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Photochemistry for pollution abatement*

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Abstract: Sunlight is a clean, cheap, and abundant reagent. Many light-initiated reactions can be carried out in water, making photochemistry an ideal tool for pollution abatement and/or elimination. We studied the photoreactivity of different families of common organic micropollutants: light-initiated processes in the absence or presence of co-oxidants, and photocatalyzed reactions using different photocatalysts and composites. Based on the experimental evidences found, detailed transformation mechanisms have been proposed that help understand the reactivity of organic micropollutants and predict their environmental fate. Our approach includes the study of the photophysics for each family of compounds, its reactivity upon direct photolysis, adsorption onto photocatalysts, photocatalytic reactivity, thermodynamics, and kinetics of the processes involved (pK_a, $E°$, rate constants, etc.), product analysis, and ecotoxicological assessment. Different commonly overlooked problems, related to the kinetics of the process, are reported, and a model is proposed that includes the possibility of adsorption on different types of active sites, leading to different reactivities.

Keywords: environmental chemistry; heterogeneous catalysis; photocatalysis; photochemistry; sustainable chemistry; water.

INTRODUCTION

Sunlight is a readily available, clean, sustainable, and traceless reagent, cheap and abundant at ground level. It can trigger and drive a large number of reactions in water, as this is almost perfectly transparent to UV–vis light [1], at least in shallow waters.

Light can initiate direct phototransformations upon its absorption [2], a process usually referred to in the literature as "photolysis" or "photodegradation", although it does not necessarily imply a fragmentation of the starting molecule, nor a "degradation".... Typical phototransformations may include a large variety of processes: isomerization, polymerization, photoionization, dehalogenation, dehydration, etc. [3].

The use of auxiliary reagents and/or photocatalysts allows generation of highly reactive primary species such as hydroxyl radicals ($HO^\bullet$), superoxide anion ($O_2^{\bullet-}$), hydroperoxide radical ($HOO^\bullet$), and others, which constitute the basis of advanced oxidation processes (AOPs) [4]. Among these, heterogeneous photocatalysis, enormously expanded in the last decade, makes use of cheap visible light sources, or even sunlight, to excite potential photocatalysts.

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The presence of photosensitizers, a variety of species that may be naturally present in waters (humic and fulvic acids, colloids, etc.) may lead, upon light absorption, to generation of excited states and/or singlet oxygen ($^1O_2$), which could subsequently transfer their energy to a non-light-absorbing species, originating photosensitization processes [3].

All these alternatives make photochemistry an excellent approach to pollution abatement, or even elimination, something prophesized as early as a century ago by Giacomo Ciamician in his seminal paper "The photochemistry of the future" [5]. However, photochemistry has been overlooked as a tool for green chemistry, probably due to technical difficulties to profit from sunlight, the high energy cost associated with the use of UV lamps, and the real fact that there may be a lot of undesired, difficult-to-control side reactions.

Persistent organic micropollutants (POPs) include a vast variety of chemicals that threaten both the environment and human health. While writing this, more than 70 million organic and inorganic compounds are known, of which over 50 million are organic, and only a bit fewer than 300 000 are inventoried or regulated [6]. Among the most relevant organic micropollutants, agrochemicals, pharmaceuticals, personal care products, and a variety of others such as dioxins, polycyclic aromatic hydrocarbons (PAHs), benzofurans, etc. can be included [7,8,13,14]. Some accumulate in the environment due to their lack of reactivity, whilst others do so because of ongoing human activity. There are also large differences in their bioavailability and bioaccessibility [9]. All these facts make the development of appropriate methods for their abatement and/or degradation necessary.

In the last few years, we have studied the way different families of POPs undergo phototransformation, using UV–vis irradiation, and also in the presence of auxiliary co-oxidants and photocatalysts, that may be nanosized or nanostructured, with a view to reduce or eliminate their presence in natural waters [2,10–21]. Our results help understand the environmental fate of the studied POPs and their metabolites upon light uptake, and allow us to propose mechanisms for the aqueous photodegradation, including the participation of excited states and short-lived intermediates. With this information, it becomes possible to predict which processes may be relevant under oxidizing and/or reducing conditions, how acidity affects the different intermediates, etc. Results also allow comparison of a single process in the presence/absence of photocatalyst, and how incorporation of the photocatalyst into a composite may affect the reactivity. The common research strategy involves the study of the photophysics of each POP, its reactivity upon direct photolysis, adsorption onto solid photocatalysts, photocatalytic reactivity, thermodynamics (pK_a, $E°$) and kinetics of the processes involved (timescale ns to h), product analysis, and, if possible, ecotoxicological assessment.

Here we present the two main approaches to abatement/elimination of organic micropollutants in water, namely, direct irradiation and heterogeneous photocatalysis, and point out different problems that have been frequently omitted or overlooked.

DIRECT IRRADIATION

POPs absorb UV–vis light, depending on their structural characteristics (value of λ_{max}, magnitude of the absorption coefficient, ε) and the conditions of the medium (in aqueous media, basically the pH). Many POPs are purposefully designed to absorb little or no visible light, leaving the use of UV light as the only alternative for direct photodegradation. Though the use of UV light is more effective for degradation purposes, it is also more expensive in terms of energy cost [22], and harmful to living organisms, as it induces damage to DNA [23]. Energy efficiencies may be measured using factors such as the quantum yield or apparent quantum yield, electrical energy per order (EE/O), or the thermodynamic efficiency factor (TEF) [22].

Briefly, upon light absorption singlet or triplet excited states may be generated:

$$\mathrm{POP} + h\nu \rightarrow {}^1\mathrm{POP} \quad (1)$$

$$^1\mathrm{POP} + h\nu \rightarrow {}^3\mathrm{POP} \quad (2)$$

^{1}POP and ^{3}POP may show different reactivities. They can deactivate, leading to the corresponding photoproducts (eqs. 3, 4).

$$^1\text{POP} \rightarrow \text{Prods} \tag{3}$$

$$^3\text{POP} \rightarrow \text{Prods} \tag{4}$$

^{1}POP, as closed-shell species, generally react with other closed-shell species (Z, eq. 5):

$$^1\text{POP} + \text{Z} \rightarrow \text{Prods} \tag{5}$$

^{3}POP are radicals that may react with open-shell species (W, eq. 6)

$$^3\text{POP} + \text{W} \rightarrow \text{Prods} \tag{6}$$

and, specifically, with $^3O_2$, eq. 7:

$$^3\text{POP} + {}^3\text{O}_2 \rightarrow \text{POP-O}_2 \rightarrow \text{Prods} \tag{7}$$

To characterize ^{1}POP and ^{3}POP, and to gather information on their properties, detailed photophysical studies are needed, including quantum yields and lifetimes for the different occurring excited states, rate constants, etc. All these photophysical procecesses share the common fact that they do not lead to phototransformation. Thus, for example, the lowest excited singlet and triplet states of *sym*-triazines, common herbicides, have been studied experimentally using absorption, fluorescence and phosphorescence spectroscopy, and lifetime measurements, and have also been theoretically characterized [19]. The main absorption bands were assigned: four low-lying nπ* singlet transitions were identified in the absorption spectrum below the lowest ππ* singlet transition, with a parallel situation for the triplets. The low-lying emissions were assigned to the nπ* (S_1) (fluorescence) and nπ* (T_1) (phosphorescence). A significant coupling was found between nπ* and ππ* states, leading to a small S–T energy gap (E_G), as shown in the simplified Jablonski–Perrin diagram in Fig. 1.

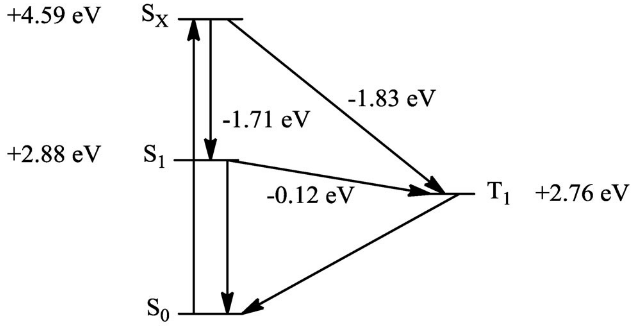

Fig. 1 Simplified Jablonski–Perrin diagram for a typical *sym*-triazine (atrazine).

Contrary to what is typically taught to undergraduate students, intersystem $^1\text{POP} \rightarrow {}^3\text{POP}$ crossing is rather common and effective, so that the relevance of the triplet state in photoreactivity may be high. Thus, the observed fluorescence quantum yields (Φ_F) are usually low, showing the importance of non-radiative deactivation pathways in the lowest excited singlet state. For example, we have obtained fluorescence quantum yields for different families of pesticides, with approximate values Φ_F (triazines) ca. $1 \cdot 10^{-4}$–$7 \cdot 10^{-4}$, Φ_F (phenylureas) ca. $2 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$, and Φ_F (sulfonylcarbamates) ca. $2 \cdot 10^{-1}$. Such low values for Φ_F imply high uncertainties in the measure of fluorescence, which may have serious implications from the analytical point of view. Phosphorescence quantum yields are typically high: Φ_P

(phenylureas) and Φ_F (sulfonylcarbamates) ca. 0.8. Very high quantum yields for intersystem crossing have been found: Φ_{ISC} (phenylureas), Φ_{ISC} (sulfonylcarbamates) ca. 0.8.

The excess energy in ^{1}POP and ^{3}POP may be released through many non-radiative pathways [3]: e^- photoejection, bond-homolysis, bond-heterolysis, isomerization, etc., opening different reaction channels that lead to phototransformation (photochemistry). In this way, different short-lived species, in particular, radical cations, neutral radicals, and hydroxyl ($HO^\bullet$) adducts, may be produced and characterized in detail [13,14,24]. We have studied the short-lived species produced in the first stages of direct irradiation of different types of POPs: amines, anilines, phenylureas, sulfonylcarbamates, sulfonylureas, triazines, etc. UVC and light of higher energies frequently induce photoionization (through photoejection), generating a radical cation and a free e^- that is immediately hydrated by bulk water (eqs. 8 and 9):

$$\mathrm{POP} + h\nu \rightarrow \mathrm{POP}^{\bullet+} + e^- \tag{8}$$

$$e^- + n(\mathrm{H_2O}) \rightarrow e^-\text{-}(\mathrm{H_2O})_n \tag{9}$$

where n is the size of the water cluster solvating the electron [25]. The solvated e^- shows a very characteristic UV–vis absorption spectrum, with a very broad band peaking at 720 nm in deaerated medium, with a very high $\varepsilon(720\ \mathrm{nm}) \approx 19\,000\ \mathrm{mol{\cdot}L^{-1}{\cdot}cm^{-1}}$ [26], that may overlap other less intense absorption bands. For this reason, in order to observe other transient species, an e^--scavenger is frequently used, such as O_2 or N_2O, that are rapidly reduced (eqs. 10 and 11):

$$\mathrm{O_2} + e^- \rightarrow \mathrm{O_2}^{\bullet-} \tag{10}$$

$$\mathrm{N_2O} + \mathrm{H_2O} + e^-_{\mathrm{aq}} \rightarrow \mathrm{N_2} + \mathrm{HO^-} + \mathrm{HO^\bullet} \tag{11}$$

although other reactive oxygen species (ROS) are generated ($O_2^{\bullet-}$, $HO^\bullet$). Phenylureas, for example, upon 193 nm laser-flash photolysis generate, with Φ ca. 0.1, e^-_{aq} that decay very fast, and N-centered radicals peaking at ca. 450 nm (Fig. 2), for which the acidity constant was determined as $-1 \le pK_a \le 1$, depending on the structure of each compound, by fitting to a sigmoidal the change in absorbance vs. pH at the maximum wavelength (Fig. 3) [13].

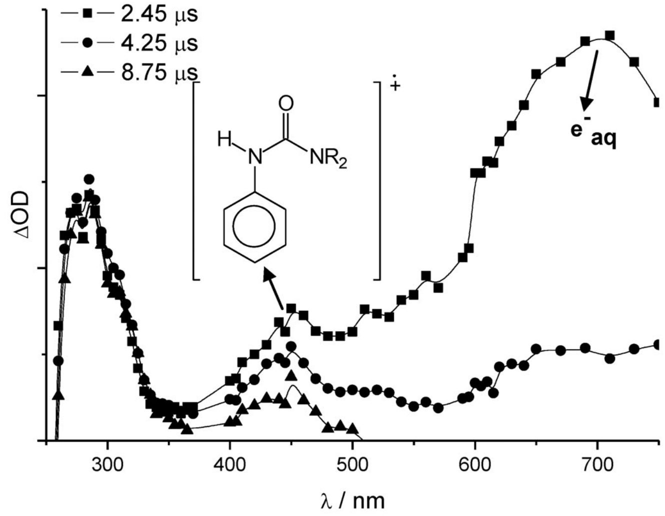

Fig. 2 Spectra obtained after 193 nm LFP of Ar-satd. 50 μM phenylurea at pH ca. 7.

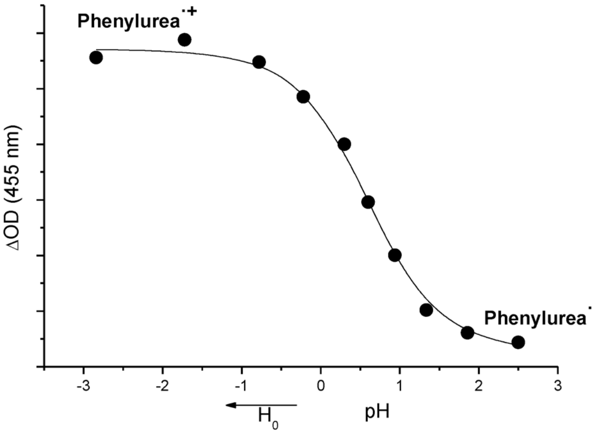

Fig. 3 Typical plot obtained for the determination of pK_a for the radical cation of phenylureas.

Therefore, the radical cation formed upon photoionization of phenylureas deprotonates immediately to yield the corresponding neutral radical $POP^•$, which exhibits a lower absorption.

The assignment of the band for the N-centered radical can be independently checked by using an alternative technique to one-e^- oxidize the starting *N*-phenylureas. Possibly the most powerful alternative to do this is pulse radiolysis [27]. This technique uses ionizing radiation, accelerated e^- that are absorbed by the medium (H_2O) rather than a chromophore of the dissolved species. In this way, primary oxidant and reducing species are generated ($HO^•$ and e^-, eq. 12), that may be selectively scavenged (eqs. 10, 11, and 13) and controlled to generate secondary oxidant and reducing species with ad hoc chemical properties ($E°$, pK_a, reactivity, selectivity, etc., eqs. 14 and 15).

$$H_2O \rightsquigarrow H_2O^{•+} + e^- \rightarrow HO^• + H^+ \tag{12}$$

$$HO^• + tBuOH \rightarrow tBuO^• + H_2O \tag{13}$$

$$Ox + HO^• \rightarrow Ox^{•+} + H_2O \tag{14}$$

$$Red + e^- \rightarrow Red^{•-} \tag{15}$$

Since e^-/e^-_{aq} are generated, it may react with the species that are present in the medium, reducing them to the corresponding radical anions ($POP^{•-}$). Thus, phenylureas may undergo one-e^- reduction to give the corresponding $POP^{•-}$, which can be characterized exactly in the same way described above for $POP^{•+}$. Thus, the radical anions for phenylureas are observed as a short-lived species peaking at ca. 350 nm and their acidity constant was determined as $4 \le pK_a \le 6$, depending on the structure of the compound [13].

The role of excited states and short-lived intermediates has been largely overlooked. Few detailed mechanistic studies are available in which the proposed mechanism incorporates information on the different intermediates and the pathways through which they are formed. From all the above shown (simplified) evidences, it becomes clear that identifying the first stages in the phototransformation of POPs gives essential information to propose an appropriate reaction mechanism. For example, in the case of phenylureas, described above, identification of the neutral radical formed by deprotonation or the corresponding radical cation (the primary species), allowed to propose a C–N bond homolysis of this to yield a radical/cation pair within a cage (Fig. 4). This explains the observed reaction products: the species within the radical/cation pair may have or not time enough to diffuse apart. If they diffuse apart (path "a" in Fig. 4), anilines and unstable carbamic acids (that then decarboxylate) are obtained as reaction products, but if they cannot diffuse apart (path "b" in Fig. 4), the cation reinserts in the aromatic ring (photo-Fries rearrangement) [28]. Of course, the photo-Fries mechanism could also originate from

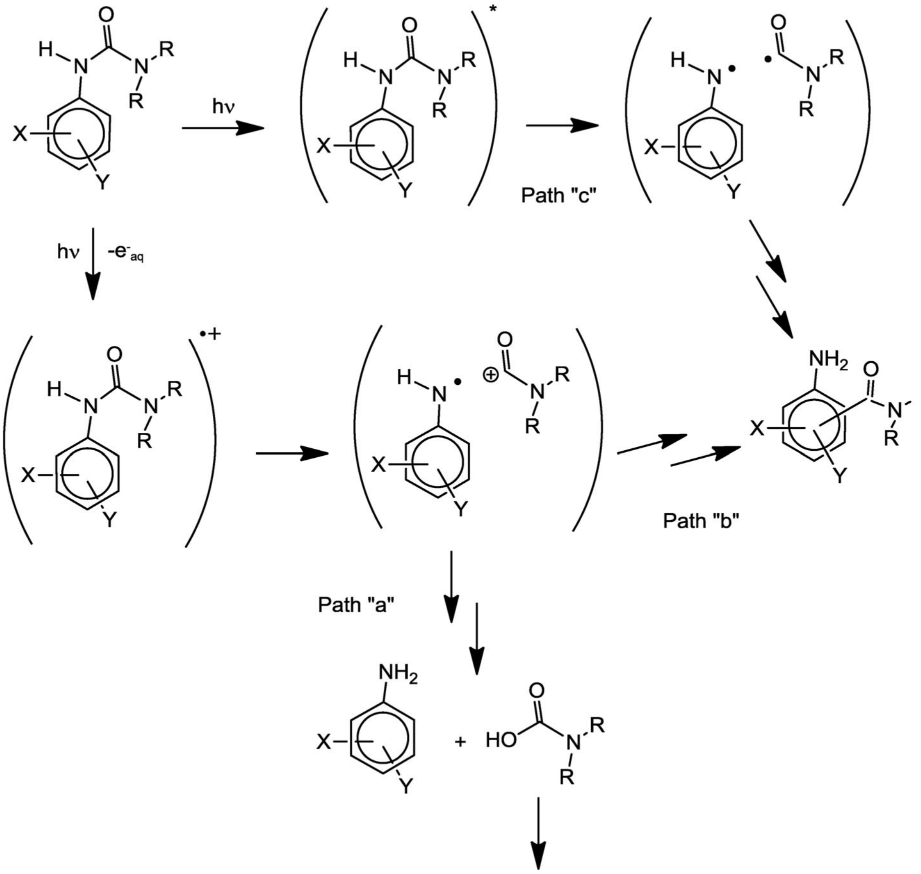

Fig. 4 Reaction mechanism for direct photodegradation of phenylureas.

a C–N bond homolysis to give a C- and a N-centered radical (path "c" in Fig. 4) that may rearrange, but that would not explain the presence of anilines as photoproducts.

HETEROGENEOUS PHOTOCATALYSIS

Briefly, heterogeneous photocatalysis makes use of a solid semiconductor that is a good adsorbent and whose E_G between the valence band (VB) and the conduction band (CB) can be covered by photons of the appropriate energy ($h\nu \geq E_G$) [29], so that an e^- is promoted from the VB to the CB, leaving a positive hole (h^+) in the VB, and generating an electron-hole pair (h^+-e^-), as shown in Fig. 5. Most h^+-e^- recombine readily, releasing heat, but in some cases both charge carriers (e^- and h^+) flow through their energy levels, migrating to the surface of the solid, where they can react with adsorbed H_2O, HO^-, and O_2, generating highly reactive primary species (eqs. 16–18) [2]:

$$h^+ + H_2O_{ads} \rightarrow H_2O^{\bullet +} (\rightarrow H^+ + HO^{\bullet}) \qquad E^o = 2.53 \text{ V [29]} \tag{16}$$

$$h^+ + HO^-_{ads} \rightarrow HO^{\bullet}_{ads} \qquad E^o = 1.89 \text{ V [30]} \tag{17}$$

$$O_{2\,ads} + e^- \leftrightarrows O_2^{\bullet -}{}_{ads} \qquad E^o = -0.33 \text{ V [31]} \tag{18}$$

The primary reactive species may also react with other molecules (POP/POP metabolites) that might be adsorbed on the surface of the solid semiconductor, in a process that may go through several

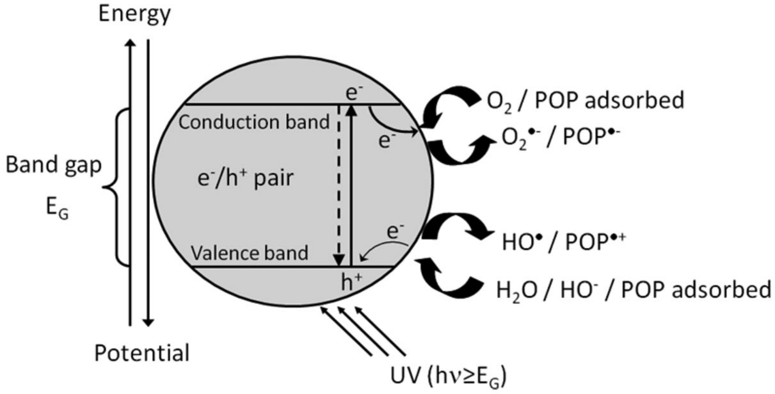

Fig. 5 Schematic representation of the main events triggering heterogeneous photocatalysis.

cycles until complete mineralization of the starting material [29], or until the surface of the photocatalyst becomes poisoned, which sometimes happens rather soon [32].

Different semiconductors are known that fulfill the fundamental requisites of being cheap, unreactive, and nontoxic, but, unfortunately, the overlap between their absorption spectrum and sunlight irradiance spectrum is usually small [29]. Many efforts have been made to improve this, including doping of the photocatalyst with different elements, introduction of defects in the crystalline network, etc., and this still a major challenge in the field nowadays. With the advent of nanochemistry, nanosized photocatalysts [33] and nanoscopic composites of photocatalysts have been produced that help improve the efficiency of photodegradation processes [34].

Heterogeneous photocatalysis is based on the surface phenomenon of adsorption. Usually the reagents and the photocatalyst are left in contact in the dark for a short period, during which adsorption equilibrium is assumed to be reached. However, the time needed to such equilibrium can be very variable depending on the structure of the reagent, from minutes to hours. In general, no kinetic, or equilibrium, adsorption studies are usually carried out, assuming ca. 30–60 min is enough. Furthermore, little is known about how adsorption equilibria are altered by irradiation; additional studies should be carried out on this topic.

Assuming the adsorption equilibrium has been achieved, there is also controversy on whether primary species such as $HO^{\bullet}$ react on the surface of the catalyst or in the bulk of the solution. $HO^{\bullet}$ has been shown to diffuse several hundred angstroms away from the surface into the bulk of the solution [35]. This was confirmed in the oxidation of furfuryl alcohol by $HO^{\bullet}$, for which a homogeneous-phase process is suggested [36]. In contrast, electron spin resonance (ESR) studies established that $HO^{\bullet}$ might migrate only some atomic distances from the surface, and therefore $HO^{\bullet}$ reactions would take place mainly on the surface [37]. These points are poorly understood, although they are key to understanding the kinetics of the process, especially in situations where adsorption is poor or impeded, or if the surface has become poisoned, but primary reactive species can still depart from it toward the bulk.

There may be also transport limitations both for molecules diffusing from the bulk of the solution toward the surface (eq. 19), and from the surface to the bulk (eq. 20), i.e., the rate of the whole photocatalytic process may be limited by the diffusion rather than one of the reactions taking place at the surface (eqs. 21–23).

$$\mathrm{POP_{bulk}} \rightarrow \mathrm{POP_{ads}} \tag{19}$$

$$\mathrm{(POP\ metabolites)_{ads}} \rightarrow \mathrm{(POP\ metabolites)_{bulk}} \tag{20}$$

$$\mathrm{POP_{ads}} + h^{+} \rightarrow \mathrm{(POP\ metabolites)_{ads}} \tag{21}$$

$$\mathrm{POP_{ads} + HO^{\bullet}_{ads} \rightarrow (POP\ metabolites)_{ads}} \tag{22}$$

$$\mathrm{POP_{ads} + O_2{}^{\bullet -}{}_{ads} \rightarrow (POP\ metabolites)_{ads}} \tag{23}$$

Little is known about the role of these processes on the overall kinetics of photocatalysis, and detailed investigations are needed.

It is not unfrequent to observe plateaus or “induction periods” at the beginning of heterogeneous photocatalysis processes. Propanolol, a nonselective β-blocker drug used against cardiovascular diseases, when subject to a pure photolytic regime, follows first-order kinetics, but upon heterogeneous photocatalysis the kinetics shows a plateau at the beginning of the process that lasts for ca. 20 min before the process accelerates (Fig. 6). This could be due to a limited transport of the drug to the surface of the photocatalyst. Besides, the reduced rate at the beginning of the process seems to indicate that $HO^{\bullet}$ does not diffuse into the bulk of the solution.

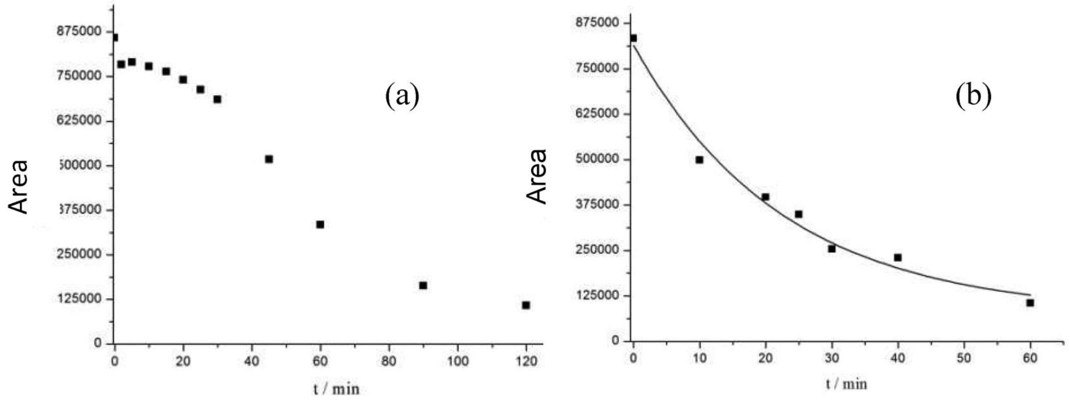

Fig. 6 (a) Photocatalysis of 30 mg L^{-1} propanolol, λ_{exc} = 366 nm, [P25] = 1 g·L^{-1}, pH = 6, T = 298 K. (b) Photolysis of 30 mg L^{-1} propanolol, λ_{exc} = 366 nm, pH = 6, T = 298 K.

The most popular photocatalyst is the well-known Degussa (Evonik) P25, with an averaged composition: 78:14:8 in anatase, rutile, and amorphous phase [38]. Despite the E_G values for rutile (3.03 eV) and anatase (3.18 eV), the combination of both in P25 shows a synergistic effect that makes it much more photoactive than the separate components. Though the high photocatalytic activity of P25 is attributed to the increase in charge-separation efficiency resulting from interfacial e^{-}-transfer from anatase to rutile, coupled in a bilayer form [39], the fundamental reason for such positive synergy is, as yet, unknown. This effect deserves more research.

Different product distributions, or even different products, have been reported, depending on the allotropic form of the photocatalyst used. For example, different product distributions are found using anatase, rutile, and P25, as photocatalysts during the photocatalysis of phenylureas (Fig. 7). Again, more research is needed to understand this effect [13].

Adsorption isotherms may show very different behavior for different surfaces, even when comparing allotropes of the same photocatalyst. Figure 8 shows this for the adsorption of phenylureas onto TiO_2 as anatase, rutile, and the commercial mixture P25. Clearly, the adsorption isotherm for P25 is not straightly derived from those for anatase a rutile, and the synergetic effect is unclear. Furthermore, the adsorption isotherm for P25 shows the formation of a complete layer, and how another layer is being formed. The common interpretation of heterogeneous photocatalysis (Fig. 5) accounts for the role of the first layer of adsorbed molecules, but not beyond. It is not unreasonable to assume that charge carriers might migrate beyond the first layer, and this needs appropriate modeling.

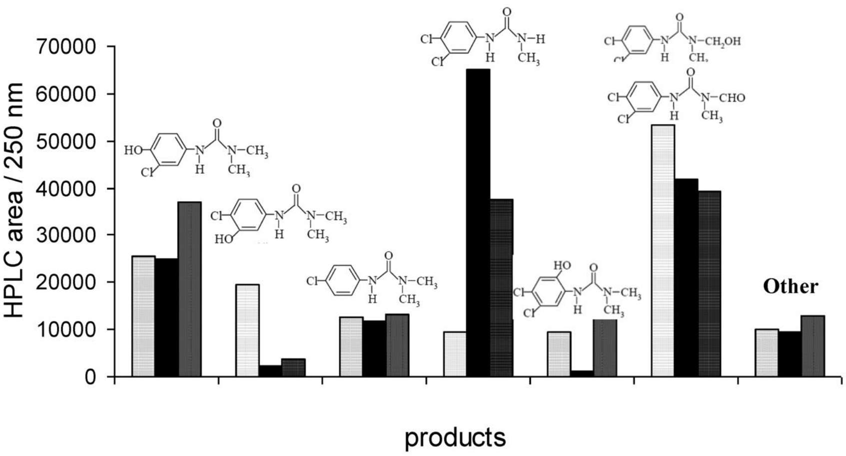

Fig. 7 Yields of main photoproducts obtained upon during UVA–vis irradiation of 12.9 μM phenylurea in 1 g·L^{-1} suspensions of rutile (▨), anatase (■) and Degussa-P25 (■).

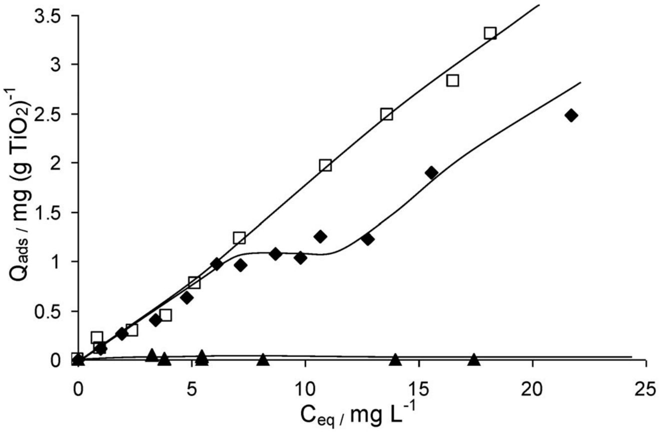

Fig. 8 Adsorption isotherms for phenylureas on P25 (◆), rutile (▲) and anatase (□). Tendency lines, shown only for the sake of clarity, are not mathematical fits.

A common, largely overlooked problem in heterogeneous photocatalysis is the occurrence of bi-exponentially shaped kinetics, that show a sharp decay of the reagent at the beginning of the process, followed by a slower decay. Typical examples are shown in Fig. 9 for the photocatalyzed degradation of carbamazepine. Typically, mixing effects or alterations due to irradiation effects are claimed, therefore, those first few points defining the sharp (fast) decay are neglected/omitted.

Usually, heterogeneous photocatalysis is interpreted in terms of Langmuir's adsorption model and the kinetics of the process according to the Langmuir–Hinshelwood model. This assumes, among other hypotheses, that the surface is homogeneous, with only one type of active adsorption sites. A typical organic molecule with aromatic groups and polar groups may show different possibilities for interaction with the surface (through the π-electrons of the aromatic groups, through nonbonding electrons of heteroatoms, or through charged groups such as carboxylate, ammonium, etc.). The preferred mode of interaction will depend on the nature of the surface and will mark the number of molecules occupying the surface. We have applied this idea under the simplified hypothesis that there are two different types of adsorption site and worked out the kinetic equations.

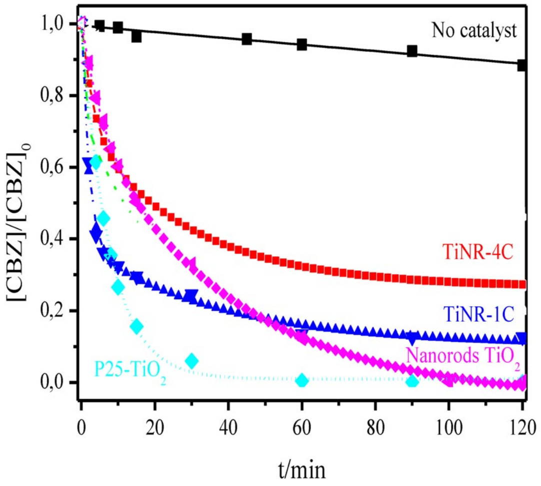

Fig. 9 Effect of different TiO$_2$-based photocatalysts on the removal of aqueous carbamazepine upon UVA–vis irradiation. $[CBZ]_0 = 8$ mg•L^{-1}, $P(O_2) = 21$ %, [catalyst] = 0.5 g•L^{-1}, T ca. 298 K, pH ca. 6.

Figure 10 shows this for the heterogeneous photocatalysis of ketoprofen, a nonsteroidal anti-inflamatory drug with analgesic and antipyretic effects: two different types of adsorption sites are supposed to be present: two interactions through the aromatic ring bearing the benzoyl group (protonated and unprotonated carboxylate) and one through the carboxylate group. There are also three adsorption/desorption equilibria that can be expressed by the ratio of the corresponding adsorption (k_{11}, k_{12}, k_{13}) and desorption rate constants (k_{-11}, k_{-12}, k_{-13}), and that need to be considered. Each of the three adsorbates may react on the surface with any of the primary reactive species (h^+, HO$^\bullet$, or e^-), giving three irreversible steps (k_{21}, k_{22}, k_{23}). Assuming the adsorption is not rate-determining, $k_{2i} << k_{1i}$ and k_{-1i}, and the desorption of the products is fast

$$r = \frac{k_{21}K_{11}[\mathrm{AH}]}{1+K_{11}[\mathrm{AH}]+K_{1P}[P_1]} + \frac{k_{22}K_{12}[\mathrm{A}^-]}{1+K_{12}[\mathrm{A}^-]+K_{2P}[P_2]} + \frac{k_{23}K_{13}[\mathrm{A}^-]}{1+K_{13}[\mathrm{A}^-]+K_{3P}[P_3]}$$

where $K_{iP}[P_j] = \Sigma_j K_{iP,j}[P_{ij}]$, i.e., the term related to the adsorption of the reaction products.

Under conditions where $1 >> K_{1j}[A_1] + K_{iP}[P_j]$ ($[A_1]$ is either [AH] or [A$^-$]) and working at constant pH, the rate equation is first order with respect to A$^-$ or AH, and gives a monoexponential decay:

$$r = \frac{k_{21}K_{11}[H^+] + \left(k_{22}K_{12} + k_{23}K_{13}\right)K_a}{\left(K_a + H^+\right)}[\mathrm{A}] = k_{\mathrm{app}}K_{\mathrm{L,app}}[\mathrm{A}] = k_{\mathrm{exp}}[\mathrm{A}]$$

i.e., $[\mathrm{A}]_t = [\mathrm{A}]_0\, e^{-k_{\mathrm{app}}t}$, where $[\mathrm{A}] = ([\mathrm{AH}] + [\mathrm{A}^-])$.

On the other hand, the decay could be bi-exponential (it could even include additional exponentials) if

i. the adsorption is rate determining, or
ii. the desorption is not fast, or
iii. the reaction photoproducts do not desorb efficiently from the active sites, poisoning the surface,

and when $[\mathrm{A}^-] >> [\mathrm{AH}]$, the following equation could be used:

$$[\mathrm{A}^-]_t = [\mathrm{A}]_{02}\, e^{-k_{2,\mathrm{obs}}t} = [\mathrm{A}]_{03}\, e^{-k_{3,\mathrm{obs}}t} + ([\mathrm{A}]_0 - [\mathrm{A}]_{02} - [\mathrm{A}]_{03})$$

where $[\mathrm{A}]_{0i}$ is the maximum coverage of the active site i (2 and 3) where A$^-$ adsorbs.

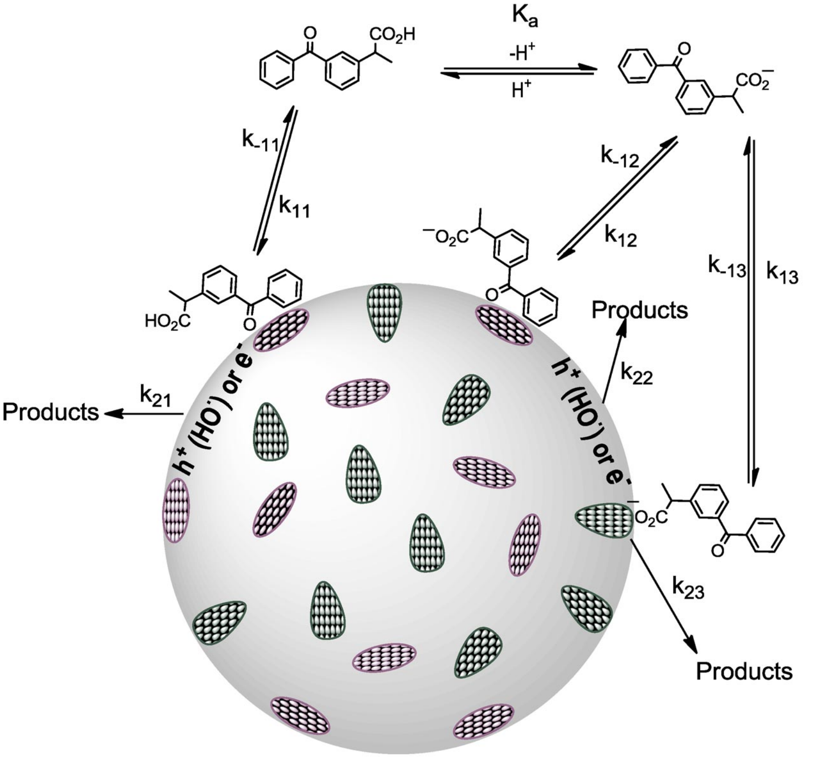

Fig. 10 Schematical representation of the different processes taking place during the aqueous heterogeneous photocatalysis of ketoprofen taking place at two different adsorption sites.

Thus, this two-active-site adsorption model can explain the frequently observed bi-exponential behavior. The curves in Fig. 9 are the best bi-exponential fits of this mathematical model to the experimental data. This adsorption model could be applied to the photocatalyzed degradation of different types of POP to verify its generality.

CONCLUSIONS

Photochemistry constitutes an excellent and promising green and cheap technology for pollution abatement, or even elimination. However, there are a number of aspects, both in direct irradiation and in heterogeneous photocatalysis, that still need study for a better control of the process. Thus, in direct irradiation (photolysis) additional work needs to be done on the role of excited states, as they determine the fate of the process, and also on the detailed mechanistic description of the process, aiming at a better control of reactivity. In heterogeneous photocatalysis, further research is required in many aspects: the effect of irradiation upon adsorption equilibria, the reactivity of primary species ($HO^\bullet$) on the surface of the catalyst vs. that in the bulk of the solution, the role of diffusion processes on the overall kinetics of photocatalysis, the origin of the observed plateaus (or “induction periods”) at the beginning of the processes, the reason for the synergetic effect in mixtures such as P25, the effect of the presence of more than one adsorbed layer, and the development of suitable kinetic models accounting for the observed bi-exponential behavior.

A model has been proposed that considers multiple active adsorption sites, and the corresponding kinetic equations derived to fit the typically overlooked bi-exponential kinetics that sometimes are obtained in this kind of work.

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