k [min^{-1}]**
Acetaminophen	261	< LOD	16.1	0.016	248	< LOD	14.1	0.019
Caffeine	300	0.05	21.7	0.008	336	0.09	1.2	0.007
Ofloxacin	56	< LOD	63.2	0.063	114	< LOD	56.7	0.034
Antipyrine	300	0.07	10.5	0.008	336	0.08	3.8	0.007
Sulfamethoxazole	300	0.02	10.2	0.012	336	0.03	4.5	0.010
Carbamazepine	300	< LOD	18.0	0.014	336	< LOD	6.6	0.013
Flumequine	56	< LOD	39.3	0.078	114	< LOD	30.0	0.036
Ketorolac	191	< LOD	21.8	0.022	248	< LOD	11.6	0.017
Atrazine	300	0.28	6.1	0.004	336	0.26	0.0	0.004
Isoproturon	300	< LOD	12.4	0.016	336	< LOD	6.9	0.011
Hydroxybiphenyl	300	< LOD	15.6	0.012	336	< LOD	6.2	0.010
Diclofenac	111	< LOD	35.2	0.032	133	< LOD	20.1	0.028
Ibuprofen	261	< LOD	11.3	0.011	294	< LOD	11.3	0.010
Progesterone	300	0.03	18.3	0.011	336	0.02	8.9	0.011
Triclosan	300	0.15	14.9	0.005	336	0.13	15.6	0.005

conditions	**initial**	**final**	**initial**	**final**
DOC [mg L^{-1}]	38	30	40	36
pH [-]	7.6	4.8	8.1	4.8
Fe [mg L^{-1}]	5	3	5	3
consumed H_2O_2 [mg L^{-1}]		110		52

The difference in the Fenton degradation of these two processes can be explained through the peroxide concentration. The relatively high initial dose of 50 mg L^{-1} H_2O_2 gives way to several other reactions of organic radicals with peroxide, self decomposition of peroxide etc. thus consuming more peroxide. When using 5 mg L^{-1} H_2O_2, the peroxide is consumed rapidly and after complete consumption, there are other radical reactions (Dorfmann Mechanism **Eq 1.47** and **Eq 1.48**) which help in the degradation of the contaminants.

The experiments showed that it is possible to degrade contaminants in simulated effluents of MWTPs after carbonate/bicarbonate stripping with acid without lowering the pH. It is possible to degrade these contaminants with initial H_2O_2 concentrations of 50 mg L^{-1} but the process is better with an initial and constant concentration of 5 mg L^{-1}.

3.4.4 Degradation of 15 contaminants in MWTP effluents

3.4.4.1 Initial concentration of 100 µg L^{-1} each

Taking all the information into account on how to treat different matrices, the last step was to treat real MWTP effluent. Although the effluent of a MWTP is subject to changes (DOC, BOD_5, COD, ions and organic compounds, etc.) it is considered stable in a certain range. The initial DOC, TIC and COD of the water used in this experiment (**Figure 3.12**) were 36 mg L^{-1}, 106 mg L^{-1} and 60 mg L^{-1} respectively.

The water from the MWPT was stripped from its carbonates/bicarbonates (0.2-0.35 mL H_2SO_4 conc. was needed depending on the particular water), circulated in the reactor until TIC was below 5 mg L^{-1}, spiked with the 15 contaminants at 100 µg L^{-1} each, and subjected to the photo-Fenton treatment. The pH changed from initial pH 8.1 to pH 6.5 after stripping and to a final pH 4.0, while DOC declined from 36 mg L^{-1} to a final 26 mg L^{-1}. The amount of consumed H_2O_2 was 70 mg L^{-1}, while Fe concentration maintained at 4 mg L^{-1}. The residual concentration at the end of the experiment at t_{30W} = 276 minutes is both 9% for Triclosan and Atrazine.

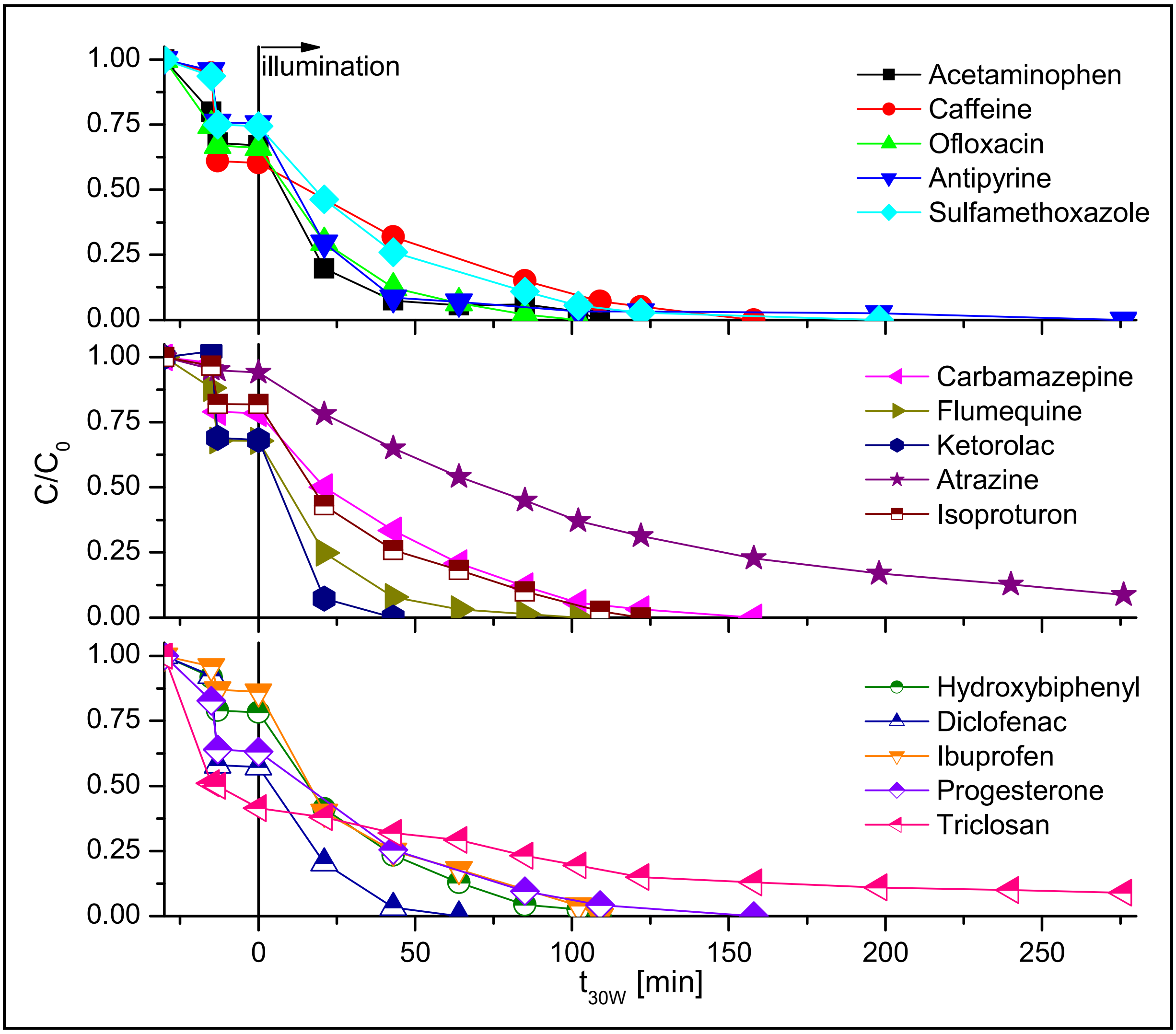


Figure 3.12 Degradation of 15 contaminants at 100 µg L^{-1} each initial concentration in stripped real MWTP effluent with 5 mg L^{-1} Fe and 50 mg L^{-1} H_2O_2 and unadjusted pH.

All other contaminants were degraded below their LOD. The degradation rate of the contaminants was faster than in the previous experiments conducted with simulated effluent water. There might be two reasons for that, first the slightly lower pH, which helps maintaining iron in solution and secondly the presence of organic substances in real MWTP effluents (like humic acids) which produce solvated electrons and hydroxyl radicals upon irradiation that could improve reaction rates compared to simulated effluent water [Fukushima and Tatsumi, 2001; Prosen and Zupančič-Kralj, 2005].

3.4.4.2 *Initial concentration of 5 µg L^{-1} each*

To work closer to reality the initial concentration of the 15 selected contaminants was lowered to 5 µg L^{-1}. The samples taken were subject to SPE (see **chapter 2.4.7**) with a concentration factor of 50. Due to some interference in the matrix, not all contaminants could be detected in all the experiments, but it affected not more than one or two compounds in each experiment. The first experiments were conducted with a typical photo-Fenton with a pH 2.9 with both 20 mg L^{-1} and 5 mg L^{-1} Fe. This was done to have an indication on how fast and how efficient the standard photo-Fenton system works. The results of these experiments can be seen in **Figure 3.13**, **Figure 3.14** and **Table 3.4**. The Fenton phase with 20 mg L^{-1} Fe contributed to the major degradation percentage. Due to the strong conditions (low pH, high iron concentration), the DOC declined significantly from initial 20 mg L^{-1} to 5 mg L^{-1} (mineralisation of 75%), while H_2O_2 consumption was 78 mg L^{-1}.

Table 3.4 Degradation behaviour of the 15 compounds at 5 mg L^{-1} each initial concentration in MWTP effluents with typical photo-Fenton at pH 2.9 and different Fe concentrations.

compound	Photo-Fenton 20 mg L^{-1} Fe		Photo-Fenton 5 mg L^{-1} Fe	
	Fenton deg [%]	<LOD in t_{30W} [min]	Fenton deg [%]	<LOD in t_{30W} [min]
Acetaminophen	70	52	94	26
Caffeine	90	10	82	13
Ofloxacin	100	0	96	13
Antipyrine	64	52	66	26
Sulfamethoxazole	84	30	85	38
Carbamazepine	90	52	43	38
Flumequine	80	3	-	-
Ketorolac	94	3	81	26
Atrazine	86	52	55	38
Isoproturon	91	30	40	38
Hydroxybiphenyl	85	52	33	64
Diclofenac	90	10	60	26
Ibuprofen	85	10	67	38
Progesterone	-	-	67	38
Triclosan	-	-	56	64
conditions	**initial**	**final**	**initial**	**final**
DOC [mg L^{-1}]	20	5	22	14
Fe [mg L^{-1}]	20	15	5	3
consumed H_2O_2 [mg L^{-1}]		78		43

The photo-Fenton conducted with 5 mg L^{-1} Fe had similar results, (slightly longer degradation time, lower Fenton degradation) but a lower DOC mineralisation (36%). This again shows that it is possible to degrade the contaminants present in the water with low initial iron concentrations and initial H_2O_2 concentrations of 50 mg L^{-1}.

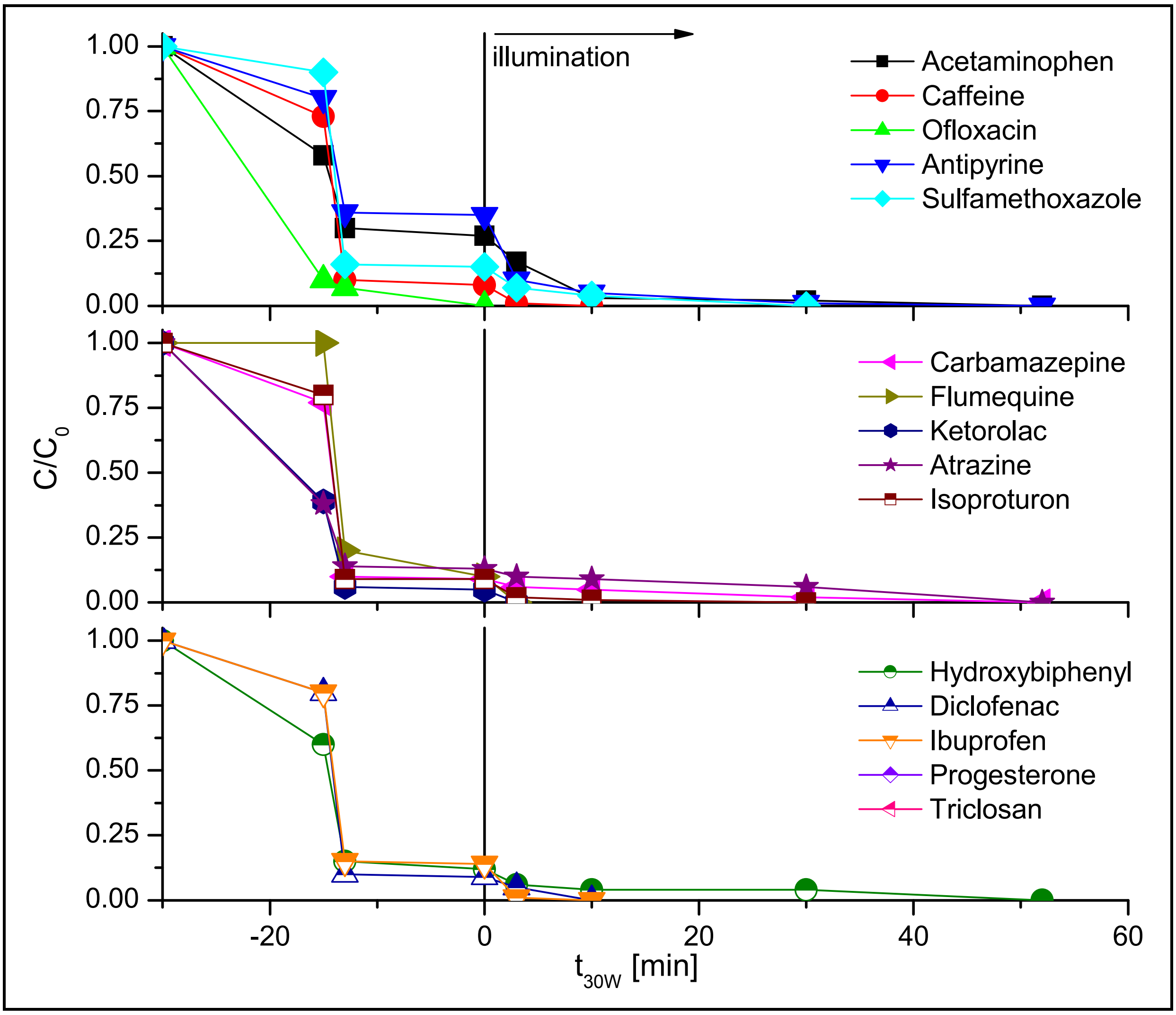


Figure 3.13 Degradation of 15 contaminants at 5 µg L^{-1} initial concentration each in MWTP effluent with 20 mg L^{-1} Fe and pH 2.9.

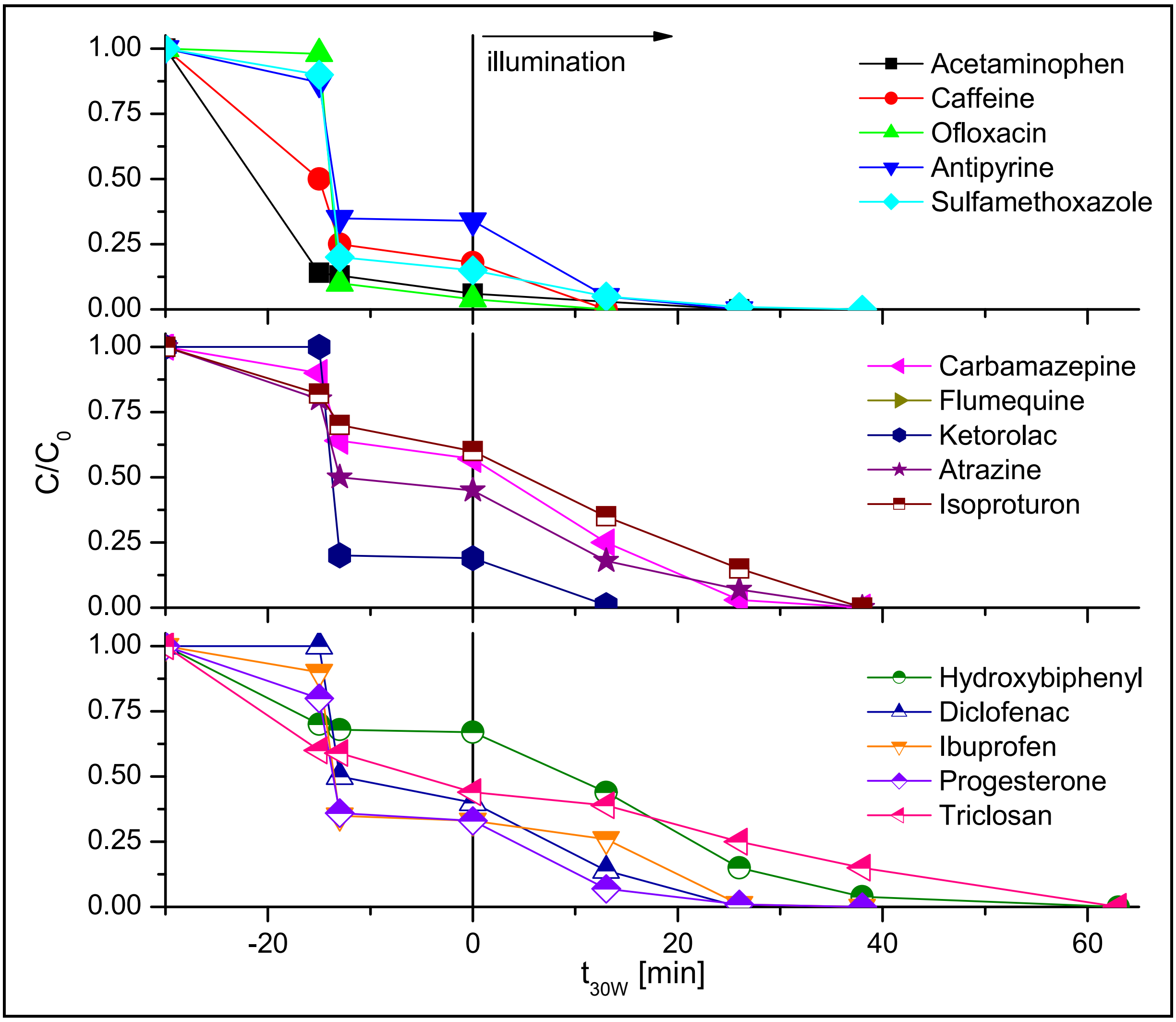


Figure 3.14 Degradation of the 15 contaminants at 5 µg L^{-1} initial concentration each in MWTP effluent with 5 mg L^{-1} Fe and pH 2.9.

When looking at the chromatograms of the samples at 248 nm (see **Figure 3.15**) for the different t_{30W}, it can be seen that the biggest decline (peaks and baseline) happens between t_{-15} and t_0 minutes, which is the Fenton phase. The second noticeable step is between t_0 and the first sample after illumination at t_{30W} = 12 minutes. The peaks which are still present at t_{30W} = 88 minutes do not coincide with the contaminants and may be degradation products or other substances present in the effluent, which can not be determined with the HPLC-UV/DAD equipment. The standard method for the determination of organic UV-absorbing constituents is described in the Standard methods [Standard Methods for the Examination of Water and Wastewater]. This UV absorption is measured at 254 nm. At this wavelength most organic and aromatic compounds strongly absorb UV light. As the UPLC-UV/DAD system only had a limited number of wavelength slots, the wavelength closest to 254 nm was selected to measure the absorbance.

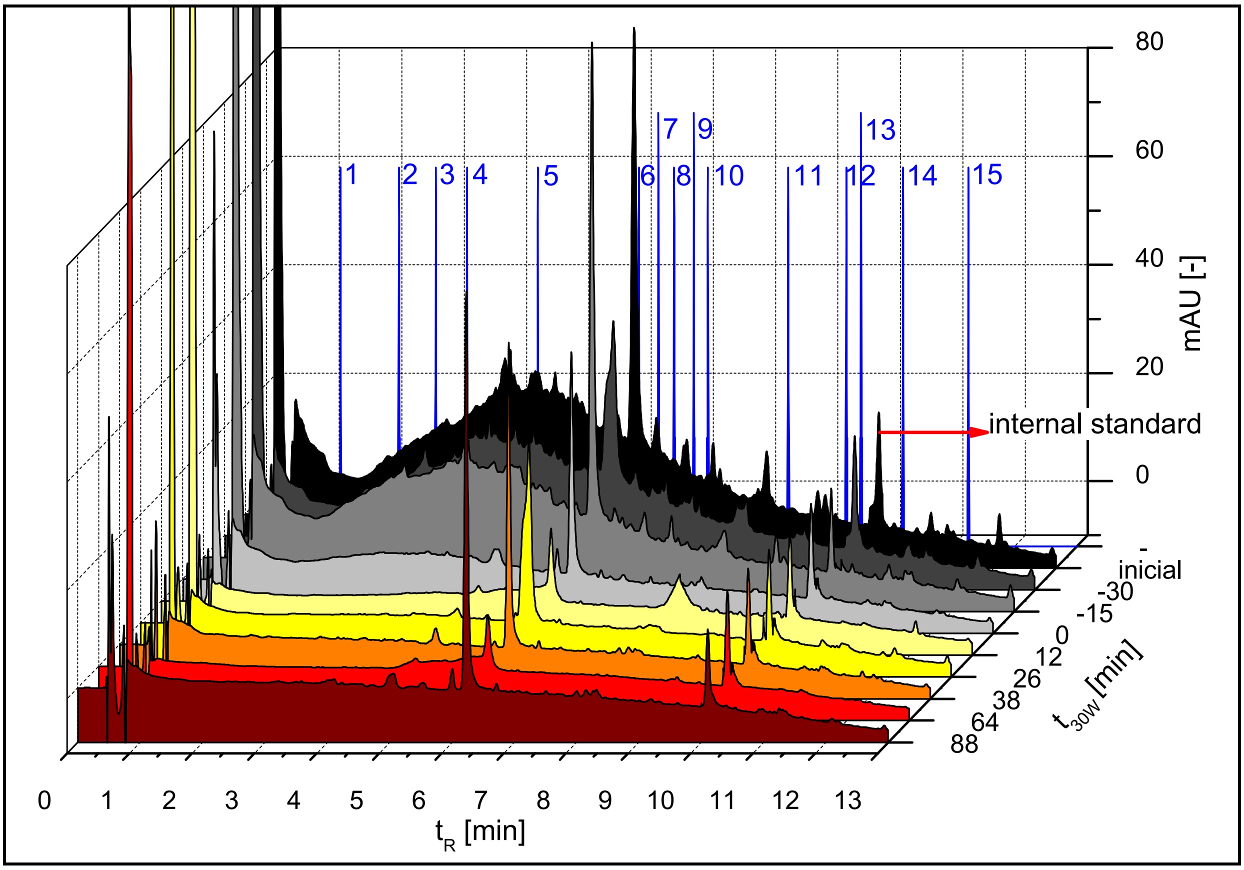


Figure 3.15 Chromatogram (at 248 nm) of the degradation of the 15 contaminants in MWTP effluents. C_0 = 5µg L^{-1} each, pH 3 and 5 mg L^{-1} Fe. The big decline between t_{-15} min and t_0 minutes derives from the Fenton phase. The blue lines mark the retention times of the 15 contaminants.

Treating spiked MWTP effluents at a level of 5 µg L^{-1} each without pH adjustment showed a different behaviour (see **Figure 3.16**). The pH maintained at pH 6.6, DOC declined from an initial 20 mg L^{-1} to a final 17.5 mg L^{-1}. Fe concentration declined from initial 5 mg L^{-1} to a final 1 mg L^{-1}. Two contaminants could not be detected due to interferences with the matrix; out of the 15 contaminants 11 were present at the end of the experiment at t_{30W} = 174 minutes: Acetaminophen (51%), Caffeine (87%), Antipyrine (48%), Sulfamethoxazole (52%), Carbamazepine (18%), Ketorolac (9%), Atrazine (53%), Isoproturon (27%), Hydroxybiphenyl (40%), Diclofenac (7%) and

Ibuprofen (13%). The two flourquinolones antibiotics Flumequine and Ofloxacin were degraded below their LOD at t_{30W} = 76 minutes and t_{30W} = 25 minutes respectively. The impact of the process onto the treated water can be observed better in **Figure 3.17**.

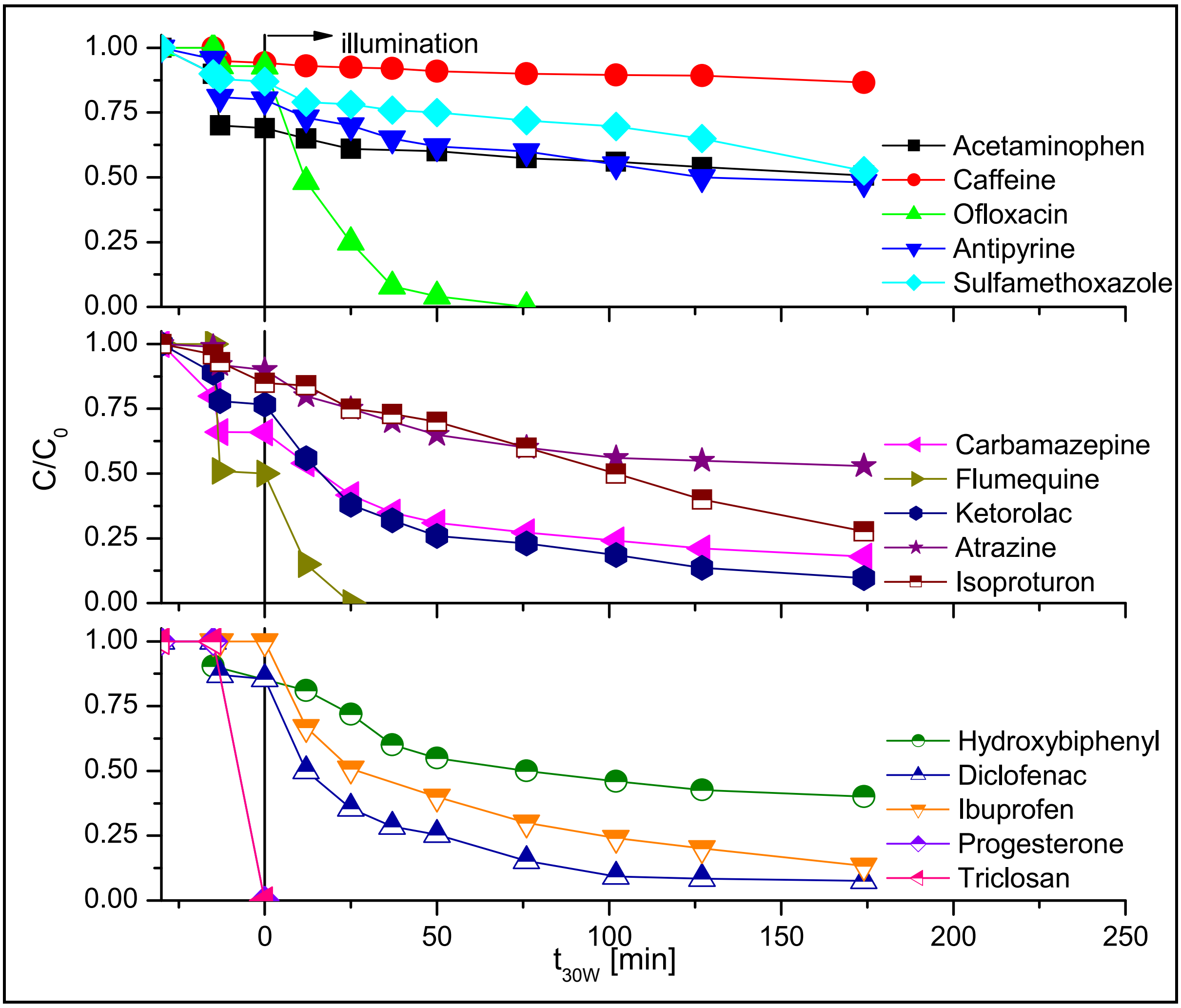


Figure 3.16 Degradation of the 15 contaminants at an initial concentration of 5 µg L^{-1} each in MWTP effluents at neutral pH. The degradation for 11 contaminants is incomplete; two could not be detected due to interferences with the matrix.

There is no significant change in the absorbance at 248 nm, neither in the Fenton phase, nor in the first few minutes of the photo-Fenton reaction. The main impact on the Fenton and photo-Fenton reaction surely is the loss of iron in this experiment

i) the iron was precipitated rapidly (in comparison to the other experiments)

ii) and the pH did not decrease significantly.

Duplicate experiments with the same conditions verified this behaviour. The degradation of contaminants present in MWTP effluents was incomplete and in some cases very unsatisfactory as the residual concentration was above 70% of the initial concentration.

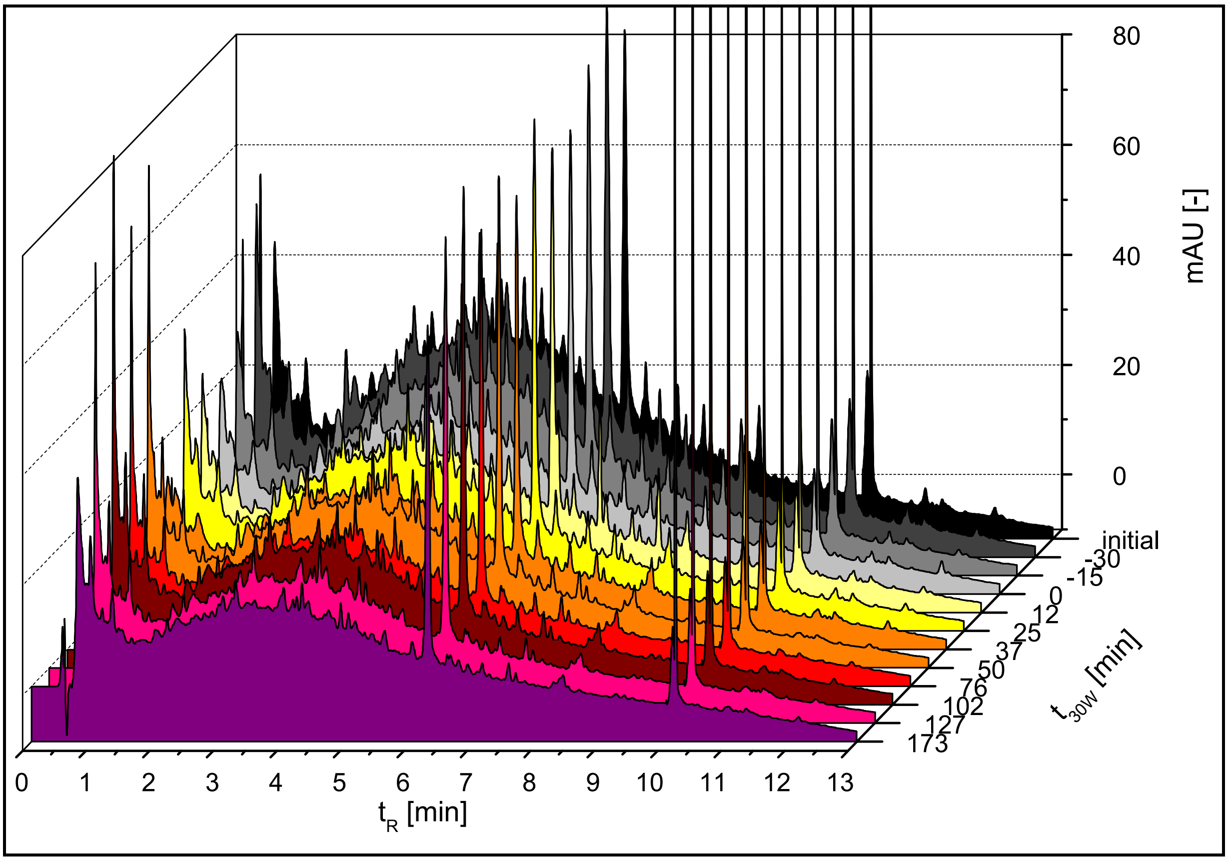


Figure 3.17 Chromatogram (at 248 nm) of the degradation of the 15 contaminants in MWTP effluents. C_0 = 5 µg L^{-1} each, neutral pH and 5 mg L^{-1} Fe. As can be observed, there is no significant decline in absorbance neither in the Fenton phase nor in the first minutes of the photo-Fenton reaction.

One way of overcoming the loss of iron it to start with an elevated iron concentration, so that the iron remaining in solution is sufficient for the degradation of the contaminants. The results for the experiment conducted with 20 mg L^{-1} Fe, a pH 6.5 and 50 mg L^{-1} H_2O_2 was equally disappointing. The only significant degradation which is observable happens in the Fenton phase (see **Figure 3.18**). Although the Fe concentration was 13 mg L^{-1} at the end of the experiment at t_{30W} = 92 minutes, the system was unable to degrade the contaminants in a significant extent during the photo-Fenton phase. DOC declined insignificantly from initial 15 mg L^{-1} to 13 mg L^{-1} (13% mineralisation), pH changed from pH 7.2 to a final pH 6.6, while H_2O_2 consumption was 70 mg L^{-1}. The compounds suffered degradation in the Fenton phase between 14% (Sulfamethoxazole) and 87% (Flumequine), and had residual concentrations between 18% (Diclofenac) and 73% (Sulfamethoxazole) with the exception of Flumequine (6%) and Ofloxacin (<LOD).

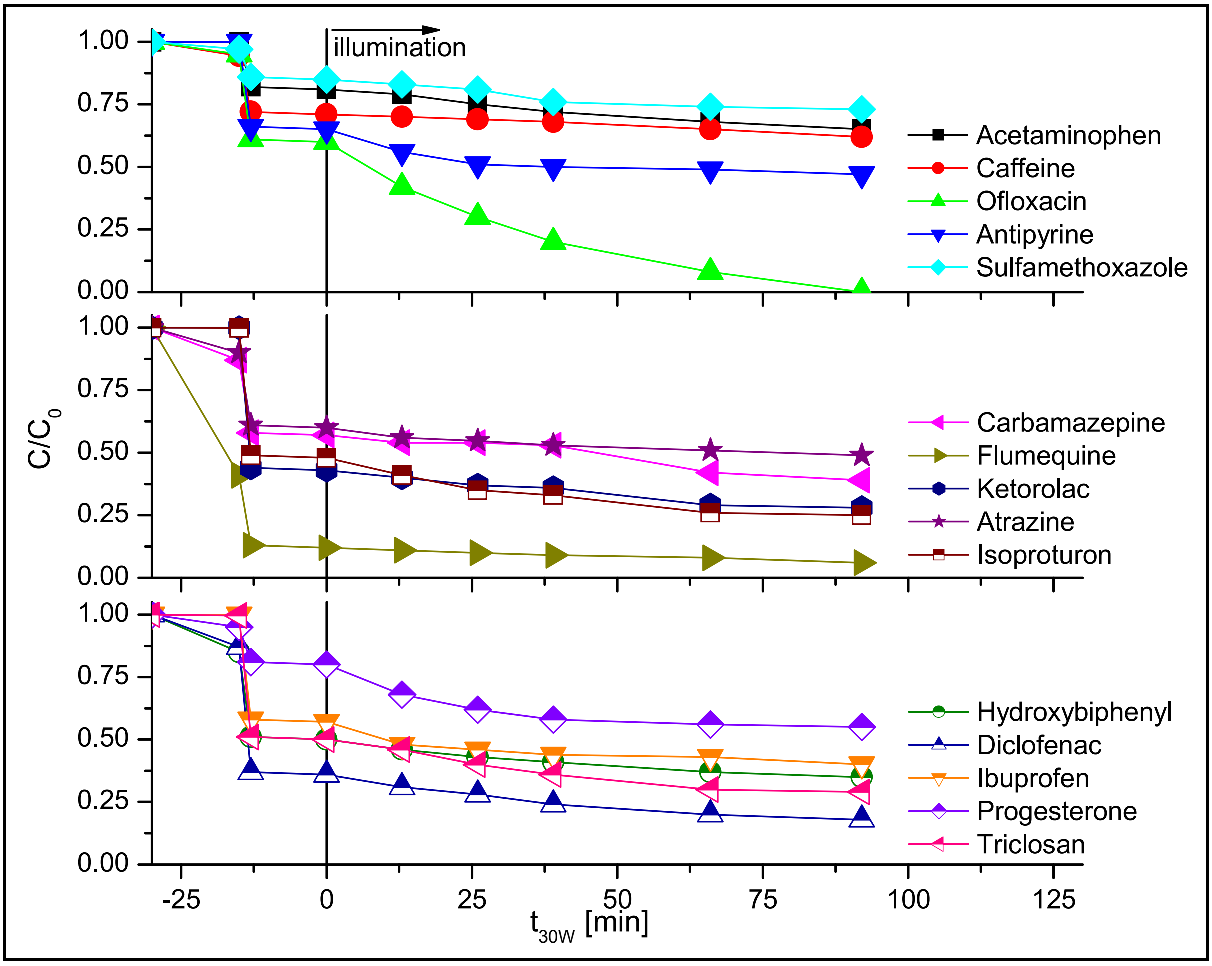


Figure 3.18 Degradation of the 15 contaminants at 5 µg L^{-1} initial concentration in MWTP effluents at neutral pH and 20 mg L^{-1} Fe.

As can be seen in **Figure 3.19**, the only significant decline in the absorbance at 248 nm was in the Fenton phase. After that, the absorbance did not change which is in good accordance with the data obtained from **Figure 3.18**. This leads to the conclusion that it is not possible to degrade the contaminants in MWTP effluents at neutral pH, neither with low concentrations of iron nor with concentrations as high as 20 mg L^{-1}. The reason why the photo-Fenton process is inhibited in these waters in unknown, but may lie in the composition of the effluents, which may contain substances that either stops the reduction from Fe^{3+} to Fe^{2+}, scavenge the $HO^{\bullet}$ radicals, form inactive complexes with iron and thus make it unavailable for the reaction etc. The solution proposed in this work to solve this problem was to find compounds which can complex the iron and at the same time keep it available for the photo-Fenton process, which are non toxic, biodegradable and cheap.

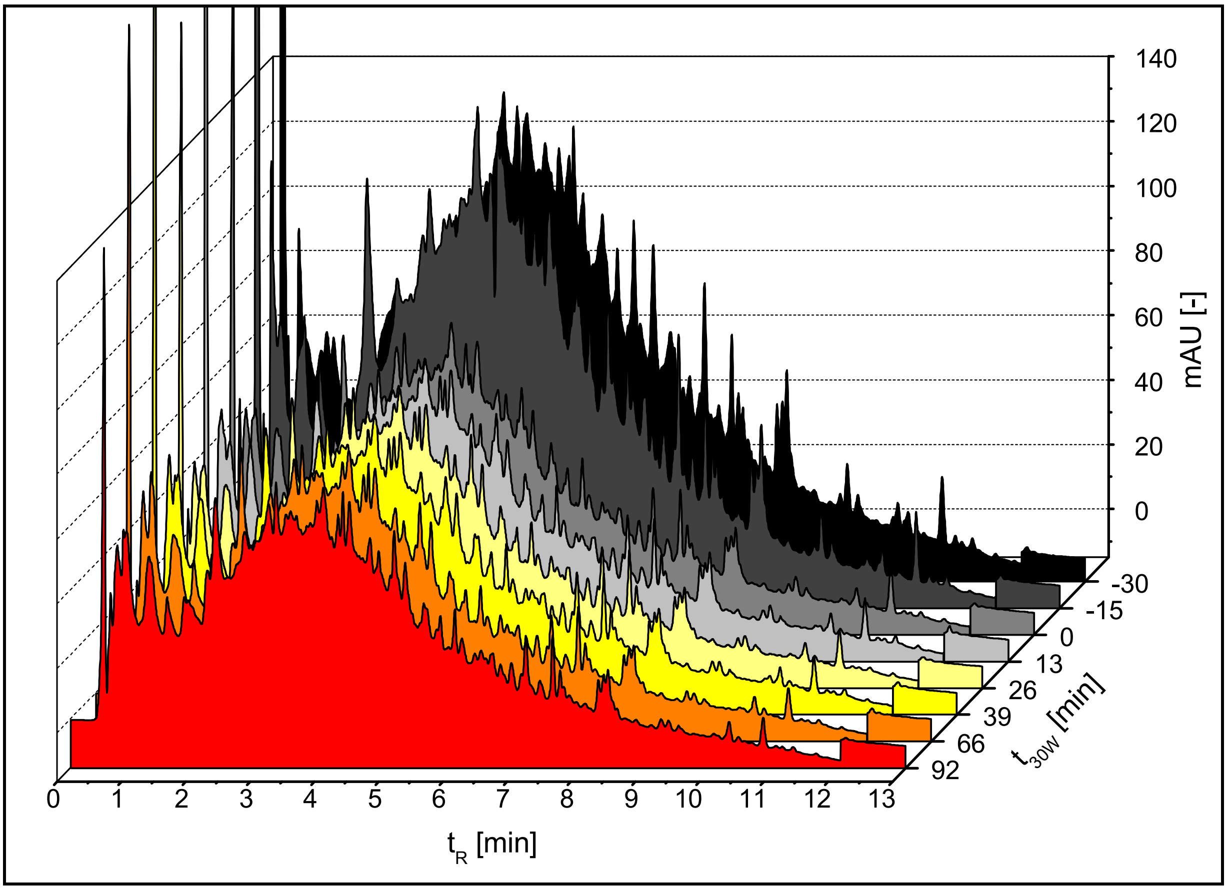


Figure 3.19 Chromatogram (at 248 nm) of the degradation of the 15 contaminants in MWTP effluent. C_0 = 5 µg L^{-1} each, neutral pH and 20 mg L^{-1} Fe. The only significant decline in absorbance is in the Fenton phase.

3.4.5 The use of Fe complexing agents for the degradation of contaminants in MWTP effluents

3.4.5.1 Experiments conducted with oxalic acid

The problems encountered with the lack of efficiency of the photo-Fenton process at neutral pH in real MWTP effluents which are correlated to the precipitation/inactivation of the photoactive iron species lead to the conclusion that it was necessary to add compounds into water, which are able to form complexes with iron and at the same time making it available for the photo-Fenton process. It is known that iron is complexed in water by polycarboxylates such as citric acid and oxalic acid and that these complexes have a high absorption in the UV-Vis region [Faust and Hoigne, 1990] (**Eq 1.56** and **Eq 1.60**). There are several examples of the ferrioxalate assisted photo-Fenton for the degradation of contaminants in water at acidic and natural pH [Huang et al, 2007; Monteagudo et al, 2008; Prato-Garcia et al, 2009], so the idea was to treat MWTP effluents spiked with the 15 contaminants at an initial concentration of 100 µg L^{-1} each with a ferrioxalate assisted photo-Fenton.

The MWTP effluent was stripped from its carbonates/bicarbonates, while pH was maintained neutral. H_2O_2 (50 mg L^{-1}) was added, after 15 minutes Fe^{2+} (5 mg L^{-1}) and oxalic acid (35 mg L^{-1}), which added to a molar ratio of Fe : Ox = 1 : 3.6 (a slight surplus on the oxalic side), were added into the reactor and after another 15 minutes the reactor was illuminated. Most of the contaminants were degraded below their LOD in t_{30W} = 18 minutes, Flumequine and Sulfamethoxazole concentrations were <LOD in t_{30W} = 46 minutes. Only Atrazine was present at the end of the experiment at t_{30W} = 56 minutes in a residual concentration of 2% (see **Figure 3.20**). DOC concentration changed from an initial 22 mg L^{-1} to a final 15 mg L^{-1} (54% mineralisation), pH changed significantly from 6.1 to 4.0, H_2O_2 consumption was 48 mg L^{-1}.

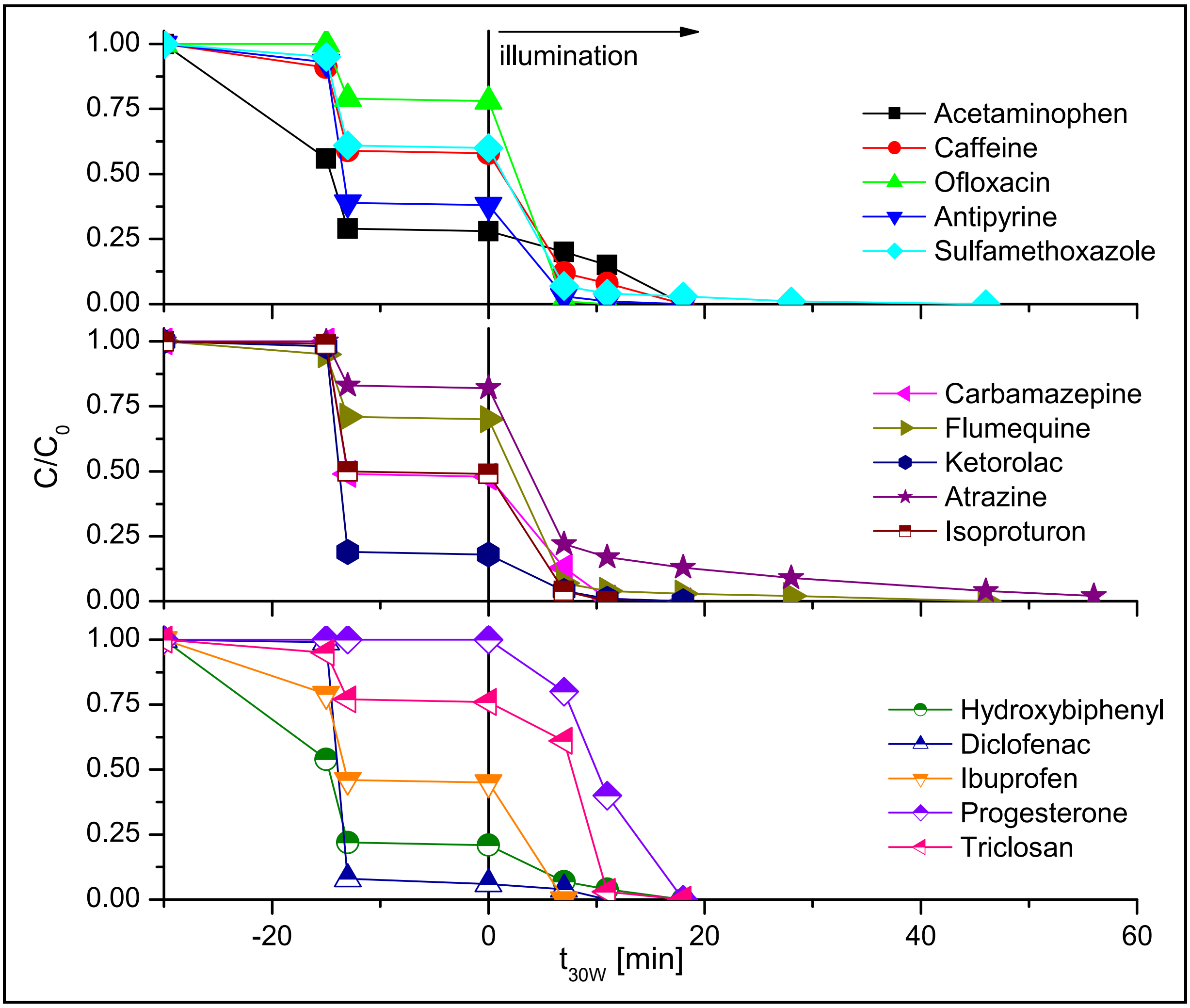


Figure 3.20 Degradation of 15 contaminants at 100 µg L^{-1} initial concentration in stripped MWTP effluents with ferrioxalate assisted photo-Fenton at unadjusted pH.

The behaviour of pH, DOC, sum of all contaminants (ΣCs) and H_2O_2 consumption can be seen in **Figure 3.21**. Due to the fact that the water was stripped of its carbonates/bicarbonates, it has lost most of its buffering capacity and the use of oxalic acid lowered the pH significantly to pH 3.3. During the process, oxalic acid was consumed and that was the reason that the pH raises during the process. The degradation was faster than in neutral pH photo-Fenton, but the process ended up with a low pH (similar to the optimal pH of normal photo-Fenton). The process seemed, although quite effective, not suitable because of the complicated process maintenance such as strippingof carbonates while keeping pH neutral, adding of oxalic acid, and neutralizing the water at the end of the process because of the low residual pH.

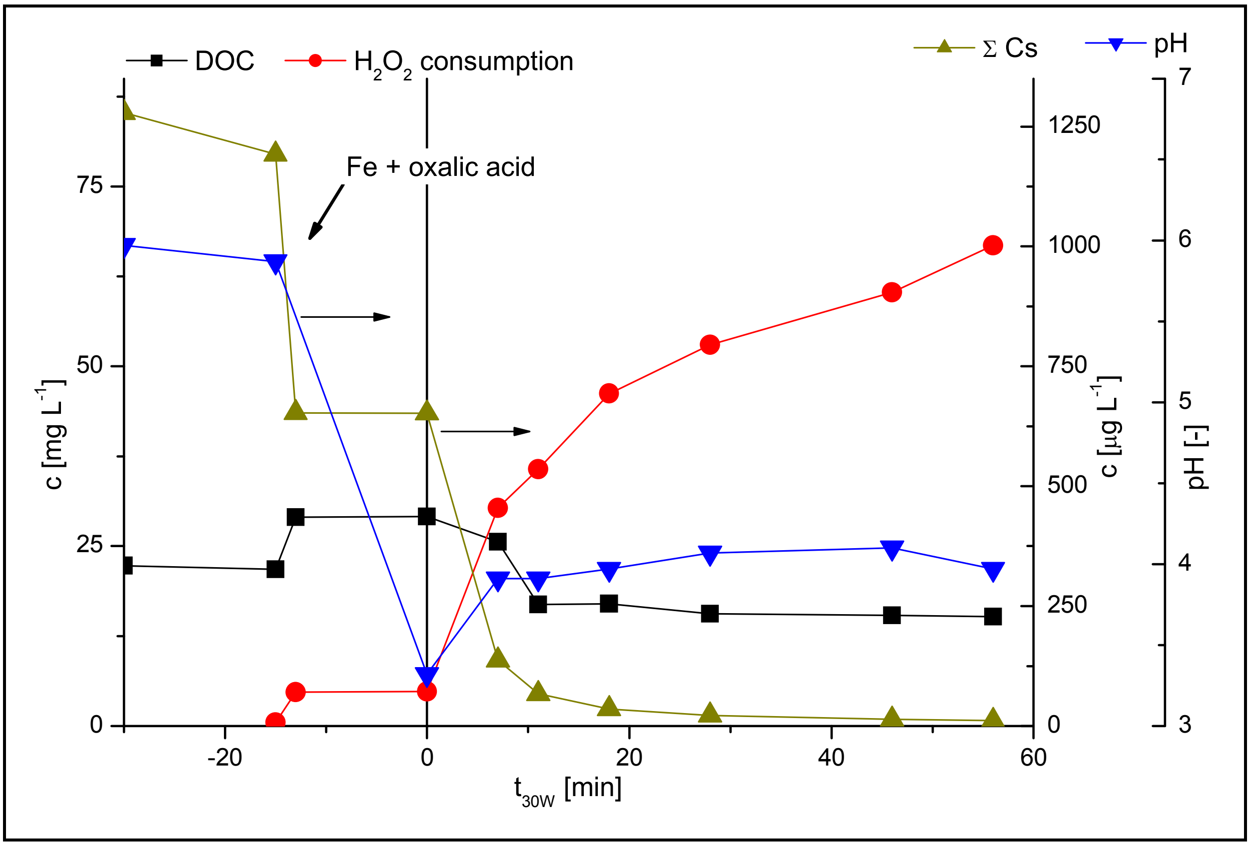


Figure 3.21 DOC evolution, H_2O_2 consumption, pH value and sum of all contaminants as a function of t_{30W} in MWTP effluents with ferrioxalate assisted photo-Fenton.

Another approach was tested whether it is possible to degrade the present contaminants in water with a ferrioxalate assisted photo-Fenton at pH neutral without the stripping of carbonates/bicarbonates. For this the water was spiked with the 15 contaminants at a level of 100 µg L^{-1}, and the iron and oxalic acid was added into the reactor like in the experiment before. The results were downright disappointing, with the sum of all contaminants at 52% of the initial concentration at the end of the experiment at t_{30W} = 196 minutes. The pH stayed in the neutral range of the water (pH 8), DOC did not change significantly from an initial 30 mg L^{-1} to 37 mg L^{-1} after oxalate adding and to a final 29 mg L^{-1}. H_2O_2 consumption was 41 mg L^{-1}. This showed that although the ferrioxalate assisted photo-Fenton is a quite potent process, the presence of carbonates/bicarbonates has a negative impact onto the degradation of the contaminants.

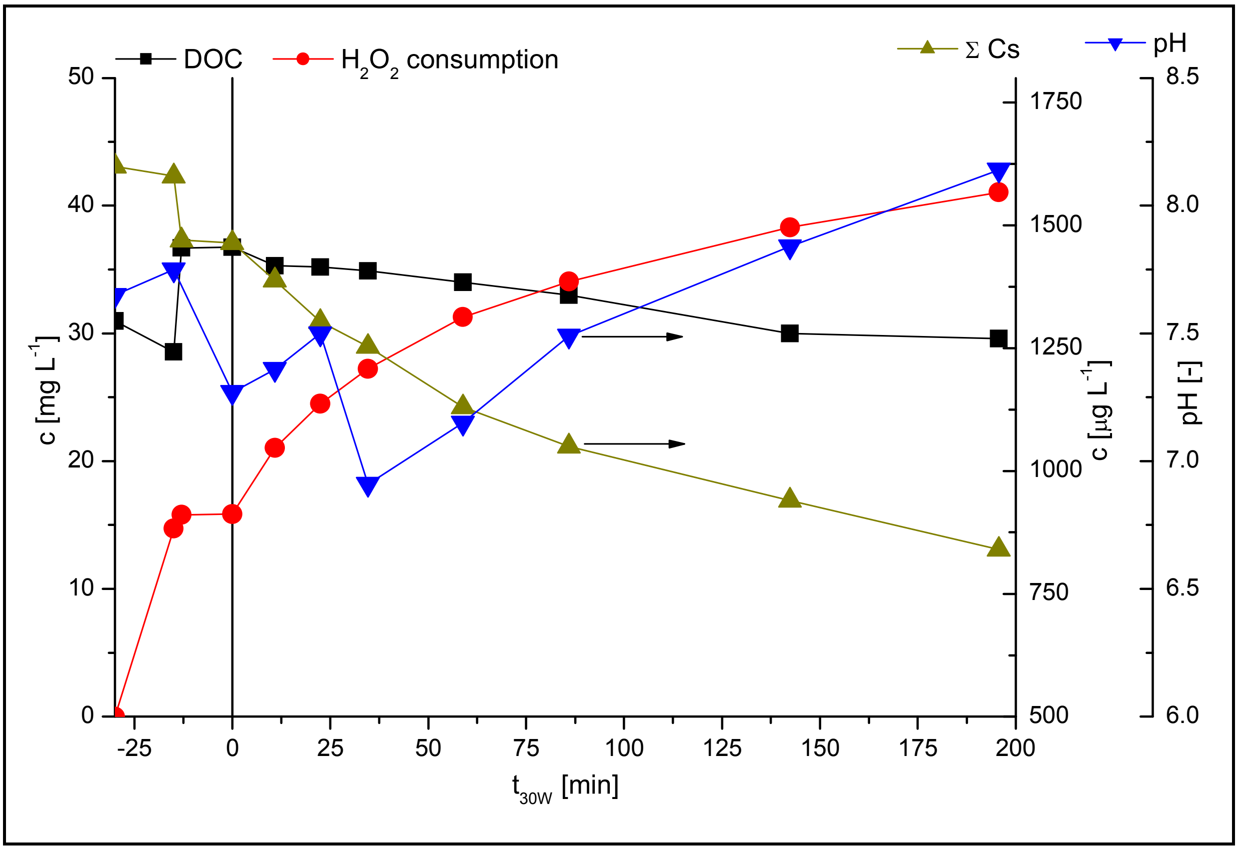


Figure 3.22 H_2O_2 consumption, DOC, pH, and sum of all contaminants evolution as a function of t_{30W} in unstripped MWTP effluents with ferrioxalate assisted photo-Fenton.

These results lead to the conclusion that although the ferrioxalate assisted photo-Fenton is a good way of degrading contaminants present in the water, the low pH at the end of the experiments is undesirable, so other substances had to be found to complex the iron while keeping the pH in the desired neutral range.

3.4.5.2 Experiments conducted with humic acids

The next substances tested were humic acids. Humic acids are a fraction of the humic substances. These are naturally occurring organic substances resulting from microbiological and chemical transformation of organic debris, they are the largest fraction of dissolved organic matter in natural water and are categorized as humic acid (HA), fulvic acid and humin, according to their solubility [Corin et al, 1996; Lam et al, 2003]. They absorb sunlight and generate exited triplet states ($^3HS^*$), various reactive oxygen species, $HO^\bullet$, singlet oxygen ($^1O_2$) and H_2O_2 [Auger et al, 1997; Sandvik et al, 2000]. They contain numerous functional groups like $-NH_2$, -CHO, =O, -OH, -COOH, etc. which enable them to support ion exchange and redox processes and to form complexes. They also contain a number of stable free radicals which can react with various substances [Auger and Richard, 1996; Farré et al, 2007; Kepczynski et al, 2007; Lipczynska-Kochany and Kocjany, 2008]. Most of the iron species in the aqueous environment exist in the form of complexes with organic acids (citric, oxalic and maleic acid) as well as humic substances [Clarke and Danielsson, 1995; Steinmann and Shotyk, 1995]. The light induced legand to metal charge transfer (LMCT) may also occur for the case of Fe(III)-humate complexes, and Fukushima et al compared the kinetic constants for the reduction of Fe(III) by humic acid in the presence of light with equivalent reactions carried out in the dark [Fukushima and Tatsumi, 1999].

The stripped MWTP effluent was spiked with the 15 contaminants, after homogenisation humic acid was added, after which peroxide and iron was added like in the experiments before. One visible effect using HA was that the water had a typical brownish colour of marsh water. During the experiments a slight discolouration could be noticed, but it has to be emphasized, that water for reuse has to meet certain quality criteria like turbidity and colour. The change in the absorbance during an experiment can be seen in **Figure 3.23**. The first experiments conducted were to determine the optimal HA concentration. Three different HA concentrations (50, 25 and 10 mg L^{-1} HA which account for a mass ration to iron of 1:10, 1:5, 1:2 respectively) were tested and (see **Figure 3.24**) the results showed that the experiment with 10 mg L^{-1} HA showed the most promising outcome in terms of contaminant degradation.

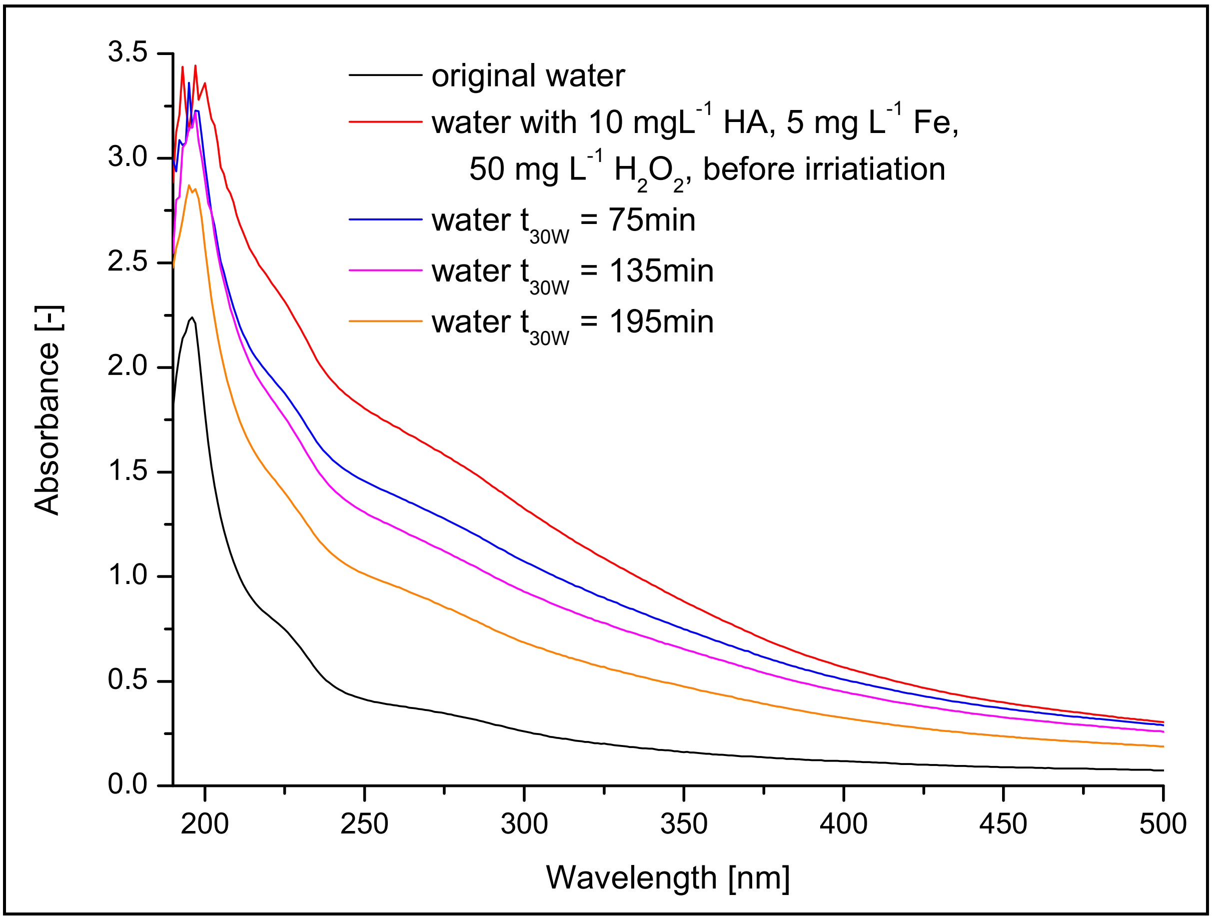


Figure 3.23 Evolution of absorbance of MWTP effluent treated with 10 mg L^{-1} HA

On the other hand, the pH at the end of the experiment was at pH 4.2 which was higher than in the experiment conducted with oxalic acid, but still quite low compared to neutral pH. The DOC in these experiments did not change significantly; iron concentration was stable (between 5 mg L^{-1} and 4 mg L^{-1} for all experiments), and the H_2O_2 consumption was 83 mg L^{-1} for 50 mg L^{-1} HA, 68 mg L^{-1} for 25 mg L^{-1} and 69 mg L^{-1} for 10 mg L^{-1} respectively.

The conditions of these experiments can be seen in **Table 3.5** with the initial and final concentration of contaminants (sum of contaminants), pH evolution during the experiments etc.

Table 3.5 Initial and final conditions of the experiments conducted with different HA concentrations

HA	**50 mg L^{-1}**				**25 mg L^{-1}**				**10 mg L^{-1}**			
t_{30W} [min]	-30	0	11	198	-30	0	7	154	-30	0	11	186
pH [-]	6.9	6.4	6.2	6.1	7.2	5.8	5.4	4.6	6.7	4.6	4.5	4.2
DOC [mgL^{-1}]	32			30	28			24	26			25
consumed H_2O_2 [mg L^{-1}]	-	17	24	83	-	17	22	68	-	12	18	69
$\Sigma Cs/\Sigma Cs_0$ [%]	100	78	65	25	100	72	56	9	100	66	43	3
ΣCs [µg L^{-1}]	1534	1200	1000	385	1549	1117	869	133	1511	996	655	42

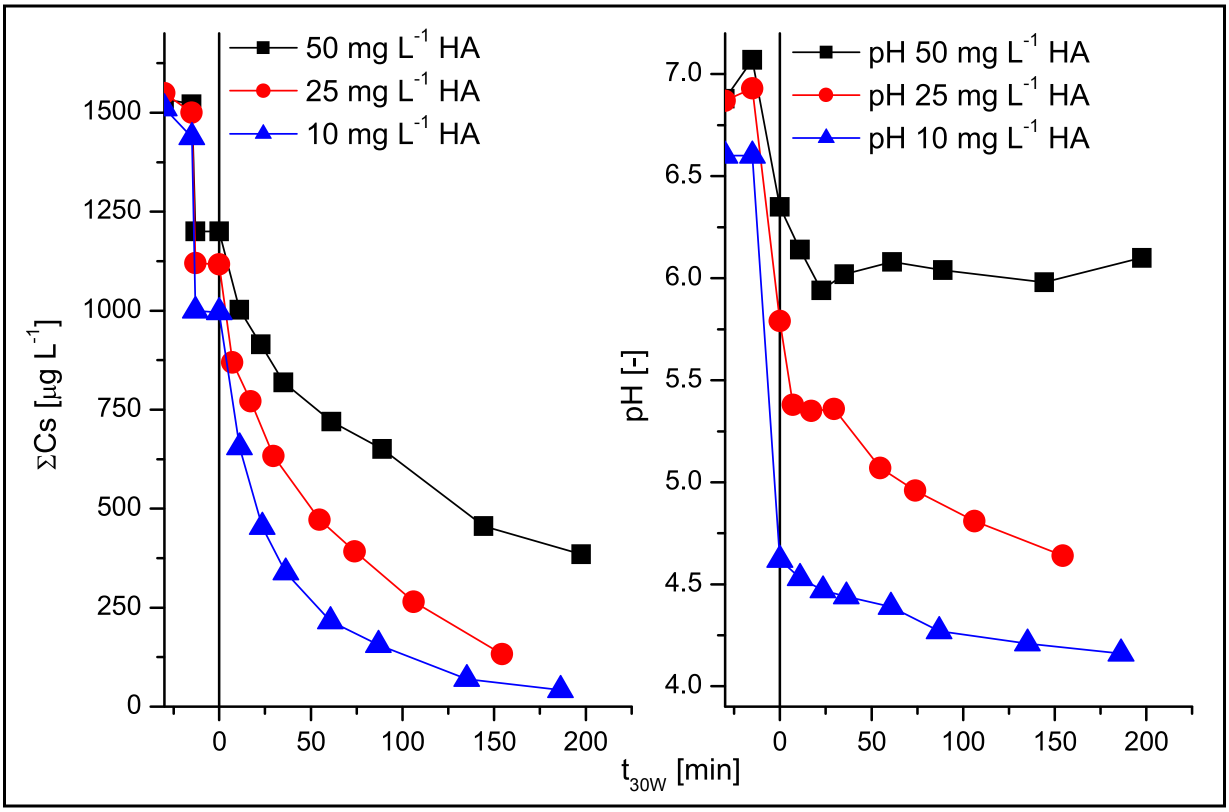


Figure 3.24 Degradation of the sum of all contaminants (initial concentration 100 µg L^{-1} each) with different humic acid concentrations in stripped MWTP effluents.

The results showed that a higher HA content lead to a slower degradation rate of the compounds present, but as well to a higher pH at the end of the experiment and therefore 10 mg L^{-1} HA was considered the more adequate concentration. To verify theses results, several experiments with 10 mg L^{-1} HA were conducted with MWTP effluents obtained from the same day with different initial pH and effluents with the same pH from different days. The results showed that in the case of the same water the evolution of pH had a huge impact onto the degradation of the contaminants. As can be seen in **Figure 3.25**, the water with pH 7.3 and pH 5.5 (same water, but different initial pH after carbonate/bicarbonate stripping) had final pH of pH 5.8 and pH 4.0 respectively and a residual concentration (ΣCs) of the contaminants of 328 µg L^{-1} (22%) and 75 µg L^{-1} (5%) respectively. Different waters with more or less the same initial pH (pH 6.7, pH 7.3 and pH 7.0) had as well different residual concentrations and different final pH. This can be explained that the waters obtained from the MWTP during different days had different composition. The conditions of the experiments conducted with 10 mg L^{-1} HA can be seen in **Table 3.6**.

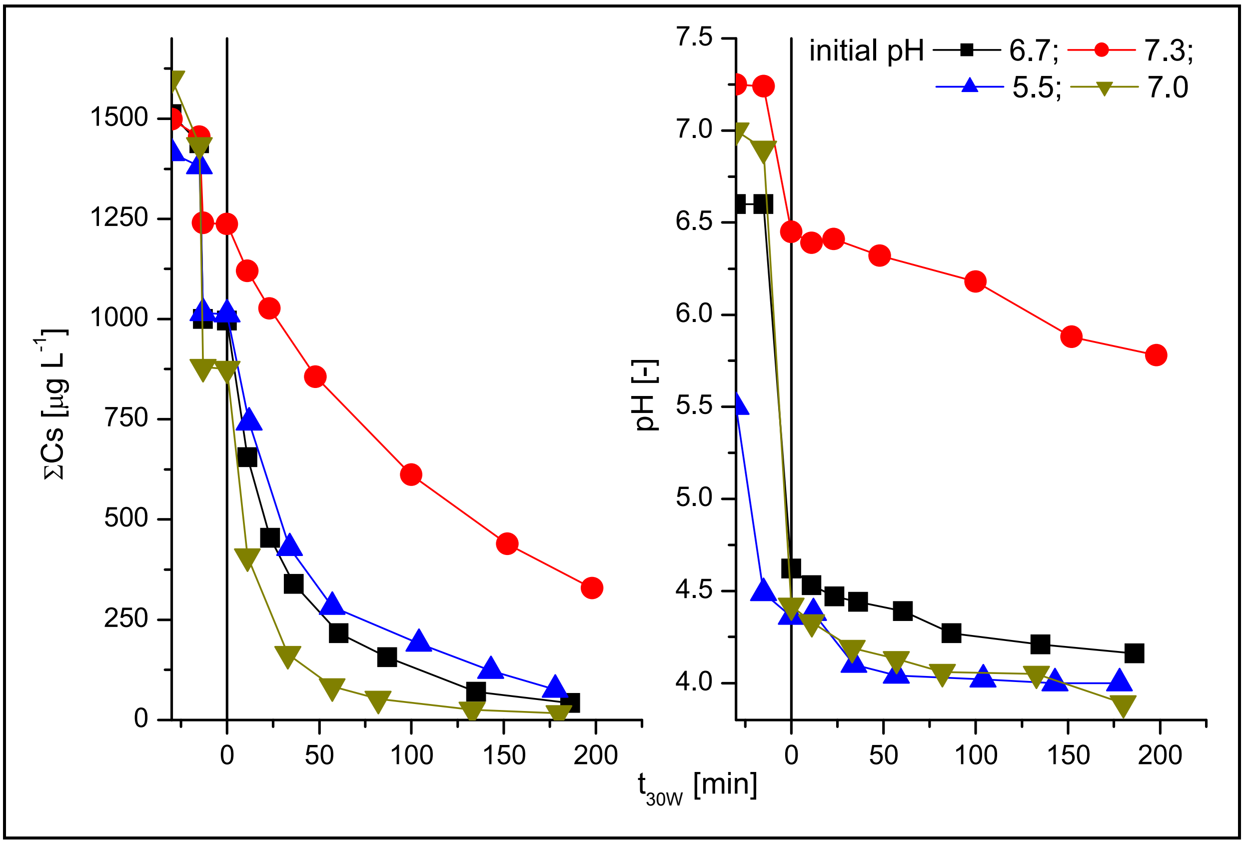


Figure 3.25 Degradation of the sum of all contaminants (initial concentration 100 µg L^{-1} each) with 10 mg L^{-1} HA concentrations in stripped MWTP effluents with different initial pH.

Table 3.6 Initial and final conditions of the experiments conducted with same HA concentrations (10 mg L^{-1}) in the same water but different initial pH and different water but same pH

experiment		1		same water different initial pH			2	
t_{30W} [min]	-30	0	11	198	-30	0	12	178
pH [-]	7.3	6.5	6.4	5.8	5.5	4.4	4.3	4.0
consumed H_2O_2 [mg L^{-1}]	-	36	41	113	-	8	13	40
$\Sigma Cs/\Sigma Cs_0$ [%]	100	83	75	22	100	71	52	5
ΣCs [µg L^{-1}]	1498	1237	1120	328	1414	1012	741	76
experiment		**3**		**different water same initial pH**			**4**	
t_{30W} [min]	-30	0	11	186	-30	0	11	180
pH [-]	6.7	4.6	4.5	4.2	7.0	4.4	4.3	3.9
consumed H_2O_2 [mg L^{-1}]	-	13	18	69	-	4	12	77
$\Sigma Cs/\Sigma Cs_0$ [%]	100	66	43	3	100	54	25	1
ΣCs [µg L^{-1}]	1511	996	655	42	1599	875	407	17

Experiments conducted with 5 mg L^{-1} HA showed a similar behaviour as can be seen in **Figure 3.26**. It is not clear why the same initial pH (pH 6.8 and pH 6.6) can lead to final pH 4 and pH 4.9, or why slightly different pH (pH 6.8 and pH 6.1) can lead to the same pH 4. The possible explanation for this may lie in the inorganic and organic composition of the MWPT effluent. All of theses waters were stripped prior to treatment of the carbonates/bicarbonates (TIC < 1 mg L^{-1}) and therefore have none or very low buffer capacity. The conditions of the waters, their pH evolvution, H_2O_2 consumption, etc. can be seen in **Table 3.7**.

Table 3.7 Initial and final conditions of the experiments conducted with same HA concentrations (5 mg L^{-1}) in MWTP effluents under similar conditions.

experiment		1				2		
t_{30W} [min]	-30	0	10	205	-30	0	13	221
pH [-]	6.8	4.3	4.3	4.0	7.2	6.3	6.3	5.6
consumed H_2O_2 [mg L^{-1}]	-	16	22	72	-	9	13	49
$\Sigma Cs/\Sigma Cs_0$ [%]	100	65	36	1	100	77	68	31
ΣCs [µg L^{-1}]	1393	911	499	18	1575	1220	1068	490
experiment		**3**				**4**		
t_{30W} [min]	-30	0	27	211	-30	0	20	196
pH [-]	6.6	5.5	5.4	4.9	6.1	4.3	4.2	4.0
consumed H_2O_2 [mg L^{-1}]	-	4	13	34	-	4	7	25
$\Sigma Cs/\Sigma Cs_0$ [%]	100	76	54	22	100	67	46	9
ΣCs [µg L^{-1}]	1471	1120	796	329	1546	1029	718	138

The same range of degradation can be achieved with different peroxide consumptions. In all the experiments DOC evolution was negligible.

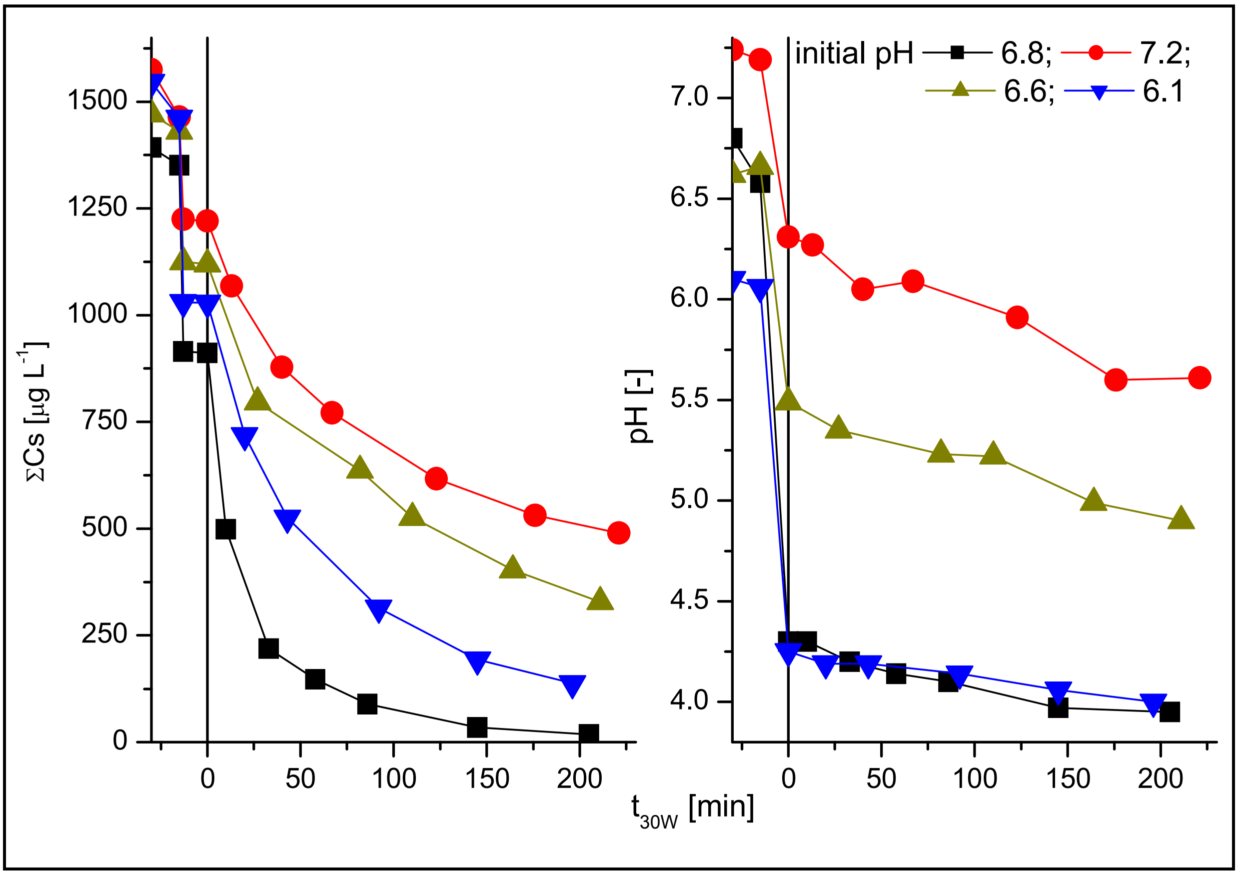


Figure 3.26 Degradation of the sum of all contaminants (initial concentration 100 µg L^{-1} each) with 5 mg L^{-1} HA concentrations in stripped MWTP effluents with different initial pH.

Another set of experiments war run, this time with a concentration of 2 mg L^{-1} HA. There was again a great variance in the results, which are consistent with the prior experiments, see **Figure 3.27** and **Table 3.8**. Again the typical behaviour can be observed, where the most efficient degradation happens at the lower pH. The mean residual concentration of the experiments conducted with 10 mg L^{-1} HA was 7.8% (116 µg L^{-1} as a sum of all present contaminants) in comparison to 15.8% (244 µg L^{-1}) for the experiments conducted with 5 mg L^{-1} HA and 16% (232 µg L^{-1}) for experiments conducted with 2 mg L^{-1} HA. This leads to the conclusion, that if humic acids are applied for this type of degradation of contaminants in water, the optimal HA concentration is 10 mg L^{-1} (in the tested range of 50 to 2 mg L^{-1}).

Table 3.8 Initial and final conditions of the experiments conducted with same HA concentrations (2 mg L^{-1}) in MWTP effluents under similar conditions.

experiment	1				2				3			
t_{30W} [min]	-30	0	11	205	-30	0	12	163	-30	0	10	209
pH [-]	6.7	4.4	4.4	4.0	7.2	5.9	5.5	4.7	7.3	6.4	6.4	5.8
consumed H_2O_2 [mg L^{-1}]	-	7	12	61	-	9	13	61	-	11	14	40
$\Sigma Cs/\Sigma Cs_0$ [%]	100	65	37	2	100	78	64	9	100	82	75	37
ΣCs [µg L^{-1}]	1481	954	543	24	1555	1208	989	135	1460	1204	1100	539

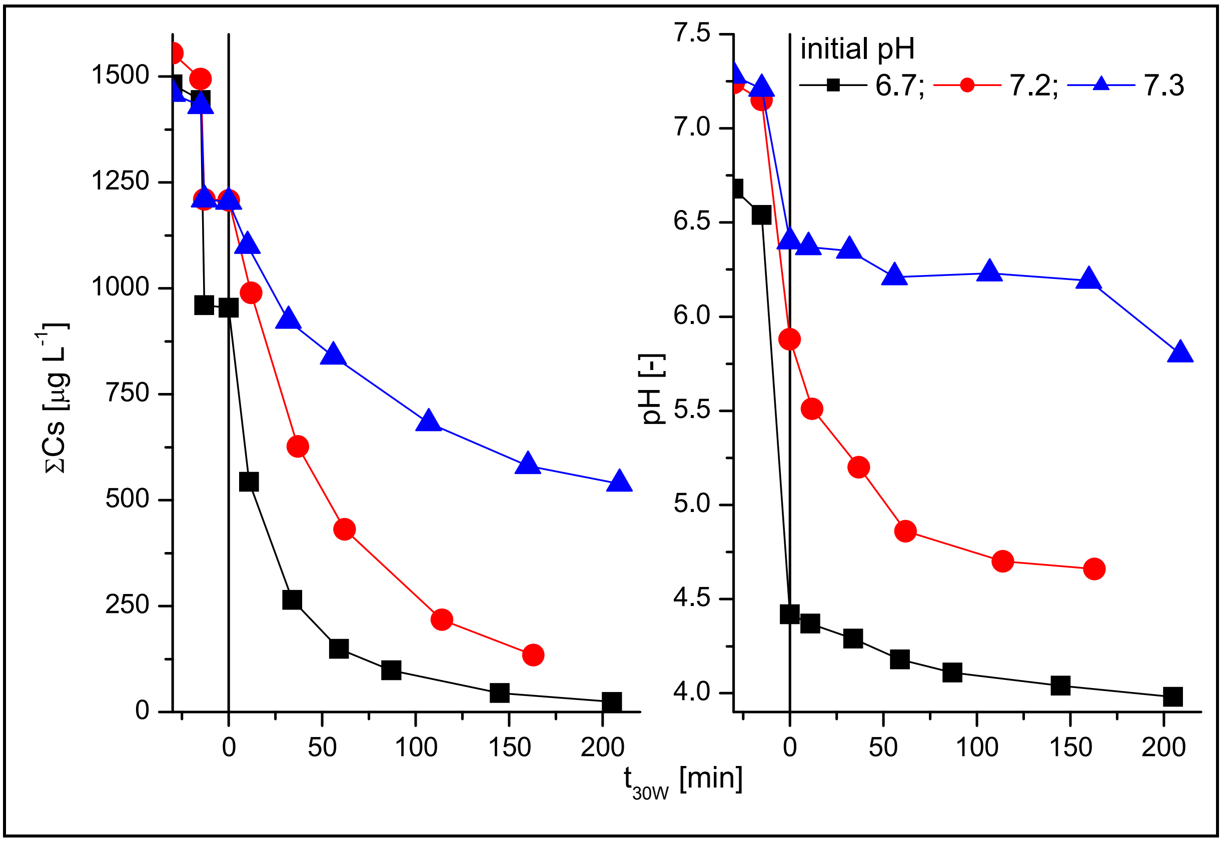


Figure 3.27 Degradation of the sum of all contaminants (initial concentration 100 µg L^{-1} each) with 2 mg L^{-1} HA concentrations in stripped MWTP effluents with different initial pH.

The residual pH depends strongly on the initial pH and the properties of the treated effluent. The conclusion for the pH is that if the initial pH is between pH 6 and pH 7, the residual pH is around pH 4 and an almost complete degradation of the contaminants (as a sum of all contaminants present) could be attained. If the initial pH is above pH 7, the residual pH is higher than pH 5 and the residual contaminant concentration is above 20%.

As in former cases, one test was done to evaluate the impact of carbonates/ bicarbonates present in the water when using HA. This experiment was done with 10 mg L^{-1} HA, and the IC was 84 mg L^{-1}. The results were similar to the ones obtained before (unstripped effluent photo-Fenton and unstripped effluent ferrioxalate assisted photo-Fenton). So it is necessary to remove carbonate/bicarbonate content before treatment also when using HA.

To test the impact on lower initial concentrations of the 15 contaminants, another experiment with 10 mg L^{-1} HA and an initial concentration of 5 µg L^{-1} of each of the contaminants was performed. The results can be seen in **Figure 3.28**.

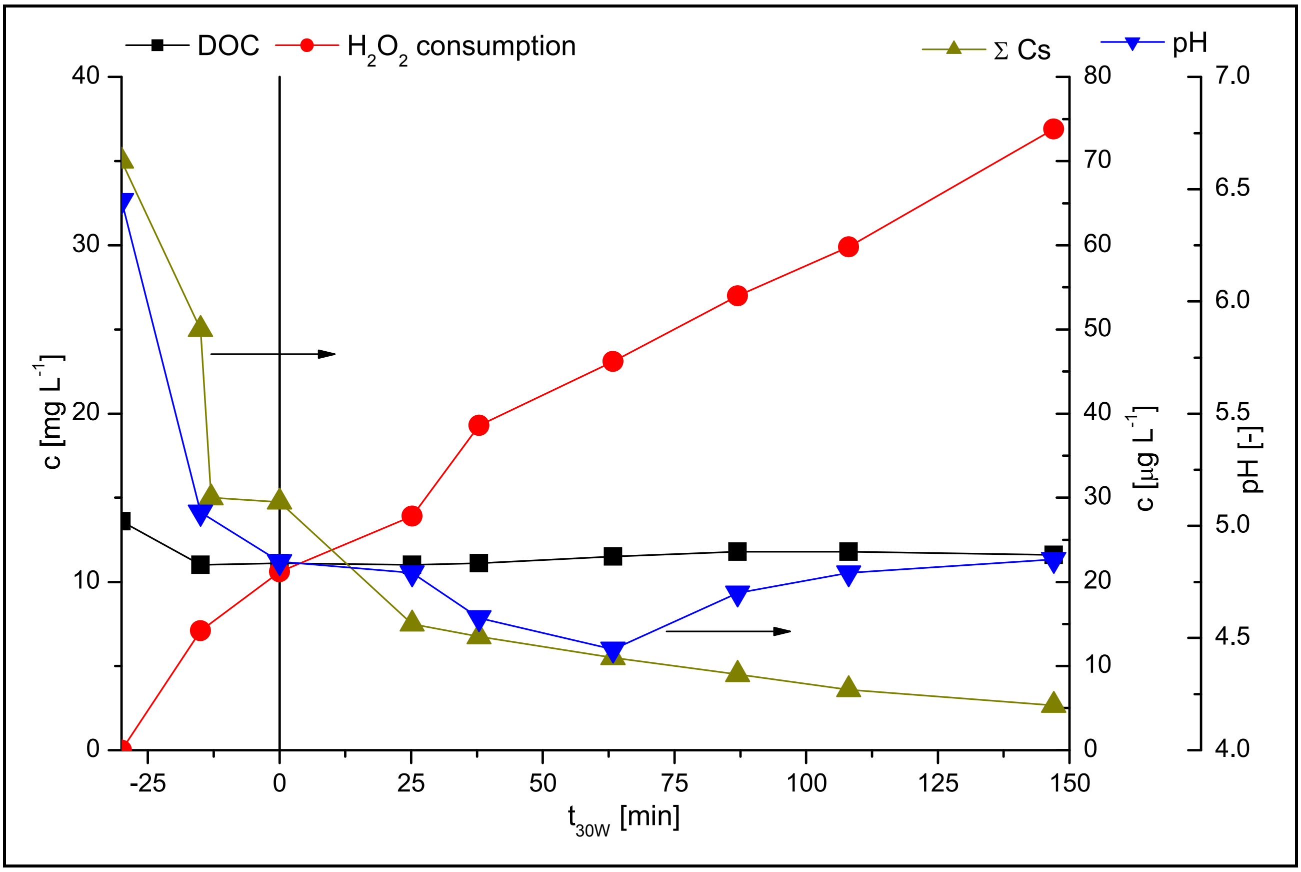


Figure 3.28 H_2O_2 consumption, DOC, pH, and sum of all contaminants (ΣCs) evolution as a function of t_{30W} in carbonate/bicarbonate stripped MWTP effluents with 10 mg L^{-1} HA. Initial concentration of 5 µg L^{-1} of each contaminant.

The experimental time was t_{30W} = 147 minutes, 37 mg L^{-1} of H_2O_2 were consumed, pH changed from initial pH 6.4 to a final pH 4.6, while DOC did not change significantly from 14 mg L^{-1} to 12 mg L^{-1}. The iron concentration throughout the experiment was stable at 4.6 mg L^{-1}. The residual contaminant concentration was 5.4 µg L^{-1} (7 % of the initial concentration), which consisted of 1.34 µg L^{-1} Acetaminophen, 0.5 µg L^{-1} Caffeine, 0.09 µg L^{-1} Sulfamethoxazole, 0.11 µg L^{-1} Carbamazepine, 0.03 µg L^{-1} Flumequine, 1.57 µg L^{-1} Atrazine, 1.29 µg L^{-1} Hydroxybiphenyl and 0.42 µg L^{-1} Triclosan. All other contaminants are degraded below their LOD in t_{30W} = 108 minutes.

As a conclusion it can be stated, that the use of humic acids augments the photo-Fenton process. The final pH shows great variance, from pH 4 to pH 5.5 depending on the initial pH, the water composition etc. The results indicated that this process works, although slower and not that efficient than photo-Fenton at pH 2.8 and ferrioxalate assisted photo-Fenton. These results lead to the idea to use a different source of organic acids or humic acids in regard of cost and operational related considerations.

3.4.5.3 Experiments conducted with a mixture of MWTP influent and effluent

MWTP effluents were mixed with influent in a ration of 1:10 and a ration of 1:3 (see **Figure 3.29**). The idea behind this approach was to make use of substances occurring naturally in waste water which could form photoactive $Fe^{3+}L$ species. The mixture was stripped of its carbonates/bicarbonates and treated in the same way as before with a spiking level of the 15 contaminants at 100 µg L^{-1} each. Both results were rather disappointing. The raw influent water did not provide sufficient complexing agents to maintain the iron available for the photo-Fenton process.

The experiment conducted with a 1:10 radio (not shown) had a final contaminant concentration of 916 µg L^{-1} (60% of the initial concentration), pH was stable at pH 7.5, DOC did not change (36 mg L^{-1}), H_2O_2 consumption was 118 mg L^{-1} at a t_{30W} = 178 minutes.

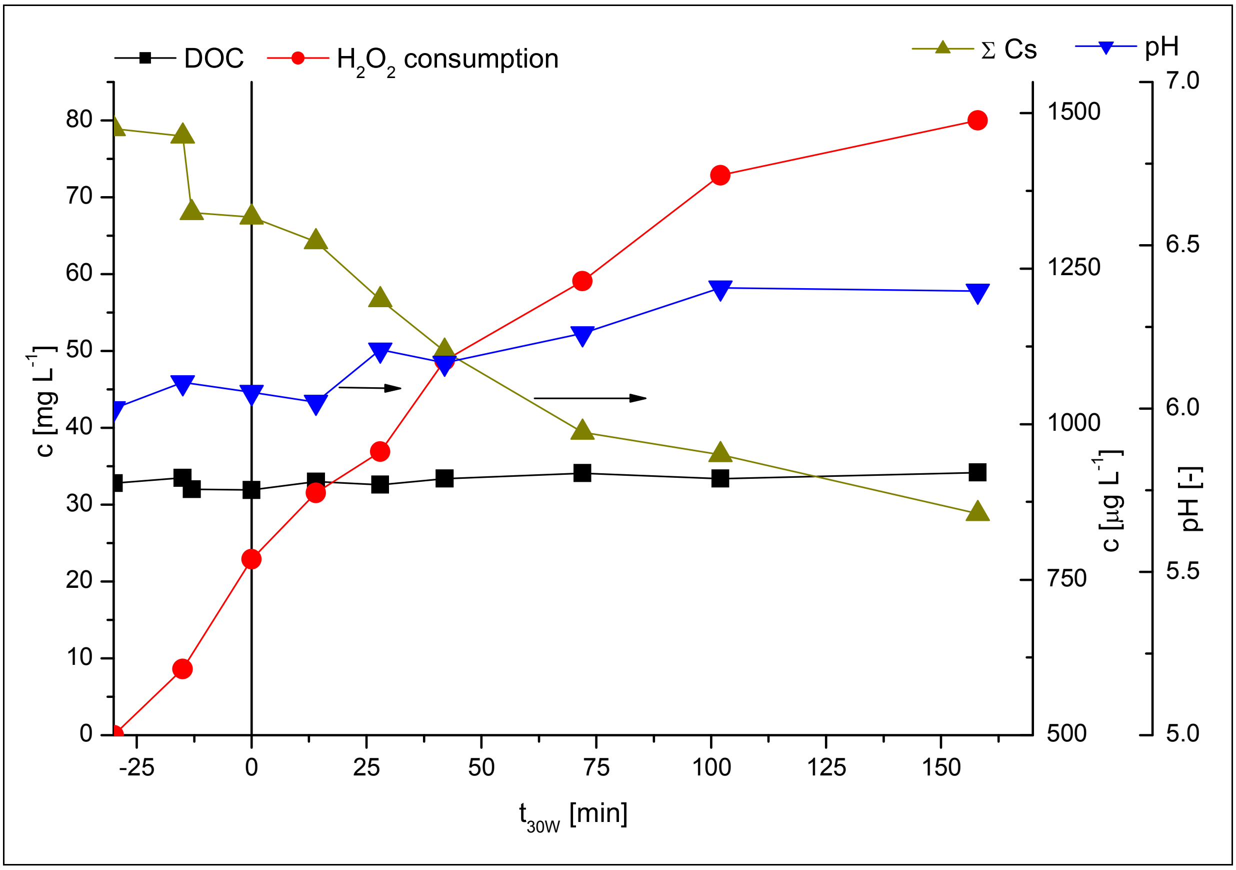


Figure 3.29 H_2O_2 consumption, DOC, pH and sum of all contaminants (ΣCs) evolution as a function of t_{30W} in carbonate/bicarbonate stripped MWTP effluents with a mixture of influent mixed with influent (ef : in = 1 : 3).

The experiment conducted with a 1 : 3 mixture of influent to effluent (see **Figure 3.29**) had a final contaminant concentration (sum of all contaminants) of 856 µg L^{-1} (58% of the initial concentration), initial pH was pH 6 and final pH was 6.4, DOC did not change (33 mg L^{-1}), and H_2O_2 consumption was 80 mg L^{-1} at a t_{30W} = 158 minutes.

3.4.5.4 Experiments conducted with EDDS

The rather disappointing results lead to the conclusion that another complexing agent had to be found to make this process work. There are a number of agents, which have a high complexing potential. One among them is the well known substance (Ethylenediaminetetraacetic acid) EDTA a hexadentate chelating agent. But the disadvantage of EDTA is that it emerges nowadays as a persistent organic pollutant [Yuan and VanBriesen, 2006] because it its widespread use. It degrades to ethylenediaminetriacetic acid, which then cyclises to the diketopiperizide, a cumulative, persistent, organic environmental pollutant. A good alternative is the biodegradable chelating agent EDDS ((S,S)-Ethylenediamine-N,N'-disuccinic acid), both structures can be seen in **Figure 3.30**. The useful chelating range for EDDS with iron(III) is between pH 3 and pH 9 in comparison to EDTA, which has a chelating range of pH 2 and pH 11 [Orama et al, 2002].

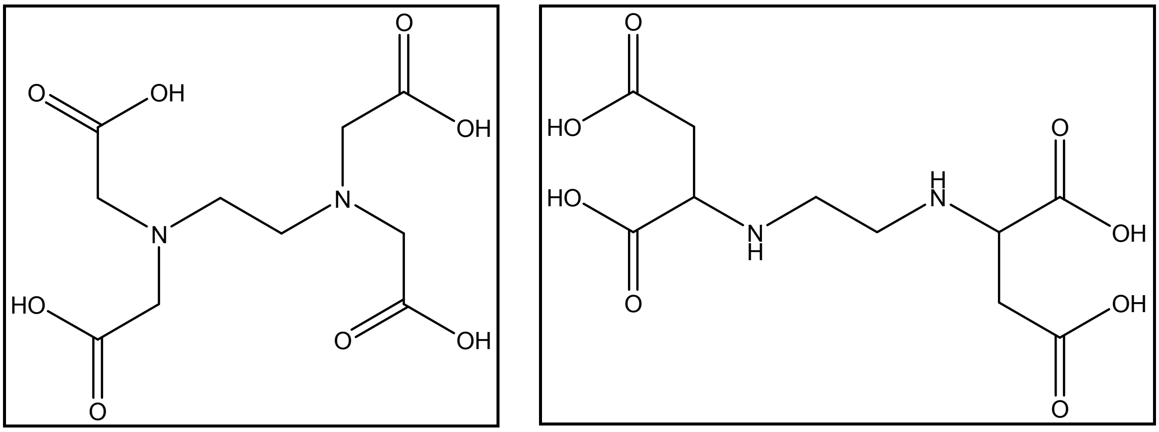


Figure 3.30 Structure of the chelating agents EDTA (left) and EDDS (right)

Initially two different EDDS concentrations (0.1 mM and 0.2 mM) were tested in stripped MWTP effluents. The stripped MWTP effluent was circulated in the reactor, peroxide was added and after homogenisation, the Fe(III)-EDDS solution was added, 15 minutes later, the reactor was illuminated. Through the use of the Fe(III) salt, no Fenton reaction takes place in the reactor. The first experiment was conducted with 0.1 mM EDDS, 50 mg L^{-1} initial H_2O_2 concentration, 5 mg L^{-1} Fe (0.1 mM) and an initial concentrations of 100 µg L^{-1} of each contaminant. The experiment (see **Figure 3.31**) had a final pH 6.4 at t_{30W} = 196 minutes and a final concentration of contaminants (sum of contaminants) of 77 µg L^{-1}. DOC evolved from initial 22 mg L^{-1} to 38 mg L^{-1} when adding EDDS at t_{30W} = -15 minutes to a final 33 mg L^{-1}. Peroxide consumption was 119 mg L^{-1}. The sum of 77 µg L^{-1} consists of 15 µg L^{-1} Antipyrine, 12 µg L^{-1} Sulfamethoxazole, 35 µg L^{-1} Atrazine, and 15 µg L^{-1} Hydroxybiphenyl. All other contaminants were degraded below their LOD before t_{30W} = 196 minutes.

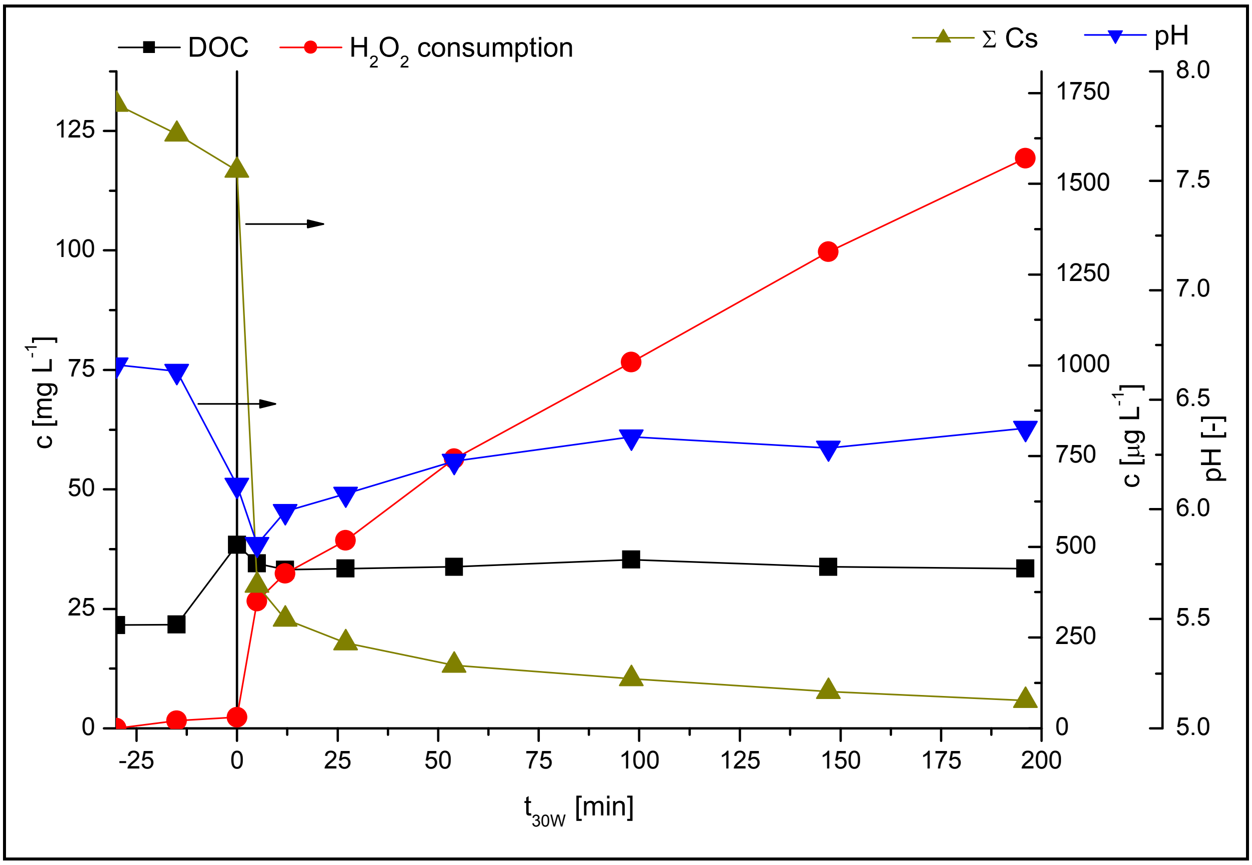


Figure 3.31 H_2O_2 consumption, DOC, pH and sum of all contaminants (ΣCs) evolution as a function of t_{30W} in stripped MWTP effluents with 0.1 mM EDDS.

Taking into account that the EDDS in itself is subject to degradation during the treatment, another experiment with 0.2 mM EDDS was performed. This experiment (see **Figure 3.32**) had a final pH of pH 7.1 at t_{30W} = 168 minutes, a final concentration of contaminants (sum of contaminants) of 61 µg L^{-1}, a final DOC of 43 mg L^{-1} (initial 20 mg L^{-1}) and consumed 92 mg L^{-1} H_2O_2. The 61 µg L^{-1} consisted of 11 µg L^{-1} Antipyrine, 5 µg L^{-1} Sulfamethoxazole, 30 µg L^{-1} Atrazine and 15 µg L^{-1} Hydroxybiphenyl. All other contaminants were degraded below their LOD before t_{30W} = 168 minutes. A direct comparison of the experiments can be seen in **Table 3.9**. Both EDDS concentrations were able to degrade the contaminants more efficient than the former experimental setups. The experiment with 0.2 mM EDDS seem to be more efficient in terms of degradation time and peroxide consumption. It should be remarked that 90% of degradation was achieved after t_{30W} = 8 minutes with 0.2 mM EDDS.

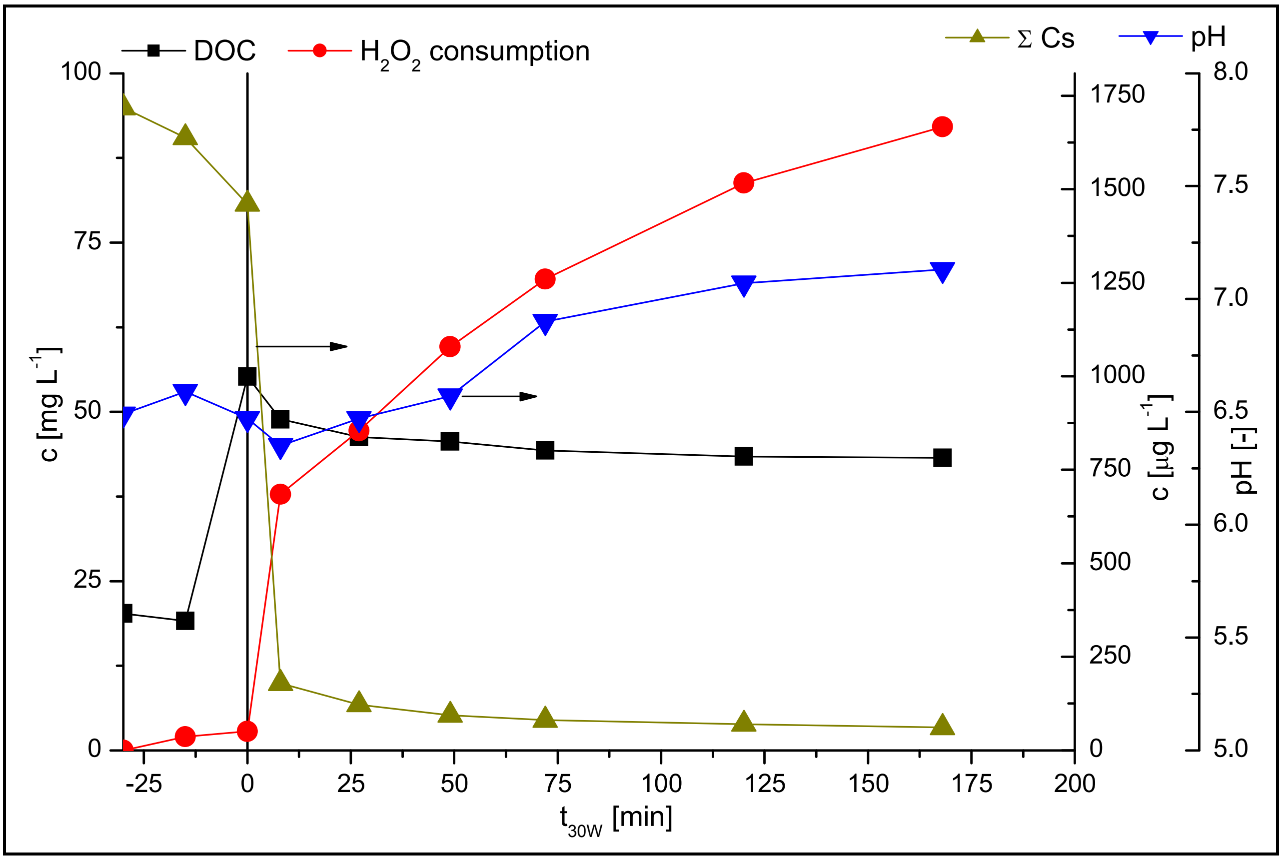


Figure 3.32 H_2O_2 consumption, DOC, pH and sum of all contaminants (ΣCs) evolution as a function of t_{30W} in stripped MWTP effluents with 0.2 mM EDDS.

Table 3.9 Comparison of the two experiments conducted with MWTP effluents and 0.1 mM and 0.2 mM EDDS and 100 µg L^{-1} initial concentration of each contaminant.

experiment	0.1 mM EDDS				0.2 mM EDDS			
t_{30W} [min]	-30	0	5	196	-30	0	8	168
pH [-]	6.7	6.1	5.8	6.4	6.5	6.5	6.3	7.1
DOC [mg L^{-1}]	22	38	35	33	20	55	49	43
consumed H_2O_2 [mg L^{-1}]	-	2	27	119	-	3	38	92
$\Sigma C/\Sigma C_0$ [%]	100	89	23	5	100	85	10	4
ΣC [µg L^{-1}]	1719	1537	394	77	1718	1460	179	61

The next step was the evaluation of the efficiency of the treatment of MWTP effluents spiked at a level of 5 µg L^{-1} of each of the 15 contaminants with 0.2 mM EDDS. The results can be seen in **Figure 3.33**. In t_{30W} = 80 minutes, the residual concentration of the contaminants is 0.5 µg L^{-1}, which consists of 0.05 µg L^{-1} Caffeine, 0.14 µg L^{-1} Antipyrine, 0.31 µg L^{-1} Atrazine, and 0.01 µg L^{-1} Hydroxybiphenyl.

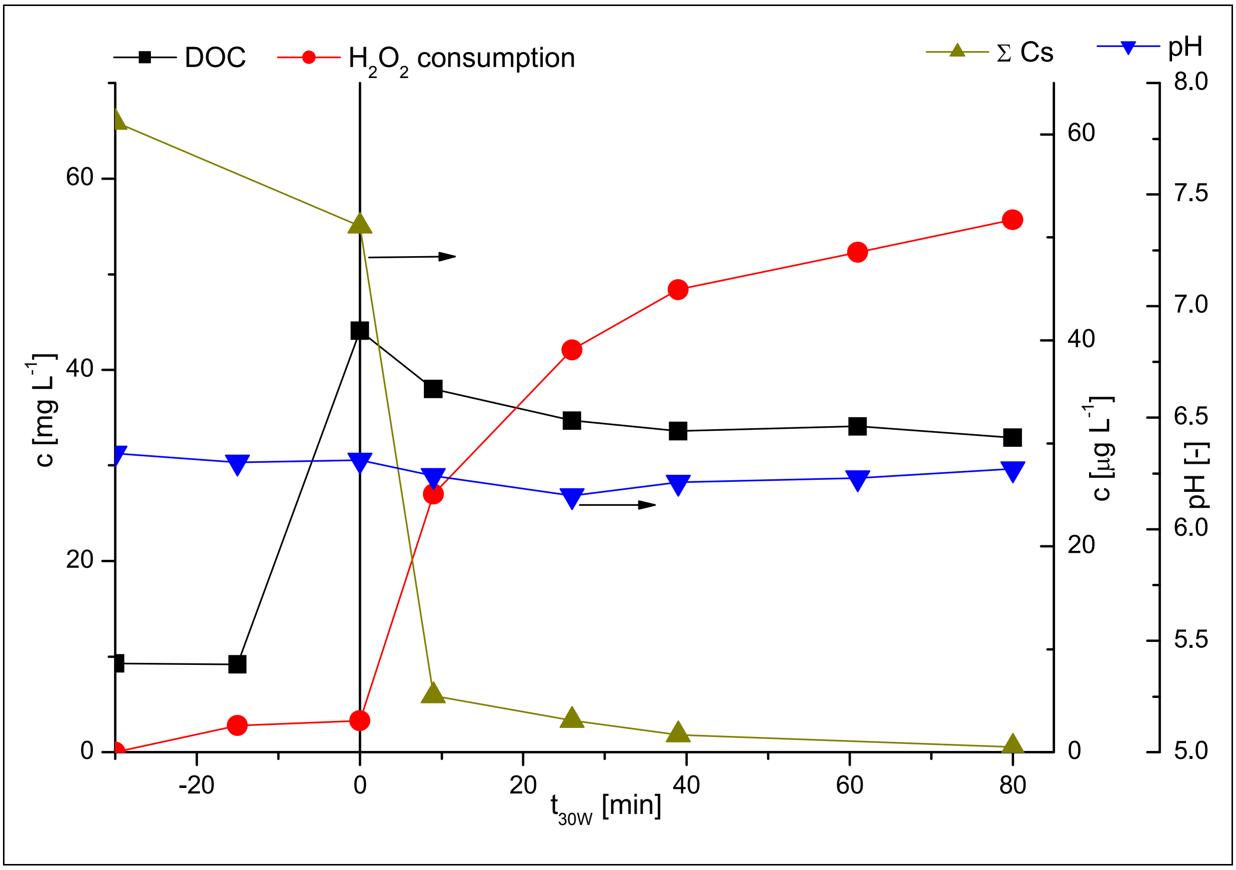


Figure 3.33 H_2O_2 consumption, DOC, pH and sum of all contaminants (ΣCs) evolution as a function of t_{30W} in stripped MWTP effluents with 0.2 mM EDDS. Initial concentration of 5 µg L^{-1} of each contaminants.

The pH during the experiment stayed around pH 6.3, H_2O_2 consumption was 56 mg L^{-1} and DOC at the end of the experiment was 33 mg L^{-1}. All other contaminants are degraded below their LOD. As this experiment was such a success (indeed 91% of degradation was achieved in $t_{30W} < 10$ minutes), this setup was tested in the presence of carbonates/bicarbonates (unstripped effluent) and if they had a negative impact onto the degradation behaviour. The results can be seen in **Figure 3.34**. The sum of the concentration of the contaminants at the end of the experiment $t_{30W} = 153$ minutes is 3 µg L^{-1}, 56 mg L^{-1} H_2O_2 was consumed, DOC concentration was 35 mg L^{-1} as opposed to 9 mg L^{-1} initial concentration, pH changed from pH 8.4 to pH 7.8. It is important to remark that 81% of degradation was achieved after less then $t_{30W} = 18$ minutes.

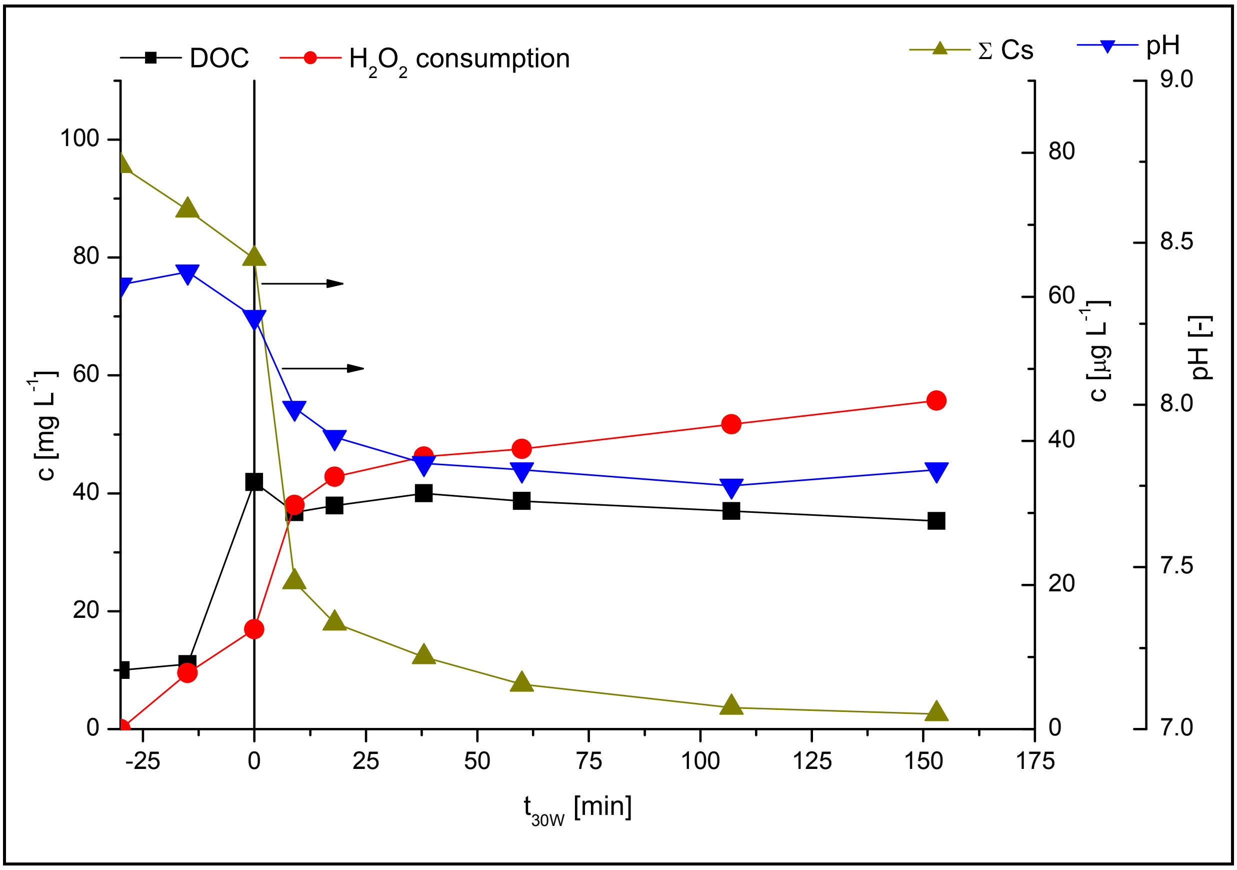


Figure 3.34 H_2O_2 consumption, DOC, pH and sum of all contaminants (ΣCs) evolution as a function of t_{30W} in unstripped MWTP effluents with 0.2 mM EDDS. Initial concentration of 5 µg L^{-1} of each contaminant.

Although the experimental time is nearly double for this experiment (t_{30W} = 153 minutes in comparison to t_{30W} = 80 minutes), the residual concentration of the individual contaminants is 0.3 µg L^{-1} Sulfamethoxazole, 0.1 µg L^{-1} Carmamazepine, 0.1 µg L^{-1} Ketorolac, 0.9 µg L^{-1} Atrazine, 0.1 µg L^{-1} Isoproturon and 0.6 µg L^{-1} Hydroxybiphenyl. It seems that the carbonate/bicarbonate content does not have that much impact onto the degradation of the contaminants when EDDS is used. The direct comparison of the two experiments can be seen in **Table 3.10**.

The results lead to the conclusion, that with the use of EDDS it is possible to degrade the spiked contaminants (both with initial concentrations of 100 and 5 µg L^{-1}) under final concentration of less than 5%. The use of 0.2 mM EDDS lead to a slightly better degradation than 0.1 mM EDDS, and it does not seem to be necessary to remove the carbonates/bicarbonates prior to treatment as shown in **Figure 3.34**.

Table 3.10 Comparison of the two experiments conducted with MWTP effluents at 0.2 mM EDDS and 5 µg L^{-1} initial concentration of each contaminant.

experiment	0.2 mM EDDS stripped				0.2 mM EDDS unstripped			
t_{30W} [min]	-30	0	9	80	-30	0	9	153
pH [-]	6.3	6.3	6.2	6.3	8.4	8.3	8.0	7.8
DOC [mg L^{-1}]	9	44	38	33	10	42	37	35
IC [mg L^{-1}]	0.5	0.7	6.2	8.0	98	99	102	103
consumed H_2O_2 [mg L^{-1}]	-	3.3	27	56	-	17	38	56
$\Sigma C/\Sigma C_0$ [%]	100	84	9	< 1	100	83	26	3
ΣC [µg L^{-1}]	61	51	5.5	0.5	78	65	20	2.1

This is a huge step forward in the modified photo-Fenton process, although it is not clear why the presence of carbonates/bicarbonates does not have a strong negative affect onto the degradation. In all 4 types of experiments the greatest degradation step happened within the first minutes of each experiment, after that the degradation was much slower. Due to the use of EDDS, the DOC of the treated water was raised significantly; this may pose problems for the reuse of the water if certain quality criteria are exceeded. But as the EDDS is an environmental friendly and biodegradable substance, one can state that the problems should be easily saved.

3.4.6 Treatment of MWTP effluents with photo-Fenton and modified photo-Fenton and evaluation of degradation of emerging and micro contaminants with LC-QqQ-MS

Parallel to the experiments conducted with the 15 model compounds, MWTP effluents were treated with photo-Fenton at pH 3, with 20 and 5 mg L^{-1} Fe, modified photo-Fenton (5 mg L^{-1} Fe) with 10 and 5 mg L^{-1} HA at neutral pH and modified photo-Fenton with 0.2 mM EDDS at neutral pH in stripped and unstripped water. H_2O_2 initial concentration was 50 mg L^{-1} and all experiments were completed regardless of irradiation within one day. These waters were analysed by LC-QTrap-MS to evaluate the degradation of the present emerging and micro contaminants.

Table 3.11 Average, minimum, maximum concentrations and frequency of detection of the contaminants.

contaminant	average [ng L^{-1}]	min [ng L^{-1}]	max [ng L^{-1}]	detected [-]
Caffeine	18527.9	331	66379	10
4-AAA	13732.0	1976	36727	10
Paraxanthine	6816.9	124	16140	10
4-FAA	6741.7	2236	9831	10
Nicotine	6524.6	136	43103	8
Cotinine	6039.4	16	18393	10
Ibuprofen	5295.0	181	12859	5
Gemfibrozil	3652.2	1291	7161	6
Furosemide	2206.8	181	7667	9
4-MAA	2090.3	93	5684	10
Hidrochlorothiazide	2046.5	314	3783	8
4-AA	1492.5	611	2542	8
Naproxen	1385.8	142	5272	9
Diclofenac	1326.9	110	3577	9
Ofloxacin	1081.5	566	2299	10
Atenolol	921.5	280	1361	10
Ranitidine	916.6	100	2675	9
Codeine	889.4	43	1603	8
Sulfamethoxazole	843.6	219	1879	10
Antipyrine	829.1	49	3503	9
Isoproturon	715.0	54	1376	2
Ciprofloxacin	705.4	192	1510	10
Acetaminophen	610.5	49	1172	2
Diuron	539.5	103	2379	6
Ketoprofen	451.6	254	735	10
Trimethoprim	331.7	26	596	10
Velafaxime	330.2	150	411	10
Azithromycin	262.7	75	405	6
Sulfapyridine	241.0	50	734	10
Pravastatin	204.9	13	505	8
Clarithromycin	195.0	109	337	10
Atrazine	180.0	6	481	6
Sulfamethazine	167.0	-	-	1
Erythromycin	164.3	70	410	8
Chlorfenvinphos	156.5	4	397	10
Citalopram HBr	149.9	82	219	10
Fenofibric Acid	132.0	38	358	10
Carbamazepine	127.7	73	201	10
Lincomycin	122.4	51	212	10
Primidone	114.6	82	138	5
Benzafibrate	111.3	12	327	9
Norfloxacin	102.0	45	186	8
Salicilic_Acid	89.0	33	211	6
Indomethacine	86.6	42	127	9
Simazine	80.3	8	248	4
Metronidazole	59.5	16	109	6
Propyphenazone	38.8	11	95	4
Sotalol	33.8	17	48	4
Propanolol	32.4	20	68	9
Metoprolol	30.0	15	38	4

Epoxide Carbamazepine	26.8	11	33	4
Mefenamic Acid	26.6	6	44	8
Famotidine	23.7	20	30	3
Mepivacaine	23.4	13	38	9
Sulfathiazole	21.3	15	30	3
Nadolol	18.6	6	29	5
Amitriptylin HCl	16.0	10	22	2
Clofibric Acid	14.6	5	28	7
Diazepan	13.0	6	21	10
Ifosfamide	12.0	-	-	1
Terbutaline	12.0	7	17	2
Fenofibrate	3.0	-	-	1

Experiments were conducted with waters obtained during the time from March 2009 until February 2011. 62 micro and emerging contaminants were detected in these waters with initial maximal concentrations between 66379 ng L^{-1} (Caffeine) and 3 ng L^{-1} (Fenofibrate). 21 of those 62 contaminants were detected in all samples, 27 out of 62 contaminants were detected between 5 and 9 times and 14 out of the 62 samples were detected between 1 and 4 times.

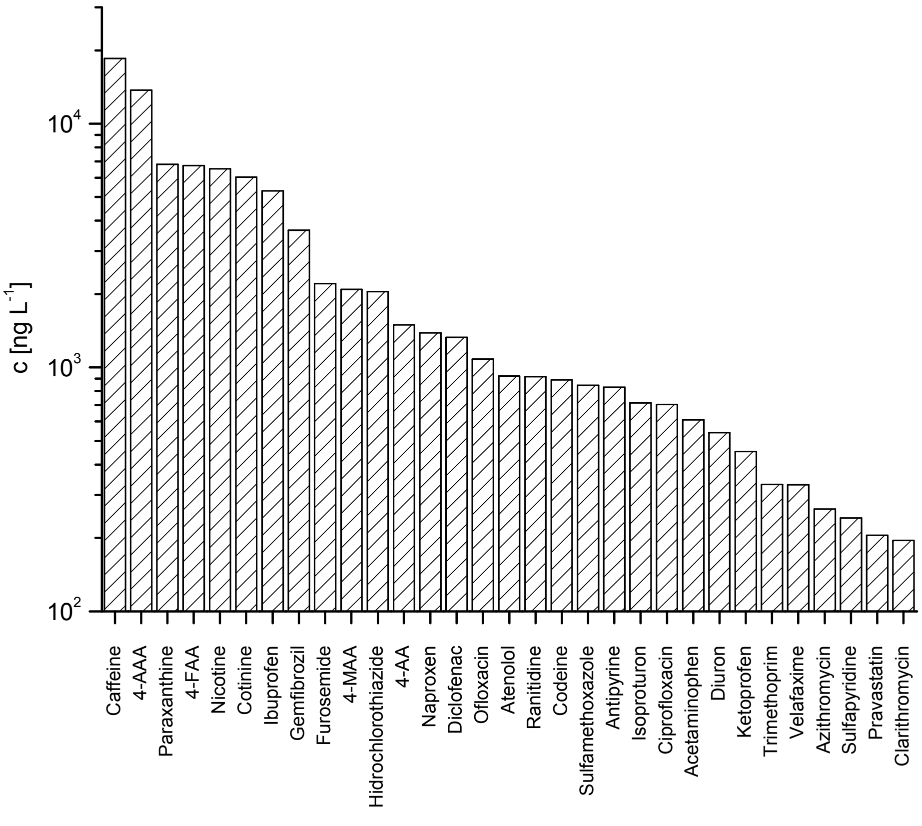


Figure 3.35 Average concentration of the detected contaminants in MWTP effluents. Concentrations between 10^4 and 10^2 ng L^{-1}.

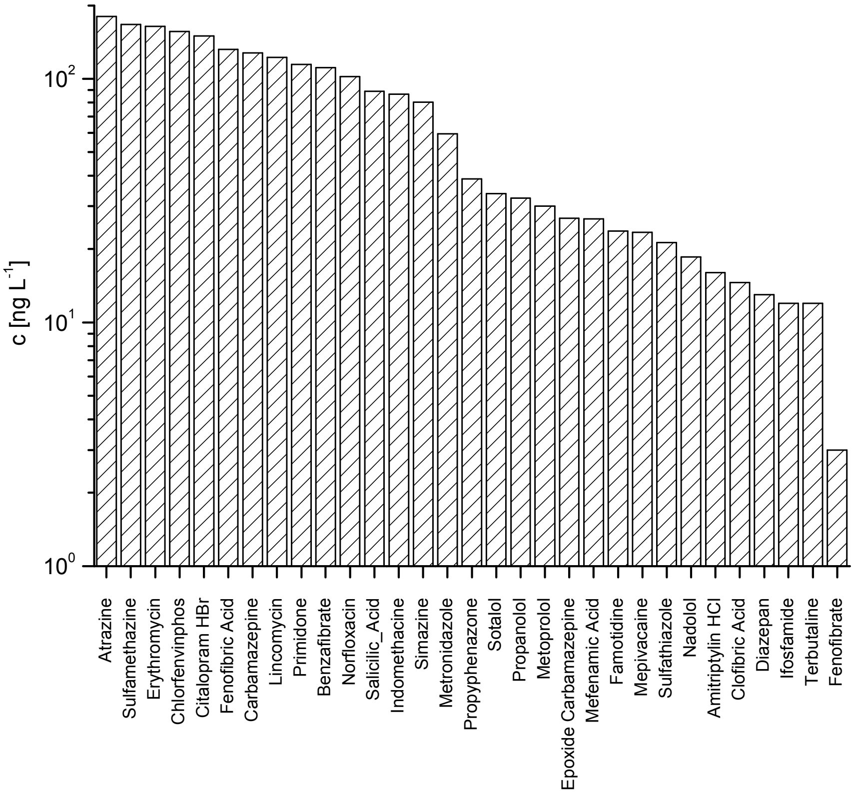


Figure 3.36 Average concentration of the detected contaminants in MWTP effluents. Concentrations between 2*10^2 and 3 ng L^{-1}. Samples were taken between March 2009 and February 2011.

The variance of the contaminants can be seen in **Table 3.11**, **Figure 3.35** and **Figure 3.36**

The MWTP effluent treated with a typical photo-Fenton at pH 3 and 20 mg L^{-1} Fe showed the baseline results, and that it is possible to degrade micro and emerging contaminants in MWTP effluents. 48 individual compounds were detected. The initial concentration of all contaminants was 81122 ng L^{-1}, which could be degraded down to 873 ng L^{-1}, a degradation efficiency of 99%, 10 contaminants were still present at the end of the experiment. The pH throughout the experiment was pH 3, DOC declined from 14 mg L^{-1} to 7 mg L^{-1}, Fe from an initial 20 mg L^{-1} to 14 mg L^{-1}, and the H_2O_2 consumed was 150 mg L^{-1}. Although the process applied was a photo-Fenton with rather harsh conditions, there were still some contaminants left at the end of the experiment at t_{30W} = 180 minutes. But it is necessary to remark that 96%

was degraded after t_{30W} = 14 minutes. The remaining contaminants with their initial and residual concentrations can be seen in **Table 3.12**. Certain substances like Atrazine have a higher resistance against oxidation, but it is unclear why for example Ofloxacin in this experiment showed an elevated resistance and in the previous experiments always was one of the first compounds which were degraded below their LOD. In general, sometimes the behaviour of certain contaminants was not very reproducible, but the overall trend of the sum of all contaminants was consistent as a function of the experimental conditions.

Table 3.12 Initial and residual concentration of the remaining 10 contaminants in MWTP effluents treated with photo-Fenton at pH 3 and 20 mg L^{-1} Fe after t_{30W} = 180 minutes.

contaminant	initial concentration [ng L^{-1}]	final concentration [ng L^{-1}]	final concentration [%]
Nicotine	1392	72	5
Caffeine	10981	38	< 0.5
4-AAA	5574	12	< 0.5
4-FAA	4777	15	< 0.5
Ofloxacin	2299	660	29
Antipyrine	4605	11	< 0.5
Atrazine	21	3	14
Chlorfenvinphos	236	22	9
Cotinine	308	32	3
Salicylic Acid	169	32	19
Σ of all contaminants*	81122	873	1

* it is the sum of all contaminants present initially in the treated water.

The next set of experiments was conducted with photo-Fenton at pH 3 and 5 mg L^{-1} Fe. The DOC changed from 26 mg L^{-1} to 17 mg L^{-1}, H_2O_2 consumption was 80 mg L^{-1} at the end of the experiment at t_{30W} = 50 minutes, Fe concentration was stable at 5 mg L^{-1}. The initial concentration of all contaminants (45 contaminants were detected) was extremely high with 179732 ng L^{-1} and declined to 5330 ng L^{-1} which derives to a degradation percentage of 97% (see **Table 3.13**). The high load of certain substances like Caffeine, Cotinine, Paraxanthine and the two metabolites 4-AAA and 4-FAA (Dipyrone metabolites) could be explained through the higher seasonal use in autumn (beginning of cold season). All other contaminants degraded below their LOD within the first minutes after irradiation.

The treatment of MWTP effluents with photo-Fenton at pH 3, 50 mg L^{-1} initial H_2O_2 concentration and both 20 mg L^{-1} and 5 mg L^{-1} Fe showed that it is possible to degrade the contaminants present in theses waters, although some of theses substances have notable residual concentrations.

Table 3.13 Initial and residual concentration of the remaining contaminants in MWTP effluents treated with photo-Fenton at pH 3 and 5 mg L^{-1} Fe after t_{30W} = 50 minutes.

contaminant	initial concentration [ng L^{-1}]	final concentration [ng L^{-1}]	final concentration [%]
Nicotine	43103	1249	3
Paraxanthine	9500	157	2
Caffeine	43660	99	< 0.5
4-AAA	36660	98	< 0.5
4-FAA	7922	19	< 0.5
Cotinine	15217	3696	24
Diuron	2379	9	< 0.5
Σ of all contaminants	179732	5330	3

When treating MWTP effluents with a modified photo-Fenton system at neutral pH with HA, the results are a little more disappointing, and again the influence of the initial and final pH can be noted. One of these experiments had an initial pH 7.1 and a final pH 6.9. The H_2O_2 consumption was 105 mg L^{-1}, DOC was stable at 18 mg L^{-1}, and the experimental time was t_{30W} = 168 minutes. 51 contaminants were detected and their initial concentration was 114231 ng L^{-1} which declined to 45857 ng L^{-1} (40% of the initial concentration). Out of the 51 contaminants 41 were still present in concentrations between 8 and 9000 ng L^{-1}.

Other experiment conducted with 10 mg L^{-1} HA had an initial pH of 6.5 and a final pH of pH 4.7. The experimental time was t_{30W} = 144 minutes, DOC was stable around 16 mg L^{-1}, 57 mg L^{-1} H_2O_2 was consumed. Out of the initial 46 contaminants detected with an initial concentration of 601749 ng L^{-1}, 14 contaminants were still present with a concentration of 9815 ng L^{-1} (1.6% of the initial concentration) at the end of the experiment (see **Table 3.14**).

Table 3.14 Initial and residual concentration of the remaining contaminants in MWTP effluents treated with modified photo-Fenton at neutral pH and 10 mg L^{-1} HA after t_{30W} = 144 minutes.

contaminant	initial concentration [ng L^{-1}]	final concentration [ng L^{-1}]	final concentration [%]
Nicotine	10068	2904	29
Atenolol	1057	18	2
Paraxanthine	13509	626	5
Caffeine	60349	2525	4
4-AAA	23148	162	0.7
4-FAA	7206	208	3
Ofloxacin	1009	28	3
Antipyrine	427	21	5
Sulfamethoxazole	1879	52	3
Simazine	446	78	18
Atrazine	5659	181	3
Chlorfenvinphos	343	212	62
Cotinine	28148	569	2
Clarithromycin	50	33	66
Σ of all contaminants	601749	7617	1

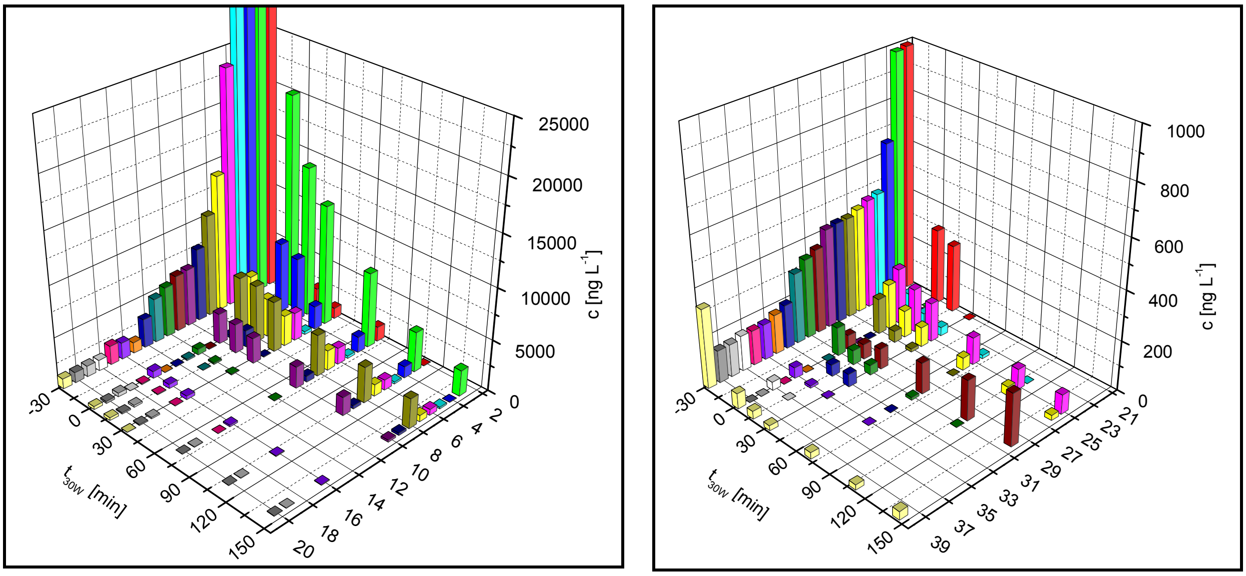


Figure 3.37 Degradation of present contaminants in MWTP effluents with modified photo-Fenton at neutral pH and 10 mg L^{-1} HA. The compound 39 is actually the sum of all contaminants with initial concentrations less than 100 ng L^{-1}.

The degradation of the 46 present contaminants can be seen in **Figure 3.37** and are ordered by concentration to make them more visible. Contaminant 39 is actually the sum of all contaminants which are present in concentrations lower than 100 ng L^{-1}

and consists of: Diazepan, Propanolol, Mepivacair, Mefenamic acid, Nadolol, Norofloxacin, Carbamazepine and Clarithromycin. Clarithromycin is still present at the end of the experiment (see **Table 3.14** and **Table 3.15**).

Table 3.15 Residual concentration of encountered contaminants in MWTP effluents treated with modified photo-Fenton at neutral pH and 10 mg L^{-1} HA after t_{30W} = 144 minutes.

number & name of contaminant		**res. concentration [ng L^{-1}]**	**number & name of contaminant**		**res. concentration [ng L^{-1}]**
1	Gemfibrozil	<LOD t_{30W} =108 min	24	Ketoprofen	<LOD t_{30W} = 69 min
2	Caffeine	2525	25	Trimethoprim	<LOD t_{30W} =108 min
3	Ibuprofen	<LOD t_{30W} =144 min	26	Antipyrine	21
4	Cotinine	162	27	Simazine	78
5	4-AAA	569	28	Erythromycin	<LOD t_{30W} = 0 min
6	Paraxanthine	626	29	Azithromycin	<LOD t_{30W} = 0 min
7	Nicotine	2904	30	Velafaxime	<LOD t_{30W} = 0 min
8	4-FAA	208	31	Chlorfenvinphos	212
9	Atrazine	181	32	Sulfapyridine	<LOD t_{30W} =108 min
10	Naproxen	<LOD t_{30W} = 0 min	33	Pravastatin	<LOD t_{30W} = 0 min
11	Diclofenac	<LOD t_{30W} = 69 min	34	Fenofibric Acid	<LOD t_{30W} = 69 min
12	4-MAA	<LOD t_{30W} = 0 min	35	Citalopram HBr	<LOD t_{30W} = 0 min
13	Hidrochlorothiazide	<LOD t_{30W} = 0 min	36	Lincomycin	<LOD t_{30W} = 0 min
14	Furosemide	<LOD t_{30W} = 0 min	37	Acetaminophen	<LOD t_{30W} = 15 min
15	Sulfamethoxazole	52	38	Indomethacine	<LOD t_{30W} = 0 min
16	Benzafibrate	<LOD t_{30W} = 69 min	39a	Diazepan	<LOD t_{30W} =108 min
17	4-AA	<LOD t_{30W} = 0 min	39b	Propanolol	<LOD t_{30W} = 0 min
18	Atenolol	18	39c	Mepivacaine	<LOD t_{30W} = 15 min
19	Ofloxacin	28	39d	Mefenamic Acid	<LOD t_{30W} = 31 min
20	Diuron	<LOD t_{30W} = 31 min	39e	Nadolol	<LOD t_{30W} = 31 min
21	Codeine	<LOD t_{30W} = 0 min	39f	Norfloxacin	<LOD t_{30W} = 0 min
22	Ranitidine	<LOD t_{30W} = 0 min	39g	Carbamazepine	<LOD t_{30W} =108 min
23	Ciprofloxacin	<LOD t_{30W} = 69 min	39h	Clarithromycin	33

The numbering of the contaminants is related to **Figure 3.37**.

One experiment was conducted with 5 mg L^{-1} HA at neutral pH. 50 contaminants were detected and the sum of the initial concentration was 111581 ng L^{-1}. The experimental time was t_{30W} = 135 minutes, pH changed from pH 7.1 to pH 6.8, DOC evolved from 32 mg L^{-1} to 28 mg L^{-1}, and 86 mg L^{-1} H_2O_2 was consumed. The residual concentration of present contaminants was 31261 ng L^{-1}, 32 contaminants were still present at the end of the experiment with concentrations between 12 and 7651 ng L^{-1} (4-AAA).

Apart from the experiment with a low final pH, all other experiments conducted either with 10 mg L^{-1} or 5 mg L^{-1} HA showed dissatisfactory results. Both quantity and residual concentration of the contaminants leave much to be desired for. The only experiment which showed more promising results had a low final pH, which is in accordance with the experiments conducted with different HA concentrations and different initial pH and the 15 model compounds (see **section 3.4.5.2**).

Two experiments were conducted with EDDS, one with stripped effluent and the other with unstripped effluent. In the MWTP effluent stripped of its carbonates/bicarbonates 43 contaminants were initially detected with an added up concentration of 43590 ng L^{-1}. This concentration declined to 2452 ng L^{-1} (6% of the initial concentration) at the end of the experiment at t_{30W} = 134 minutes, with 16 contaminants still present (see both **Figure 3.38** and **Table 3.16**). It is necessary to remark that 75% was degraded after t_{30W} = 8 minutes and 95% degradation after t_{30W} = 43 minutes.

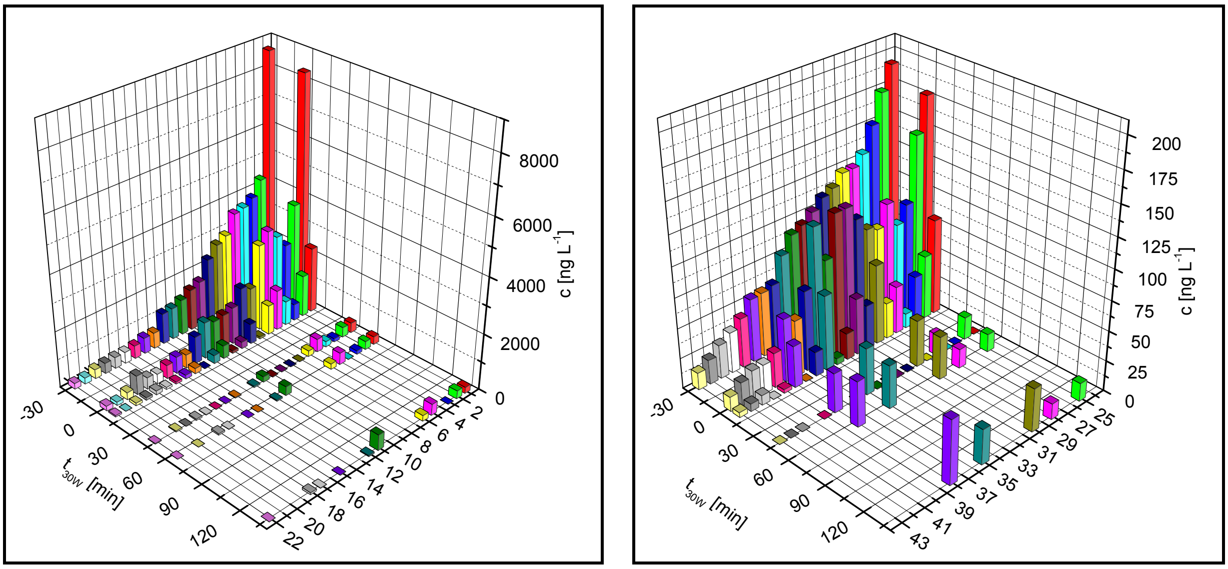


Figure 3.38 Degradation of 43 contaminants in stripped MWTP effluent treated with 0.2 mM EDDS modified photo-Fenton at neutral pH. At the end of the treatment there are 16 contaminants still present.

Table 3.16 Residual concentration of encountered contaminants in MWTP effluents treated with modified photo-Fenton at neutral pH and 0.2 mM EDDS after t_{30W} = 134 minutes.

number & name of contaminant		res. concentration [ng L^{-1}]	number & name of contaminant		res. concentration [ng L^{-1}]
1	4-FAA	217	22	Citalopram	4
2	4-AAA	288	23	Carbamazepin	539
3	Hydrochlorothiazine	<LOD t_{30W} = 134 min	24	Ciprofloxacin	<LOD t_{30W} = 43 min
4	Paraxanthine	<LOD t_{30W} = 100 min	25	Clarithromycin	15
5	Antipyrine	398	26	Diuron	<LOD t_{30W} = 43 min
6	Caffeine	195	27	4-MAA	<LOD t_{30W} = 43 min
7	Ranitidine	<LOD t_{30W} = 43 min	28	Erythromycin	13
8	Gemfibrozil	<LOD t_{30W} = 43 min	29	Lincomycin	<LOD t_{30W} = 43 min
9	Codeine	<LOD t_{30W} = 43 min	30	Atrazine	36
10	Diclofenac	<LOD t_{30W} = 43 min	31	Metronidazole	<LOD t_{30W} = 43 min
11	Sulfamethoxazole	550	32	Sulfapyridine	<LOD t_{30W} = 43 min
12	Atenolol	35	33	Fenobibric acid	<LOD t_{30W} = 43 min
13	Furosemide	<LOD t_{30W} = 8 min	34	Indomethacine	<LOD t_{30W} = 43 min
14	Ofloxacin	<LOD t_{30W} = 100 min	35	Cotinine	29
15	Trimethoprim	6	36	Benzafibrate	<LOD t_{30W} = 43 min
16	Ketoprofen	<LOD t_{30W} = 43 min	37	Isoproturon	<LOD t_{30W} = 8 min
17	Velafaxime	8	38	Nicotine	53
18	Chlorfenvinphos	<LOD t_{30W} = 100 min	39	Propanolol	<LOD t_{30W} = 43 min
19	Naproxen	<LOD t_{30W} = 43 min	40	Mefenamic acid	<LOD t_{30W} = 8 min
20	Azithromycin	<LOD t_{30W} = 100 min	41	Clofibric acid	<LOD t_{30W} = 43 min
21	Pravastatin	<LOD t_{30W} = 8 min	42	Mepivacaine	<LOD t_{30W} = 43 min
			43	Diazepan	<LOD t_{30W} = 43 min

The numbering of the contaminants is related to **Figure 3.38**.

DOC changed from initial 9 mg L^{-1} to 48 mg L^{-1} (after EDDS adding) and to a final 36 mg L^{-1}, pH did not change significantly (pH 6.5 to pH 6.3), while H_2O_2 consumption was 71 mg L^{-1}.

The experiments conducted with MWTP effluent containing carbonates/bicarbonates had slightly worse degradation behaviour than the previous one, but this was to be expected. The experimental time was t_{30W} = 126 minutes, due to the elevated buffer capacity of the water the pH stayed in the range of pH 7.6, DOC evolved from initial 14 mg L^{-1} to 47 mg L^{-1} after EDDS adding and to a final 40 mg L^{-1}, while H_2O_2 consumption was 55 mg L^{-1}. There were 46 contaminants detected with an added up concentration of 34441 ng L^{-1} which declined to 2597 ng L^{-1} (8% of the initial concentration), 25 contaminants were still present at the end of the experiment (see **Figure 3.39** and **Table 3.17**).

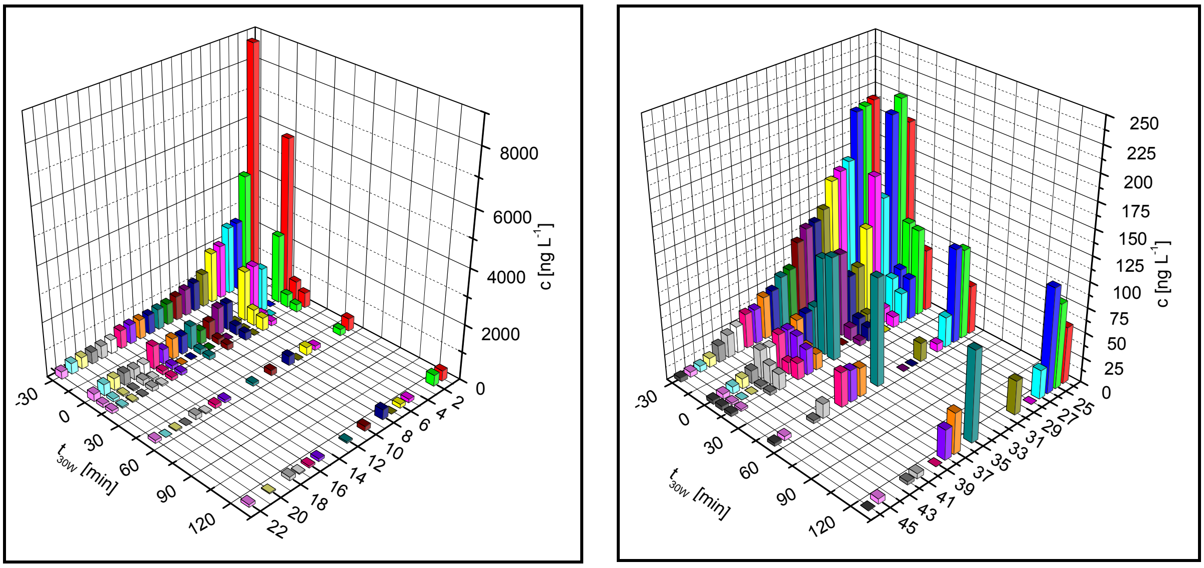


Figure 3.39 Degradation of 46 contaminants in unstripped MWTP effluent treated with 0.2 mM EDDS modified photo-Fenton at neutral pH. At the end of the treatment there are 25 contaminants still present.

Table 3.17 Residual concentration of encountered contaminants in unstripped MWTP effluents treated with modified photo-Fenton at neutral pH and 0.2 mM EDDS after t_{30W} = 126 minutes.

number & name of contaminant		residual concentration [ng L^{-1}]	number & name of contaminant		residual concentration [ng L^{-1}]
1	4-FAA	372	24	Erythromycin	57
2	Gemfibrozil	399	25	Azithromycin	85
3	4-AA	<LOD t_{30W} = 0 min	26	Carbamazepine	105
4	Ranitidine	<LOD t_{30W} = 16 min	27	Clarithromycin	29
5	4-AAA	126	28	Lincomycin	<LOD t_{30W} = 126 min
6	Hydrochlorothiazide	137	29	Sulfapyridine	<LOD t_{30W} = 16 min
7	4-MAA	<LOD t_{30W} = 126 min	30	Diuron	34
8	Sulfamethoxazole	354	31	Metronidazole	<LOD t_{30W} = 53 min
9	Furosemide	<LOD t_{30W} = 8 min	32	Fenofibric acid	<LOD t_{30W} = 53 min
10	Paraxanthine	164	33	Indomethacine	<LOD t_{30W} = 8 min
11	Diclofenac	<LOD t_{30W} = 8 min	34	Pravastatin	<LOD t_{30W} = 8 min
12	Ofloxacin	51	35	Cotinine	90
13	Naproxen	<LOD t_{30W} = 8 min	36	Norfloxacin	<LOD t_{30W} = 8 min
14	Codeine	<LOD t_{30W} = 8 min	37	Chlorfenvinphos	41
15	Atenolol	103	38	Nicotine	30
16	Ibuprofen	71	39	Salicylic acid	<LOD t_{30W} = 126 min
17	Trimethoprim	36	40	Propanolol	<LOD t_{30W} = 8 min
18	Caffeine	133	41	Benzafibrate	5
19	Ketoprofen	<LOD t_{30W} = 53 min	42	Diazepan	3
20	Velafaxime	37	43	Clofibric acid	<LOD t_{30W} = 8 min
21	Ciprofloxacin	<LOD t_{30W} = 53 min	44	Mefenamic acid	<LOD t_{30W} = 8 min
22	Antipyrine	100	45	Atrazine	5
23	Citalopram	30	46	Mepivacaine	<LOD t_{30W} = 126 min

The numbering of the contaminants is related to **Figure 3.39**.

The degradation of the present contaminants in MWTP effluents containing carbonates/bicarbonates is less satisfactory than in stripped effluents, but it was shown that this kind of process has its potential to degrade present contaminants.

A direct comparison of the experiments showed (see **Figure 3.40**) that the typical photo-Fenton at pH 3 with either 5 or 20 mg L^{-1} Fe has the best degradation efficiency, followed by modified photo-Fenton with EDDS in stripped effluent and in unstripped effluent. The modified photo-Fenton experiments conducted with HA had worse efficiencies and depended strongly on the initial pH.

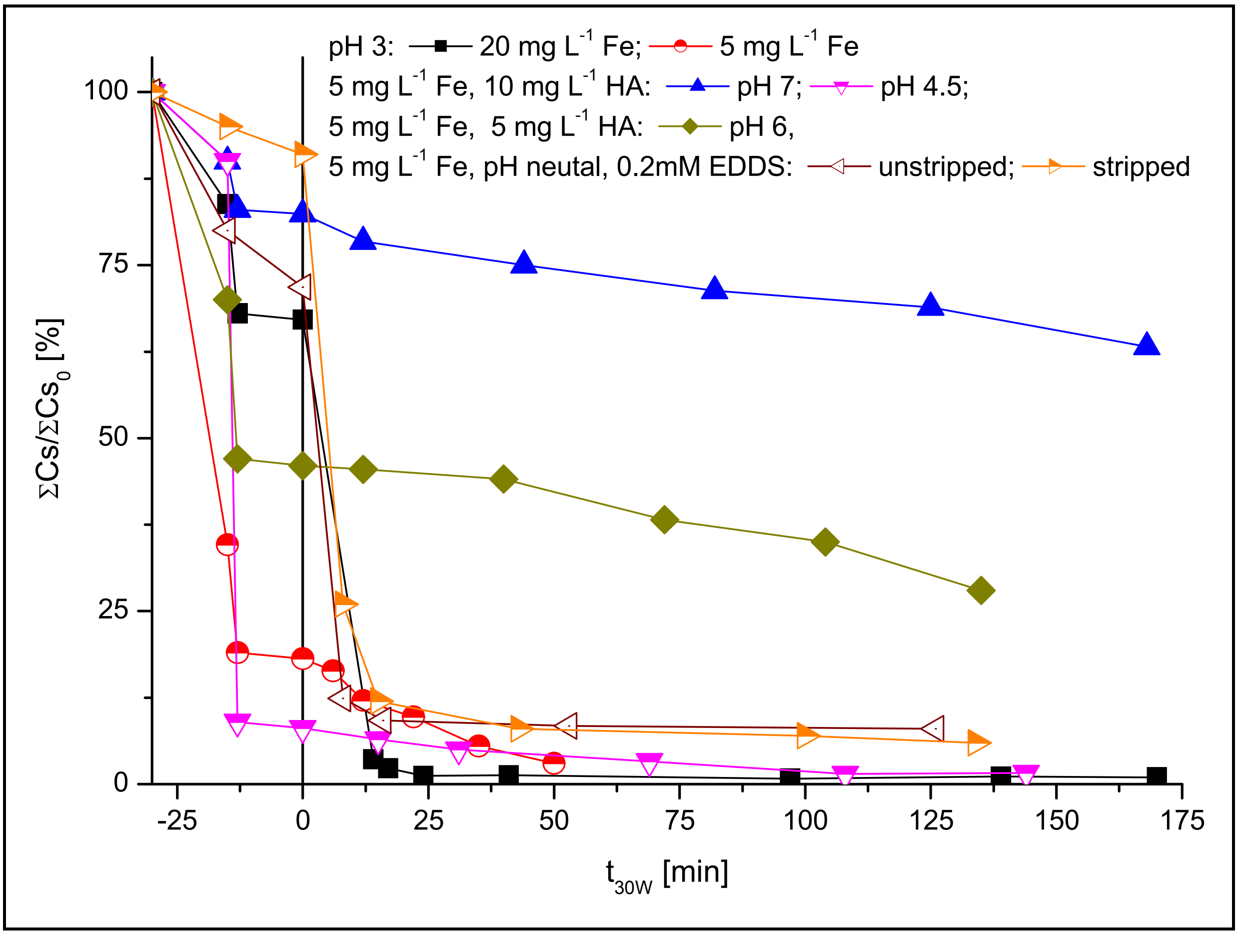


Figure 3.40 Direct comparison of the degradation efficiency of different photo-Fenton and modified photo-Fenton processes.

3.5 Toxicity evaluation with *V. fisheri*

It is a known fact that the oxidation and degradation of certain organic contaminants can produce substances which have an elevated toxicity compared to their mother compounds [Meyer and Thurman, 1996; Boxall et al, 2004; Jiao et al, 2008]. So if treated waters are reused, it should be guaranteed that this water does not contain toxic substances, or even is more toxic than before treatment. Three different waters were tested

i) simulated effluent water with an initial concentration of the 15 contaminants at 100 µg L^{-1} each,

ii) real effluent water with an initial concentration of 100 µg L^{-1} each, and

iii) real effluent water with an initial concentration of 5 µg L^{-1} each and 10 mg L^{-1} HA.

All experiments were conducted at neutral pH. In all experiments three different steps (marked 1, 2 and 3 in **Figure 3.41**) can be described. The initial toxicity (20-30% inhibition) of the simulated effluent (**Figure 3.41**) may be due to the mixture of pollutants as well as to the formation of intermediates during the Fenton reaction in the dark.

The negative inhibition observable in real effluents in step 1 (both 100 µg L^{-1} and 5 µg L^{-1} spiking) can be explained by the nutrients and salt content in the effluent waters. In all three experiments when photo-Fenton started up, the degradation of parent compounds formed more toxic degradation products, which in some cases (100 µg L^{-1}) drastically increase the inhibition (step 2). In the case of real effluents spiked at 5 µg L^{-1} levels, the inhibition was so low, due to the lower initial concentration of the contaminants and probably because of the presence of humic acid which can balance the increasing toxic effect. In the last step (3) inhibition for simulated effluent decreased, while the inhibition for real effluent (spiked at 100 µg L^{-1}) is quite constant, probably because toxic organic degradation products take longer to mineralise. The inhibition for the real effluent water spiked at 5 µg L^{-1} and treated with 10 mg L^{-1} HA even showed activation (negative inhibition), meaning that at lower initial concentrations no toxicity remained at the end of the treatment. No statements can me made about chronic toxicity of micro and emerging contaminants and their degradation products. However, it has to be emphasised that experiments at 5 µg L^{-1} are so close to reality and that this water contained both the spiked 15 contaminants and contaminants already present in the MWTP effluents. Under these circumstances, toxicity results were so conservative and excluded concerns about toxicity evolution by the photo-Fenton treatment.

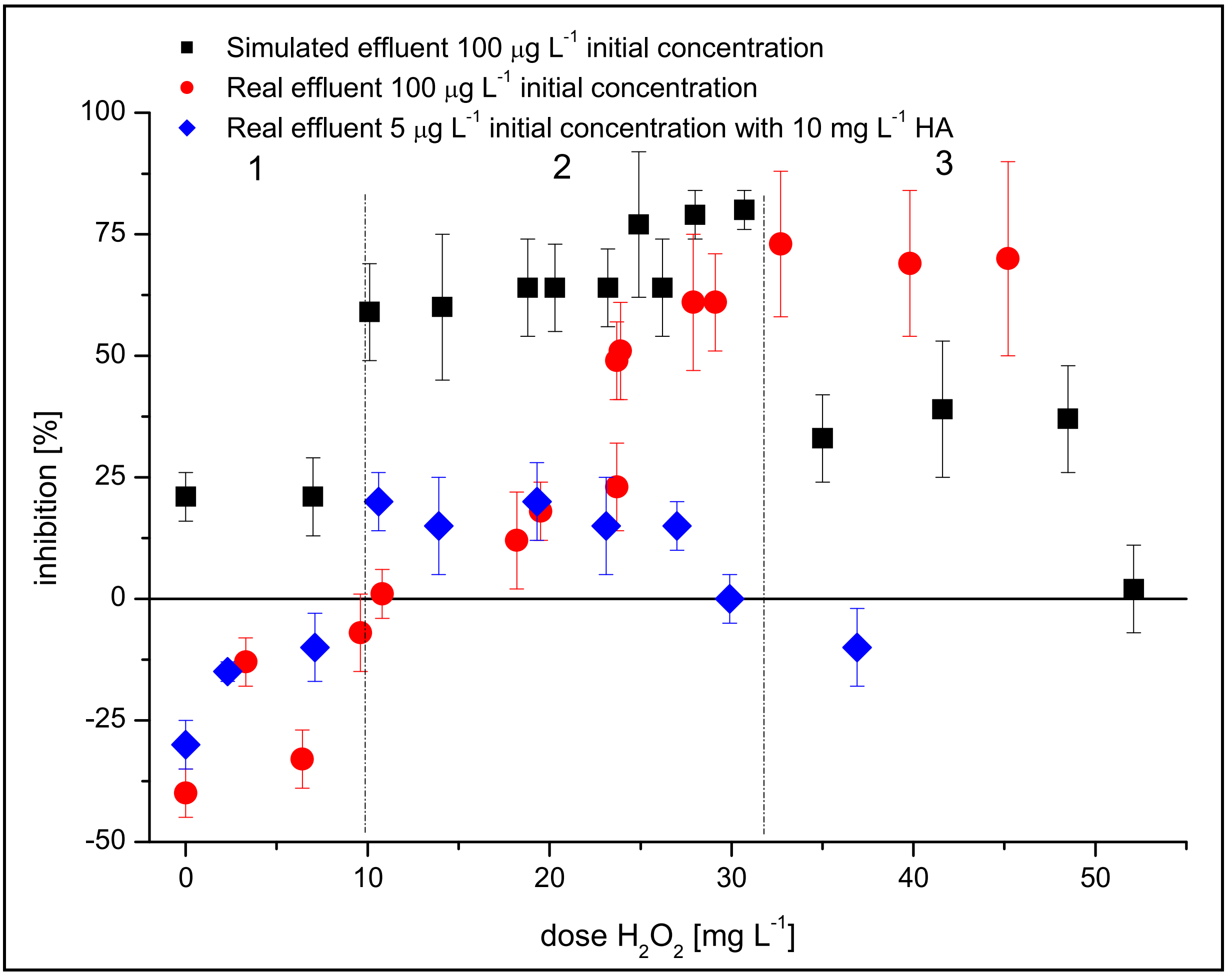


Figure 3.41 Toxicity test of simulated and real effluent water at 100 µg L^{-1} initial concentration of 15 contaminants and of real effluent water at 5 µg L^{-1} initial concentration of the 15 contaminants treated with mild photo-Fenton at neutral pH.

3.6 Evaluation of the disinfection of the treated waters with different photo-Fenton systems

Another aim of this work was the evaluation of the disinfection of the treated waters. Water suitable for reuse for irrigation has to fulfil certain criteria on the microbiological load (bacteria, parasites, etc). Samples were taken and the bacterial load (total bacteria and *coliforms*) and the change in colony forming units (CFU) during the experiments were evaluated. All results shown in this section were obtained during experiments with real MWTP effluents.

In the first experiments which were conducted with a typical photo-Fenton at pH 3, it could be observed that the low pH in itself had a significant impact on the bacterial population. The coliforms were inactivated through the low pH (detection limit <1 CFU mL^{-1}), and the CFU count for the general bacteria population is below 1 CFU mL^{-1} after t_{30W} = 13 minutes as can be seen in **Figure 3.42**. Initial microorganism load was $5.54*10^4 \pm 3.5*10^3$ CFU mL^{-1} for total bacteria and $5*10^4 \pm 2*10^3$ CFU mL^{-1} for coliforms. But it was not the intention of this work to use conventional photo-Fenton for disinfection as to acidify MWTP effluents is not a suitable process. The limits established by the Spanish legislation [Spanish real decree] (see **Table 3.18**) should also be taking into account when interpreting disinfection results, as not all waters for reuse have to have a coliforme count of CFU < 1 mL^{-1}.

Table 3.18 CFU limit according to the Spanish royal decree 1620/2007

limit CFU 100 mL^{-1}	use
0	residencial zones, water for private gardens
100	agriculture, fresh vegetables
200	parks, sport fields, golf courses, industrial use
1000	pasture irrigation for animals, trees, fish farms
10000	oilseeds, industrial use

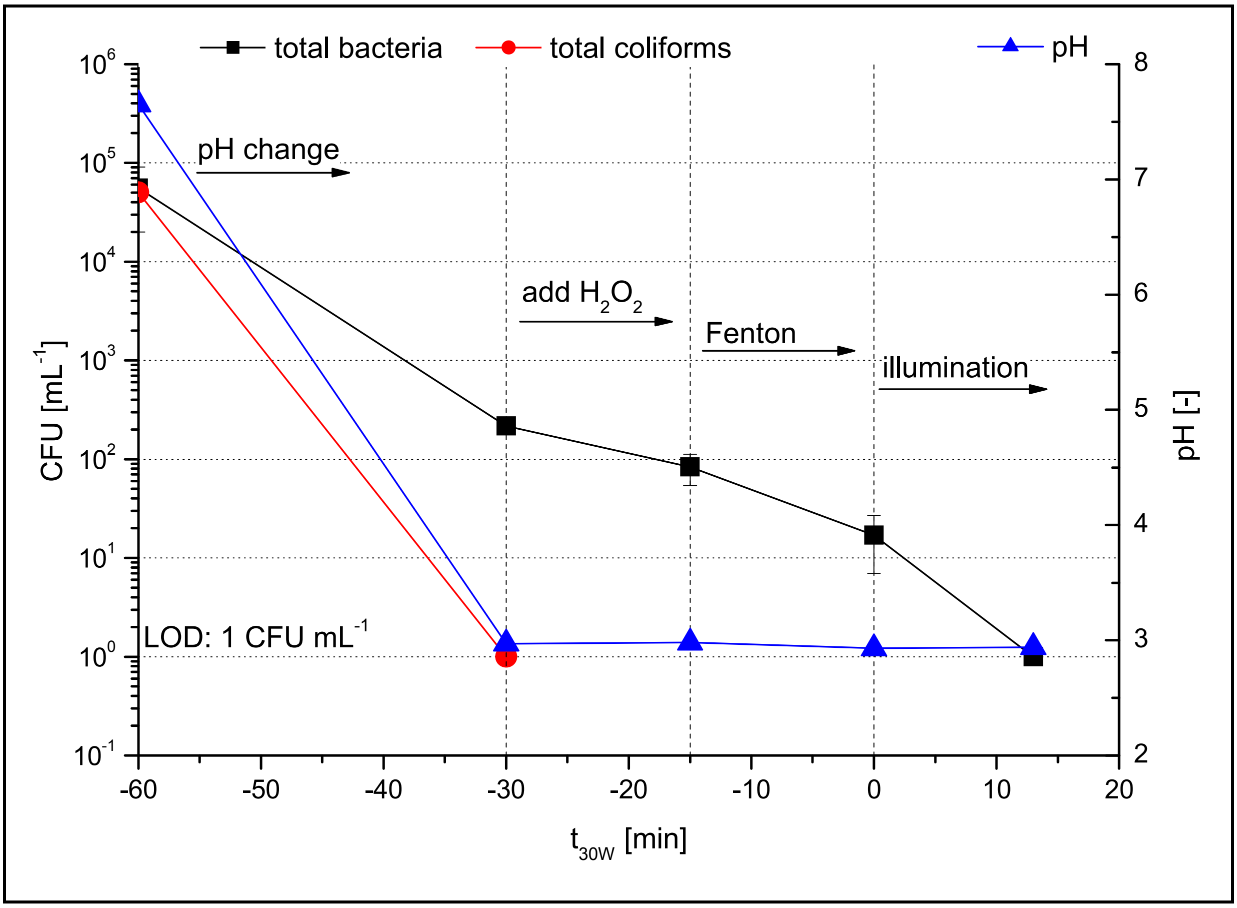


Figure 3.42 Disinfection of MWTP effluents with typical photo-Fenton at pH 3.

The disinfection of MWTP effluents with photo-Fenton at neutral pH showed a slightly different behaviour, as the pH does not have that much influence (see **Figure 3.43**). While the degradation of the contaminants in MWTP effluents at neutral pH is incomplete (see **Figure 3.16**), the disinfection is quite successful [Malato et al, 2009]. The coliforms were inactivated within the first minutes of the experiment (t_{30W} = 12 minutes) and declined from $2.1*10^5 \pm 1*10^4$ CFU mL^{-1} to <LOD, while the total bacteria count (initial $3*10^5 \pm 5*10^4$ CFU mL^{-1}) reaches the level of <LOD only after t_{30W} = 50 minutes. In general it can be stated that coliforms are more sensitive to both low pH and photo-Fenton.

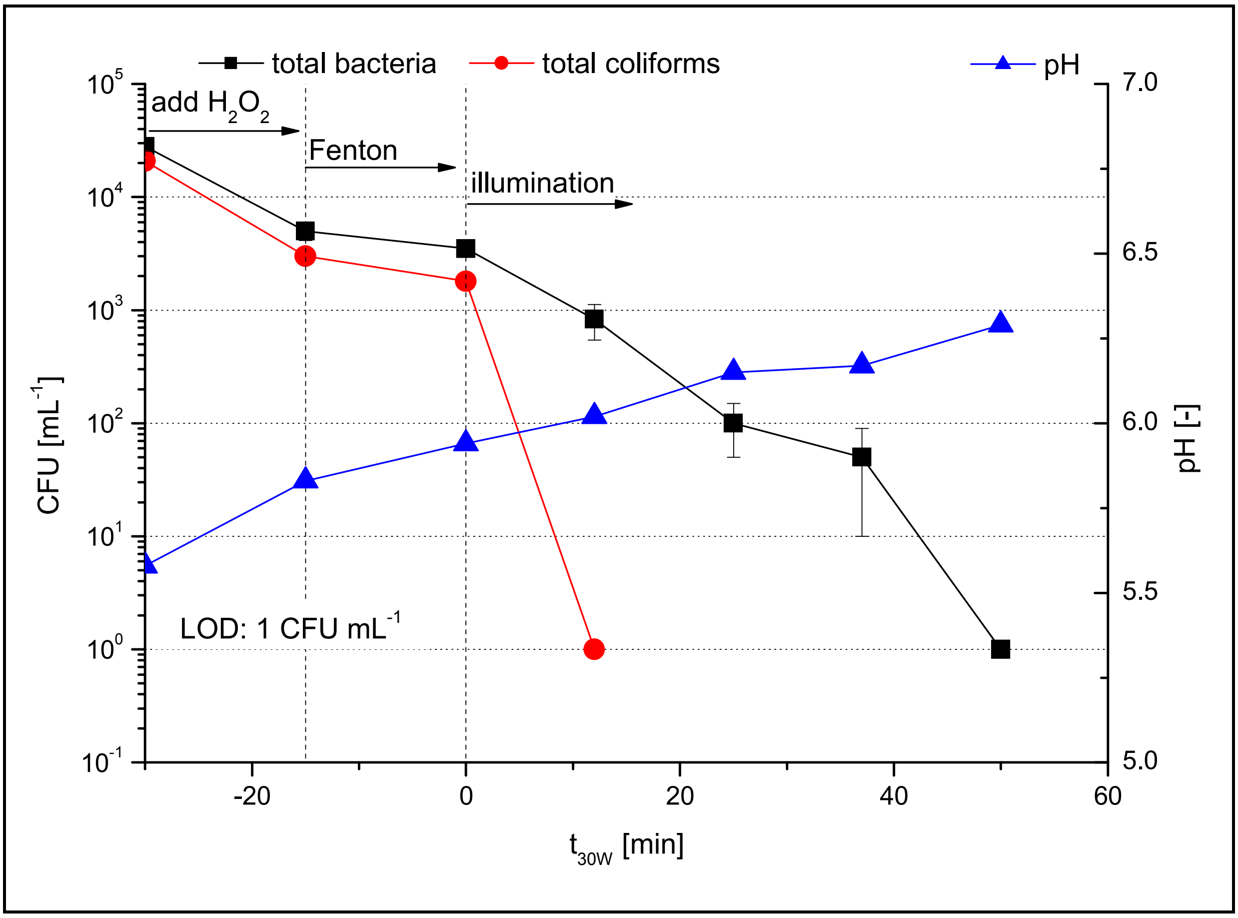


Figure 3.43 Disinfection of MWTP effluents with photo-Fenton at neutral pH.

It is a well known fact that peroxide can migrate into the cells and with the iron present in the cells can cause a Fenton reaction, which leads to cell death [Spuhler et al, 2010], but it was also demonstrated that illumination (photo-Fenton process) produces a dramatic increase in CFU disappearance.

Disinfection depended strongly on the treated water when working with photo-Fenton at neutral pH. It was not possible to reach LOD in all tested waters, and with higher pH, the disinfection rate diminished significantly. It was observed that in some cases the CFU of both coliforms and total bacteria reached a final plateau. All experiments (see **Figure 3.44**) were conducted with a mild photo-Fenton at neutral pH (pH 6-8), 5 mg L^{-1} Fe, and 50 mg L^{-1} initial H_2O_2. Although LOD could not be reached, CFU mL^{-1} declined in all experiments for a minimum of 3-log degrees for both total bacteria and total coliforms as can be seen in **Table 3.19**. As mentioned before, the disinfection of the treated waters e.g. inactivation of bacteria present depended on the particular water, but the trend seemed to be an incomplete inactivation, as final CFU counts in most cases did not reach the LOD of 1 CFU mL-1.

Table 3.19 Initial and final CFU mL-1 of treated MWTP effluents with photo-Fenton at neutral pH

	initial CFU [mL-1]		final CFU [mL-1]	
	total bacteria	**total coliforms**	**total bacteria**	**total coliforms**
pH 8	6.3*10⁴ ± 1.8*10⁴	5.8*10⁴ ± 2*10⁴	92 ± 29	10 ± 5
pH 7	1.5*10⁵ ± 1.3*10⁴	7.0*10⁵± 1.5*10⁴	50 ± 10	20 ± 5
pH 6	8.0*10⁵ ± 1.5*10⁵	4.3+10⁵± 1*10⁵	180 ± 20	50 ± 5

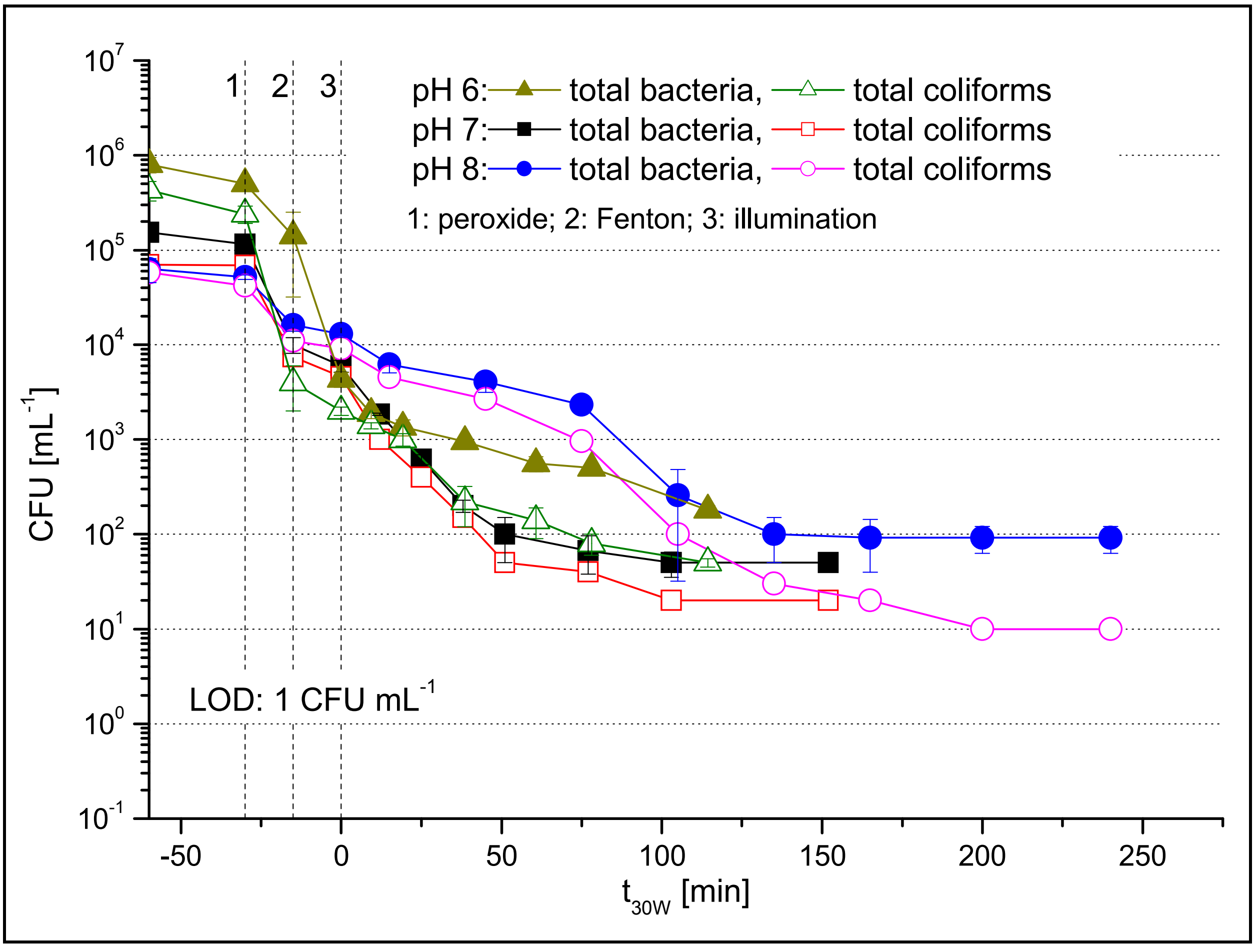


Figure 3.44 CFU count of total bacteria and total coliforms in MWTP effluents during mild photo-Fenton at neutral pH.

The experiments conducted with 10 mg L-1 HA as a complexing agent showed similar results and confirmed the efficiency when working at a slightly lower pH than pH 7. The CFU count of total bacteria for the experiment with final pH 5 declined from initial 2.9*10^5 ± 5.1*10^4 CFU mL^{-1} to final 158 ± 86 CFU mL^{-1}, total coliforms declined from initial 8.6*10^4 ± 8.5*10^3 CFU to <LOD (see **Figure 3.45**).

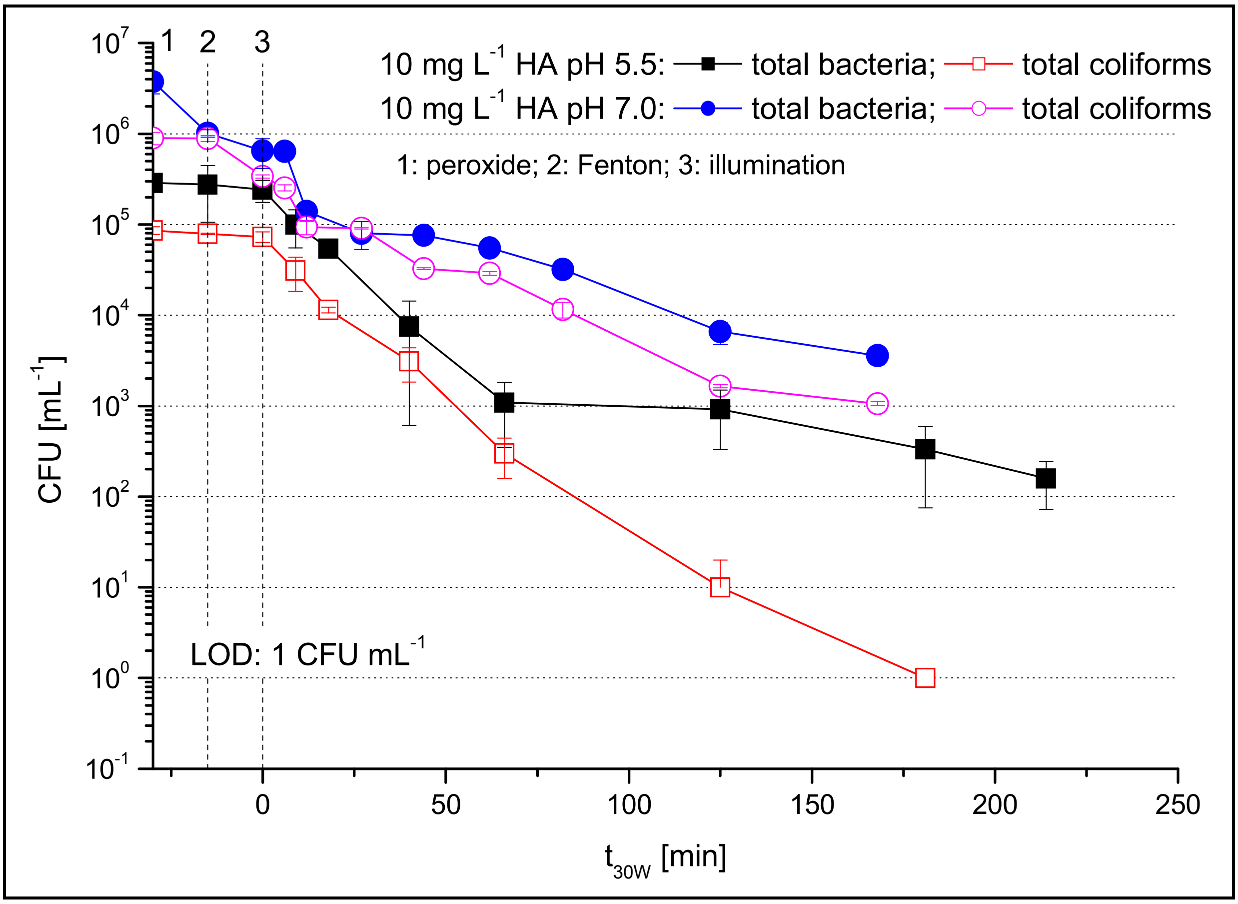


Figure 3.45 CFU count of total bacteria and total coliforms in MWTP effluents during mild photo-Fenton at neutral pH with HA as complexing agent.

Some experiments conducted with HA even showed a re growth of present bacteria after an initial decline. This can be explained through the mild conditions of the photo-Fenton and the presence of humic acids, which act as nutrients for the bacteria. Several experiments conducted with 10 mg L^{-1} HA showed the re growth of both total bacteria and total coliforms as can be seen in **Figure 3.46**. The pH during these experiments was in neutral pH range (between pH 6 and pH 7), initial H_2O_2 concentration was 50 mg L^{-1}. CFU count never reached LOD and even increased after a minimum to the end of the experiment.

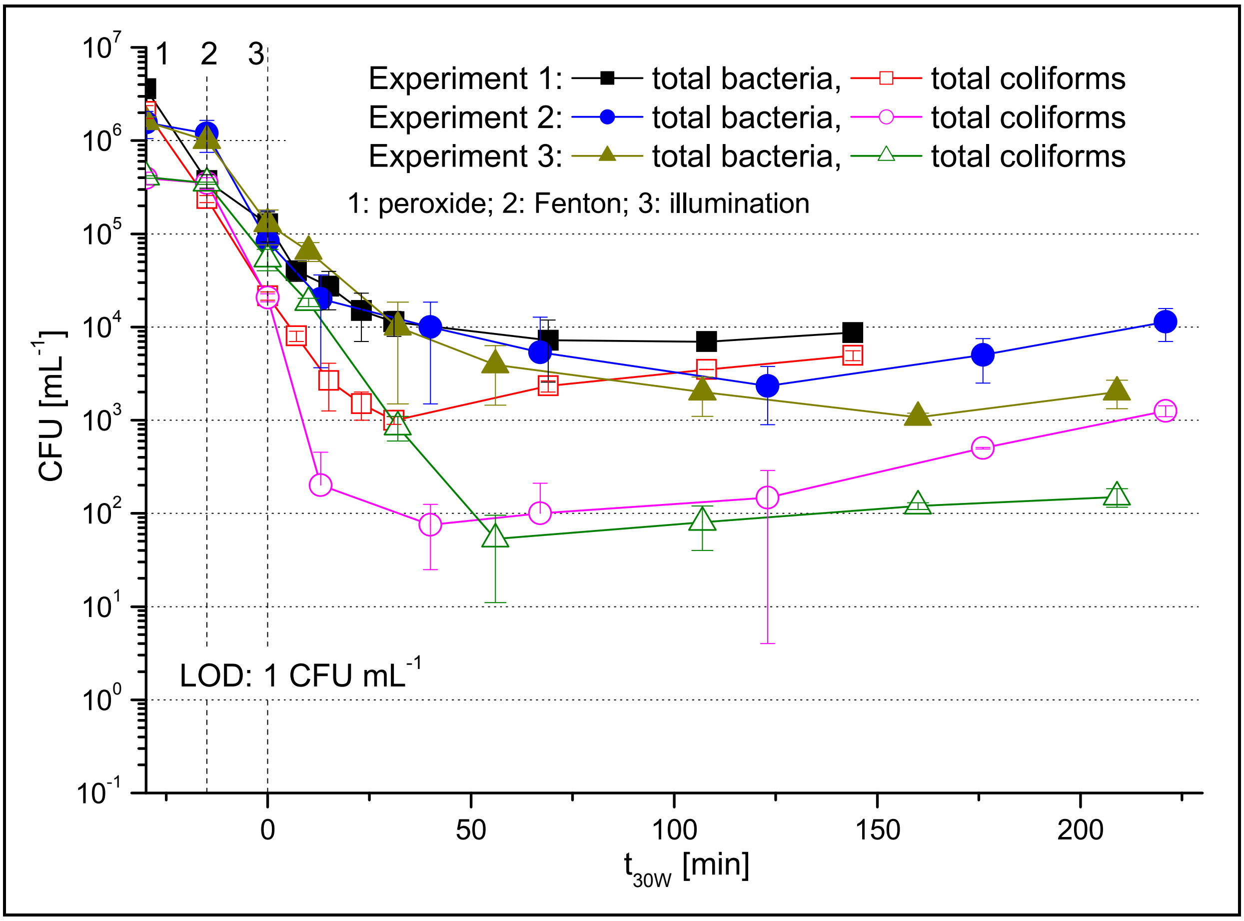


Figure 3.46 CFU count (total bacteria and total coliforms) of several experiments conducted in MWTP effluents with mild modified photo-Fenton with 10 mg L^{-1} HA under similar conditions at neutral pH.

All the experiments conducted with HA showed unsatisfactory results concerning disinfection. This led to the conclusion that even in the case of total degradation of present contaminants, the disinfection was incomplete and thus the process was not suitable for the treatment of MWTP effluents if the desired outcome is disinfected water. Although the residual CFU count did not reach the LOD, it should be noted that there was a decline of at least 2-log degrees and in most cases was higher than 3-log degrees.

The experiments conducted with EDDS showed better disinfection results, but apart from one experiment (0.2 mM EDDS in unstripped MWTP effluent) where the total coliforms count reaches LOD, the CFU count of all other experiments does not reach LOD (see **Figure 3.47**).

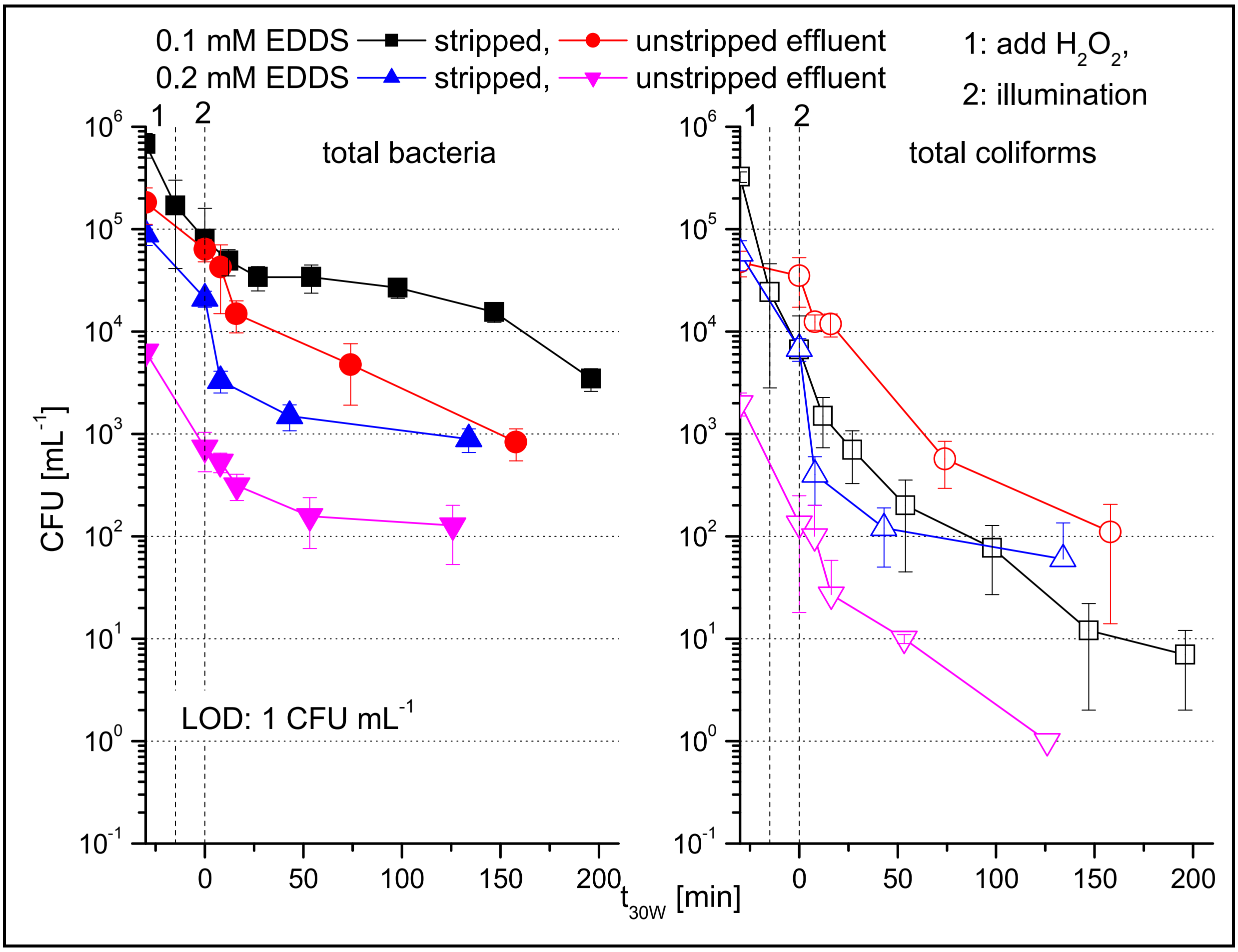


Figure 3.47 CFU count (total bacteria and total coliforms) of several experiments conducted in MWTP effluents with mild modified photo-Fenton with 0.1 and 0.2 mM EDDS in both stripped and unstripped MWTP effluents at neutral pH.

Although the results when working with EDDS were more promising than working with HA, they are still not satisfactory. The reason for this may again lay in the mild conditions of the applied process. While capable of degrading most of the present contaminants (see **Figure 3.38**) when working in stripped effluents and 0.2 mM EDDS, this process only inactivated present bacteria by 2-log degrees (total bacteria count) and 3-log degrees (total coliforms). The unstripped effluent suffers less than 2-log degrees inactivation for total bacteria count and 3-log degrees for the total coliforms. But due to the fact that the initial concentration of total coliforms in this effluent is < 10^4 CFU mL^{-1}, this result has to be looked upon cautiously. In general, it can be concluded that disinfective ability of photo-Fenton with Fe complexing agents

(EDDS and HA) was not severe enough to overcome the growth induced by high organic load.

All in all it can be said that apart from the typical photo-Fenton at pH 3, all other experiments deliver unsatisfactory results regarding the disinfection. The neutral pH and the use of complexing agents like humic acid or EDDS do not provide severe enough conditions to inactivate the present bacteria (total bacteria and total coliforms) although in all experiments there was at least a decline of 2-log degrees in CFU mL^{-1}. These results are rather disappointing and have to be investigated further, as this work was not focused on the disinfection of treated MWTP effluents.

4 Conclusions

This work focused on a development of a mild solar photo-Fenton process for the treatment of MWTP effluents. The two combined facts of water scarcity in Spain and the low percentage of water reuse demands for a new source of water for the irrigation of fields, parks, golf courses etc. One water source which is easy to access is effluent water from MWTPs. But this water still contains micro and emerging contaminants and therefore has to be treated by a tertiary process like solar photo-Fenton to remove these substances. The impact of theses substances as single compounds and as a complex mixture onto aquatic life, plant life and as a consequence onto human health is until now not fully investigated nor understood. But as these substances are xenobiotic, bioaccumulative and as a general rule have adverse effects onto organisms, it is crucial that they have to be removed from the water bodies.

Photo-Fenton is known to be an effective process for the elimination of contaminants in water, but its drawback is the necessity of low pH and relatively high amounts of iron. Therefor, a modified photo-Fenton was investigated which focused on the use of low iron concentrations (below 5 mg L^{-1}), neutral pH and low initial H_2O_2 concentrations (50 mg L^{-1}).

15 compounds were selected as model contaminants. They were selected out of a list of more than 80 substances (pharmaceuticals, drugs, hormones, pesticides, synthetic fragrances etc.) which have been found in MWTP effluents and covered not only a wide range of substances but also a wide range of behaviour in aqueous matrices and stability towards oxidation through advanced oxidation processes.

It was shown throughout the work that it was possible to use a simple UPLC/DAD system to quantify the selected 15 contaminants through a fast and reliable method. This method was able to detect and quantify these compounds at levels between

100 µg L^{-1} (initial concentration) and their LOQs/LODs without any further sample manipulation. By using solid phase extraction (SPE) the LOQ was pushed down to levels of 200 ng L^{-1} which allowed to work with initial concentrations of 5 µg L^{-1} of each contaminant to simulate conditions closer to reality. Due to matrix interferences some of the model compounds were impossible to detect, but at least 12 out of the 15 compounds could be detected at all times.

The initial concentration of 100 µg L^{-1} of each contaminant in the case of spiked waters was low enough, to optimize the photo-Fenton process under realistic conditions and high enough to follow the degradation behaviour of the selected contaminants by an easy, reliable and rapid chromatographic method.

A HPLC-QqQ-MS system was used only to state the general methodology developed with spiked waters under real conditions when treating real MWTP effluents.

4.1 Specific conclusions

4.1.1 Treatment of different waters spiked with model compounds

Due to the complexity of real MWTP effluents, the first experiments with the model contaminants were done in demineralised water. To have a base line for comparing, experiments were done with normal photo-Fenton at pH 3. This lead to the conclusion, that it is possible to degrade the present contaminants down to negligible concentrations.

The behaviour in simulated fresh water (moderately hard fresh water) showed the negative impact of present carbonate/bicarbonate species. These species act as potent radical scavengers and the degradation of the selected contaminants was incomplete. The experiments conducted in simulated fresh water without carbonates/bicarbonates were complete within reasonable time. This lead to the first significant results:

i) that it is necessary to remove carbonates/bicarbonates from the waters prior to treatment.

ii) the type of acid (hydrochloric acid or sulphuric acid) used did not have a significant impact onto the degradation behaviour.

The use of simulated effluent water without carbonates/bicarbonates showed yet again a slower degradation than in simulated fresh water. All compounds but Atrazine and Triclosan could be degraded either below their LOD or below 10% of the initial concentration within reasonable time. The use of different peroxide concentrations showed that lower initial peroxide concentrations led to a much lower peroxide consumption.

Experiments conducted with an initial concentration of 5 µg L^{-1} of each of the 15 contaminants and a pH which maintained at pH 6 showed that iron is precipitated and the process stops after an initial Fenton phase. The results of these experiments also showed that MWTP effluents are quite variable in their composition and that small changes in the initial pH can have a huge impact onto the final pH and as a consequence onto the photo-Fenton process. The results obtained led to the search of chelating agents, which maintain the iron in solution and at the same time make it available for the photo-Fenton process.

The use of oxalic acid showed promising results, but due to the low buffer capacity of the stripped effluent water, the final pH at the end of the process was below pH 4. The use of humic acids augments the degradation of the contaminants in stripped effluent water. It can be concluded, that the degradation behaviour depends greatly on the initial pH and the treated water. Lower initial pH usually resulted in a pH around pH 4 with an augmented degradation of the present contaminants. Higher humic acid concentration resulted in a slower degradation and higher pH. The humic acid enhanced photo-Fenton process worked, although slower than and not as satisfactory as normal photo-Fenton at pH 3, but it still delivered good results.

The use of influent (raw sewage) water as a source of humic substances and other complexing agents delivered disappointing results as the degradation of the used contaminants was incomplete.

The use of the chelating agent EDDS showed promising results. Not only did the pH stay in the neutral range during the experiments but the degradation of present contaminants was almost complete for both initial concentrations of 100 and 5 µg L^{-1}. The optimal EDDS concentration was 0.2 mM EDDS, which derived to a Fe:EDDS ration of 1:2. Even in unstripped effluent water, the degradation of the model compounds was widely enhanced. This means that it is possible to treat effluents without stripping, which can lead to big cost reduction. One disadvantage is the elevated DOC content of the treated waters. But it should be taking into account that EDDS is a nontoxic and biodegradable substance.

4.1.2 Toxicity evaluation with V. fisheri

The evaluation of toxicity conducted with the marine bacteria *V. fisheri* showed in some cases (initial concentration of the 15 contaminants 100 µg L^{-1} each) an elevated toxicity. In the case of initial concentration of 5 µg L^{-1} of each contaminant, no toxicity could be detected at the end of the experiment with real MWTP effluents.

4.1.3 Treatment of unspiked MWTP effluents

Photo-Fenton with the harshest conditions (20 mg L^{-1} Fe and pH 3) delivered good results. The experiments conducted with 5 mg L^{-1} Fe and at pH 3 delivered excellent results, with a residual concentration of < 3% of the initial concentration.

The treatment of effluents with both 10 and 5 mg L^{-1} HA at neutral pH showed a degradation of some contaminants which were present in these waters, but there were still numerous contaminants present at the end of the experiment. Both quantity and residual concentration of the contaminants leave much to be desired for.

The experiments conducted with EDDS in stripped and unstripped effluents showed promising results. Although the degradation of the contaminants was not complete, there was a huge decline in concentration of these contaminants to less than 10% of the initial concentration. One peculiarity of the experiments conducted with EDDS was the depletion of concentration within the first minutes after irradiation and the fact that the presence of carbonates/bicarbonates did not seem to have a huge negative impact onto the degradation. This led to the conclusion, that the EDDS enhanced photo-Fenton may have another contribution to the degradation apart from $HO^\bullet$ radicals.

4.1.4 Disinfection of MWTP effluents

Complete disinfection of the tested MWTP effluents could only be achieved through the standard photo-Fenton at pH 3. The low pH on itself was able to inactivate coliforms and the Fenton and photo-Fenton process inactivated the rest of the bacterial population within the first minutes after irradiation. All other processes conducted at neutral pH and either with humic acid or EDDS showed a decline in bacterial activity (at least 2-log degrees), but almost never reached the LOD of 1 CFU mL^{-1}. In some cases while using HA, a re growth of bacteria could be observed. The EDDS enhanced photo-Fenton did not lead to a total inactivation of bacteria, but showed better results than the HA enhanced photo-Fenton. As a general observation, coliforms showed lower resistance towards harsh conditions (pH, H_2O_2, Fenton and photo-Fenton).

4.2 Conclusions and Outlook

It can be stated that the development of a mild photo-Fenton process for the treatment of MWTP effluents can be considered a success. It was shown that it is possible to modify the photo-Fenton with different complexing agents at neutral pH. Of the tested agents, EDDS showed the most promising results and worked in

MWTP effluents containing carbonates. None of the tested photo-Fenton systems were able to degrade all contaminants present in MWTP effluents below their LOD, although some were more effective than others (photo-Fenton pH 3 > EDDS enhanced photo-Fenton pH neutral > HA enhanced photo-Fenton pH neutral). Apart from the photo-Fenton at pH 3, no total disinfection could be achieved.

The process has to be further studied but it should be emphasised that it is able to reduce the concentration of micropollutants (as sum of all contaminants) below 6% in t_{30W}= 134 minutes using less than 71 mg L^{-1} H_2O_2.
Disinfection was not completed below the LOD of 1 CFU mL^{-1}, but some uses for the required limit for coliforms is lower than 100 CFU mL^{-1}.

Further studies are necessary in order:

i) to find a better solution than EDDS for working at neutral pH,
ii) to determine if applications of photo-Fenton to retentates of membrane processes could be more efficient than direct treatment of effluents
iii) to determine why certain contaminants are more recalcitrant to the treatment than others
iv) to develop CPCs for better absorbtion of solar radiation when using low Fe loadings

to evaluate properly the use of the treated effluent for crop irrigation etc.

5 References

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Glossary

AOP	Advanced Oxidation Processes
BOD_5	Biological Oxigen Demand
CAS	Chemical Abstract Service
COD	Chemical Oxygen Demand
CPC	Compound Parabolic Collector
DAD	Diode Array Detector
DOC	Dissolved Organic Carbon
ECs	Emerging Contaminants
EC_{50}	Effective Concentration which causes a 50% mortality rate
EQS	Environmental Quality Standards
GC-MS	Gas Chromatography coupled with Mass Spectrometry
HPLC	High Performance Liquid Chromatography
IC	Inorganic Carbon
IC	Ionic Chromatography
LC-MS	Liquid Chromatography coupled with Mass Spectrometry
LC-QqQ-MS	Liquid Chromatography with triple Quadrupole Mass Spectrometry
LC-TOF-MS	Liquid Chromatography coupled with Time OF Flight Mass Spectometry
mM, M	milli mol, mol
MWTP	Municipal Wastewater Treatment Plant
PAH	Polycyclic Aromatic Hydrocarbons
PCP	Personal Care Products
PFCs	Perfluorinated Compounds
PHS	Priority Hazardous Substances
POPs	Persistent Organic Pollutants
PS	Priority Substances
Q-TRAP	Linear quadrupole Ion Trap

SHE	Standard Hydrogen Electrode
SPE	Solid Phase Extraction
TC	Total Carbon
UPLC	Ultra Performance Liquid Chromatography
UV	Ultra Violet
WDF	Water Framework Directive

Annex

The results of this investigation have been published in four articles at the moment of writing.

KLAMERTH N., Miranda N., Malato S., Agüera A., Fernández-Alba A.R. Degradation of emerging contaminants at low concentrations in MWTPs effluents with mild solar photo-Fenton and TiO_2. *Catalysis Today*, **144**, 124-130, 2009.

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Furthermore during the four years at the Plataforma Solar de Almería in the Water Detoxifiaction and Disinfection group, some collaboratory work with external investigators has been carried out, which resulted in other publications:

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