

INTERMEDIARY COMPOUNDS IN ADVANCED OXIDATION PROCESSES FOR WASTEWATER TREATMENT

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Abstract: *The research on advanced oxidation processes, like heterogeneous and homogeneous photo-catalysis, increased considerably in the last decade, due to their successfully application in removing wastewater pollutants. During these photo-catalytic processes, complex chain reactions occur that may lead to the formation of intermediates (radicals), some even more hazardous than the initial ones. The aim of the advanced oxidation processes is to achieve the total mineralization of the pollutant, which implies the process control. This paper gives a basic review about the last research done on the degradation products formed during dyes photo-degradation and their control, in aqueous solutions under visible or UV irradiation.*

Key words: *advanced oxidation processes, photo-catalysis, dyes, intermediary compounds, identification techniques.*

1. Introduction

Advanced oxidation processes (AOPs), involving single- or multiple-phase systems, are under active investigations. Some examples are given in Table 1 [26], [28]. These processes make use of ultraviolet or visible light, different oxidants (O₂, H₂O₂, O₃), catalysts (TiO₂), to generate highly reactive radicals (HO·) for the degradation of aqueous pollutants into innocuous compounds [6].

Among pollutants, dyestuff poses a major environmental concern, as they are extensively used as colorants in a wide variety of products, such as textile, paper or even food products. During their processing, some are discharged in textile effluents, causing problems to the aquatic environment (absorption and reflection of

Advanced oxidation processes Table 1

Heterogeneous processes	→ O ₂ /TiO ₂ /UV → O ₃ /TiO ₂ /UV → Fe ³⁺ /TiO ₂ /UV
Homogeneous processes	→ Fe ³⁺ /UV → H ₂ O ₂ /Fe ²⁺ /UV → H ₂ O ₂ /UV → O ₃ /UV → Cl ₂ /UV

sunlight, toxicity) [1], [7], [19].

Optimized AOPs should be used, in order to obtain the complete mineralization of the pollutant and there are already a lot of demonstrations for the successful degradation of dye pollutants by AOPs methods [12], [15].

During the photo-catalytic processes, complex chain reactions occur that may lead to the formation of colourless organic

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intermediates, sometimes more toxic than the original pollutant. The aim of the advanced oxidation processes is to obtain the total mineralization of the pollutant, thus leading to the complete photo-bleaching of the wastewaters-containing dyes.

Heterogeneous or homogeneous photo-catalysis may be applied, with careful monitoring of the process by the use of suitable analytical techniques, which may help to the prediction of possible fragmentation pathways of the pollutant during its photo-degradation.

This study is aiming to review the main photo-catalytic processes used for pollutants degradation during AOPs wastewater treatment, as well as the chromatographic techniques available for the identification of the photo-degradation intermediate products.

2. Photo-Catalysis Process

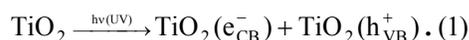
The principles of the photo-catalysis process are well established throughout the scientific community. Two basic types of photo-catalysis are explained, heterogeneous and homogeneous ones.

Heterogeneous photo-catalysis can occur by photo-catalytic (UV light) and photo-assisted degradation (VIS light). Their briefly principles are given in Figure 1, in which the dye substrate is used as the model pollutant. Among these AOPs given in Table 1, only TiO₂ and photo-Fenton photo-catalysis will be further presented.

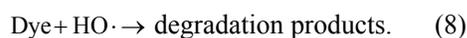
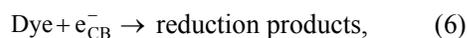
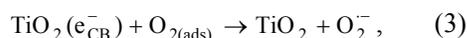
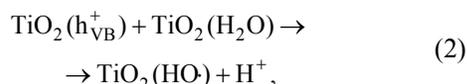
2.1. UV Heterogeneous Photo-catalysis

Under the influence of a UV source (at $\lambda \leq 400$ nm), an initial photo-excitation will take place in the semiconductor/catalyst substrate. This involves the absorption of photons by the TiO₂ semiconductor particles. UV radiation, containing photons with energy that is higher (or equal) than the band gap energy

of the semiconductor ($E_g \approx 3.2$ eV for the anatase TiO₂ polymorphic form), will induce the promotion of an electron (e^-), from the valence band (VB) to the conduction band (CB). Photo-electrons (photo- e^-) and photo-holes (photo- h^+) pairs are thus generated, according to Eq. (1):



Some of these photo-generated e^- and h^+ will participate in charge/energy transfer reactions with the adsorbed reactants (dye molecules, oxidants) on the surface of TiO₂ catalyst, leading to the formation of highly reactive radicals (HO·) and to different intermediary products (Eq. 2-8):



2.2. VIS Heterogeneous Photo-catalysis

VIS-heterogeneous photo-catalysis is regarded as the heterogeneous photo-catalysis occurring under visible light irradiation ($\lambda > 400$ nm), also called photo-sensitized or photo-assisted oxidation.

Under visible light, the initial photo-excitation takes place in the dye, which is absorbed onto the TiO₂ surface. The excited dye (Dye*) will interact with the ground state catalyst (TiO₂ surface/conduction band). Unfortunately this interaction is often restrained by the de-excitation mechanism of the dye molecule.

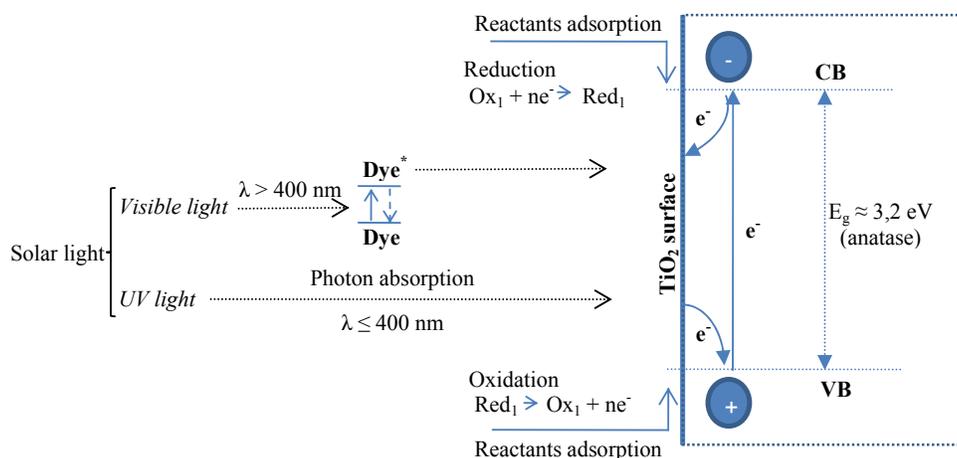
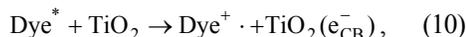
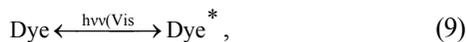


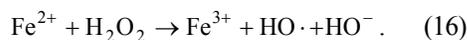
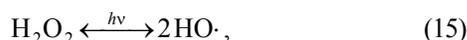
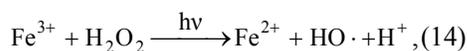
Fig. 1. Schematic diagram describing dyes photo-catalytic processes (modified from references [13] and [31])

The following equations describe, in general some of the processes, but for a more detailed understanding of the mechanisms complexity, other reviews should be studied [4], [14], [18], [21]:



2.3. Homogeneous Photo-catalysis

The homogeneous photo-catalysis occurs in aqueous solutions and is mainly based on the photo-Fenton reaction [10], [24], in the presence of the Fe^{3+} cations. Iron ions are reduced from Fe^{3+} to Fe^{2+} , and under light irradiation are forming $\text{HO} \cdot$ radicals. If a second oxidizing agent is added (H_2O_2), more hydroxyl radicals will be formed. In addition, Fe^{3+} is regenerated by reacting with H_2O_2 , forming more hydroxyl radicals (Eq. 14-16):



Finally, these highly reactive hydroxyl species will participate in the photo-degradation of the dye substrate (Eq. 8).

3. Intermediary Compounds in Heterogeneous Photo-Catalysis of Wastewater

Oppenländer [27] appreciated that probably the first study in which theoretical data are in good agreement with the experimental ones, was presented by Stefan and Bolton, in 1997. They applied an AOP system ($\text{H}_2\text{O}_2/\text{UV}$) to identify the by-products formed during propanone photo-degradation. They pointed out that the chain reactions initiated in the process, as well as the monitoring of the intermediates compounds are very complex, even for a simple pollutant like propanone is. Continuing the research, in 1999, they identified additional compounds.

Oppenländer [27] suggested that two types of mechanisms in AOPs should be considered, which are different but also interrelated. The first mechanism accepts intermediate degradation compounds, while the second one considers the mineralization of the organic pollutant.

3.1. Photo-degradation Mechanism

The second mechanism involves simple oxidation reactions in which, under the influence of UV radiation and in the presence of oxidation species, the pollutant is completely mineralized (Figure 2). This considers the optimal photo-catalysis process, but not always achieved.

More often, a chain reaction occurs, and reactive intermediates are obtained. The main products formed during the water photolysis are HO·, H· and the hydrated electron (e_{aq}^-), as given in Eq. (17).

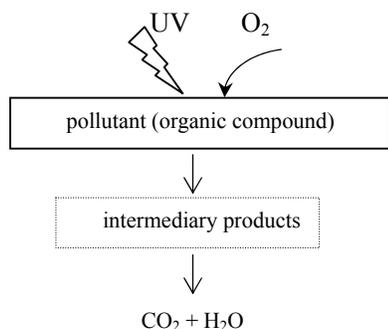
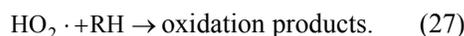
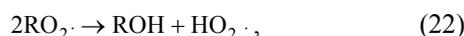
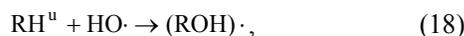
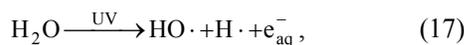


Fig. 2. *Substrate mineralization*

The hydroxyl radical follows two routes, depending on the type of the organic pollutant: unsaturated or saturated. If this is an unsaturated compound (RH^u) the oxidation occurs according the Eq. (18-19), while an unsaturated substrate (RH^s) will follow the second route, finally forming an oxidised compound (ROH), according to the Eq. (20-22). Equations (23-27) describe the main pathways and the role of hydrated electron and hydrogen

radical in producing other radicals leading to oxidation products.



By adding, in the reaction medium, other oxidants, like H_2O_2 will supplement the amount of HO· radicals (Eq. 15).

3.2. Identification of the Intermediary Compounds from Photo-catalysis Degradation

There are many photo-degradation studies, that focus on the intermediary compounds identification obtained during the treatment of wastewater with different loadings as dyes [30], pharmaceuticals [2], [36], pesticides [17], [34], benzenesulfonates [35], phenols [29], or organic solvents [20].

In their review, Rajeshwara et. al. [30] present different analytical methods available for the identification of the heterogeneous photo-catalytic degradation intermediates. Gas chromatography (GC) and liquid chromatography (LC) coupled with mass spectrometry (MS), as well as ionic chromatography (IC) is mostly used for the intermediates determination, as identification, but also are able to give more complex information about possible,

mechanisms that the pollutant follows, until mineralization is reached. The photo-catalytic intermediates that were identified have mainly hydroxyl, phenolic, amino, carboxyl, sulphonated groups resulted as

oxidative degradation.

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AOP systems with intermediary compounds detection

Table 2

Dyes	Type of dyes	AOPs	Analytical methods	Intermediary compounds	Ref.
acid orange 7	monoazo	TiO ₂ /UV	LC-MS, IC	inorganic ions; aliphatic acids; hydroxylated products; sulphonated, other polar intermediates	[1]
malachite green	triphenylmethane	TiO ₂ /UV TiO ₂ /Vis	LC-MS	mono-, di-, tri- <i>N</i> -demethylated intermediates	[3]
methyl red	monoazo	surfactant-TiO ₂ /UV	LC-MS	low molecular weight compounds	[5]
methyl orange	diazo	surfactant-TiO ₂ /UV	LC-MS	hydroxylated diazo derivatives	[5]
congo red	monoazo	TiO ₂ /Vis TiO ₂ /UV	LC-MS	hydroxyl naphthalene	[7]
acid violet 7, acid green 25	anthraquinone	TiO ₂ /UV	LC-MS, GS-MS	hydroxylated and sulphonated products	[8]
crystal violet	triphenylmethane	Pt-TiO ₂ /UV, TiO ₂ /UV	LC-MS, GS-MS	pararosaniline, benzophenone and phenol derivatives	[9]
reactive blue 4	anthraquinone	TiO ₂ /IO ₄ ⁻ /UV, electro-Fenton	GC-MS, LC, IC	poliaromatic hydrocarbons, phenols, aromatic alcohols, acids	[11]
crystal violet	triphenylmethane	H ₂ O ₂ /UV TiO ₂ /UV	LC-MS, GS-MS	aliphatic and aromatic acids, amines and phenols	[16]
acridine orange	N-heterocyclic	TiO ₂ /UV, TiO ₂ - γ - Fe ₂ O ₃ /UV	LC-MS	mono-, di-, tri-, tetra- <i>N</i> -demethylated species	[22]
ethyl violet	triphenylmethane	TiO ₂ films/TiO ₂ foil/UV	LC-MS, GC-MS	hydroxyethylated intermediates	[23]
methyl red	monoazo	TiO ₂ /UV	LC-MS	low molecular weight organic acids	[25]
methylene blue	Thiazin	Cr-Ti binary oxide/UV	LC-MS	demethylation intermediates	[32]
metanil yellow	monoazo	TiO ₂ /UV TiO ₂ /dark	GC-MS, LC, IC	phenols, aromatic amines and sulphonated derivatives	[33]
rhodamine b	xanthen	TiO ₂ -AC/MW ¹	LC-MS, GC-MS	<i>N</i> -de-ethylation intermediates	[37]

¹TiO₂ supported on activated carbon under microwave irradiation

Using a single technique is not always enough and for this reason, coupling two or more techniques is compulsory, for identification and confirmation of the oxidation compounds.

4. Conclusions

The main photo-catalytic heterogeneous and homogeneous processes and their possible radical formation mechanisms were presented.

The identification of intermediates that can form during the photo-catalytic degradation can be achieved by chromatographic methods, coupled with mass spectrometry. These techniques allow the intermediates identification, as well as possible degradative pathways formulation.

The AOPs chain reactions must be monitored aiming to control the process, in order to obtain the optimal mechanism that will finally lead to the mineralization of the substrate.

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