Photocatalytic Water Treatment

**Substrate-Specific Activity of
Titanium Dioxide**

Joana Romão

**PHOTOCATALYTIC WATER
TREATMENT:
SUBSTRATE-SPECIFIC ACTIVITY OF
TITANIUM DIOXIDE**

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Photocatalytic water treatment: substrate-specific activity of TiO_2

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TITANIUM DIOXIDE**

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Chapter 1

General Introduction

1.1 Background

One of the biggest challenges of the 21st century is the availability of clean and affordable water.¹ One third of the world's population suffers from shortages of this most precious substance for life and one billion people have no direct access to clean drinking water.²⁻⁴ Water scarcity is an increasing problem due to demographic growth, industrialization, climate change, depletion in natural water reservoirs and environmental pollution.^{1,5-7} The significant improvement in living standards since the industrial revolution and consequent intensification of agriculture and manufacturing, increases the demand for freshwater constantly.^{1,8-10} At the same time, as a result of these activities, every year, the quantity and diversity of chemical contaminants increases in (waste)water.¹¹⁻¹⁴

The presence of new contaminants in water resources^{15,16} lead the European Union Commission Services to create a new directive (2000/60/EC) on Environmental Quality Standards,¹⁷ in order to ensure the quality of drinking water and to control preservation of the environment. Looking at the existent technologies for water and wastewater treatment, the most common methods are described in Table 1.^{1,18}

Table 1. Description of current methods for water treatment.

Methods	Characteristics
Adsorption	Transfer of contaminants to a different phase without degradation. The efficiency is limited by surface area and there is a lack of selectivity.
Membranes	Physical barrier based on size exclusion, commonly associated with high energy consumption (when pressure is the driving force). The performance is highly dependent on the type of membrane material.
Chemical Oxidation	Molecular structural modification of contaminants by an oxidizing agent (i.e. chlorine, ozone). Formation of mutagenic and carcinogenic by-products may bring additional risk for human health.
Biological treatments	Decomposition of organic compounds through living systems (i.e. bacteria, algae, plants). Usually safe and low cost, the disadvantage is the high production of sludge when compared to the volume of water treated.

Inefficiency of these technologies to eliminate new emerging compounds has been claimed, while in particular levels of pharmaceutical, pesticide-related and endocrine compounds, increase in wastewater and ground water and are currently present (depending on location) in a concentration range of a few ng L⁻¹ to even mg L⁻¹.^{15,16}

Advanced oxidation processes (AOPs) based on *in situ* generation of highly reactive species ($\text{HO}^\bullet$, $\text{O}_2^{\bullet-}$) can mineralize organic contaminants into relatively harmless compounds (CO_2 , H_2O).¹⁸ AOPs include chemical oxidation (O_3 , Fenton reagents), photochemical oxidation (Ultraviolet-UV/ O_3 , UV/ H_2O_2) and heterogeneous photocatalysis (UV/ TiO_2).^{19,20} Among those, photocatalysis is attractive, because of the possibility of generating powerful reactive hydroxyl radicals ($E^0=2.8$ eV) with photon energy, without the need of additional chemicals.²¹ The mild operation conditions of temperature and pressure and the use of an inexpensive and chemically stable catalyst (TiO_2) are particularly attractive for complete mineralization of contaminants and by-products. Interest in pre- and post-processing of wastewater using sunlight has increased and so has the importance of photocatalysis technology. Two pilot plants for wastewater treatment using TiO_2 in a slurry reactor were built in New Mexico (USA) and Almeria (Spain), however the low photonic yield and low efficiency under visible light, makes this technology difficult to commercialize.^{20,22} These limitations have been focus of numerous studies in order to improve the photocatalyst, reactor design and light efficiency, but also more fundamental studies in order to fully understand the mechanistically important pathways of mineralization of organic compounds have received attention.²³⁻²⁵

1.2 Principals of Heterogeneous Photocatalysis

Heterogeneous photocatalysis is a discipline that covers several types of reactions, such as oxidation, dehydrogenation, hydrogen transfer and metal deposition, among others.²⁶ In photocatalysis, light, if of sufficient energy, will activate the catalyst and stimulate chemical reactions on the surface, such as oxygen reduction and oxidation of organic compounds. The overall process in photocatalysis can be described by five independent steps:^{26,27}

1. Mass transfer of reactants from the bulk phase to the catalyst surface
2. Adsorption of the reactants
3. Photocatalytic reaction in the adsorbed state:
 - a. Photon absorption by the catalyst
 - b. Formation of electrons (e^-) and holes (h^+)
 - c. Photo-generated charges are transferred to the catalyst surface and induce reaction
4. Product desorption
5. Mass transfer of the products from the interfacial region to the bulk fluid.

Next, steps number 3 and 4 in the photocatalytic decomposition mechanism will be discussed in more detail. The first aspect of step number 3 is the activation of a semiconductor (SC) material (TiO_2 , ZnO , WO_3) by absorption of a photon with energy greater or equal to the band gap ($h\nu \geq E_{bg}$). This will lead to charge separation of electrons (e^-) and holes (h^+) by the promotion of an e^- from the valence band to the conduction band (1.1).^{28,29}

TiO_2 is the catalyst that has been most intensively investigated and is the most promising catalyst for practical applications.³⁰ The electron-hole pairs formed participate in several oxidation or reduction reactions at the catalyst surface with the adsorbed species (1.2-1.5), leading to organic (R) compound decomposition.^{28,29}

The protonation of $\text{O}_2^{\cdot -}$ leads to the formation of a hydroperoxy radical ($\text{HO}_2^{\cdot}$) and consequently to hydrogen peroxide H_2O_2 (Equation 1.6-1.8). These species act as electron scavengers avoiding recombination and improving the reaction rate.^{28,29}

Heterogeneous photocatalysis oxidizes organic compounds into their corresponding intermediates until carbon dioxide and water are formed, if the reaction conditions (photocatalyst, light intensity, illumination time, etc) are chosen accordingly.²⁸ Another pathway for the electron-hole pair is the recombination which happens when the concentration of e^- and h^+ in the catalyst is high.²⁷ Fig.1 illustrates all the reactions on the photocatalyst surface described previously.

Fig. 1. Schematic illustration of the photocatalytic mechanism in the presence of a water contaminant.

1.3. Photocatalysts

An ideal photocatalyst is photostable, chemically inert and available at an affordable price.³¹ There are several semiconductors that have been reported as promising for water treatment, such as TiO_2 , ZnO , WO_3 , CdS , MoS_2 , BiVO_4 ,^{23,32} TiO_2 is by far the most used.^{30,33} The overall photocatalytic activity of TiO_2 is determined by its crystalline structure, surface area, density of surface hydroxyl groups and adsorption/desorption characteristics. These parameters will be discussed in more detail in the next paragraphs.

TiO_2 has three common crystalline polymorphs: anatase, rutile and brookite. The crystalline phase brookite is known to be inactive for water treatment, while studies have been made intensively in order to determine the most active crystalline phase, anatase or rutile.³⁴⁻³⁷ Ryu and Choi, tested eight commercial TiO_2 samples (Anatase, Rutile and mixtures of both phases) in slurry reactors for the mineralization of several organic compounds (phenol, organic acids, amines, dyes, etc.). For each compound the optimum degradation rate was found for different TiO_2 samples. In many cases Degussa P25 (80% Anatase, 20% Rutile) was found to be the optimum catalyst, but this is not possible to predict *a priori*.³⁵

As mentioned previously, the surface hydroxyl group concentration has been recognized to play an important role in the photodegradation process. Furthermore, as the concentration of hydroxyl groups on the catalyst surface (anatase) increases, there is a positive effect on the reaction rate. It has been proven that OH groups have a determinant role in the photocatalytic mechanism.^{38,39} Regarding surface area, this is usually closely related to a higher concentration

of active sites which allows a large amount of species to be adsorbed and to react, thus promoting the surface reaction rate.^{40,41}

Co-catalyst

Several structural modifications of TiO_2 have been made in order to suppress electron and hole recombination. One of the most common methods is the addition of noble metals, such as Pt, Au, or Pd, which can trap the electrons due their relatively low Fermi levels, as shown in Fig.2. The co-catalyst leads to a longer lifetime of the charge carriers and enhances formation of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals inducing further redox reactions.⁴²⁻⁴⁵ For example, in hydrogen production studies, Pt- TiO_2 has been applied with success, showing significant efficiency improvement when compared to TiO_2 .^{42,46,47} In this situation platinum provides active sites for hydrogen production.^{48,49}

Fig. 2. Schematic illustration of the role of a co-catalyst in a photocatalytic mechanism.

1.4. Photocatalysis: reactors and operational parameters

Reactors

Undoubtedly, reactor design plays a determinant role to obtain high photocatalytic efficiency. In photocatalysis the catalyst surface needs to be illuminated as efficiently as possible. In general, reactors can be classified into two types, depending on the photocatalyst configuration: suspended or immobilized (Fig.3).^{50,51} Using photocatalyst nanoparticles in suspension, *slurry reactors* are applied (Fig.3.a), *immobilized film reactors* have the photocatalyst immobilized on a substrate (Fig.3.b).^{50,51} In slurry reactors, larger surface area of the photocatalyst is available for reaction, limited by the UV light penetration depth in the solution. The necessity of an additional (filtration) step and the difficulty in scaling up the process are the disadvantages of slurry reactors.^{51,52} Conversely, there are also technical challenges to be overcome for

immobilized film reactors, such as the immobilization method which should not compromise the catalyst properties.⁵¹ This work was performed in slurry batch reactors, allowing a fair comparison with what is reported in literature. Besides that, the focus was the ability of the catalyst to decompose organic compounds, and to obtain more in depth mechanistic understanding.

Fig. 3. Type of photoreactors: a) Slurry reactor and b) immobilized film reactors

Operational parameters

- *Photocatalyst Loading*

The photocatalyst loading only effects the overall reaction rate in a true heterogeneous catalytic regime, which means that the initial rate is directly proportional to the amount of TiO_2 at low concentrations.³¹ A linear dependency is only observed until a certain catalyst concentration. At some point, the reaction rate levels off, and becomes independent of catalyst loading.⁵³ This is closely related to light scattering phenomena and reduction of light penetration into highly concentrated solutions.⁵⁴

- *Contaminant Concentration*

It is commonly reported that the concentration of organic contaminants in water affects the photocatalytic reaction rate. As the initial concentration of the organic compounds increases, the irradiation time required to reach full mineralization of all volumetric content, becomes also longer.⁵⁵ However, when the contaminant loading is high, this saturates the TiO_2 surface, decreasing the photonic efficiency and sometimes leading to catalyst deactivation.⁵⁶

- *Light wavelength and intensity*

In order to activate TiO_2 with a band gap of 3.0 eV, wavelengths lower than 400 nm are required to initiate the reaction. Light intensity determines the overall photocatalytic reaction rate. Low intensity can be sufficient to induce surface reactions, but in order to activate all the catalyst available and to achieve maximum efficiency, it is necessary to supply a relatively high

light intensity. However there is a limit in light intensity, after which the rate no longer increases due to increasing probability of electron and hole recombination.⁵⁷

- pH

Another important operator parameter in heterogeneous photocatalysis is the pH of the electrolyte. This can significantly affect the size of the catalyst aggregates, the TiO₂ surface charge and consequently the ionization state and the adsorption ability of the organic molecules.^{58,59} The isoelectric point (PZC) refers to the pH at which the TiO₂ surface charge is neutral. For Evonik P25 that value is pH 6.3.^{60,61}

At pH < PZC (1.9) the catalyst surface becomes positively charged, which favors electrostatic attraction forces with negatively charged compounds, enhancing rates of the adsorption. At pH > PZC (2.0) the TiO₂ surface becomes negatively charged and anionic compounds are repulsed. At pH = PZC, the neutral surface charge induces catalyst aggregation and moderate adsorption of anions and cations can be expected.⁵⁸

Kinetics

All the operation parameters, discussed previously determine the kinetics of organic compounds towards mineralization. Most kinetic models used in photocatalysis are based on the Langmuir-Hinshelwood (L-H) mechanism. This model is applied when the reactions occur between two adsorbed substrates, being a surface-bound radical and adsorbed substrate (organic compound). According to the L-H model (2.1), the initial rate of organic compound mineralization (r) is proportional to the surface coverage (θ).²⁸

$$r = -\frac{dC}{dt} = k\theta = \frac{kKCi}{1+KCi} \quad (2.1)$$

In the equation, k is the reaction rate constant, Ci is the concentration of the organic compound and K is the Langmuir adsorption constant. At mM concentration $C \ll 1$, the L-H equation simplifies to *quasi* first order kinetics (2.2).

$$\ln\left(\frac{C_0}{C}\right) = kKt = k't \quad (2.2)$$

Most of researchers have reported that the mineralization of organic species is indeed obeying such first order kinetics.^{55,62}

1.5. Aim & Approach

The importance of clean water for humanity and the need for environmentally friendly technologies for purification, increases the interest in heterogeneous photocatalysis. Despite all research performed on this topic in the last decades, the reaction mechanism and the effect of the operational parameters on the decomposition rate of emerging compounds are relatively unknown. Many studies in practical applications of photocatalysis were focused on water purification plants, however the biggest drawback is the low efficiency of TiO_2 under visible light.⁶³ A completely other scale of practical application is also of interest: to develop domestic appliances that would allow purification of tap water still containing compounds with high resistance against other purification methodologies. In addition, such appliance could also contain catalytic functions for inorganic anion mineralization and in particular the hydrogenation of nitrates. A layout of the perspective device is shown in Fig. 4.

Fig. 4. Layout of a domestic device for water purification.

There are many studies related to photocatalytic decomposition of single organic compounds, however to compare the different results reported in the literature is challenging. The main reason is because of the different type of reactors used and the corresponding differences in light distribution and penetration. Considering that most setups consist of single reactors, evaluating one reaction at a time, we have proposed the use of a relatively inexpensive 96-well microplate photo-reactor assay, to study the effect of process parameters on photocatalytic rates. All the advantages and versatility of this high throughput screening method will be discussed in Chapter 2.

In the last decade, many studies highlight the prevalence of emerging contaminants (pharmaceuticals, endocrine-disrupting) in natural water reservoirs. Currently available technologies fall short in solutions to adequately remove them. In order to evaluate the ability of TiO_2 to degrade new emerging contaminants, the previously mentioned method (in Chapter 2)

was applied for high throughput screening of TiO₂ P25 photocatalyst efficiency in degrading 1280 compounds of a pharmaceutical library, see **Chapter 3**.

Literature also reveals that steroids are a class of compounds that are not easily mineralized. For that reason further studies with a model compound, cortisone acetate, were done to characterize its optimal decomposition parameters (pH, catalyst loading, etc.), in a scaled up laboratory slurry reactor (50 ml). Furthermore, reactions were also followed by Liquid chromatography-Mass Spectrometry (LC-MS) in order to identify possible intermediates. The results are reported in **Chapter 4**.

When photocatalysis is applied for water treatment, the need to decompose several organic contaminants simultaneously is evident. Remarkably, the literature contains very few studies of photocatalytic degradation of mixtures. In **Chapter 5**, we investigated the mineralization of methyl orange, a dye-type molecule, in the presence of atrazine, a pesticide. Different reaction conditions (pH, catalyst loading, contaminants concentration, etc.) were applied.

As stated previously, a domestic appliance which would be able to convert nitrates by hydrogenation, in addition to photocatalytic mineralization, would be a major improvement in water purification technology. **Chapter 6**, was focused on photocatalytic degradation of organic compounds (methyl orange) with concurrent hydrogen production. Pt-TiO₂ was applied as photocatalyst, and the addition of methanol in the aqueous phase evaluated to reach sufficiently high hydrogen concentrations. Several reaction conditions were evaluated, including anaerobic and aerobic conditions, in order to achieve the maximum hydrogen production, and complete conversion of the organic compounds into CO₂.

Finally, **Chapter 7** provides a reflection of the work done, as well as suggestions for further studies to answer some of the remaining questions.

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Chapter 2

High Throughput Analysis of Photocatalytic Water Purification

We present a novel high throughput photocatalyst efficiency assessment method based on 96-well microplates and UV-Vis spectroscopy. We demonstrate the reproducibility of the method using methyl orange (MO) decomposition, and compare kinetic data obtained, with those provided in the literature for larger conventional photo-reactors. To demonstrate the capabilities of the method, we rapidly screened the effects of salts, potentially present in wastewater, on kinetic rates of MO decomposition, and briefly discuss the obtained data on the basis of existing literature.

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1. Introduction

Clean water remains one of the major societal concerns. Among the currently available water purification methods, the most common are biological treatment, adsorption on activated carbon, and chemical oxidation, often in combination with membrane and filtration technologies.^{1,2} However, in most of these techniques, polluting organic molecules are not completely destroyed and the operational costs are high.¹⁻³ Heterogeneous photocatalysis opens up new opportunities for water purification since it allows complete mineralization of the organic pollutants into environmentally neutral compounds, such as CO₂ and H₂O, with reactions occurring at room temperature at relatively low costs.^{1,3}

Photocatalyst activity depends on the inherent ability of semiconductor materials, such as titanium oxide (TiO₂), tungsten oxide (WO₃) or zinc oxide (ZnO), to create electron-hole charge carrier pairs when exposed to light. Depending on the type of reactor, photocatalytic systems can be characterized as immobilized or slurry systems,^{2,3} in which light distribution within the reactor and its resulting penetration to reach the catalyst particle surface, as well as mass transfer limitations need to be carefully considered.³ Typical reaction volumes for laboratory scale slurry reactors range from 50 mL to 1 L,⁴ with UV/visible illumination supplied to the reactor from the top. Typical degradation times of organic wastewater compounds (dyes^{5,6}, pharmaceuticals⁷ and herbicides^{8,9}) range from 60 to 180 min. However, photocatalytic slurry reactors are very difficult to standardize according to their operational procedures, mostly due to the previously mentioned light penetration and distribution differences, making the relative comparison between the experiments performed in different reactors difficult. Furthermore, most of these reactors only allow the study of one reactive parameter (such as organic molecules or photocatalyst concentrations) at a time,^{1,4} and batch reactors usually consume relatively high amounts of the test materials (photocatalysts, organic contaminant and oxidizing agents).

Optimization of the photocatalytic reactive conditions often needs to be performed when considering any new emerging organic contaminant to find the optimal mineralization conditions. Combinatorial chemistry and high throughput screening are two powerful concepts that enable rapid selection of the optimum reaction parameters.¹⁰ While mostly applied in conventional catalyst evaluation, some high throughput experiments recently have also been applied to photocatalyst evaluation.¹¹⁻¹³ Specifically, Maier and co-workers¹¹ established a high throughput method based on HPLC to evaluate several photocatalysts for 4-chlorophenol oxidative conversion. Xiao *et al.*¹³ developed fluorescent photo-imaging methodology for the same purpose with both publications using slurry systems. It quickly becomes apparent that

there is a tremendous potential in developing uniform, inexpensive high throughput photocatalyst screening methods to maximize organic pollutant degradation efficiency.

In this work, we report a new high throughput screening method based on the use of 96-well plates for photocatalyst efficiency assessment, while also utilizing UV-Vis spectrometry to track the degradation process of any light absorbing model organic wastewater compounds. The 96-well microplate base is widely used in many fields of sample preparation and analysis, such as drug efficiency screening in pharmacology,¹⁴ enzymatic studies in biochemistry¹⁵ and high content biological cell bioassays.¹⁶ Utilizing these well plates allows reduction of the reagent and catalyst amount, easier handling, and higher sampling throughput. We validated our proposed method by performing *in situ* photocatalytic degradation tests using a model organic wastewater compound, methyl orange (MO), with a specific focus on a few crucial reaction parameters, such as photocatalyst chemical composition, its concentration in the slurry, and the presence of salts (ionic species). The results of this method are compared with those reported in the literature in order to validate the proposed analytical system.

2. Experimental

2.1 Microplate photo-reactor setup

The experimental setup of the high throughput photocatalytic screening experiment is shown in Fig. 1 with the corresponding reactor positioning shown in Fig. 2. Selected photocatalyst slurry compositions were prepared and transferred in equal volumes into the 96-well microplate. A model organic pollutant was added and each photodegradation experiment took place in an independent microwell (well diameter of 6.4 mm and depth of 11.2 mm), situated within the microplate. The working volume was 200 μL . A multi-tubular light source ($3.21 \text{ mW}/\text{cm}^2$) with the light wavelength ranging from 360 to 380 nm was positioned 50 mm above the microplates. After each photocatalytic experiment, the resulting aqueous suspension containing the photocatalyst and the organic contaminant, was transferred by a multimicropipet into a 96-well filter microplate (Corning, hydrophilic $0.2 \mu\text{m}$ PVDF membrane). In order to separate the solid photocatalyst, the aqueous suspensions in the 96 well filter microplate were centrifuged into a third, 96-well UV transparent base plate (Corning), at 300 rpm for 3 min (Fig. 1). The extent of the organic molecule degradation was monitored using the disappearance of its corresponding absorbance spectrum in a microplate spectrophotometer (Multiskan™ GO, Thermo Scientific) using the maximum value of the absorption band. MO was chosen as a model organic molecule to validate the method. The UV-Vis spectra of MO in distilled water revealed two absorption bands at 270 nm and 465 nm, with the latter used for quantification. No significant change in absorbance of MO was observed by dark adsorption on the catalyst surface, or by illumination

in the absence of catalyst material, in agreement with literature.⁵ Photodegradation measurements were performed in triplicate to determine the reproducibility values.

Fig. 1. Scheme of the 96-well microplate based experimental protocol.

Fig. 2. Microwell photo-reactor dimensions. These dimensions were also used for MO concentration determination by UV Vis spectroscopy.

The 96-well microplate photo-reactor allows for performance evaluation at many different conditions. In this study we demonstrate two cases of application:

- In the first case, the numbers on the top of the plate (columns 1-12) were filled with three different photocatalysts ZnO, Hombikat TiO₂ (Sachtleben) or P25 (Evonik) at four different catalyst concentrations (0.1, 0.25, 0.5, and 1.0 g/L respectively), while the letters (A-E) represent different reaction times. The entire volume of each row (200 µL) was transferred after a certain reaction time (wells A1 to A12) to the 96-well filter microplate. Rows A to H represent reaction times of 0, 1, 2.5, 5, 7.5, 10, 15 and 30 minutes, respectively. All experiments were performed at natural pH of 6.1.
- In the second example, the numbers correspond to different catalyst or MO concentrations and the letters to different salts. In this case, each plate corresponds to a single reaction time. Two plates were prepared, representing reaction times of 2.5 and 5 minutes, respectively. The parameters studied were: two MO concentrations of 5 and 10 mg/L, and two P25 TiO₂ catalyst concentrations, i.e. 0.25 g/L and 0.5 g/L. The molar ratios between the MO concentration and the salts were respectively, 1:1, 1:2 and 1:4. Columns A to H represent the salts according to the following order: sodium chloride, sodium phosphate dibasic, sodium carbonate, hydrochloric acid, potassium bromide, potassium nitrate and potassium sulfate. All experiments were performed at natural pH, pH 6.1, however the addition of HCl changed the pH to 3.0 and consequently the UV/Vis absorption maximum of MO shifted to 508 nm, from which maximum the concentration was derived in this particular experiment.⁵

All chemicals including methyl orange (MO), sodium chloride, sodium phosphate dibasic, sodium carbonate, hydrochloric acid, potassium bromide, potassium nitrate and potassium sulfate were obtained from Aldrich, and used without further purification.

3. Results and Discussion

Methyl orange (MO) was selected to validate the microplate photo-reactor system via photocatalytic degradation studies with a starting concentration of 10 mg/L. MO is an organic dye that is commonly used as organic model compound in wastewater photocatalytic degradation studies.^{17,5} Initially, to evaluate both the accuracy and the sensitivity of the microplate method described here, several aqueous MO solutions were prepared (2.0, 4.1, 8.2, 16.4, 32.8 and 65.5 mg L⁻¹). UV-Vis spectra of MO have two absorption band maxima situated at 270 and 465 nm, as shown in Fig. 3.A. The band at 465 nm was used for quantification. Linear regression analysis was used to determine the linearity of this quantification method, its sensitivity and the detection limit of the UV-Vis spectrometer for the microwell based experiments, as shown in Fig. 3.B. The calibration sensitivity found was to be 0.04, the analytical sensitivity at MO concentrations of 65.5 and 2 mg L⁻¹ were 1.02 and 19.05, respectively, whereas limit of detection (LOD) was 0.15 mg L⁻¹ MO. It can be seen that the linearity of the measurements remains constant up to at least ~70 mg L⁻¹ of MO, a middle value of the concentration range that is typically found in industrial textile wastewater streams¹⁸ and used in laboratory scale photocatalytic degradation experiments.⁸

Fig. 3. Evaluation of method accuracy and sensitivity of UV-Vis analysis of MO. A) UV-Vis spectra at various MO concentrations. B) Linear regression of data obtained in A) with $R^2=0.99$

TiO₂ based photocatalysts (P25 and Hombikat) and ZnO were tested for activity because of the stability of TiO₂ in aqueous environment, and the known photocatalytic efficiency of ZnO.¹⁹ The photocatalyst concentration used ranged between 0.1 and 1 g L⁻¹, which is typical for slurry reactors.²⁰ A photocatalytic degradation efficiency of 10 mg L⁻¹ MO in the presence of 0.25 g L⁻¹ of various photocatalysts under top-illumination of 375 nm light is shown in Fig. 4. The data are the averages of three independent measurements and error bars represent the standard deviation

(STDEV) of those measurements. It can be seen that the STDEV obtained at each time point was very small at $\sim 1\%$.

Fig. 4. Photocatalytic decomposition of 10 mg L^{-1} MO at 375 nm irradiation and 0.25 g L^{-1} photocatalyst loading. Photocatalysts used were TiO_2 P25, TiO_2 Hombikat and ZnO. The error bars are the calculated standard deviations of three independent experiments.

Fig. 4 shows that most of the MO in aqueous solution, $\sim 93 \%$, was degraded after 15 minutes when using ZnO, while degradation efficiencies achieved were $\sim 89 \%$ and $\sim 52 \%$ for TiO_2 P25 and TiO_2 Hombikat, respectively. These results are consistent with those reported in the literature, where ZnO exhibits higher photocatalytic activity than TiO_2 P25,^{21,22} with the latter exhibiting greater activity than TiO_2 Hombikat.⁵

Data shown in Fig. 4 were processed to obtain the observed photocatalytic degradation rate constants, (k, min^{-1}), of which the values are listed in Table 1. These were obtained using data point linearization of the initial MO degradation slope via pseudo first order kinetics:

$$-\ln\left(\frac{C}{C_0}\right) \text{ vs. time} \quad (1)$$

Table 1. The decomposition rate constants of MO degradation in the presence of different photocatalysts. R^2 provided for the linear data fit according to equation (1).

Catalyst (0.25 g L ⁻¹)	Pseudo-first order observed rate constant (min ⁻¹)	R ²
ZnO	0.23	0.931
TiO ₂ P25	0.12	0.994
TiO ₂ Hombikat	0.04	0.933

Table 1 shows that the highest observed rate constant was obtained for ZnO (0.23 min⁻¹). However, it is known that photo-corrosion of ZnO in aqueous solutions leads to the formation of ZnOH⁺, Zn(OH)₂, Zn(OH)₃⁻ and other products, that are not active as photocatalysts.^{23,24} Thus, further experiments were performed using TiO₂ P25 as photocatalyst material.

Another parameter studied was catalyst concentration, varying in the slurry ranging from 0.1 to 1 g L⁻¹ in the presence of an initial MO concentration of 10 mg L⁻¹. The data obtained are shown in Fig. 5.

Fig 5. Photocatalytic decomposition of 10 mg L⁻¹ MO at 375 nm irradiation and using various concentrations of TiO₂ P25 (0.1-1 g L⁻¹). The error bars represent the deviation between three independent experiments.

Fig. 5 shows that the degradation of MO increases as a function of increasing concentration of TiO₂ P25. Additionally, an excellent reproducibility was obtained with almost negligible STDEV calculated. Observed initial rate constants (k , min⁻¹) were calculated using a linearization of the data points shown in Fig. 5 and are listed in Table 2.

Table 2. Observed initial rate constants of MO degradation in the presence of various loadings of TiO₂ P25. R² provided is that for the linear data fit according to equation (1).

TiO ₂ P25 Concentration (g.L ⁻¹)	Pseudo-first order observed rate constant (min ⁻¹)	R ²
0.1	0.048	0.956
0.25	0.124	0.994
0.5	0.198	0.997
1.0	0.256	0.992

Table 2 shows that the observed initial decomposition rate constant, k (min⁻¹), increases with the TiO₂ P25 concentration in the slurry. The trend is shown in Fig. 6.

Fig. 6. Effect of catalyst concentration on pseudo first order rate constant of TiO₂ P25 in decomposing MO.

The observed trend is in agreement with the findings reported in the literature.⁵ Catalyst concentration is one of the most important parameters of slurry reactors and can be correlated with its availability per unit volume for photocatalytic reaction. However, after increasing up to a certain amount, it becomes impossible to achieve a better decomposition rate due to the limited light penetration through the vessel, and deviation from linearity in the curve of Fig. 6 is apparent.²⁵ TiO₂ concentrations of 1-2 g L⁻¹ have already have been shown to significantly scatter incident light and thus can be considered as a maximum usable value.²⁵ Our data shown in Fig. 5 for 0.5 and 1.0 g L⁻¹ agrees with this observation, suggesting that in microplate photo-reactors of small volumes, the photocatalyst is utilized efficiently within the same concentration range, as typically observed in batch reactors. Additionally, photocatalytic slurry reactors are commonly supported by agitation to ensure a uniform distribution of the photocatalyst. However, in the microplate system proposed in this study, agitation could not be applied. As a result, there is a progressive deposition of the photocatalyst at the bottom of the micro-well.

This is expected to be compensated by relatively short diffusion paths of the reactant molecules within the small reactor dimensions. This will allow the molecules to reach the photocatalyst surface, at these microliter volumes, within the duration of the experiment (~ 15 min). Assuming an MO diffusion coefficient, D , of $1 \times 10^{-5} \text{ cm}^2/\text{s}$,²⁶ the diffusion length ($\sqrt{2Dt}$, where t is the reaction time to degrade $\sim 90\%$ of MO, in seconds) was estimated to be 0.2 cm , close to the vertical reactor dimensions. This means that even with a complete settling of the photocatalyst material, all of the MO molecules will have been interacting with the catalyst particles within the reaction timeframe.

The comparison between the observed rate constant of the microplate photo-reactor with other slurry reactors is difficult, since this depends on various experimental parameters, such as the reactor geometry, light source and its position in the reactor,²⁷ as well as the initial concentration of the model waste compound. Table 3 shows the observed rate constant values obtained from the 96-well microplate photo-reactors in comparison with other studies.

Table 3. Comparison of observed initial rate constants (k) of MO degradation, between the 96 well microreactor with others.

[MO] (mg/L)	[P25 TiO ₂] (g L ⁻¹)	Type of Reactor	Reactor Volume (mL)	Light Source	k (min ⁻¹)	96 Well Microreactor k (min ⁻¹)	k (Slurry Reactor) / k (well plate)	Ref.
20	0.08	Slurry /Suspension	150	Black light tubes 4 W	0.0244	0.0480	0.51	28
10	0.5	Slurry /Suspension	7.5	UV lamp 50mW cm ²	0.5200	0.1980	2.63	29
10	0.5	Slurry /Suspension	1100	UV lamp 11W	0.0076	0.1980	0.04	30
10	1.0	Slurry /Suspension	1100	UV lamp 11W	0.0097	0.2560	0.04	30
20	1.0	Slurry /Suspension	50	Black light tubes 18 W	0.0110	0.2560	0.04	31

Clearly, the rate constant value obtained in our study in the well-plate is higher than these obtained in conventional laboratory slurry reactors of larger volume. One of the disadvantages of a typical slurry reactor equipped with top illumination is that the light intensity decreases with increasing reactor depth due to absorption/scattering by photocatalyst particles or even the solution itself. Hence, only catalyst particles in the upper volume of the reactor contribute efficiently to the photocatalytic process.³² Our 96-well microplate photo-reactor circumvents the problem due to the high top surface area-to-volume ratio (A/V , cm⁻¹). Specifically, A/V of a

single well in the current system is 1.61 cm^{-1} while that reported for typical batch reactors is at least an order of magnitude smaller, as shown in Table 3. High A/V values in our microwell setup enables for an efficient utilization of the photocatalyst volume while decreasing the total required amounts of both catalyst and solution. The observed initial rate constant (k) determined in the well plate seems to correspond to the value obtained in a reactor configuration in which the reactor volume is only 7.5 mL (Table 3). In this case, the observed initial rate constant (k) value is in the same order of magnitude than the one obtained in the 96-well microplate photo-reactor. This observation confirms that the observed initial rate constant (k) values are closely related to reactor geometry.

As a second example to demonstrate the potential of our method, we have performed experiments with different salt concentrations added to the MO/catalyst mixture. Fig. 7, summarizes the results.

Fig. 7. Photocatalytic degradation of MO (5 mg L^{-1}) with P25 TiO_2 (0.25 g L^{-1}) in the presence of various anions and cations. The molar ratio between MO and the salts were respectively 1:1 (A), 1:2 (B) and 1:4 (C).

As is reported in the literature, the presence of ionic species can accelerate or retard the observed initial reaction rate.^{33,34} The ionic species chosen represent some of the most common species present in wastewater. From the ionic species tested, only phosphate and carbonate anions show a significantly negative effect on the reaction rate constant of MO degradation (Fig. 7). These results are generally in agreement with what is reported in the literature for dyes.^{33,34} Further, addition of HCl appears to promote the rate at which MO is degraded. Addition of HCl has been reported to negatively affect the rate of degradation of various substrates,^{33,34} but literature does not contain information on the effect of HCl on MO decomposition rates. The positive effect found in our studies is most likely related to the decrease in pH induced by the addition of HCl. Acidic conditions are known to favor the decomposition of MO.⁵ The photocatalytic degradation reaction of MO in the presence of the

other salts did not show any appreciable effect in the observed reaction rate constant, again in agreement with literature.^{33,34}

4. Conclusions

In summary, we propose a method of high throughput photocatalyst screening that requires very short reaction times of up to 15 min to degrade dye compounds in the concentration range typical of those found in industrial organic wastewaters. This method is applicable to a wide concentration range of model organic contaminants, powder photocatalysts and various combinations of these. Furthermore, this method minimizes the amount of the photocatalyst needed and the volume of the working solution from typical values of 50-1000 mL to only 200 μ L. Finally, this method allows the efficient utilization of all the photocatalyst present within the reactor, thus providing a more realistic value of the intrinsic rate constant in photocatalytic applications. The validity of the method was also demonstrated in an evaluation of the effect of salt concentrations on the effective rate constant. In agreement with literature phosphate and carbonate anions were found to decrease the rate of decomposition of MO, whereas acidic conditions favor the rate.

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Chapter 3

High Throughput Screening of Photocatalytic Conversion of New Emerging Contaminants

In this study, we have evaluated the effectiveness of photon induced oxidation methods in the elimination of pharmaceutical compounds belonging to a library known as LOPAC¹²⁸⁰ from aqueous solution. To this end, degradation reactions of over 800 compounds were performed in the absence and presence of TiO₂ P25 as photocatalyst and analyzed by spectroscopy. In general, few compounds were degraded effectively in the absence of the photocatalyst (3 %), while in the presence of TiO₂ P25, the majority of compounds was converted, often to a large degree. Several aspects of the compounds chemical nature (molecular weight, functional groups and pharmacological classes) were considered in order to explain the different levels of degradation obtained. In general, the molecular weight is associated with the complexity of the compounds in terms of number of chemical bonds and functional groups present; so, as this increases, the degradation efficacy decreases. Relatively high degrees of conversion were achieved for molecules with functional groups such as aldehydes, alcohols, ketones and nitriles. Relatively low degrees of conversion were found for compounds with conjugated aromatic systems. The efficacy of photocatalysis in conversion of several pharmacological classes, such as hormones and opioids, is discussed.

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1. Introduction

The fast increase of emerging contaminants in waste water (pharmaceuticals, metabolites, endocrine-disrupting drugs) raises concerns with respect to deteriorating human health and well-being, and also with respect to disturbing the general balance in the ecosystem.^{1,2} Standard wastewater treatments, either mechanical, chemical or biological, are often unable to completely degrade these emerging contaminants.^{3,4} This is supported by several reports claiming the presence of these compounds in the range of a few ng L⁻¹ to a few mg L⁻¹ in surface and ground wastewater.^{5,6} Compounds, such as caffeine, codeine, naproxen, acetaminophen, diclofenac, ofloxacin and ibuprofen were even found at concentrations up to several mg L⁻¹.⁵

Advanced oxidation processing (AOPs) has been shown to be a promising technology to degrade some of these compounds, making use of the *in situ* generation and subsequent reaction of (unselective) hydroxyl radicals (HO•).^{7,8} The disadvantage of these technologies is that sacrificial agents, such as iron salts and/or hydrogen peroxide, are needed.⁸ Heterogeneous photocatalysis has also been referred to as an alternative method leading to the complete mineralization of organic contaminants into CO₂ and H₂O.⁹ Decomposition in such process is achieved through the generation of powerful intermediary oxidative species (HO•, O₂•⁻), created by reduction of oxygen and oxidation of water by electron-hole charge pairs, and formed when a semiconductor (ZnO, WO₃, or TiO₂) is exposed to light.⁷ Photocatalysis is considered highly sustainable and the low operational costs make it a very attractive technology. Titanium dioxide (TiO₂) is the most effective photocatalyst for water treatment applications so far described, particularly due to its high stability in water.¹⁰

Photocatalysis approaches have been previously evaluated for removal of organic compounds from water, such as dyes, phenols and pharmaceuticals (diclofenac, naproxen).¹¹⁻¹³ However, to the best of our knowledge, little is known about the degradation mechanism of these compounds and which specific molecular functionality enhances the susceptibility to photocatalytic degradation.

High throughput screening (HTS) can be a powerful tool to conduct a large studies on the degradation probability of a wide variety of drug-related compounds, and help to identify when this probability is a function of specific functionality present in the molecular structure. Two analytical methods have been used for combinatorial screening of photo-degradation catalysts: the first is supported by High Performance Liquid Chromatography (HPLC)¹⁴ analysis decomposing 4-chlorophenol and the second is based on fluorescence imaging for 1,6-hexamethylenediamine.¹⁵ In a smaller scale, an interesting screening was performed to test the

substrate-specific activity of eight commercial TiO_2 samples to decompose 19 substrates.¹⁶ The complexity of coupled analytical methods and its readouts strongly limits the effectiveness of throughput, and further data mining.

In this work we describe, for the first time, a HTS assay designed to help understanding how TiO_2 photodegrading capability depends on substrate-specific properties, such as molecular weight and chemical functional groups. To this end, a LOPAC¹²⁸⁰ library, which is a library of 1280 pharmacologically active compounds divided in drug target classes such as hormones and neurotransmitters, was used. The study of the degradation of 1280 compounds was performed using a miniaturized microplate photo-reactor, in combination with a UV-Vis microplate spectrometer, as previously described in Chapter 2.

2. Experimental

2.1. Materials

To evaluate the ability of photocatalysis to oxidize pharmaceutical compounds, a LOPAC¹²⁸⁰ library was used. This was obtained from Sigma Aldrich. This library consists of 1280 different compounds which are stored in dimethyl sulfoxide (DMSO). Evonik TiO_2 P25 was used as the photocatalyst.

2.2. Microplate photo-reactor setup for LOPAC¹²⁸⁰ screening

The experimental setup used for determination of photocatalytic efficacy was previously described and validated in Chapter 2, and previously published work.¹⁷ To proceed with a photon-induced degradation study, the LOPAC¹²⁸⁰ library was distributed over sixteen 96-well plates (concentration of 2000 μM). In the absence of catalyst, 25 μL of the library solutions were diluted in demineralized water to reach the final working volume of 200 μL (final concentration 25 μM) into UV transparent 96-well microplates (Corning). To evaluate photocatalytic efficacy, an aqueous slurry of TiO_2 P25 at 0.25 g L^{-1} was prepared and transferred in equal volumes (192.4 μL /well) into the 96-well plates, followed by the addition of 27.6 μL from the LOPAC¹²⁸⁰ stock solution, resulting in a final working volume of 220 μL (final concentration of 25 μM). In both experimental conditions (photolysis and photocatalysis), the 96-well plates were illuminated from the top with a multitubular light source (3.21 mW.cm^{-2} , 360-380 nm) at a distance of 5 cm for 5 min. In the case of the photocatalytic experiment, the aqueous suspension was transferred into a 96-well filter microplate (Corning, hydrophilic 0.2 μm PVDF membrane) and the solution filtered into a new 96-well microplate by centrifugation at 300 rpm for 3 min in order to separate off the photocatalyst. Afterwards, just 200 μL was transferred into a new UV

transparent 96-well microplate (Corning) (see Chapter 2, Fig.1). This guarantees an equal volume per well and the same path length, l , required for proper application of the Lambert-Beer law ($A=\epsilon.l.c$) when using the microplate spectrophotometer (Multiskan™ GO, Thermo Scientific). Measurements were processed and used to assess the degradation profile of each compound through the intensity decrease in absorbance spectra (at peak value). Previously to any reaction, the maximum in the absorbance spectrum for each compound was determined in the spectral range of 200-800 nm, in order to find the optimum wavelength (spectra of DMSO in water was used as background) to be used in concentration determination.

2.3. Data analysis

The spectral data obtained (photolysis and photocatalytic degradation) for each compound of the LOPAC¹²⁸⁰ library were saved into a spreadsheet forming a dataset. Afterwards, information about the molecular weight, pharmacological class and functional groups was gathered and stored for all compounds. For data handling and further processing, the dataset was imported into MATLAB, used for clustering and extraction of relevant information. Series of scripts were therefore created to cover data mining steps involving data pre-processing, management and visualization (bar graphs, scatter and box plots).

Fig.1 schematically illustrates the High Throughput Screening (HTS) conceptual process for the LOPAC¹²⁸⁰ library study, including the data analysis.

Fig. 1. Schematic illustration of HTS for the LOPAC¹²⁸⁰ library.

3. Results and Discussion

3.1. Photolysis vs Photocatalysis

Prior to the determination of the photo (catalytic) conversion efficiency, UV-Vis spectra of the 1280 compounds were measured, from which several compounds were excluded since they did not show a traceable peak. From the initial 1280 compounds, only 825 compounds showed spectral intensity suitable for further analysis. The photocatalytic performance of TiO₂ P25 as photocatalyst at 375 nm was compared to photolysis (degradation in the absence of the catalyst at 375 nm) after illumination for 5 min.

For each individual reaction it was possible to analyze the absorbance decay and calculate the degradation percentages (100% represents full dis-colorization). Global degradation results for the 825 compounds from LOPAC¹²⁸⁰, either by photolysis or photocatalysis, are shown in Fig.2. TiO₂ P25 assisted photocatalysis has proved to be clearly superior as degradation method, having much higher degradation percentages achieved after 5 min of illumination, when compared to photolysis. Photolysis could only decompose few compounds up to 40% (5), 50% (3) and 70% (2). The difference in the susceptibility for photolysis and photocatalysis is clearly highlighted by the number of compounds degraded less than 1%.

Fig. 2. Ranking of the compounds in a LOPAC¹²⁸⁰ library, based on the degradation percentages achieved after 5 min illumination either by photolysis (375 nm exposure) or photocatalysis (375 nm exposure, TiO₂ P25). The distribution shows that the majority of compounds is not effectively decomposed in the absence of catalyst (over 450 compounds are degraded to less than 1% of the original concentration), whereas photocatalysis significantly enhances the number of compounds that were degraded to larger percentages of the original concentration.

In Table 1, some of the few compounds showing higher degradation percentages solely by photolysis are highlighted. Noticeably, the degradation of these compounds (oxolinic acid, TCPOBOP, Molsidomine, SIB 1893 and SB-366791) was not significantly improved in the presence of the photocatalyst. A reason explaining this may derive from a common feature of these compounds, which is the presence of functional groups comprising ester, benzene and pyridine rings. However, for the large majority it is clear that the presence of TiO₂ P25 increases the degradation percentage, the case for Apigenin (Table 1) being exemplary.

Table 1: Comparison of degradation percentages of some compounds in Photolysis and Photocatalysis

Compounds	Photolysis Degradation (%)	Photocatalytic Degradation (%)
Oxolinic acid	76	80
TCPOBOP	44	57
SIB 1893	42	40
SB-366791	57	83
Apigenin	6	63

Fig. 3. Photocatalytic degradation percentages achieved for some of the most representative compounds in LOPAC¹²⁸⁰.

Fig.3 shows some selected compounds from the LOPAC¹²⁸⁰ library and the respective photocatalytic degradation percentages after 5 min of illumination, giving a closer insight on the compound diversity included in this study. Furthermore, the results are categorized by High, Medium and Low levels of degradation. In the low degradation group are compounds such as caffeine, adenosine and cortisone while in the high degradation percentage group are (S)-pindolol and several compounds from the tyrphostin family (drugs that inhibit enzymes responsible for the activation of certain proteins).

The high reproducibility of this screening method is illustrated by Table 2, showing that compounds with similar chemical backbone tend to have similar degradation values reached by photocatalysis.

Table 2. Compounds with similar chemical functionality and the respective degradation percentages in order to prove the consistency of the 96-well microplate photo-reactor method.

Compounds	Degradation (%)	Compounds	Degradation (%)	Compounds	Degradation (%)
Cortisone	0	(-)-alpha-Methylnorepinephrine	17	Tyrphostin 23	75
Corticosterone	0	(±)-Norepinephrine (+)bitartrate	18	Tyrphostin 25	73

3.2. Molecular weight (MW)

A parameter considered to analyze the reactivity was the molecular weight (MW). Fig.4 shows the correlation between the MW distribution and the percentage of degradation, both for photolysis and photocatalysis. As previously observed, in photolysis a lower degree of degradation is predominant, (Fig. 4.a). In the presence of TiO₂ P25, a shift towards higher degradation percentages was observed for most compounds (Fig. 4.b), compared to photolysis. In Fig. 4.b, a trend in maximum degradation rates seem to be present with increasing MW, nevertheless a relation between MW and degradability of the organic molecules is not obvious. Only above 500 g mol⁻¹ the maximum achievable percentage is significantly lower. For example, for compounds with a MW around 250 g mol⁻¹ up to 97% degradation was frequently

achieved, whereas molecules with a MW higher than 500 g mol⁻¹ have predominantly lower (maximum) values. This is in agreement with the perception that more time is needed to break and oxidize all the chemical bonds. Table 3 highlights a few organic compounds with different MW and their corresponding decomposition percentage. On the basis of these data, the gray line in Fig. 4.b was drawn, reporting the local maxima. Table 3 clearly shows that when the MW increases, the complexity in the chemical backbone also increases, which likely contributes to the fact that degradation becomes more difficult. Another important factor is derived from the interaction between the compounds with the catalyst surface that can be affected by the molecular structure flexibility/rigidity which increases with the MW. In the following chapters of this thesis, the importance of sorption will be highlighted in more detail.

Fig. 4. MW distribution correlated with degradation percentage. a) Photolysis. b) Photocatalysis. Dashed grey line is only indicative, as the MW increases the maximum degradation percentage decreases.

Table 3. Compounds with different MWs that showed maximum degradation percentages (Dashed grey line, Fig.4.b).

Molecular Weight (g/mol)	248	487	840	1163	1500
Compounds
	S(-)-Pindolol	MRS 1754	Reactive Blue 2	NF 023	NF449 octasodium salt
Degradation (%)	97,37	75,99	61,07	37,82	20,47

3.3. Pharmacologically classes

LOPAC is a library with 1280 pharmacologically active compounds that are divided in drug target classes, e.g, GPCRs (G protein-coupled receptors) ligands, hormones and neurotransmitters. Neurotransmitters are subdivided in other classes, such as adenosine, adrenoceptors, histamine, imidazoline, opioids, among others.¹⁸ Fig.5. shows degradation percentages organized by different pharmacologically active classes. In this division, central values (vertical black line which indicates the mean) never exceed degradation percentages above 10% for photolysis. Leukotriene and melatonin stand out since photolysis was in general capable of achieving significantly higher values, when compared to other classes. The leukotriene class does not have a characteristic chemical group, however, comprises benzenes, esters, amines and carboxylic acids. On the other hand, the compounds within the melatonin class usually have indole (benzene and pyrole ring) and amide chemical groups, suggesting that these are susceptible to light activation.

Fig. 5. Pharmacological classes selected from the LOPAC¹²⁸⁰ library, and the corresponding degradation distribution for photolysis and photocatalysis. The blue (photocatalysis) or orange (photolysis) bars indicate the percentage range to which most of the compounds were degraded, while the grey lines (photocatalysis) or single dots (photolysis) represent significantly lower probability. The mean is indicated by the vertical black line in both cases.

Histamine, imidazoline and opioids are the least susceptible to photocatalytic degradation. The histamine class covers derivatives from imidazole with a side-chain amine, similar to many derivatives from this family present in the library. A salt of histamine (histamine dihydrochloride) was not degraded, and a similar compound, 4-Imidazoleacrylic acid, undergoes only 2% of degradation. Imidazolines, the name given to the derivatives of imidazole, also showed very low degradation percentages (Fig.5). The Imidazole molecule is difficult to be oxidized or, at least, demands more reaction time for dis-colorization. The compounds included in the opioid class resemble morphine, containing aromatic rings and a quaternary carbon atom bonded to a tertiary amine group linked to two carbon atoms. This class also shows a very low degradation percentages, as show in Fig.5. Naloxone hydrochloride, naltrexone hydrochloride, levallorphan tartrate which have a very similar chemical structure to morphine, also showed no degradation. Higher degradation percentage were obtained for naloxone benzoylhydrazone and naltriben methanesulfonate, perhaps due to the presence of an additional phenyl group or an azo bond (N=N). The oxidation reaction might started by the activation of these groups (Fig.6).

Fig. 6. Compounds from the opioid class and the corresponding degradation percentage achieved by photocatalysis.

It has been described that morphine can be completely mineralized by photocatalysis,¹⁹ however the concentration used was 3.5 μM . In the present screening study, the concentration was significantly higher, at 25 μM . The fact that other opioids, such as naltriben methanesulfonate could be mineralized by 50% confirms that this class is suitable for being degraded by photocatalysis.

The adenosine class includes, as the name implies, adenosine, adenine, caffeine molecules and derivatives. From this class, 82% of the compounds showed a degradation percentage below 50%. Theobromine is an exception with 71% of conversion reached. Caffeine is a compound present at high concentrations in sewage and it has been reported that its complete mineralization (and its intermediates) is difficult to achieve,^{20,21} confirming the results obtained in our study.

The Adrenoceptor class comprises compounds such as epinephrine (adrenaline) and norepinephrine (noradrenaline), which consists of a 1,2-dihydroxybenzene molecule with a side-chain amine and derivatives. In the case of adrenaline and noradrenaline, the degradation percentage achieved was respectively 3 and 18%, showing potential to be degraded by photocatalysis. In the literature the photocatalytic degradation reported for a compound from the same class, atenolol, is 10%,²² in agreement with the range achieved in the present study.

Hormones comprises another class of compounds represented in LOPAC¹²⁸⁰, including molecules from the corticosteroids family (compounds with three to six-carbon rings combined with a five-carbon ring). Examples of this are corticosterone, cortisone, hydrocortisone, among others. However, while these were not degraded, other steroid hormones such as progesterone and 4-Androsten-4-ol-3,17-dione achieved degradation percentages of 32% and 58%, respectively. Fig.7 shows that this class of compounds can be degraded by photocatalysis and

that small differences in the functional groups can affect the degradation percentage observed. A derivative of cortisone, cortisone-acetate, can be degraded by this method, however to mineralize this compound with a concentration of 25 μM , the same as in the library as well as the same catalyst concentration, 90 min of illumination were necessary.²³

Fig.7. Compounds belonging to corticosteroids family and their corresponding degradation percentage achieved by photocatalysis.

Melatonin and derivatives thereof, were relatively easy to degrade. This class of compounds has a specific chemical group, being an indole molecule with a side-chain amide. Likely, these groups contribute to relatively easy oxidation.²⁴

It should be noticed that not all the classes present in the LOPAC¹²⁸⁰ library are necessarily associated with (a) specific chemical group(s) or backbone unit, but rather categorized by its biological functionality. Therefore, further analysis is done targeting the effect of the chemical nature of the compounds used in this study.

3.4. Further focus on functional Groups

Each compound from the LOPAC¹²⁸⁰ library was characterized by its intrinsic chemical nature, considering its structural composition and chemical bonds. The functional groups considered were: aromatic cyclic (AC) compounds, aromatic heterocyclic (AHC) compounds, alcohols, aldehydes, amides, amines, carboxylic acid, esters, ether, halogens, ketones and nitriles. Fig.8 shows an elaborated view of the degradation percentages on the basis of these functional groups.

Fig. 8. Degradation percentage distribution over different functional groups by photolysis and photocatalysis. The blue (photocatalysis) or orange (photolysis) bars indicate the percentage range to which most of the compounds were degraded, while the grey lines (photocatalysis) or single dots (photolysis) represent significantly lower probability. The mean is indicated by the vertical black line in both cases.

In Fig. 8 it is possible to observe that, regardless of the functional groups, degradation is much higher in photocatalysis than in photolysis. Further, photocatalysis is able to break most chemical bonds after 5 min of illumination, since the central values are up to 15% decomposition. There are some functional groups that show high efficiency in degradation: aldehydes, ketones and nitriles. Looking at the compounds included in the aromatic heterocyclic (AHC) group, indole molecules stands out, which is in agreement with the results found for the melatonin class.

In order to understand why 207 compounds (Fig.2) were not degraded, their chemical structure was evaluated in more detail. Overall, these molecules contain in their chemical backbone aromatic cyclic compounds in conjugated systems and derivatives of purine, caffeine, pyrimidine, pyridine and imidazoline molecules. Nevertheless, it is very difficult to generalize, given the fact that each compound has multiple functional groups and different complexities, as shown in Tables 1 and 2.

3.5. The role of the solvents (HCl, DMSO)

In the LOPAC¹²⁸⁰ library, there are 202 compounds initially in hydrochloric acid-containing stocks (in DMSO), from which a degradation below 10% was achieved for 66 of the compounds. In photocatalysis, an acidic medium is often beneficial, but negative effects have also been reported for the presence of chloride, since the Cl^- ions deactivate the catalyst surface.^{25,26} The presence of these ions might partially contribute to the relatively low percentages of degradation obtained by these compounds, but its effect was not evaluated for this screening purpose.

The LOPAC¹²⁸⁰ library is commercially available with most compounds dissolved in DMSO, to ensure their stability and solubility. Photocatalytic degradation of DMSO has already been reported in literature^{27,28}, even defining an ISO standard (ISO/CD 10676) for the evaluation of photocatalytic performance in wastewater treatment.²⁷ This compound is of special interest due to the ability to react with hydroxyl radicals,²⁹ being methansulfonate (CH_3SO_3^-) and sulfate (SO_4^{2-}) two intermediates identified from its degradation.²⁷ In the present study, degradation of DMSO was not observed, since the maximum in the absorbance spectra of DMSO appears at 224 nm and the intensity did not significantly change after 5 min of illumination, either in the absence or presence of the catalyst. As already discussed in this thesis, the presence of a second compound in solution can interfere with the reaction time necessary to achieve full degradation of other compounds, for example, due to competition for surface sites of the catalyst. Nevertheless, all the compounds of the library were exposed to the same reaction conditions, so the comparison and evaluation of photocatalysis efficacy to degrade these compounds is deemed as viable.

UV-Vis spectrometry provides an easy, fast and reliable quantification method. However, it does not allow to follow intermediates or confirm if the molecules were completely converted into CO_2 and H_2O . In this study it is shown that photocatalytic degradation efficiency is highly dependent on the substrate chosen and the interaction with the catalyst surface. Obviously, the kinetics and formation of intermediates in the degradation process is relevant and needs to be studied in more detail, especially as a function of process conditions. Analytical techniques, such as HPLC in combination with MS, are viable techniques to reach this goal.

5. Conclusions

This study evaluates the applicability of TiO₂ P25, by far the most used photocatalyst,^{30,31} to eliminate new emerging contaminants from wastewater. These are mainly pharmaceutical compounds that may pose a risk to the environment and human health.^{5,6} LOPAC¹²⁸⁰ is a library of pharmacologically active compounds comprising FDA-approved molecules and other drugs used in industrial processes, thus making it a very suitable for the purpose of this study. This work constitutes, to the best of our knowledge, by far, the biggest screening of potential pollutants in water been made so far, giving special focus in pharmaceutical compounds which are one of the biggest concerns regarding water treatment in developed societies.

The reaction time chosen for photolysis and photocatalysis was 5 min, clearly sufficient for a significant amount of compounds to be significantly degraded. To distinguish the molecules and the corresponding functional groups leading to easy oxidation was a challenge, mainly due to the high complexity found. Still, high degradation efficiencies were achieved for molecules with functional groups such as aldehydes, alcohols, ketones, nitriles, and amides. One class of compounds that stood out in terms of low resistance against oxidation were indole derivative molecules. The compounds with conjugated aromatic systems and derivatives from compounds such as adenosine, caffeine and imidazole, were relatively difficult to convert and showed low degradation values.

The results presented here should be considered preliminary, since the screening scope does not allow deeper understanding of mechanisms and kinetics. It provides a good starting point for further investigation on the understanding about the role of the molecular complexity of a substrate in determining photocatalytic effectiveness.

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Chapter 4

Photocatalytic Decomposition of Cortisone Acetate in Aqueous Solution

The photocatalytic decomposition of cortisone 21-acetate (CA), a model compound for the commonly used steroid, cortisone, was studied. CA was photocatalytically decomposed in a slurry reactor with initial rates between 0.11 to 0.46 mg L⁻¹ min⁻¹ at 10 mg L⁻¹ concentration, using the following heterogeneous photocatalysts in decreasing order of their catalytic activity: ZnO > Evonik TiO₂ P25 > Hombikat TiO₂ > WO₃. Due to the lack of ZnO stability in aqueous solutions, TiO₂ P25 was chosen for further experiments. The decomposition reaction was found to be pseudo-first order and the rate constant decreased as a function of increasing initial CA concentration. Changing the initial pH of the CA solution did not affect the reaction rate significantly. The decomposition reaction in the presence of the oxidizing sacrificial agent sodium persulfate showed an observed decomposition rate constant of 0.004 min⁻¹, lower than obtained for TiO₂ P25 (0.040 min⁻¹). The highest photocatalytic degradation rate constant was obtained combining both TiO₂ P25 and S₂O₈²⁻ (0.071 min⁻¹) showing a synergistic effect. No reactive intermediates were detected using LC-MS showing fast photocatalytic decomposition kinetics of CA.

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1. Introduction

A wide range of potentially harmful organic compounds is being released to the environment via municipal wastewater discharge.¹⁻³ Of particular interest are active pharmaceutical ingredients,⁴ resulting in ground and surface water from their release during the manufacturing,⁵ landfill leaching⁶ and animal waste natural environmental processing.² When transferred into the environment, these drug compounds, including steroidal hormones, can undergo a variety of microbially enhanced chemical transformations.⁷ Some estrogenic hormones persisted in water⁸ at low concentrations of 1–10 ng L⁻¹ and led to pronounced biological changes in fish, such as decreased reproductive capability and alterations in species composition.^{7,9} Additionally, drug compounds, persistent in the environment, may promote development of antimicrobial resistance.¹⁰ Since sources of drinkable water inevitably involve groundwater streams,¹¹ these transformed pharmaceutical compounds have already been detected in drinking water on several occasions in ng L⁻¹ amounts.¹²⁻¹⁵ Due to this, a clear link between the discharged contaminated water and drinking water has already been established.¹⁶ The pharmaceutical compound cortisone and other corticosteroids are commonly prescribed drug compounds due to their anti-inflammatory and immunosuppressive properties.¹⁷ These corticosteroids have been of particular environmental interest in recent years due to their established presence in the municipal wastewater.¹⁸⁻²⁰ In some countries, such as the Netherlands, a typical concentration of cortisone in wastewater was found to be 381–472 ng L⁻¹.^{21,22} Very recently it has been shown that certain anabolic steroids last much longer in the environment than expected. In particular, steroid trenbolone acetate was shown to never fully degrade in the environment when exposed to solar light, undergoing hydroxylation during the day but reverting back to its initial form at night via acid chemistry.²³ The previous chapter also confirmed that steroids are not easily mineralized. Due to their persistence in the environment the urgency to investigate their treatment methods is warranted.

A promising advanced oxidation method for any organic wastewater treatment is heterogeneous photocatalysis, since it can lead to a complete mineralization of the organic pollutants, ultimately CO₂ and H₂O being the final products. This method has previously been successfully used to clean drinking water from many types of organic pollutants.^{24,25} One of the major advantages of this method is that it can be carried out under ambient conditions, e.g. in the presence of atmospheric oxygen. The photocatalytic activity depends on the ability of the semiconductor to create electron-hole charge carrier pairs, which in turn generate the primary oxidants responsible for the oxidation reactions, such as hydroxyl radicals (•OH), as well as transient hydroxyperoxide radicals.²⁶ Many photocatalysts, including but not limited to TiO₂,

WO₃ and ZnO have been reported to efficiently decompose organic pollutants.²⁷ A way to facilitate the photocatalytic degradation further is the addition of chemical oxidants, such as persulfate, that in the presence of UV light produces additional reactive radical species, such as hydroxyl and sulfate anion radicals (SO₄^{•-}).^{28,29} The combination of a photocatalyst and an oxidant can substantially improve the photodegradation of organic contaminants, as reported for photocatalytic processes taking place under UV²⁹ and visible²⁸ light.

The aim of this chapter is to identify the photocatalyst material most suitable for cortisone decomposition in aqueous solution and to provide additional information on how altering process conditions (catalyst and cortisone concentration, solution pH, persulfate oxidant presence) affect the rate constant of the decomposition reaction. In this study, we used cortisone 21-acetate (CA) as a model emerging contaminant, due to its pharmaceutical relevance, high photostability and low toxicity³⁰, to establish efficient waste-, ground- and drinking water photocatalytic cleaning procedures.

2. Experimental

2.1 Materials

Most reagents and photocatalyst materials were obtained from Aldrich and used as received. Those included NaOH, HCl, cortisone 21-acetate, sodium persulfate, WO₃ and ZnO. Hombikat UV 100 TiO₂ was obtained from Sachtleben, while Evonik TiO₂ P25 was obtained from Evonik Industries. The solvents for HPLC, acetonitrile and water, were obtained from Biosolve. XRD patterns were recorded using a Bruker D2 PHASER spectrometer. Specific BET surface area was obtained using a Micromeritics Tristar 3000 measuring apparatus. Samples were outgassed at 300°C for 24 hours prior to the BET measurements, similar to the procedures reported previously.^{31,32} XRD and BET characterization results are shown in Appendix A, Fig. 1 and Table 1, respectively.

2.2. Photocatalytic decomposition experiments

The photocatalytic decomposition experiments were performed in a medium throughput reactor equipped with a multi-stirrer plate situated within a light isolating box that had a multi-tubular light source installed, as shown in Fig. 1. The light source had an intensity of 3.21 mW cm⁻² at the liquid surface in the wavelength range of 360 to 380 nm. The aqueous photocatalyst suspensions were magnetically stirred in a 100 mL beaker at 400 rpm throughout the

experiments. The initial concentration of CA (with its molecular structure shown in Fig. 2.a) was 10 mg L^{-1} . 50 mL of CA solution was used in each experiment. The pH of the initial solution was adjusted using diluted NaOH or HCl. In the case of the reactions performed with buffer solutions, they represented 20% of the total volume. The buffers used were NaHCO_3 (0.05 M, 100 mL)/ NaOH (0.1 M, 42.4 mL)/ H_2O (57.6 mL) and $\text{Na}_2\text{B}_4\text{O}_7$ (0.025 M, 100 mL)/ HCl (0.1 M, 37.6 mL)/ H_2O (62.4 mL) for pH 10.8 and 8.1, respectively. Before performing the photocatalytic decomposition reactions, the solution was saturated with air for 15 minutes and allowed to equilibrate in the dark for 30 minutes. During the photocatalytic decomposition experiments, samples were taken out periodically, the catalyst filtered out with a Millipore filter of $0.20 \text{ }\mu\text{m}$ (Whatman SPARTAN RC 30) pore size, followed by monitoring of the reaction extent via a decrease of CA absorbance peak at 244 nm using UV-VIS spectrometry. A typical photodecomposition experiment shown in Fig. 2.b was complete within $\sim 90 \text{ min}$, as concluded from the disappearance of the 244 nm peak. In order to improve the photodecomposition kinetics of CA, a strong oxidizing agent, sodium persulfate ($1.24 \times 10^{-6} \text{ mol}$, $2.95 \times 10^{-3} \text{ g}$), was added at 1:1 mol ratio to the typical CA concentrations discussed above (10 mg L^{-1} , $1.24 \times 10^{-6} \text{ mol}$).

Fig. 1. The medium throughput photochemical reactor used in this study. It is comprised of a multi-stirrer plate and a 360-380 nm light source operating at 21°C . See text for further details.

a)

b)

Fig 2. a) Chemical structure of cortisone acetate (CA). b) UV-VIS absorbance spectrum during the photocatalytic decomposition reaction (10 mg L⁻¹ of CA and 0.25 g L⁻¹ of P25 TiO₂).

2.3. Analytical Methods

2.3.1. Total Organic Carbon (TOC) experiment

To determine the total organic carbon amount remaining, a photocatalytic experiment was performed with 10 mg L⁻¹ of CA and 0.25 g L⁻¹ of TiO₂ P25 photocatalyst. Liquid samples were collected after 0, 15 and 120 min, and analyzed for TOC content. The TOC measurements were performed using a Shimadzu TOC-L CPH instrument equipped with a high sensitivity catalyst and ASI-L autosampler. The system was calibrated in 3 ranges, 0-1 ppm, 0-5 ppm and 0-10 ppm. Analytes were prepared by Mr. N. de Vries of Shimadzu Benelux and analyzed at Shimadzu Europe Duisburg. Data were processed using TOC-L Control software.

2.3.2. Liquid chromatography-mass spectrometry (LC-MS)

To identify any reactive intermediates, 0.5 mL sample solution was taken at various reaction times, centrifuged in BD Falcon tubes at 7000 rpm, and analyzed using HPLC (Agilent 1100 Series). Separation of CA decomposition products was done using a gradient elution in water and acetonitrile mixtures of 75:25 to 50:50 for the first 10 min, 50:50 for the following 2.5 min and 25:75 for the final 5 min,^{33,34} using a flow rate 0.5 mL min⁻¹. 10 µl was injected to the reverse phase column (All Chromolith Merk C18 column 100 mm x 3 mm i.d.) using the autosampler at room temperature (21°C). Detection was performed using a Spectra System UV600LP photodiode array UV detector followed by a mass spectrometry (Bruker MS Esquire 3000+). The separated products were ionized using the positive Electrospray Ionization (+ESI)

technique. The MS ionization conditions were as follows: flow rate of 0.5 mL min^{-1} , nebulizer gas pressure of 30 psi, dry gas flow of 3 L min^{-1} and dry gas temperature of 325°C .

3. Results and Discussion

3.1. Effect of the photocatalyst nature on the decomposition of CA

First, as control experiments, decomposition rates of 10 mg L^{-1} CA under 375 nm light with no catalyst present, as well as with TiO_2 P25 in the dark, were compared to the results obtained using TiO_2 P25 in the presence of light, and are shown in Fig. 3. It can be seen that the CA concentration in solution is constant within 180 min in the first two cases, but in the presence of TiO_2 P25 with light, CA concentration decays exponentially and becomes negligible after ~ 90 min. The observed CA stability is due to the absence of photons of sufficient energy to directly photolytically decompose CA.

Fig. 3. CA (10 mg L^{-1}) photocatalytic decomposition under 375 nm irradiation without any photocatalyst (blue), with 0.25 g L^{-1} loading P25 TiO_2 in the dark (orange) and P25 TiO_2 with light (black).

Photocatalytic CA decomposition was further carried out using different semiconductors, such as TiO_2 (Evonik P25 and Hombikat), ZnO and WO_3 , in order to establish the most effective commercial photocatalyst. The concentration of the photocatalysts used was 0.25 g L^{-1} . The corresponding data are shown in Fig. 4. This type of catalyst screening is important due to the fact that it is not possible to predict *a priori* which catalyst performs best for the photocatalytic decomposition of a selected organic compound.²⁷ From the data shown in Fig. 4 it can be seen, that a complete decomposition of CA occurred after ~ 60 min when using ZnO and ~ 90 min when using TiO_2 P25. The relative order of 10 mg L^{-1} CA decomposition efficiency for the semiconductor photocatalysts investigated was $\text{ZnO} > \text{Evonik P25} > \text{Hombikat (Homb)} > \text{WO}_3$.

The best catalyst to decompose CA from the data shown in Fig. 4 is ZnO, as can be explained by its greater quantum efficiency, than that of TiO_2 ,^{35,36} as well as by the rich defect chemistry of ZnO.³⁷ However, ZnO is unstable in aqueous solutions due to its photo enhanced dissolution and reaction with water leading to the formation of ZnOH^+ , Zn(OH)_2 , Zn(OH)_3^- , Zn(OH)_4^{2-} , Zn^{2+} and other products, depending on the experimental parameters, such as pH.³⁵ These products formed are not active as photocatalysts.^{38,36}

Poor catalytic activity of WO_3 can also be observed from Fig. 4. WO_3 has a band gap of 2.4-2.7 eV, smaller than the other photocatalysts used in this work. The oxidative power of the photogenerated holes in the valence band is enough to oxidize organic compounds (+3.1-3.2 vs SHE) but the reduction potential of the photogenerated electrons in the conduction band (+0.3 - +0.5 vs SHE) is lower than needed for the one electron reduction of adsorbed oxygen (-0.046 V vs. SHE).³⁹ Poor photoactivity of WO_3 has already been reported in the photocatalytic decomposition of other organic compounds, such as methyl orange and phenol.^{40,41} With any overpotential occurring, WO_3 will not be able to transfer photoproduced electrons to the O_2 molecule, since the rate of the photooxidation of organic compounds on the surface of catalysts is proposed to be limited by the rate of electron transfer to oxygen.⁴¹ The negligible photoactivity of WO_3 can also be attributed to the high recombination rate of electrons/hole pairs.⁴¹

From the data presented, it was decided to conduct further photocatalytic experiments using TiO_2 P25, which showed the second fastest photocatalytic decomposition rate observed, without any pre-treatment, while maintaining the chemical stability.

Fig. 4. CA (10 mg L^{-1}) photocatalytic decomposition under 375 nm irradiation and 0.25 g L^{-1} photocatalyst loading. Photocatalysts used were Hombikat and P25 TiO_2 , WO_3 and ZnO. Error bars shown are based on triplicate measurements.

3.2. Effect of TiO_2 concentration on the decomposition rate of CA

The first parameter that was optimized in this work to ensure an effective CA photocatalytic degradation rate using TiO_2 was the photocatalyst concentration. The photocatalytic degradation rate of 10 mg L^{-1} CA was evaluated at TiO_2 P25 slurry concentrations of $0\text{--}1.0 \text{ g L}^{-1}$, as shown in Fig. 5. The inset shows that the initially observed decomposition rate constant, $k \text{ (min}^{-1}\text{)}$, increases proportionally with the TiO_2 P25 concentration until it reaches a *plateau* for a photocatalyst loading of 0.25 g L^{-1} . In a slurry reactor based photocatalytic process, the amount of the photocatalyst is an important parameter due to the fact that after a certain amount, it is not possible to achieve a better decomposition rate due to limited light penetration in the vessel, that is, the photoactive volume of the suspension decreases.⁴² Additionally, Konstantinou and Albanis have also related this phenomenon to increased light scattering and subsequent reduction in light penetration through the solution.⁴² The optimum concentration of TiO_2 P25 of 0.25 g L^{-1} was observed, and was in the lower end of the range of $0.07\text{--}8.0 \text{ g L}^{-1}$, reported for various compounds.⁴³ It is also in agreement with the values reported by Li Puma for tubular and solar compound parabolic collector based reactors.⁴⁴ The optimal concentration depends on the physical parameters of the reactor itself, as well as on the light source parameters (power, wavelength).⁴² The light intensity used in the present study was relatively low, causing a relatively low catalyst concentration *plateau*.

Fig. 5. CA (mg L^{-1}) photocatalytic decomposition under 375 nm irradiation at different concentrations of TiO_2 P25 ($0\text{--}1 \text{ g L}^{-1}$). Inset: observed rate constant, $k \text{ (min}^{-1}\text{)}$, as a function of TiO_2 P25 photocatalyst loading.

3.3. Effect of the initial CA concentration on the decomposition rate at a constant 0.25 g L⁻¹ TiO₂ P25 loading

Next, the effect of the initial CA concentration on its photocatalytic decomposition kinetics was explored. The rate constant, k (min⁻¹), was calculated using a linear plot of $-\ln(C/C_0)$ vs time, whereas the initial rate was obtained by multiplying initial concentrations, C_0 , by the obtained rate constant. The dependence of the photocatalytic decomposition rate on the initial organic compound concentration is important in elucidating the rate determining step in the reaction mechanism for any practical application.⁴² Fig. 6 shows the decomposition of CA as a function of the illumination time in solution containing different initial concentrations, while the loading of TiO₂ P25 was kept constant at 0.25 g L⁻¹. It can be seen that the decomposition curves of different initial CA concentrations (5-40 mg L⁻¹) all show an exponential decay. This effectively means that the total process kinetics depend on the initial concentration of the organic compound and the decomposition kinetics are pseudo-first order. A decrease in the photocatalytic decomposition rate constant from 0.06 to 0.01 min⁻¹ for 5 to 40 mg L⁻¹ of CA, respectively, can be seen in the inset of Fig 6.a. Furthermore, it can be seen that the calculated initial reaction rate, r_o , is effectively independent of the initial concentration, since the values obtained are similar, ranging from 0.31 to 0.46 mg L⁻¹ min⁻¹ with no detectable trend in changes observed. It can be proposed, that, as the CA concentration increases, the photocatalyst surface becomes covered with adsorbing CA molecules, thus decreasing the kinetic transfer of the photogenerated holes or hydroxyl radicals to the CA molecule.^{45,46} More importantly, it can also be proposed that, as CA concentration increases, O₂ present in aqueous solution as electron scavenger needs to compete with CA molecules to reach the surface of the photocatalyst, thus decreasing the formation of HO₂[•] radicals. via the superoxide intermediate mechanism, important for the decomposition of organic contaminants.⁴⁵ Using the rate constants obtained here, cortisone degradation in the environment can be estimated. Here, it is typically present at very low concentrations of ng L⁻¹. Hence, cortisone will degrade at environmentally relevant concentrations very quickly, when in contact with a photocatalyst in the presence of light, with a typical estimated half-life of ~11 min, as calculated using the observed rate constants reported here. Consequently, its photocatalytic decomposition might be a viable method to remediate cortisone contamination in drinking water. In the following sections we will discuss two other parameters of relevance for optimizing process conditions.

Fig. 6. Photocatalytic decomposition of varying concentrations of CA (5–40 mg L⁻¹) under 375 nm irradiation using TiO₂ P25 (0.25 g L⁻¹). Inset: observed rate constant, k (min⁻¹) in blue and initial rate, r_0 (mg L⁻¹ min⁻¹) in red as a function of CA concentration. Lines are given for the eye guidance only.

3.4. Effect of the solution pH on the photocatalytic decomposition rate of CA

The pH of the solution can affect the surface charge of the photocatalyst particles, their aggregate size, as well as their electronic properties, thus having a strong effect on the total efficacy of heterogeneous photocatalytic water purification.⁴⁷ Photocatalytic decomposition experiments of 10 mg L⁻¹ CA using TiO₂ P25 (0.25 g L⁻¹) as a photocatalyst were performed to obtain the optimal pH value and are shown in Fig 7. Solution pH values investigated ranged between 3.1 and 10.8, a range broader than that typically found in the environment of 6 to 9.⁴⁸ It can be seen that the photocatalytic decomposition of CA at different pH values exhibits similar decomposition kinetics, as inferred from the very similar exponential CA concentration decay.

Fig. 7. CA (10 mg L⁻¹) photocatalytic decomposition under 375 nm irradiation at different pH values of without buffers (pH 3, 5, 7, 8.2 and 10.8) and with buffers (pH 8.1 and 10.8) using TiO₂ P25 (0.25 g L⁻¹).

Any variation in the operating pH is known to affect the surface charge of the catalyst: the pH will directly affect the ionization state of the TiO₂ surface according to the reactions (1) and (2).⁴²

The reported point of zero charge (pzc) value for TiO₂ P25 is pH 6.3.⁴² Thus, the TiO₂ surface is expected to become positively charged in acidic environment (pH < 6.3) and negatively charged in basic conditions (pH > 6.3). Since one of the major photocatalytic reactants is a hydroxyl radical generated by reaction of the photoinduced hole by a water molecule,⁴⁹ photocatalytic efficiency should decrease with increasing pH. This is not the case in Fig.7, with degradation reactions proceeding at essentially the same rates throughout the whole pH range. We measured the pH values of 10 mg L⁻¹ CA solutions before and after their photocatalytic decomposition experiments. It was observed that at low pH values (3.3 and 5.1), the decrease was very small, 3.1 and 4.3, respectively. However at the initial pH values of 7.1, 8.3 and 10.8, the final pH was 5.1, 6.0 and 7.0 respectively, close to the pzc reported for TiO₂ (6.3). This can be due to the release of protons or the acetic group during CA decomposition into the solution via the cleavage of the C-O bond. Notably, reported pKa of CA is 12.6⁵⁰, much higher than the pH of the solution investigated, so no dissociation is expected prior to the decomposition by the *in situ* generated radical species. We can propose that several hydroxyl radical generation mechanisms proceed at different pH values, as well as other oxygen based radical generation (O₂^{•-}) steps, with the resulting final photocatalytic decomposition rate being almost the same. As a test, two pH values, 10.8 and 8.2, were chosen for analogous tests using a buffered solution. After the photocatalytic reaction the pH values were 9.6 and 8.0, respectively, and the decomposition rates showed very similar behavior to those shown in Fig. 7. Hence, no pH dependency was observed on the decomposition rate, allowing performing CA degradation in practice at the native pH of the aqueous solution treated. The observed decrease in pH can be proposed due to the formation of acids during the oxidation reactions.⁵¹

3.5. Photocatalytic decomposition of CA in the presence of S₂O₈²⁻ and S₂O₈²⁻/TiO₂

Another possibility of further improving the photodecomposition kinetics of CA is the addition of strong aqueous phase oxidants. The oxidizing ion S₂O₈²⁻ was used in the form of sodium persulfate (1.24x10⁻⁶ mol) to investigate the ability of strong oxidizers to decompose CA (10 mg L⁻¹ corresponds to 1.24x10⁻⁶ mol in 50 mL working volume). Fig. 8 shows that the solution of

CA with the persulfate anion present in the dark had a decrease of 21% in its initial concentration within the first 2 h, equalizing afterwards. After 6 h of irradiation, the CA was almost totally decomposed in the presence of $\text{S}_2\text{O}_8^{2-}$ (with no TiO_2) with an estimated rate constant of 0.004 min^{-1} . TiO_2 P25 alone shows a higher CA photodecomposition rate constant of 0.040 min^{-1} in the presence of 375 nm irradiation. Finally, complete decomposition of CA is achieved after 30 min when a combination of $\text{S}_2\text{O}_8^{2-}$ and TiO_2 P25 is irradiated with a rate constant of 0.071 min^{-1} , more efficient than with only the photocatalyst present. The activity obtained in the presence of both the oxidizing agent and the photocatalyst demonstrates synergy between the persulfate and TiO_2 P25. This warrants a discussion on the related decomposition pathways.

Fig. 8. CA (10 mg L^{-1}) photocatalytic decomposition in the presence of sodium persulfate using TiO_2 P25 (0.25 g L^{-1}). Specific reactive conditions include the presence of $\text{S}_2\text{O}_8^{2-}$ in the absence of UV light, $\text{S}_2\text{O}_8^{2-}/\text{UV}$, TiO_2 P25/ UV and $\text{S}_2\text{O}_8^{2-}/\text{TiO}_2$ P25/ UV .

One of the drawbacks of metal oxide semiconductor material based photocatalysts is a relatively fast charge carrier – electron/hole - recombination yielding a low overall process efficiency.⁵² The addition of an electron acceptor/scavenger can further improve the photocatalytic decomposition of organics via several mechanisms, namely by (a) decreasing the electron-hole recombination by accepting the conduction band electron, (b) increasing the reactive radical concentration and thus the corresponding oxidation rate and (c) generating more radicals and other oxidizing species.^{52,53} Persulfate ion has recently been used alone, in combination with TiO_2 as photocatalyst^{28,29} or in advanced oxidation with transition metals,⁵⁴ to enhance the total process performance to remove organic contaminants via the resulting sulfate anion radical generation ($\text{SO}_4^{\cdot-}$). These generated sulfate anion radicals then can further react with H_2O to produce hydroxyl radicals at the wavelengths comparable to those used in this work^{52,53} via reactions (3) and (4)

The data presented in Fig. 8 show, however, that the mechanism of CA photocatalytic decomposition does not proceed exclusively via reaction with hydroxyl radicals in solution generated by $\text{S}_2\text{O}_8^{2-}$, but also by catalyst surface mediated steps, equation (5).²⁹

Hence, the presence of $\text{S}_2\text{O}_8^{2-}$ in the vicinity of the photocatalyst surface leads to the formation of other radical species, such as $\text{SO}_4^{\bullet-}$, an oxidant species that increases the efficiency of the photocatalytic reactions. It is important to reiterate that the calculated pseudo first order rate constant for the experiments with $\text{S}_2\text{O}_8^{2-}$ alone, TiO_2 P25 alone and $\text{S}_2\text{O}_8^{2-} + \text{TiO}_2$ P25 were 0.004, 0.040 and 0.071 min^{-1} , respectively, showing a synergistic behavior due to the more efficient electron transfer to $\text{S}_2\text{O}_8^{2-}$ than to O_2 , with the former being a stronger oxidant ($\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-} = +2.01 \text{ V}$ vs $\text{O}_2/\text{O}_2^{\bullet-} = -0.13 \text{ V}$),^{55,56} as depicted in Fig. 9. While O_2 is a major electron scavenger without $\text{S}_2\text{O}_8^{2-}$ present, with $\text{S}_2\text{O}_8^{2-}$ secondary reactions to form other radicals, such as $\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$ can contribute to accelerating CA decomposition.

Finally, a photocatalytic experiment was performed with 10 mg L^{-1} of CA and 0.25 g L^{-1} of TiO_2 P25 at natural pH (~ 7), in which samples were collected after 0, 15 and 120 min and analyzed for total organic carbon content, showing respectively 6.74, 6.58 and 0.89 mg L^{-1} . It can be seen that after 2 h, only $\sim 8.9\%$ of TOC was still left in the solution. This value is important since it shows that photocatalytic processes lead to almost complete mineralization of CA and can be used as a viable water treatment technique. However, sample matrix effects of natural waters need to be accounted for, to obtain the more accurate values.

Fig. 9. A proposed mechanism of CA degradation in the presence of electron acceptors (O_2 and $S_2O_8^{2-}$) mediated by the photocatalyst surface with the corresponding relevant standard redox potentials at pH 0 of TiO_2 , $O_2/O_2^{\bullet-}$ and $S_2O_8^{2-}/SO_4^{\bullet-}$.

3.6. Photocatalytic degradation of CA followed by LC-MS.

A photocatalytic treatment of CA (10 mg L^{-1}) was performed for 60 min with TiO_2 P25 and the resulting samples were taken after 0, 1, 3, 5, 10, 30 and 60 min for LC-MS analysis. Fig. 10 shows the corresponding chromatograms. A clear decrease with time in the initial CA concentration with the retention time of 8.3 min can be observed. The peak with the retention time of 5.7 min exhibits an MS spectrum chiefly due to the 403 m/z fragment, and is an isomer of the CA peak at 8.3 min. The peak at 4.1 min exhibits an MS spectrum with the fragment at 361 m/z ($[M+1]$) due to the removal of the acetyl group via hydrolysis (Fig. 1 in Appendix B). Lack of identifiable intermediates can be proposed to take place due to two reasons. First, a rapid conversion of CA at the TiO_2 surface proceeds resulting in an efficient mineralization of the molecule, as supported by TOC analysis. Furthermore, resulting intermediate species are strongly bound to TiO_2 , minimizing the visibility of decomposition fragments. Finally, resulting concentrations of the intermediates might be lower than the instrumental resolution, thus preventing their detection.

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Fig. 10. LC-MS time resolved chromatograms obtained during the photocatalytic degradation of CA (10 mg L^{-1}) with TiO_2 P25 (0.25 g L^{-1}) at 375 nm. Peaks due to instrumental contamination are marked with asterisks.

4. Conclusions

In this work, the photocatalytic decomposition of cortisone acetate (CA) was investigated using a medium throughput screening system in the presence of catalysts, as well as a strong sacrificial oxidizing agent. No photocatalytic decomposition in a pure photolytic regime, and very little CA adsorption on the photocatalyst particles was observed. The best catalysts to perform the photocatalytic decomposition of CA were ZnO and TiO_2 P25. The latter was chosen for further studies due to the poor stability of ZnO in water. The optimal amount of TiO_2 P25 was found to be 0.25 g L^{-1} . No pH dependency was observed on the decomposition rate, allowing to perform CA degradation at the native pH of the aqueous solution treated. Finally, photocatalytic decomposition using TiO_2 P25 was more efficient than with the persulfate ion alone. However, the combination of $\text{TiO}_2/\text{S}_2\text{O}_8^{2-}$ under 375 nm radiation yielded the overall fastest decomposition rate constant. Thus, the use of the electron acceptors ($\text{S}_2\text{O}_8^{2-}$) in combination with photocatalysts for practical applications can be seen as the most effective way of improving the photocatalytic decomposition reaction rate. When LC-MS was used to follow

the photocatalytic degradation of CA, no intermediate compounds were detected at any significant amount. This fact is important for water cleaning applications, since the toxicity of the intermediates is usually an issue during the photocatalytic treatment. Several pathways can be proposed for this observation. First, the initial compound could have been promptly converted to CO₂ and H₂O, which is not confirmed by our TOC data. Next, the concentrations of intermediate compounds formed are very low and can't be detected by our instrument. Most importantly, an adsorptive chemistry on the photocatalyst particles can be proposed. This is substantiated by the fact that the photocatalyst used, TiO₂ P25, was of high BET surface area (53 m² g⁻¹) and is known to chemisorb many organic molecules. Hence, the reactive oxygenate intermediate would bind to titanium surface sites thus not appearing during the solution analysis.

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Appendix A

Table 1. Characterization of the photocatalysts.

Catalyst	Manufacturer	BET surface area, m ² /g	Crystalline Phase
ZnO	Sigma-Aldrich	6	Wurtzite
P25 TiO ₂	Evonik	53	70% Anatase 30% Rutile
Hombikat TiO ₂	Sachtleben	313	100% Anatase
WO ₃	Sigma-Aldrich	7	Monoclinic

Fig. 1. XRD patterns of the photocatalysts used in this work.

Appendix B.

MS spectra from the peak at 4.1 min

MS spectra from peak at 5.7 min

MS spectra from the peak at 8.3 min

Fig. 1. The representative MS spectra of the eluted species at 4.1, 5.7 and 8.3 min showing CA and cortisone fragments.

Chapter 5

Photocatalytic Degradation of Organic Contaminant Mixtures in Water

The photocatalytic decomposition of Methyl Orange (MO) and Atrazine was studied in a slurry reactor individually, and simultaneously. From the several photocatalysts tested - TiO_2 P25, TiO_2 Hombikat, 0.5% Pt/P25- the highest rate constants for both substrates were obtained with TiO_2 P25. When simultaneously present, MO had a strong detrimental effect on the rate observed for Atrazine decomposition for all the catalysts. Various process parameters were varied (catalyst loading, MO initial concentration, pH) to determine the cause of this observation. The results reveal the importance of adsorption of the substrate on the catalyst surface in obtaining a high degradation efficiency. In particular when the pH increases from 3 to 11, Atrazine decomposition was no longer inhibited by MO. Apparently the surface charge of TiO_2 significantly affects the degradation order of contaminants when present in mixtures. Consequences of the results for practical application of photocatalysis for water decontamination are briefly discussed.

This chapter is based on: Romão, J.; Mul, G.; “Photocatalytic Degradation of Organic Contaminant Mixtures in Water”. (Submitted)

1. Introduction

Clean water is one of the biggest concerns of society, while of particular interest are the recently increasing concentrations of so-called emerging contaminants (pharmaceuticals, pesticides, metabolites).¹⁻³ The main techniques applied to perform purification of wastewater, such as adsorption by the use of activated carbon, biological treatment and filtration, do not eliminate the emerging contaminants completely. A novel water purification method needs to be developed.^{4,5} Heterogeneous photocatalysis, which can be classified as an advanced oxidation method, is considered a promising technology for water treatment.⁶⁻¹⁰ The main advantage of photocatalysis is that complete mineralization to CO₂ and H₂O of a wide range of organic pollutants can potentially be achieved at room temperature and at relatively low costs.^{5,11}

The key for obtaining a high efficiency in photocatalysis is to optimize the reaction conditions to which the semiconductor is exposed. Mass transfer and light transfer issues need to be resolved, to create electron-hole pairs and subsequently radical species (hydroxyl radicals, superoxide anions), necessary for the desired oxidation reactions.^{12,13} TiO₂, WO₃ and ZnO are some of the semiconductor photocatalysts suitable for decomposition of organic contaminants in water, as reported in the literature.⁹ Nonetheless, TiO₂ is by far the most used catalyst in wastewater treatment, due to its high stability and photocatalytic efficiency.^{5,14}

Many studies focused on decomposition of organic contaminants, such as dyes, pharmaceuticals, herbicides and pesticides. Several reaction parameters have been optimized, such as: i) catalyst loading, ii) initial concentration of the organic compound, and iii) the pH.¹⁴⁻²⁰ There is a need to evaluate all these conditions, since the most effective conditions are very much dependent on the molecular structure of the organic compound.^{11,21} For example, an optimum TiO₂ loading of 2 g L⁻¹ was reported for decomposition of Acid Orange, while for another dye, Amino Black 10B, 5 g L⁻¹ appears to be most beneficial.⁹ Most studies reported on water decontamination are performed using a single organic contaminant. There are two reports in literature from Serpone *et al.*²² and Encina *et al.*²³ which describe the decomposition of two compounds, derivatives from chlorophenol, in the same solution. In both studies, it is reported that the competition of the chlorophenol compounds for the active sites of the catalyst, cause a decrease in the rate constant of one of the molecules. These studies are very relevant since in municipal wastewater multiple components are present, and evaluation of the mutual effects of these contaminants on their photocatalytic degradation rates is necessary to evaluate the feasibility of practical application.

The main aim of this research is to evaluate the photocatalytic degradation rates when there are several compounds with very different chemical composition in solution. This study is focused on the degradation of two organic molecules at the same time, and the optimized degradation conditions for such mixtures are evaluated. Decomposition of Atrazine, a known pesticide, and methyl orange (MO) and acid orange (AO), as representative for dye molecules which are often used as wastewater model compounds, were studied. Fig.1 shows the chemical structures of these compounds.

Fig. 1. Chemical structures of the organic compounds used in this study.

The process parameters evaluated in this study were catalyst composition (TiO₂ P25, TiO₂ Homb, 0.5% Pt/P25), light intensity, catalyst loading, initial concentration of the organic compounds and pH.

2. Experimental

2.1 Materials

All reagents were obtained from Aldrich and used as received. Those include NaOH, HCl, chloroplatinic acid, methanol, methyl orange, atrazine and acid orange. The photocatalyst material, Hombikat UV 100 TiO₂, was obtained from Sachtleben, and P25 TiO₂ from Evonik Industries. The solvents (water and acetonitrile) used for HPLC analysis were purchased from Biosolve.

2.2. Preparation of Pt/TiO₂ P25

Functionalization of TiO₂ P25 with Pt nanoparticles was performed using a photodeposition method.²⁴ To this end, an aqueous suspension of TiO₂ P25 and chloroplatinic acid (H₂PtCl₆, 0.5 g L⁻¹) was stirred for 30 minutes in the dark. Subsequently MeOH was added (1M, 3 ml) and the suspension illuminated (radiation intensity 3.21 mW cm⁻² at 375 nm) for 5 h. The powder was

collected by centrifugation, and washed three times with ethanol (20 ml) and distilled water (20 ml) consecutively. The powder was dried over night at 90°C. The Pt loading was estimated to be 0.5 wt %. (Detailed characterization of the catalyst is reported in Chapter 6, paragraph 3.1)

2.3. Photocatalytic decomposition experiments

The photocatalytic degradation experiments were performed in parallel screening equipment (Chapter 4, paragraph 2.2). The reactors consisted of glass flasks filled with 50 ml of an aqueous photocatalyst suspension, stirred at 350 rpm. The initial concentration of methyl orange (MO), atrazine and acid orange (AO) was $1.25 \times 10^{-5} \text{ mol L}^{-1}$ and the most often applied photocatalyst concentration equivalent to 0.25 g L^{-1} . For the photocatalytic degradation experiments of the individual organic compounds, the catalyst was suspended in 25 ml of a solution of $2.5 \times 10^{-5} \text{ mol L}^{-1}$. Subsequently 25 mL of MilliQ water was added to each of these solutions. For analysis of the mixtures, 25 mL of each contaminant solution of $2.5 \times 10^{-5} \text{ mol L}^{-1}$ were mixed, and finally the catalyst added. The pH of the initial solutions was adjusted using diluted NaOH or HCl, when applicable. The reactors were positioned on a multiple stirrer plate, and enclosed in a box containing eight tubular light sources with an intensity of 3.21 mW cm^{-2} (in the wavelength range of 360 to 380 nm)¹⁹. Before performing the photocatalytic decomposition reactions, the solutions were stirred and kept in the dark for 30 minutes.

2.4. Liquid chromatography-mass spectrometry (LC-MS)

In order to determine the decomposition rate of the organic compounds, samples were taken periodically. The samples were immediately centrifuged at 7000 rpm for 5 minutes to remove the catalyst particles. Subsequently the samples were analyzed by HPLC (Agilent 1100 Series). Separation of the organic compounds in the sample was achieved using a mixture of water and acetonitrile (75:25) as eluent, and applying a flow rate of 0.3 ml min^{-1} . The sample volume injected into the reverse phase column (All Chromolith Merk C18 column 100mm x 3mm i.d.) was 10 μL at room temperature (21°C), using an autosampler. Detection was performed using a Spectra System UV600LP photodiode array UV detector, followed by mass spectrometry (Bruker MS Esquire 3000+). The separated products were ionized using positive Electrospray Ionization (+ESI) in the case of MO and Atrazine, and negative Electrospray Ionization (-ESI) for AO. The MS ionization conditions were: a flow rate of 0.5 ml min^{-1} , a nebulizer gas pressure of 30 psi, a dry gas flow of 0.3 L min^{-1} , and a dry gas temperature of 325°C. In Appendix A, a chromatogram from the initial mixture of MO and Atrazine, and the respective Mass Spectra, are shown for reference.

2.5. Calculating rate constants

Rate constants were calculated using data point linearization of the slope of first or zero order kinetics. The respective relations are shown in equations (1, first order) and (2, zero order), in which c is the concentration after a certain time interval, and c_0 the initial concentration:

$$-\ln\left(\frac{c}{c_0}\right) \text{ vs. time} \quad (1)$$

$$c \text{ vs. time} \quad (2)$$

3. Results

3.1. Effect of Photocatalyst Composition on degradation rate of MO and/or Atrazine at neutral pH (7.5)

Hombikat (TiO₂ Homb), and Evonik P25 (TiO₂ P25) were initially investigated to determine the most effective commercial catalyst in MO and Atrazine degradation (Fig.2). Fig. 2.a. shows the results for TiO₂ P25. The rate of MO degradation in the absence (□) or presence of Atrazine (■) is very similar (first order rate constants of 0.16 min⁻¹ or 0.17 min⁻¹, respectively). The degradation rate of Atrazine is higher in the absence of MO (○), showing a first order rate constant of 0.35 min⁻¹. However, in the presence of MO (●), the Atrazine concentration only very slowly decreases in the first 15 min (zero order behavior $k = 2.57 \times 10^{-7} \text{ mol L}^{-1} \text{ min}^{-1}$), while a high decomposition rate is only obtained after MO is fully degraded (first order rate constant of 0.12 min⁻¹). When TiO₂ Homb was used, different degradation profiles can be observed (Fig. 2.b). The degradation of MO individually (□) or in the presence of Atrazine (■) is much slower as compared to obtained for TiO₂ P25, and complete mineralization was only achieved after 45 min of illumination. The difference in degradation rate of Atrazine (as a single compound) induced by P25 or Hombikat is even more pronounced (○), while the presence of MO appears to have a less dramatic detrimental effect on the rate (●). The rate constants derived from the experiments at different conditions can be found in Table 1.

a)

b)

Fig. 2. Photocatalytic decomposition of MO and Atrazine individually and in mixtures ($1.25 \times 10^{-5} \text{ mol L}^{-1}$) with 0.25 g L^{-1} of photocatalyst. a) TiO_2 P25, b) TiO_2 Homb.

3.2. Effect of Light intensity on performance of P25 and Hombikat

Fig. 3, shows the decomposition profiles for Atrazine and MO in a mixture at lower light intensity. Obviously the degradation rate of MO is slower at lower light intensity for both catalysts (TiO_2 P25 and TiO_2 Homb). Atrazine decomposition is clearly delayed much more significantly by the presence of MO at low light intensity, as compared to high light intensity,

and particularly evident for TiO₂ Homb. The MO substrate specificity of TiO₂ Homb is 100% at low light intensity.

a)

b)

Fig. 3. Photocatalytic decomposition of MO and Atrazine in mixtures ($1.25 \times 10^{-5} \text{ mol L}^{-1}$) with 0.25 g L^{-1} of photocatalyst at a light intensity of 1.25 mW cm^{-2} . a) TiO₂ P25, b) TiO₂ Homb.

Fig. 4, shows the light dependency of the rate constants of simultaneous decomposition of MO (a) and Atrazine (b) for both catalysts, where the highest rate constants are obtained for P25. Increasing the light intensity leads to a non-linear increase in the rate constant of MO for both catalysts. However, the effect of light intensity is much more significant for Atrazine, since the (zero order) rate constant increases exponentially.

a)

b)

Fig. 4. Comparison of rate constants at different light intensities with TiO₂ P25 and TiO₂ Homb, as photocatalyst for a) MO and b) Atrazine.

3.3. Promoting activity of TiO₂ P25 with Pt nanoparticles

A commonly applied surface modification of TiO₂ is deposition of metal nanoparticles on the surface in order to improve electron-hole separation efficacy and promote oxygen reduction catalysis.²⁵⁻²⁷ The sample prepared contained approximately 0.5 wt.% Pt on TiO₂ P25. Fig. 5 shows that MO in the absence (□) or presence of Atrazine (■) yields similar degradation profiles, in agreement with the data for TiO₂ P25. However, the addition of Pt nanoparticles significantly decreases the efficacy of TiO₂ P25 in MO degradation (compare with Fig. 2).

Lower rate constants can be calculated for MO individually (0.08 min^{-1}) and in a mixture with Atrazine (0.10 min^{-1}), when compared to TiO_2 P25 (0.17 , and 0.16 min^{-1} , respectively). In the case of Atrazine decomposition ($\circ$), an only slightly lower rate constant for $0.5\% \text{ Pt/P25}$ (0.31 min^{-1}) or TiO_2 P25 (0.35 min^{-1}) was obtained. Again the presence of MO has a dramatic effect on the Atrazine degradation rate. The lower rate constant for the platinumized catalyst compared to TiO_2 P25 (Fig. 2) observed for Atrazine decomposition in the presence of MO ($\bullet$), is likely due to the slower MO degradation rate (Table 1). Since Pt addition did not improve the performance of the photocatalyst, TiO_2 P25 was used for further studies.

Fig. 5. Photocatalyst degradation of MO and Atrazine individually and in mixture ($1.25 \times 10^{-5} \text{ mol L}^{-1}$) with 0.25 g L^{-1} of $0.5\% \text{ Pt/P25}$.

Table 1. Rate constant (k_1 , min^{-1} first order, $k_0 \text{ mol L}^{-1} \text{ min}^{-1}$ -zero order*) values for the mixture of MO and Atrazine with a catalyst loading of 0.25 g L^{-1} at pH 7.5

Catalyst	Light Intensity (mW cm^{-2})	MO	MO (At)	At	At (MO)
TiO_2 P25	3.21	0.17	0.16	0.35	$2.87 \times 10^{-7*}$
TiO_2 Homb	3.21	0.05	0.08	$1.82 \times 10^{-7*}$	$1.49 \times 10^{-7*}$
TiO_2 P25	1.20	-	0.11	-	$6.28 \times 10^{-8*}$
TiO_2 Homb	1.20	-	0.06	-	$1.58 \times 10^{-8*}$
$0.5\% \text{ Pt/P25}$	3.21	0.08	0.10	0.31	$2.31 \times 10^{-7*}$

3.4. Effect of TiO₂ P25 concentration on the decomposition reactions

Catalyst loading is an important parameter to optimize photocatalytic efficacy and for single compound degradation studies, usually a TiO₂ concentration of 1 g L⁻¹ leads to optimized efficacy.^{20,28} The result of 1 g L⁻¹ of catalyst to degrade MO and Atrazine is shown in Fig. 6.a. The decomposition reactions of MO (□) and Atrazine (○) individually were completed within 10 min, while MO degradation was little affected by the presence of Atrazine (■). Decomposition of Atrazine (●) required 45 min of illumination to be completed in the presence of MO. As compared to a catalyst concentration of 0.25 g L⁻¹, the rate constant for MO increased from 0.17 min⁻¹ to 0.30 min⁻¹ and for Atrazine from 0.35 to 0.72 min⁻¹. MO showed a similar rate constant value when decomposed in the presence of Atrazine, while for Atrazine in the presence of MO the increase in rate constant by increasing the catalyst concentration was insignificant (2.87x10⁻⁷ min⁻¹ for 0.25 g L⁻¹, 3.24x10⁻⁷ M min⁻¹ for 1.0 g L⁻¹, see Table 2). In Fig. 6.b, decomposition of MO and Atrazine in the presence of a catalyst concentration of 2.0 g L⁻¹ is shown, when present in a mixture. In this case, the Atrazine (●) decomposition rate was significantly improved, needing only 20 minutes to achieve full conversion, and showing first order, rather than zero order behavior (rate constants 0.21 min⁻¹, or 3.24x10⁻⁷ mol L⁻¹ min⁻¹, respectively). Table 2, shows the trends in rate constants individually and when present in mixtures as a function of catalyst loading.

a)

b)

Fig. 6. Photocatalytic degradation of MO and Atrazine individually and in a mixture ($1.25 \times 10^{-5} \text{ mol L}^{-1}$) using a) 1 g L^{-1} and b) 2 g L^{-1} of TiO_2 P25.

Table 2. Rate constant (k_1 , min^{-1} - first order, $k_0 \text{ mol L}^{-1} \text{ min}^{-1}$ -zero order*) values for the mixture MO and Atrazine at pH 7.5 with several catalyst loading.

Catalyst	Concentration (g L^{-1})	MO	MO (At)	At	At (MO)
TiO_2 P25	0.25	0.17	0.16	0.35	$2.87 \times 10^{-7}^*$
TiO_2 P25	1.0	0.30	0.24	0.72	$3.24 \times 10^{-7}^*$
TiO_2 P25	2.0	-	0.61	-	0.21

3.5. Effect of the MO concentration on the decomposition reaction in the mixture

The results obtained with a lower MO initial concentration, 1.52×10^{-7} instead of 1.25×10^{-5} M are shown in Fig.7. In this reaction condition, Atrazine decomposition is completed after 15 min ($k = 0.23 \text{ min}^{-1}$), with a rate constant very similar to obtained for the catalyst loading of 2 g L^{-1} ($\text{TiO}_2 \text{ P25}$). The same is true for MO (0.66 and 0.61 min^{-1} , respectively). The rate constants increased significantly when compared to the reaction in which both compounds have the same initial concentration (Table 3).

Fig. 7. Photocatalytic degradation of MO ($1.52 \times 10^{-6} \text{ mol L}^{-1}$ and Atrazine in a mixture ($1.25 \times 10^{-5} \text{ mol L}^{-1}$) using 1 g L^{-1} of $\text{TiO}_2 \text{ P25}$

The rate constants determined in the various experiments reported in this paragraph are summarized in Table 3.

Table 3. Rate constant (k_1 , min^{-1} first order, $k_0 \text{ mol L}^{-1} \text{ min}^{-1}$ -zero order*) values for the mixture MO and Atrazine at pH 7.5 with several MO initial concentrations.

Catalyst	MO initial concentration (M)	MO	MO (At)	At	At (MO)
$\text{TiO}_2 \text{ P25}$	1.25×10^{-5}	0.17	0.16	0.35	2.87×10^{-7} *
$\text{TiO}_2 \text{ P25}$	1.52×10^{-6}	-	0.66	-	0.23

3.6. Effect of the solution pH on the photocatalytic degradation reactions

Since the adsorption of dyes is anticipated to play a dominant role in determining degradation efficacy, the pH of the solution was varied as well. The degradation profiles of MO and Atrazine in acidic (pH = 3) and basic (pH = 11) conditions are shown in Fig.8.

a)

b)

Fig. 8. Photocatalyst degradation of MO and Atrazine individually and in mixture ($1.25 \times 10^{-5} \text{ mol L}^{-1}$) with 0.25 g L^{-1} of $\text{TiO}_2 \text{ P25}$. a) pH 3. b) pH 11.

Photocatalytic degradation profiles at acidic pH are comparable to observed at neutral conditions (compare Fig. 8.a and Fig. 2.a, respectively). To degrade MO as a single compound ($\square$) or in the mixture ($\blacksquare$) requires 15 and 30 min of reaction time, respectively. Atrazine ($\circ$) needs the same illumination time of 15 min to be fully mineralized, while MO delays the degradation time to 45 minutes ($\bullet$). In summary, the reactions are somewhat slower in the order of 5-10 minutes in acidic pH than in normal pH. Fig 8.b, shows the photocatalytic degradation reactions at pH 11. The decomposition reaction of MO as a single molecule ($\square$) and in a mixture ($\blacksquare$) was now only completed after 30 min of illumination. The decomposition reactions of Atrazine at pH 11, in both situations ($\circ, \bullet$), needed 45 min. The degradation rate of all the reactions were delayed when compared to normal pH. The most interesting observation is that MO and Atrazine in the mixture were degraded equally fast at pH 11 (Fig 8.b). The rate constants determined in the various experiments reported in this paragraph are summarized in Table 4.

Table 4. Rate constant (k_1 , min^{-1} - first order, k_0 $\text{mol L}^{-1} \text{min}^{-1}$ -zero order*) values for the MO and Atrazine at different pH's.

Catalyst	pH	MO	MO (At)	At	At (MO)
TiO ₂ P25	7.5	0.17	0.16	0.35	2.87×10^{-7} *
TiO ₂ P25	3	0.13	0.11	0.14	1.80×10^{-2} *
TiO ₂ P25	11	0.08	0.08	0.07	0.06

3.7. Acid orange and MO decomposition

Acid orange (AO) in combination with MO was another mixture studied with TiO₂ P25 (0.25 g L⁻¹) as a photocatalyst. As Fig. 9 shows, both dyes were adsorbed on TiO₂ P25 surface in the first 30 minutes in the dark. The decomposition of both dyes as single molecules ($\square$, $\triangle$) was completed after 15 minutes of illumination with the rate constant, 0.17 min^{-1} . In the mixture, AO ($\blacktriangle$) was completely mineralized after proximally 20 minutes with a slightly lower rate constant (0.12 min^{-1}), while MO ($\blacksquare$) needed more than 30 minutes (0.05 min^{-1}). In this case, MO was the compound inhibited in photocatalytic rate, while both compounds showed first order decomposition behavior. This second example enforces the theory that the compound with the highest affinity for the catalyst surface will be the first to be fully degraded. The rate constants determined are summarized in Table 5.

Fig. 9. Photocatalyst degradation of MO and AO individually and in a mixture ($1.25 \times 10^{-5} \text{ mol L}^{-1}$) with 0.25 g L^{-1} of TiO_2 P25.

Table 5. Rate constant (k, min^{-1}) values for the several photocatalytic degradation conditions of MO and AO individually and in the mixture.

Catalyst	pH	Concentration (g L^{-1})	MO	MO (AO)	AO	AO (MO)
TiO_2 P25	7.5	0.25	0.17	0.05	0.18	0.12

4. Discussion

4.1. Catalyst comparison

4.1.1. TiO_2 P25 vs TiO_2 Hombikat

Literature is inconclusive in generalizing which of the two forms of TiO_2 is the most effective in wastewater decontamination. Degradation of some dyes is achieved with higher efficiency using TiO_2 Homb, while for other contaminants TiO_2 P25 is more effective.²¹ When degraded individually, the observed faster MO and Atrazine degradation rates obtained for TiO_2 P25 as compared to TiO_2 Homb are in agreement with the literature.^{16,18} The most frequently advocated explanation for the higher efficiency of TiO_2 P25 is the presence of a mixture of crystalline phases, where rutile with the smaller band gap absorbs relatively low energy photons and transfers electrons generated to the anatase phase, resulting in high probability of the holes to react with the adsorbed substrates.^{15,29} Besides these optical properties, sorption of molecules is also very relevant when comparing catalyst materials, which is a function of BET surface area,

and more importantly surface density of specific hydroxyl groups.^{15,21,26,30} It has been reported that a specific OH group of TiO₂ P25 might be relevant for inducing the high activity.³¹ In view of the substrate specificity, we propose favorable surface chemical processes are at the origin of the higher activity of TiO₂ P25 than TiO₂ Homb.

4.1.2. Catalyst comparison at low light intensity

Light intensity is one of the parameters that has been frequently studied in determining photocatalytic reaction rates (of single compounds).³⁰ Depending on the intensity range, either first, half, or zero order dependency of light intensity on the rates has been determined. The effect of light intensity on preferential decomposition of compounds when present in mixtures, has not been previously addressed. We observe that the decomposition of MO shows comparable behavior as frequently reported in the literature, i.e. the reaction rate constant shows non-linear dependency on light intensity. This is typically explained by an increasing probability of electron-hole pairs to recombine at increasing light intensity, since the concentration of these charge carriers will increase significantly. The exponentially increasing values of the rate constant for Atrazine in a mixture are easily explained on the basis of the faster MO decomposition rate. The results show clearly that adsorption of MO is a determinant step that mitigates Atrazine decomposition. In particular at low light intensity, only when MO is decomposed completely, and consequently some catalyst sites are available, Atrazine starts to be decomposed.

4.1.3. Platinized TiO₂

The goal of depositing Pt on the TiO₂ P25 surface was to improve the efficiency and analyze if the substrate specific activity of the organic compounds would change. In the literature, it is usually claimed that Pt deposition helps to prevent electron-hole pair recombination. Indeed, for an Anatase catalyst, a positive effect of Pt nanoparticles on the MO reaction rate was reported.³² However, it has been reported that the effect of metal deposition on the photocatalyst efficiency is highly dependent on the catalyst (Hombikat, Degussa P25 and Rutile) and the preparation method of the Pt particles, among other parameters.^{26,33,34} In this study, by comparison to TiO₂ P25, Pt particles did not significantly affect the Atrazine decomposition rate. In agreement with this observation, Colón *et al*, claim that Pt induced promotion of electron hole pair separation is not relevant when the catalyst is TiO₂ P25.²⁶ The presence of the rutile and anatase phase already induces optimized electron-hole pair separation efficiency.²⁶ The negative effect of Pt nanoparticles on the MO decomposition rate is more difficult to explain, but suggests the preparation method applied induced changes in TiO₂ surface composition negatively affecting catalyst performance.³⁵ The role of Pt addition on photocatalytic activity of TiO₂ is associated

with several factors that determine a positive or negative influence in the reaction rate constant, is difficult to define *a priori*.

4.2. Effect of process conditions on efficacy of TiO₂ P25

4.2.1. Catalyst and MO concentration

Increasing catalyst loading (from 1 g L⁻¹ to 2 g L⁻¹) or lowering the initial concentration of MO by ~10 times relative to Atrazine, significantly increases the Atrazine rate constant. This is in full agreement with a decomposition pathway in which adsorption of the substrates is a dominant factor. Typically an increase in catalyst concentration results in higher rate constant, until it reaches a *plateau*,^{16,18} as it was observed in this work (Fig.7). In particular up to a catalyst concentration of 2 g L⁻¹, the rate constant of Atrazine (in the presence of MO) increased significantly (and changed from zero order to first order). The initial concentration of the organic compounds has also been frequently reported to affect the oxidation rate.^{18,19} A high substrate concentration can lead to TiO₂ saturation, deactivating the catalyst, and decreasing the photonic efficiency.⁵ Also in the experiment in which the initial concentration of MO was 10 times lower than Atrazine, the Atrazine decomposition reaction rate was barely affected by the presence of MO. What these two parameters have in common, is that the availability of catalyst sites for Atrazine adsorption increases. This leads to the mitigation of the negative effect of MO in Atrazine decomposition, which means sorption on the catalyst surface of Atrazine is very likely the rate determining step.

4.2.2. Effect of pH

The adsorption of molecules on TiO₂ surfaces, is strongly pH dependent. As a function of pH, the surface charge of the photocatalyst changes. This is illustrated by the following reactions (PZC implies Point of Zero Charge):

What is evident from reactions (1) and (2), is that the surface charge changes once the TiO₂ P25 surface is exposed to acidic (positive) or basic (negative) conditions. Consequently, the affinity of the organic contaminants for the surface is also likely to change.^{4,36} For TiO₂ P25 the PZC is in the order of 6.3.³⁷ The change in surface sign from positive in acidic conditions, to negative in basic conditions, can be used to explain the observed differences in extent of inhibition of MO on the degradation rate of Atrazine.^{38,39} The weak adsorption of Atrazine on TiO₂ in acidic conditions is in agreement with the absence of functional groups (-COO⁻) that could strongly

bind with the photocatalyst surface (Ti^{4+} , $-\text{O}-$, $-\text{OH}$).¹⁸ The negatively charged sulfate group of MO (Fig. 1) is likely a strong anchoring group for the positively charged TiO_2 surface in acidic conditions. The degradation rate constant for MO as a single molecule (0.08 min^{-1}) and in mixture (0.08 min^{-1}) at pH 11 is significantly lower than at pH 7.5 (0.16 and 0.17 min^{-1} , respectively). This result is explained by repulsive electrostatic forces at these basic pH values. The fact that MO at this pH is not blocking the surface means that Atrazine can reach the surface and be decomposed at the same time. Fig.10, shows a schematic representation of the reaction mechanism that we suggest for decomposition of the mixtures, in both reaction conditions, pH 3 and 11.

Fig. 10. Schematic representation of photocatalytic decomposition of MO and Atrazine (At) at a) pH 3 and b) pH 11 over P25.

Based on the results presented in this study, we propose a degradation mechanism at pH 3 in which MO is degraded first by holes and hydroxyl radicals generated on the catalyst surface. At the same time Atrazine is only slowly decomposed, mainly by radicals desorbing from the surface and present in solution ($\text{HO}^\bullet$, $\text{O}_2^{\bullet-}$), corresponding to the zero order rate constant. After MO and surface intermediates are completely converted into CO_2 and H_2O , Atrazine adsorbs, resulting in a faster decomposition rate and first order kinetics. The fact that the surface bound

concentration of MO at pH 11 is relatively low (Fig. 10.b), implies that Atrazine can be co-adsorbed, and simultaneously converted.

In the degradation mixture of 4-chlorophenol and 2,6-chlorophenol, reported in the literature,²³ a competition for the catalyst surface is also observed, resulting in lower rate constant values, which is in agreement with our results. Encinas *et al.* also mention the possible participation of hydroxyl radicals in the decomposition mechanism.²³ However, the fact that both compounds are chlorophenol derivatives makes it difficult to assign rate differences to specific interactions with the catalyst surface.

5. Conclusions

In this work, the photocatalytic decomposition of aqueous solutions with more than one organic compound was investigated using a top illumination reactor and LC-MS. The best catalyst with which to perform the photocatalytic decomposition of Methyl Orange (MO) and Atrazine as single compounds, or mixtures thereof, was TiO₂ P25. Significantly higher rates were obtained as compared to TiO₂ Homb, while addition of Pt (0.5% Pt/P25) was detrimental to the performance of TiO₂ P25. At a TiO₂ P25 loading of 0.25 g L⁻¹, substrate selective activity was observed, the degradation of MO being preferred over Atrazine. Increasing the catalyst loading from 0.25 g L⁻¹ to 2 g L⁻¹ resulted in decomposition of both compounds simultaneously. When the MO initial concentration was 10 times lower than Atrazine, again the Atrazine decomposition rate was not affected significantly by the presence of MO. The same is true for reaction conditions of basic pH. These results prove that adsorption is one of the determinant steps in photocatalytic degradation, and suggests that the low rate of Atrazine decomposition in the presence of MO is associated with particularly weak adsorption of Atrazine on the TiO₂ P25 surface, as observed in acidic conditions. Another mixture tested was MO and Acid Orange (AO) using TiO₂ P25 (0.25 g L⁻¹). In this case, even though both compounds have similar structures, MO degradation was significantly delayed by the presence of AO. Applying photocatalysis for wastewater treatment is definitely a challenge, and parameters optimized for degrading single compounds, might not be necessarily applicable when multiple compounds are present. Modification of the catalyst surface can be used to determine which molecule is preferentially decomposed, and might be used to induce simultaneous decomposition at a specific pH.

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Appendix A

Fig. 1. LC-MS time resolved chromatograms obtained during the photocatalytic degradation of MO and Atrazine with TiO_2 P25 (0.25 g L^{-1}) at 375 nm.

Fig. 2. MS spectra of a) MO and b) Atrazine

Chapter 6

MeOH Assisted Photocatalytic Degradation of Methyl Orange with Simultaneous Production of H₂

Platinized TiO₂ prepared by photodeposition of Pt was evaluated for photocatalytic activity in the simultaneous conversion of methyl orange (MO), and (MeOH assisted) formation of hydrogen. Low concentrations of methyl orange were found ineffective for generation of hydrogen in measurable quantities upon illumination of Pt/TiO₂ in water. On the other hand, significant quantities of hydrogen were obtained when MeOH was the reactant. Surprisingly, when methyl orange was added to the MeOH/water solution, hydrogen formation was significantly suppressed. The origin of this detrimental effect of MO lies in the strong and preferred adsorption and conversion of the dye, on the Pt sites of the catalyst. This suppresses the Pt catalyzed formation of hydrogen. Interestingly, similar to hydrogen formation, dye discolorization is stimulated by the presence of MeOH, without the formation of new chemical compounds, confirming the role of MeOH as a hole scavenger in the photocatalytic process. In aerobic (but oxygen lean) conditions, MeOH assisted hydrogen formation and dye discolorization are inhibited, explained by preferred adsorption and reduction of O₂ to O₂^{•-}, and consecutive reaction thereof with MeOH.

This chapter is based on: Romão, J.; Salata, R.; Park, S.; Mul, G.; “MeOH Assisted Photocatalytic Degradation of Methyl Orange with Simultaneous Production of H₂”. (Submitted)

1. Introduction

Potable water in several domestic areas not only contains organic toxins, but also a significant amount of nitrate, which both have adverse effects on human health.^{1,2} To mitigate these issues, photocatalysis is a promising technology, in particular if oxidation of organic toxins to CO_2 ,^{3,4} could be combined with the *in situ* generation of hydrogen,^{5,6} needed for reductive elimination of nitrates by heterogeneous catalysis.⁷

The photocatalytic process of oxidative decomposition and hydrogen formation involves identical photo-excited states, i.e. electrons and holes (Fig.1). The main difference is that for efficient mineralization of organic contaminants aerobic conditions are necessary, and oxygen is typically the electron acceptor, while for hydrogen evolution, protons need to be reduced, and anaerobic conditions are usually beneficial.^{8,9} Photogenerated holes when reaching the semiconductor surface induce the formation of radical species, such as hydroxyl radicals by oxidation of water, or organic radicals by reaction with surface adsorbed organic compounds (Fig.1). Usually conversion of the radical species and organic contaminants subsequently leads to formation of CO_2 and H_2O .^{3,9} Several reports also demonstrate that decomposition of contaminants is feasible in anaerobic conditions, with simultaneous formation of hydrogen (Fig.1).^{10,11}

Fig. 1. TiO_2 loaded with Pt and the processes occurring which are relevant for photocatalytic decomposition of organic compounds with simultaneous H_2 production.

The catalyst most commonly used to induce the above illustrated reactions, is TiO₂ (and specifically P25)^{12,13}, with a bandgap of 3.2 eV and a conduction band (E_{CB}) energy lower than the standard redox potential of hydrogen (E (H⁺/H₂) 0 V at pH 0), which makes hydrogen production thermodynamically feasible.¹⁴ Unfortunately, hydrogen evolution is usually associated with low photonic efficiency.⁹ The reason is a high recombination rate between the photogenerated holes and electrons, diminishing the probability the desired redox processes on the semiconductor surface.⁹ This problem can be overcome by loading TiO₂ with noble metals, such as Pt, Pd, Au, Cu, or Rh.^{8,9,14,15} These metals create effective surface sites for hydrogen production, thus minimizing recombination of electrons and holes.¹⁴

Another solution to suppress recombination is the use of electron donors, such as the previously indicated organic contaminants (Fig. 1), which can react irreversibly with the photogenerated holes stimulating hydrogen production.^{16,17} Several sacrificial agents (organic compounds), have been studied for this purpose, such as alcohols,^{16,18} sugars,¹⁹ organic acids,^{16,20} and several others.^{5,21} Alcohols are the organic compounds that induced the highest rates in hydrogen evolution, due to their high susceptibility towards oxidation.²²

The aim of this work is to study the decomposition of organic compounds combined with hydrogen production. The organic compounds chosen were Methyl Orange (MO), a dye that is often used as model compound in studies involving decontamination of wastewater, and MeOH, since this is known to enhance hydrogen production efficiently.⁸

2. Experimental

2.1. Materials

All reagents were obtained from Aldrich and used as received. Those include chloroplatinic acid, MeOH and MO. The photocatalyst material, P25 TiO₂, was obtained from Evonik Industries. The solvents (water and acetonitrile) used in the HPLC analysis were purchased from Biosolve.

2.2. Preparation of Pt-TiO₂

Deposition of Pt nanoparticles on TiO₂ P25 with an estimated weight loading of 0.5 wt % was performed using a photodeposition procedure.^{23,24} To this end, an aqueous suspension of TiO₂ P25 (0.5 g L⁻¹) and chloroplatinic acid (H₂PtCl₆, 0.5 g L⁻¹) was stirred for 30 minutes in the dark and then MeOH was added (1 M, 3 ml). The suspension was illuminated (radiation intensity 3.21 mW cm⁻² at 375 nm) for 5 h. The powder was collected by centrifugation, and washed three

times consecutively with ethanol (20 ml), and finally with distilled water (20 ml). The powder was dried overnight at 90°C.

2.3. Photocatalytic experiments

The equipment used for photocatalytic reactivity evaluation consists of three parts: a reactor, a gas chromatograph and a LabView interphase to control gas flow rates induced by mass flow controllers. A cylindrical batch reactor was used with an internal volume of 50 mL. In the lid of the reactor a small window (fused silica which allows 90% transmission) was incorporated, to allow illumination of the solution from the top. The light source used was a 120 Watt high pressure mercury lamp from Dr. Gröbel UC-Elektronik GmbH, with a spectral range from 280 to 650 nm, from which the light was introduced in the reactor through an optical fiber. An argon (Ar) flow (5 mL min⁻¹) was continuously purged through the reactor during the experiment. A gas chromatograph (GC), equipped with a Parabond Q column (10m) and a TCD detector was used for determination of H₂, O₂ and N₂ concentrations.²⁵

The working volume of the aqueous photocatalytic suspension was 15 mL, which was continuously agitated by magnetic stirring at 300 rpm. In this study several aqueous solutions were prepared to compare photocatalytic activity, including MeOH (2.48 M) or mixtures of MeOH (2.48 M) and Methyl Orange (0.06 mM). All reactions were performed at neutral pH (~7). Two photocatalysts were tested with a concentration of 1 g L⁻¹, being TiO₂ and 0.5% Pt/TiO₂. Before initiating the photocatalytic reaction, the aqueous solution was purged with argon or argon with 20 % O₂ (5 ml min⁻¹, to saturate the aqueous solution), for 30 minutes in the dark. The total time of illumination was 60 minutes.

2.4. Analysis of MO decomposition

From the same reactor used for determination of hydrogen production, samples were taken out periodically and centrifuged at 7000 rpm for 5 min to remove catalyst particles. Subsequently the samples were analyzed by UV-Vis spectroscopy and liquid HPLC (Agilent 1100 Series). The HPLC method involved the separation of the organic compounds in the sample using a mixture of water and acetonitrile (75:25) as eluent, and applying a flow rate of 0.3 ml min⁻¹. The sample volume injected into the reverse phase column (All Chromolith Merk C18 column 100mm x 3mm i.d.) was 10 µL at room temperature (21°C), using an autosampler. Detection was performed using mass spectrometry (Bruker MS Esquire 3000+). The separated products were ionized using positive Electrospray Ionization (+ESI). The MS ionization conditions were: a flow rate of 0.5 ml min⁻¹, a nebulizer gas pressure of 30 psi, a dry gas flow of 0.3 L min⁻¹ and a dry gas temperature of 325°C.

3. Results

3.1. Characterization of 0.5% Pt/TiO₂

The Pt/TiO₂ sample was analyzed by X-Ray Fluorescence (XRF, Bruker S4 Pioneer) in order to quantify the platinum loading. The loading determined by XRF amounted to 0.44 wt%. The particle size of Pt was determined by transmission electron microscopy (TEM, Philips CM300ST-FEG) and the composition of the presumably Pt particles confirmed by Energy Dispersive X-ray spectroscopy (EDX, Noran System Six). The results of the TEM and EDX analyses are shown in Fig. 2. From the TEM micrograph it could be determined that the Pt particle size varies between 3 and 5 nm (Fig.2.a).

Fig. 2. Characterization of 0.5% Pt-P25. a) TEM. b) EDX.

3.2. Effect of Pt deposition on hydrogen production activity of TiO₂

Fig.3 shows the results obtained from the illumination of aqueous suspensions with and without MeOH in the presence of two photocatalysts (TiO₂ and 0.5% Pt/TiO₂). In the absence of MeOH, hydrogen production was not observed for both catalyst compositions. From the aqueous solution with MeOH (2.48 M) hydrogen evolved in measureable quantities significantly higher for the Pt/TiO₂ catalyst than for the TiO₂ catalyst (see insert for the trend in activity in Fig.3). The initial rise in concentration is due to non-steady state behavior (flush out) of the continuously stirred tank reactor, (CSTR), which requires approximately 10 minutes. Then a steady state in hydrogen rate of approximately 0.1 $\mu\text{mol H}_2 \text{ g}^{-1}\text{cat min}^{-1}$ is reached for TiO₂, although initially the rate is somewhat higher. The initial rate induced by 0.5 % Pt/TiO₂ amounts to 7.5 $\mu\text{mol H}_2 \text{ g}^{-1}\text{cat min}^{-1}$, which slowly decays to a steady state rate of 5.5 $\mu\text{mol H}_2 \text{ g}^{-1}\text{cat min}^{-1}$ (Fig.3).

Fig. 3. Hydrogen concentration as determined in a CSTR for TiO_2 and 0.5% Pt/TiO_2 photocatalysts from aqueous suspensions with (2.58M) or without MeOH, as a function of illumination time. The inset shows a magnification of the result obtained for MeOH with TiO_2 .

3.2. Effect of process parameters on H_2 production in anaerobic conditions.

3.2.1. Effect of the initial MeOH concentration

Different initial concentrations of MeOH were used in order to determine the optimum for hydrogen production (Fig.4). For all MeOH concentrations tested, an initial maximum in hydrogen production rate is observed (after 10 minutes), followed by a significant decrease in rate until steady state is reached, variable in quantity for each initial MeOH concentration. Fig.4.b shows that the order in MeOH concentration of the hydrogen formation rate is likely significantly lower than 1, to be expected since the MeOH concentration range was relatively high. The phenomena are similar to those reported by Patsoura et al.¹⁷

a)

b)

Fig. 4. a) Time dependent hydrogen concentration determined for a 0.5% Pt/TiO₂ catalyst as a function of initial MeOH concentration. b) Rate constant values found for MeOH at different initial concentrations (M). The trend line is meant to guide the eye.

3.2.2. Effect of MO on MeOH induced hydrogen formation

The effect of MO on the MeOH induced hydrogen production rate was determined for various MO concentrations, at a fixed concentration of MeOH of 2.48 M. The results of these experiments are summarized in Fig. 5. First, in the absence of MeOH, hydrogen production was below the detection limit of the TCD detector. Apparently MO is not able to stimulate hydrogen formation over Pt/TiO₂ to a significant degree at the concentration levels tested (0.09 M). Further, at a low concentration of 0.06 M, the presence of MO had very little effect on the MeOH induced hydrogen production. However, increasing MO concentration, some remarkable changes were observed. First, the hydrogen formation appears to be delayed and the delay time increases as a function of MO concentration. Second, the amount of hydrogen produced is initially higher in the presence of MO, while the transient reaching steady state levels also requires somewhat longer times. The highest hydrogen production rate obtained was in the presence of 0.09 mM of MO ($9.1 \mu\text{mol H}_2 \text{ g}^{-1} \text{ cat min}^{-1}$) while between 0.15 to 0.31 mM a slight decrease in rate was observed. The maximum hydrogen concentration peak observed at minute 8 for 0.06 and 0.09 mM, starts to shift being at minute 23 at the highest concentration of MO (0.31mM).

Fig. 5. MeOH induced hydrogen concentration transients over 0.5% Pt/TiO₂ as a function of MO initial concentration.

In order to determine the photocatalytic decomposition of MO, samples were collected after certain illumination intervals and analyzed by UV-Vis spectroscopy and LC-MS. The results of MO mineralization in the absence or presence of MeOH are shown in Fig.6.a. After 10 minutes of illumination full dis-colorization of MO was achieved, while in the presence of MeOH this

required even less time. To identify potential compounds formed from MO in the applied anaerobic conditions, LC-MS analysis was performed. In anaerobic conditions, a species with m/z of 172 (Fig.6.b) was obtained after 10 minutes of illumination, which we could assign to the formation of a hydrogenated fragment of MO, to be discussed later.

a)

b)

Fig. 6. a) Photocatalytic dis-colorization of MO (0.09 mM) in the absence or presence of MeOH (2.48 M) at anaerobic conditions (Ar). b) Analytical analysis by LC-MS of samples with MeOH at $t=10$ min.

3.3. Quantification of H₂ production in oxygen lean conditions

As stated in the introduction, photocatalytic hydrogen production is likely very much dependent on the presence or absence of oxygen in the water feed. In purification devices to be applied in practice, the water feed will likely contain oxygen (air). It is therefore relevant to study the effect of solved oxygen on the transients described in Fig. 7. To introduce oxygen in the solution, argon with 20% volume of O₂ was purged for 30 minutes prior to starting illumination. During illumination the purge consisted again of pure Ar. Fig.7 shows the effect of dissolved oxygen on the MeOH induced hydrogen production transients, in the absence or presence of MO. Clearly, in the absence of MO, the presence of oxygen (□) induces a delay of about 5 minutes before the hydrogen concentration maximizes and decays to steady state. In the presence of MO (○), the delay in hydrogen production is significantly longer (10 minutes) and the attainable steady state hydrogen concentration lower.

Fig. 7. Hydrogen concentration produced over 0.5% Pt/TiO₂ from aqueous suspension with MeOH (2.48M) and MO (0.06 mM) as function of illumination time in anaerobic and aerobic conditions.

In order to further understand the importance of oxygen in MO decomposition, the photocatalytic decomposition of MO in the absence or presence of MeOH was again followed by UV-Vis spectroscopy (Fig.8.a) and LC-MS (Fig.8.b) analysis. Fig.8.a, shows that the presence of oxygen significantly prolongs the illumination time needed to achieve full discolorization (90 minutes), while again the presence of MeOH accelerates this, reducing the time needed for full color elimination to 30 minutes. LC-MS analysis revealed that the intermediate with m/z of 172 was no longer present in aerobic conditions after 10 or 30 minutes of reaction, 30 minutes being the time at which full dis-colorization was obtained.

a)

b)

Fig. 8. a) Photocatalytic decolorization of MO (0.09 mM) in the absence or presence of MeOH (2.48 M) in aerobic conditions (solution saturated with a flow of 5 mL/min of 20% O₂ in Ar for 30 min). b) Analytical analysis by LC-MS from the samples with MeOH after 10 and 30 min illumination, and the corresponding MS spectra (305.9 and 327.9 m/z) of the MO peak at 2.2 min (samples t=10min).

4. Discussion

4.1. The necessity of Pt for H₂ evolution from MeOH solutions

In the present study, hydrogen production in the absence of MeOH was not observed for both photocatalysts (TiO₂ and 0.5% Pt/TiO₂, Fig.1), and neither when MO was reacted in anaerobic conditions, Fig.3. While the absence of hydrogen formation for TiO₂ P25 is in agreement with the literature,²⁶ several studies have reported formation of hydrogen for Pt containing catalysts, with simultaneous contaminant molecule decomposition.^{5,15} Principally, photogenerated electrons (rutile E_{CB}= -0.09 V, anatase E_{CB}= -0.29 V) have enough energy to reduce protons to hydrogen. However, the overpotential for hydrogen generation is high for TiO₂ surfaces.^{9,10,21} The addition of Pt is one of the most used strategies to lower this overpotential by providing active sites for hydrogen generation and thus limiting recombination between electrons and holes.¹⁰ The absence of hydrogen production with 0.5% Pt-TiO₂ in the present study is probably related to the detection limit of the equipment, which is not able to measure concentrations below 1 ppm (Fig.1 and Fig.3). The values reported in the literature are typically in the ppb range.^{17,21} In the presence of MeOH, it was possible to observe hydrogen production (maximum at ~0.15 μmol H₂ g⁻¹ cat min⁻¹) over TiO₂, which was significantly increased to ~7.5 μmol H₂ g⁻¹ cat min⁻¹ for 0.5% Pt/TiO₂ (Fig.3). The mechanism of MeOH induced hydrogen formation over 0.5% Pt/TiO₂ will be discussed in the following paragraphs.

4.2. MeOH assisted hydrogen formation

In anaerobic conditions, two reactions of MeOH in aiding the production of hydrogen can be proposed. In the first oxidative reaction (1), MeOH will help to increase the efficiency of proton reduction over Pt by reacting with photogenerated holes, avoiding electron-hole recombination.²⁴

The other reaction is dehydrogenation of MeOH, occurring over the surface of the Pt/TiO₂ nanoparticles inducing the formation of hydrogen and formaldehyde as shown in reaction (2).

8,22,15

Consecutive reactions of formaldehyde to formic acid (3), and formic acid to CO₂ (4) have also been proposed to contribute to hydrogen formation in anaerobic (reductive) conditions.

From the catalytic data reported in the present study, whether oxidation or dehydrogenation of MeOH contributes most significantly, cannot be determined, and isotopic labeling (using deuterated MeOH) is required. However, we prefer the oxidation mechanism, based on the initial transient in hydrogen production rate. We speculate this initially decreasing rate is related to poisoning of Pt sites by CO formed in the (partial) oxidation mechanism. CO is a well-known poison for Pt anodes in direct MeOH fuel cells (DMFC) and in fact is reported to prevent the commercial application thereof.^{27,28} At some point the rate of formation, and consecutive oxidation of CO to CO₂ are in equilibrium, and the hydrogen formation rate reaches steady state.

4.3. Explaining H₂ formation transients from MeOH and MO mixtures in anaerobic conditions

Some remarkable observations regarding the MeOH induced hydrogen formation in the presence of MO at anaerobic conditions can be made (Fig.7): i) hydrogen formation is delayed by the presence of MO, ii) the maximum in hydrogen formation is enhanced in quantity and shows a slower transient to steady state, and iii) MO dis-colorization is faster in the presence, than in the absence of MeOH. These observations suggest that the Pt catalyst is substrate selective with favorable affinity for MO as compared to protons. Adsorption and azo-bond cleavage of MO likely progresses over Pt sites, inducing reduction of color intensity and the formation of the mass fragment 172 m/z as illustrated in Fig. 9.

Fig. 9. First step in MO photocatalytic degradation, and possible fragments formed from the azo-bond cleavage.

Since no other intermediates were observed which could be assigned to possible MeOH-MO reactions, we assume that the acceleration of this reaction induced by MeOH is due to favorable hole scavenging and occurrence of reaction (1). Once MO has fragmented, the Pt surface is available for proton reduction to produce hydrogen, explaining the concurrent rise in hydrogen production with the decreasing color intensity of MO. What is obvious is that MO fragments

(Fig. 9) enhance the maximum attainable hydrogen production in the presence of MeOH. We speculate this might be related to sulfate formation on the TiO_2 surface by consecutive oxidation of mass fragment m/z 172. Sulfate formation has been previously reported to promote activity and photonic efficiency of TiO_2 based photocatalysts.^{29,30}

4.3. Explaining H_2 formation transients from MeOH and MO mixtures in oxygen lean conditions

Dissolved oxygen delays MO dis-colorization, as well as hydrogen evolution observed in Fig. 7 and 8. The significant delay by the presence of oxygen in the dis-colorization of MO is in agreement with the hypothesis that dis-colorization needs photogenerated electrons and occurs over Pt sites (Fig.10). We anticipate that oxygen competes for these electrons. After the delay, oxygen in solution is mostly converted and the reactions follow the processes discussed for anaerobic conditions. We assume that the acceleration of MO dis-colorization induced by MeOH is again due to favorable hole scavenging, enhancing photonic efficiency. The fate of the superoxide and hydroperoxyl radicals formed by reduction of oxygen,¹² is likely to react with MeOH, rather than MO, given the significantly higher concentration of MeOH. This lowers the concentration of MeOH, on which hydrogen formation was demonstrated to be dependent in Fig. 4.

Fig. 10. Schematic representation of all the reduction reactions that occur on Pt surface and MeOH oxidative reaction.

5. Conclusions

The data reported in this study demonstrate that photon-electron stimulated Pt nanoparticles have multiple catalytic functions. The following order in reactant selective reduction activity was observed experimentally: $O_2 > MO > H^+$. This order in reactivity is based on: i) MO discolorization and hydrogen formation (by H^+ reduction) are negatively affected by the presence of oxygen and ii) MeOH induced hydrogen formation is inhibited by the presence of MO. We demonstrate that MeOH is oxidatively converted by reaction with holes, diminishing probability of electron-hole pair recombination, and explaining the promotion of MeOH in the dye discolorization reaction (both in the absence or presence of oxygen). CO is likely a dominant product of MeOH oxidation in anaerobic conditions, in agreement with CO poisoning of Pt being at the origin of the frequently observed maximum in hydrogen production. For practical application of concomitant MeOH induced hydrogen formation and dye degradation, Pt/TiO₂ induced photocatalysis is not practically feasible, due to the strong reactant selective activity of the Pt nanoparticles. Moderation of the Pt particles, e.i. by alloying, allowing simultaneous, rather than consecutive processing of oxygen reduction, dye conversion, and/proton reduction to hydrogen, might lead to improvements. At the same time, the photonic efficiency of dye degradation might be improved by combining TiO₂ with favorable semiconductor substrates, such as silicon, commonly used in construction of photocatalytic microreactors.

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Chapter 7

Outlook

In the experimental chapters of this thesis, the use of heterogeneous photocatalysis was demonstrated viable for pollution control, and more specifically wastewater treatment. A broad versatility in compound degradation, mechanistic understanding and reactor engineering can provide for very promising new developments in upcoming applications. In this final chapter, I will shortly elaborate on relevant research problems, which might be of interest as follow-up.

Reactor Challenges

The variety of reactors proposed in the literature for performing photocatalytic studies is vast. Conversely, the standardization of methods that could allow easier comparison among peers is of great interest. For instance, the use of our 96-well microplate photoreactor method presented in Chapter 2, fulfils in great part these requirements, since it allows to obtain close to intrinsic values of reaction rate constants. In order to sustain the relevance of this reactor (96-well plate), it would be important to complement this study with theoretical studies to determine mass transfer and light propagation limitations within the reactor/material. Besides, it would also be very interesting to test the use of a 96-well photoreactor for immobilized catalyst systems, by applying a catalyst coating on the bottom of the well. This would avoid filtration steps, and also allow a fair comparison between photocatalyst activity in immobilized and slurry systems. The detection method applied – UV/Vis Spectrometry – is not the ideal method, since it is not possible to follow the formation of possible intermediates. However, the volume in the 96 well (200 μ L) is sufficient for more detailed analysis, such as Liquid Chromatography

As far as practical application is concerned, microfluidic approaches might be promising in the development of domestic appliances. Although several aspects of such devices have been briefly discussed in this thesis, the stability of the photocatalyst has not. This is essential to determine the lifetime of the appliance. If deactivation is observed, photocatalyst formulations need to be developed with enhanced lifetimes, or means need to be available to regenerate the catalysts.

A novel compound library

In the literature and confirmed by the data presented in this thesis, a big diversity in susceptibility of organic compounds and model contaminants (dyes, phenol, among others) towards photocatalytic conversion has been observed. In this thesis, a pharmaceutical library – LOPAC¹²⁸⁰ – was used for determining photocatalytic activity differences. However the complexity of the molecules made it very challenging to determine trends and draw conclusions. To better address the usage of complex datasets to characterize photocatalyst effectiveness, rational design of libraries might be applied, looking forward to include qualitatively and statistically representative molecules. This would allow a better understanding

of the interaction of specific chemical groups with the catalyst surface, and to determine if it is possible to predict the photocatalytic activity.

Practical Applications

When the aim is to provide a domestic appliance for water purification, an important parameter is the illumination time needed to reach full conversion. While fast rates for single component mineralization have been reported, the results in this thesis show the photocatalytic decomposition of such compound might be significantly retarded when present in the same aqueous solution with another compound (Chapter 5). Further studies are necessary in order to fully understand sorption of molecules chemically different on the catalyst surface and how that determines the reaction mechanism. For this purpose, FTIR spectroscopy can be a relevant tool, but the low concentration of the organic compounds in solution, and the fact that the medium is water, implies that this is not an easy task. Attenuated Total Reflection accessories are recommended to use for initial trials.

Photocatalytic decomposition combined with hydrogen production

The production of hydrogen through photocatalysis has attracted a lot of attention, however the combination with decomposition of organic compounds has not been validated in much detail. In this thesis, it was proven that it is possible to decompose methyl orange and produce hydrogen by methanol decomposition. Still, few key aspects can be improved for a better understanding, such as to prove the possibility to generate hydrogen from methyl orange in the absence of MeOH. Although it was possible to generate hydrogen by photocatalysis the efficiency is still very low for practical application. The photocatalyst is the key for the success of this technology and also the biggest challenge, since this needs to be effective for the mineralization of organic compounds and have catalytic functionality to generate hydrogen. In further studies, catalyst improvement might be the focus, starting by coupling semiconductors with other co-catalysts, such as Au or Ag.

Regarding the commercialization of photocatalytic oxidation for water cleaning, especially in small devices, more effort should be devoted to establishing a kinetic model, to be able to better predict the photocatalytic reaction rates, and the optimum reaction parameters to mineralize all the organic compounds after a certain illumination period. These are the biggest challenges, before the commercialization of a device for delivering clean and safe water can be considered.

Summary

In this thesis, heterogeneous photocatalysis is presented as a promising technology for water purification. Photocatalysis is revisited from an experimental and engineering point of view, comprising some theoretical fundamentals towards the commercialization of domestic appliances for water purification. **Chapter 1** introduces the basic principles of photocatalysis and the reaction parameters that play a role in optimizing reaction rates.

In **Chapter 2**, it is presented a novel and inexpensive 96-well microplate photo-reactor, is presented suitable for high throughput screening. This method is applicable to a wide range of model organic contaminants and photocatalysts, and only requires very short reaction times, up to 15 min, in the concentration range typically reported in literature. Furthermore, the working volume of the reactor is 200 μL , minimizing the amount of catalyst and organic compounds needed. Finally, a very important aspect is that limitations in light penetration through the aqueous solution (reactor height is 1 cm) are absent, resulting in an efficient utilization of all the catalyst particles available within the reactor, providing a close to intrinsic value of the rate constant.

One of the latest concerns in water purification technology, is the prevalence of pharmaceuticals in the environment and their potential detrimental effects on human health. High throughput screening of a pharmaceutical library with 1280 compounds was performed to evaluate the ability of TiO_2 to degrade these new emerging contaminants. The results are described in **Chapter 3**. In general terms, TiO_2 was suitable to oxidize many new emerging contaminants, but the decomposition efficiency was found dependent on the chemical composition of the compounds investigated. By comparing conversion after 5 minutes of illumination, it was possible to identify some of the functional groups/chemical classes that are relatively easily oxidized. The compounds showing a high degradation tendency possessed functional groups, such as aldehydes, alcohols, ketones, nitriles, or amides. One class of compounds that stood out as being easy to degrade, were indole derivatives. The compounds that were barely oxidized consisted of conjugated aromatic systems and were derivatives from compounds such as adenosine, caffeine and imidazole, among others.

The high throughput screening performed previously in Chapter 3 also revealed that steroids are a class of compounds that are difficult to oxidize. For that reason, further studies were done with cortisone acetate (model compound) with focus on optimizing the mineralization parameters (pH, catalyst loading, etc), in a laboratory scale slurry reactor (50 ml). The decomposition

reaction, presented in **Chapter 4**, was followed by Liquid Chromatography-Mass Spectrometry (LC-MS). Several photocatalysts were tested, of which ZnO and TiO₂ P25 were found to be the best. TiO₂ P25 was chosen for further process parameter optimization, due to the poor stability of ZnO in water. The optimum catalyst loading was determined to be 0.25 g L⁻¹, while varying pH had very little effect on the decomposition rate. Furthermore, the use of a strong oxidizing agent (S₂O₈²⁻) in combination with TiO₂ P25, increased the reaction rate significantly. Although, the photocatalytic decomposition reaction was followed by LC-MS, intermediate compounds were not detected.

In **Chapter 5**, a study of photocatalytic degradation of mixtures of organic compounds in aqueous solution is described. Such study is very relevant for practical application of photocatalytic water treatment, since then simultaneous decomposition of several organic contaminants is required. The mineralization of Methyl Orange (MO), a dye molecule representative of those used in the textile industry, and Atrazine, a typical pesticide derivative, was investigated individually and when present in mixtures. The rate constant of MO is similar in the presence or absence of Atrazine, while the rate constant of Atrazine decomposition decreases significantly when MO is present, at pH 7. Other parameters such as pH, catalyst loading and relative concentration of the organic compounds showed to be relevant for the order in degradation efficacy. In this chapter, the decomposition mechanism and the importance of adsorption on the catalyst surface in order to achieve faster rate constants of Atrazine in the presence of strongly adsorbing compounds, are discussed.

Chapter 6 is focused on photocatalytic degradation of organic compounds in oxygen lean conditions over Pt-TiO₂ as catalyst, to achieve concurrent production of hydrogen. This can be relevant if photocatalytic oxidation of contaminants is to be combined with catalytic hydrogenation of inorganic contaminants (nitrates) in a domestic appliance. In this study, MeOH was used as sacrificial agent to induce hydrogen formation. It was found that in anaerobic conditions, higher hydrogen production rates were obtained, however full conversion of MO was not achieved. In oxygen lean conditions, the following order in reduction activity of Pt nanoparticles was observed: O₂ > MO > H⁺. The rate of hydrogen formation from MeOH is strongly influenced by the initial concentration of oxygen and MO present in the photocatalytic reactor.

Finally in **Chapter 7**, the work performed is analyzed and discussed, followed by suggestions for future research on photocatalysis applications for water treatment.

Samenvatting

Heterogene fotokatalyse wordt besproken in dit proefschrift als een veelbelovende technologie voor waterzuivering. **Hoofdstuk 1** introduceert de basisprincipes van fotokatalyse en de reactieparameters die een rol spelen bij het optimaliseren van reactiesnelheden. De focus van dit proefschrift ligt op de analyse van omzetting van relatief nieuwe verontreinigingen die in (drink)water voorkomen, zoals medicijn derivaten. Zowel een eerste screening van een veelvoud aan verbindingen als gedetailleerde studies van (mengsels van) een aantal componenten worden geadresseerd. Tevens wordt aandacht besteed aan de mogelijke commercialisering van huishoudelijke toepassingen voor waterzuivering, waarbij ook vorming van waterstof tijdens de ontleding van medicijn derivaten aan de orde komt: waterstof zou in een vervolgstap kunnen worden gebruikt om nitraten uit drinkwater te reduceren naar stikstof.

In **Hoofdstuk 2** wordt een nieuwe en goedkope 96-well microplaat foto-reactor geïntroduceerd, geschikt voor snelle evaluatie van de effectiviteit van fotokatalysatoren in de ontleding van verontreinigingen in drinkwater. Deze methode is toepasbaar op een breed scala van organische contaminanten en fotokatalysatoren en vereist slechts zeer korte reactietijden tot 15 minuten in het concentratiebereik gewoonlijk gerapporteerd in de literatuur. Bovendien is het werkvolume van de reactor 200 μl , wat de benodigde hoeveelheid katalysator en organische substanties vermindert. Ten slotte is een erg belangrijk aspect dat licht penetratie door de waterige suspensie (de reactorhoogte is 1 cm) volledig is, resulterend in een efficiënt gebruik van alle beschikbare katalysatordeeltjes binnen de reactor. Daardoor wordt een nagenoeg intrinsieke waarde van de reactiesnelheidsconstante verkregen.

Eén van de meest recente zorgen in waterzuiveringstechnologie is de aanwezigheid van (restanten van) geneesmiddelen in het milieu en de mogelijk schadelijke gevolgen voor de volksgezondheid. Een farmaceutische bibliotheek met 1280 substanties werd gebruikt om het fotokatalytische vermogen van TiO_2 te evalueren om deze nieuwe opkomende verontreinigingen af te breken. De resultaten worden beschreven in **Hoofdstuk 3**. In het algemeen is TiO_2 geschikt om veel nieuwe opkomende verontreinigingen te oxideren, maar de ontledingsefficiëntie is afhankelijk van de chemische samenstelling van de onderzochte substanties. Door de conversie na 5 minuten belichting te vergelijken was het mogelijk om enkele functionele groepen te identificeren, die moleculen betrekkelijk makkelijk laten oxideren. Deze functionele groepen zijn onder andere aldehyde, alcoholen, ketonen, nitrillen en amiden. Een andere klasse van substanties die opvalt door de makkelijke afbreekbaarheid zijn indool derivaten. De substanties

die nauwelijks worden geoxideerd bestaan uit geconjugeerde aromatische systemen en zijn derivaten van substanties zoals onder andere adenosine, cafeïne en imidazool.

Uit hoofdstuk 3 blijkt dat steroïden een klasse van moeilijk oxideerbare substanties zijn. Daarom werd de oxidatie van cortison acetaat (modelsubstantie) in een suspensiereactor op laboratoriumschaal (50 ml) uitgevoerd, met de nadruk op het optimaliseren van de mineralisatie parameters (pH, katalysatorbelading, etc.). De ontledingsreactie werd gevolgd met vloeistofchromatografie-massaspectrometrie (LC-MS) en de resultaten worden besproken in **Hoofdstuk 4**. Verscheidene fotokatalysatoren werden getest, waarbij zinkoxide (ZnO) en titaandioxide (TiO₂) P25 als besten bevonden werden. TiO₂ P25 werd gekozen voor verdere optimalisatie vanwege de slechte stabiliteit van ZnO in water. De optimale katalysatorbelading werd bepaald op 0,25 g L⁻¹, terwijl het variëren van de pH zeer weinig effect had op de ontledingssnelheid. Het gebruik van een sterk oxidatiemiddel (S₂O₈²⁻) in combinatie met TiO₂ P25 verhoogt de reactiesnelheid aanzienlijk. De fotokatalytische decompositiereactie werd gevolgd met LC-MS, maar tussenproducten konden niet worden gedetecteerd.

In **Hoofdstuk 5** wordt de studie van fotokatalytische degradatie van mengsels van organische substanties in waterige oplossing beschreven. Een dergelijke studie is zeer relevant voor de praktische toepassing van fotokatalytische waterzuivering, aangezien gelijktijdige ontleding van verschillende organische verontreinigingen dan is vereist. De mineralisatie van methyl oranje (MO), een stof die representatief is voor kleurstof moleculen die gebruikt worden in de textielindustrie, en atrazine, een typisch pesticide derivaat, werd afzonderlijk en in mengsels onderzocht. De reactiesnelheidsconstante van MO is vergelijkbaar in de aan- of afwezigheid van atrazine, terwijl de reactiesnelheidsconstante van atrazine decompositie aanzienlijk afneemt wanneer MO aanwezig is. Andere parameters zoals pH, katalysatorbelading in de slurry reactor en relatieve concentratie van de organische substanties vertoonden relevantie voor de grootte van orde in degradatie werkzaamheid (dan wel nulde orde, dan wel eerste orde). Het ontledingsmechanisme en het belang van adsorptie op het katalysator oppervlak om snellere reactiesnelheidsconstanten van atrazine te bereiken in aanwezigheid van sterk adsorberende substanties, worden in dit hoofdstuk besproken.

Hoofdstuk 6 richt zich op fotokatalytische afbraak van organische substanties in zuurstofarme omstandigheden met platinum geladen TiO₂ (Pt-TiO₂) als katalysator om gelijktijdige productie van waterstof te bereiken. Dit is zeer relevant als fotokatalytische oxidatie van contaminanten gecombineerd moet worden met katalytische hydrogenering van anorganische verontreinigingen (nitraten) in een huishoudelijke toepassing. Methanol (MeOH) was noodzakelijk om de vorming van waterstof te induceren. In totaal anaerobe omstandigheden werden hogere waterstof

productiesnelheden verkregen dan in zuurstofarme omstandigheden. Echter, volledige conversie van MO werd dan niet gehaald. In zuurstofarme omstandigheden werd de volgende volgorde in reductie activiteit van Pt nanodeeltjes waargenomen: $O_2 > MO > H^+$. De vormingssnelheid van waterstof uit MeOH wordt dus sterk beïnvloed door de aanvankelijke concentratie van zuurstof en MO aanwezig in de fotokatalytische reactor.

Tot slot wordt in **hoofdstuk 7** het uitgevoerde werk geanalyseerd en bediscussieerd, gevolgd door suggesties voor toekomstig onderzoek naar fotokatalytische toepassingen voor waterbehandeling.

Sumário

Nesta tese, a Fotocatálise Heterogénea (o catalisador encontra-se em suspensão) é apresentada como uma tecnologia promissora para purificação da água. No **Capítulo 1** faz-se uma introdução aos princípios da fotocatalise e aos parâmetros desta que irão ser estudados de modo a otimizar a velocidade de reação. Nesta tese iremos explorar a fotocatalise quer do ponto de vista teórico, quer para compreender o seu potencial de aplicação em dispositivos miniaturizados para fins domésticos de purificação de água.

No **Capítulo 2**, apresenta-se um novo método desenvolvido para estudos de fotocatalise em maior escala e a custo reduzido, que se baseia num foto-reactor de 96 poços (microprato de 96 poços), adequado para execução múltiplas reações em paralelo. Este método pode ser aplicado a uma larga variedade de contaminantes orgânicos assim como fotocatalisadores, requerindo curtos tempos de reação, até 15 min, e funcionando no intervalo de concentrações tipicamente descritos na literatura. Além disso, o volume do reactor de apenas 200 μL minimiza a quantidade de uso de catalisador e de moléculas modelo. Um aspecto relevante é a ausência de limitações na penetração da luz na solução aquosa (altura do reactor de apenas 1 cm), resultando numa utilização eficiente de todo o catalisador disperso em suspensão proporcionando um valor próximo da real velocidade de reação.

No desenvolvimento de tecnologia para a purificação de água, uma das maiores preocupações é a prevalência de productos farmacêuticos e os seus efeitos na saúde humana. De modo a elucidar a multiválcencia da fotocatalise, o catalisador dióxido de titânio (TiO_2) foi utilizado na decomposição de uma livraria com 1280 compostos farmacêuticos. Os resultados obtidos com o foto-reactor de 96 poços são descritos no **Capítulo 3**. Em termos gerais, o TiO_2 foi capaz de oxidar muitos dos composto farmacêuticos, estando a eficácia dependente da natureza química da molécula em estudo. Analizando os resultados de degradação após 5 minutos de iluminação, foi possível identificar alguns dos grupos funcionais e classes mais facilmente oxidáveis nos compostos orgânicos. Nestes, os que apresentam maior percentagem de degradação possuem grupos funcionais tais como aldeídos, álcoois, cetonas, nitrilos ou amidas. Uma das classes de compostos que se destacou por atingir as mais elevadas percentagens de decomposição foram os derivados de indol. Os compostos farmacêuticos que apresentaram baixas percentagens de decomposição apresentam na sua estrutura química conjugações aromáticas e derivados de adenisina, cafeína e imidazol, entre outras classes.

O Capítulo 3 revela ainda que os esteróides são uma classe de difícil oxidação, o que levou a um estudo mais detalhado, tendo como modelo a molécula acetato de cortisona. O estudo das

diferentes condições de reação (pH, concentração do catalisador, etc.) foi executado num reactor de escala laboratorial (50 ml). A reação de decomposição, apresentada no **Capítulo 4**, foi seguida por Cromatografia Líquida - Espectrometria de Massa (LC-MS). Foram testados vários fotocatalisadores, tendo o óxido de zinco (ZnO) e TiO₂ P25 (comercial) apresentado os melhores resultados relativos à velocidade da reação. TiO₂ P25 foi escolhido para estudos subsequentes, devido à instabilidade de ZnO em água. Por conseguinte, a concentração ótima de catalisador determinada foi de 0.25 g L⁻¹, tendo a variação de pH mostrado-se irrelevante para a cinética da reação. Adicionalmente, o uso de um agente oxidante (S₂O₈²⁻) combinado com o catalisador (TiO₂ P25) mostrou aumentar significativamente a velocidade da reação. Apesar da reação de decomposição ser seguida por LC-MS, não foram identificados compostos intermediários.

O **Capítulo 5** reporta o estudo da degradação de vários compostos orgânicos em solução. Para este efeito foram estudadas as condições de degradação da molécula modelo Alaranjado de Metila (do inglês “methyl orange”, MO), que representa uma classe de compostos usados frequentemente na indústria têxtil e a Atrazina, um pesticida; ambos caracterizados individualmente e quando presentes em simultâneo na mesma solução aquosa. Apesar da constante de velocidade de reação do MO se ter mostrado semelhante quer na presença ou ausência da Atrazina, a pH 7, a constante de velocidade de decomposição da Atrazina diminui significativamente quando MO está presente. Outros parâmetros como o pH, a concentração de fotocatalisador e moléculas em solução, mostraram-se relevantes para determinar a ordem de decomposição entre os dois compostos em solução. Neste capítulo é ainda discutido o mecanismo de decomposição, assim como a importância do fenómeno de adsorção à superfície do catalisador.

O **Capítulo 6** foca-se na decomposição fotocatalítica de compostos orgânicos, usando como catalisador TiO₂ modificado com platina (Pt-TiO₂), reação na qual ocorre produção simultânea de hidrogénio. Este facto poderá ser útil na aplicação de um dispositivo de purificação de água, no qual a produção de hidrogénio permite combinar a oxidação fotocatalítica com a hidrogenação catalítica de compostos inorgânicos (por exemplo, nitratos). Neste caso, o metanol (MeOH) foi usado como um doador de prótons para coadjuvar a reação. Verificou-se neste estudo que a concentração de hidrogénio produzida foi mais elevada quando a reação ocorre em condições anaeróbicas, não tendo a decomposição de MO sido completa. Na presença de oxigénio, a capacidade de redução à superfície das nanopartículas de Pt foi observada na seguinte ordem: O₂ > MO > H⁺. A concentração de hidrogénio produzido a partir de MeOH é fortemente influenciada pela concentração inicial de oxigénio e MO presente no reactor.

Por último, no **Capítulo 7** é feita uma reflexão global sobre os resultados obtidos e apresentadas sugestões para futuros estudos, e pondera-se acerca da aplicabilidade da fotocatalise para o tratamento de águas residuais.

List of Publications

Journal papers

Joana Romão, Mohamed Hamdy, Guido Mul, Jonas Baltrusaitis; “Photocatalytic decomposition of cortisone acetate in aqueous solution”, *Journal of Hazardous Materials*, 2015, 282, pp 208-215.

Joana Romão, David Barata, Pamela Habibovic, Guido Mul, Jonas Baltrusaitis; “High Throughput Analysis of Photocatalytic Water Purification”, *Analytical Chemistry*, 2014, 86 (15), pp 7612–7617.

Joana Romão, David Barata, Nelson Ribeiro, Pamela Habibovic, Hugo Fernandes, Guido Mul; “High Throughput Screening of Photocatalytic Conversion of New Emerging Contaminants”. (Submitted)

Joana Romão, Guido Mul; “Photocatalytic Degradation of Organic Mixtures in Water”. (Submitted)

Joana Romão, Rafal Salata, Sun-Young Park, Guido Mul; “MeOH Assisted Photocatalytic Degradation of Methyl Orange with Simultaneous Production of H₂”. (Submitted)

International conference proceeding

Jonas Baltrusaitis, **Joana Romão**, Guido Mul, “Photocatalytic Degradation of Cortisone Acetate in Water”, 245th National Spring Meeting of the American-Chemical-Society, 7-11 April 2013, New Orleans, LA.

Oral communications

Joana Romão, G. Mul., “*Photocatalytic Degradation of Organic Contaminant Mixtures in Water*”, 27th International Conference on Photochemistry, June 2015, Jeju Island, Korea.

Joana Romão, G. Mul., “*Photocatalytic Degradation of Organic Contaminant Mixtures in Water*”, Netherlands Catalysis and Chemistry Conference (NCCC), March 2015, Noordwijkerhout, Netherlands.

Joana Romão, G. Mul., “*Photocatalytic water cleaning technologies*”, Symposium at Universitat Politècnica de València, April 2014.

Poster presentations

Joana Romão, Rafal Salata, Guido Mul; “*Photocatalytic Degradation of Organic Contaminants in Aqueous Mixtures Combined with Hydrogen Production*”, European Materials Research Society (E-MRS), May 2015, Lille, France – BEST POSTER AWARD

Joana Romão, Guido Mul; “*Photocatalytic Degradation of Organic Contaminant Mixtures in Water*”, Netherlands Catalysis and Chemistry Conference (NCCC), March 2014, Noordwijkerhout, Netherlands.

Joana Romão, Guido Mul; “*Photocatalytic Degradation of Cortisone 21-Acetate in Water*”, XIth European Congress on Catalysis, 1-6 September 2013, Lyon, France.

Joana Romão, Guido Mul, Jonas. Baltrusaitis; “*Steroid Degradation by Photocatalysis*”, Netherlands Catalysis and Chemistry Conference (NCCC), March 2013, Noordwijkerhout, Netherlands.

Joana Romão, Guido Mul, Jonas. Baltrusaitis; “*Photocatalytic Degradation study of Cortisone 21-Acetate in Water*”, Netherlands’ MicroNanoConference’12, 10-11 December 2012 (Poster Pitch), Ede, Netherlands

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The Author

Joana Romão was born on 13th June 1987 in the Barreiro, Portugal. In 2009, she graduated in Organic Chemistry at Faculty of Science and Technology, University Nova de Lisboa (Portugal). In the same year, she enrolled in the Master of Bioorganics at the same university. Her master thesis, “Development of cyclodextrin-hydrogel polymeric systems in supercritical carbon dioxide (scCO₂) for drug delivery”, was performed under the supervision of Dr^a Maria Manuel Marques and Dr^a Teresa Casimiro. In July 2011 she completed the MSc.

In October 2011 she moved to Enschede to join the group of Photocatalytic Synthesis as PhD candidate, being supervised by Prof. Dr. Guido Mul. During the past 4 years, she explored the potential of applying photocatalysis for water cleaning, either by developing new platforms for high throughput screening, studying the fundamentals of reaction mechanisms or optimizing sustainable degradation protocols. The challenges and achievements are described in this thesis.