
Monica Pavel, Crina Anastasescu, Razvan-Nicolae State, Anca Vasile, Florica Papa and Ioan Balint

“Ilie Murgulescu” Institute of Physical Chemistry of the Romanian Academy, 202 Spl. Independentei, 060021 Bucharest, Romania
* Correspondence:ibalint@icf.ro

Abstract: It is well-documented that large-scale pollution generated by human activity has a dramatic impact on ecosystems. In this context, removing harmful chemicals via photocatalysis has tremendous potential as a depollution method, utilizing freely available solar light and catalytic materials with low or negligible ecotoxicity. The main drawbacks, which aren’t often addressed in the available literature, are the formation of harmful intermediate products, low reaction rates, limited catalyst stability, and difficult catalyst recovery. In most cases, published works assess the efficiency of tested photocatalysts from pollutant degradation studies, whereas identifying and quantifying by-products is not often conducted. This review summarizes the recent advances reported for the photocatalytic removal of some organic (e.g., alcohols, carboxylic acids, volatile organic compounds, phenol) and inorganic (e.g., NO$_3^-$) contaminants. The efficiency of various UV- and visible-light active photocatalysts and the reaction degradation pathways were explained, emphasizing the main factors contributing to their mineralization. The reaction mechanisms, the identification and quantification of degradation intermediates, and the implication of reactive active species (ROS) were discussed and analyzed for each category of model target pollutant. Additionally, the actual challenges and future photocatalytic approaches to improve environmental remediation were presented.

Keywords: photocatalysis; air cleaning; wastewater treatment; reactive oxygen species; degradation pathways

1. Introduction

The economic prosperity brought by industrialization is associated with the dramatic degradation of the environment (i.e., water and air pollution, loss of natural resources, climate change, etc.). The uncontrolled release of numerous hazardous contaminants, such as dyes, chemicals, heavy metals, organic solvents, petroleum products, and solid wastes, is strongly contaminating the environment.

Advanced oxidation processes (AOPs) have attracted considerable interest due to their significant potential for environmental remediation [1]. Among them, heterogeneous photocatalysis employing semiconductor materials and various light sources is a promising route for the removal of persistent pollutants to produce harmless end products. During the photocatalytic process in the presence of the light of suitable energy (with higher energy than the respective band gap of the material), an electron (e$^-$) is excited from the valence band (VB) of a semiconductor to the conduction band (CB), generating a positive hole (h$^+$) in the valence band. Photogeneration of charge carriers (e$^-$/h$^+$) initiates the photocatalytic degradation process. The valence band hole oxidize surface absorbed water molecules or OH$^-$ to produce hydroxyl radicals (•OH). The photoexcited electrons reduce oxygen molecules and produce hydroperoxyl radicals (HO$_2$•) or superoxide radicals (•O$_2$$.^-$). During the photocatalytic process (Equations (1)–(4)), these reactive oxygen species
(ROS) and free electrons/holes react with the surface adsorbed molecules (e.g., organic, inorganic compounds) and convert the pollutants to unharmful products.

\[
\text{Semiconductor} + h\nu \rightarrow h^+ + e^- \quad (1)
\]

\[
e^- + h^+ \rightarrow \text{energy} \quad (2)
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ \quad (3)
\]

\[
e^- + \text{O}_2 \rightarrow \cdot\text{O}_2^- \quad (4)
\]

The efficiency of a photocatalytic reaction is mediated by the capability of the photocatalyst to generate longer-lived electrons and holes, leading to the formation of reactive free radicals. It also depends on the type of photocatalytic material and the operational parameters such as solution pH, irradiation time, and the presence of holes scavengers (sacrificial electron donors). Another factor affecting photocatalysis is the state of the material, e.g., powder form or its immobilization on support. Organic pollutants may contain a great diversity of elements, such as C, N, O, S, Cl, etc. During the successive degradation steps, each carbon atom requires at least four photo electrons (e\(^-\)) and four photo holes (h\(^+\)) in order to be mineralized into CO\(_2\). Consequently, it is clear that the high number of electrons and holes required for the mineralization of large organic molecules impede the efficiency of the depollution process. During the successive degradation steps, the photo charges break the large molecule down into smaller units via intricate redox processes. Consequently, photocatalytic technologies are easier for pollutants with one carbon atom in their molecule, such as formic acid, methanol, or formaldehyde. For larger organic molecules, the photocatalytic technologies should be associated with other methods, such as treatment with strong oxidants (e.g., ozone, persulfate ion, hydrogen peroxide) to raise the mineralization extent of the pollutant \[2–5\]. In depollution technologies, the fundamental problem is the extent to which the pollutant is photomineralized. Most papers analyze only the degradation of the target compounds into intermediates, which may be as harmful as the pollutant itself, without assessing the amount of carbon dioxide.

This work surveys the basic mechanisms involved in photocatalytic mineralization of the most common gaseous/liquid pollutants and a large area of efficient engineered materials used for their removal under light exposure. The novelty comes from the discrimination between the photocatalytic mechanisms/materials inducing the unknown or scarcely quantifiable intermediates and those leading to harmless end products such as CO\(_2\), Cl\(^-\), or N\(_2\). The manuscript is divided into four main subsections (Figure 1). The first subsection describes the photocatalytic removal of alcohols and carboxylic acids in gaseous and liquid phases. Methanol, ethanol, and oxalic acid were described as model molecules. The second subsection is related to the removal of volatile organic compounds (VOCs) from indoor air and wastewater. The class of the chlorinated VOCs is exemplified by trichloroethylene (TCE), perchloroethylene (PCE), and dichloroacetic anion (DCA) compounds, while the group of the aromatic VOCs is illustrated by benzene, toluene, xylene, and ethylene pollutants. The third subsection presents the photocatalytic mineralization of harmful aromatic compounds from wastewater, focusing on phenol model molecules. Finally, the fourth subsection refers to the photocatalytic removal of aqueous inorganic nitrogen-based compounds from wastewater concentrating on nitrate (NO\(_3^-\)) reduction. All these target pollutants were chosen due to their widespread usage, toxicity, and environmental pollution.

Challenges and future directions of photocatalytic environmental remediation are discussed. The potential of novel emerging photocatalytic technologies transferable to industrial applications is also analyzed.
Figure 1. Schematic illustration of the manuscript structure and its objectives.

2. Photocatalytic Removal of Organic and Inorganic Pollutants

Environmental pollution is a pervasive problem with consequences for human health, living organisms, and ecosystems. To solve this issue, the total transformation of the parent harmful compounds to eliminate their toxicity and persistence is necessary. In the following, recent advancements reported for the removal of recalcitrant organic and inorganic molecules are presented, taking a look at their reaction degradation mechanisms.

2.1. Photooxidation of Primary Alcohols and Carboxylic Acids in Gaseous and Liquid Media

The photocatalytic oxidation (PCO) of organic compounds to CO₂ should be the ideal degradative process in depollution technologies, especially when solar light, which is a cheap, regenerable energy source, is used [6]. The photooxidation of alcohols is investigated as a model reaction for the abatement of organic pollutants [7]. The degradation of the intermediary carboxylic acids, which resulted in alcohol’s photodegradation pathway, is also of great interest. In the meantime, alcohols can be an efficient and convenient hydrogen source via dehydrogenation or sacrificial reagents in photocatalytic water splitting.

Methanol is often chosen for fundamental studies concerning primary alcohols due to its structural simplicity but also as a prototype for organic pollutants in applicative research devoted to the environmental field. The oxidative sequence of methanol photomineralization to CO₂ involving only a few organic intermediates is an appropriate choice for the investigation of oxidative degradation mechanism [8,9] but also for establishing the activity ranking of various photocatalysts. The numerous studies on methanol photooxidation, both in gaseous phase and liquid media, centered especially on titania [10], support the idea that the driving force over semiconductor-type materials is the capacity of the catalyst to photo generate appropriate density of charges (e⁻/h⁺) combined with prevention of charge recombination.

2.1.1. Basic Data on Methanol Photodegradation on TiO₂

In what comes, we should list the key factors controlling the photomineralization of methanol on different engineered materials. The methanol degradation pathway is related to methanol surface coverage on photocatalysts as well as to the density of surface hydroxyl groups and adsorbed oxygen. For example, by exposing the adsorbed methanol on anatase (101) to UV irradiation, Setvin et al. [11] observed that the main reaction products are formaldehyde (CH₂O) and methyl formate (CH₃O–CHO), formed by distinct reaction pathways. The first results from methanol interaction with the co-adsorbed oxygen or terminal OH⁻ groups leading to methoxy anion formation:

\[ \text{CH}_3\text{OH} + \text{OH}^- \rightarrow \text{CH}_3\text{O}^- \rightarrow \text{H}_2\text{O} \]  \hspace{1cm} (5)
By accepting a hole, methoxy radical is generated:

$$\text{CH}_3\text{O}^- + h^+ \rightarrow \text{CH}_3\text{O}\cdot$$ (6)

This is further converted to formaldehyde. On the other hand, methyl formate (\(\text{CH}_3\text{O}^-\text{CHO}\)) is obtained at high methanol surface coverages. Shen et al. [12] reported an increased photoactivation rate of methanol on annealed rutile (110) surface, facilitating both oxygen and methanol adsorption. The authors identified the thermally activated cleavage of the \(\text{O}^-\text{H}\) bond as being the first step, followed by the photo-catalytically driven \(\text{C}--\text{H}\) bond cleavage. Also, the surface defects of TiO\(_2\) photocatalyst proved to increase the photo dissociation rate of methanol [13]. Shen et al. [8] showed that the methoxy group, formed on the catalyst surface, acts as a more efficient hole scavenger compared to the molecular methanol. On the methanol-saturated surface of rutile nanoparticles exposed to UV irradiation [14], the conversion of the methoxy group to formate, requiring two photo-electrons, is enhanced in the presence of oxygen. In this case, oxygen also acts as the main electron scavenger, competing with methanol oxidation.

A great number of semiconductor materials have been developed for the removal of organic pollutants from air and water by photomineralization. Noble (Au, Pt, Ag, Pd) and d-(Cu) metals deposition on TiO\(_2\) is typically used to extend the light absorption range of TiO\(_2\) and ZnO [15–17] but to bust the photocatalytic performances via better charge separation at Schottky domains created at metal/semiconductor interfaces [18–20]. The great majority of works concerning the photooxidation of alcohols (methanol) advance the following mechanistic pathways: (a) direct hole oxidation route and/or (b) oxidation intermediated by hydroxyl radicals (\(\bullet\text{OH}\)) resulting from the following reactions:

$$h^+ + -\text{OH} \text{ (surface hydroxyl)} \rightarrow \bullet\text{OH}$$ (7)

$$\text{O}_2 + e^- \rightarrow (\text{O}_2^-)_{\text{ads}} \text{ (on catalyst surface)}$$ (8)

$$(\text{O}_2^-)_{\text{ads}} + 2\text{H}^+ + e^- \rightarrow \text{H}_2\text{O}_2 \rightarrow 2\bullet\text{OH}$$ (9)

When \(\text{O}_2\) is not able to reach the surface because of high organic coverage, the direct hole route is favored [21].

### 2.1.2. Methanol and Ethanol Oxidation in Gaseous Phase on Bare and Modified Catalysts

Despite the great number of papers focusing on the photooxidation of methanol, only a few of them discriminate between degradation (oxidative degradation to intermediates) and mineralization (oxidation to \(\text{CO}_2\)). El-Roz et al. [22] carried out a mechanistic study using an operando-FTIR system coupled with gas phase analysis techniques (gas-IR and MS) on TiO\(_2\) P25 photocatalyst. The authors found that methanol concentration is a key factor in tailoring oxidation selectivity. Under light irradiation of 365 nm, the maximum methanol conversion to \(\text{CO}_2\) and \(\text{H}_2\text{O}\) was observed for 500 ppm CH\(_3\)OH in the gas phase (20% \(\text{O}_2/\text{Ar}\)), according to the reaction:

$$\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 3\text{H}_2\text{O}$$ (10)

For 1200 ppm CH\(_3\)OH in the gas phase, the favored product was methyl formate:

$$2\text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{OCHO} + 2\text{H}_2\text{O}$$ (11)

According to the authors, the oxidation sequence starts with the dissociative chemisorption of methanol, leading to the formation of surface methoxy groups which are oxidized to formate and finally to \(\text{CO}_2\), the last step being considered as rate limiting for the methanol photooxidation. Additionally, methyl formate secondary product can result from a reaction between adsorbed formate and methoxy group.

Photocatalytic oxidation of methanol in visible light over AuNPs modified WO\(_3\) was studied by DePuccio et al. [23] using a continuous flow gas-phase reactor. Distinct
photocatalytic tests performed comparatively on AuNPs/SiO$_2$ and bare WO$_3$ indicated that the surface plasmon resonance (SPR) phenomenon (induced by AuNPs) and the band gap excitation of WO$_3$ are responsible for two distinct mechanisms involved in methanol oxidation. One mechanism is responsible for methyl formate generation, whereas the other leads to the formation of formaldehyde. When AuNPs are deposited on WO$_3$, the SPR triggered by light absorption enhances the separation of the photogenerated charges by WO$_3$, increasing thus the photocatalytic activity. Over bare WO$_3$, the formation of CO$_2$ was not observed, contrasting with Au/WO$_3$, where CO$_2$ was the major reaction product (39%).

Ethanol photocatalytic oxidation is also highly important for depollution applications since it largely emerges from industrial activity. In addition, it is noteworthy to investigate the differences in photoreactivity brought by the carbon–carbon bond in comparison to methanol.

Muggli et al. [24] studied the photocatalytic oxidation of ethanol using transient reaction techniques and isotope labeling. The Carbon-13 labeled ethanol (CH$_3^{13}$CH$_2$OH) adsorbed on Degussa P-25 was exposed to light (maximum intensity ≈ 390 nm) and 0.2% O$_2$ in He. The CO$_2$, H$_2$O, and acetaldehyde formation have been observed for ethanol saturation coverage, whereas for lower coverage, only CO$_2$ and H$_2$O were obtained. The α-carbon of ethanol proved to be preferentially oxidized. This finding is also certified by the resulting intermediates (acetaldehyde and acetic acid) [25]. The reactions below depict the whole process.

\[
\text{Ethanol-derived Acetaldehyde (ads) → } (a) \text{ & (b)} \]
\[
(a) \rightarrow \text{acetic acid } \rightarrow \text{CO}_2 + \text{formaldehyde } \rightarrow \text{formic acid } \rightarrow \text{CO}_2 \text{ (fast)}
\]
\[
(b) \rightarrow \text{formic acid + formaldehyde } \rightarrow \text{formic acid } \rightarrow \text{CO}_2 \text{ (slow)}
\]

According to the authors, the presence of acetaldehyde on the catalyst surface, together with other intermediates, decreases the reactivity of (b). The enhancement of the acetaldehyde oxidation rate is required to increase the overall CO$_2$ formation.

Yu et al. [26] studied the photocatalytic conversion of ethanol to CO$_2$ in the presence of O$_2$ by using in situ infrared (IR) spectroscopy. The surface coverage of adsorbed H$_2$O and ethanol on P25 Degussa was identified as a key parameter in deciding the favored reaction pathway. The involved oxidizing species involved in the reaction are formed according to the following equations:

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{h}^+ + \text{e}^-
\]
\[
\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{OH}^- + \text{H}^+
\]
\[
\text{OH}^- + \text{h}^+ \rightarrow \cdot\text{OH}
\]
\[
\text{O}_{\text{2ads}} + \text{e}^- \rightarrow \text{O}_2^-
\]
\[
2\text{O}_2^- + 2\text{H}_2\text{O}_{\text{ads}} \rightarrow 2\cdot\text{OH} + 2\text{OH}^- + \text{O}_2
\]

The authors summarized the ethanol photo-oxidation by using h$^+$ and •OH as it comes:

\[
(\text{CH}_3\text{CH}_2\text{OH}_{\text{ad}}/\text{CH}_3\text{CH}_2\text{O}_{\text{ad}} \rightarrow \text{H}_2\text{O} + \text{CO}_2)
\]

I. For low ethanol coverage and adsorbed H$_2$O on the TiO$_2$ surface, an •OH-initiating oxidation mechanism leading to HCOO$^-$$_{\text{ads}}$ as a major intermediate was proposed by the authors. The envisaged parallel/series reactions were:

\[
\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}}/\text{CH}_3\text{CH}_2\text{O}_{\text{ads}} \rightarrow,
\]
\[
(a) \rightarrow \text{adsorbed C}_1\text{-oxygenated species (HCHO}_{\text{ads}}, \text{HCOOH}_{\text{ads}}, \text{and HCOO}^-_{\text{ads}})
\]
\[
(b) \rightarrow \text{adsorbed C}_2\text{-oxygenated species (CH}_3\text{COOH}_{\text{ads}} \text{ and CH}_3\text{COO}^-_{\text{ads}}) + \text{C}_1\text{-oxygenated species}
\]
\[
(c) \rightarrow \text{adsorbed CH}_3\text{CHO}_{\text{ads}}
\]
II. For high ethanol coverage, decreased in the amount of adsorbed water on the TiO₂ surface was registered due to the fact that the direct interaction between the photogenerated holes and adsorbed ethanol is favored. This leads to the hydrogen abstraction from α-carbon (CH₃CH₂OH_ads/CH₃CH₂O_ads) and the formation of CH₃COO⁻_ads as primary, intermediate species, according to the reactions:

\[
\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}} + h^+ + \text{O}_{\text{lattice}} \rightarrow \text{CH}_3\text{COO}^- + 2\text{H}^+ \quad (25)
\]

\[
\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}} + 2h^+ + \text{O}_{\text{lattice}} \rightarrow \text{CH}_3\text{COOH} + 2\text{H}^+ \quad (26)
\]

In this system, the oxidation of ethanol to CO₂ is carried out preferentially by highly oxidizing •OH radicals to the detriment of holes.

Modifying P25 with Ag nanoparticles, Fukuhara et al. [27] obtained an active photocatalyst for the degradation of ethanol in the UV and visible range. They monitored the heat released by ethanol partial and total oxidation (Equations (27)–(29)):

\[
\text{C}_2\text{H}_5\text{OH} + 1/2\text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}, \Delta H^0 = -172.91 \text{ kJ mol}^{-1} \quad (27)
\]

\[
\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}, \Delta H^0 = -1277.38 \text{ kJ mol}^{-1} \quad (28)
\]

\[
\text{CH}_3\text{CHO} + 5/2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}, \Delta H^0 = -1104.47 \text{ kJ mol}^{-1} \quad (29)
\]

The results revealed different light-induced acting mechanisms for Ag nanoparticles and TiO₂. Under UV irradiation, TiO₂ promotes the partial oxidation of ethanol to acetaldehyde, whereas O₂ activation accounts for CO₂ and H₂O yield. Under visible light, the complete oxidation of ethanol to CO₂ and generation of H₂O occur over Ag₀ nanoparticles.

The presence of oxygen was highlighted as a key factor for CO₂ production on Ag-TiO₂ catalyst under UV-Vis irradiation (Figure 2). Figure 2b shows that O₂ is activated under UV light on TiO₂, whereas the surface of the Ag nanoparticle promotes the partial oxidation of C₂H₅OH to CH₃CHO and the cleavage of the C–C bond leading to CO₂ and CH₄ formation.

![Figure 2](image_url)
2.1.3. Methanol, Ethanol, and Oxalic Acid Oxidation in Liquid Phase on Pristine and Modified Catalysts

Kawai et al. [28] proposed the following mechanism for methanol degradation on TiO$_2$-suspended powder in deaerated aqueous media under 500 W Xe-lamp light irradiation:

$$\text{MeOH} \rightarrow \text{HCHO} + \text{H}_2 \quad (30)$$

$$\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{HCO}_2\text{H} + \text{H}_2 \quad (31)$$

$$\text{HCO}_2\text{H} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (32)$$

At the beginning of the process, H$_2$ was the main gaseous product obtained along with small amounts of CO$_2$. The photogenerated holes are used for the oxidation of MeOH, HCHO, and HCO$_2$H intermediates, whereas the photogenerated electrons are responsible for H$_2$ production via proton reduction.

Villareal et al. [29] explored the photoelectrochemical oxidation of methanol and formic acid dissolved in water on polycrystalline anatase electrodes. The authors found that methanol oxidation to CO$_2$ is carried out by surface-bound hydroxyl radicals. This mechanism suggests weak interaction between methanol and oxide surface. In contrast, formic acid appears to be oxidized directly to CO$_2$ by the valence band-free holes, indicating strong adsorption on the catalyst surface, despite the competitive adsorption of water.

Methanol photooxidation in aqueous media has also been studied by Haselman et al. [30] on platinum-modified TiO$_2$. An ATR-FTIR setup was used for time-resolved investigations of both Pt particle growths during in situ photo deposition on TiO$_2$ thin films and the photooxidation of methanol under UV irradiation in aqueous environments. The authors certified that methanol is oxidized in aqueous solutions to H$_2$ and CO$_2$ by the photogenerated holes. Also, for 2.7% Pt loading on TiO$_2$, the methanol photooxidation to CO$_2$ takes place via the formation of formaldehyde intermediate, while for lower Pt loading (1.4%), methyl formate is obtained. The reaction mechanism depends on the availability of specific active sites (on platinum and defects).

The solar light-driven generation of CO$_2$ and H$_2$ from a water/methanol mixture has been carried out by Papa et al. [32] on PVP-protected bimetallic nanoparticles (Pt-Cu and Pt-Ag) by a modified protocol of the alkaline polyol method. Active photocatalysts for aqueous methanol mineralization have been obtained by supporting them on TiO$_2$ (2.16 mmol CO$_2$ h$^{-1}$ g$_{\text{cat}}$$^{-1}$ for Pt-Ag/TiO$_2$ and 1.68 mmol CO$_2$ h$^{-1}$ g$_{\text{cat}}$$^{-1}$ for Pt-Cu/TiO$_2$) under 125 W medium pressure Hg lamp and 10% O$_2$/Ar.

Photocatalytic experiments confirmed that not only semiconductor materials show photocatalytic activity but also large band-gap insulators such as tubular SiO$_2$ may work as extremely active photocatalysts in the methanol/water mixture when exposed to solar light [33]. SiO$_2$ nanotubes with a high surface density of light-absorbing defects were obtained by a modified sol-gel method, using DL tartaric acid as an organic template.

The formation of Si$_3^+$ defects by calcination enhanced light absorption characteristics, the importance of thermal treatment being illustrated in Figure 3a.

The CO$_2$ generation rate in Ar flow was 2.4 µmol h$^{-1}$ and increased at 12 µmol h$^{-1}$ in the presence of O$_2$. The evolvement of CO$_2$ and H$_2$ from aqueous methanol exposed to solar (AM 1.5) and visible light irradiation ($\lambda > 420$ nm) demonstrated that the light absorbing defects, having the energy levels located within the forbidden gap of SiO$_2$, are able to work as photocatalytic sites (Figure 3b).

ROS photogeneration over the SiO$_2$, SiO$_2$-TiO$_2$ nanotubes and P25, together with their impact on the aqueous methanol photodegradation, were also investigated [34]. The TiO$_2$
proved to work as a photocatalyst by intermediation of •OH radicals, while the SiO₂–TiO₂ generated O₂⁻. In contrast, the organic substrate was activated and degraded on the surface of SiO₂ by the intra-band gap, isolated surface quantum defects.

Oxalic acid is found in biological systems but also as an emerging residue from industrial activities (textile industry, etc.). Oxalic acid is often chosen as a model pollutant for testing the photoreactivity of dicarboxylic acids because its photodegradation process conducts mainly to CO₂. Other presumable intermediates, such as formic acid and carbonate, have not been clearly revealed [35].

The earlier mentioned SiO₂ material with different morphologies and modified with platinum proved to be efficient for the photomineralization of oxalic acid in the 200–800 nm range [36]. For this system, the degradation mechanism proposed the following sequences:

- Involving of the photogenerated holes in the oxalate oxidation at the catalyst surface (Equation (33))

\[ 2h^+ + C_2O_4^{2–} \rightarrow 2CO_2 \]  

(Equation (33))

- Enhancing of the photoelectron transfer to the oxygen and proton by the platinum presence (Equation (34))

\[ 2H^+ + 0.5O_2 + 2e^- \rightarrow 2H_2O \]  

(Equation (34))

The spherical SiO₂ particles were inactive, whereas the rate of CO₂ evolvement over tubular-shaped SiO₂ particles was 45 µmol g⁻¹cat h⁻¹. Platinum deposition on tubular SiO₂ further increased the CO₂ formation rate to 428 µmol g⁻¹cat h⁻¹, the efficiency of the modified catalyst being comparable with that of semiconductor-based materials.

Kosanić et al. [37] conducted the same photocatalytic process in oxygenated aqueous solution over TiO₂ powder (Degussa P25) under UV irradiation (300–400 nm) and correlated the CO₂ production with the illumination time. The authors advanced the following mechanism initiated by the •OH radicals:

\[ HC_2O_4^- + •OH \rightarrow OH^- + •COOH + CO_2 \]  

(Equation (35))

\[ •COOH + O_2 \rightarrow •HO_2 + CO_2 \]  

(Equation (36))

\[ •HO_2 + •HO_2 \rightarrow H_2O_2 + O_2 \]  

(Equation (37))

Doping of TiO₂ nanopowders with iron allowed the use of simulated solar light irradiation (AM 1.5) for the mineralization of oxalic acid in an aqueous solution. The redox sites created by introducing Fe³⁺ into the TiO₂ lattice were able to absorb the visible component of solar light [38]. The photocatalytic activity was found to increase due to the
enlargement of catalyst surface area and to the decrease in optical band-gap. The highest recorded CO$_2$ formation rate was 245 $\mu$mol h$^{-1}$. The proposed mechanism considered that the C$_2$O$_4^{2-}$ mineralization takes place either by •OH attack or by direct reaction with holes.

Kiatkittipong et al. [39] compared the photocatalytic generation of CO$_2$ in an aqueous solution under UV irradiation ($\lambda_{\text{max}} = 254$ nm) over various titanate nanoribbons. It was found the following sequence of the photocatalytic activity, in accordance with the increasing of the crystallinity (decreasing of bulk defects) due to the calcination step: TiO$_2$ > Na$_2$Ti$_3$O$_{11}$ > Na$_{1.48}$ H$_{0.52}$ Ti$_3$O$_7$ ~ H$_2$Ti$_3$O$_7$.

Cauxa et al. [40] used oxalic acid as an electron donor for water splitting performed on g-C$_3$N$_4$ and loaded with platinum (0.37 wt.%) under UV-Vis irradiation (using a cut-off filter for obtaining $\lambda > 380$ nm). Based on registered CO$_2$: H$_2$ ratios, the authors assumed that oxidation of water also occurs in addition to the photooxidation of oxalic acid since more hydrogen was produced. Also, the presence of hydrogen peroxide was identified in the oxalic solution after photocatalytic tests suggesting the free radical formation before the complete degradation of oxalic acid to CO$_2$. This is in accordance with the mechanism proposed by Kosanić et al. [37].

Karunakaran et al. [41] performed a systematic study on oxalic acid photomineralization under natural sunshine triggered by various particulate semiconductors (TiO$_2$, CuO, ZnO, Pb$_2$O$_3$, PbO$_2$, Bi$_2$O$_3$). The authors identified the operational parameters influencing CO$_2$ production as being the following: oxygen presence, the concentration of the oxalic acid solution, and the area of the catalyst bed. The photocatalytic efficiency relative to the oxalic acid mineralization was the following: ZnO > CuO = TiO$_2$ = Bi$_2$O$_3$ = Pb$_2$O$_3$ > PbO$_2$ for the next reaction conditions: 50 mL of 0.25 M acid, [O$_2$] dissolved = 24.7 mg L$^{-1}$, 1.0 g — catalyst loading, 15.68 cm$^2$ — catalyst bed, 10 min sunshine. Additionally, for each catalyst and the same reaction conditions, the degradation of the formic, acetic and citric acid was also performed. Table 1 presents the registered reactivity sequence:

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Reactivity Sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>oxalic acid &gt; acetic acid &gt; citric acid</td>
</tr>
<tr>
<td>CuO</td>
<td>formic acid &gt; oxalic acid &gt; acetic acid &gt; citric acid</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>formic acid &gt; oxalic acid &gt; acetic acid &gt; citric acid</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>formic acid &gt; oxalic acid = acetic acid &gt; citric acid</td>
</tr>
<tr>
<td>Pb$_2$O$_3$</td>
<td>formic acid &gt; oxalic acid = acetic acid &gt; citric acid</td>
</tr>
<tr>
<td>PbO$_2$</td>
<td>formic acid &gt; oxalic acid = acetic acid &gt; citric acid</td>
</tr>
</tbody>
</table>

2.2. Volatile Organic Compounds (VOCs) from Air and Wastewater

This section deals with the latest discoveries on VOC abatement from air and water using various photocatalysts and photocatalytic techniques.

2.2.1. Overview of Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs), such as alcohols, aromatics (e.g., benzene, toluene, xylene), aldehydes, and halocarbons are a major group of air pollutants [42] produced mostly from outdoor (industrial processes and transportation) or indoor sources (domestic products, building materials, and food industry). They can cause major health issues like respiratory diseases, heart issues or even cancer [42–44]. VOCs also represent a precursor of PM 2.5 (particulate matter are fine inhalable particles with diameters of 2.5 $\mu$m or smaller), which determines important environmental challenges all over the world [43]. On the other hand, chlorinated VOCs cause severe contamination in aquatic environments, TCE (trichloroethylene) and PCE (perchloroethylene), used at a large scale as solvents or in dry cleaning, are the most encountered types of VOC contaminants [45,46]. In the specific case of chlorinated compounds, the monitoring of Cl$^-$ release in time in the water phase or TOC (total organic compound) evolution can be a measure of pollutant removal efficiency [47].
With the exception of a few studies \[48–50\], most investigations ignore this aspect focusing only on the quantification of the chlorinated compound by GC measurement.

Many techniques have been used to remove those volatile organic compounds from the air or from water. These include adsorption, thermal catalysis, ozone oxidation or photocatalytic oxidation, the latter attracting more and more attention lately. The heterogeneous catalysis can offer various advantages if compared to other AOPs (advanced oxidation processes), such as moderate operation temperatures or pressure and low cost if sunlight is used as an irradiation source. On the other hand, even if photocatalysts offer good results, at least in lab-scale experiments, other AOPs proved to be as efficient, especially ozonation. For example, ozonation and activated carbon adsorption are accepted technologies for water remediation \[51\], but they do not meet the aim of our study.

Generally, three mechanisms regulate the photocatalytic mineralization of VOCs: light harvesting, photogenerated charge carrier (electrons and holes) separation, and charge injection into VOCs and their intermediates from the surface of the catalyst. In order to improve the effectiveness of charge carrier separation, various methods have been applied, such as metal doping, nonmetallic element doping, and the production of heterojunction from several materials with matching energy bands \[43\]. This can also be explained as follows: when a semiconductor photocatalyst is irradiated by light, an electron-hole pair is generated. Thus, an electron is excited from the valence band to the conduction band resulting in a hole \(h^+\) remaining in the valence band. This oxidizing hole can interact directly with an adsorbed molecule or can oxidize water to produce hydroxyl radicals, which are themselves oxidizing agents \[51\].

Therefore, in this review we focused on chlorinated and aromatic VOCs removal from the environment (water and air) using various photocatalysts working under different irradiation sources.

2.2.2. Chlorinated VOCs Abatement from Air and Water

Monteiro et al. \[52\] studied the photocatalytic oxidation of perchloroethylene using a photoreactor having a compound parabolic collector. The TiO\(_2\)-based paint was used as a coating for two configurations of monolithic structured cellulose acetate. The photocatalytic experiments were performed under solar irradiation (spectral range of 300 < \(\lambda\) < 800 nm). They obtained in the best experimental conditions (initial concentration = 1100 ppm, feed flow rate = 75 cm\(^3\) min\(^{-1}\), relative humidity \(\approx\) 40% and incident UV irradiance \(\approx\) 38.4 W m\(^{-2}\) in the presence of oxygen) a PCE conversion of around 60%. Also, they observed that if the relative humidity is low, Cl radical chain propagation reactions could be included in the photocatalytic oxidation mechanism of PCE and that the photoreaction can still occur in the absence of oxygen.

The authors proposed a reaction mechanism according to the schemes below (Figure 4). It relies on the supposition that the reaction of PCE degradation starts with the addition of •OH radicals, thus leading to a dechlorination reaction where •Cl radicals are formed. In detail, Figure 4a shows the attack of hydroxyl radical to PCE pursued by chlorine radical release yielding trichloroethenol. Figure 4b represents the addition of •Cl to PCE, thus forming chloroalkyl radical, which is then oxidized by superoxide radicals creating a peroxo radical. The peroxo radical can be transformed into chloroethoxy radical by reacting with a second peroxo radical which suffers a CC bond scission forming CCl\(_2\)O and CCl\(_3\) radicals. CCl\(_3\) converts into chloroform or carbon tetrachloride by reacting with H\(^+\) or •Cl, while CCl\(_2\)O produces phosgene that may be hydrolyzed into CO\(_2\) and HCl. Figure 4c shows the chlorination of PCE resulting in chloroalkanes. Here, PCE suffers a reaction with •Cl forming chloroalkyl radical that can be hydrogenated or chlorinated, resulting in pentachloroethane or perchloroethylene. Finally, Figure 4d represents the formation mechanism of trichloroethyl acetate and trichloromethyl acetate. If •OH is added to chloroalkyl radical and dichloroacetyl chloride, pentachloroethanol and dichloroacetic acid could be obtained. Dichloroacetic acid could be further chlorinated to obtain trichloroacetic acid. At the surface of the catalyst, dichloromethanol can be formed. In the end, ethyl,
trichloroacetate and methyl trichloroacetate may be produced after reactions between trichloroacetic acid and pentachloroethanol or dichloromethanol.

![Diagram of chemical reactions involving trichloroacetate and methyl trichloroacetate](image)

Figure 4. (a) •OH radical addition to PCE followed by •Cl radical generation; (b) •Cl addition to PCE followed by $O_2^-$ radical addition forming chloroalkanes and phosgene; (c) chlorination of PCE by addition of •Cl producing chloroalkanes; (d) esterification of ethyl, trichloroacetate and methyl, trichloroacetate. Reproduced with permission from ref. [52]. Copyright 2015 Elsevier.

Egerton et al. [53] presented their work regarding the influence of platinum on the UV (irradiation by a Philips PL-L 36W 09 actinic lamp, UV peak intensity at $\sim 360$ nm) photocatalytic degradation of dichloroacetate anion (DCA) by rutile and anatase forms of titania. They did the Pt deposition photochemically, with Pt(II) being more active than Pt(0). The activity of undoped rutile was lower than that of anatase, while after doping, the activity of rutile increased. In the end, both titania catalysts performed similarly. The authors observed that undoped Pt/anatase catalysts did not oxidize DCA when under visible light irradiation. On the other hand, Pt/rutile managed to oxidize DCA, being three times faster than experiments where Pt-free catalysts were used under UV irradiation.

Grzechulska-Damszel et al. [54] worked on a study regarding the photocatalytic decomposition of very low amounts (15 $\mu$g dm$^{-3}$, these concentration levels corresponding to those available in groundwater) of trichloroethylene (TCE) and tetrachloroethylene (PCE) in water using TiO$_2$. The authors performed various tests, including blank tests and tests
without light irradiation and observed that low (when catalysts were used in dark mode) or no degradation occurred. For the photocatalytic tests, the authors used commercial titania and a commercial reaction system (Trojan UVMax, Trojan Technologies, London, ON, Canada, UV/Vis radiation in the range of 250–800 nm, with high maximum at 254, 436 and 546 nm) commonly used for water disinfection. The photocatalyst was used either as suspended particles or as an immobilized refill (titania was coated onto a glass fabric). When subjected to light irradiation (UV-Vis lamp), either TCE or PCE alone was removed at about 95% in under 90 min, while when a PCE/TCE mixture was tested, around 95% degradation was still obtained after 150 min. Therefore, the authors concluded that low amounts of TCE and PCE can be removed from the water when using a titania-based photocatalytic process and recommend the use of the immobilized system, being more beneficial from an economic point of view.

Suarez et al. [55] studied the photocatalytic activity of TiO$_2$/zeolite hybrids for VOC oxidation. Two UV-A lamps (8 W Philips and 6.5 mW cm$^{-2}$ irradiance) were used as the irradiation source. The authors synthesized titania with various morphologies (nanoparticles of almost 5 nm and decahedral anatase particles (DAP) having around 100 nm) and used commercial TiO$_2$ for comparison reasons. They obtained the catalytic hybrid by incorporating TiO$_2$ on ZSM5 using either freeze drying, incipient wetness impregnation or mechanical mixing. After characterization, they evaluated the photocatalytic performance of the studied catalysts on trichloroethylene photooxidation (and also formaldehyde) under UV-A irradiation and continuous airflow. The authors observed that the incorporation of titania, regardless of its type, into ZSM5 improved the photocatalytic performance up to 10 times compared to single titania particles. Even though DAPs had the highest VOCs reaction rate, it was concluded that TiO$_2$ nanoparticles homogeneously distributed on the zeolite material showed the highest VOCs photooxidation and CO$_2$ formation rates of the series (titania NP/ZSM5 > DAP/ZSM5 > commercial titania/ZSM5).

A study regarding the effect of photocatalysis on the degradation of trichloroethylene (TCE) in aqueous solutions using a photocatalyst-coated plastic optical fiber (POF) was done by Chen et al. [56]. They used TiO$_2$ and ZnO as photocatalysts and two diodes (LEDs) with low light intensity as the light source (40 mW cm$^{-2}$, 395 nm and 20 mW cm$^{-2}$, 365 nm). Parachlorobenzoic acid (pCBA) was utilized as a hydroxyl radical for the calculation of hydroxyl radical conversion rate (ROH, UV). After performing experimental tests, the authors observed that titania-coated POF was more efficient in degrading TCE in basic solutions, while ZnO-coated POF had better results in acid solutions. This was expected due to the fact that the mechanism of TCE removal by titania is photocatalysis, while by zinc oxide is adsorption. Another noticeable fact was that if the coating time increases, thus increasing the coating thickness, the degradation efficiency decrease. On the other hand, the enhancement of light intensity improved the photocatalytic efficiency. pH played an important role in the photocatalytic tests and was observed by the authors that if it is increased from 4 to 10, the (ROH, UV) increases from 2 $\times$ 10$^3$ to 8 $\times$ 10$^3$ M·s·cm$^{-2}$·mJ$^{-1}$ for titania and from 8 $\times$ 10$^2$ to 2 $\times$ 10$^3$ M·s·cm$^{-2}$·mJ$^{-1}$ when zinc oxide was used.

State et al. [45] investigated the photocatalytic removal of TCE (trichloroethylene) under simulated solar irradiation (AM 1.5) using Au/TiO$_2$ and Pd-Au/TiO$_2$. The authors obtained the mentioned photocatalyst using incipient wetness and deposition precipitation methods. After performing the photocatalytic tests, it was observed that TCE was converted to more than 80% of Cl$^-$ and CO$_2$ no matter the catalyst used. Also, in order to obtain TCE conversion directly to Cl$^-$ and C$_2$ (ethane, ethylene) using the H$_2$ generated photo catalytically in situ, the authors performed the photocatalytic degradation of TCE over the same catalytic materials in the presence of methanol traces. Thus, it was evidenced that when Pd-Au/TiO$_2$ was used, hydro dechlorination (HDC) and photomineralization reactions of TCE took place simultaneously (Figure 5), while Au/TiO$_2$ was inactive. A reaction mechanism was proposed: the organic substrate was the source of protons (and thus of H$_2$) and carbon of CO$_2$. The •OH radicals supply the O$_2$ for the development of oxidized organic intermediates and, finally, of CO$_2$. 
Hsu et al. [46] evaluated the possibility of using LaFeO$_3$ as a photocatalyst for trichloroethylene (TCE) degradation from the water via heterogeneous oxidation. The authors synthesized LaFeO$_3$ using the sol-gel method. TCE was chosen as an organic pollutant to be removed because it is one of the most encountered water pollutants in Taiwan. The authors’ results indicated that up to 95% removal efficiency from water could be obtained when using 2 g per liter photocatalyst (LaFeO$_3$) and 1 h illumination from a Xe lamp up to 400 W. Other parameters were also studied, such as light intensity, catalyst loading, the influence of TCE concentration or pH contribution on TCE removal. They reported the highest energy efficiency to be 10.8 mg TCE/kWh. The TCE removal efficiency decreases if the initial TCE concentration increases, while the removal efficiency increases if the catalyst loading increases. Also, by increasing the pH value, the removal efficiency rises due to the addition of OH$^-$ groups. In the end, the authors revealed that the processes of adsorption, photodegradation and photocatalysis take place simultaneously and reach equilibrium after 1 h, and a removal mechanism had also been identified, suggesting that the overall removal efficiency reached 82% (20% accounting for adsorption and 39% for photolysis).

In the study of Raciulete et al. [48], the photocatalytic activity for TCE removal under simulated sunlight irradiation (using a 150 W short-arc Xe lamp (1000 W·m$^{-2}$, Peccell-L01) over RbLaTa$_2$O$_7$ perovskites with mostly nanowire and platelet morphologies was investigated. Two RbLaTa-based layered perovskite samples were prepared via a solid-state synthesis route. The authors observed that the sample synthesized in mild conditions (e.g., 1200 °C for 18 h) favored the photo-mineralization of TCE to Cl$^-$ and CO$_2$ due to the presence of a high density of hydroxyl groups (Figure 6). Contrariwise, the activity of the sample annealed in harsh conditions (e.g., 950 and 1200 °C, for 36 h) remained modest for TCE removal, whereas its surface carbonate was beneficial for the formation of intermediate products. With the purpose of enhancing the overall photocatalytic performances of RbLaTa-based layered perovskites, the samples were subjected to protonation [47]. The strategy involved the slow replacement of the interlayer Rb$^+$ of RbLaTa$_2$O$_7$ hosts by H$^+$ via the cation exchange route. The authors showed that the obtained HLaTa$_2$O$_7$ protonated perovskites were able to photomineralize TCE under simulated solar irradiation. The enhanced activity of protonate perovskites was ascribed to favorable roles played by their increased specific surface area and high density of hydroxyl groups.

Figure 5. Photomineralization and photomineralization/hydro dechlorination mechanisms. Reproduced with permission from ref. [45]. Copyright 2017 Elsevier.
Photocatalytic degradation of various chlorinated environmental pollutants (VOCs), such as various chlorinated ethene and methane derivatives, in real groundwater samples, was studied by Dutschke and coworkers [57]. They developed an appropriate experimental setup in order to apply advanced oxidation processes (AOP) to real groundwater samples. Their setup used an O₃-bubble column reactor with a carrier-bound TiO₂/UV system (365 nm LEDs). The authors did a comprehensive study and discussed the influence of flow rate, O₃ concentration and radiation dose on the process performance. After parameter optimization (shown in Table 2) [57] using Box–Behnken experimental design, they obtained almost complete degradation rates for DCE: 99%, TCE: 99%, and PCE: 98%. A degradation rate of 85% was obtained for TCM (trichloromethane) without the formation of transformation products. The formation of tetrachloromethane (PCM) due to induced chlorination represented a problem during their photocatalytic experiments, but this was overcome by using suitable O₃ doses and irradiation in order to produce enough hydroxyl radicals, thus PCM will not appear as a transformation product during the degradation of other chlorinated organic pollutants.

**Table 2.** Optimized parameters for chlorinated VOCs degradation. Reproduced with permission from ref. [57]. Copyright 2022 Elsevier.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>30 L h⁻¹</td>
</tr>
<tr>
<td>Ozone concentration</td>
<td>1289 mg m⁻³</td>
</tr>
<tr>
<td>Irradiance</td>
<td>33.6 W m⁻²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VOC</th>
<th>Degradation (SE) in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCE</td>
<td>C₂H₂Cl₂ 99.4 (±0.3)</td>
</tr>
<tr>
<td>TCE</td>
<td>C₂HCl₃ 99.3 (±0.2)</td>
</tr>
<tr>
<td>PCE</td>
<td>C₂Cl₄ 98.0 (±0.2)</td>
</tr>
<tr>
<td>TCM</td>
<td>CHCl₃ 84.8 (±7.8)</td>
</tr>
<tr>
<td>PCM</td>
<td>CCl₄ 14.0 (±11.4)</td>
</tr>
</tbody>
</table>
2.2.3. Aromatic VOCs Abatement

Lyu et al. [43] tried to improve photocatalytic mineralization under UV irradiation (using four UV lamps at 8 W, 254 nm) of volatile organic compounds by developing a homojunction-adsorption layer on anatase TiO$_2$. Injection and separation of photogenerated charge carriers can improve the mineralization efficiency of VOCs. Therefore, they used toluene as model VOC, and they grew microporous TiO$_2$ onto the surface of anatase TiO$_2$ to obtain a homojunction-adsorption layer, thus optimizing the adsorption ability and photoactivity of the catalyst for photocatalytic mineralization of the model VOC (toluene). Various techniques were used to analyze the physical properties and mineralization of toluene. Results showed that the growth of microporous TiO$_2$ increased the surface area of the catalyst by 160% compared with anatase TiO$_2$, as well as induced microporous structure. This enhanced the adsorption of toluene at a low concentration of 5.5 mg m$^{-3}$ and limited the release of the adsorbed organic compounds. The authors also reported that a homojunction occurred at the interface of microporous TiO$_2$ and anatase TiO$_2$, leading to improved separation of photogenerated charge carriers. They concluded that due to this enhanced adsorption ability and photoactivity, the mineralization efficiency of toluene over micropore-anatase TiO$_2$ composite was 1.78 and 2.12 times higher than that over M-TiO$_2$ and anatase TiO$_2$, respectively.

Wang et al. [42] prepared the rGO-TiO$_2$ composites through a modified refluxing-solvothermal method and used them as catalysts for photocatalytic degradation of single VOC (p-xylene and ethylene) and VOC mixtures (benzene, toluene, p-xylene) under simulated solar irradiation (using 250 W and 500 W xenon lamps). The authors reported that their developed catalyst had higher photocatalytic degradation activity for a single VOC and even 2.6 times higher activity for a VOCs mixture compared to commercial P25 TiO$_2$. Also, the photodegradation efficiency of P25 decreased from 80% to 63.8%, while the synthesized catalyst kept its efficiency unchanged (around 93%). The improved performance of rGO-TiO$_2$ was attributed to an enhanced separation efficiency of electron-hole, better light harvesting ability and increased VOC adsorption capacity.

Ji et al. [58] studied the photocatalytic oxidation of gaseous benzene using as photocatalyst mesoporous TiO$_2$ prepared by one-step hydrolysis method and varying the calcination temperature. They observed that the calcination temperature interferes with the catalytic activity of synthesized titania, also affecting its structural properties. The authors also used commercial P25 titania for comparison reasons, but this had poor efficiency and deactivated quickly, while their obtained mesoporous titania had a much better stability and photocatalytic activity for benzene abatement. They reported that samples calcined at 400 °C had the best photocatalytic activity. Additionally, the authors used VUV (vacuum UV) irradiation and observed that it enhances benzene degradation, obtaining a removal efficiency of around 80%, while under UV irradiation (2 × 4 W, 254 nm, Cnlight) was just 10%. They concluded that this procedure, where VUV photolysis together with ozone generated from the VUV irradiation (2 × 4 W, Cnlight), is suitable for benzene degradation at room temperature if mesoporous titania is used.

Fiorenza et al. [59] developed ZnO-based photocatalysts for various VOCs mineralization. For the solar photocatalytic tests, they used an irradiation source, a solar lamp (Osram Ultra Vitalux 300 W, irradiance of 10.7 mW/cm$^2$). They synthesized core-shell ZnO@Au NPs and used them for gas-phase oxidation of toluene (C$_7$H$_8$) (but also of formaldehyde (CH$_2$O) and ethanol (C$_2$H$_5$OH)), obtaining 95% conversion for toluene and 85% conversion for formaldehyde resulting only in water and CO$_2$ as by-products. The same catalyst used in the photooxidation of ethanol also performed well, leading to a conversion of almost 60% having as by-products acetaldehyde with its subsequent oxidation to CO$_2$ (attaining up to 72% selectivity to CO$_2$). When performing the stability of the catalysts, the authors reported very good stability even after five consecutive runs. In the end, they concluded that the performance of the developed catalysts was due to the interaction between the zinc shell and gold core that prevented Au agglomeration, thus improving the photo-stability of the material and total VOC oxidation.
Nanodiamond (ND)-decorated zinc oxide photocatalysts were developed by Liu et al. [60] and used for the photooxidation of toluene utilizing UV-365 irradiation. They prepared various types of ZnO with different exposed crystal faces in order to evaluate the performance of the catalysts and the differences in activity. They observed that bare nanodiamond decorated ZnO having a higher amount of active (0001) exposed crystal faces obtained a total toluene removal in 2 h, the active species being superoxide radicals and photogenerated holes. After performing DRIFT analysis, the authors also explained a decomposition pathway for toluene; namely, toluene reacts with •O$_2^-$ generating benzoic acid and benzaldehyde, and the benzoic acid is oxidized to oxalic acid and decomposed to carbon dioxide and water. In the end, the authors proposed a mechanism for toluene photodegradation by nanodiamond decorated zinc oxide catalyst (Figure 7). Thus, zinc oxide and nanodiamonds can generate e$^-$ and h$^+$ if excited under UV light. After obtaining the ND-ZnO, the electrons can pass from the ND to ZnO and can form an electric field. Afterward, the h$^+$ transfers from ZnO to ND and reacts to toluene. At the same time, e$^-$ from ND transfers to zinc oxide and interacts with O$_2$ forming •O$_2^-$, thus mineralizing gaseous toluene and intermediates. As the valence band edge potential of the mentioned photocatalyst is more negative than the redox potential of •OH/H$_2$O, there were no •OH radicals generated during the process. Therefore, the photo-generated h$^+$ could have contributed directly to the reaction of toluene oxidation.

![Figure 7. Proposed mechanism for photocatalytic degradation of toluene upon ND-decorated ZnO photocatalysts. Reproduced with permission from ref. [60]. Copyright 2019 Elsevier.](image)

Zhang et al. [61] reported the preparation of Ag/ZnO/nBC photocatalyst consisting of zinc oxide, cellulose nanocrystal-derived nano biochar (nBC) and silver nanoparticles, which was used in the photodegradation of various volatile organic compounds using a 300 W xenon lamp. They observed that VOC molecules are adsorbed on the surface of the mentioned catalyst via oxygen-containing groups (–OH, –C=O, and –CO), thus obtaining high photocatalytic efficiencies for the degradation of methyl alcohol (92%), acetone (81%), formaldehyde (89%) and phenol (90%).

2.3. Aromatic Water Contaminants

Nowadays, the removal of low-concentration organics recalcitrant for minimizing environmental and human health risks is of growing concern [62,63]. Among different aromatic substrates, phenol is a representative pollutant due to its presence in petroleum refinery wastewater affecting the ecosystems. It is often used as a model chemical for investigating the degradation of more complex and harmful compounds. Therefore, we will consider this pollutant focusing on its photocatalytic mineralization. This section of the paper outlines the general physicochemical properties of the phenol and its usages, describing the mechanism of the photocatalytic reaction. It also discusses and evaluates various types of photocatalysts and their performance in the photomineralization of phenol.
2.3.1. Phenol: General Properties and Uses

Phenol is a well-known contaminant introduced continuously into the environment through its usage in industry and human activities (Figure 8) [64]. Phenol is an aromatic compound, colorless to light-pink, with a burning taste and a distinctive odor. It is moderately soluble in water, soluble in most organic solvents, and less soluble in aliphatic hydrocarbons.

![Figure 8. Phenol concentration in the effluent of major industries. Reproduced with permission from ref. [64]. Copyright 2019 Elsevier.](image)

Phenols are produced naturally during the decomposition of plants and microorganisms, being released slowly in soils compared to other soil organic matter [65]. The oxidation of cumene (Hock process) is by far the dominant technology for the synthesis of phenol, with a production rate of more than 6.7 × 10^6 tons per year [66]. Other industrial processes include the toluene oxidation with benzoic acid as an intermediate product and the recovery of phenol from coal tar. Phenol is commonly used in different branches of industry comprising plastics and related materials, production of polycarbonates, epoxies, Bakelite, detergents, nylon, pesticides, explosives, dyes, textiles production, and pharmaceuticals [67]. Because of its impact on human health, the United States Environmental Protection Agency (USEPA) enlisted the phenol as a pollutant of priority concern. It is highly irritating to the skin and genotoxic, while repeated exposure causes weight reduction and infertility; it has endocrine-disrupting effects and can damage the liver, kidneys, and nervous system [68]. The World Health Organization (WHO) recommended a maximum permissible concentration of phenol in drinking water of 2 mg L^{-1} [69]. However, even at very low concentrations, contamination of drinking water supplies represents a human threat, directly affecting the health of ecosystems.

2.3.2. Mechanism of Photocatalytic Removal of Organic Pollutants

Most authors agreed that the photocatalytic degradation of organic substrates (in this case, the phenol) follows Langmuir–Hinshelwood kinetics (Equation (38)) [70]:

\[
\frac{dC}{dt} = -\frac{kKC}{1 + KKC}
\]  

(38)

where \( r \) represents the initial rate of reaction, \( C \) is the concentration of the reactant, \( t \) is the irradiation time, \( k \) is the rate constant, and \( K \) is the adsorption coefficient of the reactant. When the concentration of the pollutant is in the millimolar range, Equation (38) can be simplified to the apparent rate order equation (Equation (39)) [71]:

\[
\ln \frac{C_0}{C} = kKt = K_{app}t
\]  

(39)

where \( C \) and \( C_0 \) are the concentrations of pollutants at time \( t \) and \( t_0 \), respectively, and \( K_{app} \) is the apparent-first order rate constant (in min^{-1}). It is assumed that the reaction occurs on the surface of the photocatalyst. The mechanism of the photocatalytic reaction
implies two steps: (i) the degradation of phenol to intermediates (e.g., hydroxylated and short-chain compounds) and (ii) the mineralization of the by-products to carbon dioxide and water [72].

Sobczynski et al. [73] admitted that during the UV irradiation of TiO$_2$, the phenol reacted with photogenerated holes (h$^+$) or photoinduced hydroxyl radicals, resulting in a variety of hydroxylated reaction by-products. The photocatalytic reaction proceeded via multiple steps, in which the principal intermediates were hydroquinone, catechol, and p-benzoquinone. Also, another variety of aliphatic intermediates formed in the reaction mixture, which finally converted to non-toxic end products (Figure 9).

Guo and co-workers [74] focused on the identification of the intermediate produced by phenol photodegradation on TiO$_2$ using GC-MS and HPLC tools. They agreed that the main reaction intermediates were hydroquinone, resorcinol, catechol, 1,2,3-benzenetriol, (E)-2-butenedioic acid, 2-hydroxy-propaldehyde hydroxy-acetic acid, 3-hydroxy-propyl acid, and glycerol. The •OH radicals are highly reactive species that attack the phenyl ring of the phenol yielding to catechol, resorcinol, and hydroquinone. Further, the phenyl rings will break up to give malonic acid, followed by short-chain organic acids (e.g., maleic, oxalic, acetic, formic acids, glycolic acid), and finally, CO$_2$. Based on the detected by-products, the authors established that besides hydroxyl radicals, the •H was also a significant active free radical in the degradation pathways. During the photocatalytic process, H$^+$ or •H is scavenged by oxygen to form HO$_2$• radicals, which finally convert to hydroxyl radicals. However, these authors concluded that the principal reactive species responsible for organics degradation was •OH radical.

Wysocka et al. [75] carried out the photocatalytic degradation of phenol over Me-modified TiO$_2$/SiO$_2$@Fe$_3$O$_4$ nanocomposites (Me = Pd, Au, Pt, Cu) obtained by ultrasonic-assisted sol-gel method. In their study, the Pd- and Cu-TiO$_2$/SiO$_2$@Fe$_3$O$_4$ photocatalysts displayed the highest photo-oxidation rate of phenol and mineralization. •O$_2^-$ and •OH were the active species involved in the photodegradation process. These radicals attack the phenyl ring yielding catechol, hydroquinone, and benzoquinone generation, followed by oxalic acid and CO$_2$ formation (Figure 10). Conversely, different pathways occurred for the hydroquinone and catechol oxidation. Catechol was directly oxidized to oxalic acid and further mineralized to harmless products. The hydroxylated by-products were oxidized to aliphatic carboxylic acids and finally to CO$_2$. The authors found that for Pt-TiO$_2$/SiO$_2$@Fe$_3$O$_4$ nanocomposite, a lack of catechol after 60 min of irradiation resulted in a low mineralization rate. It has been postulated that the enhanced photocatalytic activity of Pd- and Cu-modified photocatalysts were due to increases in the number of adsorption sites and efficient charge carrier separation. In the case of the Au-TiO$_2$/SiO$_2$@Fe$_3$O$_4$ sample, the keto-enol tautomeric equilibrium retarded the rate of the phenol mineralization.
Figure 10. Schematic illustration of the phenol photocatalytic degradation mechanism for TiO$_2$/SiO$_2$@Fe$_3$O$_4$ magnetic catalysts modified with: (a) copper; (b) gold; (c) palladium, and (d) platinum nanoparticles. Reproduced with permission from ref. [75]. Copyright 2018 MDPI.

The photomineralization reaction depends on several factors, such as (i) the synthesis conditions (e.g., synthesis route, thermal treatment), (ii) the physicochemical properties of the catalyst (e.g., phase composition, morphology, particle size, surface area, porosity, band-gap energy), and (iii) the operational parameters (e.g., solution pH, initial concentration of the organic substrate, the mass of catalyst, wavelength, reaction temperature, radiant flux, and design of the reactor) [76].

2.3.3. Phenol Removal over Various Catalytic Materials

Titanium dioxide is by far a benchmark for numerous photocatalytic applications due to its high chemical stability, low cost, possibility to tune the band gap with other semiconductors, and biological inertness. However, photocatalysis on TiO$_2$ is still limited by its UV band wavelengths, weak adsorption of hydrophilic pollutants, and agglomeration
of nano-sized particles. Therefore, it is a permanent rush to develop new light harvesters which aim to outperform titanium dioxide. The most common cleaning technologies are (i) biological (aerobic/anaerobic), (ii) physical (sedimentation, screening, filtration, floating, flocculation, and aeration), and (iii) chemical (neutralization, ozonation, precipitation, adsorption, and oxidation) processes.

A novel Z-scheme-based photocatalyst composed of Bi$_2$O$_3$/Bi$_2$MoO$_6$ heterojunction was proposed by Fu et al. [77] for efficient photodegradation of phenol with 96.4% degradation efficacy. In this system, a TOC removal efficiency of 75.5% was achieved. The spatially separated redox charge carriers, the excellent light harvesting capability, and the fast-charge transportation features of the catalysts were the factors determining their enhanced performances.

Zhang and co-workers [78] prepared a Bi$_2$S$_3$/Bi$_2$WO$_6$ composite by a hydrothermal method which efficiently weakens the recombination rate of photoinduced charge carriers and narrows the photonsponse range. The composite photocatalyst exhibited enhanced photocatalytic activity in the degradation of phenol under visible light irradiation, being 6.2 times higher compared to bare Bi$_2$WO$_6$. The photodegradation rate of phenol (Figure 11a) reached 51.6% in the presence of the Bi$_2$S$_3$/Bi$_2$WO$_6$ composite after 2 h of visible light irradiation, whereas only 12% of phenol was degraded by Bi$_2$WO$_6$. The photogenerated electrons (Figure 11b) were introduced from the conduction band (CB) of Bi$_2$S$_3$ to the CB of Bi$_2$WO$_6$ due to the intimate contact between the two semiconductors. Simultaneously, holes on the valence band (VB) of Bi$_2$WO$_6$ were transferred to that of Bi$_2$S$_3$ under the band energy potential difference. Therefore, efficient separation of the photoinduced e$^-$/h$^+$ pairs took place while their recombination was hindered.

![Figure 11](image-url)

**Figure 11.** (a) Photocatalytic degradation of phenol under visible light irradiation as a function of time; and (b) Diagram for energy band levels of Bi$_2$S$_3$/Bi$_2$WO$_6$ composites and the possible charge separation process. Reproduced and adapted with permission from ref. [78]. Copyright 2012 American Chemical Society.

Different BiFeO$_3$ morphologies synthesized by three synthesis routes (e.g., co-precipitation CP, hydrothermal HT, sol-gel SG) were investigated by Chien et al. [79] for the photodegradation of phenol as a model organic pollutant. The SG-BiFeO$_3$ sample exhibited remarkable direct sunlight photocatalytic degradation of phenol (98.95%), superior to those of the HT-BiFeO$_3$ (77.4%) and CP-BiFeO$_3$ (66.9%) in 120 min. The radical scavenger studies implied that the photogenerated hole (h$^+$), hydrogen peroxide (H$_2$O$_2$) and hydroxyl ($\cdot$OH) radicals were the dominant reactive species. Under direct solar irradiation, the photogenerated electron on the BiFeO$_3$ surface migrated from the filled VB to the CB band and left an equal number of holes in VB (Figure 12). The promoted CB electrons of BiFeO$_3$ (+0.53 eV) reacted with the oxygen molecules to generate H$_2$O$_2$ ($E^0$(O$_2$/H$_2$O$_2$) = +0.695 eV). Simultaneously, the holes situated in the VB band of BiFeO$_3$ (+2.59 eV) would react with the OH$^-$ ($E^0$(•OH/OH$^-$) = +1.99 eV) to generate the •OH radicals. Subsequently, these
radicals (h\(^+\), H\(_2\)O\(_2\) and •OH) react with the surface-adsorbed phenol, converting it into mineralized products.

![Figure 12. Mechanism of the phenol photocatalytic removal over BiFeO\(_3\) under direct sunlight irradiation. Reproduced with permission from ref. [79]. Copyright 2022 Elsevier.](image)

Jiang et al. [80] fabricated a series of BiOI-ZnO nanocomposites with various BiOI contents and tested their photoreactivity for phenol degradation under simulated solar irradiation. The phenol photodegradation rate reached 99.9\% within 2 h, whereas only 40\% of phenol removal took place over pristine ZnO. In the BiOI-ZnO system, the internal electric field formed between n-p heterojunctions of two oxide phases forced the electron and hole charge carriers to move in the opposite direction. Thus, the internal electric field between the component oxides facilitates the separation and transfer of the photocarriers. Since the CB of BiOI is much more negative than that of ZnO, the generated electron in BiOI favors the diffusion through into the CB of ZnO. Concomitantly, the photogenerated h\(^+\) in VB of ZnO moves to p-type BiOI. As a result, more photogenerated carriers migrated to the catalyst surface, contributing to the reaction. Figure 13 illustrates the proposed mechanism for the enhanced removal of phenol by the BiOI/ZnO photocatalyst. In this research study, the superoxide species (\(\bullet O_2^-\)) and holes were established as the main reactive species in the photocatalytic reaction.

Zhang et al. [81] take a look at the photocatalytic mineralization of phenol over a single BiPO\(_4\) under UV-C irradiation. After studying the influence of several operating parameters, it was established that the mineralization of phenol was favorable in acidic conditions; the catalytic process decreased with increasing initial phenol concentration, and the chloride ions promoted the rate of mineralization. The BiPO\(_4\) photocatalyst mineralized more than 95\% of phenol (10 mg L\(^{-1}\)) after 5 h of illumination. Further after, Wang et al. [82] investigated the photodegradation of phenol under simulated solar irradiation of CeO\(_2\), Bi\(_4\)O\(_7\) and 10\% CeO\(_2\)/Bi\(_4\)O\(_7\) photocatalysts. The authors indicated that for the individual CeO\(_2\) and Bi\(_4\)O\(_7\), the phenol removal rates were only 12\% and 40\%, respectively. The 10\% CeO\(_2\)/Bi\(_4\)O\(_7\) photocatalyst degrades 92\% phenol within 120 min, corresponding to the TOC value of 53\%. Since the Fermi energy level of CeO\(_2\) is higher than that of Bi\(_4\)O\(_7\), the electrons in CeO\(_2\) will be transferred to Bi\(_4\)O\(_7\) until the Fermi levels of Bi\(_4\)O\(_7\) and CeO\(_2\) are equalized. The energy band of Bi\(_4\)O\(_7\) bends downward, and the energy band of CeO\(_2\) bends upward. Hence, a built-in electric field is formed at Bi\(_4\)O\(_7\)/CeO\(_2\) interface. The electrons flow from Bi\(_4\)O\(_7\) to CeO\(_2\) and holes from CeO\(_2\) to Bi\(_4\)O\(_7\), forming thus a typical type II heterojunction. The trapping experiments of active species evidenced that h\(^+\) and •O\(_2^-\) played significant
roles in phenol removal. However, the single Bi$_4$O$_7$ was almost deactivated, while the 10% CeO$_2$/Bi$_4$O$_7$ demonstrated improved stability after three cycling experiments.

A series of ternary Bi$_7$O$_9$I$_3$/g-C$_3$N$_4$/Bi$_3$O$_4$Cl photocatalysts were synthesized via the oil bath method by Yuan et al. [83] and tested for phenol photocatalytic removal. The optimal TOC removal rate reached up to 93.57% under visible irradiation within 160 min. After performing the trapping-species experiments and EPR characterization, the authors indicated that •OH and •O$_2^-$ were the oxidizing species responsible for the pollutant removal. The same study indicated that a dual S-scheme charge migration was generated at the interface of Bi$_7$O$_9$I$_3$, g-C$_3$N$_4$, and Bi$_3$O$_4$Cl, which favors efficient charge separation.

Table 3 summarizes various studies regarding the experimental conditions and the main reactive species participating in phenol photomineralization over some photocatalysts.
### Table 3. Photocatalytic degradation of phenol over various materials.

<table>
<thead>
<tr>
<th>Type of Photocatalyst</th>
<th>Experimental Conditions</th>
<th>Light Source</th>
<th>Reaction Time</th>
<th>Degradation Efficiency</th>
<th>TOC Removal Efficiency</th>
<th>Main Active Species</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/MnO$_2$ follow sphere</td>
<td>[phenol] = 5 mg L$^{-1}$ [photocatalyst] = 20 mg</td>
<td>Simulated solar light (XHA 300 W Xe lamp AM 1.5 G filter) Solar light</td>
<td>180 min</td>
<td>100%</td>
<td>91%</td>
<td>superoxide radical</td>
<td>[84]</td>
</tr>
<tr>
<td>2% Au/TiO$_2$</td>
<td>[phenol] = 30 mg L$^{-1}$</td>
<td>Solar light</td>
<td>3.5 h</td>
<td>100%</td>
<td>-</td>
<td>-</td>
<td>[85]</td>
</tr>
<tr>
<td>Pr(0.072%)-TiO$_2$</td>
<td>[phenol] = 50 ppm, [photocatalyst] = 1 g L$^{-1}$, pH = 6.58</td>
<td>UV light</td>
<td>2 h</td>
<td>94.4%</td>
<td>-</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td>EY-TiO$_2$/Pt(0.5%)</td>
<td>[phenol] = 40 ppm, [photocatalyst] = 0.8 g L$^{-1}$, 0.2 M TEOA, neutral pH</td>
<td>Visible solar light</td>
<td>2 h</td>
<td>100%</td>
<td>-</td>
<td>superoxide radical</td>
<td>[87]</td>
</tr>
<tr>
<td>TiO$_2$-BiOBr-Bentonite</td>
<td>[phenol] = 20 ppm, [photocatalyst] = 150 mg/100 mL solution</td>
<td>Visible light</td>
<td>70 min</td>
<td>100%</td>
<td>83%</td>
<td>superoxide radical and e$^-$ (major role) h$^+$, •OH (appreciable role)</td>
<td>[88]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$rGO@AgI</td>
<td>[phenol] = 50 ppm [photocatalyst] = 0.2 g/350 mL solution</td>
<td>UV-C light, $\lambda = 254$ nm</td>
<td>9 h</td>
<td>99%</td>
<td>-</td>
<td>mainly •OH</td>
<td>[89]</td>
</tr>
<tr>
<td>mont-La(6%)-Cu$_6$Cd$_4$S$_7$ nanocomposite</td>
<td>[phenol] = 20 mg L$^{-1}$ [photocatalyst] = 60 mg/L</td>
<td>Medium-pressure Hg-vapor lamp, near UV-Vis irradiation</td>
<td>4 h</td>
<td>86%</td>
<td>77.8%</td>
<td>•OH and h$^+$ radicals</td>
<td>[90]</td>
</tr>
<tr>
<td>TiO$_2$/rGO</td>
<td>[phenol] = 20 ppm</td>
<td>UV light</td>
<td>180 min</td>
<td>97.87%</td>
<td>-</td>
<td>•OH, superoxide radical, and h$^+$</td>
<td>[91]</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$/rGO</td>
<td>[phenol] = 200 ppm [photocatalyst] = 60 mg/L</td>
<td>Visible light</td>
<td>15 min</td>
<td>100%</td>
<td>-</td>
<td>-</td>
<td>[92]</td>
</tr>
<tr>
<td>PAN-CNT/TiO$_2$-NH$_2$</td>
<td>[phenol] = 10 ppm, pH = 5 [photocatalyst] = 20 mg</td>
<td>UV light</td>
<td>7 min</td>
<td>99.2%</td>
<td>-</td>
<td>•OH and superoxide radical</td>
<td>[93]</td>
</tr>
<tr>
<td>CdS/rGO/Fe$^{2+}$</td>
<td>[phenol] = 10 ppm [photocatalyst] = 20 mg/20 mL</td>
<td>300 W Xe lamp irradiation ($\lambda &gt; 420$ nm)</td>
<td>60 min</td>
<td>100%</td>
<td>43.66%</td>
<td>•OH</td>
<td>[94]</td>
</tr>
<tr>
<td>N-TiO$_2$/HPCF (Hierarchical Porous Carbon Foam)</td>
<td>[phenol] = 30 mg L$^{-1}$ [photocatalyst] = 50 mg/50 mL aq. Ph</td>
<td>500 W Xe lamp, simulated sunlight irradiation</td>
<td>2 h</td>
<td>97%</td>
<td>78% after 6 h of illumination</td>
<td>-</td>
<td>[95]</td>
</tr>
<tr>
<td>(2:1) Bi-Bi$_2$O$_3$I$_3$/Ag-AgI</td>
<td>[phenol] = 10 ppm [photocatalyst] = 50 mg/100 mL aq. Ph</td>
<td>300 Xe lamp, $\lambda &gt; 420$ nm</td>
<td>120 min</td>
<td>100%</td>
<td>95.38%</td>
<td>•OH (more significant role than h$^+$)</td>
<td>[96]</td>
</tr>
<tr>
<td>Pt/TiO$_2$-ZnO@ZIF-8</td>
<td>[phenol] = 5 ppm</td>
<td>UV light</td>
<td>24 min</td>
<td>99.7%</td>
<td>-</td>
<td>-</td>
<td>[97]</td>
</tr>
<tr>
<td>CeO$_2$/TiO$_2$</td>
<td>[photocatalyst] = 20 mg/40 mL aq. Ph</td>
<td>300 W high-pressure UV mercury lamp, UV irradiation</td>
<td>120 min</td>
<td>99.1%</td>
<td>-</td>
<td>•OH, h$^+$</td>
<td>[98]</td>
</tr>
</tbody>
</table>
Hydrothermal synthesis of BiOCl-activated carbon (AC) was reported by Sharma et al. [99] as an efficient photocatalyst for phenol removal. After 120 min of UV-light irradiation, more than half of the phenol photodegraded by the sample with 1 wt.% AC/BiOCl. The results showed a TOC value of 11.92 mg L\(^{-1}\) for phenol mineralization. SnO\(_2\):Sb nanoparticles (with 0.2%, 0.4%, and 0.6% concentration of Sb) turned out to be competent catalysts for phenol removal under UV and solar light irradiation [100]. The authors claimed that the change in the phenol concentration influenced the solution pH due to the formation of by-products during the reaction. The degree of mineralization reached 97% over 0.6% SnO\(_2\):Sb nanoparticles within 120 min reaction time, while 71% and 45% values were achieved for 0.4% and 0.2% SnO\(_2\):Sb samples, respectively.

Sandulescu et al. [101] showed a comprehensive view of the photocatalytic oxidation of phenol under sunlight irradiation over bare and noble metal-loaded TiO\(_2\). Experiments indicated that the supported noble metals act as a visible light absorber, assisting the separation of photo-charges and reduction of O\(_2\) to O\(_2^−\). The O\(_2^−\) oxidizes mildly phenol to oxygenated products. In a parallel process, •OH radicals yielded by TiO\(_2\), mineralized phenol to CO\(_2\) by fast reaction sequences.

Photocatalytic removal of phenol under UV light was investigated by Mendoza-Damian et al. [102] by studying the effect of Sn\(^{4+}\) content on the SnO\(_2\)-ZnAl LDH photocatalytic properties. The 0.3 mol% of the Sn\(^{4+}\)−containing ZnAl LDH displayed the highest photocatalytic activity, with a phenol mineralization efficiency of 90.98%. The improved efficiency was due to a higher light absorption capacity and synergistic effect between the SnO\(_2\) and ZnAl LDH heterostructure.

Raciulete et al. [103] developed a multi-step ion-exchange methodology by exchanging Rb\(^{+}\) with Cu\(^{2+}\) spacer in the layered RbLaTa\(_2\)O\(_7\) host to achieve photocatalysts capable of wastewater depollution. The photocatalytic degradation of phenol under simulated solar irradiation, employed as a model reaction, showed that Cu−modified layered perovskites displayed an increased photocatalytic activity compared to the RbLaTa\(_2\)O\(_7\) host. Experiments demonstrated that the product intermediates over Cu-modified perovskites were hydroquinone (HQ), 1,2-di-hydroxy-benzene (1,2-DhBZ), and benzoquinone (BQ). Among the Cu−modified layered perovskites, the sample reduced at 800 °C was the most effective photocatalyst regarding the efficiency of phenol mineralization, yielding 2.82 μmoles h\(^{-1}\) of CO\(_2\) and 1.78 μmoles h\(^{-1}\) of H\(_2\).

### 2.3.4. Photocatalysis Coupled with Ozonation Process

Purification of wastewater, including phenolic compounds, has been realized by several treatment methods, such as photocatalytic degradation, electrochemical methods, adsorption, Fenton’s reaction, and ozonation processes [104–106]. Ozone is a powerful oxidizing agent that destroys organic pollutants in wastewater by producing reactive oxygen species (ROS). Photocatalytic ozonation proved to be an efficient and promising advanced oxidation process available to remove widely spread organic contaminants in wastewater. The difference between photocatalytic ozonation and catalytic ozonation in an aqueous solution lies in the chain reactions initiation. The photochemical reaction is triggered by an electron transfer from a semiconductor to oxygen or ozone. The catalytic ozonation mechanism usually begins with the reaction between the hydroxyl anion with ozone [107]. In both processes, superoxide anion (O\(_2^−\)) is primarily formed and subsequently reacts with ozone to give ozonide ion (O\(_3\)•), consequently resulting in the formation of hydroxyl radical [108]. To a lesser extent, superoxide anion (O\(_2^−\)) can also act as an oxidant, ultimately leading to the mineralization of the organic compounds. Photocatalytic ozonation shows a synergetic effect since it can decrease the electro-hole recombination due to the great electron trapping of ozone, together with the interaction of O\(_3\) with the superoxide radical. Both mechanisms are responsible for forming the ozonide radical, which further transforms into a hydroxyl radical, showing more powerful oxidant behavior [109]. Therefore, this technology can enhance the hydroxyl radical’s generation, even at low pH, increasing the mineralization rate. The application of photocatalytic ozonation on wastewater treatment is expected to
be more effective than photocatalysis and/or ozonation technologies alone. During the ozonation process, the resulting hydroxyl radical in the water phase reacts with organic contaminants leading to their mineralization [110].

Very recently, Yu et al. [111] synthesized single-crystal WO3 nanosheets (NSs) by a hydrothermal method and checked their photocatalytic activity for phenol photomineralization under visible light. The excellent performances of WO3 NSs were attributed to their lamellar morphology with single-crystal microstructure and good dispersion, providing continuous interior channels for the charge carrier transportation from the bulk to the surface of WO3 nanosheets. The authors investigated the degradation efficiency (R_D) and mineralization ratio (R_m) of phenol under different systems (Figure 14a), including ozonation alone (O3), ozonation combined with visible light exposure in the absence of photocatalyst (Vis/O3), catalytic ozonation in the presence of photocatalyst (WO3 NSs/O3 and WO3 NPs/O3), photocatalysis (WO3 NSs/Vis) and photocatalytic reaction conducted in the presence of ozone (WO3 NSs/Vis/O3 and WO3 NPs/Vis/O3). They found that the mineralization ratio for WO3 NSs/Vis/O3 reached 96% after 150 min, and it rose continuously to 98% at 240 min, while the R_m was 83% for WO3 NPs/Vis/O3 at 240 min. After WO3 nanoparticles (NPs) and nanosheets exposure to visible light, the electrons and holes were generated (Figure 14b). These photogenerated carriers were separated and transferred from the bulk to the surface of WO3 and reacted with O3 and HO−/H2O to produce hydroxyl radicals. The produced hydroxyl radicals attack the intermediates of phenol degradation. Subsequently, the complete mineralization of phenol occurred.

![Figure 14. (a) Mineralization ratio (R_m) and degradation efficiency (R_D) of phenol in various oxidation processes; (b) Proposed mechanism of phenol mineralization in WO3 nanosheets under visible light irradiation. Reproduced with permission from ref. [111]. Copyright 2022 Elsevier.](image-url)

Similarly, Nishimoto and co-workers [112] demonstrated that the WO3 catalyst possesses excellent performance for the photocatalytic water treatment under visible-light irradiation combined with ozonation. The authors employed two different catalysts (e.g., WO3 and N-doped TiO2), comparing their capability for TOC removal. Bare WO3 exhibited a superior response for the photomineralization of phenol in the presence of ozone, which readily reacted with its photogenerated electrons in the conduction band. Tawabini and Zubair [113] presented a combined UV and ozone process for phenol removal while inhibiting the formation of bromate in water. Photolysis by UV partially degrades the pollutant. Although combining the UV/O3 techniques, total removal of 50 ppm of phenol in less than 5 min occurs. The authors observed that after the optimization of the operational parameters (e.g., continuous ozonation rate of 1 L/min, addition of 1.5 ppm ammonia for adjusting the pH), the bromate formation was diminished drastically to non-detected levels. In the same way, by coupling catalytic ozonation with photocatalysis, nearly 100% degradation performance for phenol removal within 2 min was obtained over MgO/g-C3N4 catalysts by An et al. [114]. The operational conditions were a visible-light source equipped with a...
For the developed photocatalyst, the MgO played a dual role: (i) accelerating the photogenerated charges separation of g-C$_3$N$_4$ and (ii) facilitating the conversion of ozone into •OH, thus enhancing the catalytic ozonation process.

2.4. Aqueous Inorganic Nitrogen-Based Pollutants

This section has as its main objective the presentation of the mechanisms underlying the photocatalytic degradation reaction of nitrates ions (NO$_3^−$) and the factors that lead to obtaining final products that do not affect the environment and life in general. In addition to the traditional physical treatment (adsorption, membrane filtration, ion exchange, reverse osmosis) and (electro)chemical treatment (conventional chemical denitrification, zero-valent metal nanoparticles, hydrogen driven catalytic denitrification, electrochemical reduction, electrocoagulation, electrodialysis) processes for nitrate removal [115,116], investigations related to nitrate controlling have been carried out in recent years on the possibility of using photocatalytic processes [117].

2.4.1. Overview of Nitrate Anion and Its Reaction Intermediates (Nitrite and Ammonium Ions)

Photocatalytic reduction of nitrate to molecular nitrogen presents a promising approach to removing nitrate from drinking water sources. However, unwanted products such as nitrite (NO$_2^−$) and ammonium (NH$_4^+$) result from the nitrate reduction reaction. The values of these unwanted products have been regulated over the years. The standard recommended levels of nitrates, nitrite and ammonium concentration in drinking water, 50 ppm NO$_3^−$, 3 ppm NO$_2^−$ and 0.5 ppm NH$_4^+$, respectively, are introduced by the World Health Organization (WHO) [118]. To reduce the recombination of photo-generated electrons and holes, metal loading or holes scavengers are generally needed, causing, in this way, secondary pollution of drinking water [119].

Continuous efforts have been devoted to the achievement of heterogeneous photocatalytic nitrate reduction, which is potentially a green and low-cost operation; however, achievements are not as much as expected. In general, photocatalytic nitrate reduction includes two successive reactions, from nitrate to nitrite and then from nitrite to nitrogen radical. The nitrogen radicals will further combine to form N$_2$. Sometimes ammonia (NH$_3$) may be generated as the over-reduced product. The unwanted NH$_3$ is more toxic than NO$_3^−$, and the problem is that the use of the majority of traditional photocatalysts cannot avoid the formation of NH$_3$, leading to a low selectivity to N$_2$ [120–130]. If the formation of undesired by-products (e.g., NO$_2^−$ and NH$_4^+$) is prevented, photocatalytic technology could be one of the most promising options to solve the problems of environmental pollution and energy shortage due to its advantages such as adaptability, low cost, and no secondary pollutants [131]. Dark catalytic hydrogenation of nitrate has been considered a promising alternative to overcome the economic and environmental disadvantages of separation technologies without generating waste streams [132]. N$_2$ selectivity and water matrix effects are important factors that should be assessed for any technology based on catalytic and/or photocatalytic processes proposed for nitrate removal [133,134].

2.4.2. Efficient Nitrate Removal from Wastewater over Different Materials

Photocatalytic nitrate reduction is one of the emerging transformative technologies capable of yielding harmless gaseous products. The e$_{CB}^−$/h$_{VB}^+$ pair recombination is the main drawback of photocatalytic processes and affects their overall efficiency. The strategies for improving the charge carrier separation have already been reported and discussed thoroughly in several reviews [117,135–138]. It is widely accepted that NO$_2^−$ is the first stable intermediate product obtained from nitrate reduction, and it can remain in solution as NO$_2^−$ or undergo further reduction to N$_2$ or to NH$_4^+$. Some authors have been unable to detect quantifiable amounts of NO$_2^−$ at the end of the photocatalytic reduction of NO$_3^−$ because it can be easily reduced after its formation [139–143]. Because of its faster
reduction, several works study the direct reduction of $\text{NO}_2^-$ . The reduction of nitrite is the divergent point that defines the selectivity towards harmless $\text{N}_2$ or undesired $\text{NH}_4^+$.

Few studies quantify the direct yield towards $\text{N}_2$. The quantification of $\text{N}_2$ by gas chromatography was reported by Kominami et al. [141] and by Zhang et al. [144]. Experimental work by Zhang et al. [144] concluded that $\text{N}_2$ was the only gas product released using an Ag/TiO$_2$ photocatalyst. N$_2$O has been identified as an intermediate released in other reductive treatments, such as hydrogenation [145–147]. Even though $\text{N}_2$ is an inert species, other nitrogen-containing gas species such as $\text{N}_2\text{O}$, NO, and other $\text{N}_x\text{O}_y$ are hazardous species with high environmental implications in atmospheric chemistry [148,149]. The last major product obtained during $\text{NO}_3^-$ and $\text{NO}_2^-$ reduction is the ammonium cation, released from an alternative pathway to the one of the HNO intermediate. The selectivity of nitrate depends on the ratio of surface coverage of $\text{N}$ species to reductant species. A low coverage or high concentration of reducing mediators could deteriorate the selectivity for the formation of $\text{NH}_4^+$. An appreciable pseudo-concentration of adsorbed nitrogen intermediates, mainly $\text{HNO}$ and $\text{NO}_2^-$, would favor the pathway leading to $\text{N}_2$–gas species. Many reactions are highly pH-dependent; therefore, acidic pH is necessary to ensure sufficient $\text{H}^+$ to allow fast kinetic rates. Therefore, the pH dependence is not only related to the surface charge that modulates the adsorption of species on the photocatalyst surface but also to the $\text{H}^+$ source to ensure the complete reduction.

Doped semiconductor photocatalysts can provide higher conversion of nitrate and selectivity to nitrogen gases than pristine TiO$_2$, but results are comparable to composite catalysts, raising the question of whether interstitial/substitutional doping is necessary compared to photo deposition methodologies [150]. An excessive metal loading in the composite can be detrimental, becoming a recombination center instead of the desired electron sink [151]. Optimizing metal loads to about 1.0% w/w typically minimizes this detrimental effect [152]. Monometallic composites are the most prevalent types reported in the literature. The metals’ performance was also related to the intrinsic capability of each platinoid to stabilize $\text{H}_{\text{ads}}$ because materials with higher overpotential for $\text{H}_2$ evolution presented a predominant yield of $\text{NH}_4^+$. The most influential factors affecting the efficiency of proton reduction on the metal surface are (i) the hydrogen overpotential during water splitting and (ii) the $\text{H}_{\text{ads}}$ stabilization [153]. In support of this hypothesis, Hamanoi et al. [154] proved experimentally that a decrease in $\text{NO}_3^-$ conversion is observed when hydrogen evolution is increased. Furthermore, bubbling $\text{H}_2$ enhances the reduction of $\text{NO}_3^-$ to $\text{NH}_4^+$, demonstrating that the adsorption of $\text{H}_2$ on platinoids surface catalytic sites as $\text{H}_{\text{ads}}$ contributes to the reduction process [117,127].

Photocatalysts based on pristine TiO$_2$ and related mono/bimetallic composites or bimetallic systems are intensively studied [155–158], but conventional metal-modified photocatalysts usually suffer from metal leaching, aggregation, and gradual deactivation and need to be significantly improved in terms of $\text{N}_2$ selectivity. New materials were developed or used for the first time for photocatalytic denitration (perovskite-based photocatalysts, layered double hydroxides (LDHs) with hydrotalcite-like structures, nonlinear optical material LiNbO$_3$) [159].

It is well known that photocatalytic oxidation has been investigated extensively for its capability of producing highly oxidative $\bullet \text{OH}$, but little attention has been paid to the photocatalytic reduction of oxidative pollutants such as nitrate in water. Photocatalytic denitrification appeared as a feasible approach to accomplish this aim since it was first reported by Schlög and co-workers in 1999 [160]. During the photocatalytic denitrification process activated by light irradiation, the photocatalyst generates electrons ($e_{\text{CB}}^-$) in the conduction band (CB) and holes ($h_{\text{VB}}^+$) in the valence band (VB) of the semiconductor. Then, the nitrate is reduced through direct interaction with $e_{\text{CB}}^-$ or reaction with reductive $\text{CO}_2\bullet$ radicals produced from the reaction between $h_{\text{VB}}^+$ and hole scavengers (e.g., formic acid) [161–163]. According to literature, the latter mechanism generally rules the photocatalytic denitrification for several materials like conventional TiO$_2$, ZnO, ZnS, CdS, and SrTiO$_3$ [128,164–168]. It is difficult to control the formation of $\text{CO}_2\bullet$ radicals due
to the dependence on the used hole scavengers. Liu et al. [169] reported the photocatalytic denitration by nonlinear optical (NLO) material, i.e., lithium niobate (LiNbO$_3$) in the presence of formic acid (FA) serving as a hole scavenger. A 110 W high-pressure Hg lamp was employed as a 365 nm UV light source. LiNbO$_3$ achieved 98.4% total nitrate removal and 95.8% N$_2$ selectivity under neutral pH conditions. During the process, the nitrate may be reduced by (i) reductive CO$_2$•$^-$ radicals produced from the reaction between h$_{VB}^+$/$^\bullet$OH and hole scavengers, (ii) electrons generated at CB, as well as (iii) hydrogen produced from water splitting at CB. They concluded that photocatalytic denitrification should be dominated by reactions involving the conduction band (CB) either through interaction with electrons or hydrogen produced from water splitting. They showed that the role of H$_2$ is very limited, and more than 98% of NO$_3^-$ is reduced directly by electrons at the conduction band of LiNbO$_3$.

Photocatalytic denitrification using various non-toxic hole scavengers is the most common technique reported in the literature. The photocatalytic degradation of nitrates in an aqueous solution has been examined by Anderson and co-workers [118], using different Au/TiO$_2$ photocatalysts and oxalic acid as a hole scavenger. It has been shown that oxalic acid and nitrate can be simultaneously degraded over Au/TiO$_2$ to produce predominantly CO$_2$ and nitrogen, but complete nitrate removal was not achieved.

Luiz et al. [139] studied TiO$_2$ and TiO$_2$ doped with Zn$^{2+}$, Cu$^{2+}$, and Cr$^{3+}$ (metal doped TiO$_2$ (Cu-TiO$_2$, Cr-TiO$_2$ and Zn-TiO$_2$)). The prepared materials were used as photocatalysts to reduce nitrate and oxidize formic acid under the irradiation of a low-pressure mercury lamp (UV radiation at 254 nm, output power of 17 W). The results obtained from the nitrate photoreduction experiments indicated that the metal-doped TiO$_2$ activity decreases in the order: 4.4% Zn-TiO$_2$ > 4.4% Cu-TiO$_2$ > 4.4% Cr-TiO$_2$. Zn-TiO$_2$ exhibits the greatest selectivity towards N$_2$ (95.5%), a nitrate conversion up to 92.7%, and a high reaction rate (14.2 µmol NO$_3^-$/(min g$_{\text{catalyst}}$))$^{-1}$.

Doudrick et al. [128] examined the photocatalytic reduction of nitrate in water using titanium dioxide (Evonik P90) loaded with silver nanoparticles and formate as a hole scavenger (electron donor). Photocatalytic experiments were performed using a UV light source (450-W medium-pressure mercury–vapor lamp). Under acidic conditions (pH = 2.5), nitrogen gases (~85%) and ammonium (~15%) were the final by-products. The authors evidenced that radicals are unlikely to be responsible for nitrate reduction, so a photocatalyst with the proper Fermi level must be selected to meet the thermodynamic requirements. Because the pH was a factor in their experiments, proton localization at the reaction sites was important for treatment at ambient pH and for achieving harmless by-products, which can be accomplished by selecting the proper co-catalysts (e.g., Ag, Cu). Although photocatalysis is not fully suitable for drinking water applications yet, P90/Ag removes nitrate efficiently and with high selectivity.

There are some reports presenting the photocatalytic reduction of NO$_3^-$ in the absence of sacrificial agents, but their activity is not sufficiently satisfactory [130,157,170–180]. Wei et al. [181] aimed to develop photocatalysts for the chemical reduction of NO$_3^-$ in visible light (fluorescent lamps irradiated with a power intensity of 2.64 mW/cm$^2$, $\lambda$ = 419 nm) and in the absence of sacrificial agents. The use of Ni$_2$P as a potential base-metal alternative to precious metals as a catalyst for the hydrogenation of NO$_3^-$ under mild, near-ambient conditions (1 atm, 60 °C) has been demonstrated [182]. This potential catalyst exhibited complete NO$_3^-$ reduction with very high selectivity for ammonia (NH$_3$) [182]. Considering that the light source and the photocatalyst are two key factors in the photocatalytic reduction of NO$_3^-$, Wei et al. [181] synthesized Ni$_2$P/semiconductors (Ni$_2$P/Ta$_3$N$_5$, Ni$_2$P/TaON, and Ni$_2$P/TiO$_2$) and used these heterostructures as photocatalysts for the reduction of NO$_3^-$ in water (Figure 15a,b).

Starting with a 2 mM (28 g/mL NO$_3^-$) solution at pH 2, Ni$_2$P/Ta$_3$N$_5$ and Ni$_2$P/TaON achieve 79% and 61% NO$_3^-$ conversion, respectively, and conversion rates of 196 µmol g$^{-1}$ h$^{-1}$ and 153 µmol g$^{-1}$ h$^{-1}$, respectively, after 12 h under 419 nm irradiation. Control experiments confirmed that Ni$_2$P/semiconductor heterostructures and light illumination are
requires for the photocatalytic reduction of NO$_3^-$). Based on these findings, Wei et al. proposed two possible electron migration pathways and assumed that the dominant pathway in these heterostructures is light absorption by the semiconductor followed by electron injection into Ni$_2$P (Figure 15c,d) [181].

Silveira and co-workers [134] presented the promising use of FeTiO$_3$ and oxalic acid as reducing agents for the selective photo-reduction of nitrate to N$_2$. They studied the feasibility of using natural ilmenite as a catalyst for NO$_3^-$ photo-reduction with oxalic acid as a reducing agent. The generation of NO$_x$ via NO$_3^-$ and NO$_2^-$ reduction is also observed. The complete NO$_3^-$ and C$_2$O$_4^{2-}$ removal and a selectivity towards N$_2$ > 93% was achieved by using the stoichiometric C$_2$O$_4^{2-}$ amount after 210 min, without the generation of undesirable NH$_4^+$. Formic acid is known as one of the most efficient hole scavengers for nitrate reduction. The deep reduction to N$_2$ is quite difficult because the process requires a significantly high density of electrons at the catalytic sites. Yue et al. [120] proposed that the reactions occur on the surface of the catalyst particles, as shown in Figure 16.  

The authors [120] systematically investigated the performance of CuInS$_2$ in photocatalytic nitrate reduction under visible light irradiation by loading co-catalysts. A 300 W Xe lamp was used to provide visible light irradiation. Band-pass or cut-off filters were applied to obtain monochromatic beam light ($\lambda = 400, 450, 500, 550, 600$, or 650 nm) or pure visible light ($\lambda > 400$ nm), respectively. In particular, with the assistance of the LSPR effect of Au, the high record of the nitrate conversion rate of 8.32 mg N h$^{-1}$ was achieved under pure visible light. Overall, CuInS$_2$ holds high potential in the application of photocatalytic nitrate removal under solar irradiation. Yue et al. [120] advanced the idea that the reaction mechanism takes place via adsorption–reduction reactions where nitrate ions are reduced directly by photo-generated e$^-$s. This mechanism is supported by the fact that the introduc-
tion of additional halide anions in an aqueous solution reduces the photocatalytic efficiency due to the competition between the adsorption of ion species. Yue and co-workers [120] The efficiency of solid formate as a hole scavenger was evaluated. It was shown that both glucose and sucrose appear to be effective, with only a slight decrease in photocatalytic efficiency. On the contrary, harmful molecules (including benzene, phenol, and benzoic acid) and other typical h+ scavenger agents (such as methanol and ethylene glycol) were also applicable with the rationale of simultaneously decomposing two pollutants.

**Figure 16.** Photocatalytic nitrate reduction on CuInS2 loaded with co-catalysts in the presence of sacrificial agents. The abbreviations (aq), (ads), and (g) mean ions in an aqueous solution, adsorbed on the surface and in the gas form, respectively. Reproduced with permission from ref. [120]. Copyright 2016 Royal Society of Chemistry.

Titania (TiO2) and metal-loaded titania using Pt [123,151,165], Pd [141,151,165], Rh [151], Ru [151], Au [118,121], and Ag [127,128,144] are widely used and effective in the reduction of nitrate with high selectivity toward N2 [125,127,128,144,165].

Zhang et al. [144] obtained high conversion (98%) and almost 100% selectivity for nitrogen for nitrate photocatalytic reduction by using catalyst nontoxic fine Ag clusters obtained by photo-deposition of silver precursors on nano-sized titanium dioxide particles (denoted as Ag/TiO2), formic acid as hole scavenger, and a 125-W high-pressure Hg lamp, main wavelength around 365 nm, as a light source. The formation of more detrimental products, nitrite and ammonium, was thereby avoided, and residual formic acid can be completely decomposed into a harmless CO2 by further irradiation. Hou et al. [183] presented the novel core-shell structured Ag/SiO2@cTiO2 composites for photocatalytic reduction of high-concentration nitrate (2000 mg L−1). Photocatalytic denitrification experiments were performed with the light source of a 500 W high-pressure mercury lamp (main wavelength around 365 nm). Due to the electron sink effect, Ag NPs in the TiO2 shell could trap the photogenerated electrons and prolong the lifetime of charge carriers. The photogenerated electrons could be transferred from the CB of the TiO2 shell to Ag NPs for prevention of its oxidation to Ag+. Therefore, Ag/SiO2@cTiO2 could reduce high-concentration nitrate to N2 effectively.

Lin et al. [119] developed a bio electro-photocatalytic system under UV irradiation (Figures 11 and 17a) which exhibits a high selectivity for photocatalytic reduction of nitrate to N2.

A 30-W low-pressure mercury lamp was used as the light source. The proposed nonconventional bio electro-photocatalytic system has the advantage of a greater denitrification rate, higher selectivity to N2, absence of harmful by-products formation (nitrite or ammonium), the introduction of hole scavenger in nitrate solution is avoided, and cost-effectiveness (Figure 17b–d). Compared with the conventional denitrification mechanism shown in their work [119], this type of a bio electro-photocatalytic reaction pathway has a lower energy barrier (Ea) (Figure 17b), suggesting that the complete photocatalytic reduction of nitrate to N2 without cumulation of harmful byproducts is energetically possible.

\[
\begin{align*}
N\text{O}_3^-(aq) &\rightarrow N\text{O}_3^-(ads) \quad [1] \\
2N\text{O}_3^-(ads) + 10e^- + 12H^+(aq) &\rightarrow N_2(g) + 6H_2O(l) \quad [2] \\
N\text{O}_3^-(ads) + 2e^- + 2H^+(aq) &\rightarrow N\text{O}_2^-(aq) + H_2O(l) \quad [3] \\
N\text{O}_3^-(aq) &\rightarrow N\text{O}_3^-(ads) \quad [4] \\
2N\text{O}_3^-(ads) + 6e^- + 8H^+(aq) &\rightarrow N_2(g) + 4H_2O(l) \quad [5] \\
HCOOH + 2H^+ &\rightarrow CO_2(g) + 2H^+(aq) \quad [6]
\end{align*}
\]
The photocatalytic denitrification reaction can be described below (Equation (40)):

$$10e_{cb}^- + 2NO_3^- + 12H^+ \rightarrow N_2 + 6H_2O$$

(40)

The absence of nitrite generation in the bio electro-photocatalytic denitrification setup is indicative that the reaction pathway is different compared to the conventional denitrification reaction mechanism. The authors provided a valuable solution to increase the efficiency and selectively of photocatalytic denitrification by coupling an electron generation device with a photocatalytic denitrification process and simultaneous activation of nitrate atom pairs for the final formation of $N_2$ from nitrate [119,120].

In the study conducted by Liu et al. [184], a novel two-step reduction process was constructed for the selective removal of nitrate in an aqueous solution of Na$_2$SO$_3$ using Cu/Fe bimetal photocatalyst. The produced nitrite by the reduction of nitrate on the Cu$^{0}$ surface could not be converted to ammonia rapidly on the surface of iron oxide layer, leading to the accumulation in time of nitrite. In the next step, the accumulated nitrite was...
efficiently and easily reduced to nitrogen by Na$_2$SO$_3$, which worked as an efficient electron donor for nitrite reduction. The selectivity for N$_2$ was over 90%, and the yield of ammonia was below 10% during the two-step reduction process.

Shang et al. [185] investigated the influence of exposed facets of silvered TiO$_2$ photocatalysts on photo denitrification. They found that the nitrate reduction percentage and selectivity to N$_2$ for Ag$_2$O/Ag/101-TiO$_2$ reached 99.1 and 81.1%, respectively, due to the formation of the junction at TiO$_2$-metallic Ag interfaces and to Z-scheme charge transfer pathway mediated by adjacent Ag.

Recently, Silveira et al. [186] presented a study of the capability of the natural ilmenite (FeTiO$_3$) to reduce nitrate from ultra-pure and mineral water. They claim that natural ilmenite can be a great applicant for reducing NO$_3^-$ in contaminated water. In ultra-pure water, the nitrate is totally converted to NO$_x$ (2%) and N$_2$ (98%) after 210 min. If using oxalate in the mineral water, the nitrate is removed, but NO$_2^-$, NO$_x$, and N$_2$ appear as products. In another study [187], the nitrate reduction in saline waters was explored for the first time employing the FeTiO$_3$/oxalic acid photocatalytic process. A 150 W medium mercury lamp was used. Acidic pH values must be maintained to avoid oxalic acid precipitation by Ca$^{2+}$ present in the water matrix. Under those conditions and compared to ultrapure water, salinity (in the range of 5–33 g/L) has a small influence on nitrate reduction, which is related to the evolution of C$_2$O$_4^{2-}$ concentration.

Wang et al. [188] prepared a novel SiW$_9$/TiO$_2$/Cu composite catalyst and studied the impact of catalyst loading, initial nitrate concentration, polyoxometalate loading, formic acid and O$_2$ on the removal of nitrate under UV light. Nitrate removal up to 76.53% and 82.09% of N$_2$ selectivity was obtained under specific experimental conditions: initial nitrate concentration of 30 mg/L, concentration of formic acid, 30 mmol/L, SiW$_9$/Cu loading level 8.33%, the catalytic dosage of 0.8 g and presence of N$_2$.

Graphitic carbon nitride (g-$\text{C}_3\text{N}_4$) has been broadly used in the area of photocatalysis due to its suitable features such as very good stability, graphene-like structure, ease of synthesis and the capability to produce photocarriers. Liu et al. [189] obtained Ag$_y$Pd$_{10-y}$/g-$\text{C}_3\text{N}_4$ Mott–Schottky heterojunction by growing AgPd nanowires (NWs) on the surface of nitrogen-rich g-$\text{C}_3\text{N}_4$. Their strategy opens a new way for making photocatalytic hydrogen production in tandem with the reduction of NO$_3^-$ and NO$_2^-$ in water, also extending it to remove metal ions. The Ag$_3$Pd$_7$/g-$\text{C}_{1.95}\text{N}_4$ catalyst exhibited the highest photocatalytic activity and selectivity for photocatalytic reduction of NO$_3^-$ and NO$_2^-$, and the removal rates of NO$_3^-$ and NO$_2^-$ are 87.4% and 61.8%, respectively, under 365 nm irradiation, at 25 °C.

Soliman et al. [190] studied the reduction of nitrate in water under solar radiation using activated carbon prepared from date palm stone decorated with single and bimetallic nanoparticles. In their work, acetic acid, formic acid, oxalic acid, and ammonium oxalate have been investigated as holes scavengers for nitrate reduction. The obtained results for activated carbon modified with Pd-Ag (using formic acid as a hole scavenger with 0.05 M) showed that the conversion of nitrate (85% after 35 h of natural solar irradiation) takes place mainly through nitrogen gas (N$_2$) rather than nitrite (NO$_2^-$) or ammonium (NH$_4^+$).

The photocatalytic activity strongly depends on the applied experimental conditions, including the mass of the photocatalyst, the incident beam intensity, the type of sacrificial agents, the nitrate concentration in the starting aqueous solution, and so on. Table 4 shows some photocatalytic performance results of different materials reported in the literature, with an emphasis on selectivity towards harmless nitrogen, although an accurate comparison is difficult because of variations in experimental conditions.
Table 4. Comparative results of the photocatalytic performance obtained on different materials.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Light Source</th>
<th>Sacrificial Agent</th>
<th>NO$_3^-$ Conversion (%)</th>
<th>NO$_2^-$ Selectivity (%)</th>
<th>NH$_4^+$ Selectivity (%)</th>
<th>N$_2$ Selectivity (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Ag/P25</td>
<td>High-pressure Hg lamp 300 W</td>
<td>Formic acid 0.04 M</td>
<td>99.6</td>
<td>2.3 (yield of NO$_2^-$, mgN L$^{-1}$)</td>
<td>9.3 (yield of NH$_4^+$, mgN L$^{-1}$)</td>
<td>88.4</td>
<td>[125]</td>
</tr>
<tr>
<td>5% Ag$_2$O/P25</td>
<td>High-pressure Hg lamp 300 W</td>
<td>Formic acid 0.04 M</td>
<td>97.2</td>
<td>2.4 (yield of NO$_2^-$, mgN L$^{-1}$)</td>
<td>14.0 (yield of NH$_4^+$, mgN L$^{-1}$)</td>
<td>83.1</td>
<td>[125]</td>
</tr>
<tr>
<td>Fe/TiO$_2$</td>
<td>High-pressure Hg lamp 110 W</td>
<td>Formic acid 40 mM</td>
<td>100</td>
<td>0</td>
<td>13.0</td>
<td>87.0</td>
<td>[127]</td>
</tr>
<tr>
<td>Cu/TiO$_2$</td>
<td>High-pressure Hg lamp 110 W</td>
<td>Formic acid 40 mM</td>
<td>100</td>
<td>0</td>
<td>37.0</td>
<td>63.0</td>
<td>[127]</td>
</tr>
<tr>
<td>Cr-TiO$_2$</td>
<td>Low-pressure Hg lamp 17 W</td>
<td>Formic acid 450 mg L$^{-1}$ (-9.8 mM)</td>
<td>56.29</td>
<td>-</td>
<td>-</td>
<td>98.53</td>
<td>[139]</td>
</tr>
<tr>
<td>Zn-TiO$_2$</td>
<td>Low-pressure Hg lamp 17 W</td>
<td>Formic acid 450 mg L$^{-1}$ (-9.8 mM)</td>
<td>91.67</td>
<td>-</td>
<td>-</td>
<td>95.45</td>
<td>[139]</td>
</tr>
<tr>
<td>Ag/TiO$_2$</td>
<td>High-pressure Hg lamp 125 W</td>
<td>Formic acid 0.04 mol/L</td>
<td>98.4</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>[144]</td>
</tr>
<tr>
<td>Ag/TiO$_2$</td>
<td>High-pressure Hg lamp 125 W</td>
<td>Oxalic acid</td>
<td>16.7</td>
<td>2.20</td>
<td>0.37</td>
<td>84.6</td>
<td>[144]</td>
</tr>
<tr>
<td>Pd-Cu/TiO$_2$</td>
<td>-</td>
<td>Formic acid</td>
<td>62</td>
<td>0</td>
<td>6.0</td>
<td>94.0</td>
<td>[164]</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>High-pressure Hg lamp 110 W</td>
<td>Humic acid 1.0 mmol/L</td>
<td>90.1</td>
<td>-</td>
<td>-</td>
<td>86.2</td>
<td>[169]</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>High-pressure Hg lamp 110 W</td>
<td>Formic acid 1.0 mmol/L</td>
<td>98.4</td>
<td>0.13</td>
<td>1.2</td>
<td>95.8</td>
<td>[169]</td>
</tr>
<tr>
<td>Ag$_2$O/Au/101-TiO$_2$</td>
<td>-</td>
<td>-</td>
<td>98.57</td>
<td>3.55</td>
<td>2.42</td>
<td>94.03</td>
<td>[185]</td>
</tr>
<tr>
<td>Ag$_2$O/Au/101-TiO$_2$</td>
<td>-</td>
<td>-</td>
<td>99.10</td>
<td>4.56</td>
<td>14.34</td>
<td>81.10</td>
<td>[185]</td>
</tr>
<tr>
<td>Fe/TiO$_2$</td>
<td>UV-A lamp 20 W nzv Fe/TiO$_2$</td>
<td>Formic acid 27 mM</td>
<td>80.0</td>
<td>0</td>
<td>39.1</td>
<td>60.9</td>
<td>[191]</td>
</tr>
<tr>
<td>SiW$_9$/TiO$_2$/Cu</td>
<td>High-pressure mercury lamp 125 W</td>
<td>Formic acid 30 mmol/L</td>
<td>76.53</td>
<td>-</td>
<td>-</td>
<td>82.09</td>
<td>[188]</td>
</tr>
<tr>
<td>Ag$_3$Pd$<em>7$/g-C$</em>{1.95}$N$_4$ Ag-Pd NPs/activated carbon</td>
<td>Two light bulbs 40W</td>
<td>Formic acid 0.05 M</td>
<td>85</td>
<td>traces</td>
<td>traces</td>
<td>High selectivity to N$_2$</td>
<td>[190]</td>
</tr>
<tr>
<td>Ag-Pd NPs/activated carbon</td>
<td>Natural solar radiation</td>
<td>Formic acid 0.05 M</td>
<td>85</td>
<td>traces</td>
<td>traces</td>
<td>High selectivity to N$_2$</td>
<td>[190]</td>
</tr>
</tbody>
</table>
Having a high solubility in water, the nitrate anion is recognized as one of the most widespread contaminants. That is why research is still needed for the development of efficient technologies in the purification of contaminated waters [192].

To completely clarify the nitrate and nitrite photocatalytic reduction mechanism, future studies should quantify the gaseous reaction products in order to elucidate which gaseous species are released during photocatalytic treatment. However, the precise assessment of gases released in the photocatalytic reduction process is extremely challenging from an experimental point of view. It is highly advised to look into reactors that can provide high mass transfer, efficient nitrate reduction, and, on the other hand, a good recovery of N-gases. Combining with other technologies would be a wise choice for improving photocatalytic processes.

3. Prospectives and Photocatalytic Approaches in Depollution Technologies

The novelty of this study comes from the fact that this work makes a clear discrimination between oxidative degradation of pollutants, typically leading to the formation of various intermediates, and mineralization, consisting of oxidation to unharmful CO\textsubscript{2}.

The first condition to apply photocatalysis in depollution technologies is that the organic pollutant should be mineralized to unharmful CO\textsubscript{2}. The advantage of using solar light in depollution is obvious. Other restrictive conditions hindering the large-scale application of photocatalysis in pollutant removal are the low reaction rates and photocatalytic material-related. Despite the considerable advances in the abatement of numerous recalcitrant compounds, there are remaining challenges to overcome for large-scale practical application. In the meantime, the by-products should be identified and quantified, and their environmental toxicity should be assessed.

The stringent goals in photocatalytic depollution technologies are: (i) high selectivity to CO\textsubscript{2}; (ii) performant materials characterized by non-toxicity, low band gap, stability, low production costs, high recyclability and (iii) high reaction rates. The efficiency and selectivity of a photocatalyst to carbon dioxide or other unharmful compounds depend on the type of the photocatalytic material and the operating reaction parameters [193]. Another challenge consists in the fact that the majority of photocatalytic systems are based on TiO\textsubscript{2} or ZnO, which have large band gap energies (3.1–3.3 eV), thus are mostly active in UV radiation which accounts for only 5% of sunlight [194,195].

3.1. Low Reaction Rates

Due to the low reaction rates, for practical reasons, the photocatalytic technologies should be combined with other techniques such as ozonation [3,196], filtration technology [7], sonication [197–199], thermal activation [200–202]. For instance, Preda et al. [3] investigated the aqueous ammonia oxidation over iron-modified titanate nanorods by using combined treatment with ozone and simulated solar light irradiation. Increasing ammonia conversion was registered relative to the photocatalytic process carried out without ozone, but also the NO\textsubscript{3}\textsuperscript{−} formation was significantly reduced by comparison with the dark ozonation assays. The main achievement of this combined procedure was the increased selectivity of ammonia degradation to gaseous nitrogen-containing end products.

Denny et al. [7] reported the advantages of coupling the photocatalytic and filtration technologies in terms of particulate pollutants elimination together with VOC removal from the air stream. In order to enhance the photodegradation of gas phase ethanol to CO\textsubscript{2} and to reduce the production of intermediates such as acetaldehyde, a fluidized bed aerosol generator (FBAG) was adapted to prepare TiO\textsubscript{2}-loaded ventilation filters as an irradiation source used a UV-light-emitting diode (UV-LED).

According to Adewui [197], photocatalytic processes assisted by ultrasound can be significantly improved and used for the treatment of pollutants in water, sonophotocatalysis (SPC) implying either sequential photocatalytic reaction and ultrasonic irradiation or simultaneous light and ultrasonic irradiation of the investigated system. The main advantages of sonophotocatalysis are clearly emphasized by this review [197]: the better transfer
of organic compounds from the bulk solution to catalyst surface, increase the dispersion of chemicals, an extra generation of hydroxyl radicals that are very efficient oxidizing agents as well as the photogenerated holes. The photocatalytic oxidation targeting the mineralization of intermediates such as carboxylic acids can be enhanced by complementary use of ultrasounds [197], many pharmaceuticals and dyes from wastewaters being subjected to sonophotocatalytic studies [198,199].

The “thermo-photo-catalysis” concept, which addresses both environmental and energy fields, was detailed by Nair et al. [200], revealing the main advantages of this dual approach: thermal acceleration of the photocatalytic reactions (known for the limited reaction rates), the occurrence of some photocatalytic processes in the visible-infrared domain (scarcely available in terms of hole/electron photoexcitation), the same efficiency for the pollutant removal as in simple thermocatalytic process but using lower temperatures.

A coupling of advanced oxidation/reduction processes and biological processes for water depollution have been investigated, including ozonation-, Fenton-, electrochemical-biological processes, and also sequential chemical-biological processes [203]. The ozonation in the presence of UV irradiation has become one of the most used advanced oxidation processes for the degradation of organic compounds in general as acids, alcohols, and organochlorines of low molecular weight. Unfortunately, both UV and ozone are quite expensive to generate and need the consumption of large amounts of electric energy. Within the development and application of wastewater treatment technologies, should be taken into account efficiency, cost, and reliability. If the intermediate products obtained require additional removal, then the purification process becomes expensive and complicated. The combination with other technologies, for example, nanotechnology [204], can also be considered.

Andronic et al. [205] tested three different composites in a pilot plant for solar treatment of wastewater using phenol, imidacloprid, and dichloroacetic acid as model pollutants. The investigated photocatalysts were sol-gel TiO$_2$ (as the reference), Vis-active Cu$_x$S prepared by photochemical precipitation, and highly filterable TiO$_2$-fly ash mixture/composites. The experiments were conducted at a laboratory scale in two solar simulators and under natural solar irradiation at the pilot plant scale, at the Plataforma Solar de Almería, in a Compound Parabolic Collector (CPC) solar radiation system. The research group showed that the high phenol removal efficiency under simulated solar irradiation was attained by the reference TiO$_2$. This behavior was due to titania’s large surface area and its anatase/rutile phase composition. Contrarywise, under solar radiation in the CPC reactor pilot, all three pollutants were partially mineralized during the first 40–90 min, but by-products clog the surface, and removal continues without fully oxidizing the organic substrates. After 150 min of solar irradiation at the pilot–plant scale, the difference between the apparent phenol removal (55%) and mineralization (33%) confirms the presence of intermediates at the end of the reaction.

Combined photocatalytic processes proved to be also efficient for the abatement of larger molecule contaminants. Efforts were paid to search for the optimal technology for the removal of wastewater microcontaminants by coupling four different electrochemical processes with a solar CPC reactor at a pilot plant scale [206]. Thus, the anodic oxidation (AO), solar-assisted AO, electro-Fenton (EF), and solar photoelectro-Fenton (SPEF) processes were employed for monitoring the treatment of microcontaminats. This research group selected two different water matrices: one coming from a synthetic retentate with medium content of chlorides (in the range of 550 mg L$^{-1}$, from natural water), while the other one was actual urban wastewater with a higher concentration of chlorides (in the range of 1200–2000 mg L$^{-1}$), spiked with a mix of four microcontaminants (pentachlorophenol, terbutryn, chlorphenvinfos, and diclofenac). These combined technologies successfully removed contaminants of an actual urban wastewater treatment plant secondary effluent up to 80% of the total amount. However, the main disadvantage was that this process was not efficient for dissolved organic carbon (DOC) removal.
Coupling photocatalysis, catalytic, and photocatalytic ozonation, proved to be excellent processes for the abatement of a mixture of seven insecticides at a pilot plant scale [207]. The authors studied a complex mixture of pesticides (e.g., simazine, terbutryn, buprofezin, procymidone, azoxystrobin, imidacloprid, and thiamethoxam), and three sources of TiO₂ (N-TiO₂, pure TiO₂, P25 Degussa) at bench and pilot plant scale to finally combine with ozonation looking for an increase in the degradation efficiency. Ozonation was demonstrated to be the most effective process for the abatement of the targeted mixture of microcontaminants.

3.2. Non-Toxicity

Usually, bare and modified semiconductors are used for photocatalysis, especially TiO₂-based ones, but unusual photocatalysts such as the highly-defected SiO₂ nanotubes proved to be active under solar irradiation [33]. Their activity for methanol and oxalic acid photodegradation in liquid media proved to be close to that registered for TiO₂. Therefore, it can be considered a valuable solution for depollution technologies being a low-cost, non-toxic, and environmentally friendly material able to work under solar light, a regenerable energy source.

3.3. Industrial Technologies

The establishment of photocatalytic depollution technology is a very difficult task due to the fact that real industrial conditions and parameters are less stable and controllable than laboratory conditions, with few companies (Purifics Photo-Cat) applying AOP in industry [194,195]. There is a need to develop pilot scale-up systems that can confirm the technologies presented in this review and eventually be able to use them in industrial applications. Also, another aspect that needs attention is whether photocatalysis will be used alone or as an intermediary step (pre or post-treatment) in a depollution process (maybe used together with ozonation or with physical or biological processes [208].

Conventional photocatalytic nitrate reduction techniques have been developed to produce potable waters, such as adsorption, ion exchange, chemical reduction, membrane filtration, electrochemical, and biological denitrification [209]. These conventional techniques further produce secondary toxic by-products. One of the main problems in the practical application of photocatalysts is the development of methodology for photoreactor scale-up [210]. There are some chemistry, material, and reactor challenges currently limiting large-scale applications of photocatalysis processes of inorganic pollutants [203].

Figure 18 summarizes the challenges and future perspectives to improve photocatalytic remediation technologies.

Figure 18. Schematic representation of the challenges and photocatalytic approaches in depollution technologies.
4. Conclusions

Herein, an extensive screening of the scientific literature related to the photocatalytic removal of various organic and inorganic hazardous compounds is presented. The review focuses on the photomineralization of a few relevant hazardous compounds into CO$_2$ and other harmless products. Specifically, information is provided on (i) photooxidation of primary alcohols and carboxylic acids in gaseous and liquid media (e.g., methanol, ethanol, oxalic acid) in gaseous and liquid media, (ii) photocatalytic removal of chlorinated and aromatic VOCs from indoor air and water (e.g., trichloroethylene, perchloroethylene, dichloroacetate anion, benzene, toluene, p-xylene, ethylene), (iii) photomineralization of phenol from wastewater, and (iv) efficient removal of nitrate and its conversion, as far as possible, to compounds that do not affect human life and the environment. The degradation of persistent pollutants is critically analyzed, highlighting the main factors affecting the overall process, such as ROS involvement. Particular attention has been paid to the reaction mechanisms established during the photocatalytic removal of inorganic pollutant NO$_3^-$ in connection with the selectivity to harmless nitrogen. The effects of working parameters (e.g., irradiation time, the procedure of operation) on performance are also discussed, along with the intrinsic properties of the applied materials (e.g., surface active sites and structure).

From a large amount of available data, it is clear that further research should be conducted in order to find efficient photocatalysts that are able to mineralize the pollutants into the non-toxic CO$_2$. Only such photocatalysts can be considered for environmental remediation.

Pollutant elimination by only photocatalysis is a highly demanding task and difficult to carry out. Therefore, combining photocatalysis with other techniques is imperative. Photocatalysis as a depollution method has limited efficacy, but from the environmental point of view, it has great significance because the sun is a cheap and endless source. In fact, in nature, all the existent pollutants are exposed to solar irradiation. Thus, photocatalytic studies are highly relevant to the actual environment. Oxide materials (e.g., minerals) are slowly degrading pollutants under solar light, and the fate of intermediates is less known. Thus, the photocatalytic pollutant degradation mechanism in laboratory experiments is very important because it is relevant to the natural depollution processes.

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