Chapter 1
Photocatalysis: Introduction, Mechanism, and Effective Parameters

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Abstract The widely investigated heterogeneous photocatalysis offers an environmentally friendly, efficient, and versatile solution for several environmental problems. Among others, the removal of harmful organic pollutants and the generation of H_2 via water splitting are well-known and most widely studied applications. The process is based on the charge separation caused by the excitation of semiconductor photocatalyst via photon absorption. Due to the intensive development of material science, in addition to the well-known TiO_2 and ZnO, several new semiconductor materials have been designed and synthesized to increase the efficiency of heterogeneous photocatalysis and utilization of solar and/or visible light. This chapter describes the principles and mechanisms of heterogeneous photocatalysis, including the formation of photogenerated charge carriers, the role of different reactive species, and the effect of key parameters on the efficiency.

Keywords Advanced oxidation processes · Photogenerated charge carriers · Green photochemistry · Reaction parameters · Matrix effect

1.1 Introduction

1.1.1 Heterogeneous Photocatalysis for Environmental Applications

In the past decades, humanity started to face numerous emerging environmental problems, mainly related to transport, industrial, and agricultural activities. These problems require efficient and urgent solutions. The pollution of air and water with non-biodegradable pollutants may have unforeseeable consequences to the envi-

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ronment and may even endanger human health and life. These pollutants may be organic (e.g., pesticides, pharmaceuticals, hydrocarbons, dyes) or inorganic compounds, like heavy metals (e.g., chromium, mercury, lead), or other dissolved inorganic ions (e.g., nitrite, nitrate, arsenic) [1, 2]. The effect of these pollutants varies, several of them show toxic, carcinogenic, mutagenic, or have endocrine-disrupting effects (EDCs). They can accumulate in the ecosystem, so emissions below the limit values can also pose serious risks.

Advanced oxidation processes (AOPs) have been extensively investigated in the past decades, as they are a promising technique to solve and prevent many environment-related problems. The most well-known application of AOPs is the removal of trace amounts of organic, non-biodegradable pollutants, as classic biological-physical wastewater treatment methods are generally not adequate for this task [3]. AOPs are generally based on the in situ formation of reactive species that are able to oxidize many non-biodegradable pollutants. Some AOPs, like ozonation, Fenton-process, gamma-radiolysis combined with other methods (e.g., UV, O_3, H_2O_2) have been already established in water treatment plants, while many others are still many are still under further development [4]. One of the widely researched AOPs is heterogeneous photocatalysis.

Another serious issue is the excessive use of carbon-based fuels, which is responsible for the probably most well-known environmental problem of the last decades: global warming caused by the increased release of CO_2 and other greenhouse gases. Burning hydrocarbons and coal also contributes to the pollution of air with gaseous and solid pollutants, resulting in several environmental and health problems, like the formation of smog in densely populated and industrial areas. Another aspect of the problem is that reserves of coal and hydrocarbons are finite, and the search for accessible and cheap renewable substitutes is ongoing in the research field of alternative energies.

The fundamentals of green chemistry have been laid down in the 1990s, promoting environmentally friendly chemical processes. The principles of green chemistry aim primarily at the prevention of environmental and health hazards: the use of the least harmful chemicals, low waste production, and energy consumption [5, 6]. Since even today these principles are still not accomplished in many cases, and due to already occurred environmental damage, cost-effective solutions are still needed to reduce these problems. The use of catalysts is one of the key elements of green chemistry. Catalysts are materials used to increase reaction rates by introducing new reaction pathways with lower activation energies. Heterogeneous photocatalysis is a field of heterogeneous catalysis, in which a photochemical reaction is accelerated or initiated thanks to the presence of photocatalysts (generally semiconductors) and photons with appropriate energy to activate them. In the activated semiconductor particles, conduction band electrons $\left(e_{cb}^{-}\right)$ and valence band holes $\left(h_{vb}^{+}\right)$ are formed and initiate redox reactions with species adsorbed on the catalyst surface. In the presence of water and dissolved oxygen, the formation of different reactive species takes place, often leading to the formation of a highly reactive and non-selective oxidant, hydroxyl radical (HO$^{\bullet}$), which generally has an important role [7].

1.1.2 A Brief History of Heterogeneous Photocatalysis

The first mentions of photocatalytic reactions date back to the start of the twentieth century [8, 9], but they received wider attention after Fujishima and Honda displayed photocatalytic water splitting to produce hydrogen using a TiO_2 electrode [10]. Ever since, heterogeneous photocatalysis has received widespread scientific attention, thanks to the wide range of application possibilities. The number of studies investigating the mechanisms of photocatalysis, developing new photocatalytic materials, or otherwise incorporating photocatalytic materials into their work, is steadily growing. Many disciplines are related to the research of heterogeneous photocatalysis (Fig. 1.1). The application possibilities of heterogeneous photocatalysis seem limitless—they have been applied during selective oxidation/reduction in organic synthesizes, environmental application, self-cleaning surfaces, healthcare applications, and cancer treatment [11].

As mentioned earlier, photocatalytic processes can offer solutions to many problems, especially using the Sun as a light source, but they still face a number of challenges. A "perfect" photocatalyst needs to have several properties: it must be highly photoactive, chemically and biologically inert, withstand photocorrosion, non-toxic, inexpensive, and it must have the ability to be activated by solar light. TiO_2 meets most of these requirements, except it is primarily active in the UV region. Other photocatalytic materials often suffer from problems, like low stability or high production costs [12]. In the past decades, the modification of TiO_2 (or other effective photocatalyst) and the synthesis of new photoactive semiconductors are the keys to the application of heterogeneous photocatalytic processes under visible light irradiation. Efficient reduction of TiO_2's bandgap (below 2.5 eV), synthesis of new photocatalysts, enhancement of their photonic efficiency and/or activity are still great challenges [13].

Among these photoactive semiconductors, pristine metal-oxides such as TiO_2 and ZnO are often referred to as first-generation photocatalysts because they were
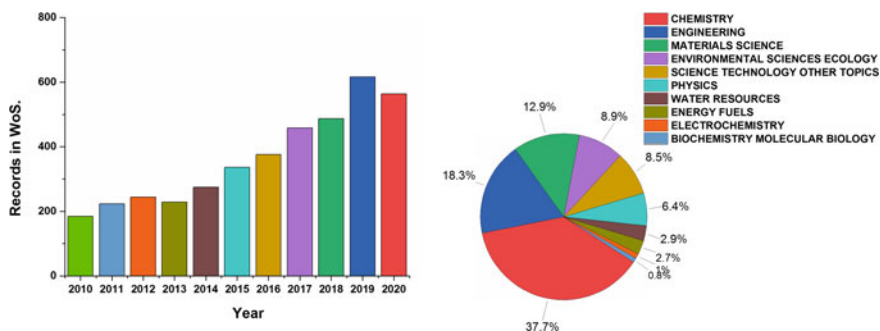
Fig. 1.1 Number of publications containing "heterogeneous photocatalysis" in the abstract, keywords, or title from 2010 to 2020, and their distribution among different fields of sciences. Data from Web of Science

the first semiconductors to be studied and applied in photocatalytic applications. These photocatalysts usually have bandgaps with energies higher than 3.1 eV (the wavelength of activating photons is lower than 400 nm) and therefore cannot be activated efficiently with solar irradiation—only 3–5% of the solar spectrum is in this range. Furthermore, the recombination of the charge carriers is a recurrent phenomenon in these first-generation photocatalysts, critically lowering their photonic efficiencies [12, 14–17].

Aiming to increase the sensitivity of these photocatalysts toward longer wavelengths as well as to reduce the recombination rate of the charge carriers, first-generation photocatalysts have been modified via several processes including elemental doping with metal and non-metal elements [18], dye sensitization [19], mesoporous structures [20], and creation of heterojunctions [12], giving rise to the second generation of photocatalysts. The doping process has received great attention and is considered an effective strategy to increase the efficiency of photocatalytic processes and extend light absorption [21]. In elemental doping, impurities are intentionally added to the structure of semiconductors [21]. The addition of phosphorous atoms to the structure of silicon semiconductors is one example of the addition of donor atoms, forming the n-type semiconductors (*n* represents the additional negative charge transferred by the donor atom). Similarly, the addition of acceptor, such as boron in silicon, results in p-type semiconductors [21, 22]. These modifications aim at better spectral sensitivity and photoactivity under exposure to sunlight. However, metal doping, for instance, can generate additional recombination or non-active absorption centers [15]. The incorporation of carbon nanotubes and graphene to semiconductors can increase adsorption sites for the substrates, serve as electron acceptors or channels to avoid charge carriers' recombination, and can induce the sensitization toward photons with higher wavelengths [12].

Another issue that has to be solved (especially when the photocatalyst is suspended in an aqueous solution) is the separation of the semiconductors from the media, which usually requires extra equipment and energy, increasing the cost of photocatalytic processes. To overcome this obstacle, photocatalysts have been immobilized into solid substrates or combined with co-catalysts, resulting in the third generation of photocatalysts [16] (immobilization methods are discussed later, in Sect. 1.5.1).

Among the several possible uses of heterogeneous photocatalysis, its potential in environmental applications is particularly notable. The application possibilities are numerous: the purification of water and air, degradation of hazardous waste, disinfection, cost-effective catalytic synthesis, and the production of hydrogen as a renewable, environmentally friendly fuel (Fig. 1.2). Another green aspect can be the use of recycled materials and waste during the production of photocatalytic materials, as it reduces both production costs and the amount of discarded waste. The metals needed for the synthesis of semiconductors, like zinc and titanium, might come from industrial wastes such as blast furnace slag [23], while catalyst supports, templates [24], and even dopants [25] can be produced from agricultural wastes [26]. The recently very popular g-C_3N_4 catalysts and other carbon-based photocatalytic materials can also be synthesized from organic waste [27, 28].

Fig. 1.2 Main environmental applications of heterogeneous photocatalysis
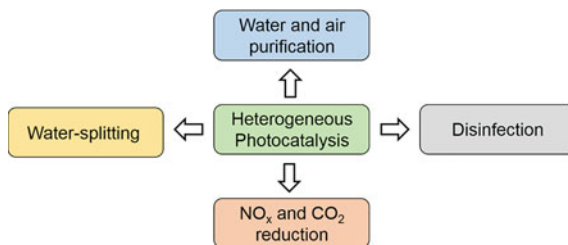
Biological materials can be used as size or shape controlling agents to enhance the synthesis of catalysts and even as additives to enhance the photocatalytic activity [29, 30].

A potential drawback of heterogeneous photocatalysis is the possibility of the release of catalyst particles into the environment. There are studies about the (eco)toxicity of nanoparticles in the environment, and the problem is even more complicated with photoactive materials [31]. The problem becomes more complex with the countless new nanomaterials with different chemical structures, particle sizes, and photoactivity [32].

1.2 Formation of Charge Carriers and Reactive Oxygen Species

Photocatalysis can be defined as the change in the rate of a chemical reaction or the initiation of this reaction in the presence of a catalyst excited by radiation with suitable wavelengths. In the case of photocatalysis, the formation of charge carriers with relative high reduction/oxidative potentials takes place, and these charge carriers are able to promote nonspontaneous reactions—or those with a positive change in Gibbs free energy—such as water splitting and the degradation of pollutants in water or air [17]. In a typical catalytic process, the kinetics of the reactions change, while thermodynamic parameters and reaction products are typically not altered.

Semiconductors are materials with conductivity in the range between metals and insulators, and in which the density of electric charge carriers is altered by external factors or agents—such as temperature and exposure to radiation [33]. When photons act as one of those agents, semiconductors can promote or accelerate reactions and the phenomenon of photocatalysis takes place; therefore, semiconductors activated by an absorbed photon are known as photocatalysts.

The formation of charge carriers is possible due to the semiconductors' electronic structure, characterized by a filled valence band and an empty conduction band separated in energy levels by a given bandgap. In the absence of an external stimulus—or the exposure to irradiation—electrons occupy the valence band. When the photocatalyst is exposed to radiation, photons with an energy equal to or greater than the energy of the bandgap (E_{bg}) are able to transfer electrons from the valence

to the conduction band, leaving positive charges (or holes) behind [22]. Initially, the electron in the conduction band and the hole in the valence band—which will be herein represented as e_{cb}^- and h_{vb}^+, respectively—are not free charge carriers nor free entities, but together consist the so-called exciton, which is a quasiparticle stabilized in semiconductors by electrostatic Coulombic forces—the attraction between e_{cb}^- and h_{vb}^+ and repulsion between different electrons in the conduction band. The exciton is an energy carrier, since it was formed by the absorption of a photon, but not a charge carrier. The separation of the energy carriers into free charge carriers occurs when enough excitons are formed—or enough electrons occupy the conduction band—so that the Coulombic attraction between e_{cb}^- and h_{vb}^+ is exceeded by repelling forces [13, 34]. Most of these charge carriers undergo recombination processes in the semiconductor bulk or surface [22, 35], but a few of them can migrate to the surface of the photocatalyst, where they initiate oxidative and reductive reactions [36]. The recombination processes can be radiative, with the subsequent release of heat, or consist of non-radiative relaxation processes that propagate vibrational motions through the lattice of the semiconductor [13, 37].

The oxidation is initiated by the h_{vb}^+, a powerful oxidant with reduction potentials (vs. NHE) varying from +1.0 to +3.5 V depending on the material of the semiconductor, its properties, and the pH of the medium, as represented in Fig. 1.3 [38]. Similarly, reductive mechanisms are initiated by the e_{cb}^-, which can have reduction potentials (vs. NHE) in the range of +0.5 to −1.5 V. The following chart represents the electrochemical reduction/oxidation of species in various photocatalysts, with reduction potentials expressed versus the normal hydrogen electrode (NHE) [17, 38].

The fast recombination of the charge carriers is the main limitation of photocatalytic processes. It occurs in the timeframe of nanoseconds in the absence of
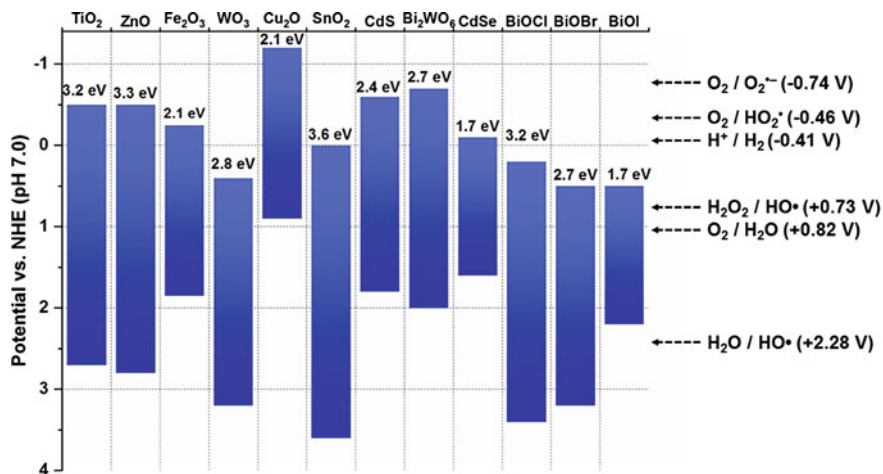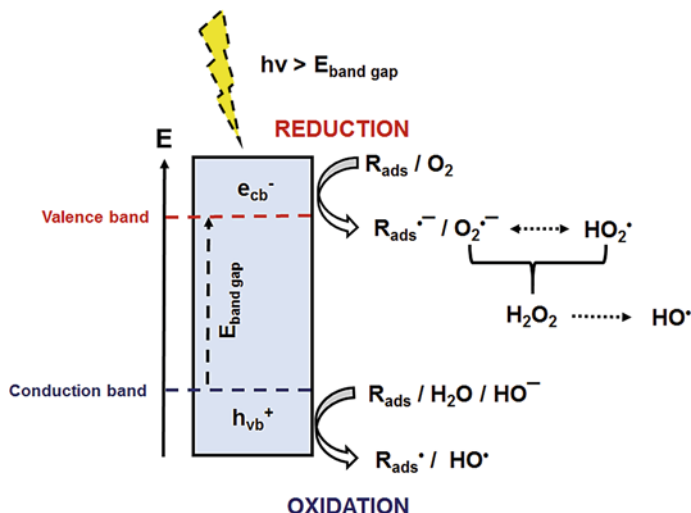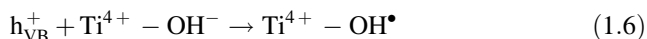

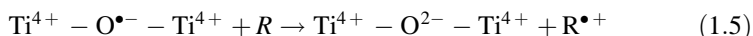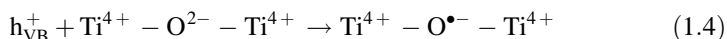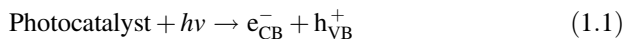Fig. 1.3 Bandgap energies of several different semiconductors

Fig. 1.4 Formation of reactive species in O_2 containing aqueous suspension of TiO_2 photocatalyst

suitable electron donors and/or acceptors, which must be adsorbed on the surface of the photocatalysts. The h_{vb}^+ can be trapped either by chemisorbed substrates or by surface oxygen/hydroxyl groups, depending on the pH of reaction media. The transfer of electrons from chemisorbed species to h_{vb}^+ occurs through an inelastic direct charge transfer pathway, while other substrates that interact weakly with the surface of the semiconductors can also undergo redox processes through indirect electron transfer mechanisms that depend on the capture of the charge carrier by surface atoms of the photocatalyst. Those mechanisms are particularly relevant to the oxidation of organic compounds in the liquid phase [39, 40]. A representation of the charge carriers formation and their reaction with adsorbed species in a general photocatalyst structure is given in Fig. 1.4.
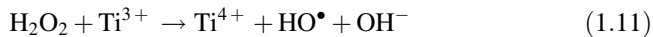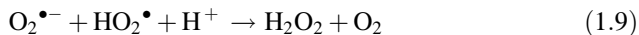
The nature of the electron donor or acceptor is modified according to the reaction medium (aqueous or gaseous phase) and with the chemical environment (pH, presence of ions, etc.). In aqueous media, water molecules can donate electrons to the h_{vb}^+ (1.2), while dissolved oxygen acts as an electron acceptor (1.7). The products of these reactions are various Reactive Oxygen Species (ROS), which can initiate chain-reaction mechanisms and promote several processes such as the degradation of organic compounds (including alkanes, alkenes, PCBs, phenols, aromatic carboxylic acids, dyes, pesticides, etc.) as well as the reductive deposition of heavy metals (such as Cr^{6+}, Pt^{4+}, etc.) to the surface. In the same manner, in the gas phase, molecules such as CO_2 can accept the e_{cb}^- and suffer reductive processes to form formic acid, methanol, etc., while adsorbed water molecules will react with the h_{vb}^+. The mechanisms underlying the formation of reduction products of CO_2 are debatable, most of the authors suppose a series of one-electron transfer reactions [17].

The following reactions (1.1–1.11) show the reaction of charge carriers with electron donors or acceptors. Photogenerated charge carriers can react with adsorbed substances or be trapped in various ways by surface or subsurface groups of the photocatalyst. R_{ads} represents a chemisorbed organic species, $Ti^{4+} - O^{2-} - Ti^{4+}$ a subsurface oxygen, $Ti^{4+} - OH^{-}$ is a surface hydroxil group of the TiO_2 photocatalyst.

$$\text{Photocatalyst} + hv \rightarrow e_{CB}^{-} + h_{VB}^{+} \tag{1.1}$$

$$h_{VB}^{+} + H_2O \rightarrow HO^{\bullet} + H^{+} \tag{1.2}$$

$$h_{VB}^{+} + R_{ads} \rightarrow R^{\bullet +} \tag{1.3}$$

$$h_{VB}^{+} + Ti^{4+} - O^{2-} - Ti^{4+} \rightarrow Ti^{4+} - O^{\bullet -} - Ti^{4+} \tag{1.4}$$

$$Ti^{4+} - O^{\bullet -} - Ti^{4+} + R \rightarrow Ti^{4+} - O^{2-} - Ti^{4+} + R^{\bullet +} \tag{1.5}$$

$$h_{VB}^{+} + Ti^{4+} - OH^{-} \rightarrow Ti^{4+} - OH^{\bullet} \tag{1.6}$$

$$e_{CB}^{-} + O_2 \rightarrow O_2^{\bullet -} \tag{1.7}$$

The $HO^{\bullet}$ is the main active species in the degradation of substrates in the aqueous phase. This statement is endorsed by its high reduction potential ($HO^{\bullet}$, H^{+}/ H_2O, $E^0 = +2.80$ V) and its high reaction rates with numerous substances [41]. In photocatalytic reactions, the formation of $HO^{\bullet}$ is determined by the nature of the photocatalyst. For instance, TiO_2 occurs in three main crystal phases, known as anatase, rutile, and brookite; among those, only anatase and rutile are widely used as photocatalyst. The formation of mobile $HO^{\bullet}$ which can diffuse 7.5 µm in water is reported in anatase, whereas only superficial $HO^{\bullet}$ (1.6) is reported in rutile [42, 43].

$HO^{\bullet}$ can also be formed in an aqueous solution via formation of $O_2^{\bullet -}$ (1.7 and 1.8). In the case of TiO_2, beside the reaction with molecular O_2 (1.7), the e_{cb}^{-} can be trapped by Ti^{4+}. The formed Ti^{3+} sites can act as a reductive agent and initiate the following mechanism (1.8–1.11) [44]:

$$Ti^{3+} + O_2 \rightarrow Ti^{4+} + O_2^{\bullet -} \tag{1.8}$$

$$O_2^{\bullet -} + HO_2^{\bullet} + H^{+} \rightarrow H_2O_2 + O_2 \tag{1.9}$$

$$H_2O_2 + hv \rightarrow 2HO^{\bullet} \tag{1.10}$$

$$H_2O_2 + Ti^{3+} \rightarrow Ti^{4+} + HO^{\bullet} + OH^{-} \tag{1.11}$$

$HO^{\bullet}$ react mainly through three different pathways: one-electron abstraction, hydrogen atom abstraction, and addition to double bonds. The one-electron abstraction generally happens in the presence of inorganic ions or easily oxidized
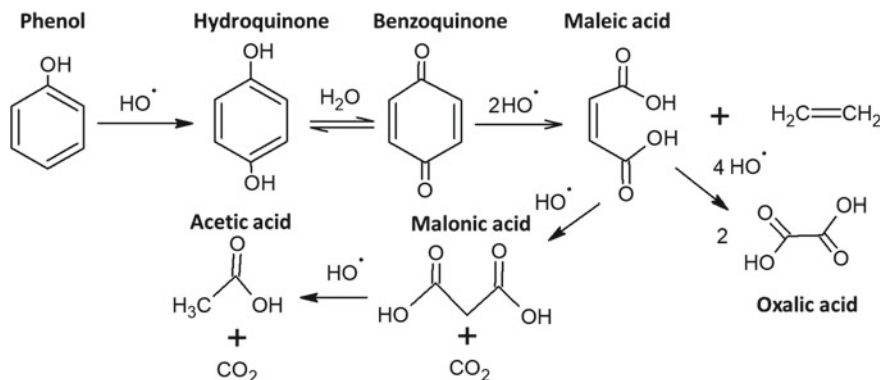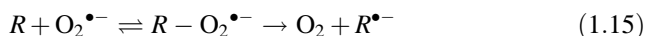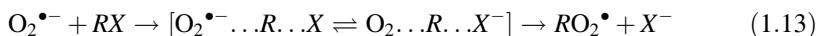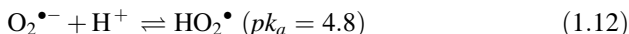
Fig. 1.5 HO˙ initiated transformation of phenol

organic compounds, hydrogen atom abstraction takes place mostly in the presence of saturated hydrocarbons, aldehydes, alcohols, and carboxylic acids, while the addition to double bonds is one of the main mechanisms for the degradation of unsaturated and aromatic organic compounds [44, 45]. Because the direct transfer of electrons requires the rearrangement of charged reaction centers, this is rarely observed. It can occur between HO˙ and metals through intermediate complexes [45]. Due to its electrophilic character, HO˙ readily reacts with the C=C bond and aromatic ring, as Fig. 1.5 shows, in the case of the phenol as a model substrate.
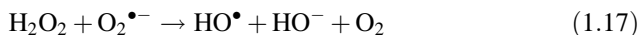
Enhanced reaction rates are usually observed in the gas phase due to the absence of solvation effects. Similar HO˙-based reactions take place in the gas phase as well as under tropospheric conditions. It is known that tropospheric aerosol particles contain carboxylic acids such as oxalic, malonic, and succinic acid. These organic compounds originate from reactions between HO˙ radicals and aromatic compounds [46].

In the case of the gas phase removal of contaminants, the relative contribution of HO˙ (either from adsorbed water or surface −OH groups) and the role of charge transfer reactions and/or other reactive particles in the transformation of organic or inorganic substances strongly depend on the chemical properties of the pollutant, on its chemical structure and on the surface properties of the photocatalyst. During the transformation of toluene in the gas phase, the dominant role of HO˙ was confirmed [47]; however, HO˙ radicals have a minor contribution to the transformation of chlorinated compounds. In the case of perchloroethylene, for instance, the inhibition effect of water–vapor [48] and the consequences of the modification of the TiO_2 surface [49] indicated a significant contribution of direct charge transfer and reaction with superoxide anion radical ($O_2^{\bullet-}$) [50]. $O_2^{\bullet-}$ has been observed during several photo-assisted reactions, especially in sensitized processes, in which singlet oxygen and $O_2^{\bullet-}$ radicals are the main active species [51]. $O_2^{\bullet-}$ is formed by the direct transfer of electrons from the conduction band to O_2 molecules adsorbed on the surface of photocatalysts [52, 53]. It may act as an oxidant ($O_2^{\bullet-}$, $2H^+/H_2O_2$, $E^0 = +0.94$ V), although the intermediate species formed during the reduction of superoxide (i.e., O_2^{2-}) are very unstable [54–56].

The $O_2^{\bullet-}$ reacts by disproportionation, one-electron transfer, nucleophilic substitution, and deprotonation [57]. The main characteristic of $O_2^{\bullet-}$ is its ability to act as a strong Brønsted base. As a consequence, mechanisms involving this radical should not play an important role in protic solvents. The $O_2^{\bullet-}$ can attack positively charged compounds or centers due to its powerful nucleophilicity [54, 57]. This reaction is particularly relevant in the presence of alkyl halides, whose mechanism is schematically represented in reaction 1.13 [57]. Superoxide radicals can react through outer- or inner-sphere electron transfer mechanisms as shown in reactions 1.14 and 1.15 [57].

$$O_2^{\bullet-} + H^+ \rightleftharpoons HO_2^{\bullet} \ (pk_a = 4.8) \tag{1.12}$$

$$O_2^{\bullet-} + RX \rightarrow [O_2^{\bullet-}...R...X \rightleftharpoons O_2...R...X^-] \rightarrow RO_2^{\bullet} + X^- \tag{1.13}$$

$$O_2^{\bullet-} + R \rightleftharpoons O_2 + R^{\bullet-} \tag{1.14}$$

$$R + O_2^{\bullet-} \rightleftharpoons R - O_2^{\bullet-} \rightarrow O_2 + R^{\bullet-} \tag{1.15}$$

The $O_2^{\bullet-}$ plays a major role in the formation of hydrogen peroxide, (1.9) [52]. Despite having a high reduction potential (H_2O_2, $2H^+/2H_2O$, $E^0 = +1.77$ V), the direct oxidation of substrates by hydrogen peroxide is considered irrelevant. Most probably, the hydrogen peroxide reacts with photogenerated charges on the surface of photocatalysts or with $O_2^{\bullet-}$ [54], resulting in $HO^{\bullet}$ formation (reactions 1.16 and 1.17).

$$H_2O_2 + e_{CB}^- \rightarrow HO^{\bullet} + HO^- \tag{1.16}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow HO^{\bullet} + HO^- + O_2 \tag{1.17}$$

Besides hydrogen peroxide, singlet oxygen is another non-radical oxidative species whose presence is reported in most photo-assisted systems associated with the formation of $O_2^{\bullet-}$. Singlet oxygen is formed after the oxidation of $O_2^{\bullet-}$ by photogenerated holes [58, 59]; however, the relevance of singlet oxygen in oxidation mechanisms is questionable due to its low reduction potential ($^1O_2/O_2^{\bullet-}$, $E^0 = +0.65$ V) and short half-life in aqueous media (2 μs) [59, 60]. Table 1.1 presents the values for the reduction potential of the most important ROS observed during photocatalytic processes relative to the standard hydrogen electrode system as compiled by Buettner [61].

All the previously described ROS have been detected during photocatalysis, and one of the preferred techniques for this purpose applies the electron paramagnetic resonance (EPR) spectroscopy. These short-lived ROS can only be detected using spin-trapping techniques, which consist of reacting the radicals with a spin-trapping agent to form an organic adduct with higher stability. The most used spin-trapping agents are nitroxides, such as the 5,5-dimethyl-1-pyrroline-N-oxide (abbreviated as DMPO) and the 2,2,6,6-tetramethyl-piperidine-1-oxyl (known as TEMPO) [62]. TEMPO is a specific spin-trapping agent used to identify the singlet oxygen during

Table 1.1 Redox couples and reduction potential of ROS relative to the standard hydrogen electrode (SHE)

Couple	E^0 (V)
$O_2, H^+/HO_2^{\bullet}$	−0.46
$O_2/O_2^{\bullet-}$	−0.33
$H_2O_2, H^+/H_2O, HO^{\bullet}$	+0.32
$^1O_2/O_2^{\bullet-}$	+0.65
$O_2^{\bullet-}, 2H^+/H_2O_2$	+0.94
$HO^{\bullet}, H^+/H_2O$	+2.31
$HO_2^{\bullet}, H^+/H_2O_2$	+1.06

photocatalysis; DMPO can detect most of the radicals present in a photocatalytic system, although it has been shown that a few radicals are unstable and transformed to DMPO-OH (the adduct formed between DMPO and HO$^{\bullet}$ radicals). This conversion particularly occurs in aqueous solutions and was observed in the presence of carbonate radicals and $O_2^{\bullet-}$ [63, 64].

Besides EPR, the presence of oxidative species can be inferred with the addition of scavenger agents, which are species able to react quickly and specifically with the radicals and charge carriers, therefore quenching their effect in photocatalytic reactions. For instance, carboxylate or carboxyl groups can coordinate with the metals present on the surface of photocatalysts, thus forming inner-sphere complexes that favor the transfer of electrons directly from the ligand molecule to the valence band of the photocatalyst or photogenerated holes [65]. For this reason, oxalate and formic acid have been applied in mechanistic investigations of photocatalytic systems to act as hole traps [66]. Other scavenger species widely applied in mechanistic investigations are alcohols such as *tert*-butanol (TBA) and methanol. The elevated second-order rate constant of the reaction between TBA and HO$^{\bullet}$ ($k_{TBA+HO^{\bullet}} = 6 \times 10^8$ M^{-1} s^{-1} [67]), along with the lower rate constant between TBA and other radical species [67], allows for a high selectivity for HO$^{\bullet}$ radicals [65, 68, 69]. Other scavenger agents have been applied in mechanistic investigations to verify the presence of singlet oxygen and $O_2^{\bullet-}$, such as azide ion and parabenzoquinone, respectively [68].

1.3 Application of Heterogeneous Photocatalysis

1.3.1 Removal of Pollutants from Aqueous and Gaseous Media

Heterogeneous photocatalysis has great potential for removing hardly biodegradable organic contaminants from waters, such as pesticides, pharmaceuticals, and other persistent organic substances [11, 70]. This process has shown great potential for the transformation and the mineralization of organic pollutants from aqueous or

gaseous media via radical reactions. Only in a few cases is an intermediate formed (e.g., cyanuric acid during the conversion of atrazine) for which heterogeneous photocatalysis is not suitable for further oxidation and degradation [71, 72]. Chlorinated molecules easily lose the Cl^- during photocatalytic processes, while from organophosphorus compounds phosphate ion is produced [71]. From nitrogen-containing molecules usually NO_3^- and NH_4^+ ions are formed. During the degradation of compounds containing azo groups, the formation of N_2 was reported [73]. The byproducts of the degradation of organic compounds in photocatalysis are highly dependent on the oxidation state of the atoms in the compound. For instance, when the nitrogen atom is at the oxidation state of -3, as in amino groups, it evolves to NH_4^+ with the same oxidation state for the nitrogen atom. Subsequently, the NH_4^+ can be oxidized to NO_3^-. In azo groups, however, the oxidation state of the nitrogen atom is $+1$, thus the formation of N_2 is favored [71, 73].

The photocatalytic removal of volatile organic compounds (VOCs) in gas phase follows a similar mechanism. In gas phase, $HO^\bullet$ is usually originated from the water–vapor and oxygen content of the air [17]. Another possible use in the gas phase is the reduction of inorganic pollutants, like CO_2, SO_2, and NO_x. The photocatalytic reduction of CO_2 has especially great interest nowadays since this process can be used to remove the most well-known greenhouse gas while enabling the production of useful products (CH_4, CO, methanol) [17, 74–76]. Besides VOCs, the highly toxic NO_x compounds (mainly NO and NO_2) are among the most widespread anthropogenic air pollutants. Heterogeneous photocatalysis offers a way to degrade NO_x to less harmful nitric acid, although the method is still under constant development [17, 77]. The gas phase applications of heterogeneous photocatalysis have been widely investigated in the last two decades, and several methods were applied, from indoor air purifiers to self-cleaning building materials (glass, concrete) with photocatalysts as surface coatings or mixed into the components [78, 79].

1.3.2 Photocatalytic Water Splitting

In the field of green chemistry and alternative energy sources, hydrogen is considered a promising alternative to replace fossil fuels due to its close to unlimited reserves in the form of water and zero emissions of harmful products. Although its cheap production and implementation in practice are still not solved, its application is steadily growing in certain areas [80]. Photocatalytic and photo-electrocatalytic water splitting to produce H_2 has received widespread attention, especially if they can be initiated by solar light, which could theoretically make the process have close to zero operating costs. During photocatalytic water splitting, the reaction of e_{cb}^- with H^+ produces H_2, while h_{vb}^+ contributes to the formation of O_2 [81]. In the case of photo-electrocatalytic processes, an external circuit is used to transport the

e_{cb}^- to a cathode (e.g., Pt), where reduction reactions can take place [82]. Several photocatalysts, like TiO_2, ZnO, CdS, WO_3, or carbon-based photocatalysts [12, 38, 83, 84] have been investigated for their potential in water splitting. Considering the generally low efficiency of the method, several directions were taken to improve it, like adding doping agents (typically cations as V^{4+}, Mo^{5+}, and Ru^{3+}, or anion as N, F^-, S^{2-}) or introducing electron trapping centers (typically noble metals as Au, Ag, Pt, Pd) to improve the separation of photogenerated charges.

The fast recombination of photogenerated charges is the main reason for the low efficiency, while another reason is the backward reaction resulting in H_2O formation, which can be hindered via the addition of electron mediators [81]. The addition of sacrificial electron donors (organic acids, or inorganic ions like I^- or S^{2-}) to react with h_{vb}^+ and promote the formation of H_2 via reduced charge recombination is also possible [81]. To achieve effective photocatalytic H_2 production, the exact reaction mechanisms still need further studies. A suitable, visible light active photocatalyst is still a great challenge for material science to undertake due to the generally low photostability and conduction band potential of visible light active catalysts [12, 38].

1.3.3 Photocatalytic Disinfection

Application of heterogeneous photocatalysis for disinfection was reported at first in 1988 by Matsunaga et al., who employed TiO_2 to inactivate *L. acidophilus*, *S. cerevisiae,* and *E. coli*. Since then, photocatalysis has been largely applied in disinfection systems, and the gram-negative bacteria *E. coli* is by far the most studied organism in these applications since it is an indicator of fecal contamination in water, non-pathogenic to humans, and it is easily cultivated in academic laboratories [85]. Similarly, due to its elevated stability, high efficiency, and low toxicity, TiO_2 is the most investigated semiconductor in disinfection systems.

The application of photocatalysts for disinfection has been investigated in several fields, including in the food industry [86], healthcare [87], and it is especially effective in indoor air cleaning [88]. There are also several applications of photocatalytic surfaces in the production of self-cleaning glasses and in medical devices that prevent hospital-acquired infections [89]. Considering that solar disinfection systems are widely recognized for inactivating pathogenic microorganisms in water, photocatalytic materials have been also investigated to improve the degradation efficiency in these already well-established systems [71].

The disinfection effect is more pronounced the more intense the contact between the microorganism and the surface [89, 90]. In these conditions, the direct photocatalytic damage of a microorganism structure can be caused by interfacial charge transfers between the photocatalyst and the external cell membrane, and therefore, the inactivation depends on the components of the membrane. These components include phospholipids and lipo-polysaccharides that, in the case of *E. coli*, have

been proven to react directly with the h_{vb}^+ of TiO_2 [90, 91]. Other damages inflicted to cell structures can be caused by the exposure to radiation directly in the DNA structure that happens mostly in the UVC range of the solar spectrum, and also by ROS formed during photocatalysis—especially the $HO^•$ [92]—or during the interaction of radiation and specific intracellular structures [71, 85]. The inactivation mechanism in photocatalytic processes is therefore extremely complex and includes several steps resulting not only from the presence of a photocatalyst but also from the irradiation itself. These steps can include the formation of ROS, DNA and RNA attack by either the direct absorption of light or the attack of internally formed ROS, chain reactions, and other mechanisms that will ultimately lead to cell mutation, membrane ruptures, loss of organelle functions, etc. [85, 90].

The use of the TiO_2/UV process has been proved to inactivate several pathogenic microorganisms, like bacteria, algae, and viruses [93]. TiO_2, in its pure or modified form, has been used widely, but other photocatalytic materials, carbon-based semiconductors, like g-C_3N_4, have also been recently applied with promising results [94]. Photocatalytic treatment of wastewater not only offers a solution for the removal of harmful organic contaminants but also inactivates many pathogens in the effluent [93]. The long sterilization period (60 h) are also feasible [95].

1.4 Improving the Efficiency of Photocatalysis

1.4.1 Combination with Other Methods

The efficiency of each method can be improved by their appropriate combination. Sonophotocatalysis is a process derived from the combination of sonochemical treatment with photocatalysis. The ultrasound exposure alone results in $HO^•$ and $H^•$ formation. Its combination with heterogeneous photocatalysis results in synergistic increases in the $HO^•$ formation rate [96]. Combining photocatalysis with ozonation may also result in synergistic effects. Ozone is a potent but selective oxidant. In the presence of a photocatalyst, it also acts as an electron acceptor and $HO^•$ source, inhibits recombination of excitons, and dramatically increases the rate of $HO^•$ formation. [97]. Photocatalytic pretreatment can remove several toxic organic contaminants, so its use can significantly increase the efficiency of biological water treatment [98].

Another possibility of the combination is the application of photocatalysts in membrane reactors (PMRs—photocatalytic membrane reactors). PMRs can be categorized into two main groups: PMRs using suspended photocatalysts and PMRs applying photocatalytic material-modified membranes [99–101]. When suspended catalysts are applied in PMRs, the photocatalytic decomposition of the organic pollutant is the main process, which is followed by membrane separation for the recovery of the nanoparticles. This application provides a high surface area

for the photocatalytic processes—compared to immobilized catalysts—resulting in high decomposition efficiency. The separation of the nanoparticles by membrane filtration results in excellent photocatalyst recovery, which is beneficial both from economic and environmental aspects. However, significant fouling of the membrane caused by a high amount of nanoscaled photocatalytic material can result in high energy requirements [100, 101].

This immobilization of photocatalytic nanoparticles in/on the membrane materials promises significant beneficial properties since the immobilized photocatalysts can enhance the hydrophilicity of the surface, which is important to suppress the adhesion of hydrophobic contaminants. These contaminants could quickly form serious water barriers on the membrane surfaces, being responsible for reduced water flux, decreased membrane lifespan, and increased energy consumption [99, 102–105]. In addition, immobilized photocatalytic nanoparticles can be used in self-cleaning membranes, which can be purified without the addition of chemicals. These membranes are also promising to suppress biofouling by preventing biofilm formation. The main disadvantages of these kinds of PMRs are the lower photocatalytic activity compared to the suspension method and technical difficulties, like providing continuous irradiation of the membrane surface and ensuring a good dispersion of the immobilized particles while also maintaining the porosity of the membranes [99–101, 105].

1.4.2 Photosensitization of Semiconductors

As briefly mentioned in the previous paragraphs, the nature of the reductive/oxidative species formed in photo-assisted processes relies on the electronic structure of the semiconductors. In recent years, different substances and compounds have been added to semiconductors to modify or interfere with their electronic structure. The purpose of these modifications is always to harvest photons with lower energy, thus increasing the efficiency of photocatalysts under solar irradiation.

The first observation of the so-called photosensitization process was published by O'Regan and Grätzel in 1991, who reported that TiO_2 could be modified with a dye to generate an electrical output. This was therefore the first mention of the Grätzel solar cell, which has inspired works in the field of photovoltaic cells ever since [16, 106–109].

Visible light initiated photocatalysis can be available in combination with TiO_2 and a sensitizing dye, coordination complexes of metals (e.g., ruthenium), or short bandgap semiconductors [110]. Organic dyes and several metal-complexes can effectively absorb light in the visible range of the electromagnetic spectrum; thus, they can be used as a photosensitizer. The dye can undergo photolysis or sensitize the semiconductor and thereby inject an electron into its conduction band (Fig. 1.6). However, Terenin and Akimov proposed that sensitization occurs by energy
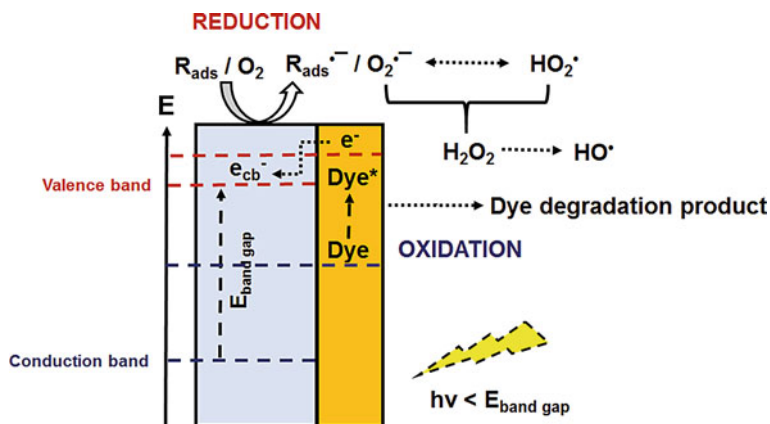
Fig. 1.6 Schematic figure of the photosensitization process (dye is adsorbed on the photocatalyst particle)

transfer from the excited dye molecule to surface-trapped electrons, and not electron transfer to the conduction band of the semiconductor [111].

To increase the absorption range of photocatalysts, inter-particle electron transfer pathways can be promoted by coupling two different semiconductors, such as TiO_2 with other visible-active photocatalyst, such as CdS [16] or WS_2 [112]. In these cases, the conduction band potential of the visible-active catalyst must be higher than that of TiO_2 (Fig. 1.7).
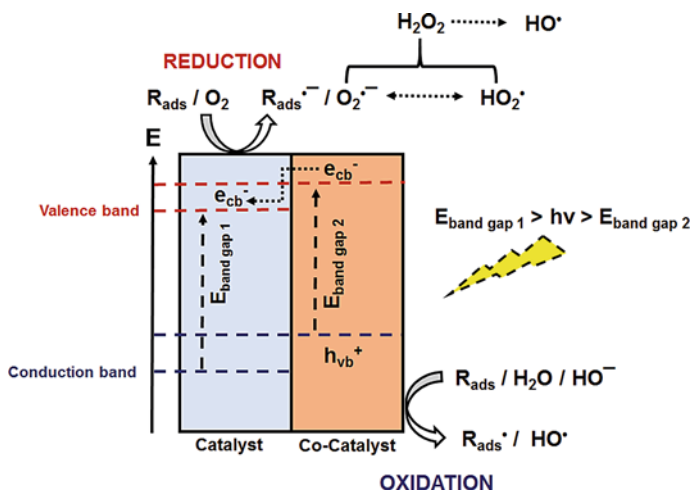
Fig. 1.7 Simplified depiction of the processes taking place in the case of a wide bandgap catalyst with a co-catalyst activated by visible light

1.5 Effective Parameters

1.5.1 Reactor Design

In the design of reactors for heterogeneous photocatalysis, the most important considerations are the mass transfer of target molecules to catalyst surface and maximizing the illuminated catalyst surface area. The photocatalysts are applied generally in two different ways: suspended in slurry reactors or immobilized as coatings. According to the light source and reaction chamber orientation, reactors can be classified as immersion, external and distributive types. The light for irradiation is distributed from the light source to the catalyst employing reflectors or optical fiber. Optical fiber reactors have the advantages of a fixed-bed reactor configuration while achieving a slurry system's equivalent efficiencies.

Suspended catalysts are always better in terms of photocatalytic efficiency due to their larger surface area and faster mass transport, but the high recovery and separation costs of nanoparticles hinder the practical application [11]. The immobilization of the catalyst is a cost-efficient way in terms of instrumentation and operating costs but significantly reduces photocatalytic activity. Due to the decrease in the surface area available to light, in this case, the fouling of the catalyst is more prominent [113]. Several immobilization methods already exist, and the most common ones are thermal, sol–gel methods, but the deposition of vapors and electrophoretic deposition has also been investigated thanks to their potential to create thin catalyst films. The most widely used supports are glass, silica-based materials, different polymers, and carbon-based materials (like activated carbon). Several other, less common supports have also been experimented with, like clays, sand, fibers, ceramic paper, and zeolites [114, 115]. The immobilization of the catalyst is a key element in terms of practical applications and finding the best method for different photocatalysts and reactor setups is an important challenge to overcome.

1.5.2 Light Intensity

The intensity of the light is another critical parameter, as the increased amounts of photons absorbed by the catalyst increase the formation of excitons. This theoretically leads to better photocatalytic activity, but the beneficial effect of higher photon fluxes is limited. Photochemical reactions are generally characterized by quantum yields or quantum efficiencies. The comparison to standard photocatalytic reactions (e.g., phenol degradation with TiO_2 P25) [116] is another possibility. The *quantum yield* (Φ) stands for the ratio of events (transformation of substrates or formation of products) and absorbed photons (1.18). Several factors complicate the determination of Φ in heterogeneous systems. During photocatalytic reactions polychromatic light is generally used, therefore, the exact quantification of photons

via actinometry might be imprecise. Another issue is the reflection of photons by the photocatalyst particles, as it reduces the number of photons absorbed, resulting in a significantly lower *apparent quantum yield* (Φ_{app}) [117].

$$\Phi = \frac{\text{amount of transformed substrates or formed products}}{\text{amount of photons absorbed by the photocatalyst}} \qquad (1.18)$$

$$\Phi_{app} = \frac{\text{amount of transformed substrates or formed products}}{\text{amount of photons reaching the reactor}} \qquad (1.19)$$

According to Hermann, due to the generally low Φ of photocatalytic reactions, the use of very high intensities is not recommended. In the case of complete surface coverage and precise determination of effective photon flux, high value can be reached (Φ = 30–40%), but in the case of trace pollutants, Φ is generally lower than 1% [72]. In many cases, the light intensity has a negligible effect [11, 14], but relatively high intensity can also promote charge carriers' recombination [118]. The effect of irradiation intensity also depends on the wavelength, the type of photocatalyst and reactants [113].

The light source is a dominant part of the reactor. The intensity of the light depends on the type of the light source, the electric power input, and the efficiency of the conversion of electrical energy into light. The utilization of solar radiation is advantageous because the cost of electricity can be avoided; however, highly efficient solar photocatalysis systems require complex design. The primary design consideration in solar photoreactors concerning the irradiation source is whether to use non-concentrated or concentrated sunlight [119].

As artificial light devices, UV lamps [120], lasers [121], or light-emitting diodes (LEDs) can be applied [122]. In most cases, conventional UV lamps are used. The efficiency of fluorescent lamps is limited by energy loss incurred in photon energy conversion and heat loss. Due to their intensive development and several advantageous properties, there has been an increased interest in applying LED light sources in the field of water treatment, even in the case of heterogeneous photocatalysis. UV LED reactors can fall under any immersion, external or distributive types and the various configurations reported in the literature [119].

1.5.3 Reaction Temperature

In homogeneous systems, higher temperature usually increases the reaction rate [123], but this effect is more complicated in photocatalytic heterogeneous systems since increasing temperatures hinders the adsorption of substrates on the catalyst surface and favor the recombination of charge carriers [11]. In gas phase at low temperatures, typically below 0 °C, the efficiency is also decreased due to the slow desorption of products [71]. In aqueous phase, the most favorable temperature

range has been determined to fall between 20 and 80 °C, although it also depends on other reaction conditions and the goal of the application [11].

As a result of the relationship between temperature and adsorption, non-Arrhenius behaviors—or processes in which the rate constant is not linearly increased with the increase of temperature—are described during the heterogeneous photocatalysis conversion of many organic compounds, particularly in gas phase catalysis [44]. Examples of this behavior can be found in studies of volatile organic compounds abatement, such as trichloroethylene, benzene [124], *tert*-butyl ether, and *tert*-butyl alcohol [125] over TiO$_2$. This phenomenon is attributed to changes in the adsorption rate over the catalysts, which markedly decreases with the increase of temperature in solid/gas systems [124, 125].

1.5.4 Catalyst Load

The concentration of the photocatalyst directly influences the surface available for the adsorption of reactants and for photon absorption. Increasing the catalyst loading increases the reaction rates, but only up to a given concentration; therefore, the determination of the optimal loading has great importance [11]. In slurry reactors, above a given catalyst concentration, the efficiency does not change or even reduces due to increased light scattering and reduced penetration depth of the photons [14]. The role of aggregation also increases at higher catalyst loadings and leads to the reduction of photocatalytic efficiency [113]. The optimal catalyst concentration also depends on the reactor size and design [118].

In the case of immobilized catalysts, the optimal catalyst coating thickness must be determined. A thin film results in partial absorption of photons, while an overly thick one results in areas where unreactive dark zones are found, thus resulting in a waste of photocatalyst material [78].

1.5.5 Initial Concentration of the Reactant

Since photocatalytic reactions are generally described to occur on the surface of the catalyst (1.20), the role of adsorption is highly important.

$$A_{ads} + B_{ads} \rightarrow C_{ads} \tag{1.20}$$

The reaction rates of photocatalytic processes are generally described by the Langmuir–Hinshelwood (L–H) kinetics. According to the L–H model (1.21), the concentration of substrates and their interactions with the surface determine the reaction rate:

$$r_0 = \frac{k \times K \times c_0}{1 + K \times c_0} \tag{1.21}$$

where r_0 is the initial reaction rate, c_0 is the initial concentration, k is the reaction rate constant, and K is the apparent equilibrium constant [126].

Another frequently mentioned kinetic model is the Eley–Rideal (E-R) mechanism. In contrast to the L–H model, which requires the pre-adsorption of substrates for the reactions to occur, the E-R model suggests one reactant (e.g., HO$^\bullet$) is adsorbed while the other is in the solution/gas phase; therefore, the reaction only requires proximity to the surface of the catalyst [127]. This model can be useful to explain some experimental results, for instance, the similar transformation rate of coumarin with negligible adsorption (<1%), and 3-carboxy-coumarin with significant adsorption ($\sim 30\%$) on TiO_2 surface [128]. The reaction with HO$^\bullet$ can take place in the aqueous phase, as HO$^\bullet$ is reported to desorb from the surface of anatase phase TiO_2 and react with pollutants in solution [42].

At low reactant concentrations, the concentration increases the reaction rates, as the limiting factor is not the formation rate of excitons and reactive radicals. Above a given concentration, the reaction rates do not increase further, due to the limited number of photons or active sites available. The accumulation and adsorption of products formed during the photocatalytic reaction might also affect the efficiency, as it can block the active sites of the catalyst, leading to the poisoning of the catalyst particles [113].

The optimal concentration of the reactants must be determined individually, as it highly depends on their chemical structure. At higher concentrations, the adsorbed reactants might absorb the light and decrease the efficiency of photocatalytic processes [14]. We might conclude that heterogeneous photocatalysis is especially useful to transform reactants present in a low concentration (like trace amount of pollutants).

1.5.6 Electron Acceptors and Donors

The most important electron acceptor is O_2; on the one hand, it prevents the recombination of photogenerated charges, and on the other hand, it also plays a role in the formation of reactive particles. The presence of dissolved O_2 is highly important in an aqueous medium, but generally, there is no significant difference between reaction rates determined in air or O_2 saturated suspensions [78]. The role of O_2 is also crucial for the mineralization of organic pollutants [11] due to the formation of organic peroxyl radicals. The addition of electron acceptors, like H_2O_2, $S_2O_8^{2-}$, BrO_3^-, CCl_4, or dissolved ions (e.g., Ag^+) leads to improved charge separations and HO$^\bullet$ formation, resulting in higher photocatalytic efficiency. The reactive species formed from these additives may also contribute to the photocatalytic process. In some cases, however, these electron acceptors may also act as

radical scavengers, lowering the overall efficiency. Above the optimal concentration, the $HO^{\bullet}$ and h_{vb}^{+} scavenging effect of H_2O_2 exceed its positive effect as electron acceptor [113]. The addition of electron acceptors also makes the photocatalytic system quite complicated, and unexpected changes might occur; for instance, in the case of Ag^+ or Fe^{3+} addition, they might even change the catalyst by precipitating in their metallic form [129].

Electron donors are especially employed in the case of H_2 generation via water splitting. Several organic electron donors have been employed, like alcohols and organic acids. In the case of CdS-based photocatalysts, the use of sulfite and sulfide ions has been proved to be beneficial to H_2-production [129].

1.5.7 Effect of Matrices

In the aqueous phase, the pH of the matrix is one of the key parameters, as it has a complex effect on heterogeneous photocatalysis. The pH affects the surface charge of the catalyst particles; above the point of zero charge (PZC), the catalyst becomes negatively charged, while at lower pH it becomes positively charged. This affects the adsorption of substrates on the surface due to electrostatic interactions. The aggregation of suspended catalyst particles also depends on pH, as particle–particle interactions result in lowered surface area and a loss of photocatalytic activity. The optimal pH range greatly depends on the catalyst, the reactants, and the goal of the application [11, 113].

Matrices may contain dissolved or floating microscopic organic components, which generally decrease the efficiency of photocatalytic processes. Suspended solids reduce the efficiency of all photochemical processes due to increased light scattering/reflectance.

Dissolved organic compounds often act as a scavenger of $HO^{\bullet}$ and/or h_{vb}^{+}, resulting in lower mineralization efficiency [11]. Their adsorption on the catalyst surface can increase the aggregation of suspended particles and occupy adsorption sites otherwise available for target compounds [130]. To solve this issue, there have been efforts to produce photocatalytic materials that show selectivity to the substrates. Coatings with selectively adsorbing materials [131] and molecular printing [132] increase the selectivity of photocatalysis for the removal of pollutants, while the adsorption of ions on TiO_2 has been used to increase its efficiency in CO_2 reduction and increase the formation of useful products like CH_4 [133].

The presence of inorganic ions has complex and varied effects. Adsorbed inorganic ions affect the surface charge of the catalysts and dramatically change adsorption properties and reaction mechanisms [134]. They may occupy adsorption sites and even displace surface $-OH$ groups, resulting in reduced hole trapping and decreasing photocatalytic activity [135]. There are, however, special cases in which inorganic ions appear to enhance photocatalytic activities, like fluoride ions (F^-).

These ions replace the surface Ti–OH groups of TiO_2 with Ti–F groups, and significantly increase the transformation of organic pollutants. However, for those compounds where adsorption is required for degradation, a negative effect was observed [136, 137]. The effect even highly depends on the crystal structure, as increased efficiency of phenol degradation was observed on fluorinated anatase, while reduced transformation rates on rutile [138, 139].

The most frequent anions in natural waters are Cl^-, HCO_3^-, PO_4^{3-}, SO_4^{2-}, and NO_3^-. During the transformation of organic pollutants, both positive and negative effects have been reported. They may scavenge $HO^{\bullet}$ or react with h_{vb}^+ to form reactive species, such as $Cl^{\bullet}$, $CO_3^{\bullet-}$, $PO_4^{\bullet-}$, and $SO_4^{\bullet-}$. These are much more selective species toward organic substances than $HO^{\bullet}$; therefore, their effect on the transformation rate depends on the chemical structure and reactivity of the substrate [140].

Other ions, like Fe^{3+} or NO_3^-, have the potential to increase the efficiency of photocatalytic processes by enhancing charge separation and promoting $HO^{\bullet}$ formation [113]. NO_3^- and NO_2^- may react with e_{cb}^- to form N_2, and this can be utilized to remove these ions as they are harmful in drinking water reserves, although the method still needs further development [141]. Cations like Fe^{3+} and Al^{3+} generally have a negative impact on the efficiency, while the most abundant cations in natural matrices, Na^+, Ca^+, and Mg^{2+} rarely affect that [140].

Reducing the matrix effect is a major challenge in large-scale applications of heterogeneous photocatalysis for water treatment.

1.6 Conclusions

Photocatalysis is one of the promising alternatives for environmentally friendly green solutions in water treatment, air cleaning, and energy production. Researchers with different backgrounds are involved in its development and concentrate their efforts on producing new photocatalytic materials that can cut costs and have adequate quantum efficiencies for the various applications. One of the prominent topics in this field is the heterogeneous photocatalysis driven by sunlight. Besides finding the proper materials for this application, researchers have to find cheap alternatives for catalysts manufacturing. The complexity of factors affecting photocatalysis efficiency and operation cost poses a significant challenge for implementing systems, especially those including removing pollutants from waters having complex matrix.

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