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Humic-Like Substances as Auxiliaries to Enhance Advanced Oxidation Processes

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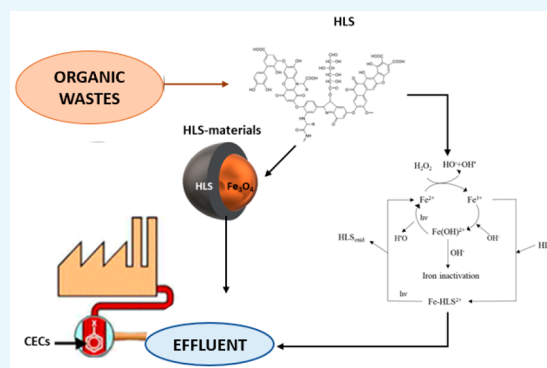
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ABSTRACT: The application of humic-like substances (HLSs) in advanced oxidation processes for wastewater treatment is summarized in this work. HLSs share important characteristics with humic substances, and they can be isolated from different wastes using procedures that are related with their pH-dependent solubility. They are able to generate, upon irradiation, reactive species such as hydroxyl radicals and singlet oxygen or triplet excited states. Although photochemical removal of pollutants can be reached by HLSs, in general, irradiation times are very long. HLSs are good metal-complexing agents, and the Fe–HLS complex is able to participate in (photo)-Fenton-like processes at mild pH, preventing iron deactivation. Finally, novel hybrid materials with environmental applications have been synthesized using HLSs; in some cases, they also contain iron oxides, which allow a better separation but also the ability to drive heterogeneous (photo)-Fenton processes.



INTRODUCTION

The increasing demands for water in our society make the treatment and reuse of polluted effluents increasingly necessary. Hence, alternatives to traditional wastewater treatment technologies have been developed in the last decades: new processes have been proposed; other ones have been modified to make them more efficient or sustainable; and new materials with relevant environmental applications have been synthesized and characterized.

Humic substances (HSs) are receiving increasing attention. These are ubiquitous macromolecules that are formed by decomposition of debris from living organisms and are reported to be among the most abundant fractions of natural organic matter (NOM).¹ HSs can be classified in three groups: (1) fulvic acids, with lower molecular weight and solubility in the whole pH range, (2) humic acids, with intermediate molecular weights and solubility in alkaline conditions, and (3) humines with the highest molecular weight and insolubility in water.² HSs have been commonly associated with problems for wastewater treatment. Phenomena such as fouling of membranes or filters or generation of undesirable byproducts in chemical oxidative processes can be attributed to their presence in water, and hence most efforts are focused on developing efficient methods to remove NOM and, in particular, HSs.³ On the other hand, HSs have been demonstrated to play a key role in the self-remediation of aqueous ecosystems, in most cases based on their ability to generate reactive oxygenated species upon irradiation.^{1,4} As a matter of fact, the role of HSs in the fate of different families of

pollutants is receiving increasing attention, and gaining further insight into these processes is now a hot topic in environmental chemistry.⁵

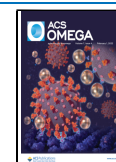
There is very little information on the use of natural HSs in photochemical processes for wastewater treatment, despite that they are commercially available for uses such as agriculture. However, substances sharing important chemical and physical characteristics can be isolated from different types of wastes. They have received different names, although they all can be labeled as humic-like substances (HLSs). The isolation of these molecules from wastes constitutes an important step forward toward the implementation of a circular economic strategy, more specifically when they are used for environmental purposes.⁶

Although several uses have been proposed for HLSs, mainly related with agronomy, the aim of this work is to summarize the most important findings on the application of these substances in wastewater remediation processes, which can be divided in two big groups: (a) as photocatalysts or as auxiliaries to drive (photo)-Fenton processes and (b) as starting products for the synthesis of materials. Finally, other

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environmental uses such as adsorbents or for soil remediation are beyond the scope of this work.

■ SYNTHESIS, CHARACTERIZATION, AND PHOTOCHEMICAL PROPERTIES OF HLSS

The usual procedure for the isolation of humic acids (HAs) is based on the pH-dependent solubility of those substances, which can be dissolved at basic pH but are scarcely soluble at acidic pH. Hence, alkaline digestion to extract the HA from the solid samples (e.g., soils), followed by precipitation by acidification, are commonly the key steps of the process.⁷ This general scheme has been used to isolate HLSs from different sourcing materials such as organic fractions of biowastes submitted to composting,⁸ mixtures of different biomasses,⁹ sewage sludge,¹⁰ or olive mill wastes.¹¹ In order to avoid the final acidification to precipitate the HLS, the isolation of the HLS can be done by ultrafiltration using ceramic membranes, where the HLS is the retentate that is then dried.¹¹ As high amounts of salts are formed in the isolation process, dialysis can be employed to obtain a final product free of these inorganic impurities.^{8,9}

As HLSs are actually a type of dissolved organic matter, methods for characterization of NOM are employed, mostly focused on determining the molecular size, structural characteristics, physical properties, as well as chemical composition and behavior. In particular, spectroscopic methods provide very interesting information on the nature of NOM and their photochemical properties. In this context, excitation emission matrices (EEMs) consist of a bidimensional plot of fluorescence emission of NOM (λ_{em}) when excited at different wavelengths (λ_{exc}); examples of EEM can be found in Figure 1. EEMs provide very useful information on

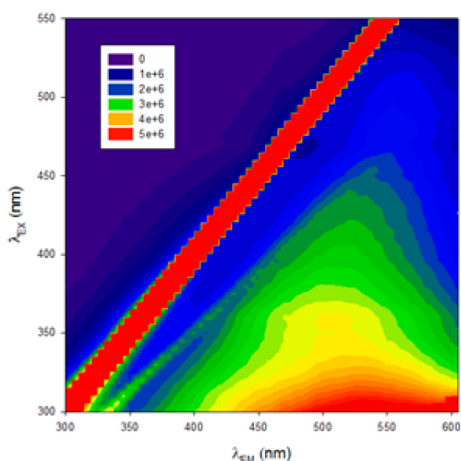


Figure 1. Typical EEMs of a HLS, in this case isolated from olive mill wastes.

the fluorophores present in the sample; in particular, some regions of the EEM can be attributed to the presence of humic or fulvic components, as well as proteins.¹² In general, HSs show absorption bands in the 300–500 nm region of the spectrum, emitting fluorescence at 400–600 nm. However, in order to obtain more accurate data, mathematical treatment of data has to be employed, parallel factor modeling (PARAFAC) being the most widely used.¹³ On the other hand, ¹³C NMR combined with potentiometric titration has been used to investigate the relative amount of functional groups in HLSs.¹⁴

On the hand, thermogravimetry coupled with Fourier transformation infrared spectrometry and mass spectrometry (TG-FTIR-MS) is an effective method for HS characterization since it not only gives information on the mass-loss characteristics and kinetics parameters of the thermal decomposition but also identifies the volatile components generated in real time.¹⁵

The photophysical properties of HSs have gained attention from many research groups, and key aspects are well-known, although some others still remain to be completely elucidated. In brief, HSs can absorb light in the UV–vis region ($\lambda < 500$ nm), generating singlet excited states ($^1SH^*$) that, in turn, can undergo via intersystem crossing (ISC) triplet excited states ($^3SH^*$). While $^1SH^*$, because of its short lifetime (typically ns), is not expected to interact with pollutants, $^3SH^*$ shows longer lifetimes (in the range of μs), and they can react with oxygen (to form singlet oxygen) and/or with other dissolved substances to form different reactive species, able to induce transformation of organic compounds.¹⁶ The main reactions are summarized in Figure 2.

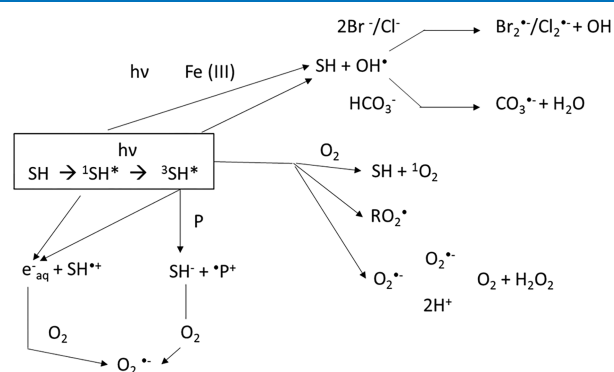


Figure 2. Summary of the key pathways for the photochemical generation of reactive species in aqueous solution mediated by HS. Adapted with permission from Richard and Canonica.¹⁶

In addition, HS and HLS contain in their structure carboxylic and phenolic acids, quinones, or amine groups, which can either participate in ion exchange processes or are good complexing agents,¹⁸ which results in new pathways to generate reactive species, such as a Fenton or photo-Fenton process.^{17,18}

On the other hand, HSs are colored macromolecules that exhibit significant absorbance in the UV–vis (at wavelengths below 450–500 nm). This can produce an inner filter effect, preventing photons from reaching the total volume of solution to treat, thus diminishing the process efficiency.¹⁹ In addition, because of the organic nature of HSs, they compete with pollutants for reactive species.²⁰ Besides, recent studies have demonstrated that the quenching rate constant of dissolved organic matter increases with the phenolic content since phenols can act as antioxidant-reducing produced radical cations, thus reforming the parent compound.²¹ Finally, HSs have been demonstrated to enhance the photodegradation of hydrophobic pollutants, as they favor a better interaction between the scarcely water-soluble molecules and the system that generates the reactive species.²²

HLSS IN HOMOGENEOUS SYSTEMS: PHOTOCATALYSTS AND AUXILIARIES FOR THE PHOTO-FENTON PROCESS

The use of HLSs isolated from urban wastes (with the names of soluble bio-organic substances, SBO, or biobased substances, BBS) as photocatalysts to remove pollutants has been studied, in most cases using xenon lamps²³ and real or simulated sunlight.²⁴ These substances have been demonstrated to enhance the photodegradation of different families of compounds, such as dyes,^{25,26} chlorophenols,²⁷ polynuclear aromatics,²⁸ and emerging pollutants such as pesticides^{29,30} or caffeine.³¹ Photodegradation efficiency varies depending on the pollutant and experimental conditions. For example, an increment of 65% in the photodegradation of 4-chlorophenol was observed in the presence of 100 mg L⁻¹ of HLS after 24 h of irradiation;²⁷ for naphthalene sulfonic acid, its removal increased around 70% in the presence of 150 mg L⁻¹ of HLS;²⁸ and the kinetic constant for the photodegradation of igranol 1054 was 4 times higher in the presence of 100 mg L⁻¹ of HLS;³⁰ however, no improvement was observed in the presence of HLS for caffeine photodegradation, unless H₂O₂ was added.³¹

However, the performance of the photochemical process involving HLSs as sensitizers is, in most cases, very poor, and hours or even days are required to achieve significant pollutant removal. This deficient behavior of HLSs as photocatalysts has also been observed for humic acids, and it should be mainly attributed to the low ability to generate reactive species, also considering that the inner filter effect of HLSs decreases direct photolysis of the pollutants.¹⁹

The nature of the reactive species generated by the HLS has also been investigated. The involvement of a singlet oxygen and hydroxyl radical has been determined by indirect experiments²⁶ but also monitored by EPR.²⁷ The formation of ·OH was high at low concentrations of HLS (in the range of a few mg L⁻¹), but beyond this point a clear decrease was observed, attributable to the scavenging role of HLSs for this reactive species. On the other hand, ¹O₂ increased with the HLS concentration; hence this species seems to be relevant when HLS is added at g/L concentrations. A more quantitative study measuring the quantum yields for the formation of reactive species by HLSs agreed that formation of ¹O₂ is more efficient than ·OH and also indicated that triplet excited states of HLS might also be relevant for the photochemical removal of pollutants.²⁹

In order to enhance the generation of reactive species (e.g., hydroxyl radicals) by the HLSs, the (photo)-Fenton process has been employed. Fenton is based on the ability of iron salts to catalyze decomposition of hydrogen peroxide to form hydroxyl radicals (although involvement of other reactive species should not be excluded). Light with $\lambda < 500$ nm is able to enhance the process, via photoreduction of iron, following a cycle that can be summarized by Figure 3.

Iron deactivation occurs at pH > 3 via the formation of oxides and hydroxides that break the catalytic cycle of iron. In order to avoid this fact, substances able to form (photo)-active iron complexes have been employed. In this context, as mentioned above, HLSs are good iron complexing agents, and they have been shown to accelerate the photoreduction of iron(III).³² Furthermore, the existence of an HS-driven photo-Fenton process was demonstrated in environmental con-

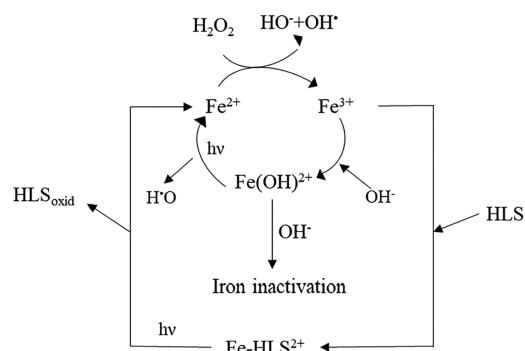


Figure 3. Summary of the key pathways for the photochemical generation of reactive species by the Fenton system in the presence and absence of HLSs.

ditions, and it is responsible for accelerating the removal of organic pollutants in aquatic ecosystems.

Experiments carried out with crystal violet in the presence of CVT230, a type of HLS isolated from urban residues, showed that at pH = 7 and under UVA-vis irradiation a clear enhancement in the removal of this dye was achieved upon addition of iron salts and hydrogen peroxide, as shown in Figure 4. The relatively good results obtained by the

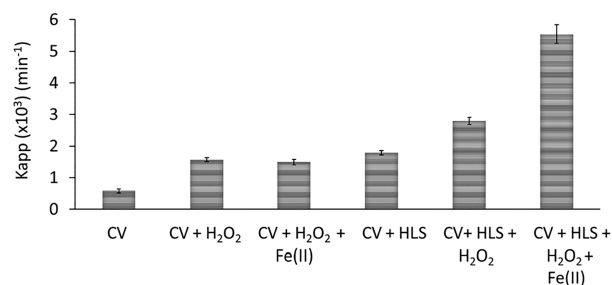


Figure 4. Pseudo-first-order rate constant for the photodecoloration of crystal violet solutions under different conditions: [CV] = 10 mg L⁻¹; [H₂O₂] = 8.3 mg L⁻¹; [Fe(II)] = 5 mg L⁻¹; [HLS] = 100 mg L⁻¹. Initial pH = 7. Adapted with permission from Gomis et al.²⁵

combination of HLS + H₂O₂ (without iron addition) could be attributed to the presence of small amounts of iron in the CVT230 composition.²⁵

A series of papers were devoted to checking the applicability of HLSs as an auxiliary to drive mild photo-Fenton reactions using a mixture of emerging pollutants.^{18,20,33,34} A clear acceleration of the process was observed at a mildly acidic medium and even a neutral medium. The best compromise between efficiency and pH is reached at pH close to 5, as beyond this point a remarkable loss of efficiency can be observed.²⁰ The stability of the complex Fe–HLS has to be considered to explain this behavior; in fact, an EEM-PARAFAC study performed with CVT230 showed that the highest complexation constants were obtained at pH = 5 (log $K = 6.77 \pm 0.08$), while they were clearly lower at pH = 7 (log $K = 5.18 \pm 0.019$).¹³

The effect of reagent concentration has also been studied. In general, a low concentration of iron has been systematically employed (ca. 5 mg L⁻¹). More interesting is the behavior of HLS concentration that showed an optimum at ca. 20 mg L⁻¹ for CVT230, and further addition of these species resulted in a loss of efficiency.²⁰ This was attributed to the fact that once there is enough HLS to complex iron further addition of this

substance only results in an inner filter effect or quenching of the reactive species by the excess of HLS. In fact, EPR measurements in the Fenton process in the presence of CVT230 showed a decrease in the signal attributed to $\cdot\text{OH}$ in the presence of high amounts of this substance.³⁵ Finally, addition of extra amounts of hydrogen peroxide is sometimes required, which might make the process unattractive under some experimental conditions.²⁵

A potentially interesting application of the HLS-driven photo-Fenton reaction is the treatment of scarcely soluble pollutants. Experiments carried out with thiabendazole proved that the effect of the HLS was more remarkable when the pollutant was above its solubility limit.²² This was attributed to the surfactant properties of HLS that favor a better contact between the pollutant and the reactive system. Finally, other applications are the treatment of textile effluents³⁶ or the use of HLSs in a photobioelectro-Fenton process at neutral medium, which avoids addition of peroxide since it is continuously produced *in situ* by electrochemical means.³⁷

The performance of HLSs in homogeneous processes (as sensitizers and in (photo)-Fenton) has been demonstrated to depend on the sourcing materials and the aging of the residues before isolation that, in turn, has a significant effect on its composition. For instance, substances isolated from a mix of green and food residues showed a better performance as photosensitizers than those that used only green residues as sourcing materials.²⁵ Aging, in general, improves the performance of the HLSs, although if the process is too long, a loss of properties can be observed.³⁰ Also in the photo-Fenton process, the more hydrophilic the HLS is, the better their ability to drive the photo-Fenton process.

Regarding the stability of humic substances when submitted to irradiation, it was observed that when CVT230 was irradiated in the UVA–vis range an increase in the hydrophilicity was observed, together with a progressive destruction of the chromophoric moieties, as shown by UV and fluorescence measurements.³⁸ Also the photo-Fenton reaction has been demonstrated to produce similar effects: lower molecular weight and more hydrophilic molecules are formed as HLSs are oxidized. This results in a decrease in their ability to complex iron and, in consequence, to drive the photo-Fenton reaction.^{33,39} However, in the case of FORSUD, a very reduced and hydrophobic type of HLS synthesized from activated sludge digestate, slight oxidation results in the formation of chelating and hydrophilic groups (e.g., carboxylates), thus improving its performance.³³

■ HETEROGENEOUS HYBRID HLS MATERIALS FOR POLLUTANT ELIMINATION

In the last few decades, advances in materials science have resulted in a broad range of new materials that find applications in AOPs, including iron-based catalysts for Fenton-like processes and nanomaterials with improved catalytic properties. An especially attractive topic is the development of inexpensive and sustainable procedures for the production of the new materials; in that context, various natural substances have been employed for this purpose.^{40–42} The main advantages of using natural substances are (i) their specific reactivity; (ii) facile synthetic procedures; and (iii) that they are often nonexpensive, readily available, and renewable materials.⁴⁰ In this context, HLSs fulfill these requirements because of their green origin, inexpensiveness, and ability to organize themselves in different supramolecular structures,

which can be in turn modified according to their composition, concentration, and pH.⁶

As mentioned above, HLSs have surfactant properties, which together with their polyelectrolytic structure make them attractive chemical auxiliaries for the fabrication of nanomaterials.⁴⁰ HLSs have been indeed applied as sacrificial tailoring agents for the preparation of mesoporous silica powders by the sol–gel method;⁴³ these powders consisted of hollow spheres, and they have been used for the removal of organic compounds as well as heavy metal ions from wastewater. HLSs have also been employed in the preparation of TiO_2 powders by sol–gel synthesis.⁴⁰ Studies on the morphology, crystal structures, and surface hydrophobicity of the obtained material indicated that, in sharp contrast with silica powders, an increase of HLSs in the reaction medium resulted in a decrease in the pore size, pore volume, specific surface area, and particle size. Recently a HS– TiO_2 material was synthesized and demonstrated its efficiency to remove amoxicillin and tetracycline as well as to enhance ROS-mediated biocide properties against pathogenic Gram-negative bacteria.⁴⁴

The presence of HLSs in magnetic materials has been studied as a green alternative treatment for wastewater remediation. HLS–Fe magnetic materials can be used to solve one of the major drawbacks of using heterogeneous processes in water remediation, which is their recovery after the treatment. The magnetic parts of the particles allow an effective recovery by physical means.⁴⁵ A logical step forward is the use of Fe–HLS in heterogeneous photo-Fenton processes for water treatment. In this context, the addition of HLSs has two main advantages: (1) grafting HLSs on the surface of magnetic materials favors the heterogeneous photo-Fenton process, most probably by complexing iron or adsorbing the pollutants, and (2) they offer a protective coating preventing surface oxidation and thus the loss of magnetism.⁴⁵ In recent years, literature is available describing the preparation and use of HLS–magnetic hybrid materials for the removal of organic pollutants.^{46–49} For example, an increase in the absorption capacity of magnetite nanoparticles coated with HLSs with the increase of particle concentration and pH value was observed for crystal violet as a model compound.⁴⁶ Among the pollutants that have been removed by an HLS–magnetite-driven heterogeneous photo-Fenton reaction can be found caffeine,^{47,48} carbamazepine,⁴⁹ 4-chlorophenol,⁴⁸ or bisphenol A.⁴¹ The ability of the HLS–magnetite materials to activate hydrogen peroxide at mild pH has also been studied in detail. For instance, magnetic particles coated with HSs were tested as a heterogeneous photo-Fenton catalyst for the activation of hydrogen peroxide (H_2O_2) and persulfate ($\text{S}_2\text{O}_8^{2-}$), employing bisphenol A as a model compound. The material showed a positive contribution on H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ activation. In that case, the highest bisphenol A degradation rates were achieved at acidic conditions (pH = 3) for both oxidants, although persulfate showed a significant efficiency even at pH = 6. The reuse of the catalyst was investigated, and a similar efficiency was observed even after three catalytic cycles. Finally, experiments carried out using real wastewater samples showed less efficiency toward pollutant removal than when compared with ultrapure water.⁴¹ It needs to be highlighted that when dealing with the use of magnetite-based materials in Fenton/photo-Fenton-like processes pollutant degradation can be at least partly attributed to iron cations that are leached from the solid material, and hence, homogeneous processes are actually

occurring, as can be found elsewhere.⁵⁰ In this particular case, the ability of HLSs to form HLS–Fe complexes able to drive photo-Fenton-like processes might cause different mechanisms to occur simultaneously (dissolved iron, complexed iron, and heterogeneous process).⁴⁸ Furthermore, taking into account the ability of HLSs to adsorb pollutants, it might favor contact between the (photo)-Fenton system and the target pollutants. Figure 5 gives a simplified summary of some of these processes.

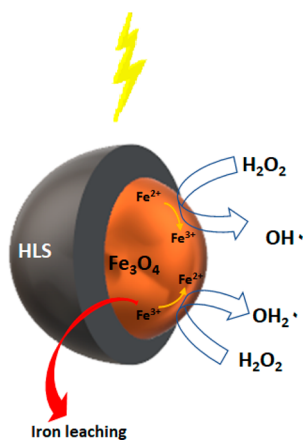


Figure 5. Summary of main processes that can occur in the photo-Fenton process carried out with hybrid materials containing HLSs and iron oxides. Adapted with permission from Gonçalves et al.⁴²

CONCLUSIONS

Humic-like substances have been demonstrated as useful auxiliary materials for wastewater treatment processes. They are in line with the circular economy paradigm of revalorizing wastes to be employed for other purposes. However, the major flaw of this strategy is the high reactive consuming processes that are used for the isolation of these substances; hence, efforts on the development of milder treatments are meaningful.

Although HLSs have been demonstrated to be good at generating reactive oxygen species, their applicability as homogeneous photocatalysts to treat real effluents is limited by the high irradiation periods that are required. On the other hand, they are able to keep the efficiency of the photo-Fenton process at mildly acidic pH, although the process is greatly influenced by the nature of the pollutants and the reaction conditions that are employed. Hence, systematic work in order to delimitate scenarios where the processes can be successfully applied is still required; some niche application can be envisaged, such as saline waters or scarcely soluble pollutants, but they remain unexplored. Also accurate economic and environmental assessment of the processes is an interesting issue to be studied in the near future.

Synthesis of novel materials with photocatalytic and adsorbing properties also seems to be a promising research line. In this case, mechanistic uncertainties are important, and determination of the amount and the role of iron leaching in the iron oxide–HLS materials seems interesting, although extending the use of HLSs to synthesize other families of materials might be of interest.

Finally, it has to be stated that the nomenclature employed for this type of materials is not normalized at all. This makes it difficult to index works dealing with these substances,

identifying what the sourcing materials are or their main characteristics. An effort on this aspect would facilitate research on this issue.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Biographies

Sara García Ballesteros is a postdoctoral researcher at the Advanced Oxidation Processes research group of the Universitat Politècnica de València. Her research interests include the isolation, characterization, and employment of HLS in water treatment as well as the use of new analytical tools (EEM-PARAFAC) for characterization and monitoring of the degradation processes.

Paula García Negueroles is a Ph.D. student at the Advanced Oxidation Processes research group of the Universitat Politècnica de València. Her Ph.D. includes the isolation from different organic sources and characterization and use of HLS as auxiliaries in the photo-Fenton process at mild conditions.

Ana M. Amat is full-professor at the Universitat Politècnica de València. She has led the Advanced Oxidation Processes group since it was founded in 2000. Her research interests include advanced oxidation processes for wastewater decontamination, with special emphasis in solar-driven photochemical processes.

Antonio Arques is full-professor at the Universitat Politècnica de València. He develops his research at the Advanced Oxidation Processes group from the same university. His research interests include the study of different strategies for the implementation of photo-Fenton processes at mild conditions, in most cases involving the use of complexing agents for iron (e.g., humic substances).

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■ ABBREVIATIONS

HS, humic substances; NOM, natural organic matter; HLS, humic-like substances; EEM, excitation emission matrices; HA, humic acid; PARAFAC, parallel analysis factor; EPR, electron paramagnetic resonance

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