Chapter XX

Hydrotalcite-like compounds and related materials as catalysts for the photodegradation of pharmaceutical compounds: Synthesis and catalytic performances

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Abstract

The presence of pharmaceutical compounds in natural water is an increasing problem as these compounds have environmental effects even at low concentrations. Adsorption has been largely used for the removal of pollutants, in the last years advanced oxidation processes (AOPs) have gained attention, as they may lead to the complete degradation of the pollutants. Several solids have been used as photocatalysts, from TiO₂, by far the most used, to some families of other materials. In the present chapter, a review on the use of hydrotalcite-like compounds, also known as Layered Double Hydroxides (LDHs), as catalysts for the photodegradation of pharmaceutical pollutants is presented.

Keywords: Hydrotalcites, Layered Double Hydroxides, Catalytic Photodegradation, Emerging Water Pollutants, Pharmaceutical Pollutants, Advanced Oxidation Processes.

1 INTRODUCTION

At present, large amounts of pharmaceutical compounds are used in several areas, as medicine, industry and cosmetics (Michael et al., 2013). This large intake may cause an increase in the presence of these compounds in natural environments, due to their discharge in untreated wastes or partially treated wastewater. This can hardly be avoided; for example, some medicines are excreted unmetabolized by living organisms in percentages that can reach even the 90% of the ingested dose. Obviously, this may lead to the contamination of surface or underground waters (Bethi et al., 2016).

Water is one of the more abundant compounds in Nature, covering about three quarters of Earth surface. However, several factors limit its availability for human intake. Human activities strongly affect the quality of water, mainly by the discarding of pollutants, which can provoke very negative effects on vegetal and animal species in the ecosystems, and on humankind itself (Qadir et al., 2010). In the last years, new contaminants have been detected in the environment, being denoted as Emerging Organic Pollutants (EOPs), listed by NORMAN Network (NORMAN, 2019), and defined as synthetic or naturally occurring chemicals that are not commonly monitored in the environment, but which have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects. More than 700 EOPs pollutants, and their metabolites and transformation products, have been reported in European aquatic environments, among them are pharmaceutical products, drugs, pesticides, personal care products and industrial additives, and some of them can also be considered as anthropogenic markers for wastewater contamination (Geissen et al., 2015). In the case of medicines, particularly antibiotics, their increasing propagation in the environment is causing the development of strongly resistant bacteria, which is an additional and very important health problem (Marti et al., 2014). It is expected that in

the next years the main cause of death, surpassing those produced by cancer, will be the presence of bacteria multiresistant to several families of antibiotic molecules. This situation has been generated by the abuse of antibiotics in human medicine and environmental pollution derived from agricultural and livestock production.

Thus, the removal of these pollutants becomes mandatory. Several procedures have been proposed and are being used for such removal, as solvent extraction, reverse osmosis, or adsorption (Park et al., 2009; Williams et al., 1999). Adsorption using materials from various porous families is probably the most popular method, as these materials have low cost, their use is simple and versatile, and they adsorb several types of pollutants (Khenniche and Aissani, 2010). The adsorption process is mainly controlled by the pH of the aqueous solution, the ionic characteristics of the adsorbent and the pollutants, as well as by the ionic strength of the medium. However, this process is based on the change of the pollutants from one phase (water) to the other (adsorbent), but does not destroy them.

In this context, Advanced Oxidation Processes (AOPs) constitute a group of techniques very attractive for the elimination of these pollutants. They cover chemical, photochemical, sonochemical, and electrochemical procedures, including Fenton, ozonation, plasma, photocatalysis, and wet air oxidation reactions, among others, and almost all the processes are based in the production of $\bullet\text{OH}$ radicals (sulfate and chlorine radicals can also be used). Other common characteristics are the operation at ambient temperature and pressure conditions (or very close to them) and that they attack all the organic compounds, that is, as they are based on the generation of strong radicals, they are not selective to the pollutants. Under optimal conditions, the process may lead to the complete mineralization of the pollutants (Miklos et al., 2018).

Several materials have been used for assisting heterogeneous photocatalytic processes. Titanium dioxide, TiO_2 under anatase structure, is the most used, functional, versatile and effective photocatalyst, based on its excellent photoelectric properties, low cost, corrosion resistance and non-toxicity for living organisms (Papoulis et al., 2013). However, TiO_2 has an important limitation, its energy band gap is 3.2 eV, and this limits its efficiency to the ultraviolet wavelength of 387.5 nm, only 3 - 5% of the solar radiation that reaches the Earth surface (Deng et al., 2016). This can be partially solved by dispersing TiO_2 on inorganic matrices, or by modifying it with several dopants as noble metals, transition metal or non-metals, etc., which can decrease the energy required for its activation.

A different strategy is to substitute TiO_2 by other catalyst. For example, clay minerals have received large attention (Garrido-Ramírez et al., 2010; Praneeth and Paria, 2017; Ramírez et al., 2010). However, hydrotalcites have received very little consideration, although these solids, also called Layered Double Hydroxides, are structurally related to clays and exist with a great variety of composition. The use of these solids for photocatalytic removal of organic compounds has been recently reviewed (Mohapatra and Parida, 2016), but their use for the degradation of pharmaceutical pollutants has been scarcely reported. In this context, the application of this family of solids for catalytic photodegradation of pharmaceutical pollutants is reviewed in this chapter. Before, the structure and methods of preparation of these materials are briefly presented.

2 STRUCTURE OF HYDROTALCITES

The hydrotalcite-like materials, or simply hydrotalcites, are a group of solids whose structure and composition are related to the mineral Hydrotalcite,

$\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4(\text{H}_2\text{O})$. These solids have a lamellar structure, with a form similar to that of brucite, $\text{Mg}(\text{OH})_2$. As they are hydroxides of two cations, they are also called Layered Double Hydroxides, and abbreviated LDHs.

As indicated, the structure and chemical composition of hydrotalcites can be considered derived from brucite. Brucite is formed by a hexagonal compact packing of hydroxyl anions, with Mg^{2+} cations occupying all the octahedral holes each two layers, thus generating a layered structure. Mg^{2+} can be substituted by trivalent cations, and each time that this substitution occurs, a positive charge is generated, that must be balanced by the incorporation of compensating anions in the interlayer region. Thus, the layers are positively charged, and compensating anions are located in the interlayer region, just the opposite than in clays, reason why hydrotalcites are also known as Anionic Clays, and can be seen as a *mirror* of clays. In the case of Hydrotalcite, one fourth of Mg^{2+} cations are substituted by Al^{3+} , that is, two of eight in the formula given before, and consequently two positive charges are generated, compensated by the incorporation of a carbonate anion. So, the hydroxyl anions in the formula are *structural*, that is, they form the octahedra of the structure, while carbonate anions are charge-balancing, and located in the interlayer. Besides, a certain amount of water also incorporates to the interlayer region, this amount depending on the ambient conditions (Mishra et al., 2018; Nalawade et al., 2009; Rives, 2001; Rives and Ulibarri, 1999; Rives et al., 2013). The resultant structure is that shown in Figure 1.

Figure 1. Structure of hydrotalcites.

It is remarkable that hydrotalcite layers can stack on different ways, giving up to different polytypes (rhombohedral and hexagonal). More interesting for the application

of these solids is the large variety of chemical composition that they can show. Thus, a large amount of divalent and trivalent cations can occupy the positions that in the parent compound are occupied by Mg^{2+} and Al^{3+} , respectively. Strictly, *Hydrotalcite* is the mineral above referenced, and *hydrotalcites* are the solids derived from it, considering the changes in composition we are commenting on now. Almost all the cations, both divalent and trivalent, with size similar to Mg^{2+} can occupy the octahedral holes maintaining the hydrotalcite structure, and hydrotalcites containing a large variety of cations have been prepared in the laboratory: Divalent: Ca, Mn, Co, Ni, Cu, Zn, Pd, Pt; Trivalent: Ga, In, Y, V, Cr, Mn, Fe, Co, Rh, Ir, Ru, lanthanides, among others. The structure is maintained if two or more divalent cations, and/or two or more trivalent cations enter the composition. Even more, when monovalent or tetravalent cations that can isomorphically occupy the octahedral positions, as Li^+ or Zr^{4+} , are incorporated into the composition, the structure is also maintained (Mishra et al., 2018; Nalawade et al., 2009; Rives, 2001; Rives and Ulibarri, 1999; Rives et al., 2013).

Besides of the size of the cations, other limiting structural factor is the degree of substitution, that is, beginning from an ideal brucite structure the amount of trivalent cations that can substitute the divalent ones. The molar fraction of the trivalent cation must be ranged between 0.20 and 0.33; in other words, the ratio $\text{M(II)}/\text{M(III)}$ must range between 2-4. Theoretical calculations have found that the maximum stability is found when the degree of substitution is 0.25 ($\text{M(II)}/\text{M(III)} = 3.0$), that is exactly the value present in the natural hydrotalcite. If the substitution degree is higher than 0.33, charged $[\text{Al}(\text{OH})_6]$ octahedral must be neighbor among them, creating a repulsion that destabilizes the structure, while for a substitution degree lower than 0.25 the amount of compensating anions is very low and the distance among them is very large, also destabilizing the

structure (Mishra et al., 2018; Nalawade et al., 2009; Rives, 2001; Rives and Ulibarri, 1999; Rives et al., 2013).

As indicated before, the degree of substitution directly determines the charge of the layers, so it conditions the amount of compensating anions. This allows to define the *anion exchange capacity*, *AEC* as the amount of anions that can be exchanged by a determined amount of hydrotalcite, by analogy with the well-known *cation exchange capacity*, *CEC*, of clays. In the natural hydrotalcite the compensating anion is carbonate, and due to its divalent charge, its amount is logically half of the substitution degree. When the hydrotalcites are prepared in the laboratory, other compensating anions can be incorporated to the structure, as nitrate, halides, borates, hydroxyl (i.e., hydroxyls as compensating cations, besides of structural hydroxyls, the resultant hydrotalcite being known as meixnerite variety), phosphate, arsenate, sulfate, sulfonates, carboxylates (lactate, terephthalate, acrylate, etc.), but also coordination compounds and polyoxometalates (polyvanadates, polymolibdates, polywolframates, etc.). In these last cases, a new metal is incorporated to the structure, besides of those composing the layers.

With all these considerations, the general formula of the hydrotalcite family can be expressed as $[M^{II}_{1-x} M^{III}_x (OH)_2]^{x+} (A^{n-})_{x/n} \cdot mH_2O$, where x is the degree of substitution of the divalent M^{II} cations by the trivalent M^{III} cations and consequently the charge of the layer, n is the charge of the anion A , and m is the degree of hydration (Mishra et al., 2018; Nalawade et al., 2009; Rives, 2001; Rives and Ulibarri, 1999; Rives et al., 2013).

When calcined, hydrotalcites tend to transform into oxides. As hydrotalcites are composed of divalent and trivalent cations, the calcination tends to form the spinels $M^{II}M^{III}_2O_4$, with an excess of the divalent oxide, as the ratio $M(II)/M(III)$ in the hydrotalcites is higher than in the spinels. The degree of substitution allows to tailor the amount of spinel in the final oxide mixture and if the compensating anions are

coordination compounds or polyoxometalates, other metals are incorporated to the final mixtures of oxides, this strongly influencing their catalytic performance.

3 PREPARATION OF HYDROTALCITES

The preparation of hydrotalcites is a relatively simple laboratory procedure, as the thermodynamic tendency to form these compounds is high when the adequate amount of cations and anions are present. Thus, the following preparation procedures can be listed (Rives, 2001).

Coprecipitation: it is the simplest procedure. In summary, it consists in the preparation of aqueous solutions of the desired metal cations in the desired ratios, their mixture, and the increase of the pH up to the precipitation of the hydrotalcite. Usually, the pH is increased by adding NaOH, Na₂CO₃ and/or NaHCO₃ solutions (or the metallic solutions are added over the alkaline solution). If not special precautions are taken, the interlayer anions should be carbonate, even if nor carbonate neither bicarbonate are used for the increase of pH; the reacting mixture, due to its strong alkaline pH, reacts with atmospheric CO₂ and the formed carbonate has a strong tendency to enter into the interlayer. With special precautions and selecting adequately the metallic salts used at the beginning of the process, nitrates, chlorides, etc., these anions can be incorporated into the interlayer.

This method has small modifications, which try to avoid the abrupt precipitation of the solid. The use of automatic titrators allows to modify the pH very slowly and to fix it very precisely to a predetermined value. Other possibility, widely used in the preparation of other families of solids, is to carry out the synthesis assisted by the hydrolysis of urea. A certain amount of urea is added to the mixture, and this is slowly heated, provoking the hydrolysis of the urea, what leads to the formation of ammonium carbonate, thus

increasing the pH. Therefore, the increase of the pH can be controlled by the intensity of the heating, with the advantage that the hydrolysis of urea is homogeneous in all the solution, and thus the precipitation leads to more uniform and smaller particles.

Figure 2. Laboratory procedure for the preparation of hydrotalcites by the coprecipitation method.

Anion Exchange: this method allows to obtain a hydrotalcite with a certain interlayer anion from the solid containing other anion. The parent solid is put into a highly concentrated solution of the second anion, and the exchange proceeds. Carbonate-hydrotalcite cannot be used as precursor, since the high affinity of this anion to the hydrotalcite interlayer avoids its exchange with other anions. The method is applicable for the intercalation of polyoxometallates and other large anions, and also if the desired anion is not stable in the initial alkaline conditions needed for the precipitation of the hydrotalcite.

Reconstruction: as indicated before, hydrotalcites are usually calcined to obtain mixtures of oxides. If this calcination is carried out at moderate temperatures, usually $\leq 500\text{ }^{\circ}\text{C}$, the solids obtained show *memory effect*, i.e., the solids are able to recover the hydrotalcite structure if they are dispersed in an anionic solution. Thus, a *normal* hydrotalcite is obtained, usually containing carbonate and prepared by coprecipitation, and calcined. The calcined solid is then dispersed in a solution containing the final desired anion and the hydrotalcite structure is now reconstructed with this desired anion in the interlayer. As in the previous method, this method is especially indicated for the preparation of hydrotalcites containing polyoxometallates and other large anions, or if the desired anions are not stable under the conditions for coprecipitation synthesis.

In some cases, the hydrotalcite synthesis is assisted by hydrothermal conditions, in recent years microwave treatments being frequent, allowing improvement in the crystallinity and homogeneity of the solids.

4. HYDROTALCITES IN THE PHOTODEGRADATION OF PHARMACEUTICALS

As indicated before, although the use of hydrotalcites as photocatalysts has been recently reviewed (Mohapatra and Parida, 2016), the use of these materials for the degradation of pharmaceutical pollutants has not been revised. A summary of the main conditions and results is included in Table 1.

The catalytic photodegradation of salicylic acid sodium under visible-light irradiation has been studied by Zhao et al. (2011). Other pollutants, although not pharmaceutical compounds, were also photodegraded, namely sulforhodamine-B, Congo Red and chlorinated phenol. The catalysts were a series of MCr hydrotalcites ($M = \text{Cu, Ni, Zn}$), prepared by mixing a solution containing the metallic nitrates with a NaOH solution, and submitting the mixture to a colloid mill rotating at 3000 rpm for a short time, followed by a separate aging process at 100 °C. Nitrate-containing hydrotalcites were thus obtained, the corresponding carbonate-counterparts being obtained by anion exchange. These catalysts exhibited 20-times higher photocatalytic performance than Degussa P25, attributable to their low band gap (1.6 eV) and their abundant surface OH groups. The authors claimed that the high dispersion of CrO_6 octahedra in the LDH layer played a key role in responding to visible light and photogenerating charge carriers. The LDH matrix provided an ordered dispersion of the CrO_6 octahedron in the layer; which promoted the efficiency of the excited electron and avoided the recombination of electron and hole. The solids showed high recyclable stability for three cycles.

Jacome-Acatitla et al. (2014) prepared MgAl hydrotalcites, with Mg/Al ratios of 2.0, 2.5 and 3.0 by the coprecipitation method ($\text{K}_2\text{CO}_3/\text{KOH}$, $\text{pH} = 9$). The resulting hydrotalcites were calcined at $450\text{ }^\circ\text{C}$. The calcined solids were employed for the catalytic photodegradation of sodium naproxen and oxytetracycline hydrochloride, under 254 nm UV irradiation. About 90% of sodium naproxen and 70% of oxytetracycline hydrochloride were mineralized by the best catalyst ($\text{Mg/Al} = 2.5$) after 5 h of reaction, better behavior than that of commercial Degussa P25 TiO_2 . Fluorescence spectroscopy study suggested the generation of hydroxyl radicals as the oxidative species, and band gap energies were 3.054 – 3.083 eV.

Catalysts based on Zn-Al-Ce were prepared by calcination of Ce-doped Zn-Al hydrotalcite precursors and used in the photodegradation of paracetamol and rhodamine B dye in aqueous solutions under simulated solar light irradiation (Zhu et al., 2016). The results showed an increase of the catalytic photoactivity due to the presence of Ce. The optimal Ce content was studied and found to be of 5% mole ratio ($n_{\text{Ce}}/n_{(\text{Zn}+\text{Al}+\text{Ce})}$), which could be attributed to the increase in the separation efficiency of electrons and holes. The most effective calcination temperature was also examined and found to be $750\text{ }^\circ\text{C}$, which was attributed to the formation of well-crystallized metal oxides. After 240 min, a 98.9% of paracetamol degradation efficiency was achieved (97.8% for rhodamine B) and the authors suggested the importance of holes, superoxide radicals and hydroxyl radicals roles during the photocatalytic process. These catalysts were also proven to be stable and reusable up to 10 cycles.

Di et al. (2017) prepared Zn-Fe carbonate hydrotalcite by coprecipitation, and calcined it at several temperatures, using the resultant solids for the degradation of ibuprofen. The solid with Zn/Fe ratio of 4 and calcined at $300\text{ }^\circ\text{C}$ exhibited the best efficiency in the degradation of the pharmaceutical (the amount degraded was not given,

although from the plot seems to be c.a. 95%, the rate constant was 1.584×10^{-2} 1/min). The solids were also used for the adsorption removal of As(III) (arsenite), obtaining a maximum adsorption capacity of 176.3 mg/g, and for the simultaneous removal of ibuprofen and arsenite, finding that the presence of ibuprofen did not affect the adsorption of arsenite but, in contrast, the presence of arsenic strongly influenced the degradation of ibuprofen, depending on the arsenic species and concentrations. The authors indicated that photogenerated h^+ played a major role in the process of ibuprofen degradation, while arsenic was removed by combined oxidation and adsorption. The reusability was also studied for six runs, with excellent behavior. The authors claimed that the process was effective using other pharmaceuticals, namely acetaminophen and diclofenac, but no data on their degradation were given.

The degradation of caffeine using the solids derived from Zn-Al carbonate hydrotalcites has been studied by Elhalil et al. (2017). Various Zn/Al molar ratios were considered, namely 1, 3 and 5, and the resulting hydrotalcites were calcined at 300, 400, 500, 600, 800 and 1000 °C for 6 h. As this calcination led to ZnO-ZnAl₂O₄ mixture, a pure ZnO sample was also prepared, and Degussa P-25 TiO₂ was also used as reference. The best caffeine removal efficiency (97.32%) was shown by the sample with Zn/Al = 3 calcined at 500 °C, and caffeine photodegradation reaction always followed a pseudo first-order kinetics. The catalytic efficiency of the solids derived from the hydrotalcites, composed of mixtures ZnO-ZnAl₂O₄, strongly depended on the calcination temperature, attributed to the progressive formation of the active phase ZnO. These solids showed better behavior than pure ZnO and also than standard Degussa P25. The authors proposed that the crystallinity and good dispersion of ZnO on the surface of the solids were important factors in the catalytic performance.

The same authors (Elhalil et al., 2019) have used as photocatalysts composites Ag-ZnO-La₂O₂CO₃ derived from hydrotalcites. The hydrotalcites were formed by the coprecipitation method, considering the ratios Zn/(Al+La) of 3 and La/Al of 0, 0.25 and 0.5. The pH was increased with Na₂CO₃/NaOH up to 8.5 when only Zn and Al formed the hydrotalcite and to 10 for the two samples containing La. The resulting hydrotalcites were calcined at 300, 400, 500, 600, 800 and 1000 °C. The dried solids were composed of LDH and LaCO₃OH phases, while ZnO, ZnAl₂O₄, La₂O₂CO₃ and LaAlO₃ were observed, in function of the temperature, in the calcined samples. Ag was deposited by a solvent-free ceramic process, grinding AgNO₃ and LDH in an agate mortar, and then calcining them in air at 500 °C for 6 h; 1, 3 and 5% Ag contents were considered. The solids were applied in the degradation of caffeine under an UV mercury lamp. The Ag-containing solids were much more active than undoped composites, and also than reference ZnO and Degussa P-25 TiO₂. The best degradation result, 99.4% after 40 min of irradiation, was shown by the solids with La/Al= 0.25 and 5% Ag. The optimal catalyst dosage for the degradation of a 20 mg/L of caffeine solution was 0.3 g/L. The catalytic activity was mainly attributed to the interfacial heterostructure in the Ag-ZnO-Al₂O₃ surface, and was observed to depend on the pH, 9.5 being the optimal value. The reusability was evaluated for the best catalyst, being excellent as it showed a degradation of 92.98% in the third cycle.

Yang et al. (2017) prepared a Zn/Fe hydrotalcite by the co-precipitation method, with molar ratio of Zn/Fe = 2.0. The anions should be nitrate and carbonate, as the nitrates were used as source of the cations, and the pH was increased with NaOH, but no special precautions to avoid the carbonate incorporation were reported. The hydrotalcite was calcined at 550 and 750 °C to form the photocatalysts, denoted as Zn/Fe mixed metal oxide (Zn/Fe-MMO) nanocomposites by the authors, which were used for the degradation

of the antibiotic tetracycline, and also of the dye methylene blue, under visible light irradiation. The catalysts were composed of wurtzite-ZnO and spinel-ZnFe₂O₄ phases. The hydrotalcite, not calcined, was also tested as catalyst, showing lower activity than the calcined composites. The degradation reached 90% after 60 minutes for the solid calcined at 700 °C, following pseudo-first order kinetics. The improved catalytic performance of this solid was attributed to the visible-light adsorption and more production of photogenerated electron-hole pairs. Based on the trapping radical tests and ESR analysis, the authors suggested that the photodegradation occurred with the generation of active radicals ($\bullet\text{O}_2^-$ and $\bullet\text{OH}$).

The preparation of ZnAl-chloride hydrotalcite (Zn/Al = 2) and its interaction with the antibiotics tetracycline and oxytetracycline was considered by Bouaziz et al. (2018). In this case, nor the hydrotalcite neither the oxides derived from its calcination were used for the degradation of the antibiotics, but the interaction between them was studied in a different way. First, the antibiotic were intercalated into the interlayer of the hydrotalcite, and two methods were considered, the anionic exchange of the chloride anions of a previously prepared sample of the hydrotalcite by the antibiotics or the preparation of the hydrotalcite in the presence of the antibiotics, that is, having the antibiotics in the solution of the cations before increasing the pH for the coprecipitation process. Unfortunately, intercalation was not successful, and the antibiotics were located on the external surface of the hydrotalcite. The antibiotics were released after 10 hours. The antibacterial activity of the solids was tested against *Escherichia coli* and *Staphylococcus epidermidis*, finding lower activity than for the free antibiotics. It is proposed that the antibiotics partially degraded in contact with the hydrotalcite. The degradation was confirmed under exposure of the solids to UV radiation or under storage at increasing temperatures (30, 60 and 120 °C).

Zhu et al. (2018) prepared ZnFe carbonate hydrotalcite ($\text{Zn/Fe} = 3$) by the urea assisted coprecipitation. Composites graphene oxide/hydrotalcite was prepared by carrying out the hydrotalcite synthesis under the same conditions but in the presence of various amounts of graphene oxide, previously submitted to sonication for its delamination. The process was completed by hydrothermal treatment for 24 h at 120 °C, centrifugation, drying and calcination at 450 °C under nitrogen atmosphere. The structure of well-crystallized hydrotalcite was observed in all the X-ray diffractograms. The calcined samples showed the presence of ZnO and ZnFe_2O_4 . These composites were used toward the degradation of paracetamol under simulated solar light irradiation and exhibited a 3.5 times improved catalytic performance as compared to pristine ZnFe hydrotalcite sample. This behavior was attributed to the graphene oxide, which may increase pollutant adsorption capacity and enhance charge separation efficiency. These composites were also applied to the catalytic photooxidation of As(III) to As(V). Interestingly, paracetamol degradation was more efficient in the mixed system paracetamol/As(III) than in the single paracetamol system, while arsenic was also efficiently removed. The catalysts showed excellent reuse properties, showing a slight decrease of performance, 8.1%, after five successive experimental runs, with the advantage that can be easily separated and recovered by an external magnet.

5 CONCLUSIONS AND PERSPECTIVES

The presence of pharmaceutical compounds in natural water is an increasing problem as these compounds have environmental effects even at low concentrations. Hydrotalcite-like compounds, also known as Layered Double Hydroxides (LDHs), although have been used as catalysts for the removal of some organic pollutants, have been very scarcely used for the photodegradation of pharmaceutical pollutants. The high versatility of these

compounds in chemical composition, the easiness of their synthesis and their good properties may strongly increase their use as photocatalysts in the next years.

ACKNOWLEDGMENTS

The authors gratefully acknowledge funding from the Spanish Ministry of Economy, Industry and Competitiveness (AEI/MINECO), and the European Regional Development Fund (ERDF) through project MAT2016-78863-C2-R. LS thanks Universidad Pública de Navarra for a pre-doctoral grant. AG also thanks Santander Bank for funding through the Research Intensification Program.

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Table 1. Applications and use conditions of hydrotalcite-like materials as catalysts for the photodegradation of pharmaceutical compounds.

Composition of the hydrotalcite	Preparation method	Calcination temperature	Pharmaceutical pollutant	Radiation	Reference
Cu-Ni-Zn-Cr nitrate and carbonate	Mixture, colloid mill and aging (nitrate solids) Anion exchange (carbonate solids)	NO (drying at 60 °C)	Salicylic acid	Visible	Zhao et al., 2011
Mg-Al carbonate	Co-precipitation	450 °C	Sodium naproxen, Oxytetracycline hydrochloride	UV	Jacome-Acatitla et al., 2014
Ce-Zn-Al carbonate	Co-precipitation	450, 600, 750, 900 °C	Paracetamol	Solar simulated	Zhu et al., 2016
Zn-Al carbonate	Co-precipitation	200, 300, 400, 500 °C	Ibuprofen	Solar simulated	Di et al., 2017
Zn-Fe carbonate	Co-precipitation	300, 400, 500, 600, 800, 1000 °C	Caffeine	UV	Elhalil et al., 2017
Zn-Fe	Co-precipitation	550, 700 °C	Tetracycline	Visible	Yang et al., 2017
Zn-Al chloride	Co-precipitation and anionic exchange	NO (drying at room temperature)	Tetracycline, Oxytetracycline	UV	Bouaziz et al., 2018
Zn-Fe*	Hydrothermal	450 °C	Paracetamol	Solar simulated	Zhu et al., 2018
Zn-Al-La carbonate**	Co-precipitation	300, 400, 500, 600, 800, 1000 °C	Caffeine	UV	Elhalil et al., 2019

* Forming composites with graphene oxide. ** Forming composites with Ag.

Figure 1. Structure of hydrotalcites.

Figure 2. Laboratory procedure for the preparation of hydrotalcites by the coprecipitation method.