Photodegradation of Emerging Pollutants Using Catalysts Supported in Organic and Inorganic Composite Materials



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Abstract Issues: Efficient solution treatment methods are necessary for the abatement of pharmaceuticals and pesticides in water, and mitigate environmental impacts. Chemical, physical and biological water treatment processes have been applied for the removal of emerging pollutants from water. However, these methods are not completely efficient due to the formation of secondary pollution, high cost and time of operation. Advanced oxidation processes can overcome these problems on water and wastewater treatment containing emerging pollutants. **Major advances**: We reviewed in this text catalytic photodegradation processes of pharmaceuticals and pesticides in aqueous media using catalysts incorporated in/on polymer-based porous rigid organic solid supports. Advanced oxidation processes are usually conducted using specific catalysts combined to ultraviolet (UV) radiation emission. Many catalysts have been studied in UV radiation-assisted water treatment techniques, including titanium dioxide (TiO₂), zinc oxide (ZnO), tin dioxide (SnO₂), cerium (IV) dioxide (CeO₂) and tungsten trioxide (WO₃), in addition to chalcogenides (CdS, CdSe). The UV radiation emission with wavelength lower than 385 nm generates

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electron-hole pairs on catalyst structures, inducing the generation of free radicals capable of photo-degrading adsorbed pollutants. The photocatalysis of organic pollutants can also take place after emission of either visible light or combination of UV/visible light. The degradation efficiencies can vary from 61.0 to 99.2% depending on the employed system. Many catalysts have low photodegradation efficiency due to their small surface area and low pollutant adsorption capacity. This problem can be overcome with the immobilization of the catalyst in solid rigid supports. Polymer-based porous composite materials have been demonstrated to be potential organic rigid solid supports to improve the photocatalytic degradation efficiency of organic pollutants due mainly to the increase of surface area. In this sense, we have shown the incorporation of metal oxides on polymer-based porous composite materials for the photodegradation of pharmaceuticals and pesticides contained in aqueous solutions.

1 Introduction

The environmental pollution caused by organic and inorganic chemical compounds has increased in the last years due to the increase of anthropological activities around the world [60]. This problem is also result of the lack of appropriate environmental remediation technologies for application on industrial-scale [47]. The industrial, urban, agricultural and animal production activities are significant sources of environmental pollution as they generate many chemical residues with ecotoxicity, affecting the ecosystem and animal/human health [70]. Many regions have been contaminated due to the inappropriate disposal of residues containing emerging pollutants such as pesticides and pharmaceuticals [24].

Emerging pollutants are synthetic, semi-synthetic, organic chemical compounds which have not been commonly detected, identified and quantified in the environment and in biological tissues [23]. Pesticides, herbicides, insecticides, fungicides, antiparasitic and antibiotics are emerging pollutants with high pollution degree which must be removed from the environment to protect humans, animals and plants [51]. The most studied chemical pollutants due to their impacts on the ecosystem and animal/human health include organochlorines, organophosphates, neonicotinoids, pyrethroids, phenylpyrazoles, benzimidazoles, triazoles, triazines, macrocyclic lactones, penicillins, tetracyclines and so forth [63]. These compounds are significant emerging pollutants for the environment due to the bioaccumulation capacity, and acute, chronic ecotoxicological and toxicological effects on non-target organisms, including humans [62].

The intensive use of pharmaceutical compounds for prophylaxis of animals, and the inadequate management of industrial and urban wastewaters are sources of entry of pesticides and medicines in the environment [60]. Hence, no-treated industrial and urban wastewaters increase the environmental pollution indices as some agricultural pesticides and pharmacological compounds can be persistent and mobile, especially in soil and water [46]. The water contamination by emerging pollutants generates great concern since it is a vector to transport chemicals into groundwater over long distances [56]. Moreover, it is not yet common to find conventional methodologies involving water and wastewater treatment plants containing pesticides and pharmaceuticals [10].

New water and wastewater remediation methodologies contaminated with emerging pollutants are mandatory to mitigate damages to the environment, animals and human beings. In this sense, various physical, chemical and biological processes have been studied/applied in the residue remediation containing pesticides and medicines [58]. These types of technologies are being frequently classified as containment-immobilization, separation or destruction [47]. Containmentimmobilization technologies are identified by the use of adsorbent compounds and physical barriers, whereas separation technologies are applied by using extracting compounds, solvents, surfactants and washing [60]. Chemical destruction technologies include ionization, hydrolysis or oxidation reactions, whereas biological destruction technologies include the use of microorganisms, microalgae, composting, landfarming, biopiles, slurry bioreactors, vermeremediation and phytoremediation [47].

Many environmental pollution remediation technologies have still limitations for the applications in real-world situations, including generation of secondary pollution due to formation of toxic by-products, undesirable physiochemical and/or biological properties in the treated environmental matrix, and high operation cost, energy consumption and operation time [23]. Moreover, negative influences of temperature, pH, moisture content, nutrients and matrix compounds are also known problems during applications of some technologies. One of the biggest challenges for applications of environmental remediation technologies is the scale-up from a laboratory plant to industrial plant [23, 47, 60]. Hence, new water and wastewater treatment technologies containing pesticides and medicines have been studied to overcome the main problems currently found in the developed methods. Moreover, detailed studies are necessary to optimize the laboratory experiments to full-scale plant aiming to treat water and wastewater contaminated with emerging pollutants such as agricultural pesticides and pharmacological medicines.

2 Methodologies for Water and Wastewater Treatment

Many emerging pollutants contained in water and wastewater industrial are difficult to biodegrade, needing efficient physical, chemical or biological treatment techniques for their elimination. The traditional aqueous solution treatment techniques commonly applied to water and wastewater purification have proved to be little effective as they require physical, physicochemical, or chemical operations to achieve adequate pollutant removal efficiencies. The most common water and wastewater treatment processes include coagulation, flocculation, electroflocculation, membrane-filtration, adsorption, and advanced oxidative processes (AOPs) [13, 48]. The most widely used methods for water and wastewater treatment are coagulation and flocculation. Both experimental procedures are based on agglomeration and growth of contaminating particles suspended in aqueous media for posterior physical removal [58]. Coagulation and flocculation are viable strategies for the water and wastewater treatment due to inexpensive implantation and operation, in addition to be easily applied at full-scale plants. However, they exhibit low removal efficiencies of emergent pollutants such as pesticides and pharmaceuticals (less than 10%) due to physiochemical properties of these compounds [2]. On the other hand, coagulation and flocculation are potential strategies in pre-treatment processes, followed by a more specific technology of emerging pollutant abatement in water [46, 71].

Electroflocculation and electrocoagulation as well as conventional flocculation and coagulation are techniques employed to agglutinate contaminants contained in aqueous solutions for posterior physical removal. However, processes using electrical current have advantages due to electrical charge action in possible oxidation–reduction reactions of compounds, destabilization of emulsions, and formation of flakes with faster kinetics [65]. Electroflocculation and electrocoagulation are relatively efficient methods for the emerging pollutant removal from aqueous solutions as they are versatile and simple to operate. These methodologies can also be important as previous steps during the execution of a conventional process with the aim of decreasing the concentrations of pollutants in solutions [49, 68].

Another method that can be applied to remove emerging pollutants from aqueous solutions is the membrane-filtration technology. This method is based on the physical separation between aqueous solution and pollutant according to selective permeability of the employed membrane. The water and wastewater purification process using membrane-filtration is very efficient, mainly at low pollutant concentrations. This technology is important to applications in urban and industrial wastewaters [33]. Aqueous solution purification processes involving semipermeable polymeric membranes have become a reality for the removal of persistent pollutants due to high retention efficiencies of impurities on such membranes [26]. The main disadvantage of this technology is the need of previous treatment processes before using the membrane-filtration in the removal of solid particles and high pollutant concentrations contained in aqueous samples. High solute concentration in aqueous solution obstruct the membrane, making the treatment process unfeasible [26, 33]. Membranefiltration technology has also been applied as an important tool in the oxidation of emerging pollutants as the membrane can be an efficient solid support to encapsulate catalysts. In this case, it takes place the pollutant physical sorption and chemical modification by applying photocatalysis techniques [38, 57].

Sorption has shown to be an important phenomenon in aqueous solution purification processes containing low pollutant concentrations. This technique involves a physical removal process of pollutants after their chemical or physical interaction in the structure of the solid material [48]. In this sense, new adsorbent solid materials have been produced to increase the applicability of sorption in the removal of several emerging pollutants with different physiochemical properties [13, 20]. The disadvantage of aqueous solution treatment processes involving sorption is related to production of secondary pollution. It takes place as the pollutant molecule trapped in the adsorbent was only transferred from the aqueous solution to the solid material structure. Therefore, the adsorbent containing pollutant must be appropriately treated before disposing, being necessary to think in alternative processes capable of removing the emerging pollutant without generating secondary pollution [20]. In this sense, advanced oxidation processes can overcome this disadvantage.

Advanced oxidation processes (AOPs) are based on oxidation reactions of harmful chemical compounds contained in aqueous solutions with subsequent conversion to no-harmful intermediates. In this case, the pollutant removal from solution takes place by physical process as described in other technologies. The oxidative conversion during an advanced oxidation process can sometimes mineralize pollutant compounds to CO_2 and H_2O or generate partial degradation with formation of oxidized compounds [37]. Briefly, the advanced oxidation process starts with the generation of free radicals, especially hydroxyl and oxygen radicals, which have high oxidation capacity of organic pollutants in solutions [24]. There are several advanced oxidation process, and photocatalytic degradation.

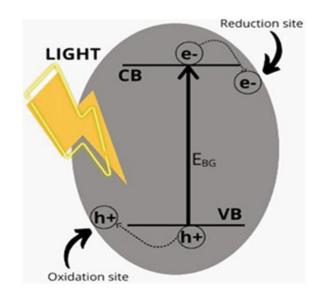
Electrochemical oxidation processes are conducted with production of free radicals after the application of an electrical potential difference between two electrodes (cathode and anode). In this case, the generated electric current provides necessary energy for the formation of free radicals [43], starting the pollutant degradation process. Ozonation is another strategy for the abatement of pollutants in water. The ozone molecule is naturally a strong oxidant agent, acting directly in pollutant oxidation processes. Moreover, it can be efficiently employed for the free hydroxyl radical (OH) formation [55]. The fenton process is applied for the free radical (OH) e HO_2) formation by using a mixture of iron (II) and iron (III) in solution [21]. The fenton process is homogeneous when iron (II) and iron (III) are dissolved in solution, and heterogeneous when iron (II) e iron (III) are immobilized in solid supports [8]. Finally, photocatalytic degradation is a technique based on the application of electromagnetic radiation as energy source for free radical formation. In this method, the pollutant removal from aqueous solution is performed by using semiconductor materials capable of absorbing electromagnetic radiation, altering their electronic shell and forming free radicals [54, 72]. When the fenton process is combined to electromagnetic radiation, it is named of photo-fenton process [52]. The pollutant photodegradation can be performed by using different energy sources such as electrical energy and electromagnetic radiation [64]. The main advantage of an advanced oxidation process is the possibility of complete degradation of the emerging pollutant in solution compared to the conventional water treatment methods involving physical removal. It avoids secondary pollution as we can see in different technologies. Overall, photocatalytic degradation is a potential strategy for the purification of aqueous solutions contaminated with emergent pollutants.

3 Catalytic Photodegradation

Heterogeneous photodegradation processes are based on the separation of charge carriers in catalyst structures after sorption of electromagnetic radiation. The sorbed energy activates the catalyst, generating an electron–hole pair (e^-/h^+) [32]. After segregation, it takes place migration of charge carriers towards the catalyst surface for the occurrence of oxidation–reduction reactions (Fig. 1).

During this process, oxygen and water free radicals are formed to degrade sorbed pollutants on the catalyst surface. Sometimes, the pollutant is degraded without the need of free radicals [28]. The photodegradation efficiency is affected by the sorbed energy wavelength, separation process of the charge carriers and sorption capacity of pollutants on the catalyst structure [61]. The sorbed energy amount on the catalyst surface per light photon must be equal or superior to energy difference between the material valence band (VB) and conduction band (CB) (band gap of the catalyst, E_{BG}) for obtaining maximum quantum efficiency. Catalysts with band gap higher than 3 eV require ultraviolet radiation to each light photon generates an electron-hole pair [32]. This commonly takes place during photodegradation processes of emergent pollutants using titanium dioxide (TiO_2) as catalyst [6]. The separation process of the charge carriers in the catalyst structure is a critical moment during photocatalysis as the electron-hole pair must remain without changes during the oxidation-reduction reactions [32]. Overall, sorbed pollutant degradation reactions on catalyst surfaces might not occur at high charge carrier recombination speeds, even at appropriate radiation wavelength. Thereby, techniques for the reduction of the catalyst particle sizes and immobilization processes of the catalyst in/on solid rigid supports have been

Fig. 1 Schematic drawing of the heterogeneous photodegradation process showing the formation of electron–hole pair (e^-/h^+) and variation of band gap energy (E_{BG}) between the valence band (VB) and conduction band (CB) after electromagnetic radiation emission on the catalyst surface



The most widely used catalyst in photodegradation processes is the titanium dioxide (TiO_2) as it has low toxicity [29]. The main challenge to use this catalyst is its large band gap energy when the aim is the activation by (solar) visible light. This disadvantage can be overcome by preparing TiO₂ nanostructure with high surface area. This type of nanostructure to allow photodegradation in milder operational conditions, decreasing the cost of the catalytic process [25]. Other metal oxides have also been employed in photocatalysis, including tin dioxide (SnO₂), cerium (IV) oxide (CeO₂) and zinc oxide (ZnO). These compounds are resistant, electromagnetic and low-cost materials when comparing with noble metals [32]. Moreover, ZnO has photocatalytic efficiency similar that found for TiO₂, however, with lower significantly cost [31]. The catalytic activity of ZnO can still be increased after combination with copper oxide II (CuO_2) due to formation of heterojunctions [1]. Metal-organic frameworks (MOFs) are materials formed by transition metals and organic compounds. These materials have proved to be attractive alternatives for the photodegradation processes of emergent pollutants [22]. MOFs and nanocomposites prepared with chalcogenides (CdS, CdSe) are structures capable of absorbing visible radiation due to lower band gap energy [27]. It is very interesting for photocatalytic processes by using solar light.

Heterogeneous photodegradation is an interesting technique for the aqueous solution treatment containing emergent pollutants such as pesticides [40] and pharmaceuticals [72]. Recent works show that the removal of pesticides and medicines from aqueous solutions by using heterogeneous photocatalysis is satisfactory as it is an eco-friendly technology [4]. For instance, heterogeneous photocatalysis can be used for the photocatalytic degradation of methyl parathion by using UV radiation and ZnO-based catalyst [4]. In this case, the morphologic structure modification of the pure zinc oxide from nanospheres to nanorods increased the degradation percentage of methyl parathion from 65 to 98% after 3 h irradiation. Additionally, the operation time was reduced to 80 min by impregnating ZnO in nanorods without efficiency loss. Zirconium-doped TiO₂ thin films proved to be efficient for the chloridazon and 4-chlorophenol photodegradation for both compounds can be obtained after 4 h of study. Moreover, several herbicides could be degraded with visible (solar) light radiation by using oxidized carbon nitride as catalyst [36].

Dichlorophenoxyacetic acid (2,4-D) is one of the most widely applied herbicides in agricultural crops. When 2,4-D enter the environment causes toxicity for humans and animals. Its high chemical stability difficult the photodegradation process [34]. Table 1 shows some applications of photocatalytic processes for the degradation of 2,4-D. Several experimental conditions have to be optimized for the efficient abatement of 2,4-D in water, including catalyst amount, initial pollutant concentration,

Photocatalyst	Conditions	Main results	References
Oxygen-doped graphitic carbon nitride	 15 mg of catalyst (0.06 mg/mL) Substrate (25 mL, 100 ppm) UV light irradiation (250 W Hg lamp or the visible light irradiation (a blue light laser) 	 Degradation of 98.7% (UV, 140 min) Degradation of 61.5% (visible, 120 min) 	[16]
Fe ₃ O ₄ @WO ₃ /SBA-15	 40 mg of catalyst Substrate (100 mL, 10⁻⁶ mol/L) UV irradiation (60 W, λ = 254 nm), 240 min 	 Degradation of 90.73% 	[34]
Au-TiO ₂ [biphasic nanobelt structure (TiO ₂ (B)/anatase) with anatase as predominant phase]	 Pyrex cylindrical reactor 1 g/L of catalyst Substrate (0.53 mmol/L) pH 3 Continuous air-bubbling, under UVA radiation (60 W), 120 min 	 Degradation of 99.2% (toxicity mainly due intermediate 2,4-dichlorophenol and was eliminated in 4 h) 	[7]

 Table 1
 Photocatalytic processes for the degradation of 2,4-dichrolophenoxyacetic acid (2,4-D)

 with different catalysts and ultraviolet (UV) radiation wavelengths

wavelength and power of the radiation source, and reaction time. Some catalysts that could be employed for the abatement of 2,4-D in aqueous media by photocatalysis are carbonaceous-based, oxide-based and zeolite-based materials. The catalytic activity increase can be efficiently obtained by doping porous solid supports and changing the catalyst morphologies. Photodegradation experiments of 2,4-D at optimized conditions can achieve a removal efficiency around 90% at short reaction times.

Photocatalytic degradation processes are also useful for aqueous solution treatments containing pharmaceuticals [67], including antibiotics and anti-inflammatories [19]. Caffeine has been utilized as model pollutant in several photodegradation studies due to its excellent stability and toxicity [5, 42], in addition to be present in medicine such as anti-flu. According to [72], less than 40 studies about photocatalytic treatments of residues containing antibiotics were published by 2014, with increase to 280 in 2019. Different strategies have been employed to increase the antibiotic photodegradation efficiencies in solutions aqueous. For example, the levofloxacin and tetracycline removal efficiency from water achieved around 95% using photocatalysis [17, 18]. Anti-inflammatories as the non-steroids are emergent pollutants which are frequently being found in urban aqueous wastewaters due mainly to their random use and disposal. Overall, non-steroids, diclofenac and ibuprofen are the most widely found emerging pollutants in surface water [9, 30]. Table 2 shows a variety of applications for the photocatalytic degradation processes aiming to reduce

Pharmaceutical	Photocatalyst	Conditions	Main results	Reference
Sodium diclofenac	BiOI-Ag ₃ PO ₄ nanocomposite	 Catalyst (0.5 g/L) Substrate (10 mL, 5 mg/L) Solar simulator radiation (40 W tungsten lamp) Time: 60 min 	Efficiency of 61%	[45]
Sodium diclofenac	Co ₃ O ₄ /WO ₃	 Batch reactor Catalyst (30 mg) Substrate (50 mL, 15 ppm) pH 10.7 Visible light radiation (80 W Hg lamp, cut-off filter) Time: 180 min 	Efficiency of 98.7%	[41]
Sodium diclofenac	Fluorine-doped ZnO	 Batch reactor Catalyst (1 g/L) Substrate (10 mg/L) pH = 6.5 Solar simulated radiation (1500 W Xe arc lamp) Accumulated energy (400 kJ/m²) 	Efficiency of 90%	[59]
Ibuprofen	Au/meso-TiO ₂	 Simultaneous photocatalytic degradation and water splitting Catalyst (50 mg) Substrate (100 mL) Substrate solution (15 mg/L), pH from 5 to 9 Simulated sunlight irradiation (300 W Xe lamp) Time: 60 min 	Complete degradation with production of 94.5 µmol/h/g of H ₂	[73]

 Table 2
 Photocatalytic degradation processes for the reduction of the concentrations of diclofenac and ibuprofen in aqueous media

(continued)

Pharmaceutical	Photocatalyst	Conditions	Main results	Reference
Ibuprofen	Z-scheme CdS/Fe ₃ O ₄ /TiO ₂ nanocomposite	 Catalyst (0.2 g) Substrate (200 mL, 10 mg/L) Visible light radiation (300 W Xe lamp, cut-off filter) Time: 180 min 	Efficiency of 94.2%	[74]

Table 2 (continued)

the concentrations of diclofenac and ibuprofen in aqueous media. A similar variability has been found between the pharmaceutical and pesticide photodegradation processes, highlighting the use of solar radiation and the increase of the quantum efficiency of metal oxide-based catalysts.

Even with several studies about photocatalytic degradation for water and wastewater treatment containing emergent pollutants, some difficulties are still found which need to be overcome. Some problems that are being studied to improve the emerging pollutant photocatalytic efficiencies in aqueous solutions include the impossibility of using visible radiation from the solar emission spectrum [30, 50], the aqueous solution matrix effect on the involved photodegradation mechanisms [39] and catalyst types. Studies have shown that the use of catalyst nanoparticles increases the photocatalytic efficiency. However, nanoparticles are difficult to remove from aqueous solutions and increase the cost/benefit of a purification process [12, 31]. In this sense, catalyst incorporation techniques in solid rigid supports are interesting strategies to overcome the separation problems of the catalyst nanoparticles from aqueous solutions. It can enable the scale-up of a photodegradation technology from laboratory plant to full-scale plant.

4 Photocatalysts Supported on Solid Materials

The use of metal oxide nanoparticles as catalysts in photodegradation processes is advantageous as they have higher active surface areas for interaction with pollutants. However, the recovery of these nanoparticles at the end of the photocatalytic process is ineffective [53]. One of the alternatives to facilitate the recovery of photocatalysts is using incorporation processes in solid rigid supports. Photocatalysts incorporated in solid rigid supports are effective due to higher activity in wider pH ranges, higher catalyst stability, higher surface area, and easy of incorporated catalyst separation at the end of the photocatalytic process [11]. Metal oxides have been incorporated in graphene-based, polymer-based, zeolite-based materials to improve the performance of advanced oxidation processes [69]. The potentials of conduction and

valence bands of photocatalysts are affected by aqueous solution pH values. These effects decrease when using photocatalysts supported in solid matrices. Hence, active photocatalysts incorporated in porous solid rigid supports have proved to be efficient reagents for photocatalytic processes in the water and wastewater treatment at wider pH ranges [11]. It enables the water and wastewater treatment containing emerging pollutants without adjusting the original solution pH. This is important as some types of emerging pollutants are contained in either acid or alkaline solutions, not being necessary the previous pH adjustment before starting the photodegradation process [6].

The physiochemical properties of the most of solid rigid supports are important for incorporation processes of photocatalysts [6]. For example, the catalytic activity of iron oxide II (FeO) increases when this catalyst is supported on clinoptilolite nanoparticles due to the increase of the active site amounts generating free radicals [3]. The incorporation of either FeO or even other catalyst in semiconductor-based materials has indicated significant improvements of photocatalytic efficiency, variation of the recombination rate between electrons and holes, and changes in the band gap energy [3, 34]. Graphene-based hydrogel nanocomposites are excellent alternatives for the incorporation of palladium due to high reduction capacity of nitroarene in aqueous solutions by photodegradation. In this case, the photodegradation efficiency was higher than 99%, with the advantage of being possible the photocatalyst reutilization in different photocatalytic processes [15]. These types of nanocomposites could be potential alternatives for the incorporation of other catalysts for the photodegradation of emerging pollutants.

Polymeric nanocomposite structures can affect the efficiency of photocatalysts after the incorporation process [27]. Thus, further researches are still needed to comprehend the interaction between solid support and photocatalyst during water and wastewater treatment involving advanced oxidation processes. Studies have highlighted that functional groups such as phosphorus, sulphur and nitrogen present in polymer matrices containing immobilized catalyst affect the heterogeneous catalysis [14]. Overall, catalysts incorporated in either inorganic or organic polymeric composite materials decrease costs of heterogeneous photocatalytic processes as it is possible to recovery the photocatalyst particles for successive studies of emerging pollutant removal contained in aqueous solutions.

Semiconductor oxides doped with known amounts of either transition metals or non-metal species are also potential alternatives for photodegradation studies of emerging pollutants [54]. These types of composites can form electron capture centres, increasing the photocatalytic efficiency and enabling their use for the emerging pollutant removal from aqueous solutions using advanced oxidation processes with application of solar light irradiation. These composites could also be easily incorporated in porous solid rigid supports. However, oxide/polymer structures affect the photocatalytic activity over the supported catalyst. Photocatalysts incorporated in composite membranes have shown excellent results in the aqueous solution purification [35]. Finally, integrated reactors have emerged as an efficient possibility in the purification of water and wastewater containing emerging pollutants. In this system takes place a membrane-filtration process followed by photocatalytic reactions with lower costs for the aqueous solution purification. Filtration membranes containing incorporated photocatalytics are advantageous due to their anti-fouling properties [66].

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