

Removal of free residual chlorine from water using ultraviolet light photolysis systems:

A review

Remoção de cloro residual livre da água utilizando sistemas de fotólise por luz ultravioleta: Uma revisão

Eliminación del cloro residual libre del agua mediante sistemas de fotólisis por luz ultravioleta: Una revisión

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Abstract

Water, an essential natural resource for society, is widely used in various sectors, whether as a raw material in industrial processes, agriculture, leisure, the production of electronic components, cosmetics, and pharmaceuticals, or, primarily, for public supply. Its application is directly related to its quality and purity, determined by the treatment process to which it is subjected. In water treatment, chlorine is commonly used as an oxidizing and disinfectant agent, acting as a barrier against microbiological contamination. However, even in low concentrations, this chemical can be harmful to sensitive equipment, compromise the quality of end products through undesirable reactions, and, if discharged in high concentrations, be fatal to aquatic organisms, causing significant impacts to the ecosystem. Therefore, research into processes and technologies aimed at controlling and removing free residual chlorine is of great importance. As an alternative to conventional removal mechanisms, the photolysis process, based on exposure to ultraviolet radiation, is gaining prominence. This article presents a review on the use of photolysis in the removal of free chlorine from water, addressing the mechanisms involved in the reactions, the types of reactors and the main parameters that influence the process.

Keywords: Photolysis; Water treatment; Ultraviolet lamps; Chlorine removal.

Resumo

A água, recurso natural essencial à sociedade, é amplamente utilizada em diversos setores, seja como matéria-prima em processos industriais, na agricultura, no lazer, na produção de componentes eletrônicos, cosméticos e fármacos, ou, principalmente, para o abastecimento público. Sua aplicação está diretamente relacionada à qualidade e pureza, determinadas pelo processo de tratamento ao qual é submetida. No tratamento de águas, o cloro é comumente empregado como agente oxidante e desinfetante, atuando como uma barreira contra a contaminação microbiológica. Contudo, mesmo em baixas concentrações, esse químico pode ser prejudicial a equipamentos sensíveis, comprometer a qualidade de produtos finais por meio de reações indesejadas e, em casos de descarte em elevadas concentrações, ser fatal para organismos aquáticos, causando impactos significativos ao ecossistema. Diante disso, a investigação de processos e tecnologias voltadas ao controle e à remoção do cloro residual livre torna-se de grande relevância. Como alternativa a mecanismos usuais de remoção, o processo de fotólise, baseado na exposição à radiação ultravioleta, vem

ganhando destaque. Este artigo apresenta uma revisão sobre o uso da fotólise na remoção de cloro livre da água, abordando os mecanismos envolvidos nas reações, os tipos de reatores e os principais parâmetros que influenciam o processo.

Palavras-chave: Fotólise; Tratamento de água; Lâmpadas ultravioletas; Remoção de cloro.

Resumen

El agua, un recurso natural esencial para la sociedad, se utiliza ampliamente en diversos sectores, ya sea como materia prima en procesos industriales, la agricultura, el ocio, la producción de componentes electrónicos, cosméticos y productos farmacéuticos, o, principalmente, para el suministro público. Su aplicación está directamente relacionada con su calidad y pureza, determinadas por el proceso de tratamiento al que se somete. En el tratamiento del agua, el cloro se utiliza comúnmente como agente oxidante y desinfectante, actuando como barrera contra la contaminación microbiológica. Sin embargo, incluso en bajas concentraciones, esta sustancia química puede ser perjudicial para equipos sensibles, comprometer la calidad de los productos finales mediante reacciones indeseables y, si se vierte en altas concentraciones, ser letal para los organismos acuáticos, causando impactos significativos en el ecosistema. Por lo tanto, la investigación en procesos y tecnologías destinados a controlar y eliminar el cloro libre residual es de gran importancia. Como alternativa a los mecanismos de eliminación convencionales, el proceso de fotólisis, basado en la exposición a la radiación ultravioleta, está cobrando importancia. En este artículo se presenta una revisión sobre el uso de la fotólisis en la remoción de cloro libre del agua, abordando los mecanismos involucrados en las reacciones, los tipos de reatores y los principales parámetros que influyen en el proceso.

Palabras clave: Fotólisis; Tratamiento del agua; Lámparas ultravioletas; Eliminación del cloro.

1. Introduction

Chlorination has become widely adopted by water and sanitation regulatory agencies as a mechanism for protecting the population's health, guaranteeing microbiological control, and disinfection. Chlorine, in the form of Cl_2 or NaOCl , as it is a strong oxidizer, is commonly used in water treatment plants so that a residual, acting as a protective barrier, is delivered to the population and industries by the distribution centers in the form of free residual chlorine (Leong, Kuo & Tang, 2008; Spellman, 2003, Bitter & Rozenberg, 2017).

Although low concentrations of chlorine in the water supply do not cause harm to people's health, chlorine concentrations of between 0.2 and 0.5 ppm are already detectable by taste. However, chlorine concentrations in effluents exceeding 0.01 mg/L already pose serious risks to marine and estuarine life, requiring prior treatment before disposal into water bodies (Black & Veatch Corporation, 2009; Crittenden *et al.*, 2012).

However, the biggest applications for chlorine removal are in the industry, in specific processes where the oxidizer is harmful to systems and equipment. As described by Crittenden *et al.* (2012), the occurrence of chlorine can accelerate the oxidative process of metal equipment such as pipes, valves, and boilers, leading to leaks and structural damage. Applying water with high chlorine concentrations in ion exchange systems can also be extremely harmful. The resins used in these systems are susceptible to oxidation, especially those based on sulfonated polystyrene, reducing their lifespan and making them inefficient in a short time (Leong, Kuo & Tang, 2008; Wrampe & Carlson, 2023).

The oxidative process is also observed in polyamide-based nanofiltration and reverse osmosis membranes. Because they are very sensitive to the presence of free chlorine, polyamide membranes undergo rapid degradation, which occurs after a few hours of use, leading to equipment loss. The rate of degradation is dependent on pH, chlorine concentration, and the presence of transition metals; however, degradation can occur between 200 and 1000 hours of use with exposure to up to 1 ppm of free chlorine (Kucera, 2010; Bitter & Rozenberg, 2017).

Pharmaceutical, cosmetics, and semiconductor industries need water with a high degree of purity, where the presence of chlorine in the water has a direct impact on the product delivered, through unwanted reactions. This makes it necessary to remove and control free residual chlorine in water (Leong, Kuo and Tang, 2008; Wrampe & Carlson, 2023).

In the presence of ammonia, free chlorine reacts to form combined chlorine, present in the forms of monochloramine (NH_2Cl), dichloramine (NHCl_2), and trichloramines (NCl_3). Although these compounds have less oxidizing capacity than free

chlorine, they can still be harmful both to processes, causing oxidation and damage to equipment, and to human health. The formation of chloramines is a common phenomenon in swimming pools (Jafvert & Valentine, 1992; Li & Blatchley, 2009).

Among them, trichloramine is especially concerning because it is highly volatile and can cause irritation to the eyes, nose, and upper respiratory tract. Chronic exposure to trichloramines and other volatile disinfection byproducts (DBPs) has been associated with damage to the lung epithelium of swimmers, as well as an increased risk of asthma development in children and lifeguards. In this context, the application of ultraviolet light disinfection systems proves to be an effective strategy not only for the degradation of residual free chlorine but also for the removal of combined chlorine, contributing to greater operational safety and health protection (Cimetiere & Laa, 2014; Shulga *et al.*, 2021).

In the last decade, the use of ultraviolet (UV) radiation has gained prominence in the process of removing free residual chlorine. Using the energy emitted by UV lamps, the photolysis of chlorine in solution leads to its mineralization, creating less reactive and harmful compounds. Therefore, this article aims to look to data on the alternative method for removing free residual chlorine from bodies of water using photolysis systems irradiated by ultraviolet light lamps, covering the principles of chlorine photolysis and factors that interfere with the process. To this end, various research sources were analyzed to consolidate information supporting the application and efficiency of this technology.

2. Methodology

A documentary research was carried out from an indirect source, of a qualitative nature (Pereira *et al.*, 2018) and, of a non-systematic review and of the specific type of narrative review (Rother, 2007). To carry out the discussion, the database used was Google Scholar, which is a free and open-source database, and with the search terms: Photolysis; Water treatment; Ultraviolet lamps; Chlorine removal. An extensive bibliographic investigation was conducted on Advanced Oxidation Processes (AOPs). Specialized textbooks and technical literature about ultraviolet radiation principles and applications were also reviewed. Reference books on water treatment provided further theoretical foundation for this study. This comprehensive approach was essential, since scientific publications and consolidated data on the removal of free residual chlorine by ultraviolet irradiation are limited. Thus, a broader theoretical basis supported the development of the present work.

3. Methodology for Chlorine Removal

The application of activated carbon filters is widely accepted in the chlorine removal process. However, due to their function and retention of organic compounds, along with the total removal of chlorine, these filters become providers of nutrients to microorganisms, enabling rapid microbiological growth. Thus, the application of granular activated carbon filters can cause biological fouling on adjacent equipment, such as ultrafiltration and reverse osmosis membranes (Kucera, 2010; Breckenridge, 2014; Pakzadeh *et al.*, 2014; Qasim & Zhu, 2018; Preece & Breckenridge, 2019; Portal Saneamento Básico, 2021).

Another widely used dechlorination process is the oxidation of chlorine through the addition of compounds based on sulfur dioxide (SO₂), such as sodium bisulfite (NaHSO₃), sodium metabisulphite (Na₂S₂O₅), or sulfur dioxide itself. The reactions of these compounds completely convert chlorine into chloride ions, which, along with the reduction of oxygen in the water and the release of assimilable nutrients, favors the proliferation of anaerobic microorganisms and the formation of biofilms on adjacent equipment (Leong, Kuo & Tang, 2008; Kucera, 2010; Breckenridge, 2014; Bitter & Rozenberg, 2017).

Thus, alternative methods for removing free residual chlorine have been gaining notoriety, such as exposure to UV radiation. As it is a physical process, the energy provided by ultraviolet lamps is able to break the bonds of chlorine molecules without the need for other chemical products (Kucera, 2010; Laa & Stefan, 2018).

Ultraviolet radiation is commonly used as a disinfection mechanism in treatment plants and industries. However, as it requires higher doses of radiation, dechlorination by UV light promotes complete water disinfection, making it a multi-barrier process for equipment and human consumption. In addition to preventing the formation of biofilms, this process also helps to improve water quality, avoiding the introduction of other chemicals and reducing total organic carbon (TOC) levels through the photolysis of organic matter (Laat & Stefan, 2018; Portal Saneamento Básico, 2021).

The treatment of chlorinated water with ultraviolet radiation is a highly effective strategy for producing high-purity water without the addition of chemical products. At the start of treatment, exposing the water to UV radiation enables the photolysis of chlorine molecules and reduces the concentration of organic carbon in the water. In addition, the need for high doses of radiation for the photodecomposition of chlorine molecules ensures an additional barrier against microbiological contamination during the process (McClellan, 2007; Pakzadeh *et al.*, 2014; Wrampe & Carlson, 2023).

4. Principles of Ultraviolet Light Photolysis

Most photochemical reactions are initiated by the absorption of photons of light emitted in the ultraviolet spectrum and a small portion in the visible spectrum, following the principles of the “Laws of Photochemistry”. The first law states that light emitted by an energy source must be absorbed by the system to cause a photochemical change. The second law, known as the Stark-Einstein law, states that for each photon absorbed by a chemical system, only one molecule is susceptible to a photochemical effect, thus delimiting the reaction process. The third and final law, known as the Bunsen-Roscoe Law, defines that the photochemical reaction process is governed by the dose of radiation absorbed by the target. Therefore, dosage becomes the most important variable in photochemical processes. As defined by the second law, for the reaction to happen, the photon's energy must equal or exceed the energy of the molecular bond. The strength of the bonds between molecules is intrinsically linked to the number of bonds between their atoms. Thus, with radiation of longer wavelengths, the energy supplied is generally insufficient to cause any changes to the medium (Blatchley, 2023).

Photochemical kinetics is then based on the mathematical description of the photon energy absorbed by the molecule and its equivalent transformation rate. The quantitative description of this process is based on Beer Lambert's law, represented by Equation 1, which relates the radiant power of a light source to an effective length and the concentration of the species in the absorbing medium (Swinehart, 1962).

$$Abs_{(\lambda)} = -\log\left(\frac{P_{(\lambda)}}{P_{(\lambda)}^0}\right) = \varepsilon_{(\lambda)} \cdot C_B \cdot l \quad (1)$$

However, it is not always the case that the absorbed energy results in a photochemical event. To this end, the term quantum yield, $\Phi_{(\lambda)}$, is used to describe the efficiency with which the absorbed photons promote a photochemical event. The quantum yield can be understood as the amount of mol decomposed or formed per number of photons absorbed. While quantum yields equal to 0 imply that no photochemical reaction can occur, quantum yields above 1 indicate that one or one or more reaction mechanisms lead to the formation of the product, often caused by chain reactions generated by the presence of intermediate radicals (Blatchley, 2023).

Considering a generic photolysis reaction, where only one reagent absorbs photon energy, the reaction rate of a photochemical process can be described by Equation 2.

$$r_B = -\frac{d[B]}{dt} = E'_i \cdot \frac{(1 - 10^{-\varepsilon_{(\lambda)} \cdot C_B \cdot l})}{l \cdot U} \cdot \Phi_{(\lambda)} \quad (2)$$

Based on Equation 2, Blatchley (2023) discusses two limiting cases for the photolysis process. The first case considers a solution in which the concentration of the target molecule is high enough for the solution to become opaque, preventing the emitted radiation from passing through the solution. The second limiting case is the case of a transparent solution, where the absorbance term tends to zero. However, as specified by the first law of photochemistry, if the absorbance were zero, any photochemical events would not happen. Therefore, in practical terms, a limit is adopted for the absorbance term $\lesssim 0.02$, obtained through a Taylor series expansion, with truncation in the second term.

Considering the equivalence between molecules and photons established by the second law of photochemistry, the description of kinetics based on the availability, or emission, of photons may become more rational than a methodology based on time. Given the need to describe the availability of photons for participation in the photochemical process, some terms are commonly used in literature. Among the most frequent are irradiance, defined as the radiant power of all wavelengths incident from all upward directions on an infinitesimal surface element, and fluence, the total radiant power incident from all directions on a small sphere divided by the cross-sectional area of that sphere (Bolton & Stefan, 2002).

Thus, for the cases of opaque solution and transparent solution, the rate equations can be represented by Equations 3 and 4, respectively.

$$r_B = -\frac{dC_B}{dt} = \frac{E'_{p,i} \cdot \Phi(\lambda)}{l} \quad (3)$$

$$r_B = -\frac{dC_B}{dt} = 2,303 \cdot \varepsilon(\lambda) \cdot C_B \cdot \Phi(\lambda) \cdot E'_{p,i} \quad (4)$$

In contrast, for a photochemical reactor using polychromatic light sources, it is necessary to include the additive contributions of all the wavelengths emitted by the lamp. Equations 5 and 6 can be written as the integral of the terms depending on the wavelengths emitted.

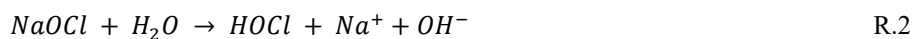
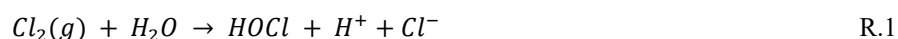
$$r_B = -\frac{dC_B}{dt} = \int_{\lambda_1}^{\lambda_2} \frac{E'_{p,\lambda} \cdot \Phi(\lambda)}{l} \cdot d\lambda \quad (5)$$

$$r_B = -\frac{dC_B}{dt} = \int_{\lambda_1}^{\lambda_2} 2,303 \cdot \varepsilon(\lambda) \cdot C_B \cdot \Phi(\lambda) \cdot E'_{p,i} \cdot d\lambda \quad (6)$$

5. Free Chlorine Photolysis

Currently, chlorine is used in treatment plants either as chlorine gas (Cl_2) or in the form of sodium hypochlorite (NaOCl), both of which undergo hydrolysis to quickly form hypochlorous acid (HOCl). As a weak acid, with a pK_a of 7.5 at 20°C , HOCl can dissociate, forming the hypochlorite ion (OCl^-). As the pH of the aqueous solution rises above 7.5, the concentration of free chlorine in the form of the hypochlorite ion becomes higher than free chlorine in the form of hypochlorous acid. (Leong, Kuo and Tang, 2008; Black & Veatch Corporation, 2009).

Reactions 1, 2 and 3 represent the hydrolysis processes of chlorine gas and sodium hypochlorite, respectively, while Reaction 3 illustrates the dissociation of hypochlorous acid into the hypochlorite ion.



In the absence of ammonia or amines, free chlorine exists as a mixture of the two components, with the fraction of each depending on pH. The combination of HOCl and OCl⁻ is referred to as the free chlorine residual. The lower the pH of the solution, the higher the percentage of hypochlorous acid, while in a solution with a higher pH, the presence of the hypochlorite ion will be more pronounced. More than 99% of free chlorine is present as HOCl at pH less than or equal to 5, and similarly, more than 99% of chlorine is in the form of OCl⁻ at pH greater than or equal to 10 (Feng *et al.*, 2007).

By emitting light with a low wavelength and high energy associated in a chlorinated solution, it's possible to promote the photolysis of diluted free chlorine. When exposed to light, especially UV light, the chlorine in solution in the form of hypochlorous acid and hypochlorite ion undergoes photolysis, generating chlorine, oxygen, and hydroxyl radicals as products (Feng *et al.*, 2007; Jin *et al.*, 2011, Preece & Breckenridge, 2019).

Reactions 4 and 5 show, respectively, the primary photolysis process of hypochlorous acid and hypochlorite ion, arising directly from the dissociation process after absorption of the emitted energy.



It can thus be seen that, through the photolysis of free chlorine, hydroxyl radicals (HO[•]), chlorine radicals (Cl[•]) and monoatomic oxygen radicals (O^{•-}) are formed. These highly reactive chemical species have an unpaired electron, causing a series of chain reactions with the medium in which they are present (Jin *et al.*, 2011).

Multiple reactions can take place after the photolysis of free chlorine, through the formation of radicals so that their concentrations, as well as the products formed, govern the subsequent reactions. Because they are highly reactive free radicals, these compounds react quickly with the surroundings through a series of chain reactions in which new types of intermediate radicals are produced, which can either consume the free chlorine available in the water or generate it again. However, information on the mechanisms of reactions following the photolysis process of free chlorine is still scarce and not widely known (Feng *et al.*, 2007; Weng, Li & Blatchley, 2012; Fang *et al.*, 2014; Cimetiere & Laat, 2014; Zhou *et al.*, 2019).

Although, it is known that during the photolysis process of free chlorine, new radicals are formed, among which the hypochlorite radical (ClO[•]) and the dichloride anion radical (Cl₂^{•-}) stand out, generated from the reaction of the chlorine radical with HOCl and OCl⁻. These radicals are in equilibrium with the medium during photolysis. Although described as less reactive in oxidative processes, the dichloride anion radical is still characterized as a relevant oxidant, with a standard potential of 2.0 V, compared to the standard potential of the chlorine radical, which is 2.4 V (Fang *et al.*, 2014; Dabic *et al.*, 2019; Lei *et al.*, 2019; Jevtic *et al.* 2022).

The speciation of radicals, strongly influenced by the pH of the solution, has a direct impact on the photolysis process and the consequent degradation of chemical compounds. In an alkaline environment, there is a greater generation of selective radicals, such as chlorine and hypochlorite radicals. In contrast, at acidic pH, the photolysis of hypochlorous acid favors the

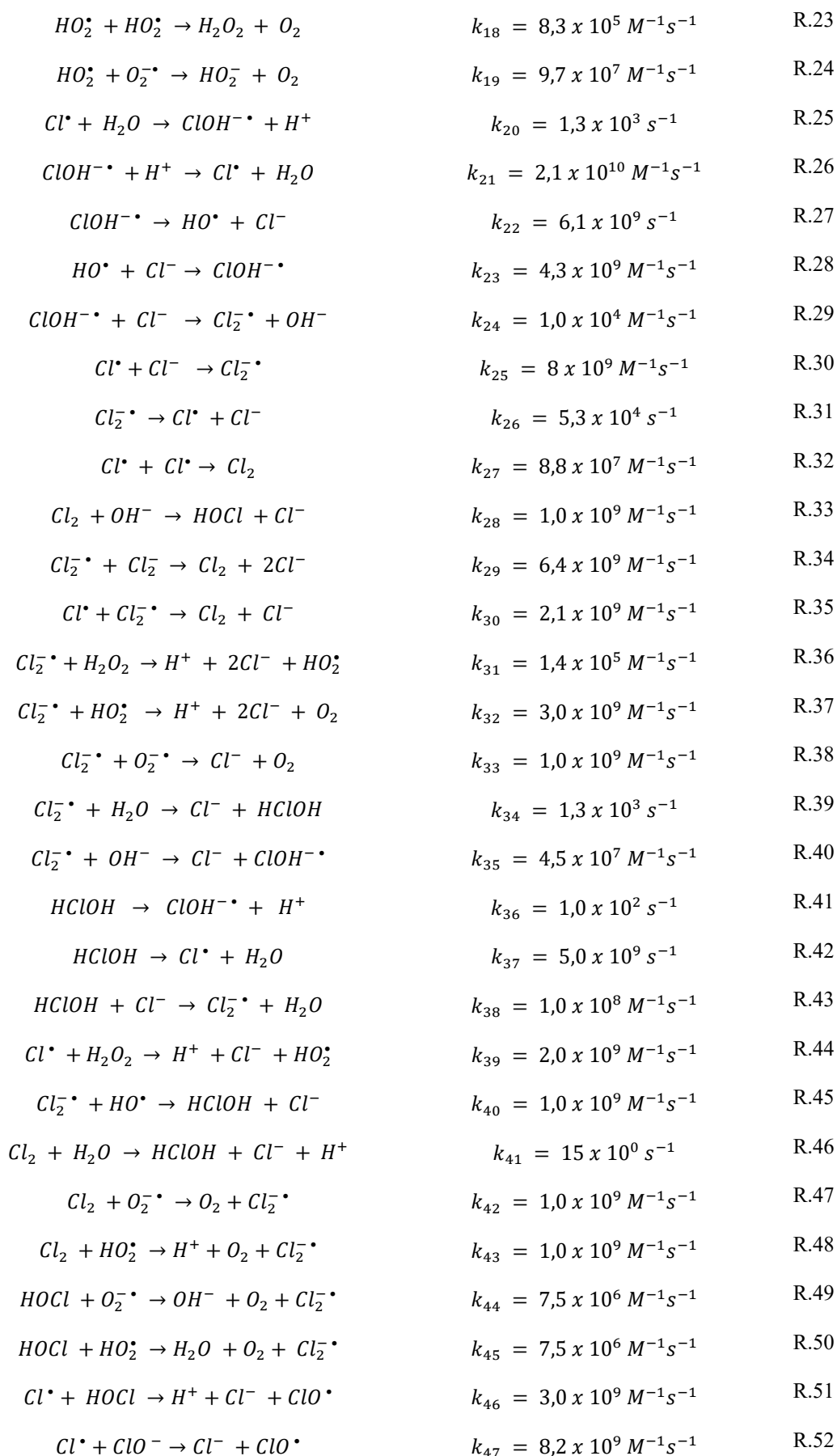
formation of the hydroxyl radical, which, being non-selective, reacts more extensively with the environment in which it is found. However, depending on the environment, chlorine-derived radicals are more reactive than the HO• radical itself (Li *et al.*, 2022).

Complementarily, when chlorine is predominantly in the form of hypochlorite ion, the generation of oxygen radicals, such as monoatomic oxygen (O•) and superoxide radical (O₂•⁻) is favored. Unlike hydroxyl and chlorine radicals, oxygen radicals have a reducing character due to their low standard potentials (e.g., for O₂•⁻, E⁰ = - 0.33 V), which contrasts with the high potentials of •OH and Cl• radicals (E⁰ = +2,7 V and +2,4 V, respectively). Thus, oxygen radicals tend to participate in termination reactions, interrupting the propagation of chain reactions and favoring the formation of stable compounds (Ilan, Czapski & Meisel, 1976; Fang *et al.*, 2014).

Table 1 shows the list of elementary reactions proposed by Zhou *et al.* (2019) for the photolysis process of free chlorine using ultraviolet radiation as the magnitude of the kinetic constants. The listed reactions demonstrate the subsequent reaction mechanism Reactions 4 and 5, up to the formation of stable chloride (Cl⁻) and oxygen (O₂) by-products.

Table 1 - Proposal of reaction mechanisms for the photolysis process of free residual chlorine.

REACTION	KINETIC CONSTANTS	
$HOCl + hv \rightarrow HO\bullet + Cl\bullet$	$\Phi_{HOCl} = 0,9 \quad \varepsilon_{HOCl} = 59 M^{-1}S^{-1}$	R.4
$OCl^{-} + hv \rightarrow O^{\bullet-} + Cl\bullet$	$\Phi_{OCl^{-}} = 0,8 \quad \varepsilon_{OCl^{-}} = 66 M^{-1}S^{-1}$	R.5
$OCl^{-} + H^{+} \rightarrow HOCl$	$k_1 = 5,0 \times 10^{10} M^{-1}S^{-1}$	R.6
$HOCl \rightarrow OCl^{-} + H^{+}$	$k_2 = 1,6 \times 10^3 M^{-1}S^{-1}$	R.7
$O^{\bullet-} + H_2O \rightarrow HO\bullet + OH^{-}$	$k_3 = 1,8 \times 10^6 M^{-1}S^{-1}$	R.8
$HO\bullet + OH^{-} \rightarrow O^{\bullet-} + H_2O$	$k_4 = 1,3 \times 10^{10} M^{-1}S^{-1}$	R.9
$HO\bullet + HOCl \rightarrow ClO\bullet + H_2O$	$k_5 = 2,0 \times 10^9 M^{-1}S^{-1}$	R.10
$HO\bullet + OCl^{-} \rightarrow ClO\bullet + OH^{-}$	$k_6 = 8,8 \times 10^{10} M^{-1}S^{-1}$	R.11
$HO\bullet + HO\bullet \rightarrow H_2O_2$	$k_7 = 5,7 \times 10^9 M^{-1}S^{-1}$	R.12
$H_2O_2 \rightarrow H^{+} + HO_2^{-}$	$k_8 = 1,3 \times 10^{-1} S^{-1}$	R.13
$H^{+} + HO_2^{-} \rightarrow H_2O_2$	$k_9 = 5 \times 10^{10} M^{-1}S^{-1}$	R.14
$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O$	$k_{10} = 2,7 \times 10^7 M^{-1}S^{-1}$	R.15
$HO_2^{-} + HO\bullet \rightarrow HO_2\bullet + OH^{-}$	$k_{11} = 7,5 \times 10^5 M^{-1}S^{-1}$	R.16
$HO_2\bullet \rightarrow H^{+} + O_2^{\bullet-}$	$k_{12} = 7,0 \times 10^5 S^{-1}$	R.17
$H^{+} + O_2^{\bullet-} \rightarrow HO_2\bullet$	$k_{13} = 5 \times 10^{10} M^{-1}S^{-1}$	R.18
$HO\bullet + HO_2\bullet \rightarrow H_2O + O_2$	$k_{14} = 6,6 \times 10^9 M^{-1}S^{-1}$	R.19
$HO\bullet + O_2^{\bullet-} \rightarrow OH^{-} + O_2$	$k_{15} = 1,0 \times 10^{10} M^{-1}S^{-1}$	R.20
$H_2O_2 + O_2^{\bullet-} \rightarrow OH^{-} + O_2 + HO\bullet$	$k_{16} = 1,3 \times 10^{-1} M^{-1}S^{-1}$	R.21
$H_2O_2 + HO_2\bullet \rightarrow H_2O + O_2 + HO\bullet$	$k_{17} = 3 \times 10^0 M^{-1}S^{-1}$	R.22



$Cl\cdot + OH^- \rightarrow ClOH\cdot^-$	$k_{48} = 1,8 \times 10^{10} M^{-1}s^{-1}$	R.53
$ClO\cdot + ClO\cdot \rightarrow Cl_2O_2$	$k_{49} = 2,5 \times 10^9 M^{-1}s^{-1}$	R.54
$Cl_2O_2 + H_2O \rightarrow HClO + H^+ + ClO_2^-$	$k_{50} = 2,5 \times 10^9 s^{-1}$	R.55
$Cl_2O_2 + OH^- \rightarrow ClO^- + H^+ + ClO_2^-$	$k_{51} = 2,5 \times 10^9 M^{-1}s^{-1}$	R.56
$ClO\cdot + HO\cdot \rightarrow ClO_2\cdot + H^+$	$k_{52} = 1,0 \times 10^9 M^{-1}s^{-1}$	R.57
$ClO_2^- + HO\cdot \rightarrow ClO_2\cdot + OH^-$	$k_{53} = 6,3 \times 10^9 M^{-1}s^{-1}$	R.58
$ClO_2\cdot + HO\cdot \rightarrow ClO_3^- + H^+$	$k_{54} = 4,0 \times 10^9 M^{-1}s^{-1}$	R.59
$ClO_2^- + Cl_2\cdot^- \rightarrow ClO_2\cdot + 2Cl^-$	$k_{55} = 1,3 \times 10^8 M^{-1}s^{-1}$	R.60
$ClO_2^- + ClO\cdot \rightarrow ClO_2\cdot + OCl^-$	$k_{56} = 9,4 \times 10^8 M^{-1}s^{-1}$	R.61

Source: Adapted from Zhou *et al.* (2019)

An important factor to consider in the photolysis process of free chlorine is the fraction of hypochlorous acid and hypochlorite ions in solution, given that both compounds have different properties in their quantum yields and molar absorption coefficients. In this way, pH plays a significant role in determining the process of free chlorine removal by photolysis. Thus, the fraction of hypochlorous acid can be simplified using Equation 7 (Feng *et al.* 2007).

$$f = \frac{[HOCl]}{[OCl^-] + [HOCl]} = \frac{1}{1 + 10^{pH - pK_a}} \quad (7)$$

The lower the pH of the solution, the more strongly the properties of hypochlorous acid will affect the photolysis process, given its higher presence in the solution. At higher pHs, the properties of the hypochlorite ion will dominate the process due to the decrease in the fraction of HOCl in the medium (Feng *et al.* 2007).

6. Variables and Factors of Interference in the Process

Due to its relevance to water treatment, along with the associated environmental impact, the photolysis of free chlorine has been widely studied, especially concerning the use of radicals formed in the process to degrade micropollutants. In the laboratory context, several parameters and factors influence the study of photolysis, ranging from the chemical characteristics of the solution to the configuration of the equipment used in the research. The main factor, therefore, be discussed, highlighting the significant aspects of the process.

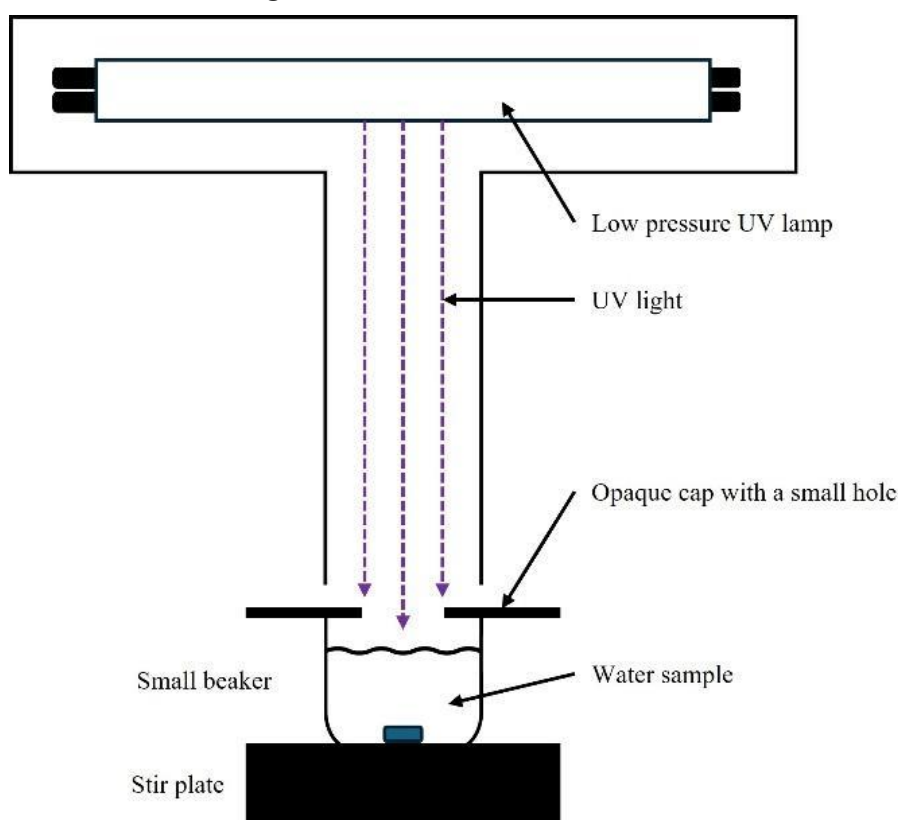
6.1 Reactor Model

The reactors used in the study of photolysis are essential for carrying out experiments to ensure that reliable data is obtained, which is necessary for modeling, simulating, and applying the process on a large scale. It is from this equipment that control of the operating conditions becomes possible, allowing simulation both in idealized conditions and in real situations.

A reactor model widely used in photochemical studies is the collimated beam reactor. Many studies in the field use this reactor model to obtain photolysis parameters, where the precision of the radiation applied directly influences the kinetics of the reaction (Bolton & Stefan, 2002; Feng *et al.*, 2007; Watts & Linden, 2007; Jin, *et al.*, 2011; Weng, Li, & Bletchley, 2012; Weng *et al.*, 2013; Fang *et al.*, 2014; Kong *et al.*, 2016; Astuti *et al.*, 2017; Wang *et al.*, 2017; Yin *et al.*, 2018; Castro *et al.*, 2021; Cobo-Golpe *et al.*, 2022; Li *et al.*, 2022).

The collimated beam is an experimental bench in which beams of light, usually in the ultraviolet or visible spectrum, are irradiated onto a liquid sample. Its configuration usually includes a radiation source, an optical system for collimation, an irradiation chamber, and sensors for monitoring the light intensity, guaranteeing high reproducibility of the experiments, as exemplified in Figure 1 (Bolton & Stefan, 2002; Feng *et al.*, 2007).

Figure 1 - Scheme of a collimated beam.



Source: Adapted from Feng *et al.* (2007).

Usually, the irradiance emitted in these systems is measured using a calibrated radiometer. However, in a homogenized solution, kept in constant agitation, the appropriate variable to consider is the average fluence rate (E'_{avg}), which must be corrected based on the properties of the system under study (Bolton & Stefan, 2002).

In a system with monochromatic light emission, where the radiometer has been calibrated according to the wavelength emitted, the average fluence rate is given by Equation 8.

$$E'_{avg} = E_0 \cdot PF \cdot RF \cdot WF \cdot DF \quad (8)$$

Where PF is the Petri Factor, which takes into account the non-idealities of the dish, RF is the Reflection Factor between the air and water interfaces ($RF = 0.975$), WF is the Water Factor, which considers the attenuation of the fluence rate due to the absorption of water, DF is the Divergence Factor, given the divergence of the light rays, and E_0 is the irradiance read on the

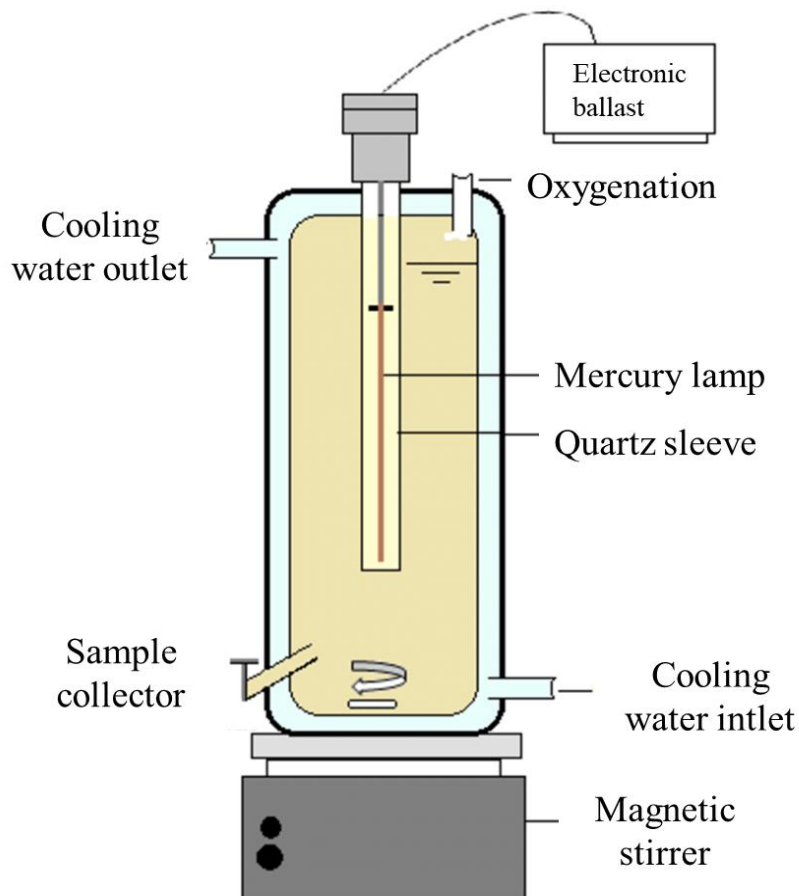
calibrated radiometer, measured at the center of the sample, where the detector must be placed at the same height at the level of the top of the solution (Bolton & Stefan, 2002).

Although this model of reactor avoids optical interference and ensures uniform distribution of radiation over the solution, the construction of this type of bench is costly and often requires specialized equipment. In addition, small misalignments can compromise the uniformity of the study, requiring strict control during experimental execution.

Another reactor model used in the photolysis study is the cylindrical UV reactor with a submerged lamp. These reactors are widely used in academic research and in the development of new technologies focused on water treatment (Cimetiére & Laat, 2014; Guo *et al.*, 2017; Wu *et al.*, 2017; Guo *et al.*, 2018; Zhou *et al.*, 2019; Giroletti *et al.*, 2022). They are a practical alternative for laboratory experiments when seeking greater interaction between UV radiation and the target compounds. A very similar reactor model was proposed by Shulga, Devi, and Dalai (2021) to study the decay of inorganic chloramines under medium-pressure ultraviolet lamp irradiation.

This reactor model, constructed from either glass or stainless steel, has a larger volume compared to the samples studied in the collimated beam setup. In the latter, despite small withdrawals for analysis, the volume can be considered constant. The radiation source is positioned in the center of the reactor and protected by a quartz tube to separate the electrical equipment from the water. To ensure a uniform radiation dose throughout the solution, the reactor is continuously stirred using a magnetic stirrer. A schematic representation of this reactor is provided in Figure 2 (Cimetiére & Laat, 2014; Guo *et al.*, 2017; Guo *et al.*, 2018; Zhou *et al.*, 2019; Giroletti *et al.*, 2022).

Figure 2 – Scheme of a Photolysis Reactor with submerged light.



Source: Giroletti *et al.* (2022).

The UV intensity and effective path length of the reactor can be determined through the actinometry process of some compounds. Zhou *et al.* (2019) used atrazine as the target compound for determining the UV intensity in the reactor, followed by defining the effective optical length through the photodegradation of hydrogen peroxide. Conversely, the determination of the photon flux emitted by the UV lamp in the photolysis reactor was carried out by Cimetiere and Laat (2014) through the photodegradation of hydrogen peroxide as the probe compound. Due to the crystalline nature of the solution used during the experiments, the effective optical length was assumed to be the distance between the quartz tube and the inner wall of the reactor.

Cimetiere and Laat (2014) determined the photon flux within the reactor from the slope of the hydrogen peroxide decay curve during photolysis. Equation 9 was applied under high hydrogen peroxide concentrations (100 mM), whereas Equation 10 was employed for very low concentrations of the probe compound (50 μ M).

$$[H_2O_2]_t = [H_2O_2]_0 - \Phi_{254} \frac{I_0}{V} \cdot t \quad (9)$$

$$\frac{-d[H_2O_2]}{dt} = k_{app} \cdot t = \ln \ln (10) \cdot L \cdot \epsilon_{254} \cdot \Phi_{254} \frac{I_0}{V} \cdot t \quad (10)$$

In both cases, the pseudo first-order rate constant of the photodegradation of the target compounds is obtained from the slope of the chemical decay line, making the process of determining the radiation dosage more complex (Cimetiere & Laat, 2014; Zhou *et al.*, 2019).

6.2 Solution pH

As described in Equation 7, the fraction of each chemical species that makes free chlorine strongly depends on pH. Due to the different properties of each species, the balance of chemical species alters the efficiency of UV radiation absorption.

As a weak acid, with a pK_a of 7.5 at 20°C, HOCl can dissociate, giving rise to the hypochlorite ion (OCl^-). As the pH of the aqueous solution increases above 7.5, the concentration of free chlorine in the form of the hypochlorite ion becomes more prominent than that of free chlorine in the form of hypochlorous acid (Leong, Kuo & Tang, 2008; Black & Veatch Corporation, 2009; Li *et al.*; 2022).

The products resulting from the photolysis of each species are also altered depending on the pH. At acidic pH, greater quantities of hydroxyl radicals (HO^\bullet) are formed. Oxygen monoatomic radicals (O^\bullet) are generated in higher concentrations at alkaline pH (Remucal & Manley, 2016; LI *et al.*, 2022).

The influence of pH on chlorine photolysis, as well as the type of lamp applied in the treatment, was observed by Cho *et al.* (2016). In their studies, the process of chlorine removal at different pH was investigated using LP, MP, and VUV lamps, in which vacuum UV (VUV) lamps are modifications of low-pressure lamps that are capable of emitting radiation at a wavelength of 185 nm.

The use of higher energy photon emission lamps allowed the dechlorination process to take place more quickly in all pHs. Thus, the VUV lamp proved most effective, followed by the MP lamp due to its higher photon emission, and lastly, the LP lamp. Similar observations regarding the effectiveness of medium-pressure UV lamps were made by Cassan *et al.* (2006) and Astuti *et al.* (2017). Meanwhile, chlorine removal proved to be more effective at acidic pH since the yield of radical formation is higher in the presence of hypochlorous acid when compared to the formation provided by the hypochlorite ion (Cho *et al.* 2016).

6.3 Quantum Yield

Quantum yield (Φ) is used as a measure of the efficiency of converting light energy into a desired product. This parameter quantifies the amount of free chlorine consumed or photo-degraded per photon absorbed during photolysis (Feng *et al.*, 2007; Jin *et al.*, 2011).

To quantify the quantum yield of free chlorine, Feng *et al.* (2007) carried out a series of experiments in which the photodegradation of chlorine was monitored. The results showed that at acidic pH and for chlorine concentrations below 71 mg/L, the quantum yield of free chlorine was constant, with a value of 1.0 ± 0.1 . However, for concentrations above 71 mg/L, the quantum yield increases linearly with a slope of $0.0025 \text{ (mg Cl/L)}^{-1}$. In contrast, the quantum yield obtained at alkaline pH and a wide range of concentrations was constant, with a value of 0.9 ± 0.1 .

In the presence of organic matter, the quantum yield of hypochlorous acid tends to increase to values above 1, ceasing to be a primary quantum yield generated by the absorption of light and indicating the influence of subsequent chain reactions. In experiments carried out by Jin *et al.* (2011), the addition of methanol (CH_3OH) to a chlorinated solution led to an increase in the quantum yield of HOCl as the concentration of CH_3OH increased, ranging from 1.0 to 16.3 as the concentration of methanol increased. This phenomenon was observed due to the chain reactions generated with the organic matter present, consuming the free chlorine available. However, the same effect was not observed in tests with OCl^- , which remained at 1.15 for the various methanol concentrations

By using LED lamps with emission peaks of 265 nm and 280 nm, Li *et al.* (2022) obtained different quantum yields for hypochlorous acid and hypochlorite ion. Table 2 shows the observable quantum yields, which consider both direct and indirect photolysis, as well as the quantum yields inert to the compounds.

Table 2 - Observable and inert quantum yields of free chlorine obtained through photolysis at 265 nm and 280 nm.

Quantum yield	LED 265 nm		LED 280 nm	
	HOCl	OCl^-	HOCl	OCl^-
Φ_{observed}	$1,59 \pm 0,18$	$0,82 \pm 0,11$	$1,46 \pm 0,20$	$0,72 \pm 0,07$
Φ_{inert}	0,88	0,45	0,83	0,40

Source: Adapted from Li *et al.* (2022).

The inert quantum yields were calculated by optimizing mathematical models to separate the direct and indirect photolysis processes, thus obtaining only the effect of radiation at different wavelengths on the process. Again, the presence of subsequent chain reactions was noticed due to the difference between the observable and inert quantum yields, where HOCl decay through these reactions contributed 41.3% and 35.2% at the respective wavelengths of 265 nm and 280 nm. For OCl^- , the contribution of the chain reactions was 35.7% for 265 nm and 37.5% for 280 nm. (Li *et al.*, 2022). Table 3 shows this compilation of distinct quantum yields obtained in different studies, comparing the results obtained experimentally.

Table 3 - Comparison of observable quantum yields for chemical species available in the literature.

Observable Quantum Yield		λ (nm)	[Cl ₂] (mM)	Reference
HOCl	OCl ⁻			
1,0 ± 0,1	0,9 ± 0,1	254	< 2	Feng <i>et al.</i> , 2007
1,5	1,3	254	0,014 ~ 0,056	Watts and Linden, 2007
1,0 ± 0,1	1,15 ± 0,08	254	1,41	Jin <i>et al.</i> , 2011
1,45 ± 0,06	0,97 ± 0,05	254	0,01 ~ 0,1	Fang <i>et al.</i> , 2014
1,11 ± 0,03	0,97 ± 0,01	268	0,1	Yin <i>et al.</i> , 2018
1,97	0,8	275	0,07	Kwon <i>et al.</i> , 2018
0,98 ± 0,02	0,82 ± 0,02	282	0,1	Yin <i>et al.</i> , 2018
-	0,87 ± 0,01	303	0 ~ 4,23	Chan <i>et al.</i> , 2012
1,59 ± 0,18	0,82 ± 0,11	265	0,042	Li <i>et al.</i> , 2022
1,46 ± 0,20	0,72 ± 0,07	280	0,042	Li <i>et al.</i> , 2022

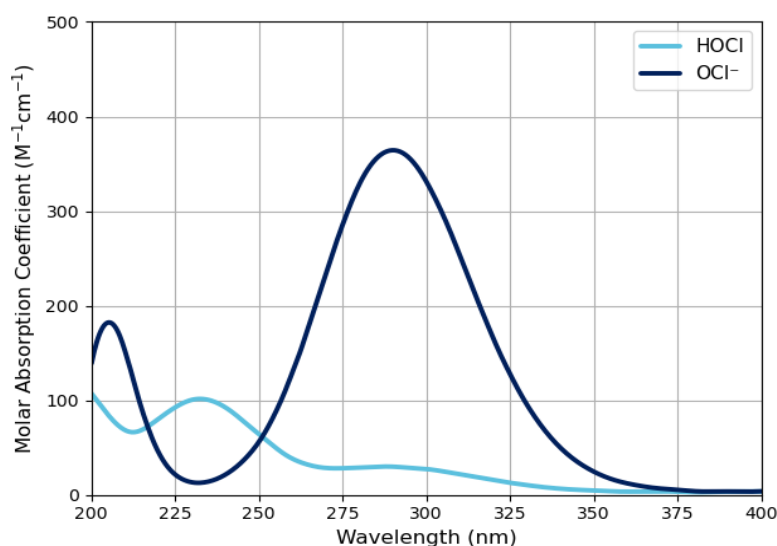
Source: Adapted from Li *et al.* (2022).

6.4 Molar Absorption Coefficient

As pointed out by Laat and Stefan (2018), free chlorine, in the form of HOCl and OCl⁻, can absorb ultraviolet light at wavelengths between 200 and 375 nm. As such, these species have the ability to undergo photolysis by UV-C, UV-B, and UV-A light. The molar absorption coefficient is a variable that quantifies a molecule's ability to absorb radiation emitted at a specific wavelength (Nowell & Hoigné; 1992a; Stefan, 2018).

Hypochlorous acid has an absorption peak at a wavelength of 236 nm, where it has a molar absorption coefficient equivalent to $101 \pm 2 \text{ M}^{-1}\text{cm}^{-1}$, while the hypochlorite ion has a molar absorption coefficient of $365 \pm 8 \text{ M}^{-1}\text{cm}^{-1}$, at a wavelength of 292 nm. (Feng *et al.*, 2007; Laat and Stefan, 2018; Li *et al.*, 2022). Figure 3 shows the absorption spectrum of hypochlorous acid and hypochlorite ions in solution under ultraviolet irradiation.

Figure 3 - Absorption spectra of hypochlorous acid and hypochlorite ion.



Source: Adapted from Feng *et al.* (2007).

However, the molar absorption coefficient values decreased for the wavelengths of a monochromatic light source. Feng *et al.* (2007) determined that the molar absorption coefficients for HOCl and OCl⁻ at 253.7 nm are, respectively, 59 ± 1 and $66 \pm 1 \text{ M}^{-1}\text{cm}^{-1}$, showing the influence of the emitted wavelength on the photolysis process of free chlorine compared with the emission peaks.

Table 4 shows a comparison between different absorption coefficients of both hypochlorite ion and hypochlorous acid, obtained experimentally, with the emission of ultraviolet radiation at different wavelengths.

Table 4 - Molar absorption coefficients of free chlorine at different wavelengths.

$\epsilon_{235} (\text{M}^{-1}\text{cm}^{-1})$		$\epsilon_{292} (\text{M}^{-1}\text{cm}^{-1})$		$\epsilon_{254} (\text{M}^{-1}\text{cm}^{-1})$		Reference
HOCl	OCl ⁻	HOCl	OCl ⁻	HOCl	OCl ⁻	
-	368	121	155	Nowell e Hoigné (1992b)		
100	350	62	58	Morris (1966)		
105	-	-	60	Thomsen <i>et al.</i> (2001)		
-	362	-	-	Chen (1967)		
101 ± 2	365 ± 8	59 ± 1	66 ± 1	Feng <i>et al.</i> (2007)		

Source: Adapted from de Feng *et al.* (2007).

The impact of the molar absorption coefficient was verified during the experiments by Li *et al.* (2022) by establishing the influence of wavelength on the photolysis process of free chlorine. First-order rate constants based on radiation fluency were evaluated by exposing chlorine solutions to LED lamps emitting wavelengths of 265 and 280 nm.

It was then noticed that the photolysis rate constant for hypochlorous acid at 265 nm was slightly higher than the constant obtained with the 280 nm lamp. However, the rate obtained for the hypochlorite ion was much more pronounced at the wavelength of 280 nm, where it was closer to the molar absorption peak of the hypochlorite ion, thus demonstrating that the photolysis process of free chlorine, as well as being pH-dependent, is also dependent on the wavelength emitted by the light source (Li *et al.*, 2022).

6.5 Water Matrix

Multiple reactions can follow the photolysis of free chlorine through the formation of hydroxyl, chlorine, and oxygen radicals so that their concentrations, as well as the products that formed them, govern subsequent reactions. Although the actual mechanism of free chlorine photolysis reactions is little known, the presence of other compounds in water significantly affects the process, leading to the consumption of free chlorine or the formation of other by-products (Watts & Linden, 2007; Cimetiere & Laat, 2014; Guo *et al.*, 2017).

In a dechlorination study of raw seawater and artificially produced seawater, it was found that organic matter in the solution provided greater production of radicals, accelerating the removal of chlorine through indirect photolysis. Cho *et al.* (2016) observed that the dechlorination process is 25% faster in raw seawater than in simulated water, indicating a scavenging effect on free chlorine due to the presence of organic matter in the water. As theorized, the production of hydroxyl radicals and chlorine radicals induces the formation of organic radicals, which in turn react with and consume free chlorine.

The formation of bromine radical species can also be observed through the reaction of hydroxyl and chlorine radicals with the bromine present in the solution. In this way, bromine ions act as scavengers of these radicals, reducing their formation and generating new bromine-based radicals. In the presence of carbonates and bicarbonates, hydroxyl radicals also suffer from the scavenging effect provided by these substances (Guo *et al.*, 2018).

Although bromine radical species can act as sequestrants for Cl^{\bullet} , this effect is more noticeable for this radical in the presence of bicarbonate. The reaction of water and free chlorine itself with chlorine radicals has a more significant scavenging effect, making the radical's disappearance by Br^{\bullet} a negligible process (Guo *et al.*, 2018).

Studies by Cimetiere and Laat (2014) showed that the photodecomposition kinetics of free chlorine in water from public swimming pools does not follow first-order kinetics due to the indirect photolysis caused by the presence of organic matter, which has a scavenger effect on free chlorine. On the other hand, the kinetics observed in runs with ultrapure and tap water from Poitiers, France, followed identical, first-order kinetics about free chlorine, indicating that the water matrix with low chemical concentrations has little effect on the process.

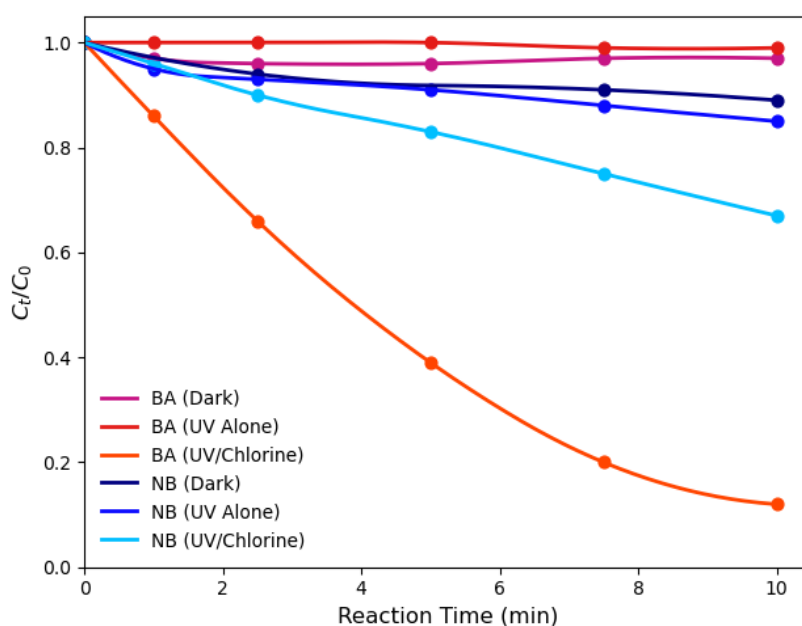
7. Free Radical Production

After breaking the bonds between hypochlorous acid and hypochlorite ion, the by-products formed are highly reactive radicals, leading to a series of chain reactions up to the formation of less reactive and more stable compounds. Although little is known about the reaction mechanism involved in the process, it is known that the recombination rate of the photoproducts generated from the photolysis of HOCl is relatively low. However, the rate of reaction between HO^{\bullet} and OCl^{\bullet} makes free chlorine an important free radical scavenger (Watts & Linden, 2007).

The use of probing compounds, so that the steady-state concentration of chlorine (Cl^{\bullet}) and hydroxyl (HO^{\bullet}) radicals can be determined, are widely used in research in this field. Thus, the production of these radicals is often monitored through the degradation of nitrobenzene (NB), a chemical degraded predominantly by the hydroxyl radical, and the degradation of a non-selective chemical, such as benzoic acid (BA) or p-chlorobenzoic acid (pCBA).

Wang *et al.* (2017) applied both nitrobenzene and benzoic acid to estimate the rate of formation of hydroxyl and chlorine radicals. In the study, the degradation of the compounds was analyzed considering their volatilization, photodegradation by UV radiation, and oxidation by the radicals formed. Figure 4 shows the results obtained, demonstrating the degradation kinetics of nitrobenzene (NB) and benzoic acid (BA) by the three mechanisms.

Figure 4 - Degradation kinetics of nitrobenzene (NB) and benzoic acid (BA) using different degradation sources.



Source: Adapted from Wang *et al.* (2017).

In aqueous solution, the degradation of NB can be attributed to oxidation by the hydroxyl radical ($k_{OH-NB} = 3,9 \times 10^9 \text{ mol/L.s}$), by its volatilization ($k_{vol-NB} = 0,013 \text{ min}^{-1}$) and direct photolysis ($k_{foto-NB} = 0,005 \text{ min}^{-1}$), where the reaction with chlorine radicals can be neglected. Based on the first-order kinetics of nitrobenzene degradation, it is possible to determine the concentration of the hydroxyl radical using Equation 11 (Wang *et al.* 2017).

$$C_{OH^*} = \frac{k_{obs} - k_{vol,NB} - k_{photo,NB}}{k_{\bullet OH,NB}} \quad (11)$$

The degradation of benzoic acid is attributed to both the oxidation of the hydroxyl radical ($k_{OH-BA} = 5,9 \times 10^9 \text{ mol/L.s}$) and the chlorine radical ($k_{Cl-BA} = 1,8 \times 10^{10} \text{ mol/L.s}$), but its degradation by volatilization or direct photolysis is very slow and can be ignored. Therefore, based on the BA degradation kinetics, and knowing the concentration of hydroxyl produced, it is possible to estimate the concentration of the chlorine radical using Equation 12 (Wang *et al.* 2017).

$$C_{Cl^*} = \frac{k_{obs} - k_{\bullet OH,BA} \cdot C_{OH^*}}{k_{Cl^*,BA}} \quad (12)$$

Watts and Linden (2007) observed the rate of hydroxyl radical formation through the degradation of p-chlorobenzoic acid (pCBA) and nitrobenzene. Both compounds are known to have high rates of reaction with the hydroxyl radical ($k_{OH-pCBA} = 5 \times 10^9 \text{ mol/L.s}$ e $k_{OH-NB} = 3,9 \times 10^9 \text{ mol/L.s}$), while their rates of degradation by photolysis can be disregarded.

During tests carried out by Guo *et al.* (2018), it was found that the concentration of HO[•] after the hydrogen peroxide photolysis process was 36.8% higher than the concentration of the radical after the chlorine photolysis process. This was due to the higher reaction rates between the hydroxyl radicals and the free chlorine itself ($k_{OH-HOCl} = 2,0 \times 10^9 \text{ mol/L.s}$ e $k_{OH-OCl^-} = 8,8 \times 10^9 \text{ mol/L.s}$) compared to hydrogen peroxide ($k_{OH-H_2O_2} = 2,7 \times 10^7 \text{ mol/L.s}$).

The formation of radicals by the probe compounds nitrobenzene and benzoic acid was also monitored by Li *et al.* (2022). The benzoic acid degradation process allowed steady-state concentration to be analyzed to understand the effect of pH on chlorine photolysis. Table 5 compiles the results estimated in the research for the photolysis of free chlorine at various pH levels using an LED lamp emitting 265 nm.

Table 5 - Estimation of radical concentration (M) by chlorine photolysis at 265 nm.

Radical	pH 5.0	pH 7.0	pH 7.5	pH 8.0	pH 10.0
HO [•]	$1,09 \times 10^{-13}$	$4,57 \times 10^{-14}$	$3,31 \times 10^{-14}$	$2,79 \times 10^{-14}$	$3,22 \times 10^{-14}$
Cl [•]	$6,15 \times 10^{-15}$	$7,1 \times 10^{-15}$	$8,04 \times 10^{-15}$	$8,71 \times 10^{-15}$	$2,42 \times 10^{-15}$
ClO [•]	$6,31 \times 10^{-10}$	$8,34 \times 10^{-10}$	$9,7 \times 10^{-10}$	$1,08 \times 10^{-09}$	$1,18 \times 10^{-09}$

Source: Li *et al.* (2022).

In general, the production of the HO[•] radicals decreased as the pH of the solutions increased. This drop is since chlorine is produced more in the form of hypochlorite ion due to the increase in pH, acting as a greater radical scavenger due to its higher rate constant when compared to hypochlorous acid ($k_{OH-OCl^-} = 8,8 \times 10^9 \text{ mol/L.s}$ e $k_{OH-HOCl} = 5 \times 10^8 \text{ mol/L.s}$). The reduction in radical formation, to the detriment of the increase in pH, ended up affecting the BA degradation process, reducing its efficiency. (Yin *et al.*, 2018; Li *et al.*, 2022).

An increase in the production of the Cl^{\bullet} radicals was observed between pH 5 and 8, being significantly intensified at a wavelength of 280 nm due to the ion's higher molar absorption coefficient. At pHs above 8, a reversal of the process was observed in which, through the formation of the intermediate radical ClOH^{\bullet} , the chlorine radical is converted into a hydroxyl radical. (Li *et al.*, 2022).

In research carried out by Fang *et al.*, 2014, and Kong *et al.*, 2016, the use of nitrobenzene and benzoic acid as probe compounds also turned out to be essential for monitoring the formation of radicals generated by the free chlorine photolysis process. Cobo-Golpe *et al.* (2022) maintained the use of nitrobenzene as a probe compound but opted to use p-chlorobenzoic acid to determine the rate of formation of chlorine radicals, as done by Jin *et al.* (2011) and Yin *et al.* (2018) used carbamazepine instead of non-selective compounds.

8. Industrial Applications of UV Photolysis of Free Chlorine

The application of ultraviolet light for the removal of free chlorine in water treatment systems has been consolidated as an efficient and non-chemical alternative in different industrial contexts. The use of these systems is particularly noteworthy in power plants and processes that use reverse osmosis or ion exchange demineralization systems for water treatment. Traditionally, dechlorination is performed by adding sodium bisulfite or using activated carbon. However, these approaches have limitations, such as the risk of incorrect dosing, proliferation of microorganisms, high operating costs, and greater maintenance requirements (Preece & Breckenridge, 2019).

Some studies have demonstrated the effectiveness of UV technology as a mechanism for removing free chlorine on an industrial scale. A notable case was performed at Southern Company's Bowen Plant (USA). Full-scale tests showed that the concentration of free chlorine in the feed water of the reverse osmosis system, initially above 1 ppm, was reduced to undetectable levels (<0.01 ppm) after UV application, ensuring protection of the membranes and extending their service life (Breckenridge, 2014; Preece & Breckenridge, 2019; Atlantium, 2020a).

Another relevant example was recorded at a power plant located in North America, with a production capacity of up to 307 MW. At this plant, replacing activated carbon filters with UV filters allowed free chlorine to be reduced to levels below 0.02 ppm, protecting the ion exchange resins used in demineralization (Atlantium, 2020b).

At a thermal power plant located in Alabama, the feed water contained approximately 0.2 ppm of free chlorine. With the application of two UV systems arranged in series, one for disinfection and the other for dechlorination, residual chlorine was eliminated to undetectable levels, enabling safe operation of the reverse osmosis system and protection of the membranes (Atlantium, 2024a).

In the industrial sector, the UV chlorine removal system was used at Archer Daniels Midland in Texas, where the use of municipal water containing approximately 4,0 ppm of chloramines was damaging the reverse osmosis system used to produce water for lime slurry. With the UV system, concentrations were reduced significantly, enabling stable operation of a 50 MW boiler and preventing biological fouling (Atlantium, 2024b).

These are some cases that demonstrate that the application of UV in the removal of free chlorine offers a robust, sustainable, and safe solution capable of protecting reverse osmosis membranes and ion exchange resins, reducing operating costs, and eliminating the need for additional chemicals. Additionally, the technology ensures the reduction of free chlorine to undetectable levels or below the recommended limits for equipment protection, combining technical efficiency and operational safety.

9. Advanced Oxidation Process Application

In recent years, a growing concern with the removal of emerging micropollutants has gained attention. Pharmaceuticals, personal care products, endocrine-disruptive chemicals, antibiotics, and disinfection by-products are gaining attention, where even at very low concentrations, they already have adverse effects on the environment and pose risks to human health. These pollutants are typically not degraded by conventional processes, making alternative treatment methods necessary (Blatchley, 2023).

Advanced oxidative processes (AOP) are based on the generation of highly reactive intermediate radicals whose function is to initiate reactions that would not normally take place or would take a long time to happen. The radicals produced are highly reactive and quickly oxidize micropollutants by thermochemical reactions, mineralizing them into less reactive compounds. The radiation dose commonly applied for water and wastewater disinfection, such as the 40 mJ/cm² recommended by the U.S. Environmental Protection Agency (2006), is effective for microbial inactivation but negligible for chlorine molecule degradation. In contrast, advanced oxidation processes require significantly higher radiation doses, exceeding those applied solely for disinfection, in order to promote radical generation. At these fluence levels, in addition to radical formation, complete disinfection of the treated effluent is also achieved (Ormezi *et al.*, 2005; Bitter & Rozenberg, 2017; Zhou *et al.*, 2019; Blatchley, 2023).

In many AOPs, the hydroxyl radical is the first product formed, making it a benchmark oxidant for these processes. HO[•] reacts with a variety of compounds at rates approaching the diffusion limit, as it is a powerful oxidant, with a standard electrode potential (E^0) of approximately 2.73 V. More recently, the use of UV combined with free chlorine has been gaining ground in industrial studies and applications (Blatchley, 2023).

The potential use of chlorine as a substitute for hydrogen peroxide as a source of radical generation has been highlighted due to its ability to overcome the limitations of the latter. Given the need to remove residual H₂O₂ from the process and its low absorption coefficient value, free chlorine has become an excellent substitute. Not only is it not necessary to remove the residual chlorine present after treatment, but the molar concentration of free chlorine required to achieve a given level of treatment in the UV/Chlorine process tends to be lower than the corresponding molar concentration of hydrogen peroxide required in the UV/H₂O₂ process. Therefore, the advantages of using free chlorine as a free radical generating source are based on the low cost of chemicals, higher treatment efficiency with lower reagent consumption, shorter treatment times, better energy efficiency due to the excellent UV light absorption characteristics of HOCl/OCl⁻, and easy implementation in chlorine disinfection systems (Zhou *et al.*, 2019; Blatchley, 2023).

Although the chlorination process is efficient in degrading compounds containing aniline groups, primary amines, reduced sulfur groups, pyrimidine, and tertiary amines substituted by electrophilic groups, its use alone results in considerably lower degradation kinetics for contaminants containing amide, imide, and azide groups, due to the low reactivity of chlorine towards these chemical structures. In this context, the combination of chlorination with ultraviolet radiation appears to be a promising alternative for the removal of emerging contaminants, whose effectiveness depends directly on the molecular structure of the compound. It should be noted that reactive chlorine radicals (Cl[•], Cl₂^{-•}, and ClO[•]) favor the degradation of molecules containing electron-donating functional groups, such as amine, hydroxyl, alkoxy, alkyl, and acyl (Yeom *et al.*, 2021).

It is important to emphasize the selective behavior of chlorine radicals observed by Guo *et al.* (2017). While the HO[•] radical tends to be non-selective during oxidation, Cl[•] reacts more quickly with benzoic acid, chlorobenzene, and phenols. On the other hand, the Cl₂^{-•} radical tends to be selective with olefins and aromatic compounds, such as hydroxyl, methoxy, or amino functional groups, and ClO[•] reacts quickly with methoxy-substituted aromatic compounds. In agreement, Wu *et al.* (2017) complement the preference of the Cl[•] radical to react with aromatic substitutes, such as toluene and anilines.

Chlorine, as a radical-generating source in the presence of UV light, is extremely effective in degrading various emerging micropollutants, making it a promising solution for treating water and effluents. The combination of ultraviolet radiation and chlorine enhances the formation of reactive species such as hydroxyl radical and chlorine radicals, which have high reactivity and the ability to mineralize complex organic compounds. The UV/Chlorine process was applied to degrade a variety of micropollutants, such as pharmaceutical and personal care products, amines, dyes, pesticides, and others (Xu, 2025). Table 6 shows a compilation of various micropollutants degraded using the UV/Chlorine process in different studies.

Table 6 - Micropollutant degradation through the UV/Chlorine advanced oxidative process.

Pollutant	Fluence Rate	[Chlorine]	pH	Reference
Methanol, p-chlorobenzoic acid, Cyclohexanoic acid	0.38 mW/cm ²	50 mg/L	5 -10	Jin <i>et al.</i> , 2011
Benzoic acid	0,58 mW/cm ²	10 - 100 µM	6 - 7.5 -9	Fang <i>et al.</i> , 2014
Atrazine	0.15 mW/cm ²	70 µM	5 - 7 - 9	Kong <i>et al.</i> , 2016
Carbamazepine	1.48 mW/cm ²	280 µM	7	Wang <i>et al.</i> , 2016
Ibuprofen	1.05 mW/cm ²	100 µM	6	Xiang <i>et al.</i> , 2016
Chloramphenicol	2.10 mW/cm ²	50 µM	7	Dong <i>et al.</i> , 2017
34 types of PPCPs	mW/cm ²	10 - 20 µM	6 - 7 - 8	Guo <i>et al.</i> , 2017
DDBAC	2.60 mW/cm ²	50 mg/L	3.6 - 7 - 9.5	Huang <i>et al.</i> , 2017
Natural organic matters (chromophres and fluorophores)	1.80 mW/cm ²	50 mg/L	7	Wang <i>et al.</i> , 2017
Metroidazole, Diethyltoluamide, Nalidixic acid, Caffeine	0.80 mW/cm ²	50-100-150 µM	6 - 7 - 8.4	Wu <i>et al.</i> , 2017
Phenacetin	0.059 mW/cm ²	300 µM	7.2	Zhu <i>et al.</i> , 2017
28 types of PPCPs	0.78 mW/cm ²	10 - 20 - 50 µM	6 - 7 - 8	Guo <i>et al.</i> , 2018
Ciprofloxacin	0.40 mW/cm ²	100 µM	7	Deng <i>et al.</i> , 2018
Benzoic acid compounds	1.97 x 10 ⁻⁶ E/L.s	0.5 - 1 - 2 - 4 mg/L	7.2	Zhou <i>et al.</i> , 2019
Brilliant Blue FCF	1.10 mW/cm ²	600 µM	3 - 11	Nikravesch <i>et al.</i> , 2020
Atenolol	3,1 mW/cm ²	100 µM	-	Gao <i>et al.</i> , 2020
Valsartan acid	1.16 x 10 ⁻⁶ E/L.s	2 - 5 - 7 - 10 mg/L	6 - 9	Castro <i>et al.</i> , 2021
Tramadol	1.04 x 10 ⁻⁶ E/L.s	1 - 10 mg/L	7	Gobo-Golpe <i>et al.</i> , 2022
Trimethoprim	0.247 mW/cm ²	3 - 6 mg/L	6 - 9	Teo <i>et al.</i> , 2022

Source: Authors.

Besides the high efficiency of the process, resulting from the high synergy between free chlorine and UV light, the process is highly flexible in its application and can be used to degrade a variety of compounds that are not degraded by the presence of HO[•] alone. Additionally, it helps reduce unwanted by-products, such as trihalomethanes, haloacetic acids, and other organochlorine compounds, although their formation may still occur under certain conditions (Wang *et al.*, 2017; Gou *et al.*, 2018; Zhou *et al.*, 2019).

However, it is essential to note that the reaction of free chlorine with various species of organic matter and nitrogen compounds present in water can lead to the formation of organochlorine by-products, which pose potential risks to human health

and the environment. Studies on the application of the UV/Chlorine process as an advanced oxidation technology highlight its effectiveness in removing emerging contaminants; however, they also report the formation of potentially hazardous compounds, such as trihalomethanes, haloacetic acids, haloacetamides, trichloramine (NCl₃), dichloromethylamine (CH₃NCl₂) and cyanogen chloride (CNCl). Therefore, the assessment of free chlorine removal efficiency must be accompanied by a critical analysis of secondary by-product formation, to ensure both the safety and the final quality of the treated water (Weng *et al.*, 2013; Cimetiere & Laet, 2014; Wang *et al.*, 2017; Kishimoto, 2019; Khajouei *et al.*, 2022).

10. Conclusion

Water treatment methods have been widely studied for decades, with chlorination established as one of the most widely used approaches for ensuring microbiological safety and effective disinfection. However, even at low concentrations, chlorine poses risks to marine and estuarine ecosystems. In addition, the increasing demand for industrial applications requiring ultrapure water, such as in the semiconductor, pharmaceutical, and cosmetics sectors, emphasizes the limitations of free chlorine, which can induce undesirable reactions. Its presence is also detrimental to systems and equipment, as it accelerates metal oxidation processes.

Ultraviolet (UV) dechlorination has emerged as a promising alternative, providing complete water disinfection while acting as a multi-barrier process. This method prevents biofilm formation, improves water quality, eliminates the need for chemical additives, and promotes the degradation of organic matter, reducing total organic carbon levels.

In this review, we present the application of photolysis for the removal of free residual chlorine from water. The discussion covers the principles of ultraviolet photolysis, the underlying mechanisms, and the operational parameters that influence efficiency. Industrial applications are also highlighted, with emphasis on the role of UV photolysis in advanced oxidation processes.

In conclusion, this review demonstrates the potential of UV photolysis as a robust and versatile dechlorination strategy capable of addressing both environmental and industrial challenges. By consolidating current knowledge and identifying key operational considerations, we aim to provide a comprehensive reference for future research and practical implementation, thereby advancing the development of sustainable and efficient water treatment technologies.

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