

École polytechnique de Louvain

Removal of anti-cancer drugs from real wastewater effluent by photocatalytic membrane reactor (PMR)

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Abstract

The presence of anti-cancer drugs, used for chemotherapeutic treatments, in surface waters raises some environmental concerns given their mutagenic and genotoxic effects. For this reason, new treatments are currently being studied for the degradation of these drugs. The aim of this study was to investigate the performances of a photocatalytic membrane reactor for the removal of three anti-cancer drugs – 5-fluorouracil, capecitabine, cyclophosphamide – from real wastewater effluent. Therefore, photocatalytic degradation experiments were performed in laboratory grade water and in secondary wastewater effluent at a TiO_2 concentration of 1.5g/L identified as the optimum for the production of active radicals. A reduction of degradation rates by more than 75% was observed for all three anti-cancer drugs in secondary wastewater effluent compared to pure water. Degradation experiments in secondary wastewater effluent filtered by reverse osmosis allowed to identify four water species responsible for the reduced degradation rates: bicarbonate, chloride, sulphate and calcium ions. Finally, an economic evaluation of this process suggested that the addition of a fine membrane like reverse osmosis as pre- or post-treatment could reduce the total cost of photocatalytic membrane reactor but further investigations are required. Overall, the results obtained in this work evidenced the need to acquire a better understanding of the mechanisms that deactivate photocatalysis in real water matrix in order to develop a more economically attractive photocatalytic membrane reactor that can efficiently degrade anti-cancer drugs in real conditions.

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List of Abbreviations

5-FU	5-Fluorouracil
AOP	Advanced Oxidation Process
CAP	Capecitabine
CFV	Cross Flow Velocity
COD	Chemical Oxygen Demand
CP	Cyclophosphamide
CSTR	Continuous Stirred Tank Reactor
LGW	Laboratory Grade Water
LGW-Cl ⁻	Laboratory Grade Water spiked with chloride ions
MF	Microfiltration
MWCO	Molecular Weight Cutoff
NF	Nanofiltration
NOM	Natural Organic Matter
pCBA	para-Chlorobenzoic Acid
PMR	Photocatalytic Membrane Reactor

RO	Reverse Osmosis
TMP	Transmembrane Pressure
UF	Ultrafiltration
WWeff	Secondary wastewater effluent
WWeff-NF	Permeate collected after nanofiltration of secondary wastewater effluent
WWeff-RO	Permeate collected after reverse osmosis of secondary wastewater effluent
WWTP	Wastewater Treatment Plant

Introduction

At a time when the awareness of public opinion about the impact that human activity has on our environment is growing, the quality of water is more and more questioned. Pollution of our lakes, rivers and other bodies of water has multiple origins, whether they are domestic, agricultural or industrial. Thanks to the increasing accuracy of detection tools, scientists have been able to point out the presence of dangerous micro-pollutants in water at concentrations down to some ng/L which could not be detected before. Even though such low concentrations might seem negligible, some contaminants are so stable and reactive that it cannot be ensured that their continuous introduction in the environment will not affect the aquatic ecosystem on the long-term. The application of the REACH legislation in Europe has certainly been a strong driver of change for the collection of information about chemicals found on the market. However, the pharmaceutical area which comprises a large variety of hazardous compounds is still exempted from registration in the REACH regulation.

Among the pharmaceuticals of concern are the antineoplastic drugs used for the treatment of cancer. The role of these drugs is to prevent the growth and multiplication of cancerous cells but, due to their unselective mode of action, they can also constitute a hazard for healthy cells [13]. After their introduction in the human body, a fraction of anti-cancer drugs is excreted through urine and/or faeces and ends up in the sewage waters. These drugs go through the wastewater treatment plant (WWTP) but the conventional technologies are currently not able to eliminate them completely so they eventually reach the surface waters [14].

The World Cancer Report of 2014 revealed that, in 2012, approximately 14 million new cases of cancer were recorded and 8 million cases led to death. It also predicted that, by 2025, the number of cases detected annually would grow by 40% [15]. This increasing occurrence of cancer will necessarily be accompanied by a growth in the quantity of anti-cancer drugs discharged in the environment, which is why their elimination has become an important concern in the scientific world over the past few years.

Given the incapacity of WWTP to eliminate anti-cancer drugs, other degradation methods have been investigated and Advanced Oxidation Processes (AOPs) stood out as one of the most promising area. AOPs' basic principle is to generate strong oxidants that can degrade the most recalcitrant pollutants [16]. This acronym regroups different techniques and one of them is called Photocatalytic Membrane Reactor (PMR). PMR is a sequential technique that combines a photocatalytic reactor for the degradation of pollutants with a membrane to avoid the loss of photocatalyst and to retain contaminants in the system [1]. Over the past few years, a large

number of articles related to PMR have been published showing the increasing interest for this technique [17][2][9][18]. However, at present, this technology is not mature enough to be applied at industrial scale. Among other issues, the poor performances of photocatalysis in natural waters, the sensitivity of membranes to fouling and the high energy consumption for artificial irradiation hinder the large-scale application of PMR [19].

This master thesis, conducted within the framework of the PhD thesis of Raphaël Janssens, aims at studying the performances of photocatalytic membrane reactor for the removal of anti-cancer drugs in real wastewater effluent and at assessing the cost of this technology. The first step will be to optimise the TiO_2 photocatalyst concentration leading to the maximum production of reactive oxygen species. Then, the effect of water matrix on the removal of anti-cancer drugs will be investigated by comparing the degradation efficiency in different water matrices: laboratory grade water, secondary wastewater effluent and filtered secondary wastewater effluent. Finally, a preliminary economic evaluation of the PMR for the continuous degradation of anti-cancer drugs will be carried out.

Chapter 1

Literature review

1.1 Anti-cancer drugs: current situation

Anti-cancer drugs (also known as antineoplastic drugs) are administered to patients undergoing chemotherapy. They are designed to prevent the proliferation of fast-growing tumoral cells in the human body by different mechanisms [20]. Depending on their mode of action, a classification of antineoplastic compounds into three categories can be established. The first class kills cells by interacting with DNA, these drugs are designated as cytotoxic. The second affects the multiplication of cancerous cells without any interaction with DNA. These are called cytostatic drugs. As for the third category, it includes the endocrine therapy drugs which have an effect on the hormonal system [10].

Once administered to patients, anti-cancer drugs are not fully metabolised and a fraction of them is excreted in the urine and/or faeces either as the parent compound, or in the form of metabolites. Eventually, they end up in waste waters [21].

Antineoplastic agents can enter the water cycle through different routes. Hospital wastewaters constitute an important one and chemotherapeutic compounds have already been detected at the level of some $\mu\text{g/L}$ in those effluents [21][22]. Another major source for the introduction of antineoplastics in the water cycle is the household sewage due to the increase of outpatient treatments.

In order to make sure anti-cancer drugs will last long enough in the human body to interact with cancerous cells, some of these drugs are designed to be very persistent [9]. However, their persistency combined with their (usually) low biodegradability make these drugs resistant to the treatments applied in conventional WWTPs. Franquet-Griell et al. [14] reported that 7 out of the 16 investigated antineoplastics were poorly eliminated by activated sludge treatment. Moreover, they demonstrated that UV disinfection sometimes applied in WWTPs did not entirely remove those drugs either. Consequently, the most recalcitrant anti-cancer drugs are constantly discharged in natural waters which could lead to their bioaccumulation in the environment [22].

Their release in the environment is particularly alarming given that these drugs, being non-selective, attack not only cancerous cells but also healthy growing cells so that they could represent a danger for any eukaryotic organisms [13]. Antineoplastic agents are known to be

carcinogenic, mutagenic, genotoxic and/or teratogenic which means they could affect the genetic material of living organisms, cause cancer and interfere with the development of embryos [23].

To this day, there is a lack of experimental investigations evaluating the long-term effects of chemotherapeutic agents on the aquatic ecosystem at concentrations encountered by living organisms [13][10]. Da Costa Araújo et al. [24] published in 2019 one of the first long-term studies describing the damage caused by two anti-cancer drugs (5-fluorouracil and cyclophosphamide) on tadpoles and their results prove that the concerns associated to the detection of anti-cancer drugs in nature are justified. In this study, tadpoles were exposed for 30 days to those drugs at their predicted environmental concentrations. At the end of the 30 days, researchers recorded morphological and mutagenic changes on tadpoles that could lead to the development of cancerous cells.

As those drugs represent a wide family of chemicals with hundreds of compounds commercially available, some studies, such as the one performed by Besse et al. [10] in 2012, established a hierarchy of chemotherapeutic agents that require more extensive studies based on the probability of drugs detection in the environment. The three compounds studied in this thesis – 5-fluorouracil, capecitabine, cyclophosphamide – have been selected from this preferential list and their predicted concentrations in French surface waters reported in Besse et al. [10] are displayed in the following table. Those concentrations are calculated based on the consumption rate of the considered drug over one year, the fraction excreted by the body, the fraction eliminated in WWTP and a dilution factor. The conservative values are obtained considering no removal of the drugs in WWTP.

Drugs	Conservative PEC [ng/L]		Refined PEC [ng/L]	
	2004	2008	2004	2008
5-Fluorouracil	38.59	39.57	7.72	7.91
Capecitabine	59.84	117.24	1.8	3.52
Cyclophosphamide	6.43	6.98	> 1.61	> 1.74

Table 1.1: Predicted environmental concentrations (PECs) of three anti-cancer drugs in surface waters for years 2004 and 2008 [10].

As the number of patients with cancer is expected to grow in the future, the consumption of antineoplastic drugs would be intensified accordingly leading to an increase of their concentration in the environment.

1.2 Solution: Advanced Oxidation Processes (AOPs)

Given the concerns raised previously and the expected increase in the consumption of anti-cancer drugs, researchers have striven to develop a treatment process for the elimination of antineoplastics from waste waters. From their experiments, Advanced Oxidation Processes (AOPs) stood out as good candidates for the removal of these drugs [22]. AOPs designate techniques that generate in-situ reactive oxygen species, such as hydroxyl radicals $\text{OH}^\bullet$, which degrade non-selectively organic compounds and micro-pollutants present in water [16].

These techniques grouped under the term AOPs differ from each other in the way they produce active radicals. They are classified into three groups: photochemical, non-photochemical and combined processes [25]. The photochemical category regroups all the processes that exploit light to produce oxidising species including photocatalysis, photo-Fenton and UV treatment coupled with hydrogen peroxide. Conversely, non-photochemical processes occur in the absence of light. Ozonation, Fenton and ultrasound can be cited as examples of this second category. Regarding combined processes, they aim to increase the oxidative capacity of the process by coupling two or more AOPs [26]. Among all these different techniques, the most popular AOPs reviewed in the literature for the removal of pharmaceuticals are $\text{UV}/\text{H}_2\text{O}_2$, UV/O_3 , photocatalysis and (photo-)Fenton [27].

However, the application of AOPs as an additional wastewater treatment faces some challenges. Several studies suggest that incomplete oxidation of micro-pollutants can lead to the formation of intermediates released in the effluent stream and potentially more toxic than the initial compounds [16][28]. Also, the target pollutant concentration in the large volumes to treat is usually low. Finally, these processes are generally very expensive because they demand high energy and reagents consumption [29].

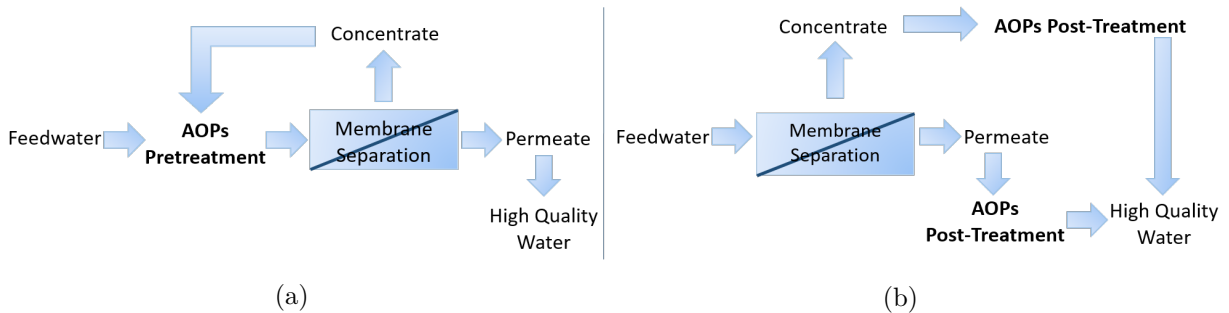


Figure 1.1: Combination of AOPs with membrane filtration in different configurations: (a) AOPs as pretreatment and (b) AOPs as post-treatment. Figure inspired by Ganiyu et al. [1].

The combination of AOPs with membrane filtration, as represented on figure 1.1, has emerged as a promising solution to overcome the aforementioned limitations, namely incomplete degradation, low concentration stream and high cost. Furthermore, this coupling is also interesting to overcome the drawbacks of membrane filtration that include fouling and disposal of the concentrate enriched in pollutants [1].

Different combinations of AOPs and membrane processes can be considered: AOPs can be used as pretreatment stage (figure 1.1a) to degrade organic pollutants and reduce membrane fouling. In that case, a fine membrane (NF or RO) is needed as a final barrier to the discharge of non-degraded pollutants or toxic by-products. The concentrate can be sent back to the AOP in order to complete pollutants removal. As a post-treatment stage (figure 1.1b), it is primarily applied to the concentrate containing micro-pollutants at high concentration avoiding the simple discharge of this stream in nature. The permeate can also undergo an advanced oxidation process to eliminate contaminants that were not rejected by the membrane. A final possible configuration is the hybrid process where degradation and separation take place simultaneously [1]. The selected combination depends on the type of AOP, the efficiency of the coupling and the cost.

The process investigated in the present work, called Photocatalytic Membrane Reactor (PMR), is a hybrid process combining heterogeneous photocatalysis with a membrane. Its application for anti-cancer drugs degradation is promising given the numerous studies that have demonstrated successful photocatalytic degradation of different pharmaceuticals in a PMR [8][30][5]. To mention just one example, Sarasidis et al. [31] studied the photocatalytic degradation of diclofenac in pure water and recorded a degradation of 99.5% between the influent and effluent of the PMR.

1.3 Photocatalytic Membrane Reactors (PMRs)

Unlike the classical photocatalytic reactor on its own, PMR offers the possibility to operate in continuous thanks to the concurrent photocatalytic degradation and confinement of catalysts in the photoreactor by the membrane [32].

Two possible configurations can be encountered for PMRs: (a) slurry PMRs where the photocatalysts are suspended in the reaction mixture and (b) immobilised PMRs where the photocatalysts are fixed on the membrane. In this work, slurry PMR is investigated because particles in suspension provide a higher active surface area which promotes photocatalytic degradation [17].

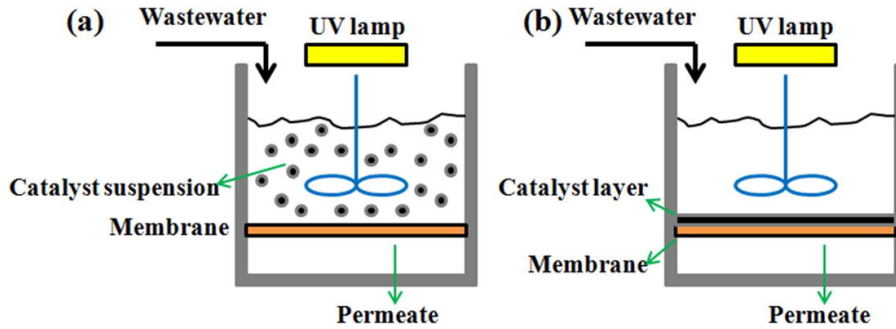


Figure 1.2: Schematic representation of a PMR in its two possible configurations: (a) slurry PMR and (b) immobilised PMR. Figure reprinted from [2].

In the slurry PMR, continuous agitation of the fluid maintains photocatalyst particles in suspension and the membrane prevents their entrainment in treated waters. The membrane actually has the dual task of confining photocatalysts in the reactor and of selectively separating targeted micro-pollutants and their degradation products from the waste waters [33]. The rejection of contaminants along with the catalyst increases their residence time in the system, which favours their complete degradation. However, this rejection property depends on the pore size of the membrane relative to the molecular weight of the pollutants. R. Hainaut et al. [12] studied the rejection properties of titania and alumina ultrafiltration (UF) membranes towards four anti-cancer drugs (5-fluorouracil, cyclophosphamide, capecitabine and ifosfamide) and noted no rejection of these pharmaceuticals. Membranes investigated in this work are the same alumina membranes as the ones studied by R. Hainaut et al. [12].

Slurry PMRs can be arranged in two different set-ups: (1) membrane module submerged in the photoreactor (as schematically represented on figure 1.2a) and (2) membrane module separated from the photoreactor as a side pressurised compartment. The latter, though less compact, presents the advantage that the membrane is not directly exposed to UV radiations and oxidising species which affect its stability [9].

The next sections of this chapter will be devoted to the description of the mechanisms behind photocatalytic degradation and the presentation of some important parameters that influence photocatalytic performances. Finally, membrane processes and their limitations will be discussed.

1.4 Principle of photocatalysis

In the *Glossary of Terms Used in Photocatalysis and Radiation Catalysis* (IUPAC Recommendations 2011) [34], photocatalysis is defined as a "change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a substance, the photocatalyst, that absorbs light and is involved in the chemical transformation of the reaction partners".

Recently, photocatalysis has gained more attention for its application to wastewater treatment due to its green attributes: mild operating conditions (atmospheric pressure and room temperature), no addition of toxic reagents and potential to degrade toxic and non-biodegradable molecules [33]. Nevertheless, some limitations, that will be presented in the coming sections, still need to be overcome to make this technology competitive against other AOPs.

1.4.1 Mechanism of degradation

Heterogeneous photocatalysis follows the same sequence of independent steps as classical heterogeneous catalysis, namely:

1. Diffusion of reactants from the fluid phase to the catalytic active sites.
2. Adsorption of the reactant(s).
3. Reaction at the catalytic surface.
4. Desorption of the product(s).
5. Diffusion of the product(s) back to the fluid phase.

However, photocatalyst differs from simple catalyst in its mode of activation: while catalytic reactions are thermally-activated processes, photocatalytic reactions are activated by light. This is the reason why photocatalytic processes can be efficiently operated at room temperature [35]. The mechanism of photocatalysis is schematically represented on figure 1.3.

Absorption of photons, whose energy is equal or higher than the band gap energy (E_g) of the semiconductor photocatalyst, causes the transition of electrons from the valence band (VB) to the conduction band (CB) leaving positively charged vacancies in the valence band (i.e. holes). The generated charge carriers then migrate towards the surface of the catalyst. A significant fraction of these charged species will not reach the surface due to the possibility for electron-hole pairs to recombine during their migration. Their recombination should be as slow as possible for an efficient photocatalytic process [36]. Charge carriers that make it to the surface without recombination can interact with adsorbed species through redox reactions.

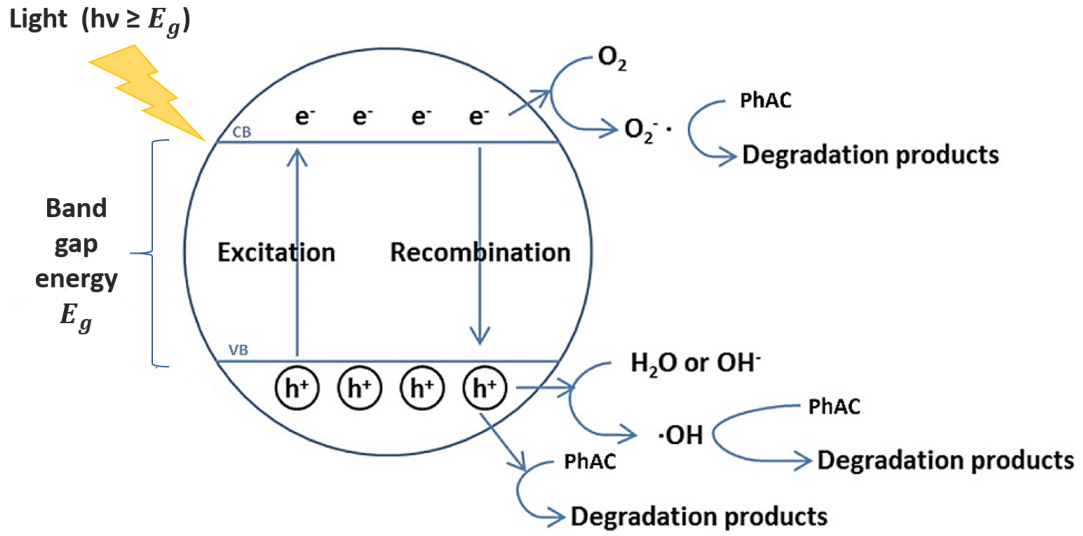


Figure 1.3: Mechanism of photocatalytic degradation for pharmaceutically active compounds (PhACs). Figure modified from [3].

Holes are oxidising species that react with water molecules and hydroxide ions to produce highly reactive hydroxyl radicals while electrons can reduce oxygen molecules into superoxide radicals $O_2^{\bullet-}$. These reactions can be written as follows, SC standing for semiconductor [32]:



Superoxide radicals can further react to form, in turn, hydroxyl radicals.

These free radicals can oxidise unselectively any organic pollutants found in the medium. Alternatively, pollutants can directly interact with holes at the photocatalyst surface. However, Lin et al. [37] demonstrated that the most probable pathway for the degradation of two anti-cancer drugs (cyclophosphamide and 5-fluorouracil) involved free hydroxyl radicals instead of holes.

It should be noted that photolysis can also take part in the degradation of pollutants. The process of photolysis consists in the cleavage of chemical bonds of a molecule after it absorbed light, without any photocatalyst being involved. The efficiency of this direct photodegradation upon light absorption varies from one compound to another and is quantified by a parameter called the quantum yield. In the case of a photolytic process, this parameter can be defined as the probability that the absorption of one photon with a given energy will cause the photolysis of one molecule [38].

1.4.2 Hydroxyl radical molecular probe

Some specific molecules called $OH^\bullet$ probe molecules are characterised by a high reactivity towards hydroxyl radicals. Therefore, in a PMR, their progressive disappearance from the solution with

time is an indirect indication on $\text{OH}^\bullet$ concentration and so on the efficiency of the photocatalytic process [39]. This experimental approach was developed in 1999 by Elovitz and von Gunten [40] to assess the oxidation potential of AOPs. A well-known example of molecular probe is the para-chlorobenzoic acid (pCBA).

When the degradation of toxic contaminants, such as anti-cancer drugs, is studied, it can be particularly convenient to limit the number of experiments conducted with these toxic compounds by using a $\text{OH}^\bullet$ molecular probe whenever possible.

1.4.3 Photocatalytic material

Semiconductor materials are often used as photocatalyst although they do not all present a photocatalytic activity. In order to participate in the interfacial redox reactions, electrons should have a sufficiently negative redox potential to reduce the adsorbed species, typically oxygen molecules, whereas holes should have a sufficiently positive redox potential to exert their oxidising power. The redox potential of charge carriers, which is specific to each semiconductor material, corresponds to the energy level at the bottom of the conduction band for electrons and at the top of the valence band for holes [36].

Among all the semiconductor photocatalysts reviewed in the literature, titanium dioxide is the most studied because of its low cost, availability, non-toxicity, long-term stability and ability to induce redox reactions [41]. TiO_2 is a polymorph which means it can exist under different crystalline phases i.e. brookite, anatase or rutile. Even though anatase is considered as the most photocatalytic active phase, it has been observed that the combination of anatase with brookite or rutile exhibited an enhanced photocatalytic activity because it decreased the rate of electron-hole recombination [41]. For this reason, TiO_2 photocatalyst generally selected in the literature is TiO_2 P25 which consists in a mixture of anatase and rutile.

As previously mentioned, the photo-activation of TiO_2 catalyst requires the absorption of photons with energy equal or greater than the band gap energy which ranges from 3 to $\sim 3.2\text{eV}$ depending on the crystalline form of titanium dioxide [42]. Therefore, UV photons only ($\lambda < 400\text{nm}$) can activate TiO_2 photocatalyst. Since UV light represents less than 5% of the solar spectrum, a photocatalytic process using TiO_2 requires artificial UV lamps to be efficient which strongly increases its operating costs and decreases its environmental attractiveness [33]. Therefore, researchers are currently working on the development of new photocatalytic materials able to exploit fully the solar light. Several strategies are investigated such as semiconductor doping or coupling of different photocatalysts [43].

1.5 Factors affecting the photocatalytic degradation

1.5.1 Initial concentration of pollutants

The Langmuir-Hinshelwood kinetic model is the most widely applied to describe the relationship between the photodegradation rate and the concentration of pollutants. It is expressed as follows:

$$r = \frac{-dC}{dt} = \frac{k_r K_a C}{1 + K_a C} \quad (1.5)$$

where k_r is the intrinsic rate constant in [mol/L/min], K_a is the adsorption equilibrium constant in [L/mol] and C is the pollutant concentration in [mol/L] [44].

Two extreme cases can be identified in order to simplify this equation:

1. For a low concentration of pollutants and/or weak adsorption ($K_a C \ll 1$), it becomes a pseudo first order reaction with an apparent rate constant k in [min^{-1}]:

$$\frac{-dC}{dt} = k_r K_a C = kC \quad (1.6)$$

After integration, it gives:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (1.7)$$

C is the pollutant concentration after a time t while C_0 is the initial pollutant concentration. This simplification is typically accepted for an initial concentration below 10^{-3} mol/L [32].

2. For a high concentration of pollutants and/or strong adsorption ($K_a C \gg 1$), expression 1.5 simplifies to a zero order reaction:

$$\frac{-dC}{dt} = k_r \quad (1.8)$$

The integration of this equation leads to:

$$C - C_0 = -k_r t \quad (1.9)$$

As already highlighted in section 1.1, antineoplastic compounds are present in hospital effluents at the level of some $\mu\text{g/L}$ and they are even more diluted in the effluent of WWTP as they are mixed with other wastewater streams. Therefore, their rate of degradation follows a pseudo first order kinetics.

1.5.2 Reactor design

To date, most of the studies about photocatalysis have been focused on batch systems for the removal of micro-pollutants from waste waters [31]. In this configuration, the extent of drugs degradation with time can be predicted with equation 1.7. However, the application of batch PMR is limited to the treatment of small volumes of water while the treatment of large volumes requires a continuous-flow reactor.

In a continuous operating mode, the permeate is continuously collected at the same rate as the feed flow rate to maintain a constant volume in the reactor. The performances of the continuous PMR depend on the separation properties of the membrane since the rejection controls the residence time of pollutants in the photoreactor.

For antineoplastic drugs, UF membranes have shown no rejection of these compounds [12]. Consequently, to estimate the efficiency of drugs degradation, the PMR can be modelled as a continuous stirred tank reactor (CSTR) assuming that a perfect mixing is reached in the reactor. In an ideal CSTR, the feed entering the vessel at time $t=0$ is instantaneously and perfectly mixed with the reactor's content. As a result, some of the species introduced at $t=0$ leave directly the reactor through the effluent stream and their residence time is close to 0 while others remain inside for a very long time. The mean residence time τ is defined as the ratio of the reactor volume V over the feed or permeate flow rate Q .

Therefore, there is a distribution of residence times due to this assumption of perfect mixing. A typical residence time distribution is depicted on figure 1.4.

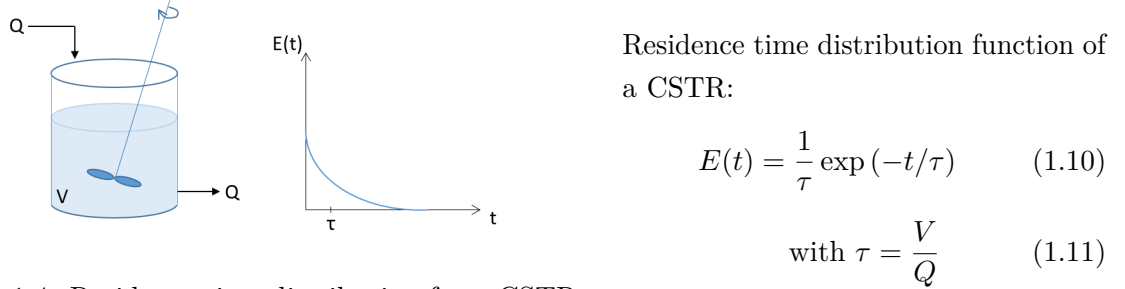


Figure 1.4: Residence time distribution for a CSTR.

The outlet concentration of pollutants in a CSTR can be predicted from the residence time distribution. To this end, the inlet flow is considered as a collection of fluid elements that behave as small batch reactors and do not interact with each other. Therefore, the conversion in each fluid element only depends on the time this element spends in the reactor and can be described by equation 1.7. The average concentration at the outlet $\langle C_{\text{out}} \rangle$ is then obtained by multiplying the fraction of fluid elements characterised by a residence time t with the concentration of the target compound in these fluid elements and by integrating over all the possible residence times.

$$\langle C_{\text{out}} \rangle = \int_0^{\infty} C(t) E(t) dt \quad (1.12)$$

Combining equation 1.12 with equations 1.7 and 1.10, it gives:

$$\frac{\langle C_{\text{out}} \rangle}{C_0} = \frac{1}{1 + k\tau} \quad (1.13)$$

These calculations are only valid for first order reactions and isothermal conditions [45].

From equation 1.13, it can be noticed that, for an average residence time in a CSTR corresponding to a given experiment time in a batch reactor, the efficiency of degradation is lower in the continuous reactor as the decrease of pollutant concentration with time is exponential in the batch mode. Moreover, it can also be observed that a higher average residence time τ

improves the degradation and this average residence time can be easily controlled by modifying the feed flow rate (equation 1.11).

1.5.3 Photocatalyst loading

It can be expected that increasing the photocatalyst concentration enhances the rate of pollutant degradation since a higher catalytic surface area is available for generation of radicals [32]. However, figure 1.5 shows that the relation between degradation rate and photocatalyst loading is not linear.

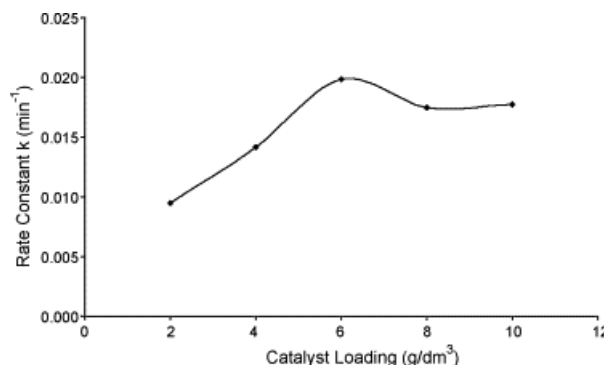


Figure 1.5: Effects of TiO₂/K catalyst loading on the optimum Congo Red degradation rate. Figure reprinted from [4].

The stabilisation of the rate constant above a certain catalyst concentration can be explained by two effects. First, an excessive photocatalyst loading increases the opacity of the solution which hinders the penetration of UV photons in the medium and limits the activation of photocatalyst particles [46]. Second, a high catalyst dosage favours a spontaneous agglomeration of photocatalyst particles in suspension [47]. This phenomenon reduces the surface area exposed to light and limits the adsorption of pollutants or any other species involved in the photocatalytic process. It should be noted that, besides catalyst loading, other parameters such as ions, organic matter and pH can influence particle agglomeration. This will be discussed in the subsequent sections.

Consequently, an optimum loading should be determined to operate at the highest degradation rate possible and avoid additional costs associated to a useless surplus of photocatalysts. This optimum depends on the photoreactor configuration, light source and selected photocatalyst.

1.5.4 Light source

Intensity and wavelength are two characteristics of the light source that influence photocatalytic degradation processes. Usually, an increase in light intensity enhances the photocatalytic degradation rate as long as intensity does not become too high. At high light intensities, the rate becomes independent of intensity [46].

The selection of an appropriate wavelength depends on the photocatalyst employed and more precisely on its band gap. As already mentioned in section 1.4.3, TiO₂ particles are

activated by UV radiations ($\lambda < 400\text{nm}$). UV spectrum can be divided in three regions based on the wavelength of radiations: UV-A (315-400nm), UV-B (280-315nm) and UV-C (100-280nm) [43]. Kertész et al. [48] studied the activation of TiO_2 particles under UV-C (254nm) and UV-A radiations (366nm) and they showed that a shorter wavelength led to slightly higher photocatalytic reaction rates.

Commonly, mercury UV lamps are used to provide artificial illumination with the drawbacks of low energy efficiency, short lifespan and environmental issues due to mercury disposal [49]. Recently, it has been proposed to replace these mercury lamps with light emitting diodes (LEDs) which have a lower environmental impact and a longer lifetime. However, their output power is lower than mercury lamps and this affects the efficiency of photodegradation. Therefore, manufacturers are currently working on the development of UV-LEDs with increased output power [19].

1.5.5 Water quality

Several authors reported a decrease in the performances of photocatalysis when photodegradation tests were carried out in real waters compared to tests performed in pure water [50][3]. For instance, Rioja et al. [5] studied the photodegradation of clofibric acid with TiO_2 in different environmental waters and their results are represented on figure 1.6. This figure shows that a degradation of less than 10% was obtained when photocatalysis was carried out in real waters whereas the same test conducted in pure water gave a degradation close to 100%.

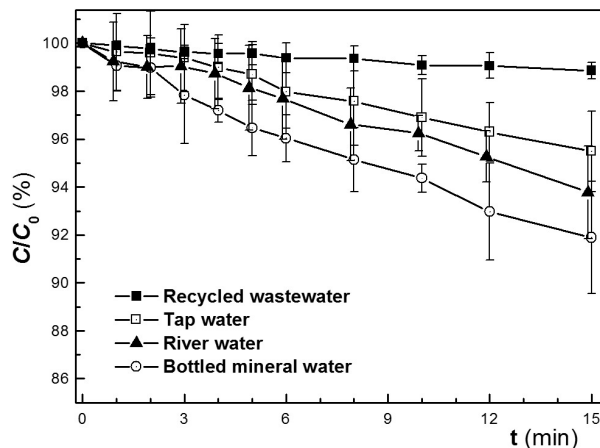


Figure 1.6: Photocatalytic degradation of clofibric acid in different water matrices. Figure reprinted from [5].

This reduction of the photocatalytic efficiency is mainly attributed to the presence of inorganic ions and organic compounds in real waters. The differences in degradation observed on figure 1.6 for the four types of matrices come from the variation in organic content and from the diversity of ions that can be found in different natural waters. Furthermore, the water pH can also have an impact on the photocatalytic process.

As the reduction of photocatalytic performances in real water constitutes a strong limitation to the successful large-scale application of PMRs, the potential effects of pH, organic matter and

inorganic ions on photocatalysis will be reviewed in more details in this section.

1.5.5.1 Solution pH

Solution pH influences the ionisation state of the photocatalytic surface which also depends on the point of zero charge (pzc) of the photocatalyst. This pzc corresponds to the pH at which the charge density of the particle surface is zero and ranges from pH 6 to pH 7.5 for TiO₂ particles according to their crystalline composition (pH 6.8 for TiO₂ P25) [32]. If the solution pH is lower than the pzc, particles are positively charged and, conversely, if the pH is higher than the pzc, the photocatalytic surface is negatively charged. Because the pH also affects the charge of target pollutants based on their pKa, a pH variation modifies the affinity between photocatalyst particles and contaminants which influences the photocatalytic efficiency [37].

Furthermore, solution pH has an effect on agglomeration of TiO₂ particles which is also related to the surface charge of photocatalyst. Charged photocatalytic particles attract oppositely charged ions present in solution and an electric double layer is formed around each particle. Thanks to this double layer, repulsive forces between particles ensure the stabilisation of the suspension. However, when pH is equal to pzc, particles are neutral and tend to agglomerate [47].

Finally, solution pH affects the main pathway responsible for the generation of free radicals. For example, it can be seen from the reactions written in section 1.4.1 that the formation of OH[•] by interaction with holes is more favourable under alkaline conditions when a large concentration of hydroxide ions is available [51].

1.5.5.2 Natural organic matter

It is acknowledged in the literature that natural organic matter (NOM) has the capacity to interfere with photocatalysis at different levels of the process [3][5][52]. First, NOMs can behave as scavengers of hydroxyl radicals limiting their availability to degrade target pollutants. Also, as organic matter absorbs light in the UV range, the competition for photon absorption between TiO₂ particles and NOMs reduces the probability of photocatalyst activation. Finally, the adsorption of NOMs on the photocatalytic surface blocks the access to active sites and, as a result, inhibits the photocatalytic reactions.

However, several researchers suggest that these inhibiting effects are only significant at high NOM concentrations. For instance, Ye et al. [3] studied the effects of different NOM concentrations spiked in pure water on the photocatalytic degradation rate and they reported that, below 5mg/L of NOM, the degradation rate was not affected. To mention another example, Drosos et al. [52] investigated the effects of different ratios of NOM (represented by humic acid) concentration over TiO₂ concentration and they observed that, for small ratios ($\sim 0.4\text{mg/g}$), photocatalytic performances were slightly enhanced. An explanation advanced was that, at low NOM concentrations, organic species, bonded to the catalyst surface, provide a highly adsorbing support for pollutants. Therefore, it increases pollutant concentration close to TiO₂ particles where the OH[•] concentration is the highest and this promotes the degradation of contaminants.

When moving away from the catalytic surface, $\text{OH}^\bullet$ concentration decreases very fast because hydroxyl radicals are highly reactive and non-selective [31].

Furthermore, the agglomeration of photocatalytic particles which causes a reduction of the available active surface area is also influenced by the presence of natural organic matter. NOM can play two opposite roles on the stability of the TiO_2 suspension: (1) they can provide steric stabilisation of the suspension by binding to the catalytic surface or (2) they can induce agglomeration of particles through the bridging effect [53]. These two effects are represented schematically on figure 1.7.

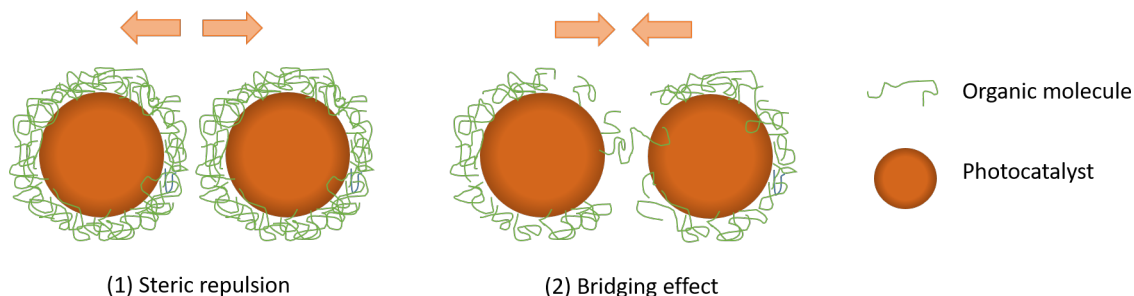


Figure 1.7: Effects of natural organic matter on agglomeration of photocatalysts. Figure inspired by [6].

The adsorption of NOM at the catalyst surface leads to a steric repulsion between the particles which limits their agglomeration. Topuz et al. [53] observed that concentrations of dissolved organic carbon $> 2\text{mg/L}$ were sufficient to stabilise the TiO_2 colloidal suspension. They also highlighted the influence of molecular weight on this stabilising effect and they noted that organic molecules with high molecular weight were more likely to prevent the agglomeration.

Regarding the bridging effect, Topuz et al. [53] did not record any enhanced TiO_2 agglomeration that could be attributed to NOM in all the natural water samples they tested. According to Tiller et al. [54], this effect is rarely observed as it appears for a narrow range of NOM concentrations at specific conditions of pH and ionic strength.

1.5.5.3 Inorganic ions

Many anions present in water have been reported to exert detrimental effects on PMR performances even at very low concentrations [3]. The most commonly found in natural waters are Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- and H_2PO_4^- . Conversely, deactivating effects of most cations on photocatalysis are less noteworthy than the ones of anions [55]. For this reason, most studies focus on the presence of inorganic anions to explain the inhibitory effects.

First, anionic species can interfere with photocatalytic performances by scavenging holes which limits their availability to produce reactive oxygen species. Anions can also react with hydroxyl radicals. These reactions lead to the formation of less reactive radicals and, therefore, slow down the rate of photodegradation [56].

Second, ions in solution are attracted by charged photocatalyst particles and form a double layer around them. This electric double layer represents a barrier that the pollutants need to

cross in order to reach the photocatalyst surface where the concentration of hydroxyl radicals is high [31]. The thickness of this double layer depends on the ionic strength of the solution [5]. Furthermore, some ions such as SO_4^{2-} can adsorb at the TiO_2 surface through van der Waals and hydrogen bonds and limit the available active sites [56].

Besides these effects, some specific ions present in real waters can also destabilise the TiO_2 suspension and cause the agglomeration of particles. This formation of larger particles affects the rate of photodegradation by reducing the active surface area. According to Ottofuelling et al. [57], divalent anion SO_4^{2-} as well as divalent cation Ca^{2+} strongly promote the formation of bigger aggregates .

From this review, it appears that ions can have multiple effects on photocatalysis which are difficult to predict without experimental investigations because it depends on the ion type and concentration. The situation for natural waters is even more complex as these waters contain a mixture of NOM and different ions which could potentially give rise to synergistic or antagonist effects.

1.6 Membrane filtration

The interest for membrane technology has increased in the past few years because it is a simple technique with a low environmental impact and energy consumption [58]. At present, it is applied in various industrial sectors such as food and pharmaceutical industries, chemical processing, wastewater treatment and more.

1.6.1 Membrane operation and classification

A membrane acts as a semipermeable barrier meaning that some dissolved substances can pass through this porous layer, forming the permeate stream, while others cannot and constitute what is called the retentate stream. This separation of solutes is made possible by the application of an external driving force. Different categories of membranes can be identified based on the driving force that applies. The most commonly used type of membranes are pressure-driven membranes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO).

Membrane process	Pore size	Pressure
Microfiltration	0.05 – 10 μm	1 – 2 bar
Ultrafiltration	0.001 – 0.05 μm	2 – 5 bar
Nanofiltration	< 2.0nm	5 – 15 bar
Reverse Osmosis	< 1.0nm	15 – 100 bar

Table 1.2: Pressure-driven membrane processes [11].

These pressure-driven membranes differ from each other by their molecular weight cutoff (MWCO) which corresponds to the lowest molecular weight of a solute rejected at 90% by the membrane and is consequently related to the pore size. Table 1.2 summarises the characteristics of each membrane, including the range of pressure necessary to force the liquid through the pores.

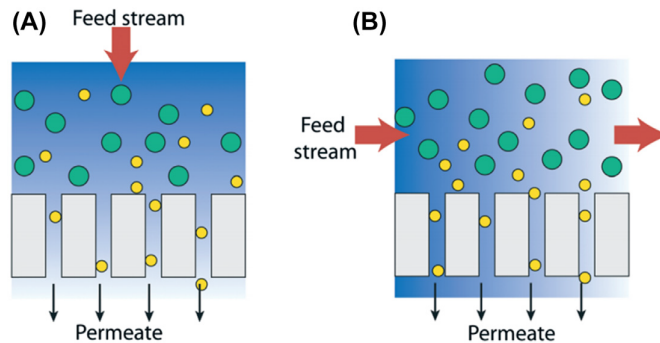


Figure 1.8: Schematic illustration of membrane operation in (A) dead-end filtration and (B) cross-flow filtration. Figure reprinted from [7].

As represented on figure 1.8, membrane processes can be operated in two different modes

depending on the feed flow direction with respect to the orientation of the membrane: dead-end filtration or cross-flow filtration. The cross-flow operation is convenient to alleviate the fouling tendency of the membrane since this operation mode limits the deposition of potential foulants on the surface by entraining them with the flow [7].

The common materials used for the fabrication of membranes are polymer and ceramic. Polymeric membranes are generally selected for their low price, availability and ease of manufacturing but they suffer from poor mechanical resistance, chemical and thermal stability. On the contrary, ceramic membranes offer a higher mechanical strength and a good thermal and chemical stability but it comes along with a higher price [11].

Some studies have highlighted that polymeric membranes are not the best suited to resist the severe conditions encountered in PMR since the exposition to UV radiations and oxidative radicals affects their stability [59]. Deteriorations can be limited if the membrane and the photocatalytic reactor are separated in two distinct units. However, Mozia et al. [60] reported that, even in that configuration, performances of polymeric membranes were impacted. They tested these membranes for 70h and recorded a strong reduction in their separation properties that was attributed to the abrasion of the membrane surface by photocatalysts. Ceramic membranes also suffer from this abrasive effect but to a lower extent than polymeric ones since, according to Szymański et al. [61], they can be operated 400h before a significant decrease in rejection is observed.

1.6.2 Rejection performances

One criteria to assess the membrane performances is its selectivity i.e. its rejection of targeted compounds. Mathematically, membrane rejection is defined as follows:

$$\text{Rejection}[\%] = \frac{C_{feed} - C_{perm}}{C_{feed}} \cdot 100 \quad (1.14)$$

In this expression, C_{feed} is the initial feed concentration of the target species and C_{perm} is its permeate concentration.

As already discussed earlier, the primary role of the membrane module in PMR is to retain in the system the photocatalyst particles whose size can range from 5 to 100nm (TiO₂ P25: 30-50nm [30]) and, for this purpose, MF and UF membranes have been proven to be effective [46].

Ideally, these membranes should also be able to confine target pollutants, anti-cancer drugs in this case, and their degradation products in the photoreactor. As previously mentioned, UF membranes are not suited for this role [12]. Consequently, the retention of antineoplastics should be investigated with membranes exhibiting smaller pore size than UF membranes such as NF or RO membranes. Cristóvão et al. [62] studied the rejection of four anti-cancer drugs with different polymeric NF membranes and they reported rejection values up to 90-99% depending on the anti-cancer drugs. Such results indicate that the combination of photocatalytic reactor with NF membrane could be more effective for anti-cancer drugs degradation than photoreactor with UF membrane because it would increase the residence time of these drugs in the reactor. However, one obstacle to the application of this photoreactor coupled with nanofiltration is that

membranes with smaller pore size are even more sensible to abrasion than UF membranes [63]. As a result, the lifetime of a NF membrane, polymeric or ceramic, would be strongly shortened in the PMR compared to UF membrane.

1.6.3 Membrane fouling

In a recent publication, Zhang et al. [2], commenting on PMR, have introduced membrane fouling as "the main technical barrier to its commercialisation". Membrane fouling can be defined as the deposition of matter on membrane surface or within the membrane pores which alters its long-term performances and is particularly critical in the case of pressure-driven membranes. Fouling reduces the permeate flux at constant transmembrane pressure (TMP) and, conversely, it increases TMP at constant flux which results in both cases in an intensified energy consumption. The severity of fouling depends on operating conditions, type of membranes and feed composition as these three parameters influence the level of interaction between the membrane and the foulants.

In PMRs, photocatalyst particles highly contribute to membrane fouling and cause what is called inorganic fouling. Furthermore, organic matter present in natural waters can accentuate membrane fouling by adsorption on photocatalytic particles or by direct interaction with the membrane. This situation is illustrated on figure 1.9 for humic acid which represents a large majority of natural organic matter found in waters according to Szimański et al. [61]. The photocatalytic degradation of organic compounds when the UV lamps are switched on makes the cake layer less dense which mitigates the resistance to permeation caused by fouling. Inorganic ions can also add to the fouling layer by interacting with the photocatalytic particles [2].

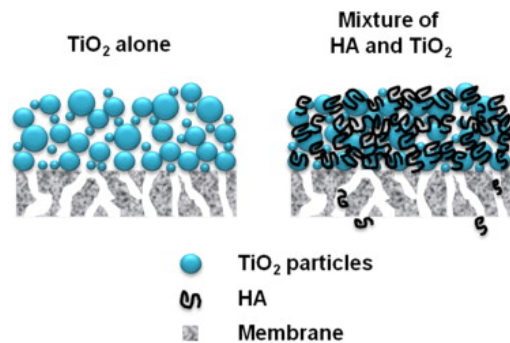


Figure 1.9: Schematic representation of membrane fouling by TiO_2 alone and by a mixture of humic acid (HA) and TiO_2 . Figure reprinted from [8].

More precisely, the mechanism of fouling in PMRs occurs in two main stages that are schematically represented on figure 1.10:

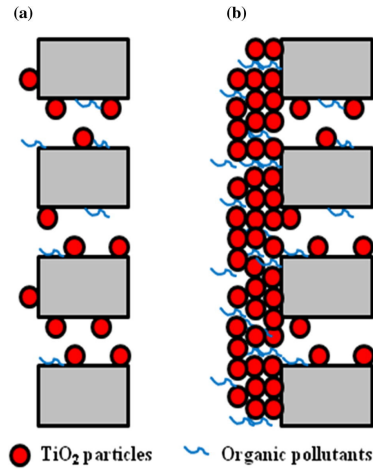


Figure 1.10: Membrane fouling mechanisms: (a) pore blocking and (b) cake layer.
Figure reprinted from [2].

- (a) Pore blocking takes place at the beginning of the fouling process when the accumulation of foulants on the membrane surface is still negligible so that photocatalyst particles and organic pollutants can penetrate and adsorb inside the membrane pores.
- (b) Cake layer is formed by the deposition of foulants layer by layer on the membrane surface. The additional resistance to permeation caused by this cake formation depends on its thickness, porosity and compressibility.

Different fouling control strategies have been developed such as aeration, backwashing, membrane modification, etc. Among all the existing techniques, one consists in operating the membrane in cross-flow filtration. As previously stated, this operation mode is effective in reducing the fouling because it can prevent the deposition of photocatalysts at the membrane surface by entraining these inorganic foulants with the flow. R. Hainaut et al. [12] studied the influence of cross-flow velocity (CFV) on the fouling of UF membranes and demonstrated that no significant fouling took place for a $CFV \geq 3\text{m/s}$. This result was confirmed by Mozia et al. [64] for similar membranes. Besides the CFV, another important parameter when talking about fouling is the transmembrane pressure (TMP) which should not be too high because a large driving force would push the foulants more strongly towards the membrane surface [2].

Cross-flow filtration is an efficient strategy to prevent the establishment of a loose cake layer, but an irreversible fouling could potentially take place after some time of operation. An effective way to remove these strongly bonded foulants is to clean the membrane using chemicals [11].

Chapter 2

Objectives

At this point of the report, the concerns raised by the increased consumption of anti-cancer drugs and their discharge in the environment have been discussed. One technology, the photocatalytic membrane reactor, has been presented as a promising solution for the removal of these drugs from wastewater, however, some limitations still need to be overcome. Notably, the detrimental effect of real waters on photocatalytic performances strongly compromises its introduction as an additional treatment in WWTP.

Given this context, the three issues addressed in the present work are the following: (i) effect of photocatalyst on anti-cancer drugs degradation, (ii) effect of water matrix on photocatalysis and (iii) economic simulation of the PMR. Based on these issues, different research questions have been established.

Effect of photocatalyst

The main objective of this master thesis is to study the performances of PMR to degrade anti-cancer drugs. In order to do so, it is first necessary to identify the optimum photocatalyst load for the investigated set-up.

- What is the photocatalyst load leading to the maximum production of hydroxyl radicals in pure water and what is the degradation rate of anti-cancer drugs at this optimised TiO_2 concentration in pure water?

Effect of water matrix

Secondly, this work aims at investigating the effects of operating the PMR with a real water matrix on the process efficiency. To meet this objective, two research questions have been identified.

- What is the effect of real waters on anti-cancer drugs kinetics of degradation?
- Which real water constituents are mainly responsible for the reduction of photocatalytic performances?

Economic simulation

Since the final selection of a treatment process mainly depends on economical factors, the third main objective of this work is to perform a preliminary cost estimation of the PMR. As the large-scale application of PMR would require a continuous mode of operation, the first step to carry out this economic analysis consists in studying the performances of PMR in continuous.

- What is the efficiency of photocatalytic degradation of pCBA in a continuous photocatalytic membrane reactor compared to a batch one?
- What is the total cost of PMR for the degradation of anti-cancer drugs in real waters? And is it interesting from an economic standpoint to combine PMR with a fine membrane as pre- or post-treatment?

Chapter 3

Materials and methods

3.1 Materials

3.1.1 Reagents: para-chlorobenzoic acid and anti-cancer drugs

The molecular probe pCBA was supplied by Sigma-Aldrich at the highest purity grade available (> 98%).

In this work, the degradation of three anti-cancer drugs was studied. These drugs, purchased from Sigma-Aldrich, are presented in the following table:

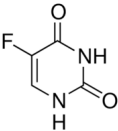
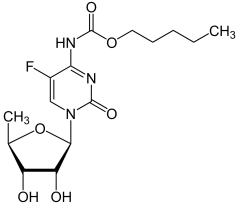
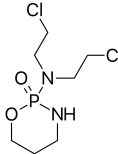
Anti-cancer drug	Abbreviation	Chemical formula	Chemical structure
5-Fluorouracil	5-FU	$C_4H_3FN_2O_2$	
Capecitabine	CAP	$C_{15}H_{22}FN_3O_6$	
Cyclophosphamide	CP	$C_7H_{15}Cl_2N_2O_2P$	

Table 3.1: Overview of the three anti-cancer drugs analysed in this master thesis.

Each of these three pharmaceutical compounds was diluted in pure water at a concentration of 1g/L and these stock solutions were stored in the dark at -20°C . For degradation experiments, each drug was spiked at 500 ppb in the reaction medium. The selected drugs concentration had to be sufficiently low to be representative of the concentrations encountered in real life but, at the same time, high enough to observe the progressive drugs degradation considering that the detection limit of the analytical equipment was 10 ppb.

3.1.2 Photocatalyst

TiO₂ Aeroxide[®] P25, purchased from Evonik Industries, was used as photocatalyst. This product consists in a mixture of 70wt.% anatase and 30wt.% rutile and is characterised by a specific surface area of approximately 50m²/g and an average particle size of 21nm.

3.1.3 Water matrices

In order to compare the efficiency of degradation, photocatalytic degradation tests were conducted in five different water matrices: laboratory grade water, secondary wastewater effluent, permeate collected after nanofiltration of secondary wastewater effluent, permeate collected after reverse osmosis of secondary wastewater effluent and pure water spiked with Cl⁻. In the following parts of this work, these five water matrices will be respectively noted LGW, WWeff, WWeff-NF, WWeff-RO and LGW-Cl⁻.

LGW was obtained from a purification water system (resistivity: 18.2M Ω at 25°C) which aims to remove ions, organics, bacteria and other particles from water.

For experiments carried out in natural waters, biologically treated wastewater was collected at the outlet of the wastewater treatment plant of Louvain-la-Neuve operated by inBW. It was stored in the dark at 4°C and used for experiments within 10 days after sampling. The composition of this water was provided by the supplier and is presented in table 3.2.

Parameters	Units	Values
Biochemical oxygen demand	mg/L O ₂	0.5
Chemical oxygen demand	mg/L O ₂	10.7
Total suspended solids	mg/L	0
Total nitrogen	mg/L N	5.42
Nitrate	mg/L NO ₃	2.97
Nitrogen	mg/L NH ₄	0.23
Total phosphorous	mg/L P	3.2
Phosphate	mg/L PO ₄	3.15
Chloride	mg/L Cl	510
pH at 20°C	-	7.1

Table 3.2: Water quality of the secondary WWTP effluent of Louvain-la-Neuve on 21st March 2018 provided by WWTP operator.

For experiments regarding water matrix effect, the objective was to successively remove specific water constituents from WWeff by selective filtration and then, carry out photocatalytic degradation tests on the resulting matrix. Therefore, WWeff was first filtered through nanofiltration membrane and then, through reverse osmosis membrane. The filtration system was an Armfield FT17 cross flow membrane filtration working at 15 bar for nanofiltration and 25 bar for reverse osmosis. NF and RO membranes were both polyamide-TFC membranes supplied by Sterlitech. Samples of WWeff and filtered WWeff were taken to analyse and compare their ionic and organic matter content. An additional water matrix consisting of pure water spiked with chloride ions was also tested.

3.2 Experimental set-up

The investigated set-up was composed of two distinctive parts: (1) the photoreactor and (2) the ultrafiltration module.

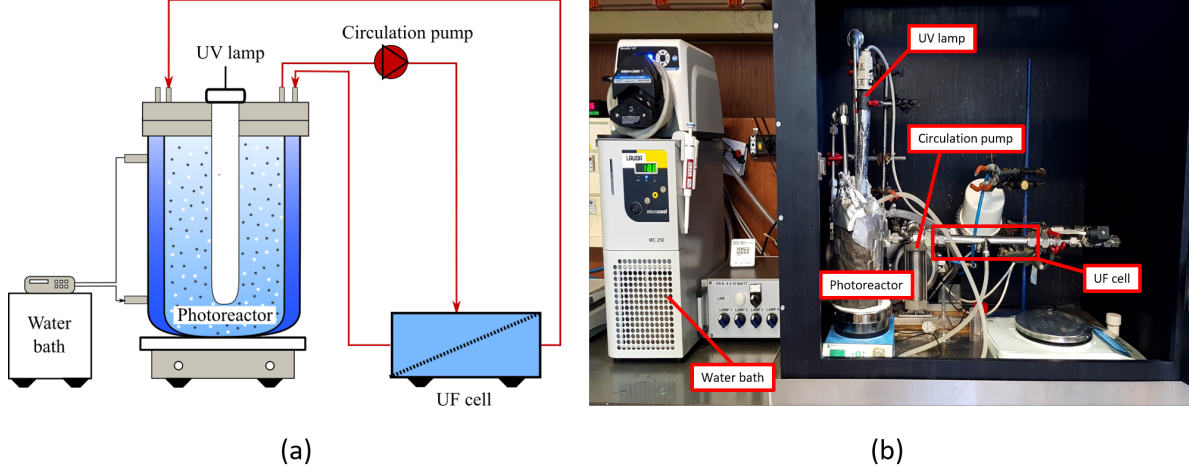


Figure 3.1: (a) Schematic diagram and (b) front view of the photocatalytic membrane reactor operated in batch. Schematic diagram modified from [9].

The photoreactor consisted in a double jacket reactor of 1L thermostated at 20°C by a cooling system (LAUDA MICROCOOL MC250). In the centre of the reactor vessel was immersed a 10W mercury low pressure UV lamp (Helios Quartz) emitting at 254nm wavelength.

In connection with the photoreactor, the ultrafiltration cell contained a ceramic tubular membrane made of $\text{Al}_2\text{O}_3/\text{ZrO}_2$. This one channel tubular membrane was 25cm long with external and internal hydraulic diameters of 10mm and 6mm respectively. It was characterised by a MWCO of 100kDa and provided an effective filtration area (A_m) of 0.0047m². TiO_2 particles retained by the membrane were sent back to the photoreactor along with the retentate. Two identical alumina membranes, supplied by Atech and denoted by their code name A172 and A194, were used for the experiments. After a certain operating time, these membranes were cleaned following a procedure described in appendix B in order to remove irreversible foulants. Two detectors were used to continuously monitor the feed cross-flow velocity (CFV) at membrane surface and the transmembrane pressure (TMP).

An air-operated diaphragm pump (OriginalTM Series metal pump, WILDEN[®] Pump & Engineering) ensured the circulation of the fluid between the photocatalytic reactor and the membrane module. This recirculation of the retentate was sufficient to ensure a homogeneous mixing inside the photoreactor. A pulse dampener was installed to absorb the pressure peaks caused by the pump.

For safety precautions against harmful UV radiations, the photocatalytic reactor was wrapped with aluminium foil and the whole set-up was placed under a box.

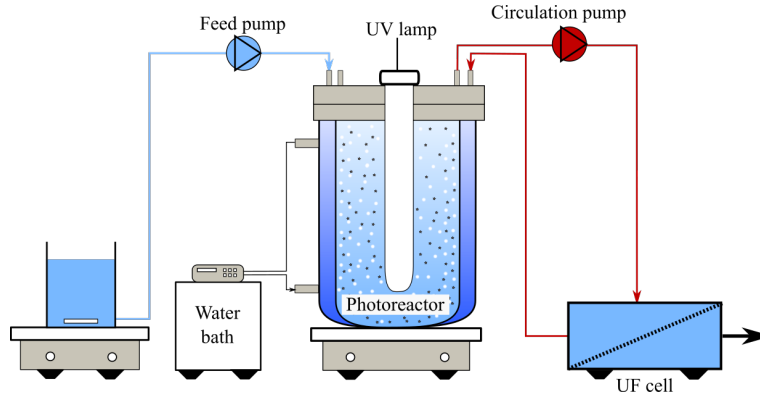


Figure 3.2: Schematic diagram of the continuous photocatalytic membrane reactor. Figure modified from [9].

Most of the experiments were performed in batch with the set-up represented on figure 3.1. In that case, no fresh solution was added during experiment and the permeate was fully recycled to the photocatalytic reactor. One test was also carried out in continuous and the modified set-up used for that experiment is represented on figure 3.2. In this operation mode, fresh solution was continuously fed to the reactor thanks to a peristaltic pump (Cole-Parmer®) while the permeate was constantly withdrawn and collected in a vessel. In this work, the first set-up will be referred to as batch PMR whereas the second one will be referred to as continuous PMR.

3.3 Experimental procedures

Prior to each experiment, the photocatalytic membrane reactor was filled with 1.6L of water selected among the five water matrices described in section 3.1.3 and the cooling system was initiated for temperature control. The TMP was fixed at 3 bar for all batch experiments and 2 bar for the continuous one and the CFV was set at 3m/s. The selection of this CFV was based on the findings of R. Hainaut et al. [12] regarding membrane fouling control strategies as discussed in section 1.6.3. A starting procedure, developed by R. Hainaut et al. [12] and detailed in appendix A, was then followed.

3.3.1 Membrane permeability

Permeability tests consist in measuring the amount of water that flows from the lumen side of the membrane to its outer shell for a defined amount of time. This amount of water measured depends on the pressure that is applied and the surface area available for filtration.

First, permeate was collected in a bucket for a specific duration. The amount of harvested water was then weighed and the volume flow of permeate through the membrane could be calculated.

$$\dot{V}_p = \frac{m_w \cdot 3600}{1000 \cdot \rho_w \cdot t_f} \quad [\text{dm}^3/\text{h}] \quad (3.1)$$

In this expression, m_w in [g] is the mass of water collected during a time $t_f = 20$ [s], $\rho_w = 1$ [kg/L] is the water density and the two numerical constants are present for units conversion.

Knowing the volumetric flow rate through the membrane, the permeate flux could be determined with the following equation:

$$J_m = \frac{\dot{V}_p}{A_m} \quad [\text{dm}^3/\text{m}^2/\text{h}] \quad (3.2)$$

where A_m is the effective surface area of the membrane.

Finally, the permeate flux divided by the TMP gave the permeability of the membrane.

$$P_m = \frac{J_m}{\text{TMP}} \quad [\text{dm}^3/\text{m}^2/\text{h}/\text{bar}] \quad (3.3)$$

Permeability measurements were first taken in the batch PMR filled with LGW only, to characterise the two alumina membranes before photocatalytic degradation tests. Then, measurements of the membrane permeability were regularly taken during photocatalytic degradation experiments to ensure that it remained constant throughout an experimental test. A decrease in permeability indicated that the membrane was fouled and needed cleaning.

3.3.2 Photocatalytic degradation experiments

3.3.2.1 In batch

After the starting procedure and prior to irradiation, 5 μ M of pCBA or 500 ppb of drugs were added in the photoreactor along with the desired concentration of photocatalyst. The solution was then mixed in the dark for 20 min to reach the adsorption equilibrium between targeted pollutants

and photocatalyst particles. Some tests were also performed in the absence of photocatalyst to look at the effects of UV radiations alone on the degradation of pollutants and, in that case, the 20 min delay was not necessary. After this adsorption step, 15mL of solution were withdrawn directly from the reactor vessel and placed in the dark to check that no degradation would occur in the absence of light. Once the UV lamp was switched on, photodegradation batch experiment started for a duration of 60 min. Periodically, samples of 1mL were taken from the permeate to be analysed later. Control samples were taken from the solution in the dark at 30 and 60 min of experiment with a syringe filter to retain the TiO_2 particles.

From these batch experiments, the objective was to derive the degradation rate constant k and this was done by using the batch reactor equation:

$$\ln \left(\frac{C}{C_0} \right) = -kt \quad (3.4)$$

After analysis of the samples, the graph $\ln(C/C_0)$ versus time was plotted and, on this graph, k corresponded to the slope of the linear regression.

3.3.2.2 In continuous

For the degradation test in continuous, the procedure was similar except that an additional volume of 1.6L of water spiked with $5\mu\text{M}$ of pCBA was prepared to constitute the feed tank. The pump flow rate was set to feed the photoreactor at the same rate as the permeate flux in order to maintain a constant volume of solution in the reactor.

Photocatalytic experiments performed in this work are presented in table 3.3 with their respective features.

Water matrix	Operation mode	$[\text{TiO}_2]$ (g/L)	Reagents	Membrane
LGW	Batch	0	pCBA	Al94
	Batch	0.1	pCBA	Al94
	Batch	0.5	pCBA	Al94
	Batch	1.5	pCBA	Al94
	Batch	2	pCBA	Al94
	Batch	3	pCBA	Al94
	Batch	0	Anti-cancer drugs	Al72
	Batch	1.5	Anti-cancer drugs	Al72
	Continuous	0.5	pCBA	Al94
	Continuous	1.5	pCBA	Al94
WWeff	Batch	1.5	pCBA	Al94
	Batch	1.5	Anti-cancer drugs	Al72
WWeff-NF	Batch	1.5	pCBA	Al94
WWeff-RO	Batch	1.5	pCBA	Al94
LGW- Cl^-	Batch	1.5	pCBA	Al94

Table 3.3: Summary of photocatalytic degradation experiments and their characteristics.

3.4 Economic simulation

The development of new technologies requires to evaluate the economic impact at each step of the development from lab-scale to industrial scale in order to identify the solutions that are more economically viable.

As already discussed in section 1.2, different combinations of AOPs and membrane modules can be considered. Photocatalytic membrane reactor itself constitutes already a hybrid process coupling photocatalysis with a membrane. An additional filtration cell able to reject efficiently anti-cancer drugs can be included to the PMR in order to improve its performances. This added membrane can serve as a pretreatment step in order to concentrate the antineoplastic compounds in the retentate and then, treat this retentate with the PMR. Filtration cell can also be added as a post-treatment and, in that case, the retentate is continuously sent back to the PMR. In this economic analysis, the costs of five different set-ups were evaluated:

- PMR alone as represented on figure 3.2.
- NF membrane as pretreatment followed by PMR (figure 3.3a).
- RO membrane as pretreatment followed by PMR (figure 3.3a).
- NF membrane as post-treatment preceded by PMR (figure 3.3b).
- RO membrane as post-treatment preceded by PMR (figure 3.3b).

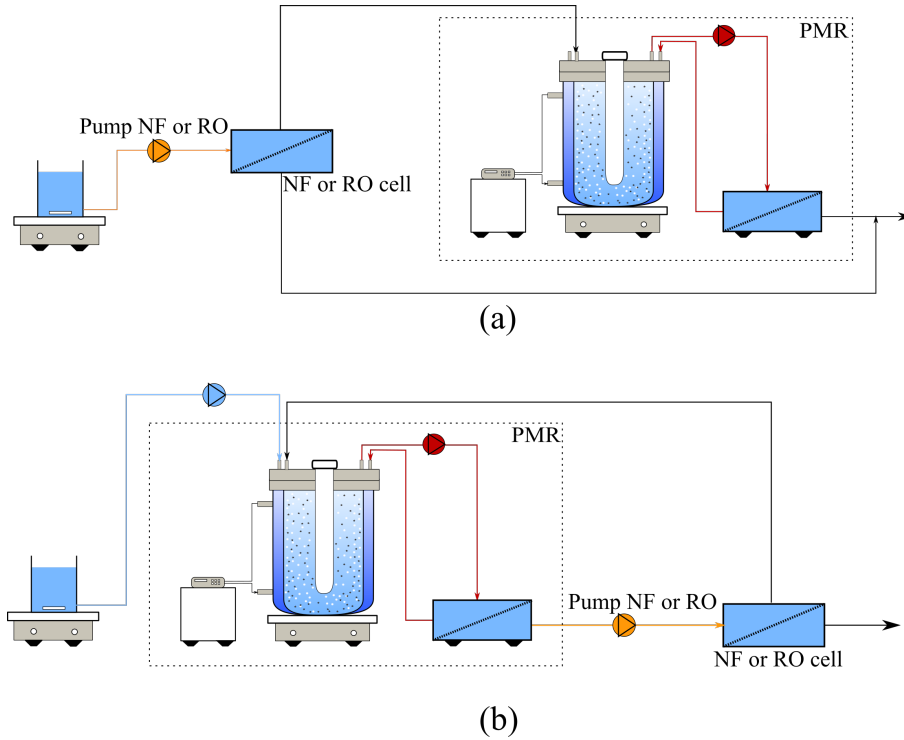


Figure 3.3: Schematic diagrams of the PMR coupled with NF or RO membrane as (a) pretreatment and (b) post-treatment. Figure modified from [9].

Before analysing the economy of a process, it is convenient to define some relevant boundaries for this analysis in order to restrict the number of elements considered. In this case, labour costs, maintenance costs, transport costs and capital expenses were excluded from the economic evaluation. Consequently, this analysis was simplified to consider only the operating expenses including photocatalyst cost, lamp replacement and energy consumption, membranes replacement and pump energy consumption.

In order to compare the operating costs of the five investigated configurations, it was necessary to define a unit of comparison. Therefore, the treatment of 1L of polluted WWeff was assumed and the concentration of anti-cancer drugs had to be decreased by one order of magnitude between the inlet and the outlet of the whole system which led to a comparison unit in €/L/order. With these hypotheses, the time to treat 1L of polluted waters was calculated for each configuration assuming that equation 1.13 could effectively predict the outlet conversion of a continuous PMR. This assumption was verified experimentally.

For the PMR on its own, the application of equation 1.13 to determine the treatment time was straight-forward. First, the mean residence time τ was calculated with equation 3.5 considering that the ratio $C_0/\langle C_{out} \rangle$ was equal to 10. In this expression, the rate constant k for anti-cancer drugs degradation was derived from batch experiments. Then, knowing the mean residence time and the reactor volume (1.6L), the feed flow rate Q was determined.

$$\tau = \frac{V}{Q} = \frac{1}{k} \left(\frac{C_0}{\langle C_{out} \rangle} - 1 \right) \quad (3.5)$$

Finally, the time necessary to treat 1L was calculated by dividing this 1L volume by the feed flow rate.

For the PMR combined with a pre- or post-treatment, the approach was quite similar except that two other parameters, i.e. rejection and recovery ratio of NF or RO cell, were introduced in the mass balance to characterise the performances of the additional membrane. Thus, knowing the inlet concentration (500 ppb) and desired outlet concentration (50 ppb) of the whole treatment process, the inlet and outlet concentrations of the PMR were deduced from the mass balance. The mean residence time in the PMR was then calculated with equation 3.5 and the feed flow rate of the whole process was determined.

The concept of membrane rejection and its mathematical definition were already presented in section 1.6.2. In this analysis, the selection of rejection percentage for nanofiltration was based on the work of Cristóvão et al. [62]. These researchers studied the rejection of two anti-cancer drugs, cyclophosphamide and ifosfamide, with nanofiltration membranes and the lowest rejection value they found was 89%. For reverse osmosis, a rejection of 95% was chosen on the basis of experiments realised by A. Leyssens et al. [65]. Regarding the recovery ratio of membranes, it represents the fraction of the membrane feed that constitutes the permeate while the rest forms the retentate. Mathematically, it is defined as follows:

$$\text{Recovery ratio}[\%] = \frac{Q_{perm}}{Q_{feed}} \cdot 100 \quad (3.6)$$

where Q_{perm} and Q_{feed} represent respectively the permeate and membrane feed flow rate. According to Mendret et al. [66], this ratio is usually comprised in the range 50-85%, therefore,

a recovery ratio of 80% was chosen for both NF and RO membranes. This value was selected in the upper part of the range 50-85% assuming that a higher recovery rate would limit the volume of water going through the PMR and reduce the costs.

Once the time of treatment was determined, the cost of each item considered in this economic analysis was estimated in €/L/order, taking into account that these items were only operated for a time corresponding to the treatment time. To take this aspect into account, the cost of each element was divided by its lifetime and multiplied by the process treatment time. Finally, the total cost of each treatment process was obtained by summing the contribution of each element. All the data necessary to carry out this economic evaluation are reported in table 3.4. For this analysis, price fluctuations were neglected so that all the costs were assumed to be fixed.

Item	Data	Source
Photocatalyst		
Cost	0.13€/g	Alibaba group
Lifetime	60h	[67]
Ceramic UF membrane		
Cost	3900€/m ²	TAMI Industries
Lifetime	400h	[61]
Polymeric NF membrane		
Cost	3022.5€/m ²	[68]
Lifetime	8760h	[69]
Polymeric RO membrane		
Cost	2586.5€/m ²	[68]
Lifetime	8760h	[69]
Lamp		
Cost	67€	Helios Quartz
Lifetime	8000h	Helios Quartz
Energy	10W	Helios Quartz
Energy		
Cost	0.27€/kWh	[70]

Table 3.4: Data collection for the economic analysis.

From this table, it can be noticed that the cost of each membrane is expressed in €/m² which means that the filtration area A_m necessary to obtain a given permeate flow rate Q_{perm} had to be calculated in order to determine the cost of membranes.

$$A_m = \frac{Q_{perm}}{P_m \cdot \text{TMP}} \quad (3.7)$$

The permeability P_m of UF membrane was 300 dm³/m²/h/bar and the TMP selected for calculations was 3 bar. For NF and RO membranes, their permeabilities were respectively 3.1 dm³/m²/h/bar and 1.3 dm³/m²/h/bar (data provided by Sterlitech Corporation [71]) and the selected TMPs were 15 and 30 bar.

Regarding UF and NF/RO pumps, their energy consumption was calculated with the following equation:

$$P = \frac{Q \cdot p}{3.6 \cdot 10^6} \quad [\text{kW}] \quad (3.8)$$

In this expression, P is the hydraulic power, p is the differential pressure in [Pa] and Q is the flow rate in [m³/h]. The feed pump that appears in configurations where the PMR stands alone and where it is combined with a post-treatment was not considered in this analysis given that its energy consumption is negligible compared to the other pumps.

3.5 Analytical methods

3.5.1 UPLC-MS

The concentration of anti-cancer drugs in samples was quantified with an ultra performance liquid chromatography coupled with a mass spectrometer (UPLC-MS). The apparatus used for analyses was an Agilent 6100 series single quadrupole LC/MS system.

First, 5 μ L of sample were extracted from the vial and injected in the HSS5 elution column along with the mobile phase at a pressure of 500 bar. Column temperature was maintained at 30°C and liquid flow rate was set at 0.25mL/min. The mobile phase consisted in a mixture of two solvents whose relative proportion in this mobile phase varied with time. The first solvent was pure acetonitrile (CH₃CN) while the second one was an aqueous solution with 5vol% CH₃CN. The three anti-cancer drugs studied were separated based on their relative affinity with the mobile phase and the stationary phase contained in the elution column and this led to different retention time in this column. Then, the role of the mass spectrometer was to detect and quantify each drug individually according to their mass-to-charge ratio.

3.5.2 HPLC-UV

High performance liquid chromatography equipped with a UV detector (HPLC-UV) was used to detect and quantify the concentration of pCBA in samples. These analyses were carried out on an Agilent 1200 Series HPLC with a diode array detector and the elution column was a Zorbax Eclipse XDB-C8 (4.6 x 150mm, 3.5 μ m) provided by Agilent Technologies.

To measure pCBA concentrations, 50 μ L of sample were extracted and injected in the mobile phase which consisted in a mixture of 80% methanol (95/5vol% MeOH/H₂O) and 20% NaH₂PO₄ 25mM (pH = 2.5). This mobile phase containing the sample to analyse was pushed through the column at a flow rate of 0.6mL/min and with an injection pressure of 90 bar. The column was maintained at 30°C during analyses. Detection of pCBA was performed with a UV absorbance detector set at a wavelength of 240.8nm.

3.5.3 COD Cell Test

Chemical oxygen demand (COD) provides an indirect measure of the organic matter content in water as it represents the amount of oxygen needed to oxidise particulate and dissolved organics present in water.

The COD of sample was determined based on a photometric method using the Spectroquant® COD Cell Test (Merck) with a detection limit of 4-40mg/L. First, 3mL of sample were added in the cell containing a solution of sulfuric acid with potassium dichromate K₂Cr₂O₇. The latter is a strong oxidising agent that is used to react with organic matter and is converted into Cr₂O₇²⁻ upon oxidation. The cell was then heated for 2h at 148°C to favour the oxidation of organics. After cooling down to room temperature, the COD of the sample was measured in a spectrophotometer which allowed to determine the concentration of Cr₂O₇²⁻ in the cell and to

convert this quantity into oxygen equivalent to finally provide the COD value in mg/L.

3.5.4 Ionic analysis

The anionic content in natural waters was quantified by ion exchange chromatography with the Ion Chromatography System Dionex ICS-2000. The anions were separated in an AS15 column according to their relative affinity with the mobile phase and the stationary phase. The mobile phase consisted of a solution of KOH 20-38mM. After separation, the quantification of the different anions was carried out by a conductometer. This technique was able to quantify the following anions: F^- , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , NO_2^- .

For bicarbonate ions, a titration method was used. The results of this analysis provided the total alkalinity of the sample which represents the water content in CO_3^{2-} , HCO_3^- and OH^- . To perform this titration, a sample of 100 mL of WWeff was collected and stored in a sealed container. Ideally, the sample had to be analysed in the 24h after water collection. For the titration itself, HCl 0.05M was progressively added in the sample and the pH was continuously monitored. First, acid was added up to pH 4.5, and the added volume V_1 was recorded. Then, more acid was added to reach pH 4.2 and the second volume V_2 was noted. Based on these two volumes, the total alkalinity was calculated in equivalent volume per litre. This equivalent volume represents the volume of acid to add in order to neutralise the water alkalinity.

$$V_0 = (2V_1 - V_2) \cdot 0.05 \cdot 10 \quad [\text{meq/L}] \quad (3.9)$$

At pH close to 7, as it is the case for WWeff, the alkalinity is mainly due to HCO_3^- so its concentration could be deduced from the equivalent volume V_0 .

Regarding cations, their concentration was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with the ICAP 6500 (Thermo Scientific). This method is based on the excitation of cations with a plasma which causes the emission of electromagnetic radiations at wavelength specific of an element. The following cations could be detected with this method: Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Si^{4+} .

3.5.5 Optical microscopy

Agglomeration of photocatalytic particles in different water matrices was investigated using the optical microscope Olympus Provis AX70. A droplet of TiO_2 solution was placed between two microscope slides of glass and was then examined under the microscope with a power magnifying lens of 10X.

Chapter 4

Results and discussion

4.1 Membrane permeability

The goals of these permeability tests in LGW were to characterise the two alumina membranes in terms of their permeability and to check that a CFV of 3m/s was sufficient to avoid inorganic fouling. LGW permeabilities obtained for the two membranes are presented on figure 4.1.

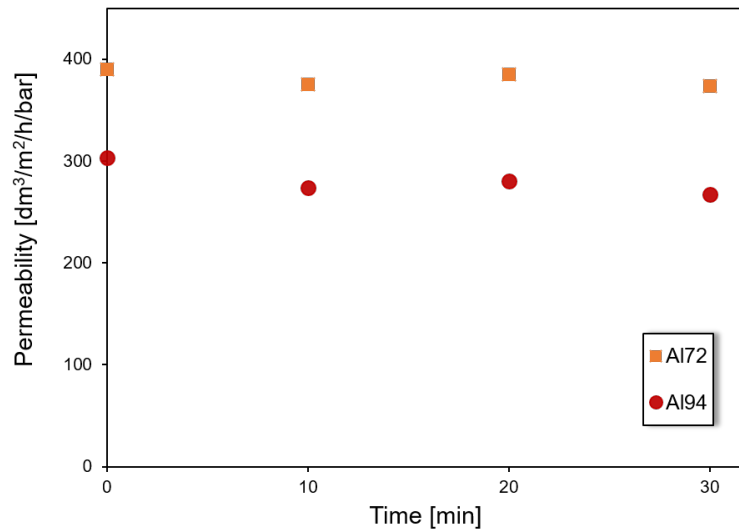


Figure 4.1: Variation of permeability with time for two alumina UF membranes (TMP: 3 bar, CFV: 3m/s).

Figure 4.1 shows that the permeability of both membranes remained constant with time which indicates that no fouling took place. It can also be noted that these two membranes, while being identical, exhibited different permeabilities. This is due to the fact that permeability depends on pore structure and this feature is difficult to control precisely during conventional manufacturing of membranes [72]. The value of permeability provided by the manufacturer for these two membranes was $300 \text{ dm}^3/\text{m}^2/\text{h}/\text{bar}$.

4.2 Effect of photocatalyst

4.2.1 Photocatalyst load optimisation

Before investigating the photocatalytic degradation of anti-cancer drugs, it is necessary to identify the optimum photocatalyst load at which these experiments should be carried out. For this reason, 1 hour degradation tests at different photocatalyst concentrations were performed in LGW with the hydroxyl radical probe pCBA. From these batch experiments, the rate constant for each set of data was derived with high correlation ($R^2 > 0.97$) and the fitting curves can be found in appendix C. The resulting k values are presented on figure 4.2. Analysis of dark controls confirmed that no degradation of pCBA occurred in the absence of light.

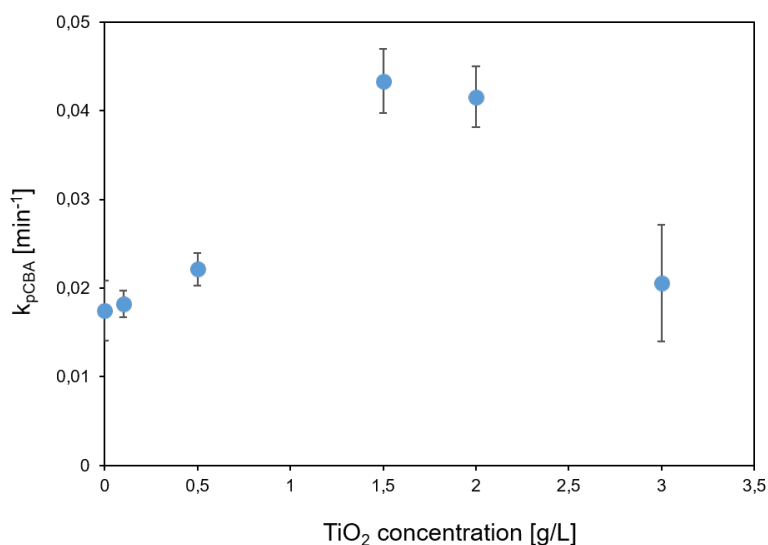


Figure 4.2: Dependence of degradation kinetic constant with TiO₂ concentration.

From the diagram above, it can be observed that the rate constant first increased with the photocatalyst load between 0 and 1.5 g/L, reached a maximum at 1.5 g/L and eventually dropped at a TiO₂ concentration of 3 g/L. This observed trend is consistent with the literature [37][4].

As already mentioned in the first chapter, this increase at low photocatalyst load is due to the larger surface area available to produce potent radicals. However, an excessive amount of suspended photocatalysts promotes the agglomeration of catalysts and obstructs the penetration of UV radiations which limits the activation of TiO₂ particles [46][47]. The trend represented on figure 4.2 indicates that, above 1.5 g/L, the negative effects of increasing the catalyst load, i.e. solution turbidity and particle agglomeration, dominated over the positive one.

Consequently, these results show that the optimum TiO₂ concentration to operate the PMR is 1.5g/L. Several authors found a similar optimum for their set-up using the same photocatalyst (TiO₂ P25) [61][73].

4.2.2 Photocatalytic degradation of anti-cancer drugs

After identification of the optimum TiO_2 loading, tests were performed with anti-cancer drugs in the presence and absence of photocatalyst to look at the effect of TiO_2 on the degradation rate. The resulting degradation profiles can be observed on figures 4.3a and 4.3b. Analysis of dark controls showed no degradation of anti-cancer drugs in the dark.

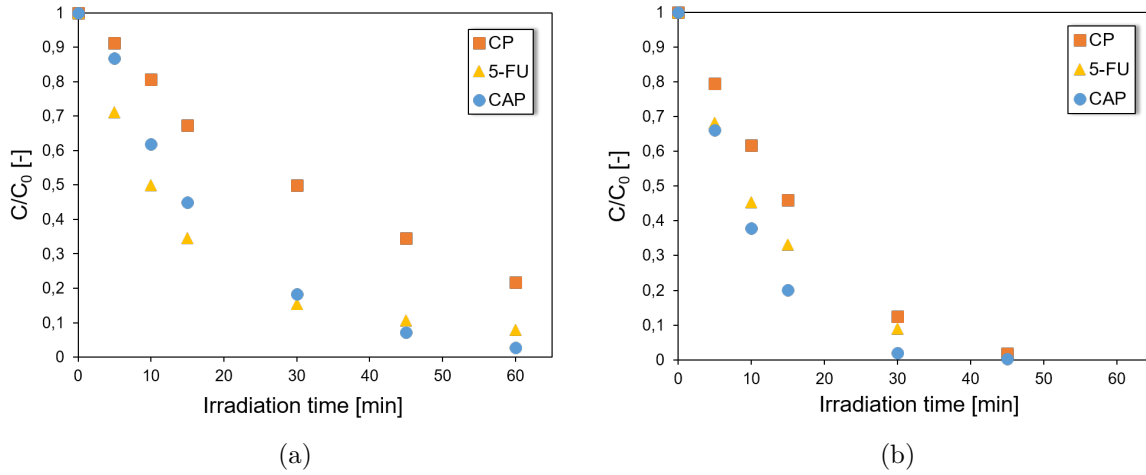


Figure 4.3: Photocatalytic removal of three anti-cancer drugs as a function of time in LGW: (a) without photocatalyst and (b) with photocatalyst at $[\text{TiO}_2] = 1.5 \text{ g/L}$.

The degradation rate constant of each drug was derived for these two batch experiments with a good correlation ($R^2 > 0.95$) as evidenced by the fitting curves in appendix C. The results, displayed on figure 4.4, show that higher degradation rates were obtained when TiO_2 was added in the reactor.

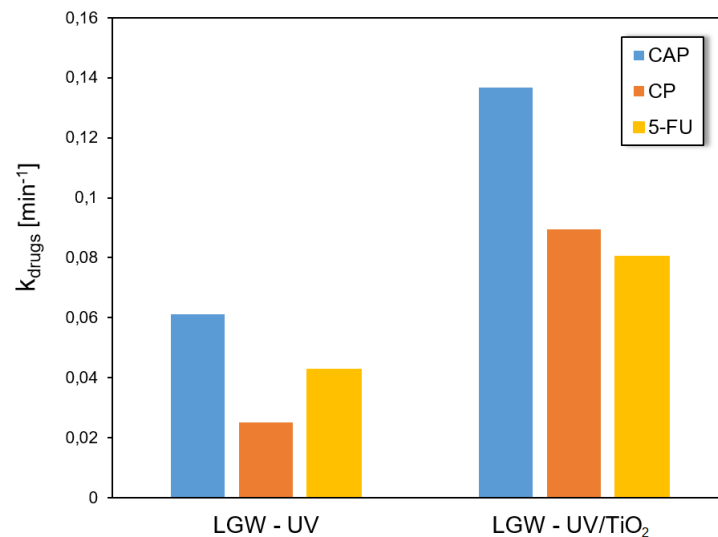


Figure 4.4: Degradation rate constants of the three studied anti-cancer drugs in LGW without photocatalyst (LGW-UV) and with photocatalyst (LGW-UV/ TiO_2).

Looking at k values obtained when the drugs were subjected to UV radiations only, it appears that direct photolysis was able to degrade CAP, 5-FU and CP with respective degradation rates of 0.06min^{-1} , 0.043min^{-1} and 0.025min^{-1} . This indicates that CAP has a higher probability to degrade upon UV light absorption. According to Franquet-Griell et al. [14], chemicals containing aromatic moieties or double bonds in their structure tend to decompose more easily under irradiation. From the chemical structure of the three investigated drugs depicted in table 3.1, it appears more clearly why CAP is a better candidate for photolysis than 5-FU and CP.

Moreover, the addition of photocatalyst led to an increase in the removal rates of CAP (+125%), CP (+260%) and 5-FU (+90%). With the addition of photocatalyst, two mechanisms can contribute to the degradation of pollutants: photolysis and photocatalysis. Unlike direct photolysis, the oxidation of pollutants by reactive radicals is a non-selective process which does not depend on the chemical structure of the drugs [14].

4.3 Effect of water matrix

4.3.1 Photocatalytic degradation in real waters

In order to investigate the effect of real waters on kinetics of degradation, tests were performed in secondary wastewater effluent. In parallel, analyses were carried out on this WWeff to characterise precisely its composition and the results are displayed in table 4.2. Anions detected at a concentration below 1mg/L are not reported in this table. For cations, only the Ca^{2+} concentration is indicated since it is recognised among scientists that the other cations do not affect significantly the photocatalytic processes [74].

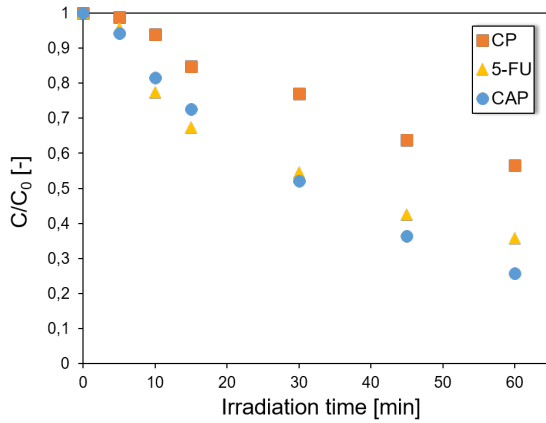


Figure 4.6: Photocatalytic removal of three anti-cancer drugs as a function of time in WWeff ($[\text{TiO}_2] = 1.5\text{g/L}$).

Parameters	Units	Values
COD	mg/L O_2	8.1
SO_4^{2-}	mg/L	63.4
NO_3^-	mg/L	2.1
PO_4^{3-}	mg/L	2.6
Cl^-	mg/L	444
HCO_3^-	mg/L	265
Ca^{2+}	mg/L	101
pH at 20°C	-	7.5

Table 4.2: Results of the WWeff analysis.

The resulting degradation profiles are compared to the ones obtained in LGW and visible on figure 4.3b. From this comparison, it appears that the performances of PMR towards anti-cancer drugs degradation were significantly reduced in WWeff. Figure 4.6 reveals that, after 60 min of experiment, the three investigated drugs were still detected in the medium at concentrations ranging from 25% to 56% of their initial concentration while a complete elimination was observed after 45 min in LGW (figure 4.3b). The rate constant in WWeff was determined for each anti-cancer drug studied ($R^2 > 0.97$) and these k values are displayed on figure 4.7 along with the ones calculated previously in LGW.

From this figure, it can be observed that the rate constants in WWeff of the three anti-cancer drugs were reduced by more than 75% of their value in LGW ($k_{\text{WWeff,CP}} = 0.01\text{min}^{-1}$, $k_{\text{WWeff,CAP}} = 0.023\text{min}^{-1}$ and $k_{\text{WWeff,5-FU}} = 0.017\text{min}^{-1}$). Different explanations, related to the presence of organic matter and ions, have been advanced in the literature review to justify this decrease in efficiency and four main routes by which real water species can deactivate photocatalysis have been identified: (i) promoting the agglomeration of photocatalytic particles, (ii) scavenging hydroxyl radicals, (iii) blocking the access to photocatalytic active sites and (iv) competing for absorption of UV photons. Although it is recognised that pH can also affect photocatalysis, in this case, its involvement in the reduction of efficiency can be safely neglected

since the pH of WWeff (table 4.2) was very close to the pH of LGW (neutral pH).

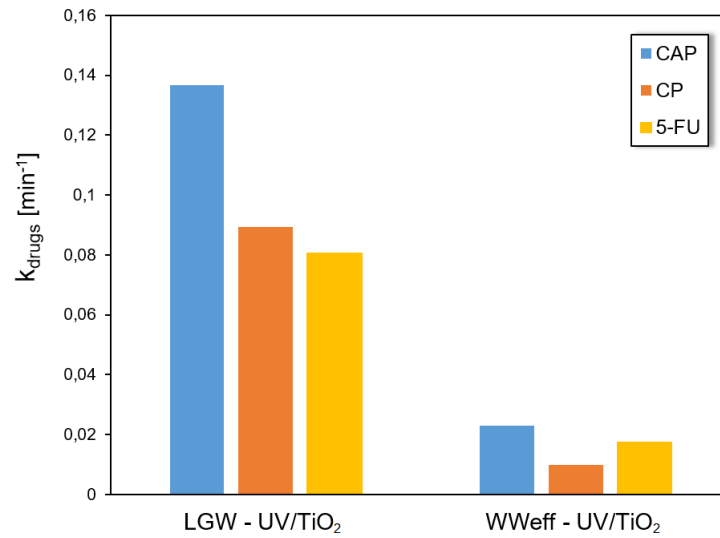


Figure 4.7: Degradation rate constants of the three studied anti-cancer drugs with $[\text{TiO}_2] = 1.5$ g/L in LGW and WWeff.

The enhanced agglomeration in the WWeff matrix used for experiments can be easily verified by observing TiO_2 particles under an optical microscope. The obtained pictures are presented below.

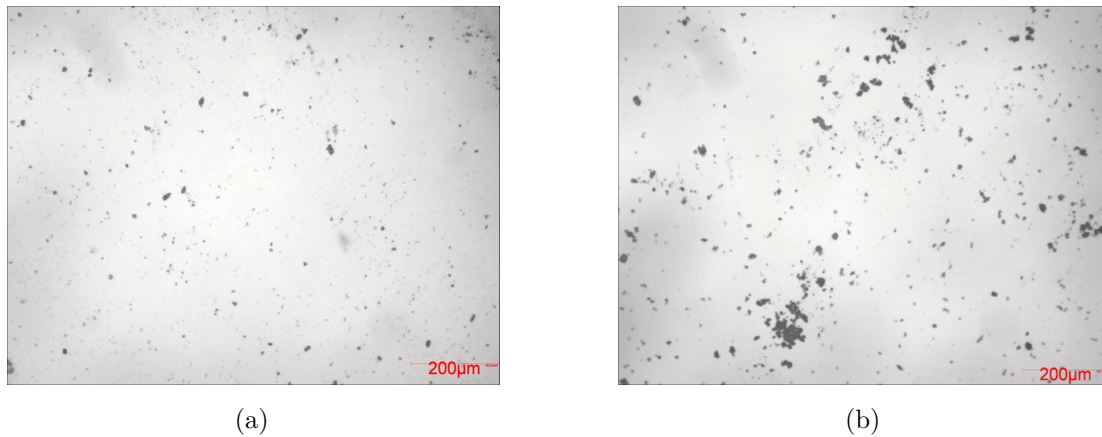


Figure 4.8: Optical microscope image of TiO_2 photocatalyst at a concentration of 1.5g/L dispersed in (a) LGW and (b) WWeff.

This agglomeration affects photocatalysis by decreasing the total catalytic surface area irradiated, which limits the production of radicals and, correlatively, the degradation of pollutants. Stability of the TiO_2 suspension is strongly influenced by the ionic strength of the solution since ions present in the medium determine the electrical double layer surrounding each particle and so the extent of electrostatic repulsion. Some specific ions have been reported to favour the aggregation of particles more than others. For example, Ottofuelling et al. [57] noted that the

formation of large aggregates was promoted in solutions containing Ca^{2+} at concentrations larger than 10 mg/L. These researchers also pointed out the role of SO_4^{2-} as a strong promoter of particle agglomeration even at concentrations down to 1 mg/L. Looking at the WWeff composition in table 4.2, it is likely that the significant concentrations of calcium and sulphate ions caused the agglomeration observed on figure 4.8b and that this effect dominated over the stabilising effect of NOM by steric repulsion. This is supported by Tiller et al. [54] who suggested that electrostatic effects govern the colloidal stability in natural waters.

Besides calcium and sulphate ions, other water species, among the ones identified in table 4.2, could also be involved in the deactivation of photocatalysis through other mechanisms than agglomeration. In order to get a better understanding of the effects of this WWeff matrix on photocatalysis, a series of experiments involving successive filtration and photocatalytic degradation tests with pCBA was implemented. Prior to filtration, one degradation experiment was carried out with pCBA and 1.5g/L TiO_2 in WWeff to enable the comparison with the other water matrices.

4.3.2 Photocatalytic degradation in filtered waters

First, WWeff was nanofiltered and the composition of this new water matrix was analysed (table 4.3). Then, a pCBA degradation test was carried out with photocatalyst spiked at the level of 1.5g/L in this WWeff-NF and the rate constant was calculated. Several authors reported that NF membranes were efficient in eliminating NOM from wastewater and it can be noticed in table 4.3 that, indeed, the organic matter content was decreased below the limit of detection of the COD Cell Test [75][76]. In these conditions, the objective of the degradation test in WWeff-NF was to check if, by removing organic matter, the photocatalytic performances would be improved with respect to the WWeff matrix.

Species	WWeff	WWeff-NF		WWeff-RO	
	C [mg/L]	C [mg/L]	Rejection [%]	C [mg/L]	Rejection [%]
COD	8.1	<4	-	<4	-
SO_4^{2-}	63.4	34	46	10.6	83
NO_3^-	2.1	1.6	24	0.4	81
PO_4^{3-}	2.6	1.8	31	n.d.	-
Cl^-	444	227	49	93	79
HCO_3^-	265	132-200 ¹	-	31-55 ²	-
Ca^{2+}	101	50-75 ¹	-	12	88

¹ Concentration range estimated based on the rejection percentages obtained for nanofiltration.

² Concentration range estimated based on the rejection percentages obtained for reverse osmosis.

Table 4.3: Composition of three water matrices: WWeff, WWeff-NF and WWeff-RO with the corresponding rejection percentages for filtered waters (n.d.: not detected).

As already discussed, organic matter can affect photocatalytic processes at different levels. It is involved in the process of stabilisation of the TiO_2 suspension thanks to the steric repulsion

between adsorbed organic molecules [53]. It can adsorb at the catalytic surface and block the access to active sites. Also, organic molecules are known to absorb UV radiations limiting the activation of TiO_2 particles and to act as scavengers of free radicals [5].

The results of the photocatalytic degradation tests can be observed on figure 4.9 and it appears that the k values in WWeff and in WWeff-NF were not significantly different ($k_{\text{WWeff,pCBA}} = 0.003\text{min}^{-1}$ and $k_{\text{WWeff-NF,pCBA}} = 0.0024\text{min}^{-1}$). This indicates that organic matter, at the concentration at which it was found in WWeff (table 4.3), had no deleterious effect on photocatalysis. Research carried out by Ye et al. [3] supports this conclusion that below a given concentration of NOM, photocatalysis is not affected. However, they obtained this result for a NOM concentration lower than 5 mg/L while, for a concentration of 10 mg/L which is closer to the concentration measured in WWeff (table 4.3), they observed non-negligible effects on the photodegradation. An explanation could be that the concentration they reported in their article is the exact NOM concentration they added in water while, in this work, the organic matter load was measured based on the COD. This measure of organic matter content tends to slightly overestimate the real NOM concentration since it takes into account any oxidisable compounds present in the water [77].

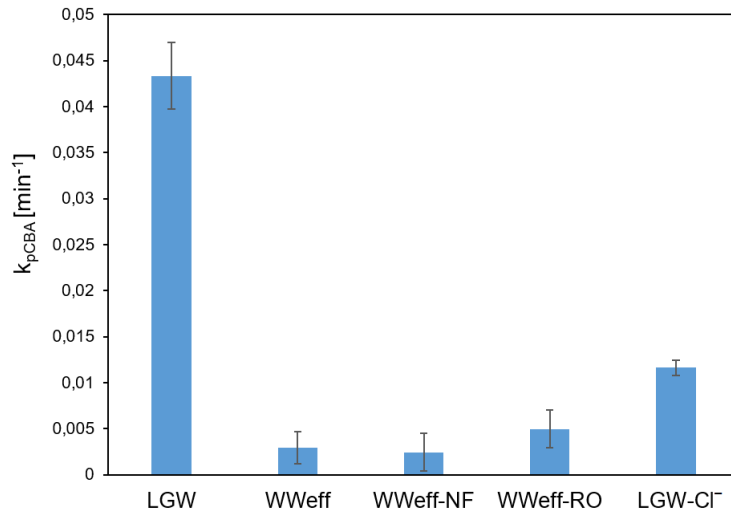


Figure 4.9: Degradation rate constants of pCBA in different water matrices with $[\text{TiO}_2] = 1.5$ g/L.

Given that the removal of organic matter did not improve the efficiency of the process, it can be assumed that ions are the source of the decrease in photocatalytic performances in WWeff. To verify this hypothesis, WWeff was filtered by reverse osmosis and a procedure similar to the one previously described for nanofiltration was followed. The objective was to significantly reduce or even eliminate some ions present in WWeff in an attempt to recover the same degradation rate as the one observed in LGW. Actually, it can be observed in table 4.3 that nanofiltration already reduced the concentration of most ions by $\sim 25 - 50\%$ but this reduction did not improve the performances.

It can be noticed on figure 4.9 that the rate constant calculated in WWeff-RO ($k_{\text{WWeff-RO,pCBA}} = 0.005\text{min}^{-1}$) is still much smaller than the one in LGW but slightly higher than the ones in WWeff and in WWeff-NF. This small increase in degradation rate could be attributed to the decrease in concentration of the detected ions by 80-90% (table 4.3).

From the composition of WWeff-RO given in table 4.3, it appears that two species were still present in the medium at relatively high concentrations: bicarbonate and chloride anions. HCO_3^- is known to be a strong scavenger of hydroxyl radicals which is their main deactivating effect. It was reported in the literature that bicarbonate ions could already impact photocatalysis at concentrations of 50mg/L and that the degradation rate decreased more and more at higher concentrations [56]. Therefore, it can be assumed that, at the level of 265mg/L in WWeff (table 4.3), these ions strongly reduced the photocatalytic efficiency.

Regarding chloride ions, these species can also scavenge $\text{OH}^\bullet$ and adsorb on TiO_2 surface which reduces the available active sites. Unlike sulphate and calcium ions, they have never been reported to interfere in the stabilisation of the catalyst suspension. Even though this anion was predominant in the solution, several authors suggested that its inhibitory effect was small compared to bicarbonate ions [5][56]. A pCBA degradation test was thus carried out in laboratory grade water spiked with 500 mg/L of Cl^- in order to check the contribution of chloride ions to the deactivation of photocatalysis in WWeff. This concentration of chloride ions was selected based on the analyses performed on WWeff (table 4.3) and on the information provided by the operator of the WWTP (table 3.2). Looking at the rate constant obtained in those conditions on figure 4.9, it is confirmed that chloride ions also had non-negligible deleterious effects on the photocatalytic process. Also, these effects were not related to particle agglomeration as evidenced by figure 4.10b and as expected from the literature. Rioja et al. [5] studied the variation of photocatalytic degradation rate with Cl^- concentration and they obtained a U-shape curve indicating that a high concentration of chloride anions is more preferable than an intermediate concentration. Particularly, they demonstrated that degradation tests performed in highly saline waters (30g/L of NaCl) exhibited similar performances as in LGW. This observation was attributed to the compression of the double layer at high ionic strength which facilitated the approach of pollutants close to the photocatalyst surface.

Finally, it could be interesting to check if photocatalytic particles also aggregated in WWeff-RO due to the influence of sulphate and calcium ions. Comparing figure 4.10a and figure 4.8a, it seems that, even though the concentrations of these two species were reduced by more than 80%, they could still affect the stability of the photocatalyst suspension by causing agglomeration of particles.

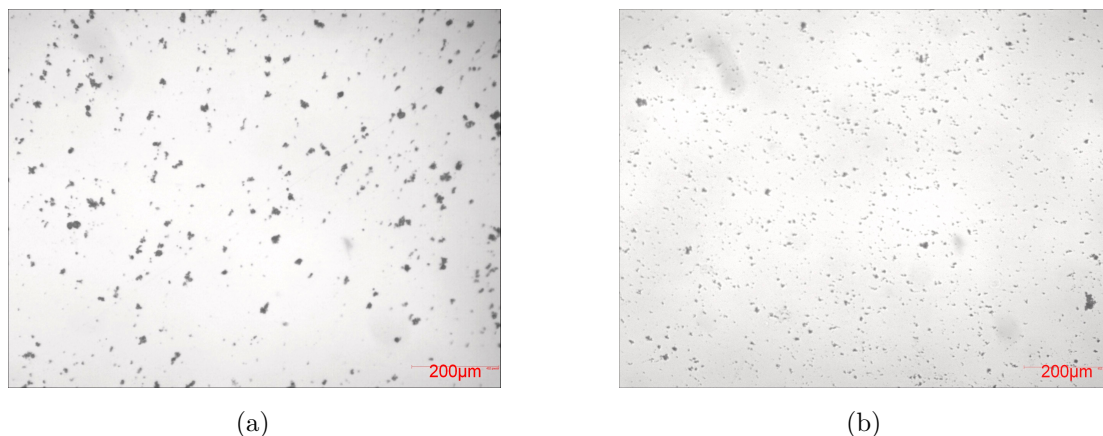


Figure 4.10: Optical microscope image of TiO_2 photocatalyst at a concentration of 1.5g/L dispersed in (a) WWeff-RO and (b) LGW- Cl^- .

To sum up, the results of this series of experiments allow to draw two main conclusions. First, organic matter at a COD level of 8 mg/L had no effect on the performances of the process. Second, many ionic species detected in WWeff were involved in the reduction of PMR efficiency for the degradation of anti-cancer drugs: bicarbonate, chloride, sulphate and calcium ions. The contribution of each ion to the decrease of degradation rate and the exact mechanisms involved are however difficult to predict given the complexity of real water matrices.

It emerges from this analysis that even a water matrix like WWeff-RO that can be considered as "clean" impeded the performances of TiO_2 photocatalysts. This suggests that the applicability of PMR as an additional process in a wastewater treatment plant might be jeopardised. This is why some authors such as Yap et al. [56] are currently working on the development of doped TiO_2 photocatalyst that would be less affected by the species present in natural waters and, so far, their research has shown promising results.

4.4 Batch vs continuous photocatalytic degradation

To compare the photocatalytic performances in different operating modes, degradation tests of pCBA were carried out in the batch PMR and the continuous one. It can be assumed that, like anti-cancer drugs, pCBA was not retained by UF membrane given that the MWCO of this membrane was much higher than pCBA's molar mass (156.6g/mol). Therefore, the continuous PMR can be considered as a CSTR for pCBA degradation assuming that the hypothesis of perfect mixing is respected.

Since degradation tests in batch lasted 60 min, to ensure a relevant comparison of performances, the influent and effluent flow rates were selected so that the mean residence time of pCBA in the continuous PMR was around 60 min. As already mentioned in the first chapter, this mean residence time represents the amount of time spent in average by pollutants in the PMR and is defined as the ratio of reactor volume over feed or permeate flow rate. In batch, the residence time simply corresponds to the experiment time (i.e. irradiation time). Consequently, a flow rate of 25 mL/min was selected for the continuous PMR and this gave an average residence time of 64 min. The comparison between bath and continuous PMR was performed for a TiO_2 concentration of 0.5g/L selected arbitrarily.

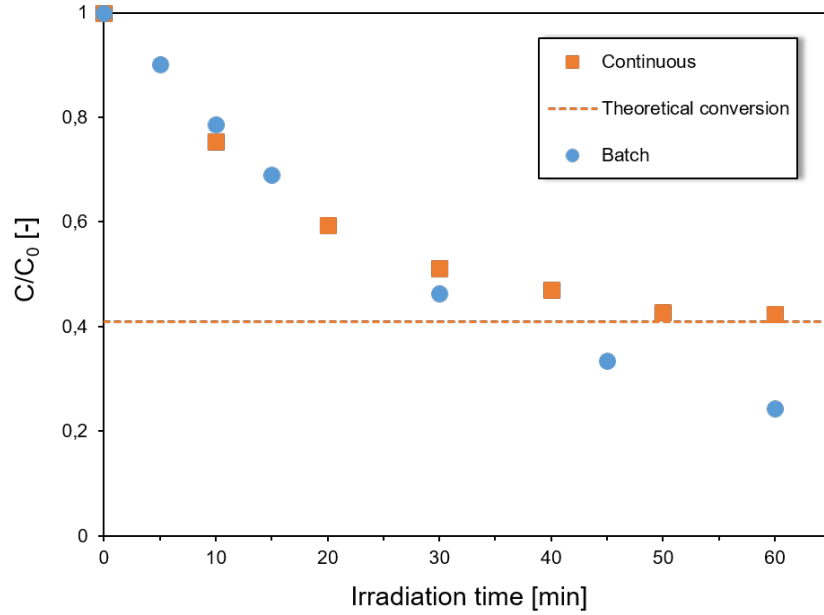


Figure 4.11: Evolution of pCBA concentration with time in batch and in continuous PMR ($[\text{TiO}_2] = 0.5\text{g/L}$ and water matrix = LGW). Theoretical conversion in continuous calculated from equation 4.1.

First, it can be observed that the concentration of pCBA continuously decreased with irradiation time in batch PMR since increasing the irradiation time is the same as increasing the residence time in the reactor. In continuous PMR, pCBA concentration stabilised after approximately 40 min which corresponds to the achievement of the steady state. The pCBA concentration in the effluent at steady state was equal to $\sim 40\%$ of the initial concentration.

It appears from these experimental tests that, for a mean residence time in continuous PMR similar to the experiment time in batch, the performances of the batch PMR were better because a degradation of $\sim 80\%$ was reached against $\sim 60\%$ in continuous. As already discussed in section 1.5.2, this is due to the distribution of residence times characteristic of a CSTR.

The pollutant concentration at steady state for a continuous PMR can be predicted theoretically using equation 4.1 that was already introduced in section 1.5.2. This equation can be applied in this case because photocatalytic reactions are pseudo first order reactions and experiments were carried out at constant temperature. Knowing the pCBA degradation rate constant for 0.5g/L of TiO_2 from previous experiments, the theoretical conversion can be calculated as follows:

$$\frac{\langle C_{\text{out}} \rangle}{C_0} = \frac{1}{1 + k\tau} = 0.41 \quad (4.1)$$

This result is consistent with the value obtained experimentally (figure 4.11). Therefore, for the economic evaluation, the above equation can be used to determine the mean residence time τ necessary to decrease the anti-cancer drugs concentration by one order of magnitude between the inlet and outlet of the treatment.

4.5 Economic simulation

The objective of the economic analysis was to evaluate the cost of PMR and find out whether the addition of a pre- or post-treatment to the PMR increased its economic attractiveness or not. The five configurations investigated are described in section 3.4 as well as the general methodology adopted to calculate their total cost.

As a reminder, each treatment process was assumed to treat 1L of solution with a decrease in drugs concentration by one order of magnitude. More precisely, as the three investigated drugs were not characterised by the same degradation rate, the requirement for each configuration was to degrade 90% of the slowest degraded drug, cyclophosphamide. Knowing the degradation rate constant for this anti-cancer drug in WWeff from previous experiments ($k_{\text{WWeff,CP}} = 0.01\text{min}^{-1}$ for $[\text{TiO}_2] = 1.5 \text{ g/L}$), the time required for treatment could be calculated for the five cases following the method described in section 3.4. The resulting treatment durations obtained for each configuration are reported in table 4.4. Though the calculated treatment times seem to be very high, it should be remembered that this evaluation is only a preliminary one performed at a really small scale. In practice, at large-scale, a larger reactor volume would be operated so that the mean residence time in the PMR would be increased without reducing the feed flow rate. Therefore, the time to treat 1L of polluted waters would be strongly reduced compared to the high values found in this analysis.

After calculation of the treatment times, the total cost of each investigated configuration was determined. The results are displayed in table 4.4 and they are also represented graphically on figure 4.12, along with the contribution of each item to the total cost.

	PMR	NF+PMR	RO+PMR	PMR+NF	PMR+RO
Treatment time [min/L/order]	568	946	189	62	28
Total cost [€/L/order]	0.23	0.37	0.08	0.05	0.03

Table 4.4: Total cost and operation time to treat 1L of polluted WWeff with a decrease in pollutant concentration by one order of magnitude for the five treatment processes studied.

As one might have expected, a longer treatment time leads to a higher cost because each item is used during a larger period. It may seem counter-intuitive that the configuration with nanofiltration pretreatment costs more than the PMR alone but this can be explained by the rejection value of 89% attributed to this membrane. Because of this rejection, the permeate concentration is higher than the target concentration in the effluent. Therefore, the PMR needs to compensate by degrading anti-cancer drugs to a larger extent which requires to increase the average residence time in the reactor by reducing the flow rate. As a result, the time to treat 1L with NF+PMR becomes much higher than PMR on its own. On the contrary, RO cell in a similar configuration performs much better than NF+PMR thanks to its 95% rejection. The configuration exhibiting the lowest cost is the one that exploits RO membrane

as post-treatment. This combination presents the advantage of increasing the residence time of anti-cancer drugs in the PMR without restricting excessively the feed flow rate. It should nevertheless be noted that applying a reverse osmosis as post-treatment to the PMR would also increase the concentration of ions and organic matter in the PMR. Results obtained in section 4.3.1 showed that photocatalysis was strongly affected by the presence of real water species. Consequently, increased concentrations of ions and organic matter might affect even more the performances of photocatalysis and the calculated treatment time in this configuration could be longer than expected. Further experimental investigations would be necessary to confirm or infirm this hypothesis. Similar remarks hold true for NF as post-treatment and RO as pretreatment though the retentate would be less concentrated in ions and organic matter than with RO membrane as post-treatment. This is due to the fact that, in the first case, the rejection percentage is lower than for RO membrane and, in the second case, the feed is concentrated only once.

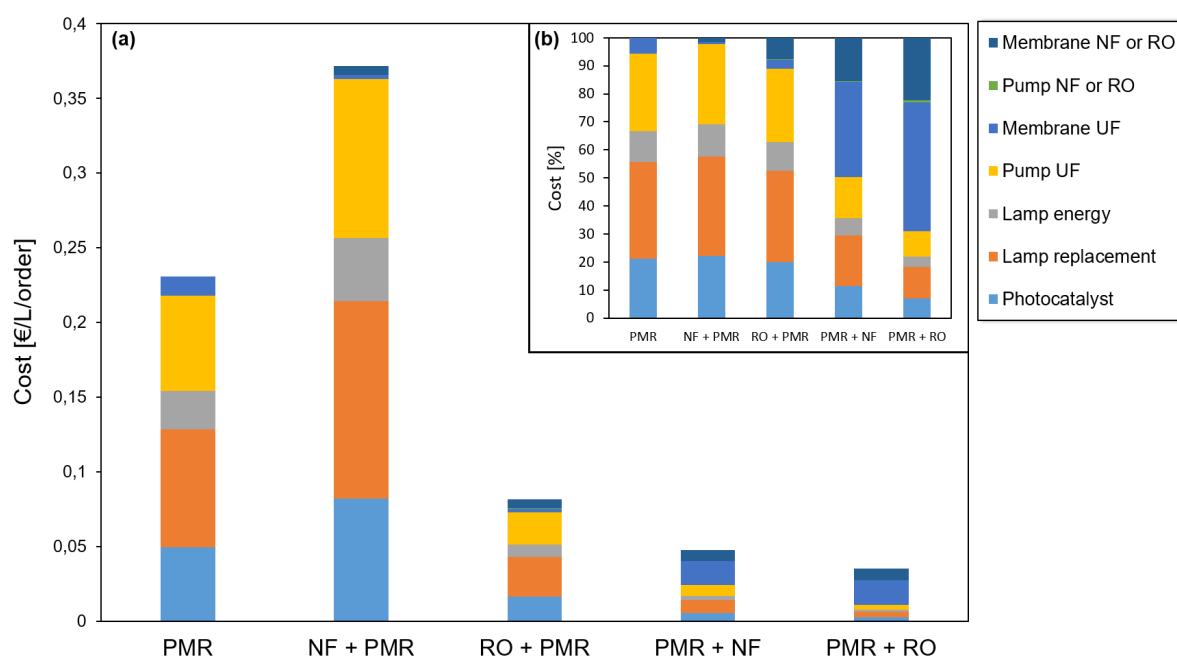


Figure 4.12: Cost estimation for PMR and PMR coupled with a membrane process: schematic diagrams expressed in (a) total cost and (b) cost percentage.

Looking at the cost distribution in each configuration, it can be observed on figure 4.12b that lamp and energy consumption of UF pump constitute together approximately 70% of the total cost for PMR, NF+PMR and RO+PMR. The high consumption of the pump comes from the fact that, to avoid fouling by deposition of TiO_2 particles on the membrane, it needs to accelerate the fluid at 3m/s which corresponds to a volumetric flow rate of 5L/min. Application of equation 3.8 in chapter 3 indicates that a power of 25W is needed to push the fluid at this rate. As already mentioned in the first chapter, fouling in PMR is an important issue and even though strategies to control this fouling have been developed, their application comes with a cost.

Regarding the contribution of the lamp, its cost could be reduced by replacing the mercury

UV lamp with LEDs. Besides their lower replacement cost, LEDs consume less energy, live longer and are environmentally-friendly [49]. Another potential solution to reduce the cost of artificial illumination would be to develop a photocatalytic material with the capacity to exploit a large fraction of the solar spectrum. In that case, the photocatalytic process could be efficiently operated under sunlight and the lamp would become dispensable. This alternative is still at the research stage but the results obtained so far by scientists are encouraging [78][79].

When the effluent of the PMR is post-treated with a membrane, it appears that the dominating cost is the UF membrane which represents respectively 34% and 46% of the total cost for PMR+NF and PMR+RO. Contributions of the lamp and UF pump are less significant in these cases because the treatment is much faster. However, for UF membrane, even though the treatment duration is short, a higher filtration area is needed to comply with the higher permeate flow rate. From equation 3.7, the surface area calculated for configurations with additional post-treatment is 10 to 100 times higher than the one obtained for the three other processes. Because ceramic membranes are expensive, a high surface area increases strongly the total cost. One way to limit this impact on the total cost would be to improve the manufacturing techniques of ceramic membranes in order to reduce the production costs.

In summary, it cannot be ensured that the combination of RO or NF membrane with PMR operated with conventional TiO_2 particles as photocatalysts is interesting from an economic point of view. Consequently, further investigations are necessary. However, assuming that photocatalysts less sensitive to real water species could be effectively developed in the future, this preliminary cost evaluation indicates that the combination of PMR with a fine membrane could reduce the total cost. Furthermore, this economic analysis highlighted two parts of PMR where costs should be primarily cut down: (i) light source and (ii) membrane fouling control strategy to avoid the deposition of TiO_2 particles. For PMR combined with a fine membrane as post-treatment, the highest contribution to the total cost is the ceramic UF membrane due to its complex manufacturing.

It appears from this analysis that the use of UF membrane in PMR strongly contributes to the increase of the total cost in the five configurations investigated because of fouling or manufacturing cost. This aspect reduces the attractiveness of PMR against other AOPs such as $\text{UV}/\text{H}_2\text{O}_2$ that do not require a filtration step. M. Makoudi et al. [80] compared the processes of $\text{UV}/\text{H}_2\text{O}_2$ and PMR for the degradation of anti-cancer drugs on an economical basis and found that $\text{UV}/\text{H}_2\text{O}_2$ was indeed better. This result was attributed to the presence of the filtration step in PMR and to the higher rate of degradation of $\text{UV}/\text{H}_2\text{O}_2$ in natural waters.

Despite the higher cost of PMR and its limited performances in real waters, its application for wastewater treatment is still intensively investigated in the literature due to its potential as a green treatment process. In particular, the possibility to activate photocatalyst with renewable energy sources like solar radiations make this technology very attractive from an environmental and economic point of view compared to $\text{UV}/\text{H}_2\text{O}_2$, for example, which demands UV lamps [27].

Conclusions

The increased discharge of anti-cancer drugs in the waste waters due to the boost of new cancer cases detected in the last few years and the inability of conventional wastewater treatment plants to eliminate these drugs have led scientists to investigate other processes for their removal. In this work, the application of photocatalytic membrane reactor for the degradation of these pharmaceutical compounds was investigated along two main axes: (i) effect of water matrix on photocatalytic efficiency and (ii) economic evaluation of the process.

Prior to studying the performances of PMR for drugs degradation in real waters, the photocatalyst load maximising the production of OH radicals in laboratory grade water was investigated and an optimum loading of 1.5g/L was identified. The degradation kinetics was studied with this optimised TiO₂ concentration in laboratory grade water for capecitabine (0.14min⁻¹), cyclophosphamide (0.09min⁻¹) and 5-fluorouracil (0.08min⁻¹).

Then, the degradation of these three anti-cancer drugs was investigated in secondary wastewater effluent at the same TiO₂ loading as pure water. A decrease in the degradation rate by more than 75% was noted in this water matrix compared to pure water. Further tests were subsequently conducted to understand the origin of this decrease and two conclusions were drawn based on the results. First, natural organic matter at the concentration encountered in secondary wastewater effluent had no effect on the degradation rate. Second, ions, and more precisely HCO₃⁻, Cl⁻, SO₄²⁻ and Ca²⁺, were identified as the cause of the decrease in degradation rate and they affected the photocatalytic performances even at concentrations below 100 mg/L.

Before the preliminary economic evaluation, the performances of PMR in continuous were studied. The results showed that the efficiency of pollutant degradation was reduced compared to a batch PMR due to the broad distribution of residence times in continuous. Also, it was observed that the application of the residence time distribution of an ideal continuous stirred tank reactor to determine the outlet conversion could effectively predict the performances of a continuous PMR.

Finally, the total cost of PMR for drugs degradation as well as the cost of PMR coupled with nanofiltration or reverse osmosis membrane as pre- or post-treatment were investigated. For PMR, the total cost calculated was 0.23€/L/order and the distribution of costs evidenced two areas for improvement in order to reduce this total cost: (i) high energy-consuming mercury lamps and (ii) membrane fouling control strategy. For the combination of PMR with an additional membrane module, no clear conclusions could be drawn about their economic interest compared to the PMR alone. Further investigations on the effect of ions and organic matter at higher

concentrations are necessary to answer precisely to this question.

To sum up, PMR shows promising results for the degradation of anti-cancer drugs in laboratory grade water. However, the strong deactivation of photocatalyst in real water matrix compromises its applicability as final wastewater treatment step in order to avoid the discharge of toxic pharmaceuticals in the environment. In this context, further research is still required to increase the efficiency of PMR in real conditions and its economic attractiveness.

Perspectives for future research

The results obtained in the present work raise other unresolved questions that can constitute a good baseline for future research.

First, regarding the effect of natural waters, one point that should be clarified is the identification of the exact mechanisms involved in the photocatalyst deactivation. This could be done by simulating real water matrices with variable concentrations of the species herein identified as principal inhibitors of photocatalysis and spike photocatalyst particles in these different solutions. Then, the adsorption of some ionic species at the catalyst surface could be verified thanks to XPS analyses. The agglomeration could also be studied more accurately following a similar method as Topuz et al. [53] who studied the correlation between calcium ions concentration and particle agglomeration using nanoparticle tracking analyser. This device can analyse precisely a suspension of nanoparticles by determining the particle size distribution. Finally, photocatalytic experiments could be performed in these different water matrices to identify which species, among the four anions identified in this work, are the main contributors to the deactivation of photocatalysis. Such rigorous analyses could be useful for the development of new photocatalytic materials more resistant to inhibitory effects.

Another important aspect that was briefly introduced in this work is the continuous operation of PMR. As previously stated, the large-scale application of PMR necessitates to run in continuous but, to this day, there is still a lack of data regarding the performances of photocatalytic degradation in this operation mode. Notably, the photocatalyst lifetime and activity when it is continuously in contact with real water species should be tested for long periods since there is a risk that the adsorption of ions and organic matter progressively decreases the activity of photocatalyst. Moreover, Rao et al. [81] reported that the formation of degradation by-products during continuous treatment process could accumulate at the TiO_2 surface and also affect its long-term efficiency. These researchers also demonstrated that deactivated photocatalysts could be efficiently regenerated by heating them at 150°C . With that in mind, it could be interesting to determine how long a continuous process can be operated with real waters before the activity of photocatalysts becomes too low and regeneration becomes necessary. It could also be useful to identify how many photocatalyst reuse cycles (1 cycle: continuous photocatalytic process followed by regeneration) can be performed before TiO_2 particles become completely inactive and need to be replaced by fresh catalyst.

Moreover, the elimination of anti-cancer drugs from waters do not ensure that the treated stream is non-toxic. For instance, Lin et al. [37] reported an increase in toxicity during

the photocatalytic degradation of cyclophosphamide that was attributed to the presence of degradation by-products. Therefore, besides the follow-up of drugs concentration during the treatment process, the toxicity of the solution should also be monitored to check that toxic by-products are completely removed from the solution. Such toxicity analyses can be performed with bioluminescent micro-organisms like *Vibrio fischeri*. Based on the reduction of light emitted by these organisms when they are added to a toxic sample, the toxicity of the tested solution can be evaluated [37].

Also, the economic simulation suggested that, to confirm the interest of adding a NF or RO membrane as pre- or post-treatment to the PMR, photocatalytic degradation experiments should be carried out in the retentate of NF and RO membranes. The objective of such experiments would be to determine the rate of anti-cancer drugs degradation in water matrices containing an increased concentration of ions and organic matter. Moreover, the economic analysis indicated other areas of investigations in order to decrease the costs of PMR and one of these areas concerns the light source which represents 45% of the total cost in the PMR. As already mentioned earlier, the use of UV-LEDs instead of conventional mercury lamps could reduce both economical and environmental impacts of the process. In future research, the efficiency of photocatalytic degradation for the removal of anti-cancer drugs could be investigated with this source of radiations. Furthermore, recent studies have worked on the development of new photocatalytic materials that can be activated by solar light and the results they obtained are promising [78][79]. Application of such catalysts could reduce even further the operating costs and environmental impacts of the process.

Finally, Deegan et al. [82] raised an interesting point regarding the occurrence and fate of numerous pharmaceuticals in natural waters. They advanced that end-of-pipe measures, though they offer a partial solution, are not sufficient to prevent the pollution of our waters. According to these authors, actions should be taken first and foremost at the source of the problem, i.e. at the level of drug design. Green chemistry principles such as use of safe solvents, high yielding synthesis, waste reduction, have already been integrated in the design of anti-cancer drugs [83]. However, it is limited so far to reducing environmental impact at the level of the production but not necessarily at the level of drug disposal. To go further, researchers should also strive to make anti-cancer drugs more selective towards cancerous cells in order to limit the risks for living organisms when these drugs are discharged in the environment. More importantly, the degradation of drugs after they had their therapeutic effect is also an aspect that should be considered in the process of drugs development.

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Appendix A

Starting procedure

Prior to degradation experiments, air bubbles trapped in the system had to be eliminated completely because they could disrupt the measurement of the CFV detector. The following procedure was developed by R. Hainaut et al. [12] to get rid of these bubbles and is reprinted here with his permission:

Nº	Steps	Cumulative operation time
1	Fill the reactor with 1.6 L of water	1 min
2	Launch the pump by opening the pressure plug valve	2 min
3	Fully open the system valve and set the operating pressure at 0.5 MPa	5 min
4	Almost close the pressure plug valve to reach very low pressure conditions (< 0.1 bar on monitor)	9 min
5	Fully open the pressure valve and almost close the system valve	12 min
6	Degasification: fully reopen the system valve and go back to low-pressure conditions	16 min
7	Close the system valve and fully reopen the pressure valve	/
8	Progressively open the system valve until the desired cross-flow velocity and pressure are reached	/

Table A.1: Starting procedure [12].

Appendix B

Membrane cleaning protocol

In order to clean the irreversibly fouled membrane, a rigorous procedure developed by R. Hainaut et al. [12] was followed. This procedure involved three steps:

1. Membranes were put in an oven at 250°C for 2h. This step aimed at eliminating organic foulants closely bound to the membranes by thermal degradation.
2. Membranes were cooled down and placed in an ultrasonic bath for 20 minutes in order to break the catalyst cake layer and further remove organic foulants.
3. The last step was the chemical cleaning itself which aimed at removing the last irreversibly bound foulants from the membranes. First, membranes were immersed in a solution of NaOH 15-20g/L at 85°C during 30 minutes. They were then rinsed with pure water before being placed in an acidic solution of H₃PO₄ (1mL/L) at 50°C for 15 minutes.

Appendix C

Determination of rate constants: fitting curves

In this appendix, the fitting curves for the determination of k values from batch experiments are represented.

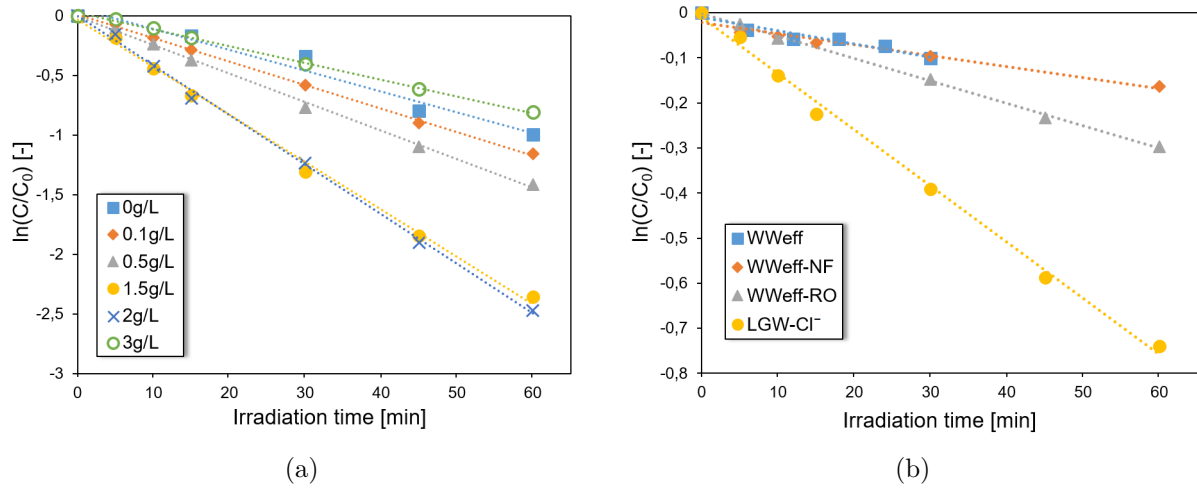


Figure C.1: Fitting curves for pCBA degradation batch experiments: (a) at different TiO_2 concentrations and (b) in different water matrices ($[\text{TiO}_2] = 1.5\text{g/L}$).

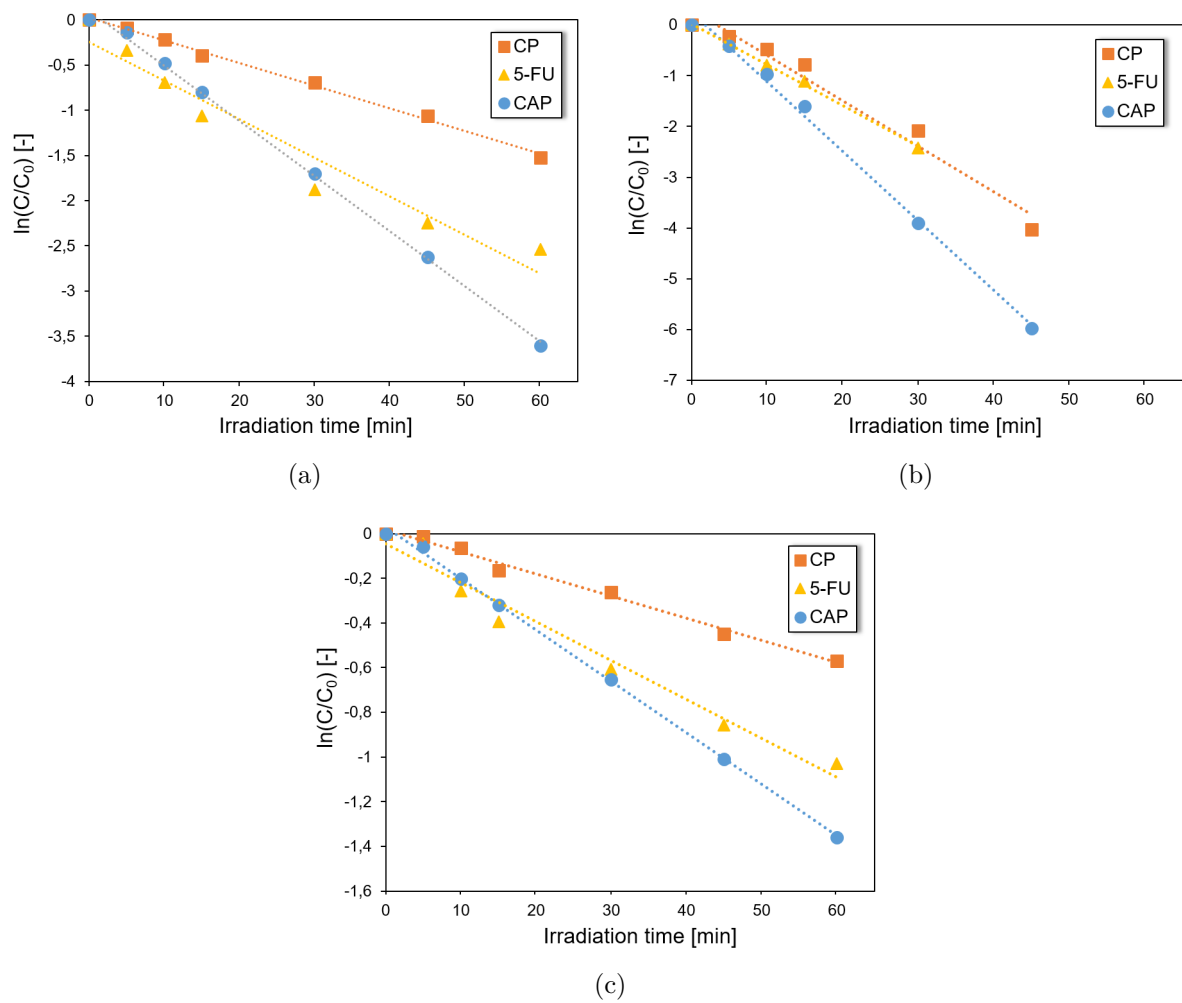


Figure C.2: Fitting curves for anti-cancer drugs degradation: (a) LGW-UV, (b) LGW-UV/TiO₂ and (c) WWeff-UV/TiO₂.

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