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EFFECT OF ORGANIC MATTER ON THE DEGRADATION OF CEFALEXIN WITH TiO_2

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ABSTRACT

In this study, the transformation mechanism of cefalexin (CFX) via TiO_2 photocatalysis and the role of humic acids extracted from two agro-industrial residues, coffee (HAc) and rice (HA_a) husks were evaluated. During the TiO_2 photocatalysis, 90% CFX degradation was found after 180 min of irradiation (365 nm); in the presence of HAc and HA_a, 37% and 61% CFX degradation were observed, respectively. This shows that the extracted humic acids do not promote the formation of reactive oxygenated species; further, they act as scavengers of hydroxyl (.OH). Additionally, it was found that CFX degradation by heterogeneous catalysis with TiO_2 is mainly associated with hole oxidation (47%) and it is caused by ·OH radicals in solution (38%). Finally, we can conclude that the role of humic acids as photosensitizers or scavengers is related to their structural properties.

KEY WORDS: Cefalexin, Degradation, Humic Acids, TiO_2, Bacterial Resistance, Organic Matter

INTRODUCTION

Contamination in aqueous systems caused by pharmaceutical compounds, particularly antibiotics, is an issue that has received significant attention in recent years. Many scientists have expressed concern owing to the appearance of these drugs in different aquatic environments (Luo *et al.,* 2014; Gothwal and Shashidhar 2015) in concentrations ranging from ng/l to µg/l. Despite being present in small amounts, the presence of these drugs generates antibiotic resistance in microorganisms (Li *et al.,* 2015) (Sharma *et al.,* 2016; Guo *et al.,* 2017). In agriculture, antibiotics are used in veterinary medicine, as biocides in fruit and crop production and as additives in the livestock and poultry industry (Sharma *et al.,* 2016). It is estimated that 80% of the antibiotics produced in the world are administered to livestock (Moyer, 2016). In 2014, pharmaceutical companies sold nearly 21 million medically important antibiotics for livestock, which was more than three times the amount of antibiotics sold for people.

In addition to the presence of antibiotics in water bodies (Botero–Coy *et al.,* 2018; Hernández *et al.,* 2019), bacteria and genes resistant to different antibiotics have been found in effluents from urban residential areas, hospitals and municipal wastewater treatment plants (Bouki *et al.,* 2013a, b; Viana *et al.,* 2013; Wi *et al.,* 2017). The onset and increased antibiotic resistance in microbial populations are inevitable owing to the principles of biology and evolution. Resistance may be intrinsic, acquired through spontaneous mutations or may occur owing to horizontal gene transfer from donor bacteria, phage or free DNA (Dodd, 2012). Microbial survival after antibiotic treatment may persist even in the absence of genetic mutation. This

phenomenon, termed collective antibiotic tolerance, involves a subset of the microbial population surviving at a normally lethal concentration of antibiotics.

Advanced oxidation processes (AOPs) are considered competitive technologies for the transformation of organic pollutants that are resistant to biological treatment (Oller *et al.*, 2011; Gagol *et al.*, 2019; Li *et al.*, 2019). AOPs represent a group of techniques characterized by the generation of hydroxyl radicals (·OH). Photocatalysis is part of the AOPs and has been widely used in the transformation processes of emerging pollutants in aqueous systems (Mangayam *et al.*, 2017; Li *et al.*, 2019).

Photocatalysis occurs on the solid surface of a semiconductor. The irradiation of this solid semiconductor excites an electron from the valence band (VB) to the conduction band (CB); thus, the semiconductor behaves like a microscopic electrochemical cell (Litter, 2005). There is a considerable variety of solids that can act as photocatalysts, including TiO_2, ZnO, CdS, FeOx, WO_3, and ZnS. Within these materials, TiO_2 is the most used in photocatalytic reactions because it can be used across a wide pH range, exhibits high chemical stability and is economic viability.

The removal of contaminants through TiO_2 photocatalysis is supported by the action of the hole or OH radical (·OH). When a photon with greater than 3.2 eV energy is irradiated on TiO_2, electronic excitation occurs from the VB to the CB, generating a hole (h+) and an electron (e–) respectively. The generated hole can oxidize the water, producing ·OH radicals (·OH) (equation 1); then, the electrons can react with the dissolved oxygen to form the superoxide anion radical (equation 2), which generates other reactive oxidized species (equation 3) (ROS). All these reactive species can attack and degrade pollutants (equation 4).

$$h^+ + H_2O/OH^- \rightarrow H^+ + {}^{\bullet}OH \qquad \text{equation 1}$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \qquad \text{equation 2}$$

$$O_2^{\bullet -} \rightarrow\rightarrow\rightarrow {}^{\bullet}OH,\ {}^{\bullet}OOH,\ H_2O_2 \qquad \text{equation 3}$$

$$ROS + \text{contaminants} \rightarrow \text{degradation products} \qquad \text{equation 4}$$

One disadvantage of TiO_2 is that it is only effective at wavelengths below 365 nm; therefore, it is not active under visible light. Therefore, exploring alternatives to broaden the spectrum of light under which TiO_2 is active is necessary. To this end, the following techniques have been employed: doping this oxide with different metals (Sandoval *et al.*, 2013; Pirbazari 2015; Durán–Álvarez *et al.*, 2016; Zanella *et al.*, 2018), preparation of mixed oxides (Durán–Álvarez *et al.*, 2016; Zanella *et al.*, 2018) and modifications using organic matter (Wu *et al.*, 2017). Humic acids (HA) are part of the organic matter and photosensitizing substances; they are capable of generating reactive species under radiation with visible light. When irradiated, these substances generate a triplet excited state (equation 5), which can (i) react with oxygen through energy transfer to generate singlet oxygen (equation 6), (ii) react with electron transfer processes to generate other reactive oxygen species (ROS) (equation 7) and (iii) may react with the pollutant and degrade it (equation 8) (Richard and Canonica 2005; Porras *et al.*, 2014; Zhang *et al.*, 2014). A recent study showed that the photodegradation of Bisphenol A with TiO_2 improved by the addition of Aldrich HAs. Wu et al. explain this fact as the formation of charge-transfer complexes between phenol groups and carboxylic acids present in the organic matter, thus favoring the separation of the photogenerated electron-hole pair (Wu *et al.*, 2017). However, other authors have found that organic matter acts as a 'scavenger' of the ·OH radicals produced via photocatalysis using TiO_2, thus reducing the degradation of the pollutant under study (Bo *et al.*, 2019).

$$HA + hv \rightarrow {}^1HA^* \rightarrow {}^3HA^* \qquad \text{equation 5}$$

$${}^3HA^* + O_2 \rightarrow HA^* + {}^1O_2 \qquad \text{equation 6}$$

$${}^3HA^* + O_2 \rightarrow HA^+ + O_2^- \rightarrow \text{other ROS} \qquad \text{equation 7}$$

$${}^3HA^* + \text{pollutant} \rightarrow {}^3\text{pollutant}^* + HA \qquad \text{equation 8}$$

Considering this, the role of the humic substances appears to be determined by the nature of the organic matter. Other authors have shown that the optical and photosensitive properties of the humic substances are related to their structural properties (Del Vecchio and Blough, 2004; Boyle *et al.*, 2009).

In this regard, this work is aimed at assessing the role of HA extracted from agro-industrial waste (rice and coffee husks) in the degradation of an antibiotic (cephalexin, CFX) via photocatalysis using TiO_2 in an aqueous system under 365 nm ultraviolet radiation.

MATERIALS AND METHODS

Samples

Stock solutions of 100 mg/l CFX (Aldrich) and 50

mg/l of the different HA were prepared. These solutions were diluted until the concentration indicated for each experiment was achieved. The HA were extracted from coffee and rice husks, and Aldrich humic acid was used as the reference.

Extraction of HA

HAs were extracted as the methodology reported by Porras et al. (2014). Humic acids were extracted from HAc coffee (*Coffea arabica*) and HAr rice (*Oryza sativa*) husks (Paredes–Laverde *et al.,* 2018). 20g HA and 200 ml 0.5 M NaOH solution were agitated for 24 h. The mixture was decanted and centrifuged at 3600 rpm for 20 min. The resulting solid was treated with 0.5 M NaOH again 2 h and subsequently decanted and centrifuged. Then, HCl was added to the supernatant of the two previous extractions until a pH close to 1 was obtained because at this pH level, the HA precipitate, where as fulvic acids remain in the solution. The mixture was decanted and centrifuged. The solid humic acid was washed with deionised water until the chloride test determined using $AgNO_3$ produced a negative result. The HA were lyophilised and stored in an amber bottle at room temperature.

Determination of acid groups in HA

Boehm titration is a method for characterizing the chemical surface of materials (Boehm 1994, 2002). It is based on the acid/base titration theory and widely used because it can effectively determine the oxygen containing functional groups from the surface of materials.

0.2g humic acid was separately immersed in 25 mL NaOH, Na_2CO_3 and 0.1-M $NaHCO_3$. After 24 h, the solutions were centrifuged and filtered, and the supernatant was titrated with 0.1 M HCl. The number of acid groups was calculated based on the following assumptions: NaOH neutralizes carboxylic groups, lactones, and phenolic groups; Na_2CO_3 neutralizes carboxylic acids and lactones; $NaHCO_3$ neutralizes the carboxylic acids.

Sample analysis

For sample analysis, an aluminium reactor fitted with five Luxtech ultraviolet lamps (UVA) emitting at 365 nm wavelength was used. A 200 ml solution was radiated with 20 ppm CFX, 5 mg/l of different HA and 100 mg/l TiO_2 with constant agitation. The samples were taken at different times, and each test was conducted twice. The samples were analysed using a Thermo Scientific Dionex UltiMate 3000 liquid chromatograph (UHPLC), fitted with an Acclaim™ 120 RP C18 (5 mm, 4.6 × 150 mm) column and a photodiode array detector. The injection volume was 20µL, and acidified water was used as the mobile phase (formic acid 10 mmol/L, pH 3) and acetonitrile (80:20).

RESULTS AND DISCUSSION

***Photo-transformation of CFX using* TiO_2**

CFX transformation using TiO_2 could occur through direct photolysis, by the direct oxidation of the substance in the hole (h+), by the action of the ·OH generated by water oxidation in h+ and/or as a result of the superoxide radical ion (O_2^-) formed by the transfer of the electron in the conducting range. To determine the contribution of these paths to CFX transformation via TiO_2 photocatalysis, the contribution of direct photolysis was evaluated. Figure 1 shows the effect of adding TiO_2 for degrading CFX. The results showed that after 180 min, CFX (20 mg/l) did not sustain direct photolysis; however, the addition of TiO_2 increased CFX degradation, achieving 90% transformation in 180 min.

Regarding direct photolysis, this result suggests that the energy emitted at 365 nm is insufficient to transform the structure of the antibiotic, which is evidenced by the lack of overlap of the signals of the emission spectrum for the lamp (Figure 2A) and the absorption spectrum of the CFX (Figure 2B).

To assess the other CFX transformation paths, the degradation of the superoxide radical ion (benzoquinone) and the hole and the absorbed ·OH(potassium iodide) was performed in the presence of an ·OH (isopropanol) scavenging substance.

Figure 3 shows that adding isopropanol caused 38% inhibition, indicating that in the photocatalytic degradation of CFX, the ·OH contribution (present in the solution) is very important and the hole and/or superoxide radical ion also play a key role. By evaluating the contribution of the superoxide radical ion (in the presence of benzoquinone), a 15% decrease in CFX degradation was obtained. These results suggest that CFX elimination by heterogeneous TiO_2 photocatalysis is mainly associated with hole oxidation (47%) and ·OH (38%). This result agrees with the findings of Li *et al.,* 2018 for CFX degradation using a Zn-oxide-based

catalyst. However, when testing TiO_2 heterogeneous photolysis in cloxacillin degradation (beta-lactam antibiotic), Serna–Galvis *et al.,* 2016 found a low contribution from ·OH in solution and hole oxidation as the main degrading mechanism. These results suggest the oxidation mechanism is associated with the structural features of the antibiotic.

CFX degradation in the presence of HA

It is well known that HAs are photosensitizing substances, which implies that they are capable of producing ROS under radiation. Previous studies showed that HA extracted from a carbonaceous material accelerated the transformation of an insecticide (chlorothalonil) (J. Porras *et al.,* 2014) and an antibiotic (ciprofloxacin) (Jazmín Porras *et al.,* 2016) under UV light in an aqueous system. Further, other authors have observed an increase in the transformation of different pollutants in the presence of natural organic matter extracted from different sources such as humic substances (Xu *et al.,* 2011), organic matter (Ter Halle and Richard 2006) and fulvic acids (S. Zhang *et al.,* 2011). Considering these results, this study tested CFX degradation using HAs extracted from two types of residual biomass: rice (Oryza sativa) and coffee husks (Coffea arabica); Aldrich HAs were used as the reference.

Figure 4 shows CFX photodegradation in the presence of the three tested HAs. It is observable that there is no antibiotic transformation during the irradiated time, which reveals a nil photosensitizing effect by such materials under the conditions in case. Boehm's titration (Boehm 2002; 1994; B. Li 2011) is a method for enabling the semi-quantitative analysis of the functional acid groups on the surface of a material, which are related with the photosensitizing capacity of the material. Table 1 shows the acid functional groups in meq/g out of the HA studied. It can be observed that all the studied HAs have a phenolic content higher than 35%.

Note that the number of these functional groups is not the only determining factor in the photosensitizing capacity of these substances. The functional groups must necessarily form a part of an aromatic structure. Previous studies (Del Vecchio and Blough 2004) have evidenced that the optical and reactivity properties of these substances are associated with the content of charge transfer complexes, which comprise acceptor (ketones and quinones) and donor groups (alcohols, phenols and hydroquinones) of electrons. The HAs with a higher content of carboxylic acids and phenols, lower molecular weight and a higher content of charge transfer complexes are more photosensitive (Aeschbacher *et al.,* 2012; Wenk and Canonica 2012; Sharpless *et al.,* 2014). The HA tested in this work were extracted from two types of biomass: rice and coffee husks. The three main components of the biomass are cellulose, hemicellulose and lignin. In general, the cellulose, hemicellulose and lignin contents may reach 40%–60%, 15%–30% and 10%–25%, respectively (Shurong *et al.,* 2017; Qu *et al.,* 2011). Considering these findings and the fact that the HAs correspond to a soluble fraction, it is highly probable that they have an aliphatic carbonaceous structure; therefore they may have a lower possibility of forming charge transfer complexes and not forming oxygenated reactive species when irradiated.

Additionally, to investigate the effect of organic matter on photocatalysis using TiO_2, CFX irradiation was performed in the presence of TiO_2 and the HAs.

Figure 5 shows that in general, HAs reduced the speed of CFX transformation in relationship with TiO_2 photocatalysis. It may be observed that this effect is different for each type of HA. This reduction is because the HAs in this system act as ·OH radical scavengers, which generates competition between CFX and the HAs by the reactive species produced during TiO_2 photocatalysis.

CONCLUSION

HAs, as a representation of natural organic matter, play an important role in the different sources of water. Considering the presence of drugs in aqueous systems, it is important to assess the effect of such substances in the degradation processes. For this study, the HAs obtained from coffee and rice husks are found to play an inhibiting role in TiO_2 photocatalysis. This suggests that HA, besides acting as photosensitizing substances, may also be substance scavenging reactive species (as in this case). On the one hand, this indicates that the role of the HAs depends on their structural features and that a thorough evaluation of the composition of these materials is necessary. On the other hand, this study made it possible to determine that the CFX degradation path via TiO_2 photocatalysis occurs mainly through hole and ·OH in solution.

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