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**Instituto de Química Campus de
Araraquara**

**HETEROGENEOUS FENTON PROCESS
BASED ON LAYERED DOUBLE HYDROXIDES
FOR URBAN WASTEWATER TREATMENT**

Ph. D. Thesis

NAYARA DE MELO COSTA SERGE

Araraquara

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**HETEROGENEOUS FENTON PROCESS BASED ON LAYERED
DOUBLE HYDROXIDES FOR URBAN WASTEWATER TREATMENT**

**Thesis presented to the Institute of
Chemistry, São Paulo State University, to
obtain the degree of Doctor in Chemistry**

Supervisor: Profa. Dra. Raquel Fernandes Pupo Nogueira

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NAYARA DE MELO COSTA SERGE

**PROCESSO FENTON HETEROGÊNEO BASEADO EM HIDRÓXIDOS
DUPLOS LAMELARES PARA O TRATAMENTO DE EFLUENTE
URBANO**

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I dedicate this thesis to my parents José Osvaldo and Ilma, my brothers Thiago and Camila, and my dear husband York.

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2) Costa-Serge, N. M.; Gonçalves, R. G. L.; Ramirez-Ubillus, M. A.; Li, C; Hammer, P.; Chiron, S.; Nogueira, R. F. P. XXX International Materials Research Congress and International Conference on Advanced Materials (Aug 14 – 19, 2022, Cancun, Mexico). The effect of interlamellar anion on CuMgFe-LDH in solar photo-Fenton degradation of the anticancer drug 5-fluorouracil. (Oral presentation).

3) Costa-Serge, N. M.; Li, C.; Nogueira, R. F. P.; Chiron, S. Solar Chemistry and Photocatalysis: Environmental Applications (Jun 5 – 10 Turin – Italy, 2022). Heterogeneous Fenton oxidation process using CuMgFe-B(OH)₄ Layered Double Hydroxide for simultaneous disinfection and antibiotics removal from urban wastewater. (Oral and poster presentation)

4) Costa-Serge, N. M.; Gonçalves, R. G. L.; Ramirez-Ubillus, M. A.; Li, C; Hammer, P.; Chiron, S.; Nogueira, R. F. P. XIX Brazil MRS Meeting (2021, online format). Influence of the interlamellar anion in CuMgFe-LDH on the degradation of the anticancer drug 5-Fluorouracil. (Poster presentation).

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7) Costa, N.M.; Gonçalves, B. R.; Neto, W.B.; Machado, A. E. H.; Trovó, A. G. XXX Encontro Regional da Sociedade Brasileira de Química (2017, Uberlândia, MG, Brazil). Tratamento de águas residuais de biodiesel por coagulação - floculação: avaliação e otimização dos parâmetros operacionais. (Poster presentation).

8) Costa, N.M.; Soares, M. S.; Soares, F. S. C. Simpósio de Integração Acadêmica Rio Paranaíba – MG, Brazil, 2013. Identificação dos compostos presentes na própolis da Região do Alto Paranaíba. (Poster presentation).

9) Costa-Serge, N. M. I Ciclo de palestra da Química 2011, Rio Paranaíba, MG, Brazil. O Ano Internacional da Química - Homenagem ao Centenário do Prêmio Nobel de Marie Curie. (Oral presentation).

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Published scientific articles

1) N. de M. Costa-Serge, R.G. Lima Gonçalves, M.A. Ramirez-Ubillus, C. Li, P. Hammer, S. Chiron, R.F. Pupo Nogueira, Effect of the interlamellar anion on CuMgFe-LDH in solar photo-Fenton and Fenton-like degradation of the anticancer drug 5-fluorouracil, Appl. Catal. B Environ. 315 (2022) 121537. <https://doi.org/10.1016/j.apcatb.2022.121537>.

- 2) C. Li, N. de M. Costa Serge, R.F.Pupo Nogueira, S. Chiron, V. Goetz, Peroxydisulfate activation by CuO pellets in a fixed-bed column, operating mode and assessments for antibiotics degradation and urban wastewater disinfection, *Environ. Sci. Pollut. Res.* 29 (2022) 71709–71720. <https://doi.org/10.1007/s11356-022-20847-1>.
- 3) M.A. Ramirez-ubillus, N. de.M. Costa-Serge, P. Hammer, R. F. Pupo Nogueira, M.A. Ramirez-ubillus, A new approach on synergistic effect and chemical stability of graphene oxide-magnetic nanocomposite in the heterogeneous Fenton degradation of caffeine, *Environ. Sci. Pollut. Res.* 28 (2021) 55014–55028.
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- 5) E.O. Marson, C.E.S. Paniagua, N.de M. Costa-Serge, R.M.F. Sousa, G.D. Silva, R.W. Becker, C. Sirtori, M.C.V.M. Starling, S.R. Carvalho, A.G. Trovó, Chemical and toxicological evaluation along with unprecedented transformation products during photolysis and heterogeneous photocatalysis of chloramphenicol in different aqueous matrices, *Environ. Sci. Pollut. Res.* (2020). <https://doi.org/10.1007/s11356-020-09756-3>.
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Submitted scientific articles

1) N. de M. Costa Serge, C. Li, R.F. Pupo Nogueira, S. Chiron. Simultaneous disinfection of urban wastewater and antibiotics degradation mediated by CuMgFe-B(OH)_4 layered double hydroxide with different oxidizing agents. Chemical Engineering Journal.

FOREWORD

This thesis was written in the format of chapters/articles in accordance with the presentation of dissertations and theses norms of the Chemistry Graduate Program at the Institute of Chemistry, UNESP – Araraquara. Two published articles and one submitted (being the first author in all of them) in refereed journals make up chapters 2, 3 and 4 of this thesis. All the results from chapter 4 were obtained at the HSM Hydrosciences Montpellier, Montpellier University, Montpellier- France, during the research internship abroad.

In chapter 1, a general introduction with the objectives is presented, starting with the problem of the presence of pollutants (chemical and biological) in wastewaters even after applying conventional treatments and the application of Layered Double Hydroxides (LDH) as an alternative for wastewater treatment in heterogeneous Fenton with different oxidizing agents to promote the removal of contaminants and inactivation of pathogens.

The next chapters present the complete scientific articles published during the Ph.D period, in the following sequence:

Chapter 2: Fenton-like degradation of sulfathiazole using copper-modified MgFe-CO_3 layered double hydroxide. Authors: Nayara de Melo Costa-Serge, Rosembergue Gabriel Lima Gonçalves, Hernán Dario Rojas-Mantilla, Celso Valentim Santilli, Peter Hammer and Raquel Fernandes Pupo Nogueira. Journal: Journal of Hazardous Materials, Volume 413, 5 July 2021, 125388. DOI: 10.1016/j.jhazmat.2021.125388. State: Received 29 October 2020, Revised 20 January 2021, Accepted 9 February 2021, Available online 12 February 2021, Version of Record 23 February 2021.

Chapter 3: Effect of the interlamellar anion on CuMgFe-LDH in solar photo-Fenton and Fenton-like degradation of the anticancer drug 5-fluorouracil. Authors: Nayara de Melo Costa-Serge, Rosembergue Gabriel Lima Gonçalves, Manuel Alejandro Ramirez-Ubillus, Chan Li, Peter Hammer, Serge Chiron and Raquel Fernandes Pupo Nogueira. Journal: Applied Catalysis B: Environmental, Volume 315, 15 October 2022, 121537. DOI: 10.1016/j.apcatb.2022.121537. State: Received 26 January 2022, Revised 17 May 2022, Accepted 18 May 2022, Available online 21 May 2022, Version of Record 26 May 2022.

Chapter 4: Simultaneous disinfection of urban wastewater and antibiotics degradation mediated by CuMgFe-B(OH)_4 layered double hydroxide with different oxidizing agents.

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Finally, chapter 5 summarizes the general conclusion of this Ph.D thesis.

Abstract

The interest in the application of Layered Double Hydroxides (LDHs) as catalysts in heterogeneous Fenton has become frequent due to their interesting structural properties, low production cost, ease of synthesis, the possibility of incorporation of different types of elements in the same structure and application under neutral conditions. The improvement and use of these materials as catalysts in secondary treated urban wastewater (STWW), would bring benefits to human health and the environment. These perspectives motivated this study, where LDHs based on CuMgFe were synthesized for the activation of different oxidizing agents, hydrogen peroxide (H_2O_2), persulfate ($\text{PDS} = \text{S}_2\text{O}_8^{2-}$), and peroxymonosulfate ($\text{PMS} = \text{HSO}_5^-$) in the generation of reactive species for the degradation of pharmaceuticals and inactivation of pathogens in STWW. Initially, two pyroaurite-type LDHs (MgFe-CO_3 and CuMgFe-CO_3) were synthesized by the coprecipitation method at constant pH to evaluate the influence of the insertion of Cu in the LDH on the degradation of the sulfathiazole antibiotic (STZ) in the dark and under LED-Vis irradiation. XPS analyzes confirmed the insertion of Cu(II) in the LDH structure and the presence of Cu(I), which increased the degradation efficiency of $150 \mu\text{g L}^{-1}$ of STZ, and achieving non detectable concentration was after 90 min using 4 mmol L^{-1} of H_2O_2 and 0.5 g L^{-1} of CuMgFe-CO_3 at pH 7.5, under LED-Vis irradiation. In view of the potential of the LDH with copper to remove the antibiotic at a pH close to neutral and the high stability of the catalyst even after 4 cycles of reuse, it was decided to study the influence of the interlamellar anion on the activity. Four LDHs of CuMgFe were synthesized, with a variation of the interlamellar anion: B(OH)_4^- , CO_3^{2-} , NO_3^- and SO_4^{2-} , for the removal of the anticancer 5-fluorouracil (5-FU) in the dark and under solar radiation. XRD and XPS results showed the phase purity of the catalysts synthesized and the intercalation of the respective anions. The degradation process in the dark showed that the interlamellar anion has a strong effect on the catalytic properties of the LDH, showing the following pseudo-first order (k) rate constant sequence: $\text{CuMgFe-B(OH)}_4 > \text{CuMgFe-NO}_3 > \text{CuMgFe-SO}_4 > \text{CuMgFe-CO}_3$. The highest efficiency of LDH with boron was explained based on FTIR and XPS results, which showed the interactions B-O and B-OH, which were responsible for inducing modifications on the electronic density of CuMgFe-B(OH)_4 , accelerating the reduction of Cu(II) and Fe(III) and thus favoring the generation of reactive oxygen species in the Fenton process. This catalyst allowed the complete degradation of $200 \mu\text{g L}^{-1}$ of 5-FU under solar radiation after 20 min and after 40

min in the dark, with degradation efficiency maintained above 90% until the fourth cycle of use in the presence of 10 mmol L⁻¹ H₂O₂ and 0.5 g L⁻¹ LDH. The excellent performance of CuMgFe-B(OH)₄ in the degradation of 5-FU, motivated the studies on the application of this catalyst in the simultaneous degradation of the antibiotics sulfamethoxazole (SMX), ciprofloxacin (CIP), cephalixin (CFX) and amoxicillin (AMX) and inactivation of *Escherichia coli* and *Enterococcus faecalis* pathogens with different oxidizing agents, H₂O₂, PDS, and PMS. In each system with different oxidants, CuMgFe-B(OH)₄ behaved differently. LDH-activated PMS was the most efficient process and provided more than 90% removal of all antibiotics after 120 min and complete inactivation of pathogens using 0.5 g L⁻¹ LDH and 4 mmol L⁻¹ PMS. However, the LDH system with H₂O₂ was efficient for disinfection, but not for the degradation of antibiotics due to the formation of complexes between the cations present in the catalyst structure and H₂O₂. The PDS activated system occurred by a non-radical pathway involving mainly singlet oxygen (¹O₂) and Cu(III) with the removal of antibiotics, but limited disinfection capacity for *Escherichia coli*.

In the experiments performed in this thesis, high stability of the synthesized LDHs and excellent performance under neutral conditions were observed, which is important for the application of these materials as catalysts.

Resumo

O interesse na aplicação de Hidróxidos Duplos Lamelares (HDLs) como catalisadores no processo Fenton heterogêneo tem se tornado frequente devido às suas interessantes propriedades estruturais, baixo custo de produção, facilidade de síntese, possibilidade de incorporação de diferentes tipos de elementos em uma mesma estrutura e aplicação em condições de neutralidade. O aprimoramento e uso desses materiais como catalisadores no tratamento de efluente de uma estação de tratamento de esgoto (ETE), traria benefícios à saúde humana e ao meio ambiente. Estas perspectivas, motivaram a realização deste trabalho, onde foram sintetizados HDLs baseados em CuMgFe para a ativação de diferentes agentes oxidantes, peróxido de hidrogênio (H_2O_2), persulfato ($\text{PDS} = \text{S}_2\text{O}_8^{2-}$), e peroximonosulfato ($\text{PMS} = \text{HSO}_5^-$) na geração de espécies reativas para a degradação de fármacos e inativação de patógenos em efluente de ETE. Inicialmente foram sintetizados dois tipos de HDLs do tipo piroaurita (MgFeCO_3 e CuMgFeCO_3) pelo método de coprecipitação a pH constante para avaliar a influência da inserção de Cu no HDL na degradação do antibiótico sulfatiazol (STZ) no escuro e sob radiação LED-Vis. As análises de XPS confirmaram a inserção de Cu(II) na estrutura do HDL e a presença de Cu(I) após a reação, o que aumentou a eficiência de degradação de $150 \mu\text{g L}^{-1}$ de STZ, onde após 90 min de reação não foi possível detectar o contaminante utilizando 4 mmol L^{-1} de H_2O_2 e $0,5 \text{ g L}^{-1}$ de CuMgFeCO_3 , em pH 7,5, sob irradiação LED-Vis. Tendo em vista o potencial do HDL com cobre em remover o antibiótico em pH próximo ao neutro e a alta estabilidade mesmo após 4 ciclos de reuso, decidiu-se estudar a influência do ânion na atividade catalítica. Quatro HDLs de CuMgFe foram sintetizados, com variação do ânion interlamelar: B(OH)_4^- , CO_3^{2-} , NO_3^- e SO_4^{2-} , para a remoção do fármaco anticâncer 5-fluorouracil (5-FU) no escuro e sob radiação solar. Os resultados de DRX e XPS mostraram que os catalisadores foram sintetizados com pureza de fase e os respectivos ânions foram intercalados. A aplicação do processo de degradação no escuro, mostrou que o ânion interlamelar tem um forte efeito nas propriedades catalíticas do HDL, apresentando a seguinte sequência de constante de velocidade de pseudo-primeira ordem (k): $\text{CuMgFe-B(OH)}_4 > \text{CuMgFe-NO}_3 > \text{CuMgFe-SO}_4 > \text{CuMgFe-CO}_3$. A alta eficiência do HDL com boro foi explicada com base nos resultados de FTIR e XPS, que mostraram as interações B-O e B-OH, as quais foram responsáveis por induzir modificações na densidade eletrônica de CuMgFe-B(OH)_4 , acelerando a redução de Cu(II) e Fe(III) e favorecendo assim a geração de espécies reativas de oxigênio no processo Fenton. Este

catalisador propiciou a completa degradação de $200 \mu\text{g L}^{-1}$ de 5-FU sob radiação solar após 20 min e após 40 min no escuro, com eficiência de degradação mantida acima de 90% até o quarto ciclo de reuso na presença de 10 mmol L^{-1} de H_2O_2 e $0,5 \text{ g L}^{-1}$ de HDL. O excelente desempenho de CuMgFe-B(OH)_4 na degradação de 5-FU, motivou os estudos para a aplicação deste catalisador na degradação simultânea dos antibióticos sulfametoxazol (SMX), ciprofloxacina (CIP), cefalexina (CFX) e amoxicilina (AMX) e inativação dos patógenos *Escherichia coli* e *Enterococcus faecalis* com diferentes oxidantes, H_2O_2 , PDS e PMS. Em cada sistema com os diferentes oxidantes, CuMgFe-B(OH)_4 se comportou diferente. O PMS ativado pelo HDL foi o processo mais eficiente e proporcionou mais de 90% de remoção de todos os antibióticos após 120 min e inativação completa dos patógenos usando $0,5 \text{ g L}^{-1}$ de HDL e 4 mmol L^{-1} de PMS. Entretanto, o sistema HDL com H_2O_2 foi eficiente para a desinfecção, mas não para a degradação de antibióticos devido à formação de complexos entre os cátions presentes na estrutura do catalisador e H_2O_2 . O sistema ativado por PDS ocorre por uma via não radicalar envolvendo principalmente oxigênio singlete e Cu(III) com remoção de antibióticos, mas com capacidade de desinfecção limitada para *Enterococcus faecallis*. Nos experimentos realizados nesta tese, observou-se uma elevada estabilidade dos HDLs sintetizados e um excelente desempenho em condições neutras, o que é importante para a aplicação destes materiais como catalisadores.

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

1 INTRODUCTION AND OBJECTIVES

1.1 Pharmaceuticals and pathogens in the environment

Synthetic or natural molecular therapeutic agents have been widely used for the treatment and prevention of diseases in human and veterinary medicine, in promoting growth in animals by inhibiting the growth of microbes in the gastrointestinal tract, as well as in agriculture for plant protection [1].

Despite the numerous benefits of these therapeutic molecules, pharmaceutical products have been considered as a new class of environmental contaminants in the last decades [1,2]. The increase in pharmaceutical consumption in recent decades has contributed to this problem, for example, total daily doses of antibiotics consumed between 2000 and 2018 in 204 countries increased by 46%, with the highest rates in Eastern Europe and Central Asia [3].

According to the World Health Organization (WHO), Brazil has the highest rate of antibiotic use in the Americas with approximately 22.8 defined daily doses for every 1,000 inhabitants, with amoxicillin and azithromycin being the most used [4]. Furthermore, recent studies have reported that China is the country that most produces and consumes antibiotics in the world with production of 248,000 tons and consumption 162,000 tons, from which 52% are used in animals and 48% in humans [5,6].

Wastewater treatment plants (WWTP) are planned to remove pollutants from sewage that can cause deterioration in the quality of receiving water bodies.

Although conventional treatments of water and wastewater, such as adsorption, flocculation and biological methods, are well established, wastewater treatment plants has variable efficiency for pharmaceutical removal and the contaminants initially present can be transformed into more dangerous contaminants than the initial ones [2,7,8].

Each WWTP has peculiarities in its project. However, WWTP usually consists of a combination of physical, chemical, and biological processes to remove solids, organic matter, and pathogens [7].

First, the conventional wastewater treatment includes screening to eliminate large solids from the effluent, and after that, the wastewater passes through sand tanks.

The primary treatment is the removal of organic and inorganic solids by sedimentation and the removal of materials that will float and the secondary treatment is used to remove organic matter and suspended solids. At this stage, activated sludge, biological filters or

biofilters are commonly employed, and air is added to the aeration tanks to provide a healthy environment for the aerobic microorganisms naturally present in wastewater [7].

The last step is tertiary treatment or advanced treatment, and chemical processes are employed for disinfection, such as chlorination, which is the most commonly applied.

In view of the high amount of pharmaceuticals that are excreted unchanged, and, unfortunately, due to the lack of strict global legislation for contaminants removal in WWTP, the permanence and persistence of these contaminants in the effluent leads to their occurrence in surface water (lakes, rivers, and seawater), groundwater, sludge, and drinking water [1,7,8]. This can have harmful effects on human health and aquatic biota, such as increased incidence of breast, testicular and prostate cancer, infertility, acute aquatic toxicity, genotoxicity and feminization of fish [5,6,9,10].

In addition, the presence of antibiotics can induce the development of antibiotic-resistant bacteria (ARB) and antibiotic-resistant genes (ARGs), which although not currently included in any international regulation, in 2015 ARB and ARGs were recognized by WHO as one of the major challenges to human health [11,12].

Spread of ARGs through diverse environmental microbes and human pathogens can occur via horizontal gene transfer (HGT) and can infect non-resistant bacteria through natural transformation, leading to further spread of antibiotic resistance by self-replication and they can also be transmitted to other bacterial species by transduction or conjugation [13].

Previous studies have reported the presence of both ARB and ARGs in wastewater samples [14][15] and ARB can survive the inhibitory action of antibiotics, limiting effectiveness in treating infectious diseases. For example, bacteria of the genus *Aeromonas* showed specific antibiotic resistance to erythromycin and ampicillin, bacteria of the genus *Klebsiella* and *Bacteroides* showed effective antibiotic resistance to ciprofloxacin, while *Escherichia* genus showed resistance to kanamycin and tetracycline [14]. This drastically affects the health of the human population. According to the World Health Organization (WHO) report of 2019, antimicrobial resistance is responsible for the deaths of 700,000 people, and it's estimated 20 million deaths by 2050 [16].

Considering the aforementioned problems, in this thesis 5 antibiotics frequently detected in wastewater treatment plant (WWTP) were selected to be investigated in heterogeneous Fenton processes: sulfathiazole (STZ), sulfamethoxazole (SMX), ciprofloxacin (CIP), cephalexin (CFX) and amoxicillin (AMX). These antibiotics belong to the family of

sulfonamides (STZ and SMX), quinolones (CIP), cephalosporins (CFX), and penicillins (AMX). Table 1.1 shows the occurrence of these antibiotics in rivers and wastewaters in different countries.

Table 1.1 Occurrence of CIP, AMX, CFX, SMX and STZ in rivers and wastewaters in different countries.

Antibiotic	Country	Concentration (ng L ⁻¹)	Reference
CIP	Egypt	220–310	[17]
	Brazil	200-700	[18]
	Turkey	80 – 3000	[19]
	Italy	1100–3700	[20]
	Spain	185–613	[20]
	Portugal	573.5 - 623.8	[21]
	Germany	82.6 – 172.3	[21]
	Finland	69.1 – 97.0	[21]
AMX	Qatar	< 10–80	[17]
	Iran	24.52–94.6	[22]
	India	62.5	[23]
CFX	Brazil	29 – 2422	[24]
	Portugal	102.4 – 111.3	[21]
	Spain	89.2 – 335.8	[21]
	Finland	201.2 – 217.1	[21]
	Cyprus	128.2 – 176.3	[21]
SMX	Tunisia	86–4145	[25]
	United States	500–1800	[26]
	Italy	280–740	[20]
	Spain	19–1150	[20]
	Portugal	62.5 - 96.6	[21]
	Germany	103.6 – 139.8	[21]
STZ	China	2	[27]
	Korea	307.4	[28]
	Taiwan	0.6-10	[1]

Recent studies have highlighted the presence of anticancer drugs in environmental systems, attributed to their increasing use for cancer treatment, low metabolism in the human body, and low biodegradability in the hospital and municipal effluents [29,30].

The genotoxic effects of these substances can affect human health and the environment, even at very low concentrations. The main source of anticancer drugs are hospital effluents, which are generally released into the sewage system without any treatment before arriving at wastewater treatment plants [29,31].

Previous studies indicated that 5-FU in concentrations of the order of $\mu\text{g L}^{-1}$ and mg L^{-1} inhibited the reproduction of crustaceans, algae and cyanobacteria, and cause damage to the DNA of mussels and zebrafish [29,32].

Therefore, in this thesis, the degradation of 5-fluorouracil (5-FU), an anticarcinogen used to treat colon, breast, gastrointestinal, head and neck cancer, was also investigated in heterogeneous Fenton processes.

In addition to the removal of micropollutants after the conventional WWTP, another big challenge is the complete inactivation of pathogens. Great progress has been achieved on the disinfection processes in drinking water and WWTP based on the chlorination and UV processes. However, several limitations still exist, including the resistance of some types of microorganisms to chlorination and UV radiation, and some disinfection by-products produced in the chlorination process that are toxic and/or carcinogenic [33,34].

Some microorganisms present in wastewater are bacteria, fungi, actinomycetes, protozoa, algae, and viruses [35]. Previous studies have reported the persistence of these microorganisms in some aquatic matrices, determined by the parameter T90, defined as the time for bacterial concentration to decrease by 90%. The T90 for *Escherichia coli* and *Enterococcus faecalis* was 4-11 and >28 days, respectively, and for the bacteria *Clostridium perfringens* was >11 days [36,37], indicating that *Enterococcus faecalis* can survive longer than others and therefore, deserves greater attention in disinfection systems.

Escherichia coli (Gram-negative bacteria) and *Enterococcus faecalis* (Gram-positive bacteria) represent general fecal indicators for water resources monitoring. The cell wall of gram-positive bacteria is made up of a thick and dense layer of phosphoric acid and peptidoglycan and is more persistent and difficult to inactivate than Gram-negative bacteria. This reflects the greater persistence of *Enterococcus faecalis* compared to *Escherichia coli* [38].

In view of the negative impact of the presence of pharmaceuticals and pathogens in wastewaters, new technologies must be developed and applied aiming for excellence in wastewater treatment, including the promotion of water reuse.

According to the WHO, the reuse of water will no longer be an option, but become a necessity. Around 6 billion people will suffer from a shortage of drinking water by 2050 [4]. Furthermore, the increasing wastewater reuse in agriculture and other non-potable applications such as street washing, industrial uses for cooling boilers, firefighting, construction, flushing toilets, increase the demand for safe technologies for effective treatment [39].

For this purpose, the combination of advanced technologies with conventional methods can be a good option to remedy the problems mentioned above, not only for the degradation of pharmaceuticals but also for the elimination of pathogens.

Some treatment processes have been commonly investigated by the scientific community, such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis and advanced oxidation processes [7]. These processes have been investigated alone or in combination.

Considered an excellent possibility for wastewater treatment, Advanced Oxidation Processes (AOPs) have the ability to produce reactive species which can oxidize organic compounds that start reactions leading to contaminants degradation to CO_2 , low toxicity, organic acids, water and inorganic salts. Furthermore, the reactive species produced in AOPs can cause the destruction of the cell envelope of bacteria, react with enzymes, and intracellular substances through different reactive species, as will be discussed in the following sections.

1.2 Advanced Oxidation Processes (AOPs)

AOPs are treatment technologies for degradation and mineralization of recalcitrant organic matter from wastewater, which have been studied for about 50 years [38]. The term AOPs, was first proposed in 1987 by research scientist William Glaze (North Texas State University) [40].

The Figure 1.1 represent the most applied AOPs for wastewater treatment: photolysis of H_2O_2 , Fenton processes, heterogeneous photocatalysis, ozonation, electrochemical processes and sulfate radical based AOP. These technologies generate reactive species such as $\text{SO}_4^{\bullet-}$, $\text{HO}^{\bullet}$, $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$, $^1\text{O}_2$ and high valence metals that oxidize organic contaminants as well as attack the

bacterial cell envelope, including peptidoglycan, lipopolysaccharide, and phospholipids, even reacting with DNA constituents and enzymes in bacterial cells [40].

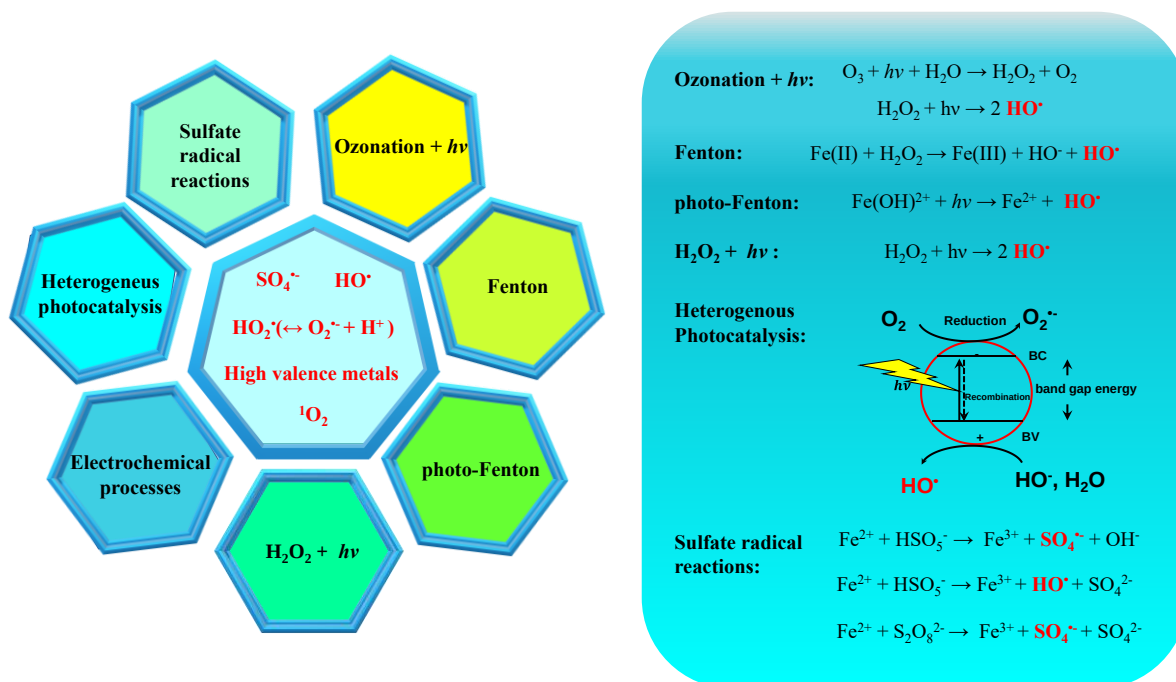


Figure 1.1 Representation of the most studied AOPs for wastewater treatment and reactions involved in the generation of reacting species.

There are reactions in natural waters, atmosphere, interstellar space, and even in biological systems that naturally occur in the environment capable of generate $HO^\bullet$, [41] but at a slow rate. Differently, with AOPs, the amount of $HO^\bullet$ is very high compared to natural processes.

AOPs are classified as homogeneous and heterogeneous because the reactions can be processed in both reaction systems. The reactive species can be produced by different processes such as chemical, sonochemical, electrochemical and photochemical [42].

The photolysis of H_2O_2 consists of the homolytic cleavage of H_2O_2 under UV irradiation ($\lambda < 280$ nm) with the generation of two hydroxyl radicals (Figure 1.1) and is an oxidative process used commercially in water treatment [43].

One of the AOPs is the Fenton process. In 1894, H.J.H Fenton discovered the high oxidizing power of ferrous ions (Fe^{2+}) and H_2O_2 for tartaric acid oxidation [40]. From this, the classic Fenton process was defined and consists of the catalytic decomposition of H_2O_2 by Fe^{2+} reducing H_2O_2 to hydroxide ions and $HO^\bullet$ and Fe^{2+} oxidation to ferric ions (Fe^{3+}) in dark conditions (Figure 1.1). The Fe^{3+} ions produced react with H_2O_2 to generate Fe^{2+} and $HO_2^\bullet$,

which has a lower reduction potential ($E^0 = 1.42$ V) compared to $\text{HO}^\bullet$ ($E^0 = 2.80$ V). The Fe^{2+} regenerated reacts again with H_2O_2 in the Fenton reaction. This reaction of Fe^{2+} regeneration is very slow. However, in the presence of radiation, this process can be accelerated and is called the photo-Fenton process as will be discussed below.

It is important to highlight that the reactions of the Fenton process represented in Figure 1.1, the water molecules that complex the iron species in aqueous solution (Fe^{2+} and Fe^{3+}) have been omitted to simplify the text. In aqueous solution, at pH 0, Fe^{3+} species are found in the form of the aquacomplex $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. The increase in the pH is accompanied by the hydrolysis of aquocomplexes, generating hydroxylated species such as $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, $[\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4]^+$, $[\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3]$, etc., depending on the pH [44] [45].

The use of UV radiation favors the regeneration of Fe^{2+} from Fe^{3+} produced in the Fenton reaction. When the Fe^{3+} complexes are irradiated with UV-Vis radiation, there is the promotion of an electron from a centered orbital on the ligand to a metal-centered orbital, called the ligand-metal charge transfer. As a consequence, an oxidation-reduction reaction leads to the reduction of Fe^{3+} to Fe^{2+} and formation of $\text{HO}^\bullet$ (Figure 1.1). Therefore, the combination of the Fenton process with irradiation, called the photo-Fenton process, causes an increase of production of hydroxyl radical [46].

The Fenton process can be classified as homogeneous and heterogeneous according to the absence or presence of solid phase, as a catalyst.

The heterogeneous Fenton process, which solid phase catalyst particles are used to activate oxidants can be interesting for operational and large-scale applications, especially when combined with solar radiation. This process have many advantages when compared to homogeneous catalysts such as possibility of reuse of the material due to the relative ease of separating the catalyst from the reaction, possibility of working in neutral conditions, no sludge generation, and efficiency even in the dark [45].

For a good efficiency of the homogeneous Fenton process, the optimum pH is around 2.8 which is a limitation. Therefore, the heterogeneous process stands out over the homogeneous process [47].

Heterogeneous photocatalysis involves the use of semiconductors. The efficiency of a semiconductor depends on some factors such as the difference between the conduction band (CB) and the valence band (VB) known as band gap energy (E_g), absolute potentials of the CB and VB and the dynamics of the photogenerated electrons, and holes such as mobility and the

rates of surface charge recombination. The generation of $\text{HO}^\bullet$ is possible from the incidence of radiation of sufficient energy to promote an electron from the VB to the CB of the semiconductor and the oxidant sites generated assist in the formation of $\text{HO}^\bullet$ (Figure 1.1) [48].

Another efficient AOP is catalytic ozonation. Ozone is a strong oxidant with a high redox potential ($E^0 = 2.1 \text{ V}$) and can oxidize inorganic and organic substances, and in a basic medium can also form $\text{HO}^\bullet$ ($E^0 = 2.8 \text{ V}$). To increase the efficiency of ozonation, the combination with UV light in the processes can improve the efficiency of the treatment [49].

An interesting technology is the generation of sulfate radical ($\text{SO}_4^{\bullet-}$) by decomposition of oxidizing agents such as persulfate (PDS, $\text{S}_2\text{O}_8^{2-}$) and peroxymonosulfate (PMS, HSO_5^-), which can also generate $\text{HO}^\bullet$ (Figure 1.1). The application of these oxidants in the Fenton process is recent [50] as will be discussed in detail below.

1.2.1 Classical and modified heterogeneous Fenton process: hydroxyl and sulfate radical reactions

Among the various AOPs, heterogeneous Fenton processes are an excellent alternative for water purification, including the inactivation of bacteria and viruses [48,51]. According to the web of science database, since 2001, 669 articles were published with the application of the heterogeneous Fenton process for wastewater treatment (keywords “heterogeneous Fenton” and “wastewater”), showing that studies in wastewater with this process are still limited.

The mechanisms behind the catalyst surface still require further investigation. Few studies report the complex interactions between solid catalysts, oxidizing agent, organic contaminants, generated reactive oxygen species (ROS), degradation by-products and other coexisting substrates [52].

The classic heterogeneous process is based on the reaction of iron containing catalysts with H_2O_2 , with the predominant generation of $\text{HO}^\bullet$. Generally, the process is denoted as modified Fenton heterogeneous process, when based on $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ reactions generated in the presence of PMS or PDS, also called sulfate radical reactions based on AOPs [53].

Recent studies have reported the application of different types of catalysts in the heterogeneous Fenton process. Iron mineral such as, magnetites, hematite, ferrihydrite, goethite, lepidocrocite, and maghemite are generally considered biodegradable, non-toxic and environmentally friendly and are the most commonly employed catalysts in Fenton [45].

Furthermore, several iron minerals can be incorporated into numerous supporting materials such as zeolites, metal-organic frameworks (MOFs), clays, graphene oxide (GO) and silica to increase thermal stability, resistance to organic solvents and high mechanical strength [54–57]. In addition to iron, other cations that participate in Fenton's reactions such as Cu, Ce, Mn, Cr, Co, and Ru can be incorporated into these materials to accelerate the degradation process [58].

Layered double hydroxides (LDHs) are a very interesting class of clay-based materials that have been extensively investigated with Cu, Mg, Fe, Co and Mn in recent decades as Fenton's catalysts, as will be discussed in detail below [59].

The oxidants most used in AOPs for environmental remediation are H_2O_2 , PDS and PMS as they present the peroxo group (O-O bond), which after undergoing catalytic decomposition, can generate radicals that act in the degradation of pollutants. Table 1.2 shows that the three oxidants have different properties and price.

Table 1.2 Properties and cost of H_2O_2 , PMS and PDS oxidants applied in AOPs [60–62]

Oxidant	E° (V)	Main generated radicals	Solubility in water at 25 °C (g L ⁻¹)	USD Kg ⁻¹
H₂O₂	1.77	HO•	Soluble	1.5
PDS	2.01	SO ₄ • ⁻	730	0.74
PMS	1.82	SO ₄ • ⁻ and HO•	298	2.2

Activated PMS can generate both types of radicals, $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ [63], however, is a more expensive oxidant. The commercial name of PMS is Oxone, in the form of a triple salt $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, and has the precursor HSO_5^- [60,64].

The advantage of using H_2O_2 is its total solubility in water compared with PDS and PMS. However, the application of PDS is advantageous since it is the most economical option among these oxidants.

In heterogeneous Fenton processes, other types of radicals and non-radical reactive species can be generated from the reactions, such as the superoxide radical and singlet oxygen [48].

The main radical species produced in the heterogeneous Fenton are represented in Table 1.3. It is possible to observe that they have a higher standard reduction potential than normal hydrogen electrode.

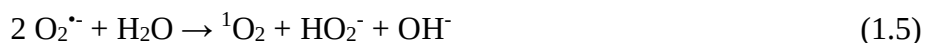
Table 1.3 Reactive oxygen species produced in classical and modified heterogeneous Fenton process [48,65,66].

Reactive Species	Redox
	Potencial (V)
$\text{HO}^\bullet + \text{e}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$	1-8 - 2.8
$\text{O}_2^{\bullet-} + \text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$	0.13 - 1.76
$\text{SO}_4^{\bullet-} + \text{e}^- \rightarrow \text{SO}_4^{2-}$	2.5–3.1
$\text{SO}_5^{\bullet-} + \text{e}^- + \text{H}^+ \rightarrow \text{HSO}_5^-$	0.81

Hydroxyl radicals are not selective and can initiate different types of reactions with different functional groups of the contaminants, forming unstable organic radicals, which are later oxidized to CO_2 , H_2O and inorganic acids from the heteroatoms present [67]. These radicals can react via hydrogen atom abstraction (Eq.1.1), electrophilic addition (generally with unsaturated or aromatic hydrocarbons) (Eq.1. 2) and electron transfer (usually with halogenated compounds) (Eq. 1.3).



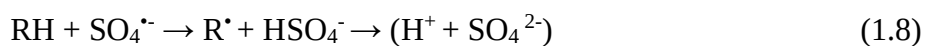
Although the literature reports many studies concerning the degradation of organic contaminants due to the action of the $\text{HO}^\bullet$, studies about the interaction of superoxide radical ($\text{O}_2^{\bullet-}$) with organic substances are still limited. The superoxide ion reacts by electron transfer, deprotonation and nucleophilic substitution and can react with water and various halocarbons to produce $^1\text{O}_2$ (Eq. 1.4 – 1.6) [68].



Sulfate radical-based advanced oxidation processes (SR-AOPs) began to be explored in 2003 [69] when cobalt/PMS showed more efficient results than the classic Fenton reagent for the degradation of 2,4-dichlorophenol and atrazine, under all investigated conditions, attributed to the greater oxidizing potential of $\text{SO}_4^{\bullet-}$ compared to the $\text{HO}^{\bullet}$.

Similar to $\text{HO}^{\bullet}$, $\text{SO}_4^{\bullet-}$ react with organic contaminants through 3 ways: i) Electronic transfer (Eq. 1.7): The $\text{SO}_4^{\bullet-}$ are strong electrophiles and capture electrons from an electron-rich site, leading to the formation of oxidized products. Therefore, compounds containing electron-donating groups are susceptible to attack by this radical such as amino (NH_2 -), hydroxyl ($-\text{HO}$), anionic oxygen species ($-\text{O}^-$), alkoxy ($-\text{OR}$), amide ($-\text{NH}-\text{CO}-\text{R}$), π electrons in aromatic compounds and other organic pollutants with unsaturated bonds [70,71].

ii) Hydrogen abstraction (Eq. 1.8): The main mode of action of $\text{SO}_4^{\bullet-}$ in alkanes, alcohols, organic acids, ethers, lipids and others, is to capture hydrogen from these molecules. iii) Addition reactions (Eq.1.9): The $\text{SO}_4^{\bullet-}$ can attack the unsaturated bond of alkenes and alkynes of organic contaminants through addition reactions.



The $\text{SO}_4^{\bullet-}$ is less influenced by dissolved organic matter (DOM) compared to $\text{HO}^{\bullet}$, ($k_{\text{SO}_4^{\bullet-} + \text{DOM}} = 6.8 \times 10^3 \text{ mgC}^{-1}\text{s}^{-1}$ and $k_{\text{HO}^{\bullet} + \text{DOM}} = 1.4 \times 10^4 \text{ mgC}^{-1}\text{s}^{-1}$) and presents greater stability, with a half-life of 30 to 40 μs , while the $\text{HO}^{\bullet}$ has 20 ns, under neutral conditions. Therefore, $\text{SO}_4^{\bullet-}$ can sometimes lead to faster degradation than $\text{HO}^{\bullet}$ reactions depending on the type of chemical structure of the contaminants present [50,72,73].

Another radical generated in the system is $\text{SO}_5^{\bullet-}$, which has a moderate oxidizing power (Table 1.3) and can be generated in the reaction between the $\text{HO}^{\bullet}$ and PMS (HSO_5^-) (Eq 1.10) and contribute slightly to the oxidation of contaminants. Under neutral and acidic conditions, the rate constant for this reaction is $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [74].

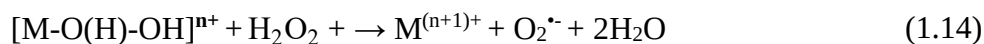
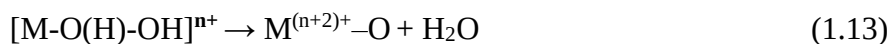
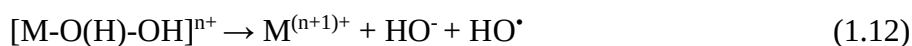


The reactive species generated in the heterogeneous Fenton process can be identified using the Electron paramagnetic resonance (EPR) spin trapping technique or using specific

scavengers such as p-benzoquinone (BQ), methanol (MeOH), and nitrobenzene used for $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$, $\text{HO}^\bullet/\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$, respectively [38].

In addition to the radicals shown in Table 1.3, other non-radical reactive species may be involved in the contaminant degradation process and disinfection such as high valence metals and oxidizing surface intermediate metastable complexes.

It has been reported that intermediate metastable oxidizing surface complexes, here designated as $\text{M}^{n+}\text{-O(H)-OH}$, can be formed on the surface of a catalyst (Eq 1.11) [75,76]. These intermediates can also react through an electron transfer to form $\text{M}^{(n+1)+}$ and $\text{HO}^\bullet$ (Eq. 1.12), like in the classical Fenton process, or through two electron transfer to form high valent metal-oxo oxidant species ($\text{M}^{(n+2)+}\text{-O}$) (Eq. 1.13), such as $\text{Cu}^{\text{III}}\text{-O}$ and $\text{Fe}^{\text{IV}}\text{-O}$ [77]. Additionally, $[\text{M-O(H)-OH}]^{n+}$ can react with other oxidant molecule to form $\text{O}_2^{\bullet-}$ (Eq. 1.14).



All the aforementioned reactive species such as Fe(IV) and Cu(III) can contribute to the degradation of the contaminants and pathogens inactivation.

An important non-radical reactive species is singlet oxygen, which has been reported as a powerful species for reacting with organic contaminants and reacting with bacterial cell constituents, promoting the inactivation of pathogens. It is an excited species of molecular oxygen that has its two electrons at the $2\pi^*$ level (Figure 1.2) with paired antibonding and antipair spins. Unlike ground-state molecular oxygen, singlet oxygen is diamagnetic.

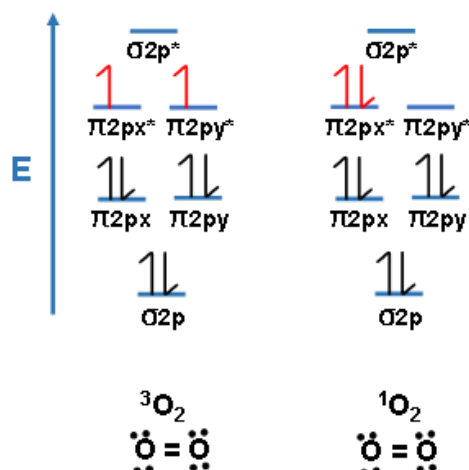


Figure 1.2 Energy diagram of the molecular orbital of oxygen in the triplet ground state and in the singlet excited state.

$^1\text{O}_2$ is a highly selective electrophile with a standard reduction potential of 0.81 ± 0.02 V vs standard hydrogen electrode, that reacts exclusively with unsaturated organic compounds via electrophilic addition, dissociated oxygen via single transfer outer sphere electron, and addition to heteroatoms (e.g. sulfur and nitrogen) [78].

Unlike oxidation by radicals, non-radical processes have the advantage of consuming lower amount of oxidants and are less influenced by organic/inorganic constituents present in the effluent, limiting the formation of toxic disinfection by-products after application of the Fenton processes.

Many catalysts have been investigated for generating radical and non-radical species in water and wastewater treatment systems. A new catalyst that has shown high potential in the generation of reactive species is the LDHs, as will be discussed in detail in the following section.

1.3 Layered Double Hydroxides (LDHs) as catalysts in the heterogeneous Fenton process

First discovered in the early 20th century, LDHs, also called hydrotalcite-type compounds, mixed metallic hydroxides and lamellar double salts are compounds of the natural anionic clay family and its analogous can be synthesized at the laboratory scale [57]. LDHs present octahedral symmetry. To understand the structure of an LDH it is convenient to use the structure of brucite $[\text{Mg}(\text{OH})_2]$, where the M^{2+} cations are at the centers of octahedrons with six hydroxyl groups (OH^-) at the vertices, while each OH^- is surrounded by three metallic

cations and they are pointed toward the corners and form infinite sheets [79]. The structure is maintained by electrostatic forces and hydrogen bonds.

The transformation of brucite into LDH (Figure 1.3) occurs due to the substitution of the trivalent cation (M^{3+}) by the divalent cation (M^{2+}) in the structure, resulting in a residual positive charge that requires the presence of an interlamellar anion with compatible charge to counterbalance the charges in the structure [80].

This process generates an expansion in the stacking of the lamellae, forming the LDH represented by the general formula: $[M(II)_{(1-x)}M(III)_x(OH)_2] (A^{n-})_{x/n} \cdot mH_2O$. $M(II)$ and $M(III)$ represent divalent and trivalent cations and the value of x represents the molar ratio of $M(III)/(M(II) + M(III))$. The range of $0.2 \leq x \leq 0.33$ is generally recognized as suitable for LDH.

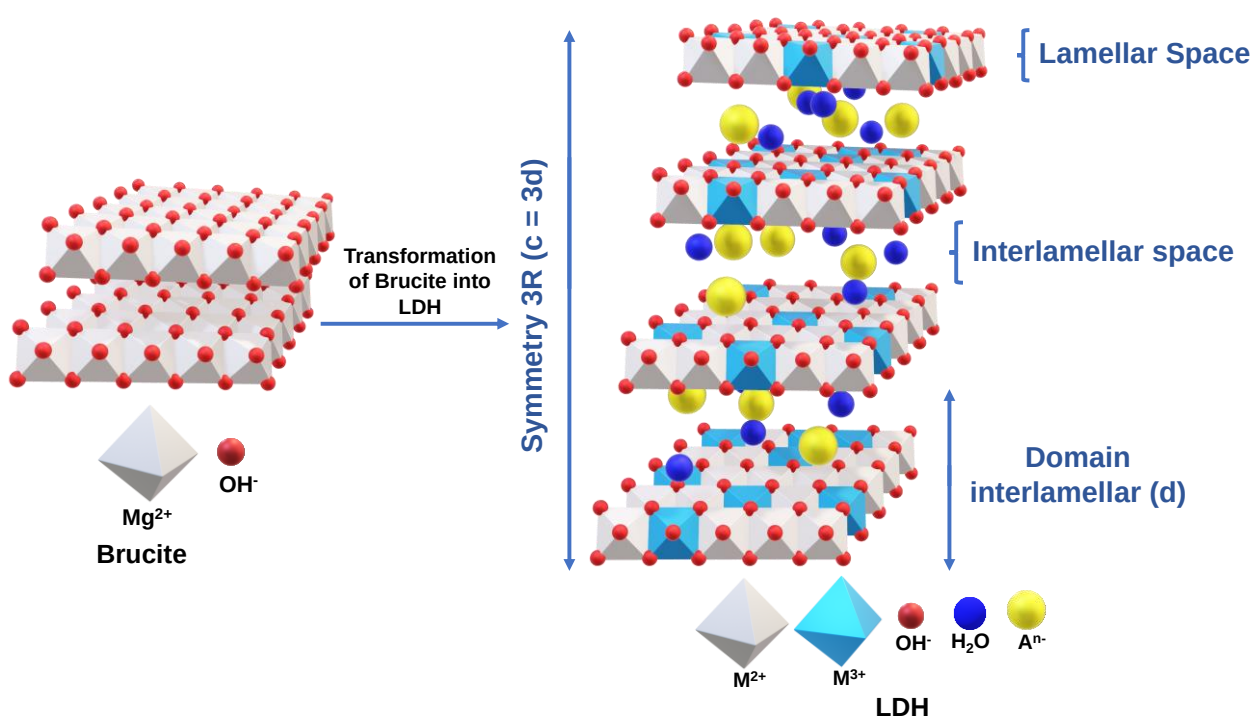


Figure 1.3 Transformation of brucite into LDH.

The interlamellar space of LDHs contains both interlayer anions and water molecules and there is a complex network of hydrogen bonds between the layer hydroxyl groups, anions and water molecules [81].

The term double in LDH does not mean that these materials are formed by only two types of cations, but formed by cations with two different valences, typically divalent and trivalent [81].

When the ionic radius of metal ions is too large, the octahedral coordination will be lost by opening one side of the octahedron into the interlamellar space leading to additional coordination with interlamellar water molecules. Therefore, to be inserted into the double hydroxide structure, the divalent metal ions must have an ionic radius in the range of 0.65–0.80 Å and the trivalent transition metal ions with an ionic radius in the range of 0.62–0.69 Å (with the main exception of Al^{3+} : 0.50 Å) [79]. The double hydroxide structure will only form if the ratio of divalent/trivalent cations is within 2:1 to 4:1 [79].

Some examples of M^{2+} and M^{3+} cations commonly inserted into the LDH structure are: Mn^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Co^{2+} , Mg^{2+} , Fe^{2+} , Ca^{2+} , Cd^{2+} , Ce^{3+} , Al^{3+} , Fe^{3+} , Cr^{3+} , Ga^{3+} , Co^{3+} and La^{3+} [57,82,83].

Chapter 2 of this thesis presents a detailed discussion of incorporation of Cu^{2+} into a 2:1 MgFe-LDH.

In the same way that different types of cations can be present in the lamellar space, different types of anions can be intercalated in the interlamellar space. A large number of anions, including inorganic anions such as F^- , Cl^- , Br^- , I^- , CO_3^{2-} , NO_3^- , ClO_4^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, CrO_4^{2-} , NiCl_4^{2-} , CoCl_4^{2-} and $\text{Fe}(\text{CN})_6^{3-}$, organic anions such as carboxylates, phosphonates, alkyl sulfates, and benzoates and biomolecules such as DNA, amino acids, vitamins, peptides, nucleosides, can be incorporated in the interlamellar space [79,80]. Chapter 3 describes in detail the influence of the interlayer anion on a pyroaurite-type LDH.

LDH is a 2D material and its versatile structure regarding the composition of layers and type of anions leads to functional diversity that allows the use in different fields such as medicine, energy conversion, environmental remediation and heterogeneous catalysis, since they can be applied as catalysts, sensors, sorbents, in batteries, supercapacitors, in drug delivery, cosmetics, antimicrobial materials [57,79,82,84].

LDHs are widely used as sorbents for a wide range of different pollutants from aqueous environment, ranging from oxyanions, phosphates, metals, radioactive materials and organic pollutants such as dyes, pesticides and herbicides [85].

Some examples of methods to synthesize these catalysts are: co-precipitation (direct method), ion-exchange route (indirect method), hydrothermal synthesis, layer-by-layer

assembly, exfoliation-restacking, in-situ synthesis, electrochemical methods, reconstruction/rehydration route (memory-effect method) [79].

The method for LDH synthesis should be selected with caution as it affects the stability of the catalyst and influences the leaching of the constituents.

The most commonly used method for LDH synthesis is the coprecipitation at constant pH due to its easy operation and good reaction yield. Furthermore, several synthesis parameters can be controlled even during the precipitation process such as temperature, pH, rate of addition of metallic salts, concentration of the alkaline solution and anionic species [79]. An image of the apparatus used for the synthesis of CuMgFe-LDH by coprecipitation method is shown in Figure 1.4, which is investigated in chapter 3 of this thesis.

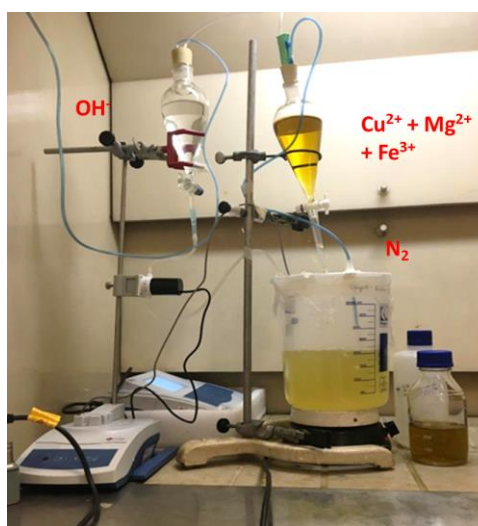


Figure 1.4 Synthesis of CuMgFe-LDH by the coprecipitation method at pH = 11 and under nitrogen atmosphere.

The coprecipitation method occurs by the slow addition of divalent and trivalent cations over the solution containing the interlamellar anion under pH control by the addition of strong base [84]. In this method, the formation mechanism of LDH is based on the condensation of the metal hexa-aqua complexes, leading to the formation of layers with almost uniformly distributed metal cations and with solvated interlamellar anions. Thus, it is possible to form the lamellar and the interlamellar space as shown in Figure 1.3 [84]. After the co-precipitation process, the material is washed with water or an organic solvent and then dried either under vacuo or heat treatment. LDH should be dried within temperatures of 400 - 500 °C because heating at higher temperatures will affect the physicochemical properties due to the formation of stable spinels [79].

Several LDHs have been synthesized by this method and have shown high crystallinity, phase purity and large specific area [86–88]. These are interesting properties to obtain high activity in the process of contaminants degradation. LDHs containing cations that participate in Fenton's reactions are interesting catalysts to be studied in wastewater treatment. According to the web of science database using the keywords “Layered Double Hydroxide” and “Fenton”, the application of LDH in Fenton processes has grown significantly in the last three years (Figure 1.5). Some of this studies reported 100% removal of contaminants from water matrices after between 60 and 100 min [89–91].

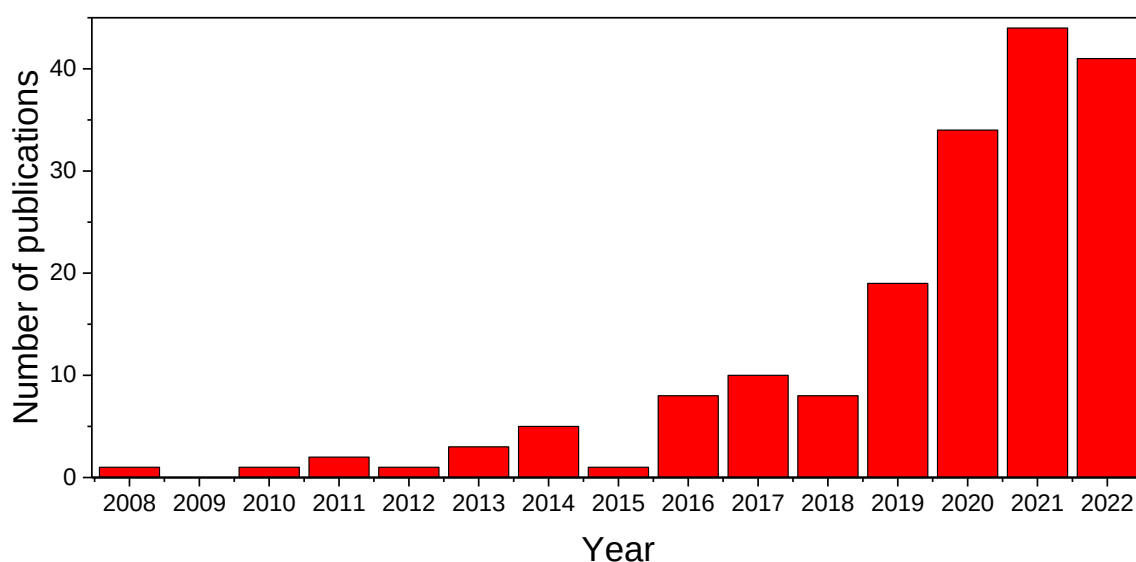


Figure 1.5 Number of published articles about use of LDH in Fenton processes since 2008. Source: Web of Science database, Institute for Scientific Information – ISI. keywords: “Layered Double Hydroxide” AND “Fenton”.

These studies reported some advantages of using LDHs in advanced oxidation processes:

- i) LDHs are easy to synthesize and are very versatile catalysts, as it is possible to select different metal ions to compose the catalyst structure and improve their catalytic properties [57].
- ii) LDH contains many active sites which favors the generation of reactive species on the catalyst surface and a small amount of catalyst may be sufficient to promote efficient degradation [59] .
- iii) LDHs with a high pH of zero point of charge (pH_{zpc}) can inhibit the formation of an acidic environment, functioning as a buffer in neutral conditions, which is interesting for

wastewater treatment. Furthermore, $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ perform well under neutrality and are beneficial for $^1\text{O}_2$ generation [59].

iv) The catalyst maintains stability even after being reused [92], due to its chemical and thermal stability of its structure that can contribute to minimal leaching, important for the application in treatment processes.

v) LDHs can be coupled to other materials such as carbon materials, metallic oxides, semiconductors and magnetic materials to form new LDH-based nanocomposites [59].

vi) The antibacterial properties of LDH have received a lot of attention recently, especially when combined with other compounds or materials [59][92].

vii) The hydroxyl groups on the surface of the catalyst can increase the antimicrobial activity, as they can be converted into $\text{HO}^\bullet$, increasing the concentration of reactive species, which together with the other radical and non-radical species generated after the catalytic decomposition of oxidants will damage DNA and other constituents of bacteria, leading to inactivation and cell death [34].

Furthermore, LDH-based catalysts can be applied to improve some limitations frequently reported in the literature. A problem often encountered in heterogeneous AOP reactions is the limited reuse, strong matrix effect, and low efficiency of oxidant utilization [45,93].

To generate reactive species in systems with LDH and oxidants, the interaction between the oxidant and the reactive redox surface of the catalysts is necessary. Nearby, several surface reactions take place such as catalytic decomposition of oxidants, the generation of radical and non-radical reactive species and reactions of reactive species with oxidants [94]. The hydroxyl group on the catalyst surface can facilitate the activation of the oxidant [95].

Another advantage of using LDH in the treatment of wastewater is the favoring formation of high valence metals on the LDH surface [75] and there is still little understanding of the oxidation mechanism and reaction kinetics of high-valent species with organic contaminants.

The reactive oxygen species generated in the heterogeneous Fenton processes can be efficient for disinfection. Reactive species preferentially attack the bacterial cell membrane including peptidoglycans and lipopolysaccharides. After the cell membrane modification (loss of function), reactive species can attack bacterial cell enzymes and proteins, including blocked DNA replication and mutations [48], which lead to bacterial inactivation.

Recently, Wang et al., 2021 synthesized Mg/Al-LDH, which has an inhibitory effect on the growth of *Vibrio parahaemolyticus*, a marine pathogen that can lead to aquaculture diseases. The process was potentialized when coupled to H₂O₂ and UV irradiation [95]. These results show the potential of LDH for the disinfection of effluents.

According to a search in the Web of Science database, no study has reported a comparison between the application of PMS, PDS and H₂O₂ with LDH. Therefore, as far as we know, for the first time the application of LDH with three different oxidizing agents in the simultaneous removal of antibiotics and disinfection of urban wastewater was demonstrated, which results are discussed in detail in chapter 4 of this thesis.

The general objective of this thesis was to investigate the influence of copper, different anions, and different oxidants on the catalytic activity of LDH for pharmaceuticals degradation via heterogeneous Fenton process and application to the effluent from urban wastewater treatment for simultaneous pharmaceuticals removal and inactivation of pathogens. In this context, the specific objectives of this thesis are:

- a) Synthesis of the LDH MgFe-CO₃ with and without Cu and of CuMgFe-CO₃, CuMgFe-NO₃, CuMgFe-SO₄ and CuMgFe-B(OH)₄ with a 3:1 molar ratio of Mg and Fe cations.
- b) Characterization of the prepared LDHs using different instrumental techniques: X-ray diffractometry (XRD), Fourier transform infrared-attenuated total reflectance (FTIR-ATR), emission scanning electron microscope (FEG-SEM), N₂ adsorption/desorption isotherm curves, UV-Vis diffuse reflectance spectroscopy (DRS), Thermogravimetric analysis (TG), differential thermal analysis (DTA), and derivative thermogravimetry (DTG), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HR-TEM).
- c) Evaluation of the catalytic activity and stability of the different materials prepared in the presence of H₂O₂, PDS and PMS in the dark, solar and under Vis-LED irradiation for pharmaceuticals degradation (sulfathiazole, sulfamethoxazole, ciprofloxacin, cephalixin, amoxicillin and 5-Fluorouracil) and pathogens inactivation (*Escherichia coli* and *Enterococcus faecalis*) in effluent from urban wastewater treatment.
- d) Identification of degradation products of SMX using Liquid chromatography–high resolution mass spectrometry (LC-HRMS) to determine the degradation pathways.

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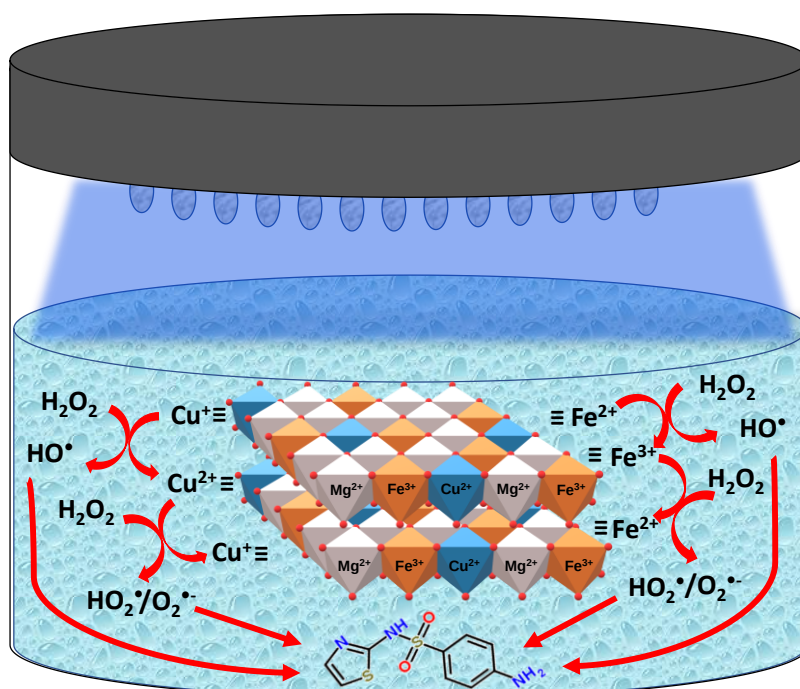
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CHAPTER 2

FENTON-LIKE DEGRADATION OF SULFATHIAZOLE USING COPPER-MODIFIED MgFe-CO_3 LAYERED DOUBLE HYDROXIDE



- ✓ CuMgFe-CO_3 and MgFe-CO_3 layered double hydroxides (LDH) showed phase purity and stability.
- ✓ Presence of surface Cu(I) was demonstrated, which increased after degradation reaction.
- ✓ Copper-LDH showed improved catalytic activity at pH 7.5 even after four cycles use.
- ✓ The role of $\text{HO}^\bullet$ and $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ radicals on sulfathiazole degradation with both LDH was demonstrated.

2 FENTON-LIKE DEGRADATION OF SULFATHIAZOLE USING COPPER-MODIFIED MgFe-CO₃ LAYERED DOUBLE HYDROXIDE

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Abstract

The catalytic activity of layered double hydroxides, with and without insertion of copper, was evaluated in a heterogeneous Fenton process for degradation of the antibiotic sulfathiazole (STZ). The characterizations with different techniques revealed lamellar structures formed by stacking of layers containing magnesium, iron, and copper cations. The insertion of copper in the lamellar structure increased the specific area of the material and the degradation kinetics, achieving complete STZ removal after 90 min. X-ray photoelectron spectroscopy analysis showed the presence of Cu(II) and Cu(I) surface sites, which contributed to the generation of

hydroxyl and hydroperoxyl/superoxide radicals. It also indicated an increase of Cu(I) content after use. For both materials, but specially for LDH without copper, addition of tert-butyl alcohol and p-benzoquinone hindered STZ degradation, indicating the importance of hydroxyl and hydroperoxyl/superoxide radicals in the degradation process, respectively. These results demonstrated the potential of copper-modified MgFe-CO₃ as a catalyst for the degradation of emerging contaminants, offering the benefits of easy preparation and high efficiency in the Fenton process.

Keywords: Pyroaurite, hydroxyl radical, hydroperoxyl/superoxide radical, Vis-LED, copper Fenton.

2.1 Introduction

Pharmaceutical residues are increasingly found in sewage effluents and surface waters, even at low concentrations. The inefficiency of conventional wastewater treatments and the lack of government regulations for the removal of emerging contaminants increase the potential of these residues to harm ecosystems and human health (Baran et al., 2011, Kosma et al., 2014). Antibiotics are hazardous contaminants that can lead to the development of antibiotic-resistant bacteria, which is recognized by the World Health Organization (WHO) as a major public health challenge (Vikesland et al., 2017, W.H. Organization, 2015, Zhang et al., 2020).

Sulfathiazole (STZ), a sulfonamide antibiotic used for the control of infections in veterinary medicine, can be considered as an emerging contaminant that is used widely and is persistent in the environment (Kim et al., 2017, Yu et al., 2016). Its occurrence has been reported at concentrations of ng L⁻¹ in environmental matrices such as effluents from swine, aquaculture, and livestock farms, as well as in surface water, urban wastewater, and effluents from sewage treatment plants (Chung et al., 2016, Ferguson et al., 2013).

Harmful effects due to the presence of STZ in aquatic environments include toxicity towards aquatic organisms and bacterial resistance (Kim et al., 2009, Ji et al., 2012, Zhang et al., 2019). Therefore, it is essential to search for effective and inexpensive alternative processes that can replace conventional biological treatments. For this purpose, advanced oxidation processes (AOPs) are potentially useful, since they offer high efficiency in the degradation of many organic contaminants, mediated by hydroxyl radicals (HO[•]) (Cheng et al., 2016, Kang and Hwang, 2000). This radical non-selectively oxidizes many organic compounds, forming carbon dioxide, water, inorganic ions, and products with lower toxicity (Qiu et al., 2019, Ganiyu et al., 2018, Gupta and Garg, 2018).

One of the most efficient AOPs is the Fenton process, which is based on the decomposition of hydrogen peroxide by iron redox reactions, generating hydroxyl radicals in solution (homogeneous processes) or at the interface with insoluble iron catalysts (heterogeneous processes) (Kang and Hwang, 2000, Candeias and Wardman, 2013, Lin and Lo, 1997, Babuponnusami and Muthukumar, 2014).

Among the desirable properties of catalysts for the heterogeneous Fenton process applied to wastewater treatment are the high stability and reusability of the catalyst, which are accomplished by various materials such as iron oxides (Yang et al., 2020a) metal-organic structures (MOFs) (Lu et al., 2021), supported on clays (Khankhasaeva and Badmaeva, 2020), graphene oxide (GO) (Wang et al., 2019) and silica (Farhadian et al., 2020).

A promising emerging class of catalysts is layered double hydroxides (LDH) based on iron and copper. LDH can be easily synthesized and present a high specific area for the generation of $\text{HO}^\bullet$ from H_2O_2 in Fenton-type reactions (Han et al., 2016, Guo et al., 2010, Wang et al., 2018).

One of the most interesting characteristics of these materials is their structural organization in the form of lamellae, represented by the general formula: $[\text{M(II)}_{(1-x)}\text{M(III)}_x(\text{OH})_2] (\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M(II) is the divalent cation, M(III) is the trivalent cation, and A^{n-} is the intercalated inorganic or organic anion with charge n (Guo et al., 2010, Mishra et al., 2018, Huang et al., 2019). These materials can be found naturally as hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$) and pyroaurite ($\text{Mg}_6\text{Fe}_2(\text{OH})_{16}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$) (Allmann, 1968).

Recently, several LDHs with different cations have been synthesized and applied mostly in the degradation of dyes using H_2O_2 as the oxidant, which degradation efficiency and stability have been discussed (Mishra et al., 2018, Wang et al., 2020, Kpinsoton et al., 2018, Saputra et al., 2020, Yang et al., 2020).

Some advantages associated with the use of modified LDH with different types of cations such as iron and copper in relation to other catalysts are high activity at neutral pH, while iron oxides, for example, demand acid medium for efficient Fenton degradation (Farhadian et al., 2020, Mishra et al., 2018, Saputra et al., 2020). The pH limitation in the Fenton process has been highlighted as the main drawback of the process, which is overcome with the application of LDH.

The most commonly used method for LDH synthesis is the co-precipitation at room temperature and pressure that allows a quick and easy intercalation of the cations that participate in Fenton's reactions such as Cu(II) and Fe(III) (Wang et al., 2018, Wang et al., 2020). This synthesis method eliminates the usual energy demanding steps of heat treatment, which can in some cases generate oxides of lower activity due to changes in the structure and the loss of active sites on the surface of the catalysts. In addition, many reported iron/carbon based materials need further treatments such as calcination at high temperatures after synthesis to build up a catalytic activity (Kpinsoton et al., 2018, Saputra et al., 2020), not necessary for LDH.

Although the co-precipitation method is the most used in the synthesis of LDH (Yang et al., 2020, Yang et al., 2020), other methods have been reported, such as solvo-thermal and hydrothermal processes, which have been applied in the electro-Fenton process for the removal of organic pollutants (Yang et al., 2020, Ghasemi et al., 2019).

The mechanism of degradation and the main reactive species involved in the LDHs based on copper and iron have not been fully clarified. While Cu(II) has been considered to favor the Fenton reaction, it has also been reported that other species are involved in degradation, such as Cu(III) and singlet oxygen (Xiang et al., 2019, Tang and Liu, 2016).

Considering the lack of application of LDH for the Fenton degradation of emerging contaminants such as antibiotics at low concentrations, and that the role of copper in the generation of different radicals is still controversial, this study evaluated the effects of the incorporation of copper in MgFe-CO₃ LDH, correlating the structural characteristics of the material with the catalytic efficiency for generating hydroxyl and hydroperoxyl radicals and degradation of the antibiotic sulfathiazole by Fenton and photo-Fenton processes under visible LED irradiation.

2.2 Experimental

2.2.1 Reagents

Sulfathiazole (99.9%), bathocuproine, tert-butyl alcohol (TBA), bovine catalase (> 10,000 units/mg protein), Na₂CO₃ and p-benzoquinone (BQ) were purchased from Sigma-Aldrich. Fe(NO₃)₃·9H₂O was from Mallinckrodt. Mg(NO₃)₂ and NaOH were from Exodo Cientifica. Cu(NO₃)₂ was from Neon. H₂O₂ (30% wt/wt), NH₄VO₃, and sodium acetate were from Synth. 1,10-phenanthroline was from Vetec. CH₃COOH was from Quimex. Methanol

(HPLC grade) was purchased from J.T. Baker. Milli-Q water from a Direct-Q® system (Millipore) was used for the dilutions and the HPLC analyses.

2.2.2 Preparation of the MgFe-CO₃ and CuMgFe-CO₃ LDHs

The LDHs were synthesized using a 450 mL solution of magnesium and iron hydrogen carbonate (3:1 molar ratio) containing 0% and 7% of Cu(II), relative to the total amount of Mg(II) (0.119 mol) and Fe(III) (0.0399 mol). The content of 7% Cu was chosen to evaluate the effect of magnesium substitution with copper and if the insertion of a small quantity of copper would contribute positively to the catalytic activity of the material since most studies have reported positive contributions to catalytic efficiency with the insertion of considerably higher amounts of Cu, between 11% and 60% in layered double hydroxide (Wang et al., 2018, Wang et al., 2020).

The synthesis was based on the co-precipitation method, using an adaptation of the procedure described by Yun and Pinnavaia (Yun and Pinnavaia, 1995). Firstly, 100 mL of Na₂CO₃ (0.116 mol) solution was added to 1.9 L of ultrapure water, under vigorous stirring, followed by dropwise addition of cations and NaOH solution (2.0 mol L⁻¹) to keep the pH at 11.0 ± 0.5, for precipitation of the metal ions as LDH.

After completing addition of the solution containing the cations, the solid in suspension was washed with deionized water, using eight cycles of centrifugation and resuspension. Finally, the materials were dried under vacuum at room temperature, and sieved through a 100 mesh sieve.

2.2.3 Characterization of the catalysts

X-ray diffractometry (XRD) was performed using a Shimadzu XRD-6000 diffractometer with a graphite crystal as monochromator to select Cu-Kα₁ radiation ($\lambda = 1.5406$ Å), at a scanning rate of 0.02° s⁻¹. Fourier transform infrared-attenuated total reflectance (FTIR-ATR) analysis was performed using a Varian spectrometer coupled to an ATR accessory (GladiATR, Pike Technologies). The LDH morphology was analyzed using a JEOL 7500F field emission scanning electron microscope (FEG-SEM).

The specific areas and porosities of the lamellar materials were determined from N₂ adsorption/desorption isotherm curves obtained at 77 K, using a Micromeritics ASAP 2010 analyzer. UV-Vis diffuse reflectance spectroscopy (DRS) was performed using a Varian Cary 5000 UV-Vis-NIR spectrophotometer, with a sample of MgO for background subtraction.

Thermogravimetric analysis (TG), differential thermal analysis (DTA), and derivative thermogravimetry (DTG) were carried out using a Shimadzu DTG-60AH analyzer. The samples were heated in an Al crucible in the range from 25 °C to 1000 °C, at a rate of 10 °C min⁻¹, under a flow of synthetic air at 50 mL min⁻¹.

Surface analysis was performed by X-ray photoelectron spectroscopy (XPS), using a UNI-SPECS UHV system equipped with an Mg K α X-ray source ($h\nu = 1253.6$ eV), at a pressure of $< 10^{-7}$ Pa. The inelastic backgrounds of the Fe 2p_{3/2}, Cu 2p_{3/2}, and O 1s spectra were subtracted using Shirley's method and the binding energy scale was corrected using the C 1s hydrocarbon group (284.8 eV). The spectra were fitted without placing constraints, using multiple Voigt profiles, employing CasaXPS software.

2.2.4 Degradation experiments

The catalytic activities of the prepared LDHs were evaluated in laboratory-scale experiments performed with 300 mL of 150 $\mu\text{g L}^{-1}$ STZ solution, at room temperature, under irradiation from 21 visible light LEDs (1.3 W; 460 ± 20 nm) and with magnetic stirring (1200–1400 rpm). The reactor used has been described previously (Rojas-Mantilla et al., 2019).

Experiments were performed to evaluate the effect of copper addition to MgFe-CO₃. The catalysts (CuMgFe-CO₃ and the MgFe-CO₃ control sample) were used in the concentration range 0.2–1.0 g L⁻¹, in the presence of H₂O₂ (0, 2, 4, and 6 mmol L⁻¹), in Fenton and photo-Fenton degradation of STZ, at pH 7.5.

Evaluation was made of adsorption of STZ on the catalyst surface, as well as the photocatalytic activity in the absence of H₂O₂. The effect of H₂O₂ photolysis on STZ removal was evaluated using 4.0 mmol L⁻¹ H₂O₂. Dark Fenton experiments were performed using the same reactor, with the LEDs turned off.

2.2.5 Chemical analysis

Aliquots were withdrawn at predetermined time intervals, with addition of bovine catalase to consume residual H₂O₂ and interrupt the reaction. The samples were then filtered through 0.45 μm nylon membranes, prior to analysis.

The concentration of STZ during the degradation process was determined by high performance liquid chromatography (HPLC), using a Shimadzu LC-20AT instrument equipped with a UV-Vis diode array detector (SPD-M20A). The column system consisted of a reversed phase Luna C18 column (250 mm $\times$ 4.6 mm, 5 μm ; Phenomenex, Torrance, CA, USA) coupled to a Phenomenex C18 guard column (4 mm $\times$ 3 mm), kept at 40 °C. The mobile phase was

0.1% acetic acid:methanol (85:15), with isocratic elution at a flow rate of 1.0 mL min^{-1} . The injection volume was $50 \text{ }\mu\text{L}$ and STZ was detected at a wavelength of 284 nm . Under these conditions, the STZ retention time was $10.07 \pm 0.05 \text{ min}$ and the limits of detection (LOD) and quantification (LOQ) were 4.8 and $16.0 \text{ }\mu\text{g L}^{-1}$, respectively, calculated using the regression equation of the calibration curve (triplicate) and three and ten times the standard deviation of the intercept, respectively. Considering that the initial STZ concentration employed in the experiments was $150 \text{ }\mu\text{g L}^{-1}$, a concentration below LOD represents at least 97% degradation, which for simplicity is referred as total removal.

The hydrogen peroxide consumption and total soluble iron and copper concentrations were quantified spectrophotometrically, using a Shimadzu UVmini-1240 spectrophotometer. The residual H_2O_2 was determined by measuring the absorbance at 450 nm after reaction with ammonium metavanadate (Nogueira et al., 2005). The concentration of copper ions in the solution after the degradation process was determined using the bathocuproine spectrophotometric method ($\lambda = 484 \text{ nm}$) (Baird and Bridgewater, 2017). The concentration of iron ions was determined spectrophotometrically, using 1,10-phenanthroline, with maximum absorption at 510 nm .

For indirect investigation of the degradation process and evaluation of the radical species involved in the degradation process, TBA and BQ were used as $\text{HO}^\bullet$ and $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ scavengers, respectively. The TBA (100 mmol L^{-1}) and BQ (at 1 mmol L^{-1}) were added to STZ/LDH suspensions in separate experiments.

The capacity for reuse of the CuMgFe-CO_3 catalyst in the Fenton process was evaluated using four cycles of 120 min , with aliquots removed before and after each cycle. After 120 min the material was recovered, washed, centrifuged and after discarding the supernatant, the material was added to 300 mL of STZ solution containing 4 mmol L^{-1} of H_2O_2 . This procedure was performed from the second to the fourth cycle.

2.3 Results and discussion

2.3.1 LDH characterization

The two catalysts (with 0% and 7% of copper) presented similar X-ray diffractograms, with (003), (006), and (009) basal plane peaks corresponding to the stacking of the lamellae, characteristic of the LDH structure (Fig. 2.1) (Wang et al., 2020, Cao et al., 2017). The diffractograms showed that no other crystalline phases were formed in the materials. Considering a hexagonal unit cell and crystalline rhombohedral system ($R3m$), the (003) and

(110) peak positions were used to calculate the lattice parameters $dhkl$, $a = 2d_{110}$, and $c = 3d_{003}$, as well as the crystallite size in the c direction (Table 2.1) (Mishra et al., 2018, Suryanarayana, 1998) The basal spacing was approximately 0.78 nm for both materials, determined using the Bragg equation (Allmann, 1968).

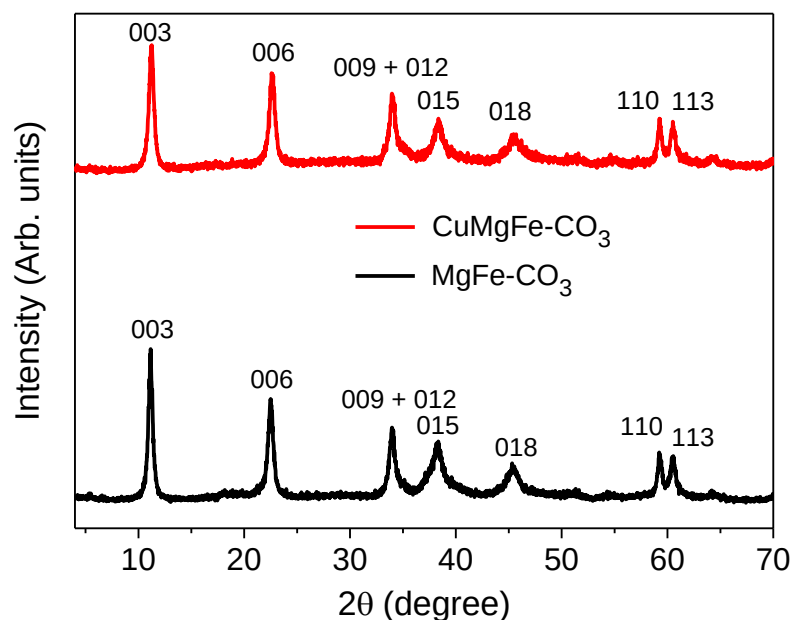


Figure 2.1 X-ray diffractograms of MgFe-CO_3 and CuMgFe-CO_3 .

The values obtained were similar to those reported elsewhere for the basal spacing of LDHs containing carbonate as the intercalation anion (Antonyraj and Kannan, 2011, Miyata, 1983, Wang et al., 2018, Wang et al., 2016). The lattice parameter a gives the distance between the cations, while the parameter c is influenced by the cation charge, nature of the intercalated anion, and water content.

The average crystallite size along c -axis were estimated using the Scherrer equation by the FWHM values of the (003) reflections. It can be observed that the parameters a and c , as well as the average crystallite size, were very similar for the two synthesized materials (Table 2.1) (Zhao et al., 2002).

This similarity could be explained by considering that the materials were prepared using the same molar ratio (3:1) of M(II)/M(III) , with CO_3^{2-} as an intercalation anion (Baliarsingh et al., 2013). In addition, the isomorphic substitution of the Mg(II) cation by Cu(II) , with almost the same ionic radius (Cu(II) : 0.073 nm; Mg(II) : 0.072 nm) (Xu et al., 2011) resulted in no significant difference of parameters “ a ” and “ c ”, which were very similar to those of pyroaurite

($\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$): $a = 0.31 \text{ nm}$ and $c = 2.34 \text{ nm}$ (Allmann, 1968, Miyata, 1983, Benselka-Hadj Abdelkader et al., 2011).

Table 2.1 Lattice parameters “a” and “c”, basal spacing (d_{003}), average crystallite size in the c direction, and specific area for the MgFe-CO_3 and CuMgFe-CO_3 particles.

Parameter	MgFe- CO_3	CuMgFe- CO_3
$d_{003} \text{ (nm)}$	0.79	0.78
$a \text{ (nm)}$	0.31	0.31
$c \text{ (nm)}$	2.37	2.36
Crystallite size in the c direction (nm)	14.13	12.75
Specific area ($\text{m}^2 \text{ g}^{-1}$)	42 ± 2	91 ± 5

On the other hand, the N_2 adsorption/desorption isotherms showed that the insertion of Cu(II) in the LDH structure resulted in an increase of the specific area from 42 ± 2 to $91 \pm 5 \text{ m}^2 \text{ g}^{-1}$ (Table 2.1). According to the IUPAC classification, the CuMgFe-CO_3 presented a type II isotherm, characterized by the absence of a plateau of the relative pressure (P/P_0) close to 1, evidencing the presence of macropores (Fig. 2.S1). The hysteresis loop between the adsorption and desorption branches was in accordance with the H3 type, which is usually observed for materials with slit-shaped pores formed by platelet aggregation, resulting in a broad pore size distribution (Gonçalves et al., 2019).

The FTIR-ATR spectra showed a broad band in the range from 3750 to 3250 cm^{-1} , corresponding to stretching of the hydroxyl groups present on the lamellae of the double hydroxide and of water molecules intercalated or adsorbed in the material (Fig. 2.2). A band centered at 1631 cm^{-1} was due to bending vibrational modes of OH^- of water molecules, while a more intense band at around 1375 cm^{-1} was due to vibrations characteristic of C-O bonds of the intercalated carbonate anions (CO_3^{2-}). Intense vibrational bands at around 660 cm^{-1} were related to stretching of metal-oxygen bonds in the inorganic lamellae (Wang et al., 2018, Benselka-Hadj Abdelkader et al., 2011, Yang et al., 2018).

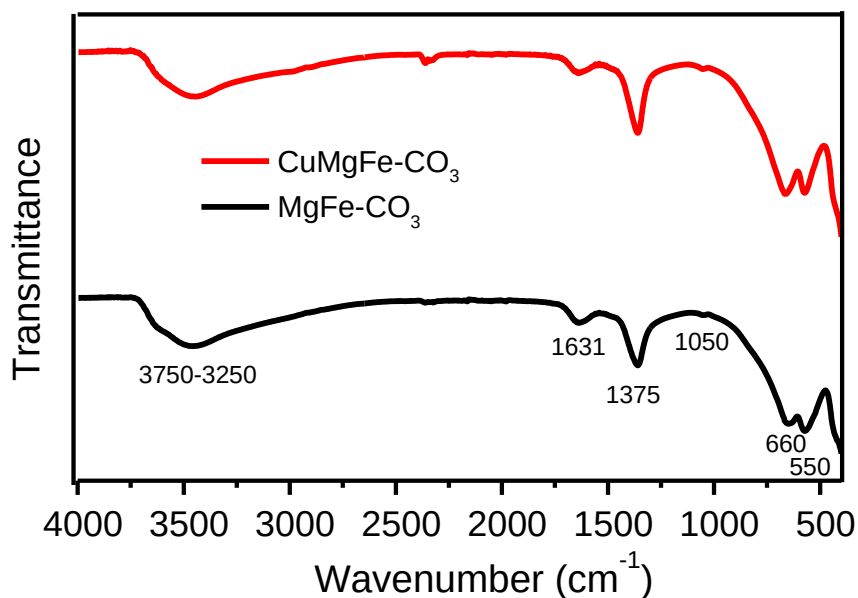
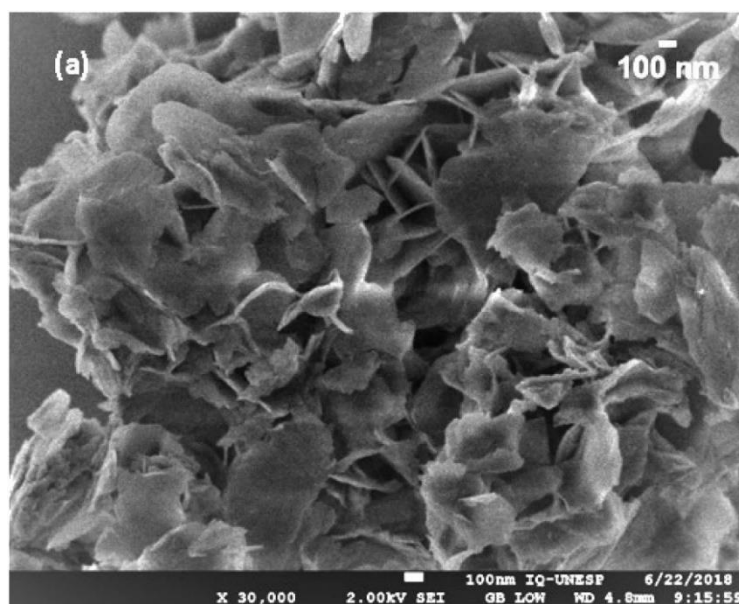


Figure 2.2 FTIR-ATR spectra of the synthesized MgFe-CO_3 and CuMgFe-CO_3 LDHs.

The FEG-SEM micrograph of the two synthesized materials were similar and resembled that of pyroaurite (Fig. 2.3) (Wang et al., 2018). This structure of agglomerated stacks of layers containing magnesium, iron, and copper cations was organized in the form of a flower ball, also described as sand-rose or platelet-like (Allmann, 1968, dos Santos et al., 2017).



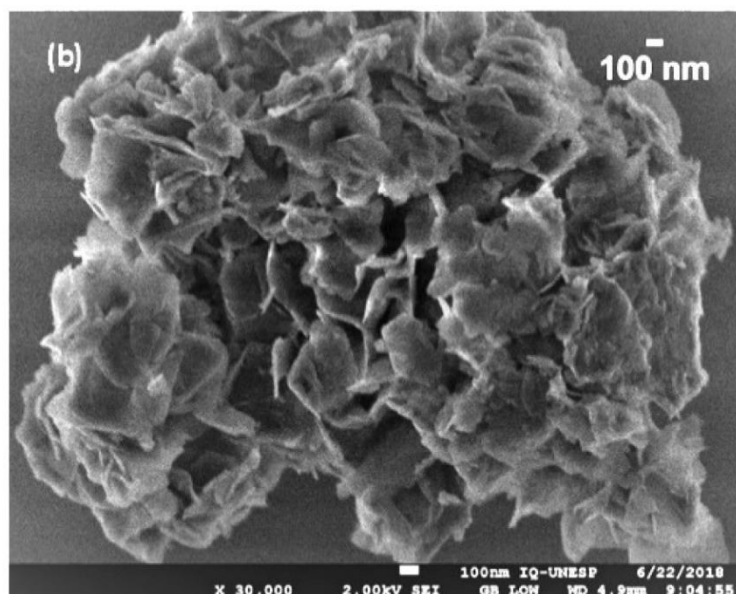


Figure 2.3 SEM images of the synthesized LDHs: (a) MgFe-CO_3 and (b) CuMgFe-CO_3 .

The UV-Vis absorption spectra of the two catalysts were similar in the UV-B region. However, the CuMgFe-CO_3 sample showed higher absorbance in the UV-A region and in the visible light region above 500 nm (Fig. 2.4). This was an interesting feature, since it would favor the use of visible radiation in the photo-Fenton process. Similar absorption profiles have been reported elsewhere for LDHs containing copper, magnesium, and iron (Gonçalves et al., 2019, Daneshvar et al., 2019, Carja et al., 2013).

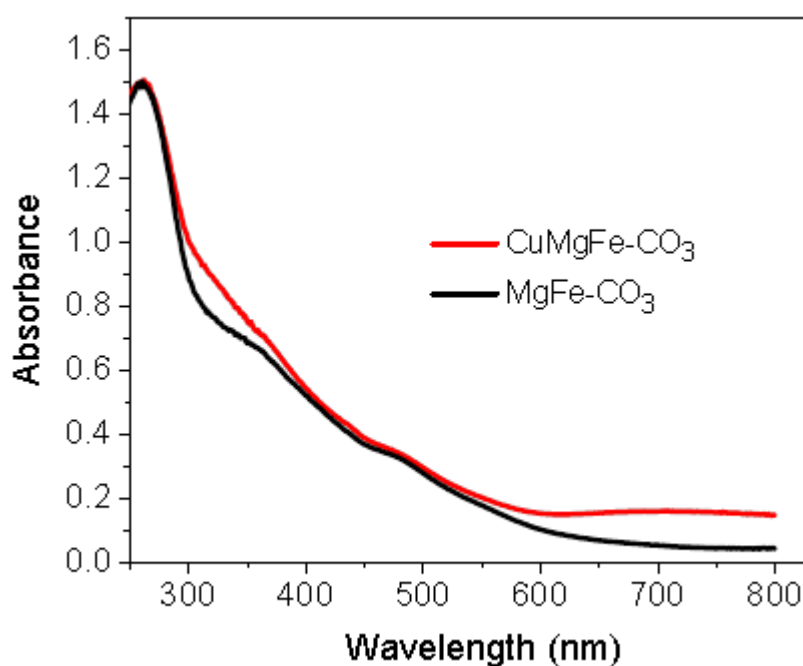


Figure 2.4 UV-Vis absorption spectra of MgFe-CO_3 and CuMgFe-CO_3 .

The TGA-DTA curve profiles for both catalysts showed two stages of weight loss, with two endothermic peaks (Fig. 2.5). The first event, at 150 °C, was associated with a mass loss of approximately 20%, which could be attributed to the elimination of absorbed and intercalated water molecules. The second peak, at around 350 °C, was related to major structural modifications, with release of the water remaining in the interlamellar space, dehydroxylation of the layers and decomposition of the intercalated carbonate anions (Wang et al., 2018, Gonçalves et al., 2020, Magri et al., 2019, Kovanda et al., 2003).

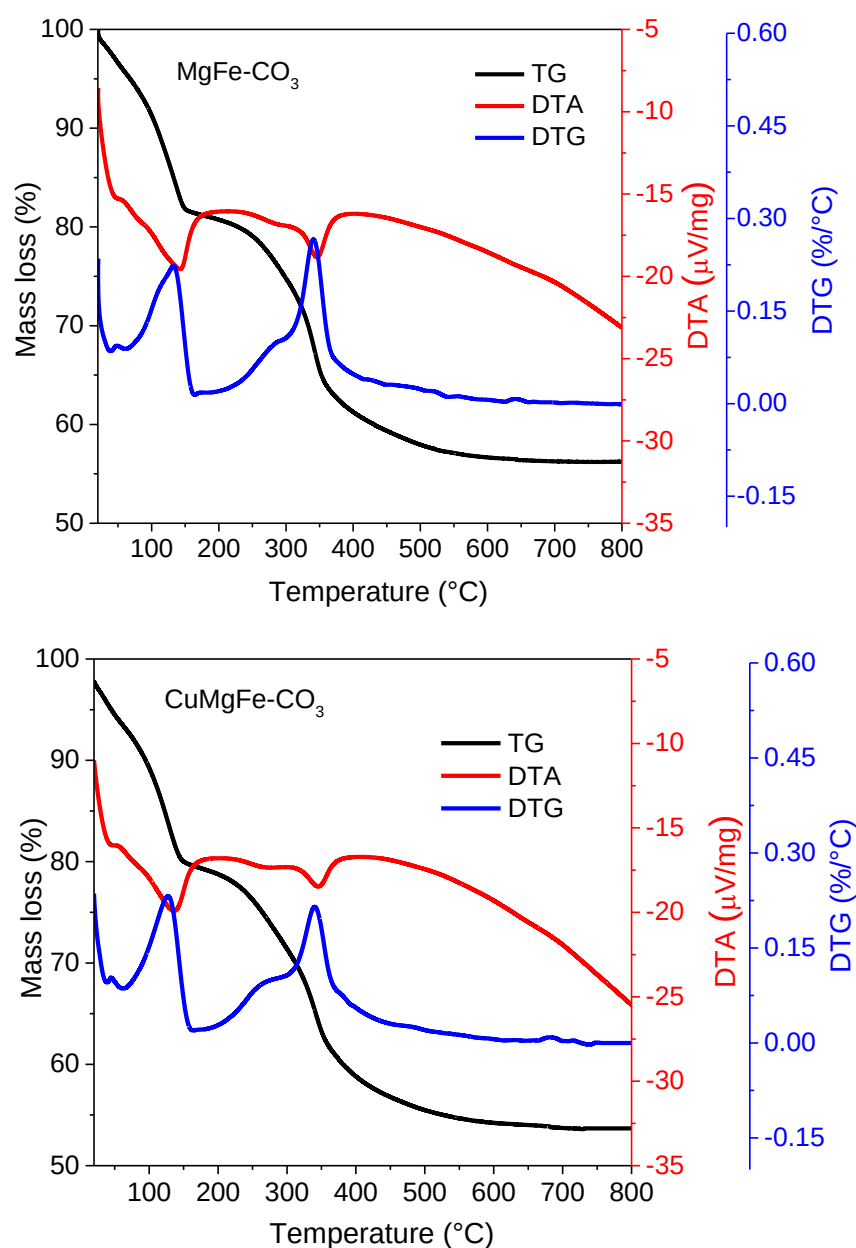


Figure 2.5 TG, dTG, and dTA thermal analyses of the synthesized materials: MgFe-CO_3 and CuMgFe-CO_3 .

2.3.2 Degradation of STZ

To assess the effect of copper insertion in the structure of LDH in the Fenton reactions, the catalyst dosage as well as the H_2O_2 concentration using both materials, with and without copper insertion, were evaluated to verify the best experimental conditions and understand the degradation mechanism involved in the process and the main reactive species present, besides of the material stability.

2.3.2.1 Effect of LDH dosage

The natural pH of the STZ solution was 5.6. However, after addition of LDH powder to the solution, a rapid increase to pH 7.5 (CuMgFe-CO_3) and pH 7.2 (MgFe-CO_3) was observed in the first minute, followed by stabilization around pH 7.8 until the end of the experiment (Fig. 2.S2). This pH increase was due to the hydroxyl groups present in the catalyst structure, which neutralized the solution. Although this pH is not optimal for the Fenton reaction, the material is not stable at $\text{pH} < 4$ and the pH increase occurred even with prior acidification of the solution (Zhang et al., 2019b).

Considering that most effluents containing pharmaceutical compounds, such as those from sewage treatment plants, are close to neutrality, there are clear advantages of carrying out the degradation reaction under near-neutral conditions. Therefore, all the experiments were performed at the natural pH obtained after dispersion of the catalyst in the solution (pH 7.5), without any pH control.

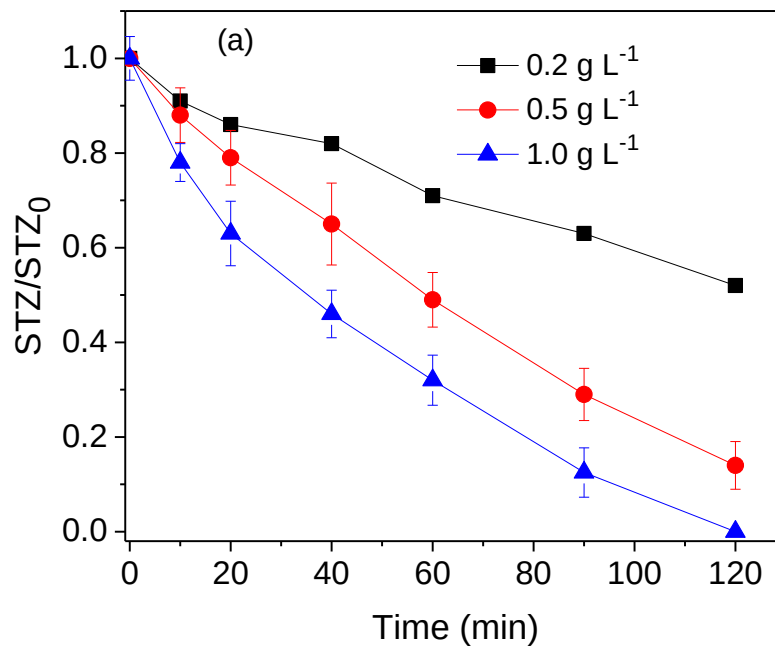
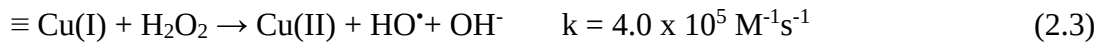
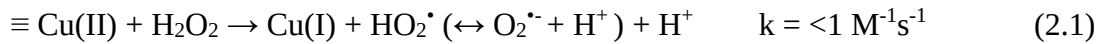
In heterogeneous Fenton processes, it is essential to determine the optimal catalyst concentration (Gonçalves et al., 2019, Yang et al., 2018, dos Santos et al., 2017, Daneshvar et al., 2019). For all the concentrations evaluated, the copper-containing CuMgFe-CO_3 LDH provided significantly higher STZ degradation, compared to the MgFe-CO_3 catalyst, under identical experimental conditions with Vis-LED irradiation (Fig. 2.6).

For the MgFe-CO_3 catalyst, there was a progressive increase in STZ degradation as the concentration was increased, achieving complete STZ removal ($\text{STZ} < \text{LOD}$; removal $> 97\%$) with 1.0 g L^{-1} of catalyst, after 120 min. For this material, the calculated stoichiometric efficiency (amount of STZ degraded in relation to H_2O_2 consumption) was 0.9% for LDH without copper (1.0 g L^{-1}) and 1% for material with copper Cu-LDH (0.5 g L^{-1}) (Fig. 2.S3), resulting in total STZ removal after 90 min. Low stoichiometric efficiencies for H_2O_2 consumption are justified due to the low initial concentration of STZ besides the low amount

of Cu(II) and Fe(III) present in the catalyst structure, which advantages were pointed out previously.

Hence, a lower concentration of copper-containing LDH (0.5 g L^{-1}) provided faster STZ degradation to undetectable levels. The LDH without copper appeared to interact less effectively with H_2O_2 , although this could be partially compensated by increasing the catalyst concentration, which increased the number of active sites for H_2O_2 decomposition and improved STZ degradation (Zhang et al., 2019, Abdullah et al., 2018, Lee et al., 2016).

As shown in Eqs. (2.1 - 2.5) , the incorporation of copper in LDH results in electron transfer from Cu(II) to H_2O_2 , increasing the rate of $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ generation and leading to reduction of Cu(II) to Cu(I) and accelerating the degradation due to the faster reaction of Cu(I) with H_2O_2 , compared to Fe(II) in the classical Fenton catalyst, generating $\text{HO}^\bullet$ and $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ in a Fenton-like process.



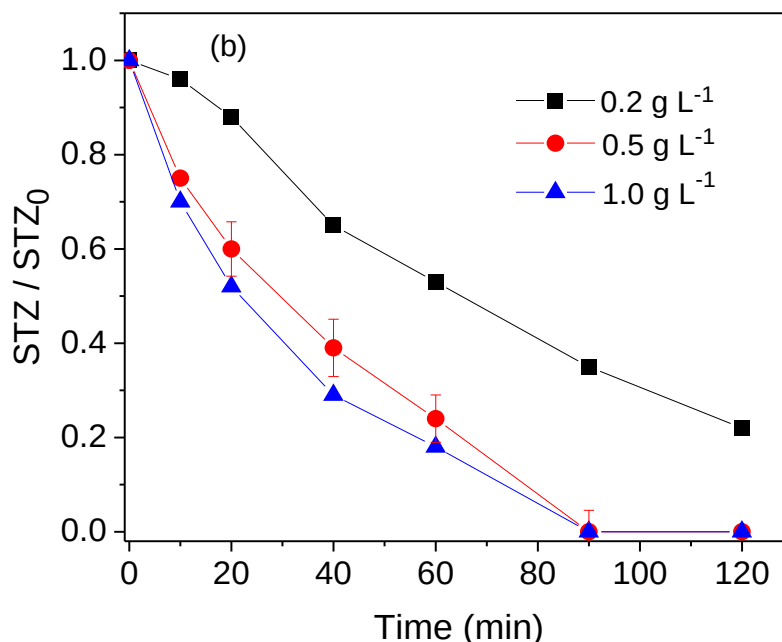


Figure 2.6 Effect of LDH concentration on STZ degradation. Conditions: pH 7.5; 150 $\mu\text{g L}^{-1}$ STZ; 4 mmol L^{-1} H_2O_2 ; Vis-LED irradiation, (a) MgFe-CO_3 and (b) CuMgFe-CO_3 .

2.3.2.2 Effect of H_2O_2 concentration

Considering that similar degradation rates were obtained with CuMgFe-CO_3 at 0.5 and 1.0 g L^{-1} , the concentration of 0.5 g L^{-1} was chosen for further experiments and comparison with the use of MgFe-CO_3 at 1.0 g L^{-1} . It should be noted that the specific area of CuMgFe-CO_3 was about 2.2-fold greater than that of MgFe-CO_3 (Table 2.1), so the surface available for reaction were approximately the same for the two materials at these concentrations.

The results for STZ degradation in the absence of H_2O_2 confirmed that H_2O_2 was essential to promote STZ degradation according to a heterogeneous Fenton reaction, since only 10% STZ removal was observed, irrespective of the insertion of copper, indicating that there was no significant photocatalytic activity of LDH under visible irradiation in the absence of H_2O_2 (Fig. 2.7). In the presence of 2 mmol L^{-1} H_2O_2 , the degradation efficiency increased to approximately 80% after 120 min, for both materials, although a slightly higher rate was observed using the copper-containing LDH.

Increase of the H_2O_2 concentration to 4 mmol L^{-1} further improved the degradation process, with the STZ concentration decreasing to undetectable levels after 90 min (with CuMgFe-CO_3) and 120 min (with MgFe-CO_3). It is interesting to note that for both catalysts, similar degradation efficiencies were obtained with 4 and 6 mmol L^{-1} of H_2O_2 , indicating that concentrations above 4 mmol L^{-1} resulted in H_2O_2 decomposition, without necessarily increasing $\text{HO}^\bullet$ generation. These results also showed the beneficial effect of insertion of copper

in the LDH structure, observed for all H_2O_2 concentrations at lower copper LDH loading. Considering that H_2O_2 concentrations above 4 mmol L^{-1} did not improve STZ degradation, this concentration was adopted in the subsequent experiments.

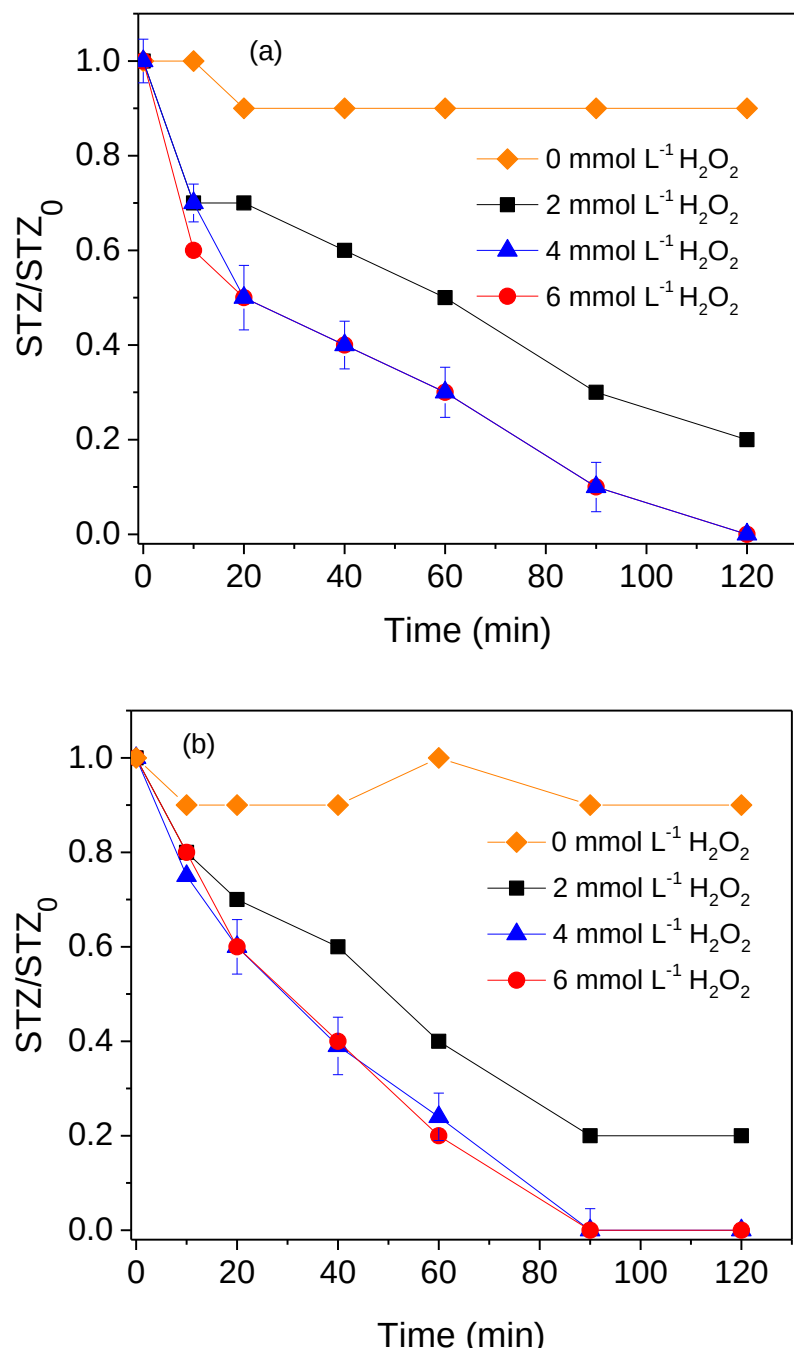


Figure 2.7 Effect of H_2O_2 concentration on STZ degradation. Conditions: pH 7.5; $150 \mu\text{g L}^{-1}$ STZ; Vis-LED irradiation; (a) MgFe-CO_3 at 1.0 g L^{-1} ; (b) CuMgFe-CO_3 at 0.5 g L^{-1} .

2.3.2.3 Effect of radical scavengers in the dark process

Experiments in the dark and in the absence of H_2O_2 , showed no adsorption capacity of either LDH despite the high specific areas of the materials (Fig. 2.S4). Similarly, H_2O_2

photolysis resulted in only 10% STZ removal, while no significant removal was observed under visible LED irradiation alone (Fig. 2.S4). In the dark, both catalysts provided efficient Fenton degradation of STZ, with approximately 90% STZ removal after 120 min

To understand the role of reactive oxygen species in the degradation mechanism, TBA and BQ were used as scavengers for hydroxyl and hydroperoxyl/superoxide radicals, respectively (Fig. 2.8).

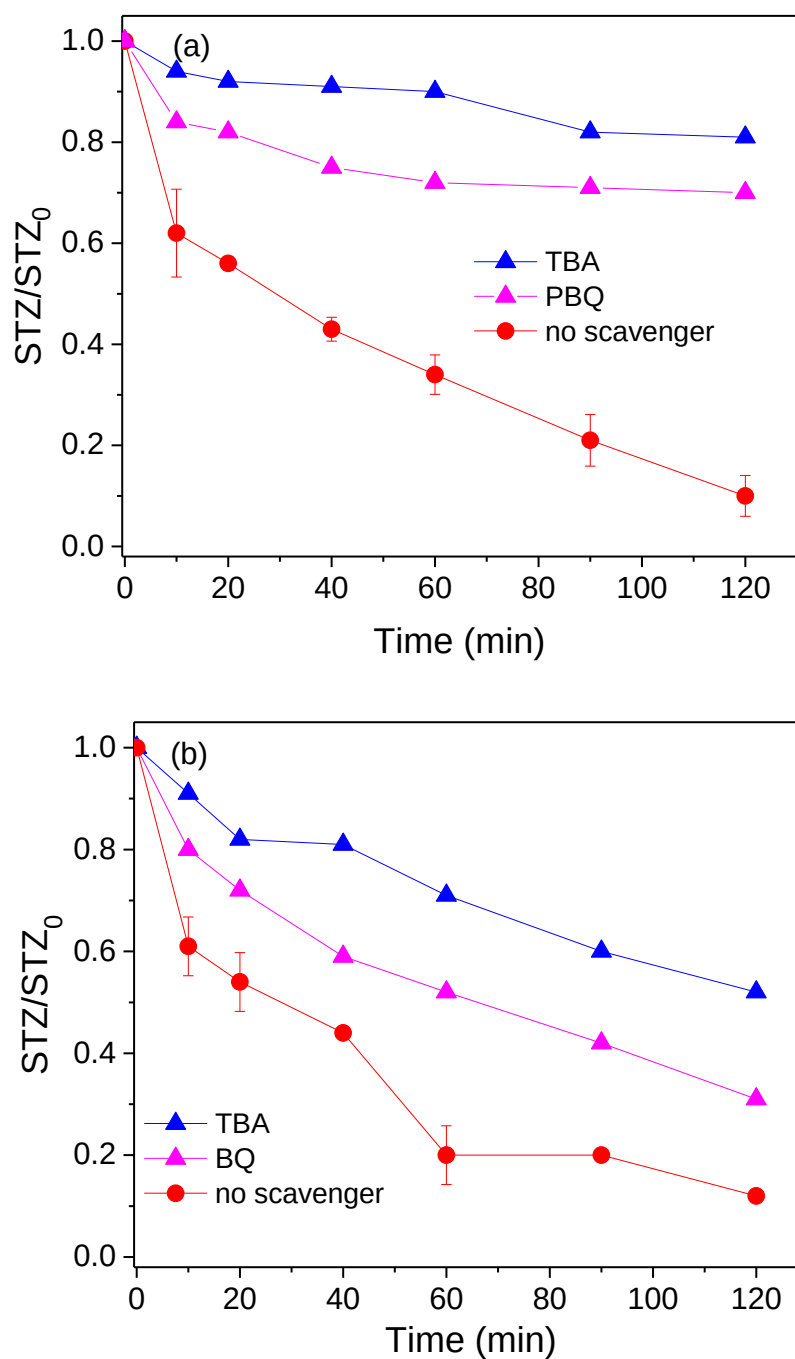


Figure 2.8 Influence of the presence of TBA and BQ on STZ degradation in the using (a) MgFe-CO₃ (1.0 g L⁻¹) and (b) CuMgFe-CO₃ (0.5 g L⁻¹). Conditions: pH 7.5; 150 µg L⁻¹ STZ; 4 mmol L⁻¹ H₂O₂; 100 mmol L⁻¹ TBA; 1 mmol L⁻¹ de BQ.

In the absence of the scavengers, 90% STZ degradation was obtained after 120 min for both MgFe-CO_3 and CuMgFe-CO_3 , which followed a first order reaction model with a rate constant (k) of 0.019 min^{-1} . However, in the presence of TBA, a known $\text{HO}^\bullet$ scavenger, STZ degradation achieved only 19% ($k = 0.002 \text{ min}^{-1}$) with LDH without copper (MgFe-CO_3) and 48% ($k = 0.006 \text{ min}^{-1}$) with LDH with copper (CuMgFe-CO_3). Similarly, in the presence of BQ, degradation achieved 30% ($k = 0.004 \text{ min}^{-1}$) and 69% ($k = 0.010 \text{ min}^{-1}$) using the LDH without and with copper, respectively.

These results indicate that both the hydroxyl and hydroperoxyl/superoxide radicals have an important role in the oxidation mechanism of STZ, with hydroxyl radical as the main oxidative species, and that LDH with copper was less influenced by the presence of radical scavengers.

2.3.2.4 Catalyst stability and CuMgFe-CO_3 reuse

For a catalyst to be a candidate for application in wastewater treatment, it is essential to confirm its stability and capacity to maintain catalytic activity during several degradation cycles. Therefore, experiments were conducted to evaluate the STZ degradation efficiency during four 120-min cycles of the Fenton process in the dark (Fig. 2.S5). The results showed that the catalytic activity of CuMgFe-CO_3 decreased only 10% after the fourth cycle, indicating a good stability of the catalyst.

In addition, the stabilities of the materials were evaluated by determining the concentrations of total soluble iron and copper after the experiments using 0.5 g L^{-1} CuMgFe-CO_3 and 1.0 g L^{-1} MgFe-CO_3 . No significant leaching was observed, with total iron concentrations $< 1.73 \mu\text{mol L}^{-1}$ and copper $< 0.35 \mu\text{mol L}^{-1}$. These concentrations corresponded to less than 1% of the contents of the metals in the catalysts, indicating high stability under the conditions employed (pH 7.5).

Possible structural changes of the LDHs during the Fenton reaction were evaluated by analyzing the materials recovered after four cycles, using XRD, FTIR, and XPS. The FTIR spectra (Fig. 2.S6) maintained similar spectrum when compared to the spectrum before degradation. It was possible to observe characteristic bands of the O-H bonds corresponding to stretching of the hydroxyl groups and water molecules, of C-O due to the interlayer carbonate anion and M-O metal-oxygen bond. Furthermore, the XRD patterns of the (003), (006), and (009) basal planes remained unchanged, indicating preservation of the layered arrangement, without any phase segregation in the LDH structure (Fig. 2.S7).

XPS analysis was used to identify the bonding states of Cu and Fe surface species of the CuMgFe-CO₃ catalyst, before and after four Fenton degradation cycles (Fig. 2.9). The Fe 2p_{3/2} high-resolution spectra were deconvoluted into four components at 709.5, 711.1, 712.3, and 514.3 eV, related to the presence of Fe(II), Fe(III) (Fe₂O₃ and FeOOH), and an Fe(III) shake-up satellite, respectively. Comparison of the spectra showed that the iron sites remained unaffected after the degradation process. Disregarding the Cu(II) shake-up satellites at higher binding energies of the Cu 2p_{3/2} spectra, the three components at 932.2, 933.7, and 934.8 eV could be attributed to Cu(I) and Cu(II) (CuO and Cu(OH)₂) species, respectively (Wang et al., 2018, Zhang et al., 2019).

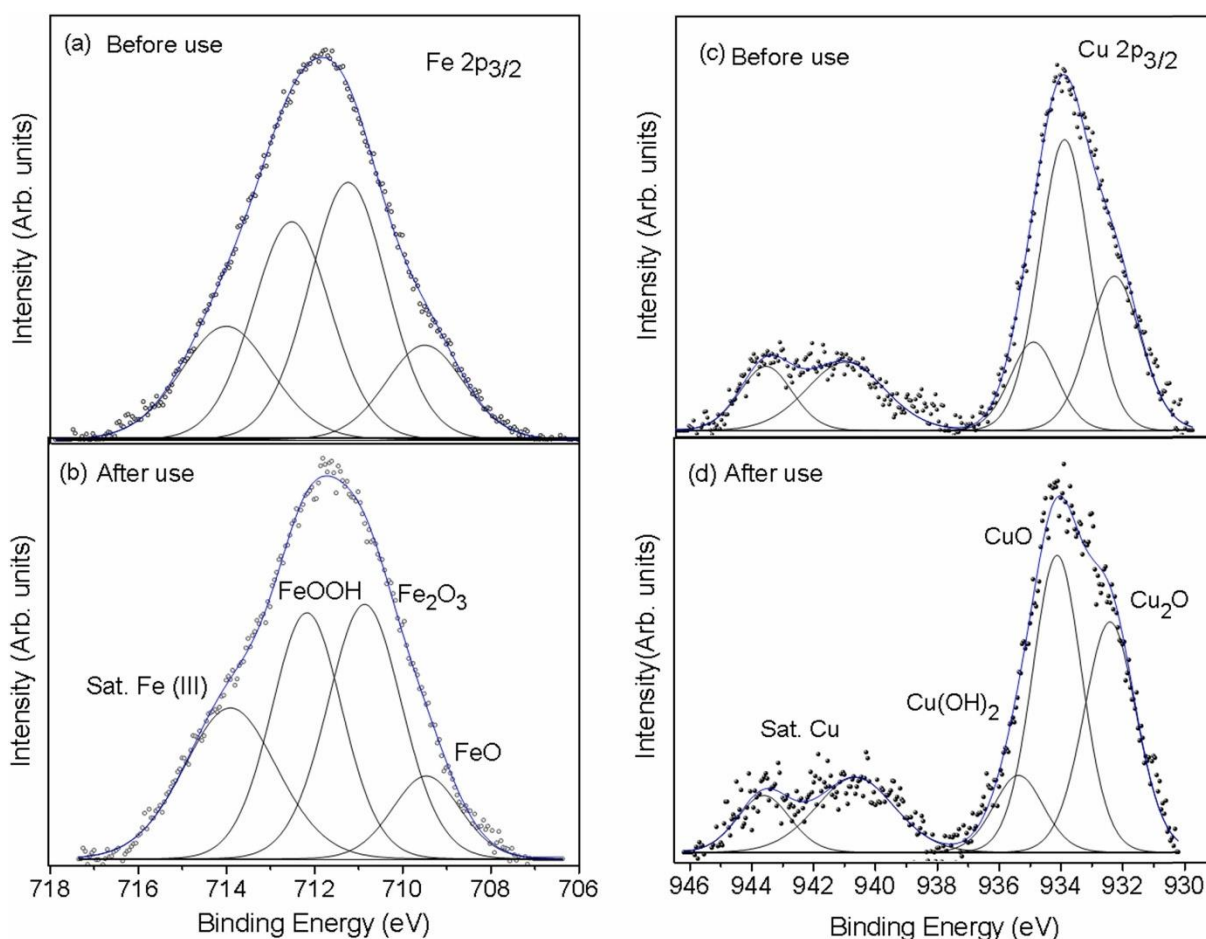


Figure 2.9 XPS Fe 2p_{3/2} (a, b) and Cu 2p_{3/2} (c, d) spectra of CuMgFe-CO₃, before (a, c) and after (b, d) four cycles of use in the Fenton process.

The presence of different Cu bonding states (Cu(I) and Cu(II)) depends on the chemical composition and the nature of isomorphous substitution of Fe and Mg sites by Cu cations (Lenglet et al., 1986, Li et al., 2004). However, it is quite common to observe in the XPS spectra the presence of a weak component assigned to Cu(I) species in samples prepared using Cu(II) precursors, due to a partial X-ray induced-reduction of Cu(II), which cannot be excluded in the

case of the LDH structure (Stellato et al., 2019, Zezin et al., 2009). The observed increase of Cu(I) after four process cycles suggested the reduction of Cu(II) during the catalytic decomposition of H_2O_2 (Eq. (2.1)). The presence of Cu(I) sites at the surface of the LDH structure is important, since this can contribute significantly to the generation of hydroxyl radicals (Eq. (2.3)).

As shown in Eqs 2.1 - 2.5, the insertion of Cu(II) in the CuMgFe-CO_3 material could lead to a synergistic effect of Fe and Cu, resulting in significantly increased generation of hydroxyl and hydroperoxyl/superoxide radicals and higher degradation efficiency, compared to MgFe-CO_3 . The results of the degradation assays and the XPS analyses suggested the formation of Cu(II)/Cu(I) and Fe(III)/Fe(II) redox pairs, with the presence of iron and copper hydroxyl groups on the surfaces of the LDHs. This provided effective decomposition of H_2O_2 to form $\text{HO}^\bullet$ and $\text{HO}_2^\bullet/\text{O}_2^\bullet$, resulting in enhanced STZ degradation, compared to the copper-free LDH.

2.4 Conclusions

The findings revealed the significant effect of copper insertion in LDH used for Fenton degradation reactions. The MgFe-CO_3 and CuMgFe-CO_3 LDHs showed phase purity and stability. XPS analysis confirmed the insertion of Cu(II) in the LDH lattice and the presence of Cu(I), which enhanced the degradation efficiency. Complete STZ removal was achieved after 90 min reaction with $4 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ and $0.5 \text{ g L}^{-1} \text{CuMgFe-CO}_3$, at pH 7.5, under Vis-LED irradiation. However, for both LDHs, experiments in the presence of the scavengers TBA and BQ evidenced the importance of both hydroxyl and hydroperoxyl/superoxide radicals in the degradation process.

The good stability and catalytic efficiency of CuMgFe-CO_3 at near neutral pH and even after four cycles use, make this material a potential candidate for heterogeneous Fenton processes employed for the effective degradation of emerging contaminants.

Credit authorship contribution statement

Nayara de Melo Costa-Serge: Conceptualization, Investigation, Methodology, Writing - original draft. Rosembergue Gabriel Lima Gonçalves: Conceptualization, Methodology. Hernán Dario Rojas-Mantilla: Investigation, Methodology. Celso Valentim Santilli: Data analysis, Funding acquisition. Peter Hammer: Data analysis, Writing - review & editing. Raquel Fernandes Pupo Nogueira: Project administration, Supervision, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Materials

Fenton-like degradation of sulfathiazole using copper-modified MgFe-CO₃ layered double hydroxide

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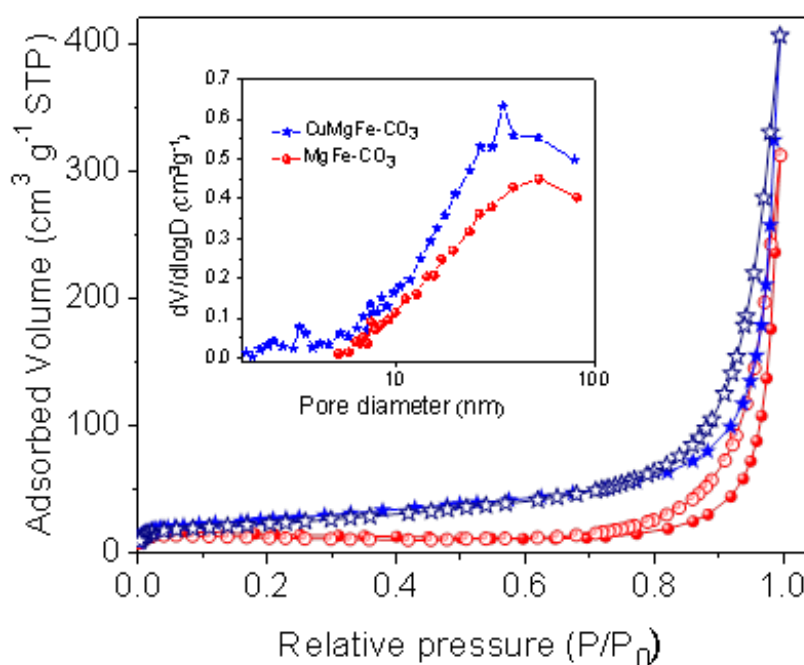


Figure 2.S1 N₂ adsorption/desorption isotherms of the MgFe-CO₃ and CuMgFe-CO₃ catalysts. The inset shows the pore size distributions of the materials.

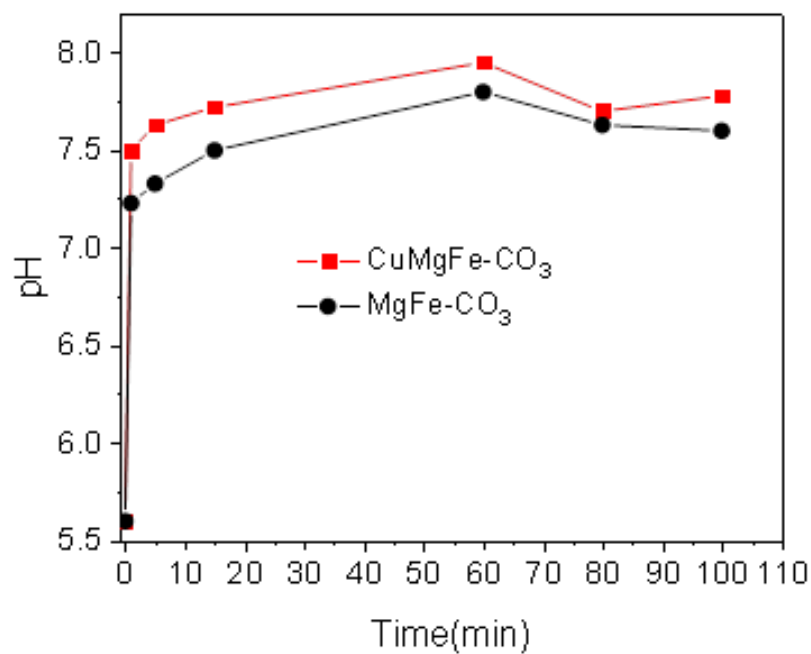
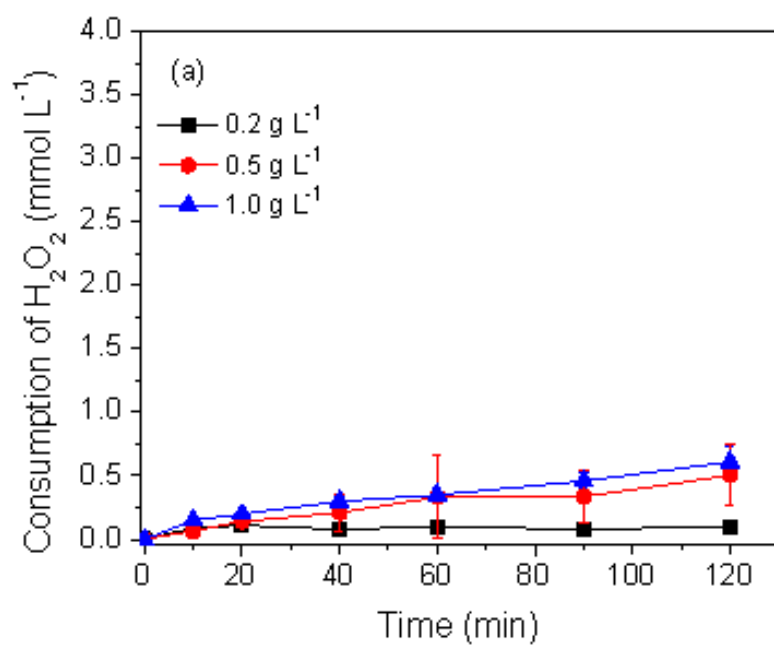


Figure 2.S2 Increases of pH in aqueous suspensions of 0.5 g L⁻¹ MgFe-CO₃ and CuMgFe-CO₃.



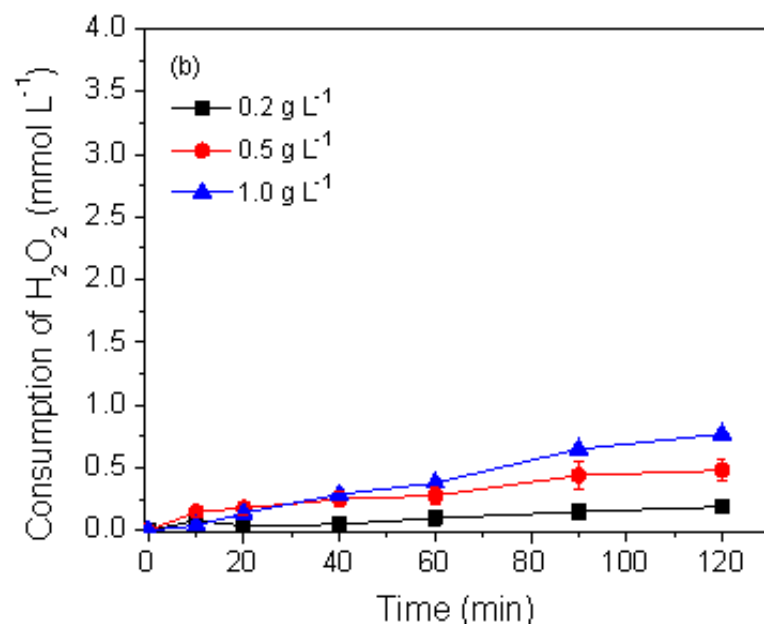


Figure 2.S3 Evaluation of consumption of H_2O_2 . Conditions: pH 7.5; $150 \mu\text{g L}^{-1}$ STZ; 4 mmol L^{-1} H_2O_2 ; Vis-LED irradiation, (a) MgFe-CO_3 and (b) CuMgFe-CO_3 .

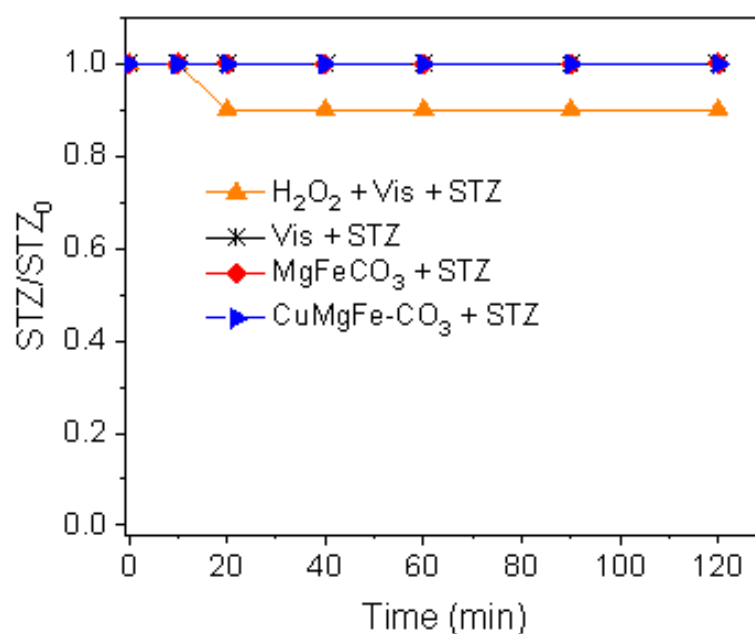


Figure 2.S4 Influences of H_2O_2 photolysis, STZ photolysis, and adsorption of STZ on the surfaces of the catalysts. Conditions: pH 5.6; $150 \mu\text{g L}^{-1}$ STZ; 4 mmol L^{-1} H_2O_2 ; 1.0 g L^{-1} MgFe-CO_3 ; 0.5 g L^{-1} CuMgFe-CO_3 .

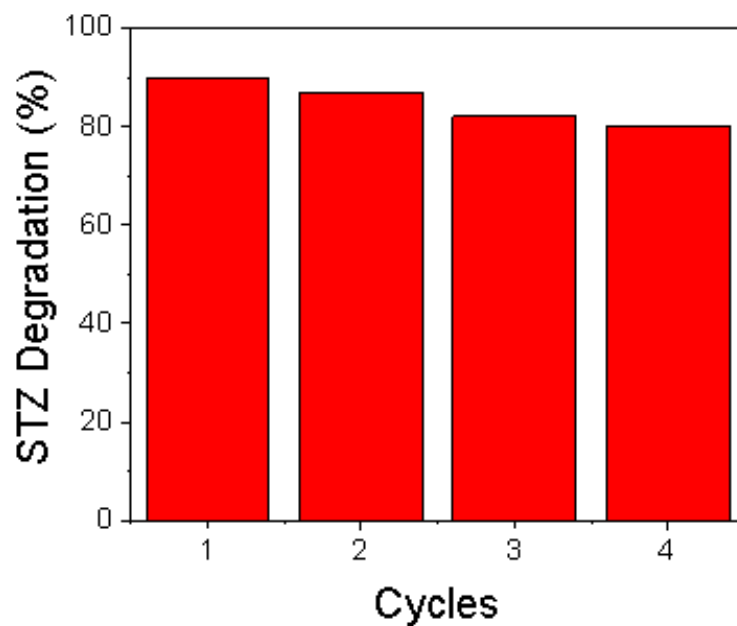


Figure 2.S5 STZ degradation during four 120-min cycles using the CuMgFe-CO₃ catalyst in the dark Fenton process. Conditions: 0.5 g L⁻¹ CuMgFe-CO₃; 150 µg L⁻¹ STZ; 4 mmol L⁻¹ H₂O₂.

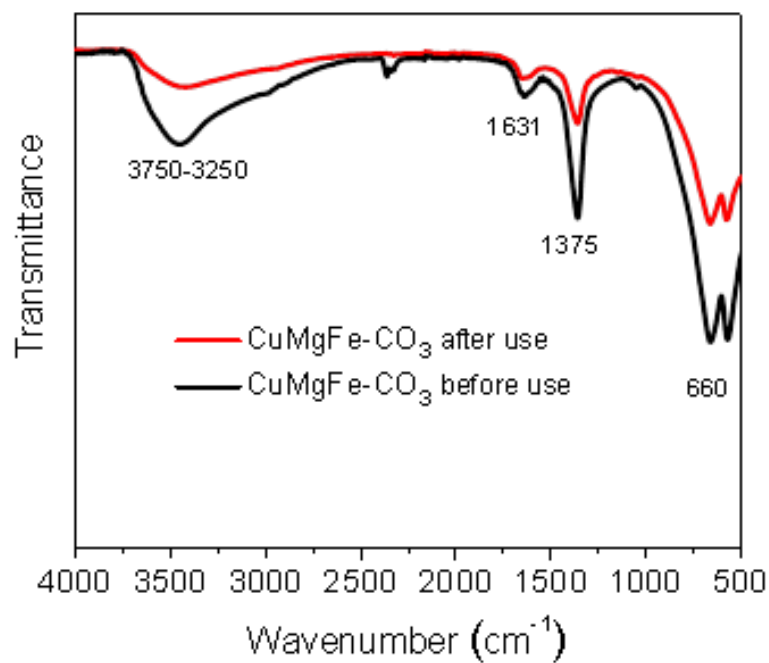


Figure 2.S6 FTIR-ATR spectra of CuMgFe-CO₃, before and after four cycles of use in the Fenton process.

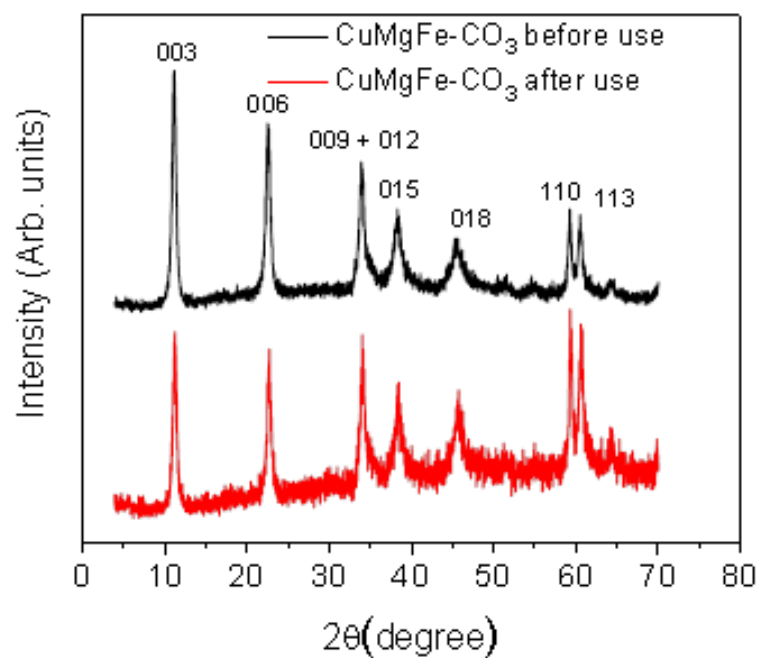
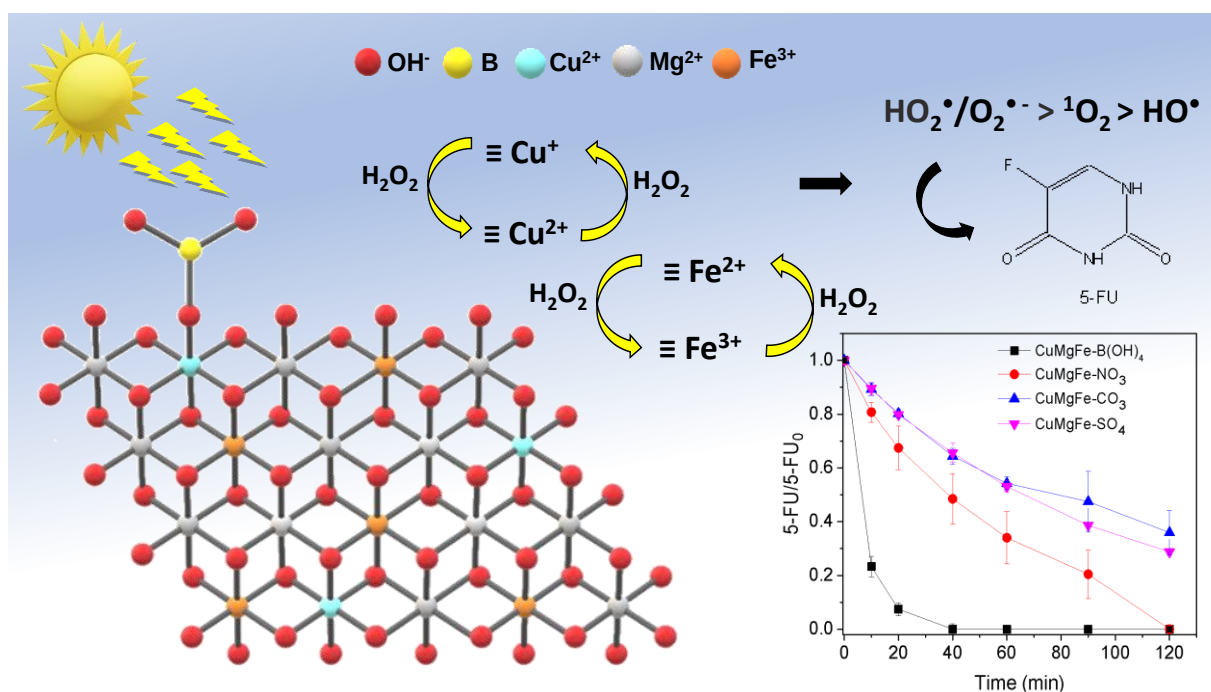


Figure 2.S7 X-ray diffractograms of the CuMgFe-CO_3 catalyst, before and after four cycles of use in the Fenton process.

CHAPTER 3

EFFECT OF THE INTERLAMELLAR ANION ON CuMgFe-LDH IN SOLAR PHOTO-FENTON AND FENTON-LIKE DEGRADATION OF THE ANTICANCER DRUG 5-FLUOROURACIL



- ✓ Interlamellar anion plays determinant role on degradation process.
- ✓ Borate on the LDH presented highest Fenton degradation efficiency.
- ✓ Borate facilitated the reduction of Cu(II) and Fe(III) species on LDH surface.
- ✓ CuMgFe-B(OH)₄ showed structure and performance stability after four cycles use.

3 EFFECT OF THE INTERLAMELLAR ANION ON CuMgFe-LDH IN SOLAR PHOTO-FENTON AND FENTON-LIKE DEGRADATION OF THE ANTICANCER DRUG 5-FLUOROURACIL

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Abstract

The influence of the interlamellar anion in Layered Double Hydroxide was investigated for the first time in Fenton-like and solar photo-Fenton processes for the degradation of the anticancer drug 5-fluorouracil (5-FU). LDHs of the MgFeCu type were synthesized by coprecipitation with the insertion of CO_3^{2-} , NO_3^- , SO_4^{2-} and B(OH)_4^- . A strong effect of the interlamellar anion was observed on the catalytic activity with pseudo-first-order rate constant sequence (k): $\text{CuMgFe-B(OH)}_4 > \text{CuMgFe-NO}_3 > \text{CuMgFe-SO}_4 > \text{CuMgFe-CO}_3$. Using CuMgFe-B(OH)_4 , 5-FU was completely degraded under solar radiation after 20 min and after 40 min in the dark, with degradation efficiency maintained above 90% until the fourth cycle of use. It was found that molecular B-O and B-OH interactions induced modifications of the CuMgFe-B(OH)_4 surface charge density, accelerating the reduction of Cu(II) and Fe(III), thus favoring reactive oxygen species generation. This performance denotes the excellent potential of CuMgFe-B(OH)_4 for 5-FU degradation.

Keywords: Hydrotalcite, hydroperoxyl/superoxide radical, singlet oxygen, borate anion.

3.1 Introduction

The increasing incidence of cancer in the global population is a major health concern. According to the Agency for Research on Cancer, it is estimated that cases of cancer may reach 28.4 million in 2040, an increase of 47%, compared to 2020 [133]. One of the consequences of increased cancer incidence is the high consumption of anticancer drugs, which leads to potential environmental risks because these compounds are only partially absorbed in the body, so the fraction excreted may contaminate aqueous environments [2,3].

The compound 5-fluorouracil (5-FU) (5-fluoro-2,4-(1H,3H)-pyrimidinedione), a widely consumed anticancer drug, has been shown to present toxic effects against microorganisms and fish, at concentration levels ranging from 5 ng L^{-1} to 20 mg L^{-1} [3-5].

Studies in European countries have found that the concentration of 5-FU in hospital wastewater may vary considerably, from 35 ng L^{-1} to $124 \text{ } \mu\text{g L}^{-1}$ [6,7], while concentrations in surface waters have been reported in the range from 4.7 to 70 ng L^{-1} [7,8]. The occurrence of 5-FU in aqueous environments is a consequence of its low biodegradation in conventional wastewater treatment plants, which is an issue that has not yet been properly addressed.

Therefore, efficient treatment strategies are needed to prevent contamination of aqueous environments by this compound [9].

One of the possible methods for effective removal of 5-FU from different aqueous matrices is the heterogeneous Fenton process, a promising advanced oxidation process (AOP) involving the catalytic decomposition of hydrogen peroxide to generate reactive oxygen species. The heterogeneous Fenton process offers several advantages, compared to homogeneous processes: i) the catalyst can be reused, ii) the process can be applied in a wider pH range, and iii) there is no sludge formation [10,11]. Although previous studies described important innovative catalysts for the removal of contaminants, only two studies investigated the removal of 5-FU using heterogeneous Fenton systems, employing magnetites containing copper ($\text{Fe}_{3-x}\text{Cu}_x\text{O}_4$) and superparamagnetic bismuth ferrite, but with relatively high concentrations of hydrogen peroxide (15 and 20 mmol L^{-1} , respectively) and artificial irradiation [12,13]. Therefore, it is necessary to develop new and easily synthesized catalysts that can provide an effective Fenton system in the dark or under solar irradiation, while minimizing the costs of energy and reagents [14,15].

Recent studies have highlighted the excellent potential of layered double hydroxides (LDHs) as catalysts in Fenton reactions for the removal of different types of organic contaminants. LDHs, also known as anionic clays, are hydrotalcite-like compounds formed by divalent and trivalent cations, with the general formula $[\text{M}^{2+}_{(1-x)}\text{M}^{3+}_x(\text{OH})_2]_{\text{lamellar}}[\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}]_{\text{interlamellar}}$ [10]. The partial substitution of divalent cations by trivalent cations results in a positive residual charge, which is compensated by anions situated in the interlamellar space [11].

Due to their unique structural characteristics, the 2D lamellae can incorporate different metals, which results in a high synergism between the cations. Further advantages of this material include atomic-level dispersion of structural cations, low toxicity, high porosity, thermal/chemical stability, low leaching of metals, and simplicity of synthesis on a laboratory scale. These features differentiate LDHs from classic Fenton-like catalysts such as iron oxides and iron/carbon composites [10,16-18].

The versatility of the LDH structure has opened several application possibilities, since the structures and catalytic activities of these materials can be improved by varying the cations as well as the interlamellar anions.

The main focus in studies concerning the use of pyroaurite-type LDHs in Fenton reactions has been to evaluate the effects of different cations in the lamellae, such as Mn, Fe,

Cu, and Co, without considering the effect of the interlamellar anion, which can also influence the catalytic activity. Based on the ability of the anion to be exchanged, the following order of stability has been reported for anion intercalation in the LDH interlamellar space: $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$ [11,15, 19].

This study investigates the connections of the interlamellar anions CO_3^{2-} , SO_4^{2-} , NO_3^- , and B(OH)_4^- on the LDH surface, and the catalytic activities for Fenton degradation. In particular, B(OH)_4^- was selected for evaluation, since recent studies have described the influence of boron species on changing the surface charge density, consequently improving redox cycles [20, 21]. Therefore, important novel aspects of this study are the evaluation of different interlamellar anions in LDH structures, together with the application of borate-based LDH in Fenton-like systems, which, as far as we know, is reported here for the first time.

Detailed characterization of the different LDHs, kinetic studies, evaluation of the reactive species generated by the use of scavengers, and determination of 5-FU transformation products were performed, in order to elucidate the effects of the anions on the efficiency of LDH used in heterogeneous Fenton degradation processes.

3.2 Experimental

3.2.1 Reagents

5-fluorouracil (>99%), bovine catalase (>10,000 units/mg protein), bathocuproinedisulfonic acid disodium salt hydrate, Na_2CO_3 , p-benzoquinone (BQ), nitrobenzene (NB), NaN_3 were purchased from Sigma Aldrich. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NaNO_3 (Mallinckrodt), $\text{Mg}(\text{NO}_3)_2$, NaOH and H_3BO_3 (Êxodo Cientifica), $\text{Cu}(\text{NO}_3)_2$ (Neon), H_2O_2 (30% w/w) and NH_4VO_3 , sodium acetate (Synth), 1,10-phenanthroline (Vetec) were used. Methanol (HPLC grade) and potassium periodate (KIO_4) were purchased from Honeywell (Germany), Na_2SO_4 was purchased from J.T. Baker, Millipore-Milli-Q, Direct-Q® Water Purification System was used for dilutions and for HPLC analysis.

3.2.2 Catalysts preparation

The molar ratio 3:1 of the cations in the catalysts synthesized is given by the Eq. 3.1:

$$\frac{n\text{Cu}+n\text{Mg}}{n\text{Fe}} = 3 \quad (3.1)$$

using 0.011 mol Cu(II), 0.109 mol Mg(II) and 0.040 mol Fe(III). The synthesis of pyroaurite-type catalysts was based on the coprecipitation method adopting $\text{pH } 11.0 \pm 0.5$ according to the

adapted methodology of Yun and Pinnavaia [22], Rozov et al. [23], and Castro et al. [24] with variation of the interlamellar anion (CO_3^{2-} , SO_4^{2-} , NO_3^- and $\text{B}(\text{OH})_4^-$).

For the synthesis of CuMgFe-CO_3 and CuMgFe-SO_4 , 0.12 mol of Na_2CO_3 and Na_2SO_4 was used. For $\text{CuMgFe-B}(\text{OH})_4$ and CuMgFe-NO_3 preparation, 0.48 mol of H_3BO_3 and NaNO_3 was used to ensure the intercalation of the respective anions, considering the difficulty of intercalation of monovalent anions in the LDH. The salts were added to 1.9 L of ultrapure water under vigorous stirring followed by a dropwise addition of metals and NaOH solution (2.0 mol L^{-1}) to keep the pH value constant. With the exception of CuMgFe-CO_3 , the synthesis was made in a N_2 atmosphere to exclude CO_2 .

After completing addition of the solution containing the cations, the suspended solids were submitted to six cycles of washing with distilled water, centrifugation and resuspension and then dried at room temperature and under vacuum. After drying, the catalysts were sieved through a 100-mesh.

3.2.3 Characterization of the catalysts

X-ray diffraction (XRD) was performed using a Bruker D8 Advance Eco equipment with $\text{K}\alpha\text{Cu}$ radiation (25 mA and 40 kV), in the range from 5 to 120° and step of 0.02°s^{-1} . Rietveld refinements based on XRD data and average crystallite sizes were obtained using TOPAS V.5 software. Fourier transform infrared (FTIR) spectra were performed using a PerkinElmer Spectrum 1000 FTIR spectrometer with a resolution of 2 cm^{-1} and averaged over four scans. The LDH morphology was analyzed using a JEOL 7500F field emission scanning electron microscope (FEG-SEM). Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HR-TEM) images were carried out using a JEOL JEM2100 LaB_6 operated at an accelerating voltage of 200 kV.

The specific area and porosity of the lamellar materials were determined by N_2 adsorption/desorption isotherms at 77 K in a gas adsorption isotherm analyzer, ASAP 2010 Micromeritics, capable of evaluating micro and mesoporous solids. UV-Vis diffuse reflectance spectroscopy (DRS) technique was performed using a Cary 5000 UV-Vis-NIR spectrophotometer (Varian) with MgO as background.

Thermal analyzes, TG (Thermogravimetric), DTA (Differential Thermal Analysis), DTG (Derivative Thermogravimetry) were performed using a Shimadzu DTG-60AH equipment. The samples were heated with a ramp of $10^\circ \text{C min}^{-1}$ in the range of 25-1000 $^\circ \text{C}$ under synthetic air flow of 50 mL min^{-1} .

The surface analysis was performed using X-ray photoelectron spectroscopy (XPS) using a UNI-SPECS UHV system equipped with an Mg K α X-ray source ($h\nu = 1253.6$ eV) at a base pressure $<10^{-7}$ Pa. The inelastic background of the Fe 2p $_{3/2}$, Cu 2p $_{3/2}$ and O 1s spectra was subtracted using Shirley's method and the binding energy scale was corrected using the C 1s hydrocarbon signal at 284.8 eV. The spectra were fitted without placing constraints with multiple Voigt profiles using the CasaXPS software.

3.2.4 Degradation experiments

Experiments in the dark were performed in a laboratory scale with 300 mL of 200 $\mu\text{g L}^{-1}$ of 5-FU solution at room temperature, containing 10 mmol L^{-1} H_2O_2 under magnetic stirring (1200-1400 rpm) in a previously described reactor during 120 min (Rojas-Mantilla et al., 2019) [25]. The experiments were performed at least in duplicate and error bars are shown for the experiments performed in triplicate.

Experiments under solar irradiation were performed in Araraquara, Brazil (21° 47' 5.3772" S) during the summer using the same experimental conditions. The irradiance was monitored in the UVA region (320–400 nm) using a PMA 2100 radiometer (Solar Light Co.) positioning the sensor at the same angle of incidence of radiation in the reactor. Aliquots were collected at a constant value of accumulated UVA dose to facilitate the comparison of the results, shown in Table 3.S1 [26].

Initially control experiments were performed to evaluate the adsorption of 5-FU on the catalyst surface as well as the photocatalytic activity in the absence of H_2O_2 and solar irradiation using 0.5 g L^{-1} of the LDHs. Subsequently, the influence of the interlamellar anion was evaluated in experiments with 0.5 g L^{-1} of the LDHs and 10 mmol L^{-1} H_2O_2 .

The investigated oxidation process was also applied for the treatment of a secondary treated urban wastewater (STWW) after spiking 200 $\mu\text{g L}^{-1}$ 5-FU. The major physical-chemical properties of the wastewater are shown in Table 3.S2.

The reuse of the CuMgFe-B(OH) $_4$ in the Fenton process was evaluated during four cycles in distilled water and three cycles in the STWW during 120 min, with aliquots collected before and after each cycle. The recovered material was washed, centrifuged and added to 300 mL of 5-FU (200 $\mu\text{g L}^{-1}$) fresh solution or STWW (spiked with 200 $\mu\text{g L}^{-1}$ of 5-FU) containing 10 mmol L^{-1} of H_2O_2 .

3.2.5 Chemical analysis

Bovine catalase (0.4 g L^{-1}) was added to collected samples to consume residual H_2O_2 . Samples were then filtered through $0.45 \text{ }\mu\text{m}$ Nylon membrane to completely interrupt the reaction. The concentration of 5-FU during degradation process was determined by high performance liquid chromatography (HPLC), using a Shimadzu LC-20AT instrument equipped with a UV–Vis diode array detector (SPD-M20A) and a Luna C18 analytical column ($150 \text{ mm} \times 4.6 \text{ mm}$, $5 \text{ }\mu\text{m}$; Phenomenex, Torrance, CA, USA), at $40 \text{ }^\circ\text{C}$, coupled to a Phenomenex C18 guard column ($4 \text{ mm} \times 3 \text{ mm}$). The mobile phase was methanol: water (5:95 v/v) with isocratic elution at 0.5 mL min^{-1} flow rate. The injection volume was $20 \text{ }\mu\text{L}$ and 5-FU was detected at 265 nm wavelength. Under these conditions, the instrumental detection limit (DL) was $1.5 \text{ }\mu\text{g L}^{-1}$. Therefore, a concentration below detection limit corresponds to at least 99% removal, which for simplicity was referred in the discussion as total removal.

The transformation products of 5-FU were identified using a Dionex Ultimate 3000 liquid chromatograph equipped with an electrospray source and an Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific, Les Ulis, France) operated in full scan MS (mass range m/z 50–900) in negative and positive ionization mode with energy of electron collisional dissociation set to 20 eV and a drying gas temperature of $200 \text{ }^\circ\text{C}$. The separation and detection conditions are shown in the Table S3.

For the indirect investigation of the radical species involved in the process, the scavengers p-benzoquinone (BQ) for $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$, methanol (MeOH) and nitrobenzene (NB) for $\text{HO}^\bullet$ and NaN_3 for $^1\text{O}_2$ were added in excess (200 mg L^{-1}) to 5-FU/LDH suspensions in separate experiments with $10 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$ [27].

The concentration of copper ions in the solution after the degradation process was determined using the bathocuproine spectrophotometric method ($\lambda = 484 \text{ nm}$) [28]. The concentration of iron ions was determined spectrophotometrically using 1,10-phenanthroline, with maximum absorption at 510 nm [29].

The formation of Cu(III)-periodate complex, with absorption at 415 nm , was verified in filtered samples using UV–Vis spectrophotometry following the protocol previously described to assess whether Cu(III) could be generated in the system [30].

3.3 Results and discussion

3.3.1 LDH characterization

X-ray diffractograms patterns with Rietveld refinement show three main peaks (003), (006) and (009) assigned to the lamellar structure and stacking planes, characteristic of the LDH structure (Figure 3.1) [31-33]. They are characteristic of hexagonal unit cell of a 3R rhombohedral system (R3m). The (003) peak was used to calculate the basal spacing (d_{003}) and average crystallite size using Bragg and Scherrer equation, respectively [16,34] with values ranging from 0.79 to 0.81 nm (Table 3.1). The basal spacing are similar to other LDHs described in the literature prepared using the same molar ratio of M(II)/M(III) (3:1) [31,33,35].

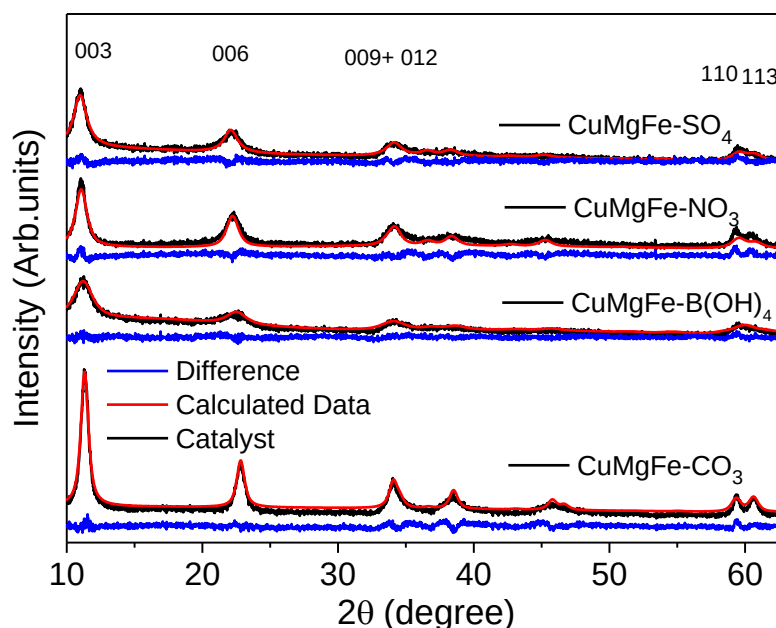


Figure 3.1 X-ray diffractograms with Rietveld refinement of CuMgFe-SO₄, CuMgFe-NO₃, CuMgFe-B(OH)₄ and CuMgFe-CO₃.

The observed differences in basal spacing, crystallite sizes and specific area among the LDH containing the different interlamellar anions (Table 3.1) are related to differences in charge and size of SO₄²⁻, NO₃⁻, B(OH)₄⁻ and CO₃²⁻ which interferes in the stabilization of the structure of the catalysts [35].

The comparison between crystallite size and specific area of prepared LDHs (Table 3.1) show smaller crystallite size and specific area for CuMgFe-NO₃, CuMgFe-B(OH)₄, CuMgFe-SO₄ than CuMgFe-CO₃, which is a consequence of the lower capacity of stabilization of the LDH structure of these anions in comparison to CO₃²⁻.

Table 3.1 Effect of different anions on basal spacing (d_{003}), average crystallite size in the c direction and specific area for the CuMgFe-CO₃ (CO₃²⁻), CuMgFe-B(OH)₄ (B(OH)₄⁻), CuMgFe-NO₃ (NO₃⁻) and CuMgFe-SO₄ (SO₄²⁻) catalysts.

Parameters	CO ₃ ²⁻	B(OH) ₄ ⁻	NO ₃ ⁻	SO ₄ ²⁻
d_{003} (nm)	0.78	0.79	0.80	0.81
Crystallite size in the c direction (nm)	11.8	4.7	7.7	6.7
Specific area (m² g⁻¹)	68	17	10	25

The structure of the synthesized LDHs was further characterized by HR-TEM image (Figure 3.S1), which images reveals that d spacing value among the catalysts are different, with highest value for CuMgFe-SO₄ and lowest value for CuMgFe-CO₃, which is in agreement with the results obtained by XRD shown in Table 3.1.

The interlayer of LDHs comprises both water and anions, and these are linked through H-bonding to the hydroxide layer [16]. Generally, the greater the charge density of the anion, the greater the electrostatic interaction with the lamellae that contributes to the tendency to be intercalated. Therefore, for the inorganic anions studied in this work, the ease of intercalation in the interlamellar space of LDH is: CO₃²⁻ > SO₄²⁻ > B(OH)₄⁻ > NO₃⁻.

Similar results have already been reported in the literature showing higher stabilization of CuMgFe-CO₃ and CuMgFe-SO₄ in the formation of primary particles of orderly growth along the 001 plane, resulting in larger platelets with a sand rose morphology [19,31]. However, the LDH with other anions such as CuMgFe-B(OH)₄ and CuMgFe-NO₃ can present a stone-like morphology [36,37]. The formation of this type of structure leads to greater packing of platelets and consequently, to a smaller surface area than LDHs prepared with CO₃²⁻, which justifies the observed crystallite sizes and specific area.

The intercalation of different anions also affects the morphology of the LDHs as identified by SEM and TEM analyzes (Figure 3.2 and Figure 3.3, respectively). A different morphology is observed for CuMgFe-B(OH)₄ when compared to the others LDHs, presenting irregular shape due to the lower ability of B(OH)₄⁻ anions to stabilize the LDH structure, leading to the formation of smaller particles.

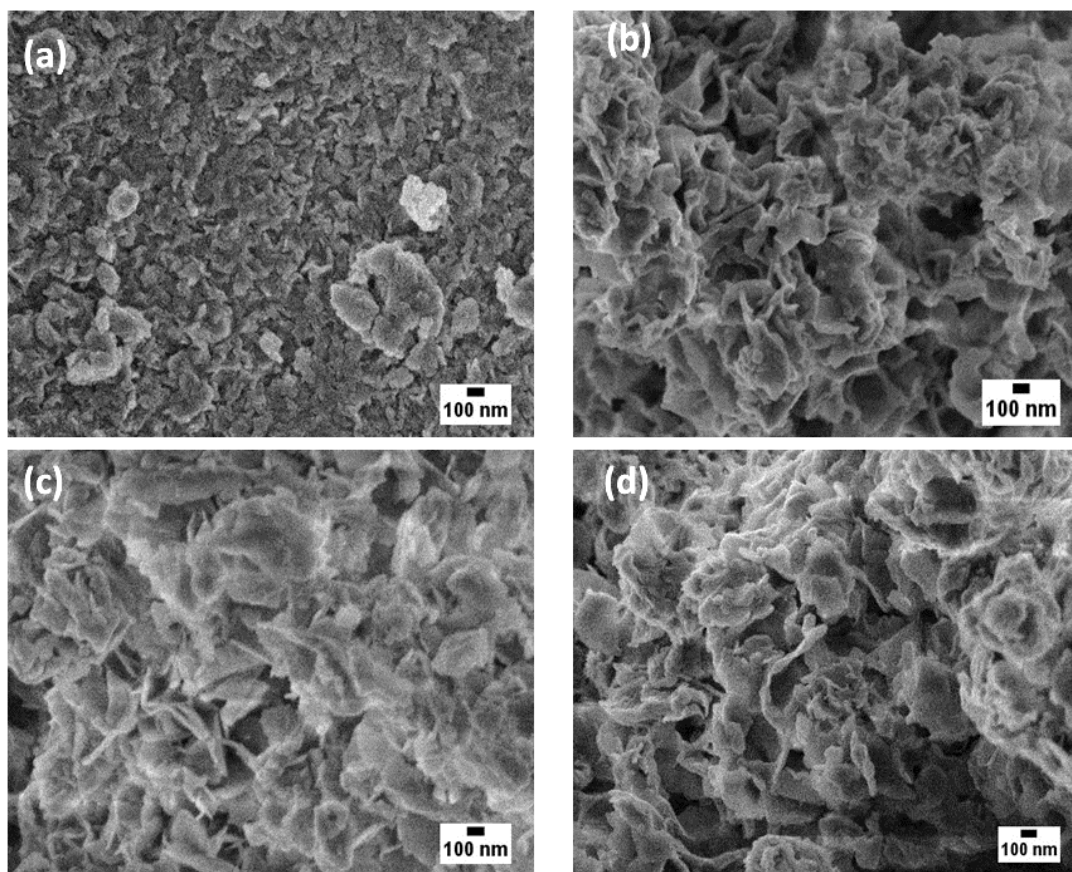


Figure 3.2 SEM images for the LDHs containing a) CuMgFe-B(OH)_4 , b) CuMgFe-SO_4 , c) CuMgFe-CO_3 , and d) CuMgFe-NO_3 .

The TEM images of the LDH, except the CuMgFe-B(OH)_4 , show pyroaurite-type lamellae forming irregular aggregates (Figure 3.3).

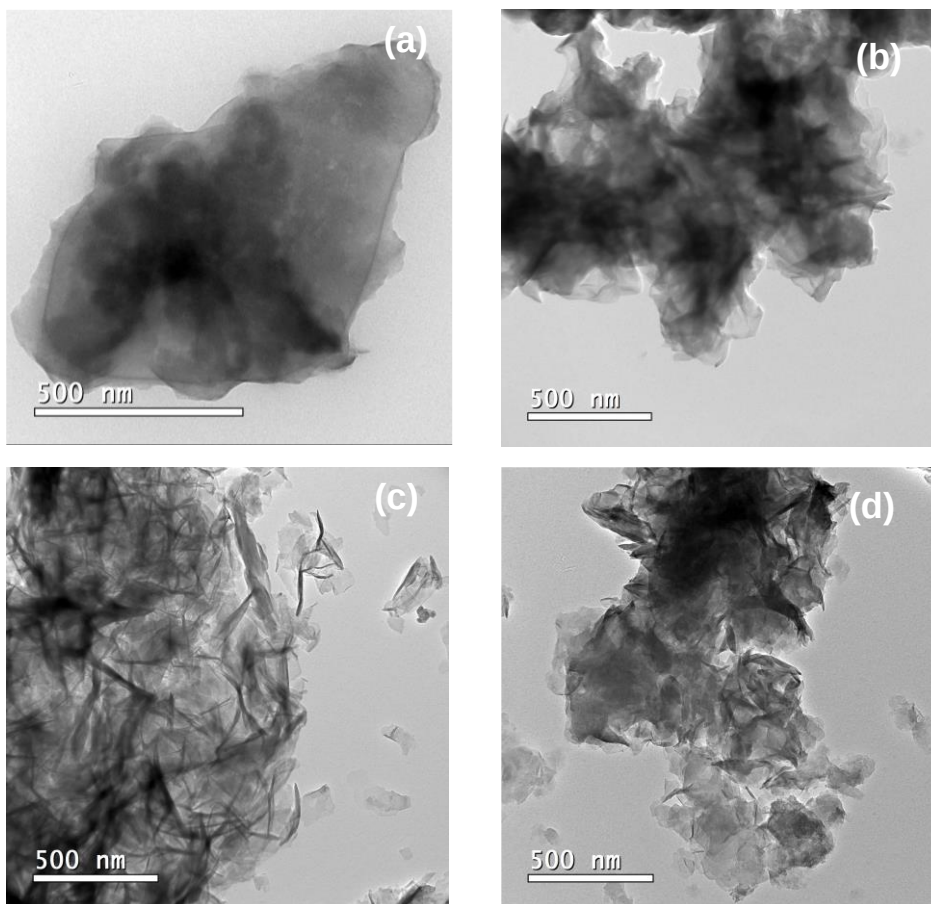


Figure 3.3 TEM images of a) CuMgFe-B(OH)₄, b) CuMgFe-SO₄, c) CuMgFe-CO₃, and d) CuMgFe-NO₃.

All the LDHs presented a type II isotherm (Figure 3.S2), with absence of a plateau of the relative pressure (P/P_0) close to 1, which indicates the presence of macropores, according to the IUPAC classification. The results also show that the materials have slit-shaped pores formed by platelet aggregation, resulting in a broad pore size distribution because hysteresis loop between the adsorption and desorption branches was in accordance with the H3 type [33,38].

The FTIR spectra of materials synthesized using different anions in the interlamellar spaces have similar characteristics (Figure 3.4). A broad band in the range from 3750 cm^{-1} to 3250 cm^{-1} corresponds to the stretching of the hydroxyl groups of the water molecules present in the interlamellar space in the structure of the LDHs [39]. Additionally, the band centered at 1640 cm^{-1} is attributed to OH⁻ modes of vibrations of water molecules in different catalysts [39]. The band at 570 cm^{-1} corresponds to metal oxygen stretching vibrations (M-O, M = Mg, Fe, and Cu) [18].

A band at 1380 cm^{-1} is present in the spectra of all materials, however, several functional groups absorb in this region. In the case of CuMgFe-CO_3 , the band at 1380 cm^{-1} and a weak band at 680 cm^{-1} are attributed to the stretching vibration of the interspersed CO_3^{2-} [40] while in CuMgFe-NO_3 it is attributed to vibrations of NO_3^- [41].

Carbonate and nitrate impurities from the precursor salts used in the synthesis are considered to contribute to absorption of CuMgFe-B(OH)_4 and CuMgFe-SO_4 at 1380 cm^{-1} , as well as the interactions between sulfate anion with the oxyhydroxide form of iron oxide [42].

A low intensity band at 680 cm^{-1} observed in CuMgFe-B(OH)_4 spectrum is attributed to asymmetric vibrations of B-O [43] and an additional band at $1200 - 1000\text{ cm}^{-1}$ of B-O-H, which can overlap with other B-O stretching vibrations [44].

The observed peak at 1120 cm^{-1} and a weak peak at 620 cm^{-1} in CuMgFe-SO_4 are attributed to asymmetric plane vibrations of the sulfate group [36,45].

These results confirm the intercalation of the anions in the LDHs structure.

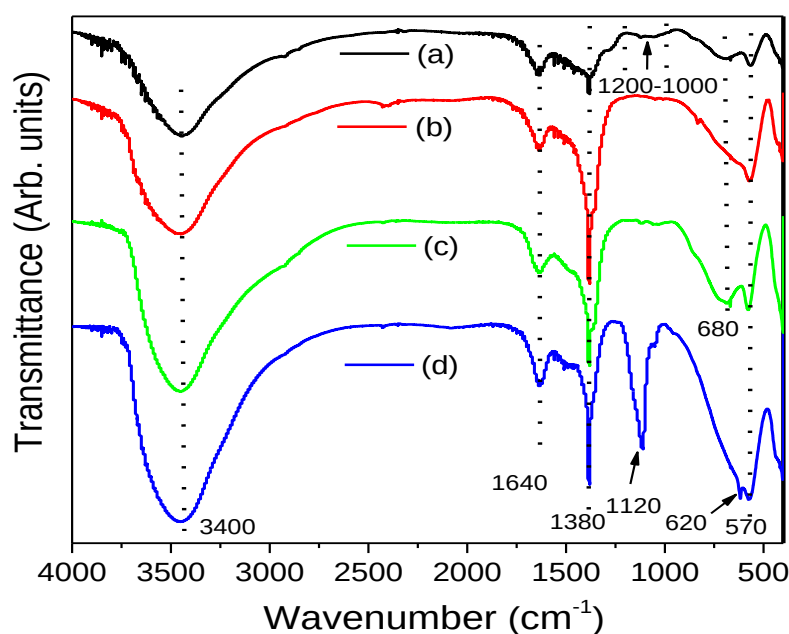


Figure 3.4 FTIR spectra of the synthesized materials CuMgFe-B(OH)_4 (a), CuMgFe-NO_3 (b), CuMgFe-CO_3 (c), and CuMgFe-SO_4 (d).

The UV-Vis absorption spectra of the investigated LDHs present similar and significant absorption up to 600 nm , which is an interesting feature for solar photo-Fenton application (Figure 3.S3), as previously reported for LDHs containing copper, magnesium, and iron [33,46].

The thermogravimetric analysis of LDHs (Figure 3.5) show that the decomposition of the LDHs occurred in four steps: (1) removal of water physically adsorbed on the external

surface of the crystallites; (2) removal of intercalated water molecules; (3) removal of hydroxyl groups from the lamellas as water and (4) removal of the intercalated anion. However, due to the conditions used in the analysis and the type of anion intercalated, some of these steps can occur simultaneously making it difficult to evaluate the decomposition events individually.

The first (endothermic) event for all LDHs occurred from room temperature up to 180 °C, with a mass loss of 15-17% attributed to the release of absorbed and intercalated water molecules. The second event (endothermic), between 185 and 500 °C, with a mass loss of 23%, can be attributed to the simultaneous release of anions from the interlamellar spaces and of the hydroxyl groups from the lamella [47]. The third endothermic event with a mass loss of 3%, which occurs from 500 to 800 °C, is a consequence of a decarbonation process of carbonate impurities in the LDHs.

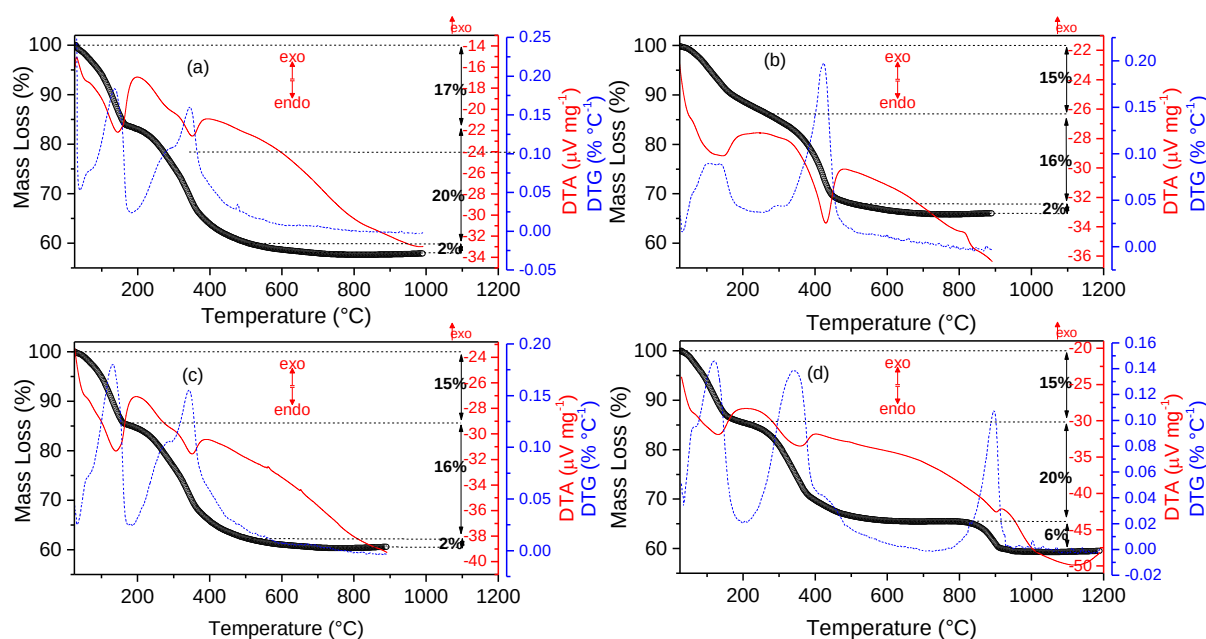


Figure 3.5 TG, dTG, and dTA thermal analyses of the synthesized materials: a) CuMgFe-CO₃, b) CuMgFe-B(OH)₄, c) CuMgFe-NO₃, and d) CuMgFe-SO₄.

The CuMgFe-B(OH)₄ thermogram (Figure 3.5b) shows a lower mass loss than the other catalysts since boron species cannot be eliminated in the gas form even at high temperature and remains in the oxide form as previously demonstrated by Demir et al., 2006 [48]. The thermal decomposition of ammonium tetraborate tetrahydrate to boron oxide appears completely overlapped at temperature higher than 350 °C [49].

XPS analysis was used to identify the bonding states of Cu and Fe surface species in the CuMgFe-NO₃, CuMgFe-CO₃, CuMgFe-B(OH)₄ and CuMgFe-SO₄ before Fenton process

(Figure 3.6). The Fe $2p_{3/2}$ high-resolution spectra were deconvoluted into four components at 709.5 eV, 711.1 eV, 712.3 eV, and 714.3 eV, related to the presence of Fe(II) (FeO), Fe(III) (Fe_2O_3 and FeOOH), and an Fe(III) shake-up satellite. The three fitted components of the Cu $2p_{3/2}$ spectra at 932.2 eV, 933.7 eV, and 934.8 eV were assigned to Cu(I), (Cu_2O) and Cu(II) (CuO and $Cu(OH)_2$) species, respectively [18,31,50]. A low-intensity component assigned to Cu(I) species is observed in all LDHs spectra. Weak Cu(I) signals have been often observed in materials prepared using Cu(II) precursors, which are attributed in part to X-ray induced-reduction of Cu(II) that cannot be excluded in the case of the LDH structure [51,52]. However, the $CuMgFe-B(OH)_4$ show higher intensities of Cu(I) in comparison to the other LDHs, evidencing the presence of this species in the material. The reduction of iron due to the presence of boron species on the surface of catalysts has already been confirmed by some authors [20,21], which may have occurred both with iron and copper in $CuMgFe-B(OH)_4$ (Figure 3.6).

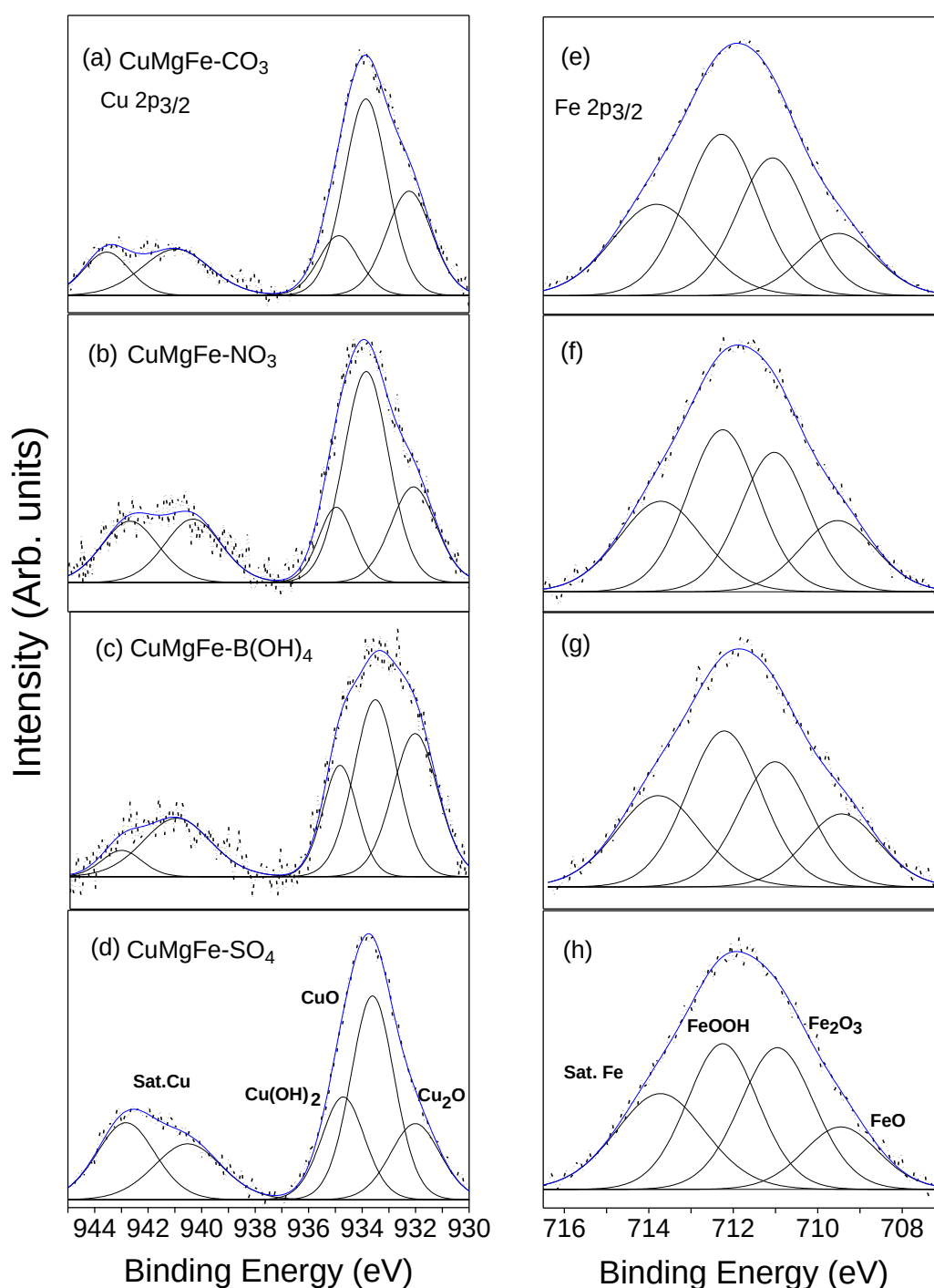


Figure 3.6 XPS high resolution spectra of Cu 2p_{3/2} (a), (b), (c), (d), and Fe 2p_{3/2} spectra (e), (f), (g), (h) of CuMgFe-CO₃, CuMgFe-NO₃, CuMgFe-B(OH)₄ and CuMgFe-SO₄, respectively.

The high resolution XPS spectra of B 1s, C 1s, N 1s and S 2p show the contribution of the anions B(OH)₄⁻, CO₃²⁻, NO₃⁻ and SO₄²⁻ confirming the insertion of the different anions in the interlamellar space of the LDHs (Figure 3.7). The N 1s spectrum shows a single peak at 407.07 eV, related to NO₃⁻ [53]. Surface contamination by adventitious carbon (CH) at 285 eV

and oxygenated groups such as C-O at 286.4 eV and carboxyl groups -OC=O at 288.8 eV, is typical for ex-situ analysis. For CuMgFe-CO₃, the carbonate component at 289.1 eV overlaps with a small contribution of carboxyl -O=C [54]. The peak at 169.8 eV of S 2p spectrum indicates that sulfur is in the form of sulfate (SO₄²⁻) [55].

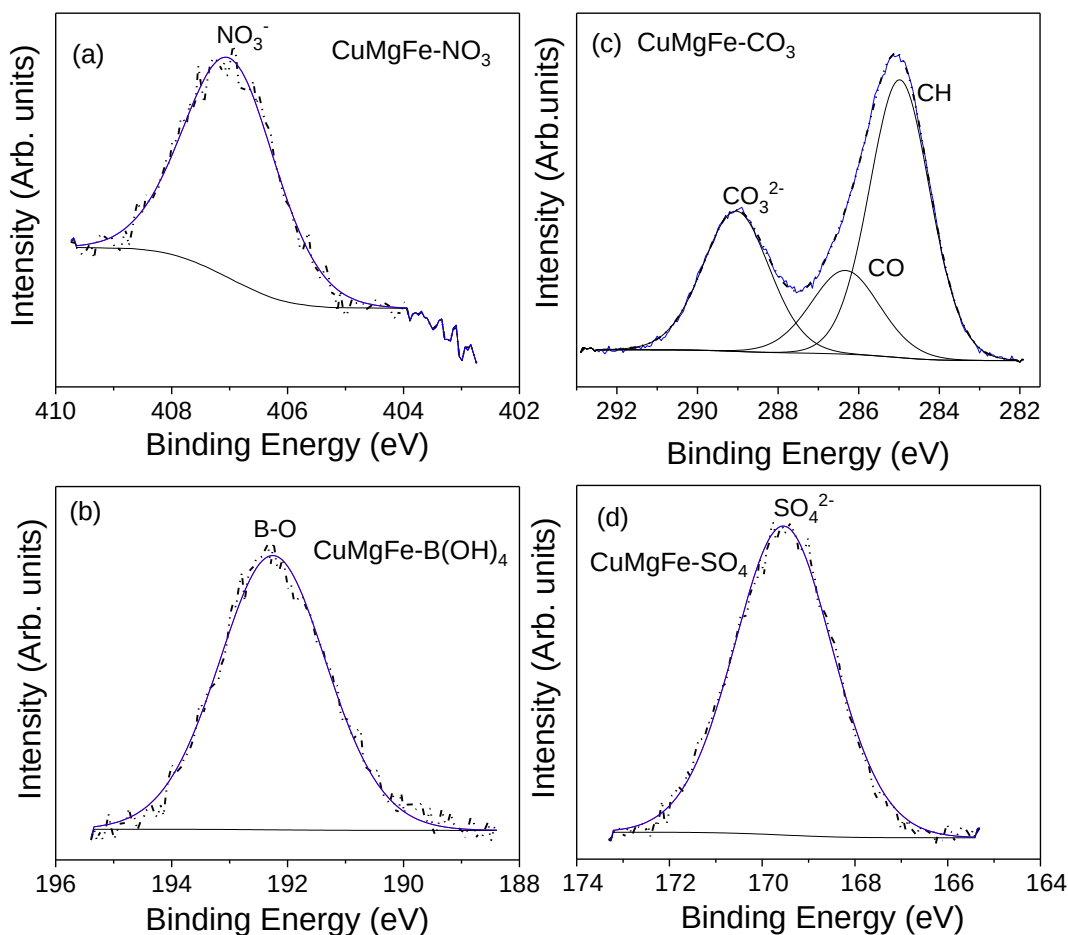


Figure 3.7 High-resolution XPS spectra of N 1s (a), B 1s (b), C 1s (c), and S 2p (d) of the synthesized LDHs.

The signal located at 192.3 eV is associated with the B-O bonds [20,21]. The chemistry of boron species in catalysts is a recent topic and no detailed information is available. Considering that the interlamellar anion in the LDH structure is situated in the interlayer galleries together with water molecules, it is difficult to confirm the type of boron species present on the surface of the catalyst. However, considering the results of XPS (Figure 3.7) and FTIR (Figure 3.4), as well as previous studies [20,21,56], it is possible to state that B-O and B-OH bonds are present in the interlamellar space of the CuMgFe-B(OH)₄, which can influence the structural characteristics and improve catalyst activity.

Notably, the characterization results for CuMgFe-B(OH)₄, allows to propose a mechanism to explain the possibility of partial reductions of iron and copper on the catalyst surface caused by the presence of boric acid (Figure 3.8). The model was proposed for copper, because a similar mechanism for iron with goethites modified with boric acid has already been reported [20].

Based on the synthesis conditions, in the Eq.2 and in the pK_a = 9.2, boric acid and borate anion may be present on the catalyst surface.



The theoretical concentration of B(OH)₄⁻ is 7.5 x 10⁻³ mol L⁻¹ in aqueous solution during preparation of CuMgFe-B(OH)₄. However, mechanistic reactions with B(OH)₄⁻ are less favorable and therefore the dominant reagent may be B(OH)₃ [44,56], which reaction on the LDH surface occurs with formation of a transition state structure and elimination of a water molecule.

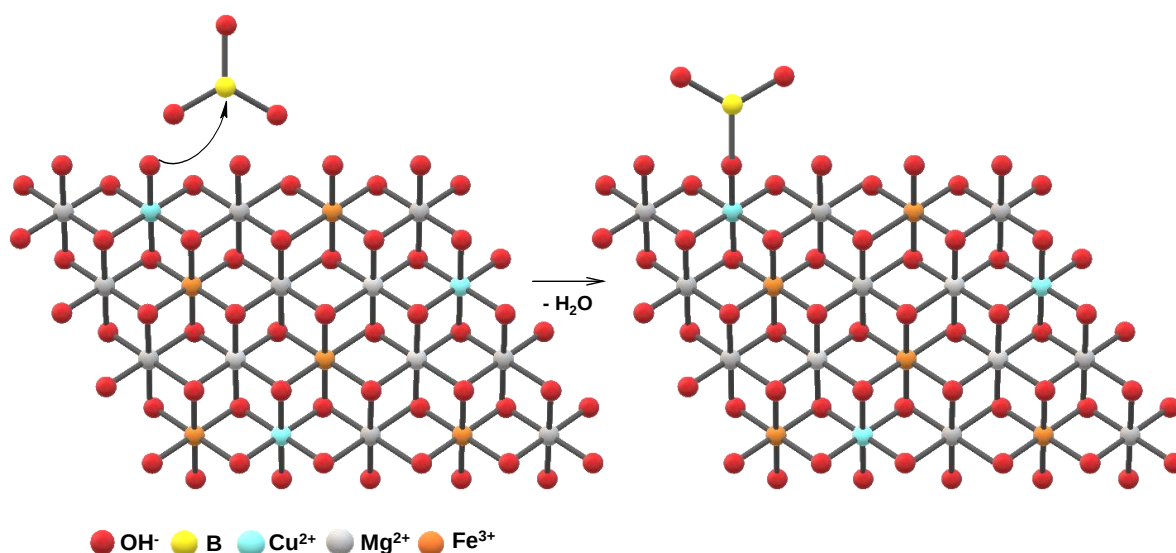


Figure 3.8 Proposed surface reaction between CuMgFe-B(OH)₄ and B(OH)₃.

The strengthening of the Lewis acid-base bond between boron and oxygen of the LDH hydroxyl group assists the stability of the hydrogen bond between the hydroxyl group of boric acid and the hydrogen of the hydroxyl group present in the CuMgFe-B(OH)₄ (Figure 3.8). After removal of the water molecule and complexation of boric acid on the surface of the LDH, a reduction of the Cu(II) and Fe(III) may occur on the surface of LDH.

The findings and the proposed mechanism revealed that B(OH)₃ can act as a promoter of the electron transfer on the CuMgFe-B(OH)₄ surface, modifying charge density and resulting

in the presence of Fe(II) and also in the high amount of Cu(I) as verified in XPS analysis (Figure 3.6c and g).

3.3.2 Effect of interlamellar anion on catalytic activity of LDH

To assess the effect of the different interlamellar anions in the structure of the LDHs, the different materials were applied in the dark and under solar irradiation for the degradation of 5-FU. The experimental conditions used were based in our previous study (0.5 g L⁻¹ of LDH; 0-6 mmol L⁻¹ of H₂O₂) [31]. After evaluating the influence of the interlamellar anion on the LDH structure, the catalyst that showed the best catalytic efficiency was selected for deeper study of the degradation mechanism involved in the process including the evaluation of the main reactive oxygen species generated, the material stability and the reuse in water and in STWW, which are presented in the following sections.

The suspensions obtained after dispersion of the CuMgFe-CO₃, CuMgFe-NO₃, CuMgFe-SO₄ and CuMgFe-B(OH)₄ in 5-FU solution resulted in the pH values of 7.0, 7.2, 7.9 and 8.3, respectively. Considering the advantages of carrying out the degradation reaction under near-neutral conditions, the experiments using all LDHs investigated were performed at natural pH, without any pH control.

Firstly, control experiments were carried out in the absence of the H₂O₂ in the dark to assess the adsorption of the contaminant on the catalyst surface (Figure 3.S4a) and a possible contribution of photocatalytic process under solar radiation without H₂O₂ (Figure 3.S4b). The results showed no significant adsorption of 5-FU on LDHs in the dark or photocatalytic degradation of 5-FU under solar radiation up to 120 min.

The interlamellar anion in LDH structure revealed to play an important role in the efficiency of the Fenton process in the dark degradation of 5-FU (Figure 3.9). Notably, LDH containing anion borate (CuMgFe-B(OH)₄) promoted a significantly higher degradation rate of 5-FU compared with other LDHs, achieving total 5-FU degradation after 40 min and following pseudo-first order kinetics with a reaction rate constant $k = 0.133 \text{ min}^{-1}$ ($R^2 = 0.997$). The second most efficient LDH was that containing nitrate (CuMgFe-NO₃), which promoted total degradation of 5-FU after 120 min with $k = 0.017 \text{ min}^{-1}$ ($R^2 = 0.997$). Surprisingly, the efficiency of LDH containing carbonate and sulfate as interlamellar anion was very similar, achieving about 70% degradation of 5-FU in the dark after 120 min with $k = 0.009 \text{ min}^{-1}$ ($R^2 = 0.990$) and $k = 0.010 \text{ min}^{-1}$ ($R^2 = 0.999$), respectively.

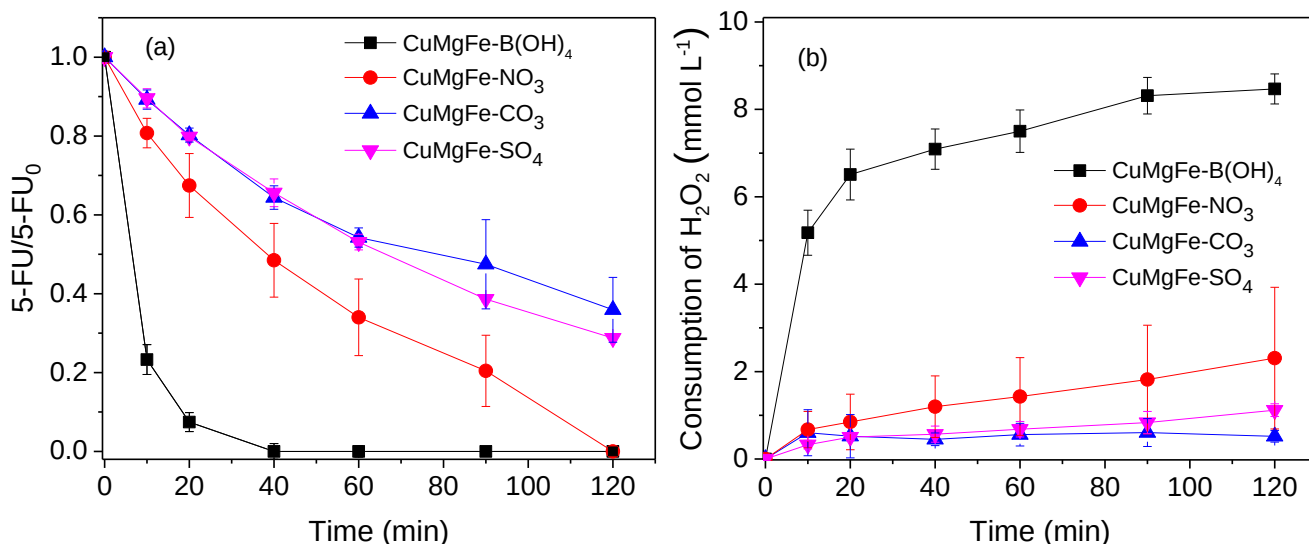


Figure 3.9 Influence of the interlamellar anion on the degradation of 5-FU in the dark (a) and consumption of H_2O_2 (b). Initial conditions: 5-FU = 200 $\mu g L^{-1}$, LDHs = 0.5 g L^{-1} and H_2O_2 = 10 mmol L^{-1} .

The divalent anions carbonate and sulfate in LDH structure resulted in similar and poorest degradation, while nitrate and borate resulted in higher catalytic activity. However, considering the much higher catalytic activity of LDH containing borate ($CuMgFe-B(OH)_4$) compared with nitrate ($CuMgFe-NO_3$), the charge of the anion cannot be considered determinant of the LDH catalytic activity.

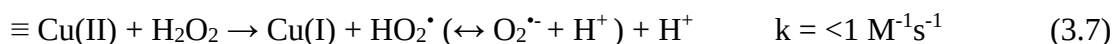
The catalytic activity of the LDHs was also reflected on the decomposition of H_2O_2 , which achieved 70% after 40 min with $CuMgFe-B(OH)_4$, while significantly lower H_2O_2 consumption was observed with other catalysts (between 23% and 5% after 120 min), indicating the higher reactivity of $CuMgFe-B(OH)_4$ toward H_2O_2 and consequently 5-FU degradation than the LDHs containing the other anions. These results allow to propose a sequence of catalytic efficiency for dark degradation of 5-FU using the investigated LDHs: $CuMgFe-B(OH)_4 > CuMgFe-NO_3 > CuMgFe-SO_4 > CuMgFe-CO_3$.

The high catalytic activity observed with $CuMgFe-B(OH)_4$ can be explained by the boron species inserted in the interlamellar space, which can modify the charge density on the material surface that facilitates Fe(III)/Fe(II) and Cu(II)/Cu(I) redox couples improving degradation kinetics. The significant amount of Cu(I) on the $CuMgFe-B(OH)_4$ surface indicated by XPS analysis (Figure 3.6), plays an important role in the generation of hydroxyl radicals, and consequently on the removal of the contaminant under dark conditions.

The effect of boron on the catalytic activity of different materials has been reported. Goethite treated with $B(OH)_3$ were responsible for the partial reduction Fe(III) species, which

consequently increased the oxidation rate of methylene blue [20]. Zhou et al., 2020 [21] investigated crystalline boron (C-Boron) in heterogeneous Fenton process and observed an increase in the redox reaction between Fe(III)/Fe(II) for diethyl phthalate removal.

The efficiency of electron transfer between H₂O₂ and copper or iron species in the material is determinant of the rate of reactive species generation (Eq. 3.3-8). According to the proposal of Figure 3.8 and as identified in XPS and FTIR analyses (Figure 3.6 and 3.4), the high amount of Cu(I) on the surface of CuMgFe-B(OH)₄ accelerated 5-FU degradation due to the faster reaction of Cu(I) with H₂O₂ (Eq. 3.8), compared with Fe(II) in the classical Fenton catalyst (Eq.3.4).



When performing the reactions under solar irradiation, the degradation efficiency was improved with all catalysts studied compared to dark (Figure 3.10). After 90 min (UV dose = 240.50 kJ m⁻²), complete degradation of 5-FU was observed in all system investigated and no significant difference was observed for the materials CuMgFe-NO₃, CuMgFe-CO₃ and CuMgFe-SO₄. Under solar irradiation, CuMgFe-B(OH)₄ also showed best activity achieving complete degradation with five times lower energy dose (48.52 kJ m⁻², 20 min), and a higher H₂O₂ consumption (Figure 3.10.b) compared to other catalysts, confirming the superiority of borate-LDH for photo-Fenton degradation. However, the notorious improvement of 5-FU with other LDHs reinforces the role of photoreduction of Fe(III) and Cu(II), achieved under solar irradiation, which contributes also in the case of CuMgFe-B(OH)₄, however to a lower extent considering the role of borate.

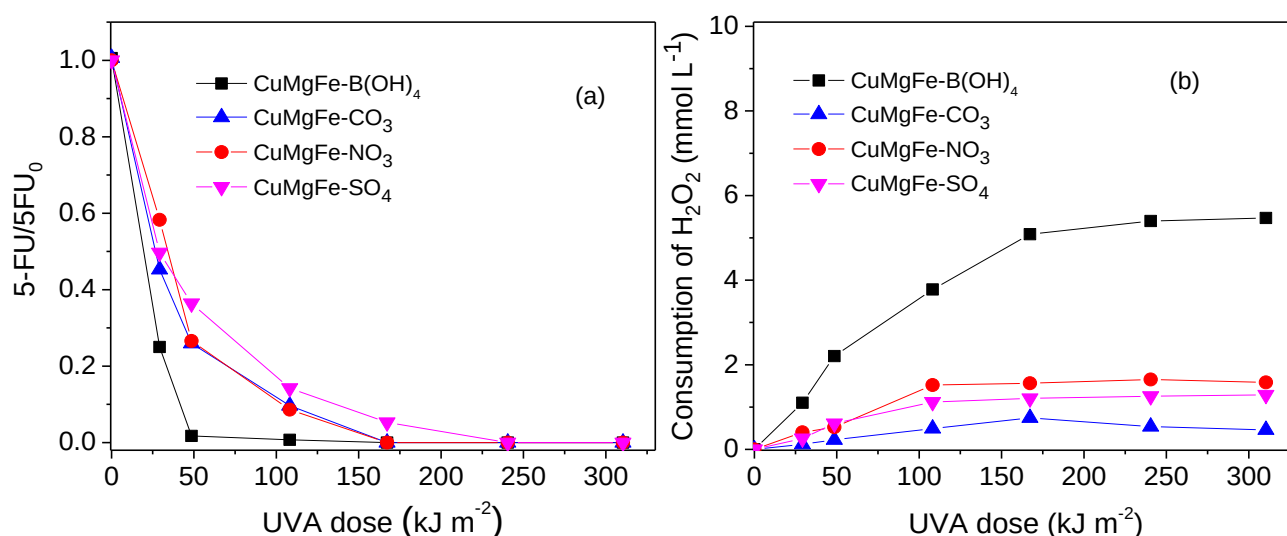


Figure 3.10 Influence of the interlamellar anion on the degradation of 5-FU under solar radiation (a) and consumption of H₂O₂ (b). Initial conditions: 5-FU = 200 µg L⁻¹, LDHs = 0.5 g L⁻¹ and H₂O₂ = 10 mmol L⁻¹.

Total soluble iron and copper concentration after the experiments using 0.5 g L⁻¹ CuMgFe-LDHs were determined to evaluate the stability of all LDHs. No significant leaching was observed, with total iron concentrations < 1.73 µmol L⁻¹ and copper < 0.35 µmol L⁻¹, detection limits of the methods.

In order to evaluate the role of reactive species generated during 5-FU degradation processes in the system CuMgFe-B(OH)₄/H₂O₂, the reaction was performed in the presence of different radical scavengers (Figure 3.S5).

Methanol and NB were used as [•]OH scavengers [27], BQ for HO₂[•]/O₂^{•-} [30] and NaN₃ for ¹O₂ [57]. The degradation reaction was strongly inhibited in the presence of BQ, showing a sharp decrease in the reaction rate constant ($k = 0.006 \text{ min}^{-1}$) indicating the strong contribution of HO₂[•]/O₂^{•-} species (Figure 3.S5). NaN₃ also showed significant inhibition of 5-FU degradation ($k = 0.031 \text{ min}^{-1}$), indicating some contribution of ¹O₂ on the degradation. These results indicate that the degradation of 5-FU can occur by radical and non-radical processes. Interestingly, MeOH and NB, showed very similar effect and indicate a minor contribution of hydroxyl radical since the reaction was only slightly inhibited with rate constants of 0.073 min⁻¹ and 0.062 min⁻¹, respectively.

Although the hydroxyl radical is usually appointed as the main species in the oxidation of contaminants via Fenton process, the contribution of other oxygen reactive species such as singlet oxygen and high-valence iron and copper species have also been reported [27,58,59].

Reactions with catalysts containing copper can also provide the contribution of Cupryl ion (Cu(III)) species, which has been indicated in the reaction of Cu(I) and H₂O₂ as possible species responsible for phenol, benzoate and antibiotic removal [27,30,60]. However, Cu(III) was not detected in the solution during degradation mediated by CuMgFe-B(OH)₄ in this study.

Notably, the scavenger experiments showed that the contribution of reactive species follows the sequence $\text{HO}_2^\bullet/\text{O}_2^{\bullet-} > {}^1\text{O}_2 > \text{HO}^\bullet$ in degradation process mediated by CuMgFe-B(OH)₄.

3.3.3 Identification of 5-FU transformation products (TPs) in the system CuMgFe-B(OH)₄/H₂O₂

For the identification of 5-FU TPs generated during the Fenton-like process with CuMgFe-B(OH)₄ a suspect screening workflow in positive and negative ionization mode in Liquid Chromatography High Resolution-Mass Spectrometry (LC-HRMS) was performed to allow for the detection of a variety of products. For this purpose, a database based on a literature search was built with possible 5-FU TPs and the corresponding molecular formula, exact mass (Table 3.S4).

Potential TPs with intensities lower than 1×10^3 cps, signal to noise ratios lower than 10, isotopic ratio higher than 10%, and mass accuracy errors higher than 5 ppm were discarded.

The TPs of 5-FU using CuMgFe-B(OH)₄ resulted from ring opening and hydroxylation forming *N*-(2-fluoro-1,3,3-trihydroxypropyl)urea (TP168), which maintained the C-F bond even after further oxidation to 3-(carboxyamino)-2-fluoro-3-hydroxypropanoic acid (TP167), which according to our knowledge was not previously reported (Figure 3.S6). The attack of C-F bond by highly reactive species resulting in defluorination followed by hydroxylation after ring opening in fluorinated aromatic compounds has been reported in different studies, which occurred also with 5-FU in this study, producing *N*-(1-hydroxy-3-oxopropyl) formamide (TP117) [59,61,62].

The Extracted Ion Chromatograms (EIC) of detected 5-FU transformation products in the system is shown in Figure 3.S7.

Degradation products identified are highly hydroxylated. The main reactive species involved were determined to be $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ and ${}^1\text{O}_2$, which together with the hydroxyl radical can assist in the degradation mechanisms. However, a detailed and specific degradation mechanisms with these reactive species is still not clear [63].

Reactions via singlet oxygen generate specific degradation products, such as peroxiranines or perepoxides, zwitterions and diradicals, which were not detected in the

degradation of 5-FU in this study [64,65]. However, it should be considered that singlet oxygen can be quickly quenched by water and contribute only slightly to the 5-FU degradation, as already reported in studies with other pharmaceuticals [27,64].

3.3.4 Catalyst stability and CuMgFe-B(OH)₄ reuse

The high-resolution Fe 2p_{3/2} XPS spectra of CuMgFe-B(OH)₄ performed after the Fenton process (120 min) in the dark (Figure 3.S8e) and under solar radiation (Figure 3.S8f) showed no significant difference compared with the spectra recorded before use (Figure 3.S8d).

However, XPS analysis of CuMgFe-B(OH)₄ revealed that after dark Fenton (Figure 3.S8b) and solar photo-Fenton process (Figure 3.S8c), the Cu(I) content on catalyst surface increased due to the reduction of Cu(II) during the catalytic decomposition of H₂O₂ (Eq. 3.7), which contributed to the generation of reactive species in the removal of 5-FU. Additionally, the high resolution XPS spectrum of B 1s after the Fenton process showed two components, one at 192.4 eV associated with the B-O bond as observed before Fenton process (Figure 3.S9), and a second at 191.6 eV related to B-OH interactions [20]. The presence of both components demonstrates that B-O and B-OH bonds are maintained in the catalyst structure even after the Fenton process.

The stability of catalytic activity of CuMgFe-B(OH)₄ in Fenton processes was evaluated after four 120 min cycles both in purified water and in STWW (Figure 3.11).

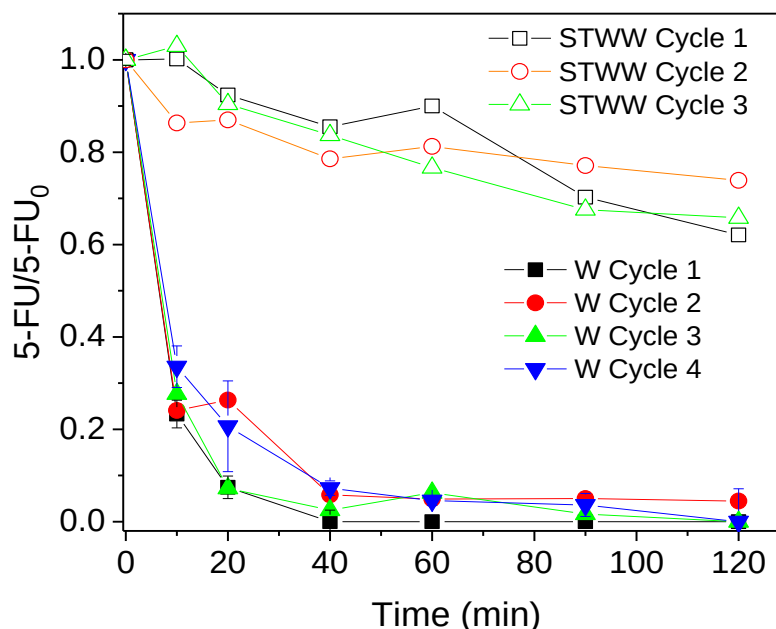


Figure 3.11 Degradation of 5-FU after four cycles reuse of CuMgFe-B(OH)_4 in purified water (W) and wastewater (STWW). Conditions: pH 7.5; $200 \mu\text{g L}^{-1}$ 5-FU; $10 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ and CuMgFe-B(OH)_4 : 0.5 g L^{-1} in the dark.

The results in water show that the material maintained catalytic activity during four cycles resulting in total removal of 5-FU after 90 min (Figure 3.11). The possible electronic changes caused by borate in the material's structure can maintaining the catalytic activity after the material use, which further highlights the catalytic properties of this LDH. The catalytic activity was also maintained in the experiments performed in STWW, although strong inhibition of degradation was observed in this case due to matrix effect, resulting in 38% degradation of 5-FU in STWW after 120 min. Natural organic matter and carbonate are common scavenger of reactive oxygen species, which reduce degradation efficiency [66]. However, the catalytic activity of CuMgFe-B(OH)_4 was maintained even in such a complex sample. Therefore, it is possible to conclude that CuMgFe-B(OH)_4 has potential for application in the removal of contaminants from water bodies in the dark and under solar radiation, highlighting its versatility and stability.

3.4 Conclusions

The findings revealed a significant effect of the interlamellar anion in the LDH structure with borate favoring a strong catalytic activity compared to LDH containing carbonate, sulfate and nitrate. The presence of CO_3^{2-} , SO_4^{2-} , B(OH)_4^- and NO_3^- in the LDH lamellae has been confirmed by FTIR and XPS. Based on XPS and FTIR analysis, it is proposed that the presence of borate facilitated the electron transfer process by the reduction of Fe(III) and Cu(II) species

in LDH surface, especially important in dark reactions. Three transformation products using CuMgFe-B(OH)₄ were identified showing ring opening and partial defluorination. The catalytic efficiency and stability of CuMgFe-B(OH)₄ at near neutral pH, and even after four cycles use, make this material a potential candidate for Fenton and solar photo-Fenton process application.

Conflicts of interest

There are no conflicts to declare.

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Supplementary Material

Effect of the interlamellar anion on CuMgFe-LDH in solar photo-Fenton and Fenton-like degradation of the anticancer drug 5-fluorouracil

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Table 3.S1 Accumulated energy dose values as a function of time in solar photodegradation experiments.

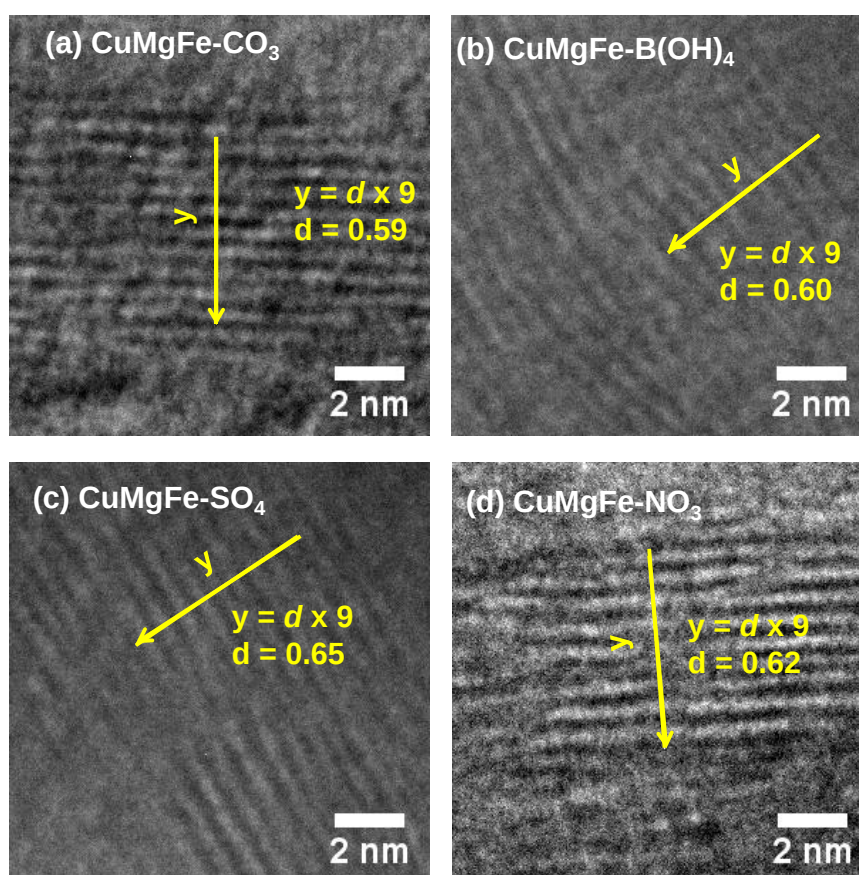
Time (min)	Accumulated energy dose (kJ m ⁻²)
0	0
10	29.19
20	48.52
40	108.19
60	167.27
90	240.50
120	310.44

Table 3.S2 Major physical-chemical properties of the investigated secondary treated domestic wastewater (STWW) after filtration on 0.45 μm cellulose filter.

Parameter	pH	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	TOC	Cu
Value	7.8	514.3 mg L^{-1}	195.3 mg L^{-1}	12.9 mg L^{-1}	58.9 mg L^{-1}	12.65 mg L^{-1}	3.75 μg L^{-1}

Table 3.S3 Chromatographic conditions for separation of transformation products of 5-FU with LC-HRMS

Mode	Solvent A	Solvent B	Gradient	Flow rate (mL min^{-1})
Positive	1% acetonitrile and 0.1% formic acid in ultrapure water.	Acetonitrile with 1% ultrapure water and 0.1% formic acid.	0 – 2 min, 95% A	0.15
			12 – 17 min, 5% A	
			18 – 22 min, 95% A	
Negative	Milli-Q water	Acetonitrile	0 – 2 min, 95% A	0.15
			12 – 17 min, 5% A	
			18 – 22 min, 95% A	

**Figure 3.S1** HR-TEM images with representation of the calculation of the interlamellar domain for the synthesized catalysts.

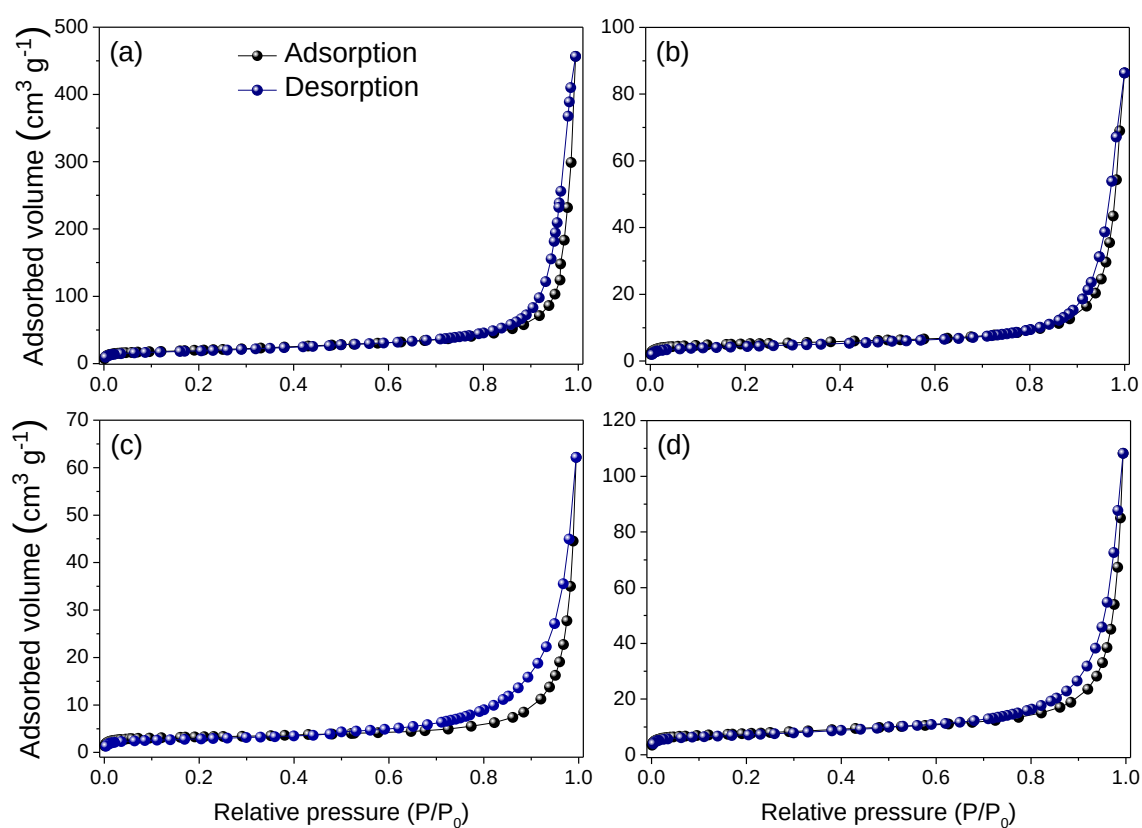


Figure 3.S2 N_2 adsorption/desorption isotherms of the CuMgFe-CO_3 (a) CuMgFe-B(OH)_4 (b), CuMgFe-NO_3 (c) and CuMgFe-SO_4 (d) catalysts. The inset shows the pore size distributions of the materials.

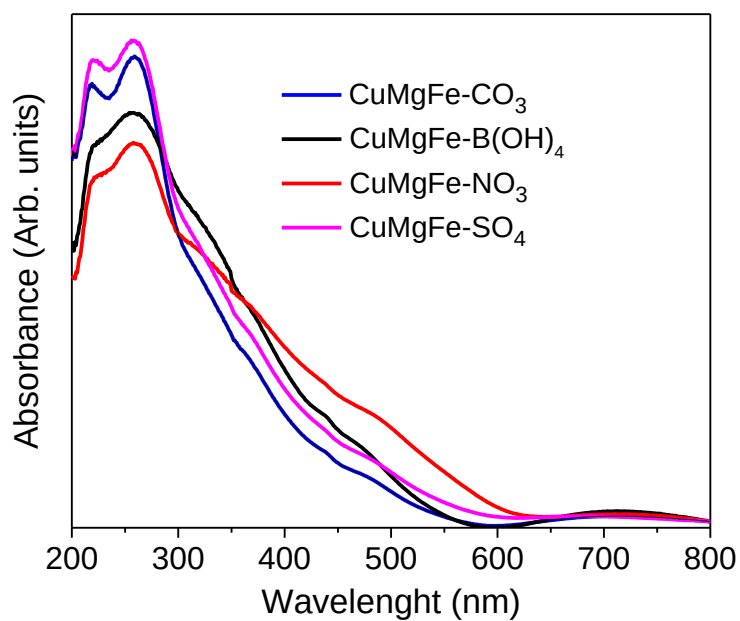


Figure 3.S3 UV-Vis absorption spectra of LDHs synthesized.

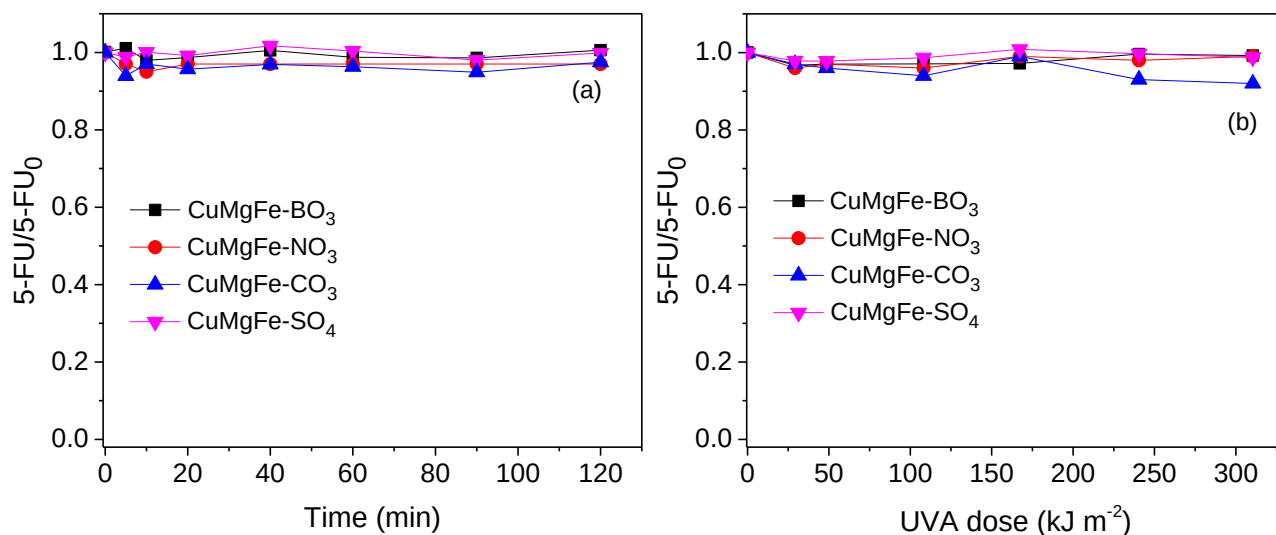


Figure 3.S4 Evaluation of 5-FU adsorption on the surface of CuMgFe-B(OH)_4 , CuMgFe-NO_3 , CuMgFe-SO_4 and CuMgFe-CO_3 in the dark (a) and under solar radiation (b). Initial conditions: $5\text{-FU} = 200 \mu\text{g L}^{-1}$, LDHs = 0.5 g L^{-1} .

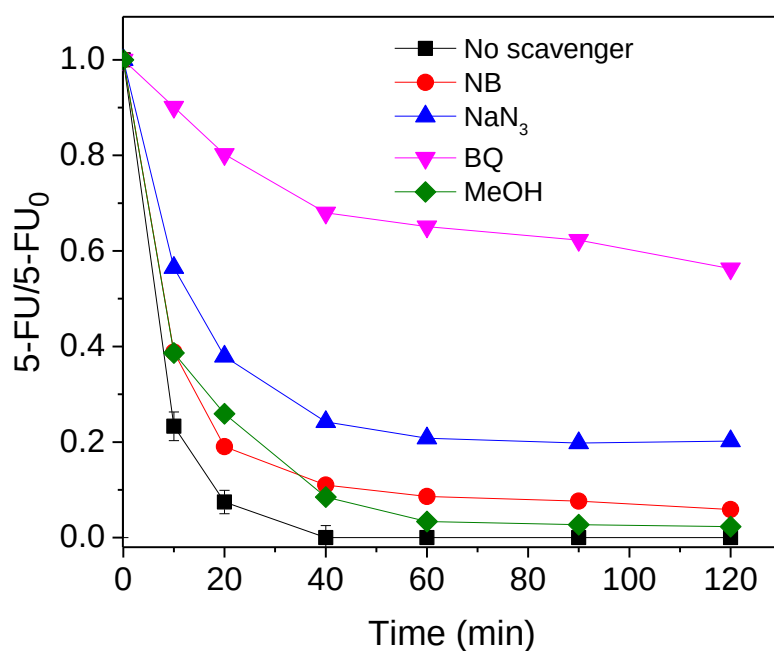


Figure 3.S5 Effect of the radical scavengers NB, NaN_3 , BQ and MeOH on 5-FU degradation in the dark. Conditions: pH 7.5; $200 \mu\text{g L}^{-1}$ 5-FU; $10 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$; 200 mg L^{-1} de BQ, NB, MeOH and NaN_3 ; 0.5 g L^{-1} of CuMgFe-B(OH)_4 .

Table 3.S4 List of previously identified 5-FU transformation products (TPs) detected using negative and positive ionization in sono-photocatalysis, UV/H₂O₂, UV/Fe²⁺/H₂O₂ and UV/TiO₂ [135–137].

Compound	Formula	m/z [M-H] ⁻
5-FU	C ₄ H ₃ N ₂ O ₂ F	129.0045
TP 147	C ₄ H ₅ N ₂ O ₃ F	147.0206
TP 105	C ₃ H ₄ FNO ₂	104.0153
TP 117	C ₄ H ₇ NO ₃	116.0343
TP 141	C ₄ HN ₂ O ₄	140.9942
TP 160	C ₄ H ₄ N ₂ O ₅	159.0047
TP 144	C ₄ H ₄ N ₂ O ₄	143.0098
TP 128	C ₄ H ₄ N ₂ O ₃	127.0152
Compound	Formula	m/z [M+H] ⁺
5-FU	C ₄ H ₃ N ₂ O ₂ F	130.902
TP 146	C ₄ H ₃ FN ₂ O ₃	147.2021
TP 151	C ₄ H ₅ FNO ₄	151.958
TP 163	C ₄ H ₅ FN ₂ O ₄	164.902
TP 167	C ₄ H ₆ FNO ₅	167.902
TP 162	C ₄ H ₆ N ₂ O ₅	163.0350
TP 144	C ₄ H ₄ N ₂ O ₄	145.0249

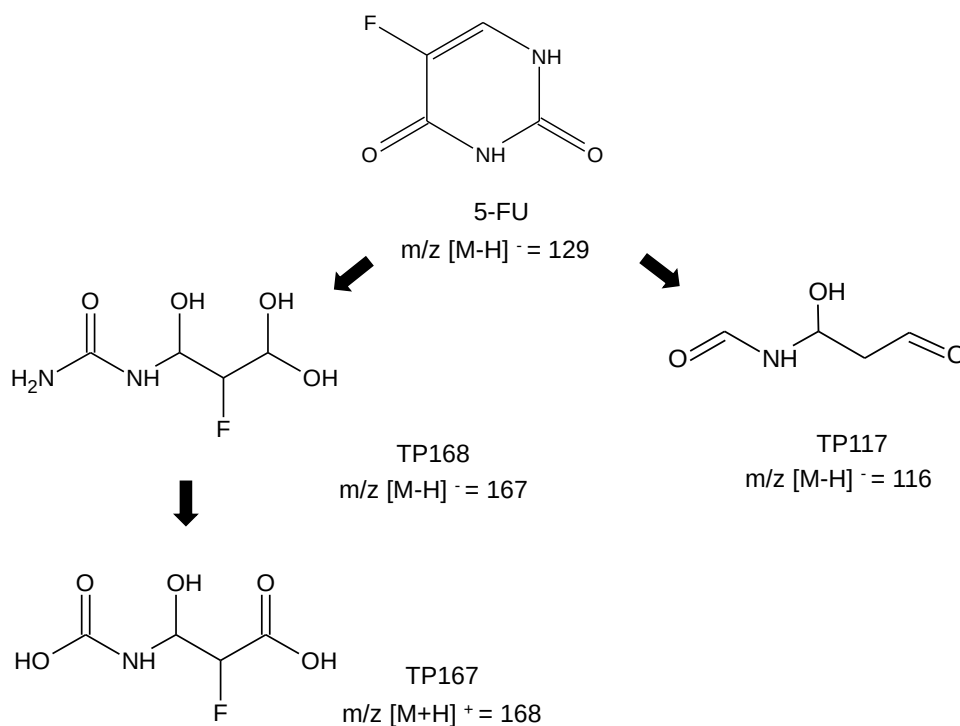


Figure 3.S6 5-FU transformation products (TPs) generated in Fenton processes using CuMgFe-B(OH)₄ in the dark.

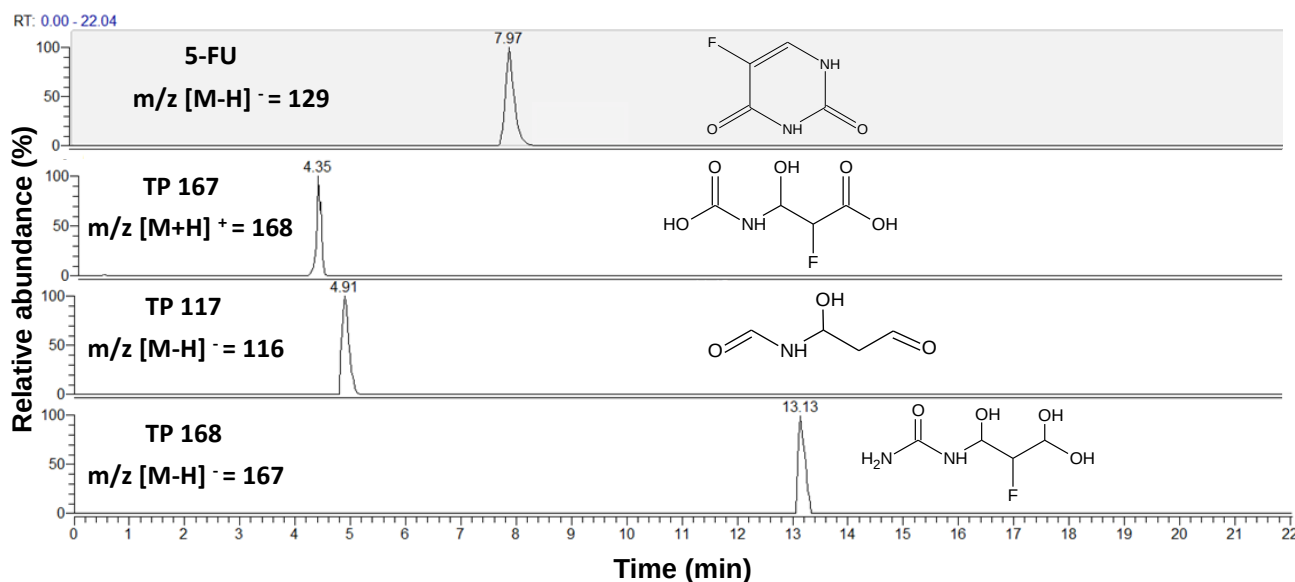


Figure 3.S7 Extracted Ion Chromatograms (EIC) of detected 5-FU transformation products in the system using CuMgFe-B(OH)₄.

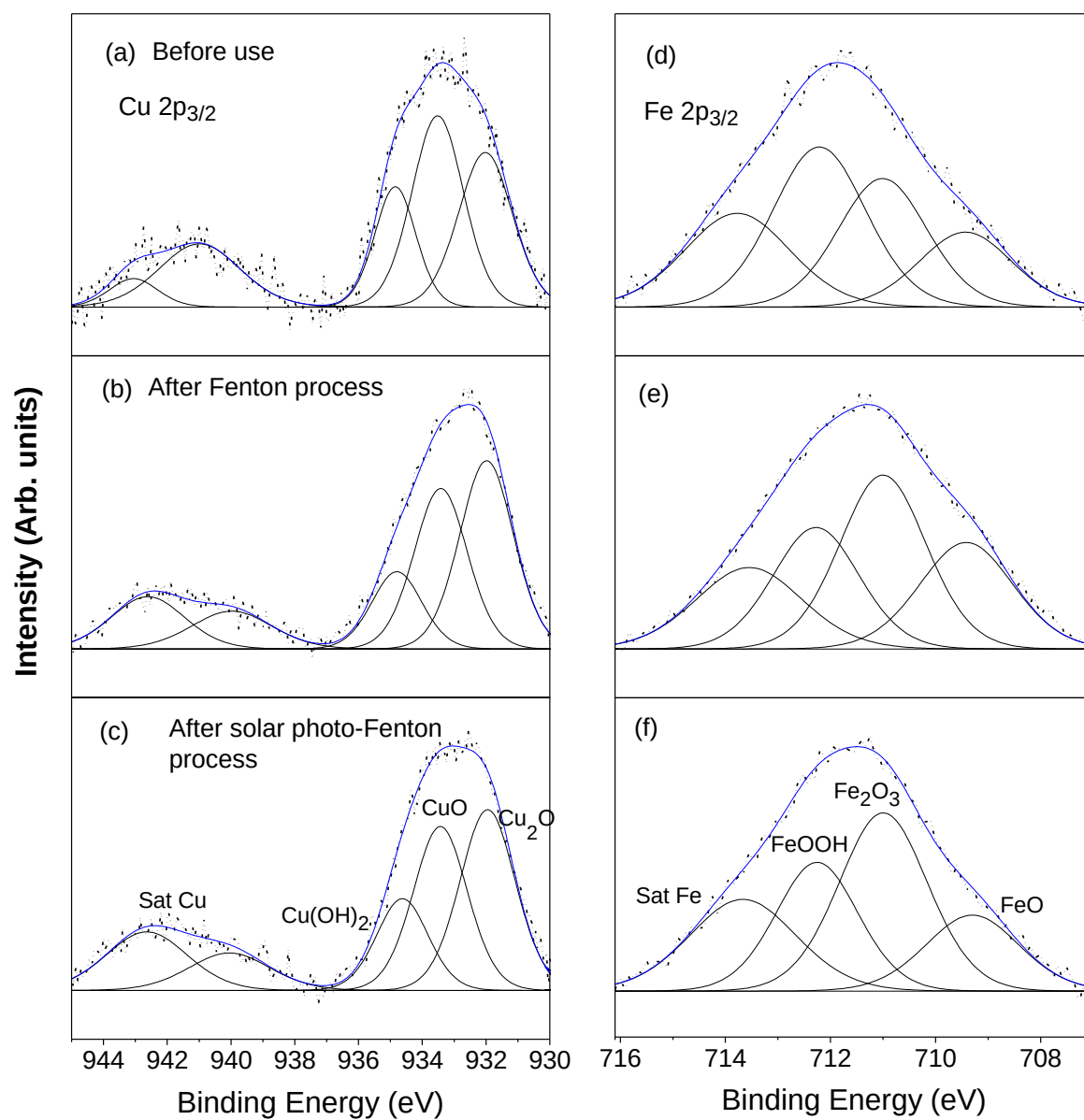


Figure 3.S8 XPS high resolution spectra of Cu 2p_{3/2} and Fe 2p_{3/2} before use (a) and (d), after Fenton process (b) and (e), and after solar photo-Fenton process (c) and (f), respectively in CuMgFe-B(OH)₄.

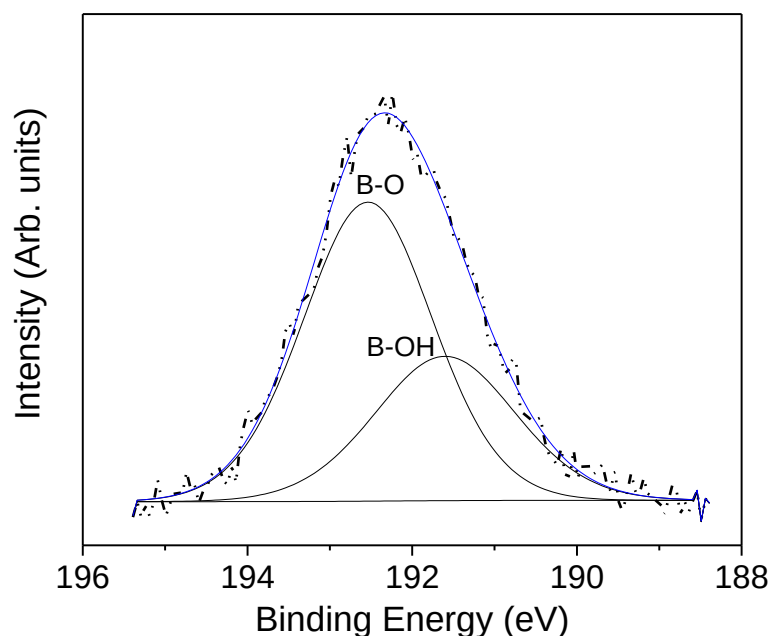


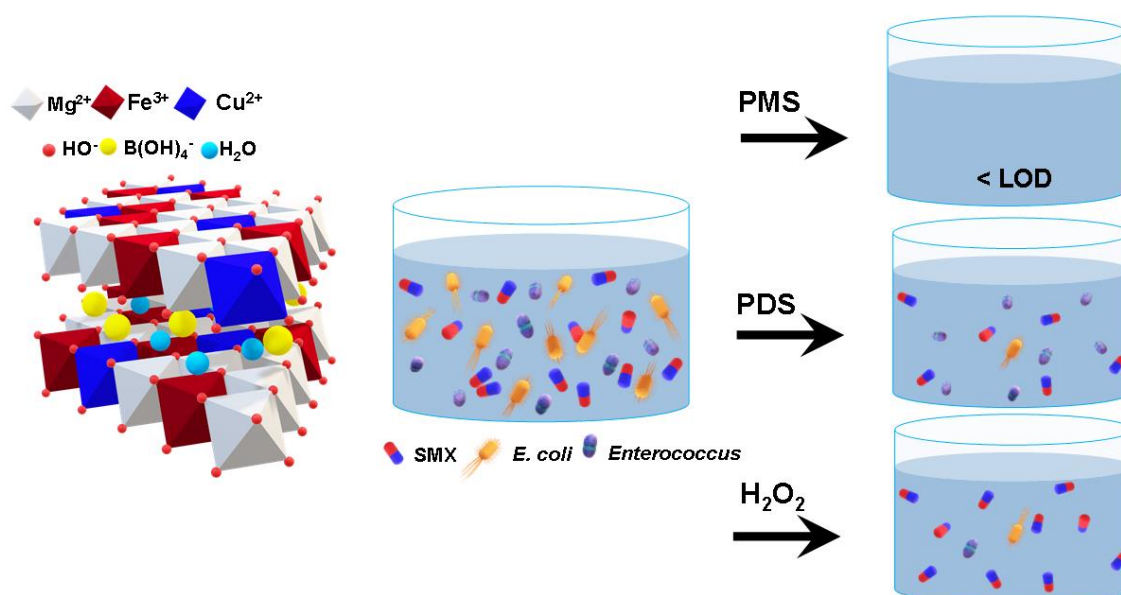
Figure 3.S9 High-resolution spectra of XPS of B 1s in CuMgFe-B(OH)₄ after Fenton process.

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CHAPTER 4

SIMULTANEOUS DISINFECTION OF URBAN WASTEWATER AND ANTIBIOTICS DEGRADATION MEDIATED BY CuMgFe-B(OH)_4 LAYERED DOUBLE HYDROXIDE WITH DIFFERENT OXIDIZING AGENTS



- ✓ CuMgFe-B(OH)_4 – LDH showed good performance with different oxidizing agents.
- ✓ SMX degradation sequence in wastewater was: LDH/PMS > LDH/PDS > LDH/ H_2O_2 .
- ✓ Toxic nitroso and nitro-SMX were not detected with LDH/PMS.
- ✓ *E. coli* and *Enterococcus* elimination followed LDH/PMS > LDH/ H_2O_2 > LDH/PDS.

4 SIMULTANEOUS DISINFECTION OF URBAN WASTEWATER AND ANTIBIOTICS DEGRADATION MEDIATED BY CuMgFe-B(OH)_4 LAYERED DOUBLE HYDROXIDE WITH DIFFERENT OXIDIZING AGENTS

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Abstract

The activation of peroxymonosulfate (PMS), peroxydisulfate (PDS) and hydrogen peroxide (H_2O_2) by CuMgFe-B(OH)_4 layered double hydroxide (LDH) was investigated for the degradation of selected antibiotics (i.e., sulfamethoxazole, ciprofloxacin, cephalixin and amoxicillin) and for bacterial disinfection (*Escherichia coli* and *Enterococcus faecalis*) in secondary treated urban wastewater in dark condition. The catalyst synthesized behaved

differently according to the oxidants used. H_2O_2 activated system was efficient for disinfection but not for antibiotics degradation due to the formation of complexes between LDH cations and H_2O_2 . PDS activated system relied on a non-radical pathway mostly involving singlet oxygen and Cu(III) with antibiotics removal but with a disinfection capacity limited to *E. coli*. The comparison of the investigated systems for the removal of SMX in the secondary treated urban wastewater (STWW) showed 18% and 48% of SMX removal after 120 min of reaction with H_2O_2 and PDS, respectively. On the other hand, with PMS, SMX was below detection limit after 20 min of reaction, demonstrating the superior performance of LDH/PMS for the treatment of STWW. Furthermore, PMS activated with LDH provided more than 90% removal of all antibiotics after 120 min and complete inactivation of the pathogens using 0.5 g L^{-1} of LDH and 4 mM of PMS.

Keywords: heterogeneous Fenton; persulfate; boron-based layered double hydroxide; sulfamethoxazole; enterococcus.

4.1 Introduction

The inefficiency of conventional urban wastewater treatment for the removal of emerging contaminants and inactivation of dangerous pathogens negatively affects water quality and can contribute to the transmission of infectious diseases [1,2]. According to the World Health Organization, water-related diseases kill about 829,000 people each year [3].

The presence of antibiotics in wastewaters can induce the development of antibiotic-resistant bacteria (ARB) and antibiotic-resistant genes (ARGs), and were recognized by WHO as one of the major challenges to human health[4–6]. This problem was aggravated with the increase in pharmaceutical consumption in recent decades. Total daily doses of antibiotics consumed between 2000 and 2018 in 204 countries increased by 46%, with the highest rates in Eastern Europe and Central Asia [7].

Among the most consumed antibiotics worldwide are those belonging to the family of sulfonamides, as sulfametoxazol (SMX) and sulfathiazole (STZ), quinolones, such as ciprofloxacin (CIP), cephalosporins as cefalexin (CFX), and penicillins, as amoxicillin (AMX). These antibiotics have already been detected in wastewater at several countries, at concentrations ranging from 24 ng L^{-1} for AMX to 3700 ng L^{-1} for CIP [8,9].

Chlorination, UV treatment using medium or low-pressure mercury lamps, and ozonation are used for wastewater treatment. However, high energy consumption and treatment

costs, as well as the formation of carcinogenic disinfection by-products, particularly in the presence of natural organic matter, are important limitations for the safe application[10]. Therefore, efficient treatment strategies are needed for simultaneous disinfection and pharmaceuticals removal from wastewater after conventional treatment processes.

The efficiency for removing organic contaminants was reported with the application of PMS alone; however toxic degradation products were generated such as 4-nitro-sulfamethoxazole [11,12]. PDS and H_2O_2 alone are not efficient for removing contaminants and demand heating, UV, or metal activation conditions for an efficient treatment process [13–15].

The investigation of catalysts applied in processes such as Fenton, heterogeneous photocatalysis, electrochemical advanced oxidation processes (EAOPs) and sulfate radical-based advanced oxidation processes (SR-AOP) are highly recommended for the elimination of pharmaceutical contaminants and inactivation of pathogens in wastewater [16,17]. However, achieving a stable catalyst with high catalytic activity for the removal of contaminants at near neutral pH, inactivation of pathogens without generation of secondary pollution, and without generation of transformation products with ecotoxicological consequences, are the major challenges.

A promising catalyst to be used in the degradation of contaminants and disinfection of wastewaters is Layered Double Hydroxides (LDH) based on iron and copper, due to the ability to activate strong oxidizers such as hydrogen peroxide ($E^\circ_{\text{H}_2\text{O}_2} = 1.77 \text{ V}$), peroxydisulfate ($E^\circ_{\text{PDS}} = 2.01 \text{ V}$) and peroxymonosulfate ($E^\circ_{\text{PMS}} = 1.82 \text{ V}$), and to generate reactive species that degrade organic matter and promote inactivation of pathogens [18, 19] with good stability and reusability.

The application of LDH in catalytic systems can circumvent the main limitations of the Fenton homogeneous process, such as chemical stability with efficient degradation even at pH close to neutrality under dark conditions, low or insignificant leaching without sludge generation [18].

The generation of $\text{SO}_4^{\bullet-}$ ($E^\circ = 2.5\text{--}3.1 \text{ V}$) and $\text{HO}^\bullet$ ($E^\circ = 1.8\text{--}2.7 \text{ V}$) in the LDH systems with PMS or PDS attracts attention for investigation aiming an efficient treatment of wastewater. Additionally, LDH shows important advantages compared with composite materials of iron and copper oxides, iron minerals supported on clay materials, carbon materials and metal-organic frameworks (MOFs), such as flexibility in chemical composition, high synergism between the cations, large surface area, well-oriented structure due to the strong

electrostatic interaction between the layers and interlayer anions, low leaching of metals as well as non-toxicity [20–23].

The application of LDH synthesized with Cu(II), Fe(III) and Mg(II) cations, CuMgFe-LDH, and carbonate as interlamellar anion, has demonstrated good performance for Fenton degradation[24]. While Cu and Fe play important role in Fenton chemistry, Mg plays a very important role in stabilizing the lamellar structure of the LDH, as recently proven by Huang et al (2022) [25], but not in Fenton chemistry.

The interlamellar anion in the LDH surface can affect its physicochemical properties, which influences the ease of the anion intercalation in the structure of the double hydroxide [21][20]. It has been demonstrated that the interlamellar anion has strong effect on the catalytic activity for the degradation of pollutants in heterogeneous Fenton process. The presence of $B(OH)_4^-$ as interlamellar anion showed beneficial effect for efficient Fenton degradation when compared to carbonate, nitrate and sulfate as interlamellar anions [20]. Boron species present on the surface of the catalyst can increase the electron density, facilitates the electron transfer process, and promote the reduction of Cu and Fe species, increasing the Cu(II)/Cu(I) and Fe(III)/Fe(II) cycle.

The generation of Cu(I) and Fe(II) on catalyst surface can accelerate Fenton like reactions for the oxidation of contaminants, especially important under dark conditions. In addition, pH adjustments are not necessary as it presents high activity at near neutral conditions. However, care must be taken during the synthesis of CuMgFe- $B(OH)_4$, which must be performed under N_2 atmosphere to eliminate CO_3^{2-} and avoid carbonate intercalation, while storage in the absence of moisture is necessary due to its high hygroscopicity.

In the heterogeneous Fenton chemistry, the contribution of additional non-radical pathways involving high valent metal (i.e., cupryl (Cu(III)) and ferryl (Fe(IV)) ions) and singlet oxygen for removing contaminants have been previously discussed [26–28] and the role of these species in the removal of antibiotics will also be investigated in this study.

Based on these features and considering the lack of studies of LDHs with other oxidizing agents for the first time, the performance and mechanism of CuMgFe- $B(OH)_4$ -LDH in activating different oxidizing agents, H_2O_2 , PDS and PMS, for simultaneous removal of the antibiotics and pathogens inactivation was investigated in this study, while the non-radical pathways involving high valent metal (i.e., cupryl (Cu(III)) and ferryl (Fe(IV)) ions) and singlet oxygen for removing contaminants is discussed. Furthermore, kinetic studies in deionized water and secondary treated urban wastewater (STWW), elucidation of transformation pathways for

SMX, proposal of the mechanism of radical and non-radical reactive species generation in the different systems for the simultaneous degradation of the antibiotics SMX, CIP, CFX and AMX, and inactivation of *Escherichia coli* and *Enterococcus faecalis* were discussed.

4.2 Experimental

4.2.1 Reagents

Sulfamethoxazole (SMX), cephalexin (CFX), ciprofloxacin (CIP), amoxicillin (AMX) (99.9%), bovine catalase (> 10,000 units/mg protein), furfuryl alcohol (FFA, > 99%), nitrobenzene (NB, > 98%), *p*-benzoquinone (BQ, >98%), sodium azide (NaN₃, > 99.5%), Oxone (KHSO₅•0.5KHSO₄•0.5K₂SO₄) were from Sigma-Aldrich. Fe(NO₃)₃•9H₂O was from Mallinckrodt (Brazil). Mg(NO₃)₂ and NaOH were from Exodo Cientifica (Brazil). Cu(NO₃)₂ was from Neon. H₂O₂ (30% wt/wt), NH₄VO₃ were from Synth. KI and K₂S₂O₈ were purchased from Honeywell (Germany). Acetonitrile (HPLC grade) and methanol (MeOH, HPLC grade) were purchased from Carlo Erba reagents (France). All solutions were prepared with ultrapure water obtained from a Milli-Q Plus system (Millipore, Bedford, MA).

4.2.2 Preparation of the CuMgFe-B(OH)₄

The synthesis of CuMgFe-B(OH)₄ was based on the coprecipitation method according to a protocol adopted previously (see Costa-Serge et al., 2021; 2022), adopting pH 11.0 ± 0.5 using 0.011 mol Cu(II), 0.109 mol Mg(II) and 0.040 mol Fe(III). The salts and NaOH solution (2.0 M) were added dropwise to 1.9 L of deionized water in the presence of 0.48 mol of H₃BO₃ under vigorous stirring keeping the pH value constant in a N₂ atmosphere to exclude CO₂.

4.2.3 Characterization of the CuMgFe-B(OH)₄

X-ray diffractometry (XRD) with Rietveld refinement, scanning electron microscopy images (SEM), high-resolution transmission electron microscopy (HR-TEM), specific area, Fourier transform infrared spectra (FTIR), UV-Vis absorption spectra, thermal analyses and high-resolution X-ray photoelectron spectra (XPS), were applied for the characterization of the prepared CuMgFe-B(OH)₄-LDH as described in previous study [20].

After reaction using PDS and PMS, the catalyst was characterized by XRD, Raman spectroscopy, SEM and XPS. DRX analysis was performed on a Rigaku SmartLab SE D/Tex ultra-250. Diffraction signal has been acquired through theta/2theta scans from 5 to 80° with 0.02° step, with an acquisition time of 1s/step. Raman spectra of the catalyst after use were

obtained with a LabRAM HR 800 model Raman Spectrophotometer (Horiba Jobin Yvon) equipped with CCD detector (model DU420A-OE-325) and a He-Ne laser (632.81 nm). The spectra were taken between 50 and 2000 cm^{-1} with acquisition time of 40 s and 2 cycles.

SEM images were obtained using a Hitachi Dual - Beam FIB-SEM NB5000, while XPS analysis were obtained using a UNI-SPECS UHV system equipped with an Mg $\text{K}\alpha$ X-ray source ($h\nu = 1253.6 \text{ eV}$) at a base pressure $< 10^{-7} \text{ Pa}$ as previously described [20].

4.2.4 Degradation and disinfection experiments

Experiments were performed at room temperature under dark conditions during 120 min. Antibiotics were spiked in 100 mL of purified water or STWW to evaluate matrix effects in a glass reactor 5 cm high and 10 cm in diameter with magnetic stirring (1200 - 1400 rpm). The experiments were carried out at least in duplicate.

Firstly, control experiments were carried out with 500 $\mu\text{g L}^{-1}$ of SMX solution and addition of 1 mM PMS, PDS or H_2O_2 to study the efficiency of each system separately.

Subsequently, the LDH/PDS system was chosen to determine the best catalyst (0 - 0.8 g L^{-1}) and oxidizing agent concentration (0 - 6 mM PDS).

Experiments were carried out in the presence (0.5 g L^{-1}) and absence of the LDH as well as in the presence of 4 mM and absence of the oxidizing agent.

Effluents were collected at the outlet of a conventional activated sludge wastewater treatment plant (STWW, 20,000 equivalent inhabitants). The physico-chemical properties of STWW are listed in Table S1. STWW was firstly filtered through a 200 μm sieve to remove the large suspended solids.

The degradation of SMX in the STWW was evaluated separately in the systems using the optimal catalyst and oxidizing agent concentration that is 500 $\mu\text{g L}^{-1}$ of SMX, 4 mM PMS, PDS and H_2O_2 in 100 mL of wastewater at natural pH ($\text{pH} = 7.5$).

The simultaneous degradation of the antibiotics SMX, CIP, CFX and AMX was evaluated in deionized water containing 2000 $\mu\text{g L}^{-1}$ of each contaminant with LDH/PDS and LDH/PMS systems with 4 mM oxidizing agent and 0.5 g L^{-1} LDH during 120 min. Control experiments in the absence of oxidant as well as in the absence of 0.5 g L^{-1} were also performed. The application of the LDH/PDS system in STWW was carried out with the addition of 250 $\mu\text{g L}^{-1}$ of the antibiotics SMX, CIP, CFX and AMX in 100 mL of the STWW, in the presence of 4 mM of PDS and 0.5 g L^{-1} of LDH during 120 min.

To evaluate the disinfection performance against *Escherichia coli* and *Enterococcus faecalis* with LDH in the different systems, as well as the ability to comply with the

requirements with the EU Regulation 2020/741 of the European Parliament and of the Council of 25 May 2020 on minimum requirements for water reuse (EU - COM 2014/015, 2014), the NF EN ISO 9308-3 and NF EN ISO 7899-1 standard protocols were used to enumerate *E. Coli* and *Enterococcus*, respectively. These methods are based on the culture of the bacteria in a liquid medium and the determination of the most probable number (MPN) according to the level of dilution.

Initially, the disinfection control experiments were carried out in the absence of the catalyst using the optimal conditions of the degradation experiments, as well as in the absence of oxidizing agent in the presence of 0.5 g L^{-1} of CuMgFe-B(OH)_4 in 600 mL of STWW and aliquots were withdrawn after 120 min of experiment.

4.2.5 Chemical analysis

Aliquots were withdrawn at predetermined time intervals and bovine catalase and Na_2SO_3 was added to ensure the consumption of residual H_2O_2 , $\text{Na}_2\text{S}_2\text{O}_3$ for consumption of PDS, and PMS, respectively, and consequently to interrupt the degradation and disinfection processes. The samples were then filtered through $0.45 \text{ }\mu\text{m}$ nylon membranes prior to HPLC analysis and also through $0.20 \text{ }\mu\text{m}$ nylon membranes for LC-HRMS.

For the kinetic studies with SMX alone, the concentration during the degradation process was determined using high performance liquid chromatography (HPLC) with a diode-array detector using an Agilent ZORBAX Eclipse XDB C8 column ($250 \times 3 \text{ mm i.d.}$, $5 \text{ }\mu\text{m}$ particle size) for kinetic studies. The separation was performed using an isocratic mode of elution with a mobile phase composed of 0.1% formic acid in Milli-Q water and acetonitrile (70:30) at a flow rate of 0.5 mL min^{-1} , $40 \text{ }^\circ\text{C}$ and $\lambda = 260 \text{ nm}$, resulting in a detection limit of $8.8 \text{ }\mu\text{g L}^{-1}$.

The concentrations of the antibiotics (SMX, CIP, CFX and AMX) in a mixture were determined using the same equipment with an Eclipse XDB C18 column ($150 \times 3.0 \text{ mm i.d.}$, $3.5 \text{ }\mu\text{m}$ particle size), mobile phase composed of 0.1% H_3PO_4 in Milli-Q water and Methanol in the proportion 75:25 at a flow 0.4 mL min^{-1} , $\lambda_{\text{SMX}} = 260 \text{ nm}$, $\lambda_{\text{AMX}} = 230 \text{ nm}$, $\lambda_{\text{CFX}} = 262 \text{ nm}$ and $\lambda_{\text{CIP}} = 280 \text{ nm}$.

The transformation products of SMX were detected using LC-HRMS. A Dionex Ultimate 3000 liquid chromatograph coupled to an electrospray source and an Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific, Les Ulis, France) operated in full scan MS (mass range m/z 50–900) in positive mode ionization were used. The collisional dissociation energy

was set to 20 eV and a drying gas temperature to 300 °C. The analytical column was an Agilent ZORBAX Eclipse XDB C18 plus column (150 × 2.1 mm i.d., 3.5 µm particle size). A gradient elution was performed using 1% acetonitrile and 0.1% formic acid (solvent A) and acetonitrile with 1% Milli-Q water and 0.1% formic acid (solvent B) as follow: 0–5 min, 95% A; 15–20 min, 5% A; 21–30 min, 95% A at a flow rate of 0.15 mL min⁻¹.

For indirect investigation of SMX degradation and evaluation of the radical species involved in the LDH/PDS system, p-benzoquinone (BQ), methanol (MeOH), nitrobenzene (NB) and furfuryl alcohol (FFA) were used as HO₂[•]/O₂^{•-}, HO[•]/SO₄^{•-}, HO[•] and ¹O₂ scavengers, respectively. The scavengers were added in excess (200 mg L⁻¹) to SMX/LDH suspensions in separate experiments with 4 mM of PDS.

The iodometric spectrophotometric method was applied to determine the residual concentration of PDS and PMS during reaction [13], while the spectrophotometric method using metavanadate was used for H₂O₂ [29]. Consumption of oxidants was calculated by subtracting residual concentration from the initial concentration, expressed in mmol L⁻¹. A Shimadzu UV mini-1240 spectrophotometer from Shimadzu (Japan) was used in all spectrophotometry analysis.

Concentrations of soluble Mg, Cu and Fe ions in solution after reaction were determined using Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) after filtration, using a Perkin Elmer Avio200 spectrometer.

4.3 Results and discussion

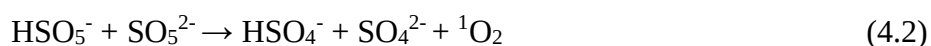
CuMgFe-B(OH)₄-LDH was characterized in detail in a previous study [20] and the main results are summarized as follows: the formation of a lamellar material with the basal planes 003, 006 and 009 was demonstrated by X-ray diffractograms with Rietveld refinement. SEM results showed irregular shape due to the low ability of B(OH)₄⁻ anions to stabilize the LDH structure, leading to the formation of smaller particles. With FTIR and XPS techniques, it was possible to identify the presence of B-O and B-OH bonds on the surface of CuMgFe-B(OH)₄.

4.3.1 SMX degradation in deionized water mediated by LDH/PDS, LDH/PMS and LDH/H₂O₂

Experiments in the absence of the LDH performed to assess the effect of each oxidant resulted in a direct oxidation of SMX of 67%, 14% and 13% after 120 min using PMS, PDS and H₂O₂, respectively (Figure 4.S1).

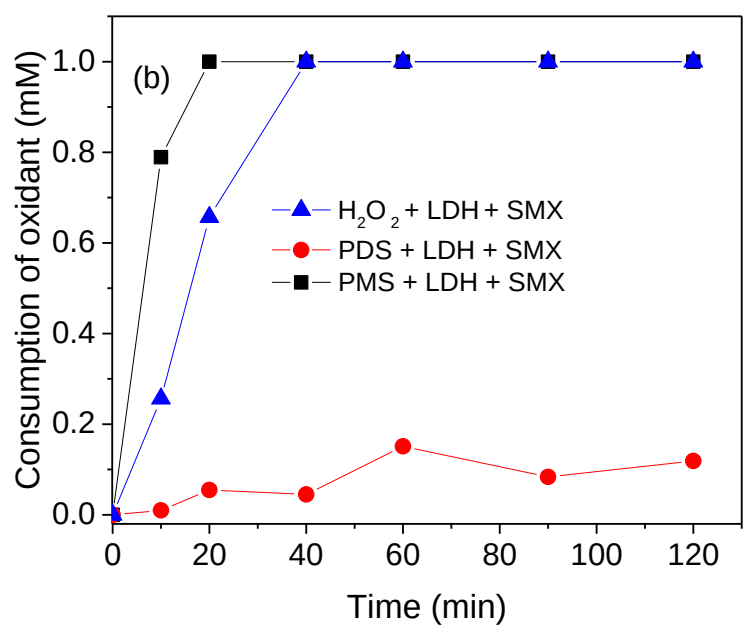
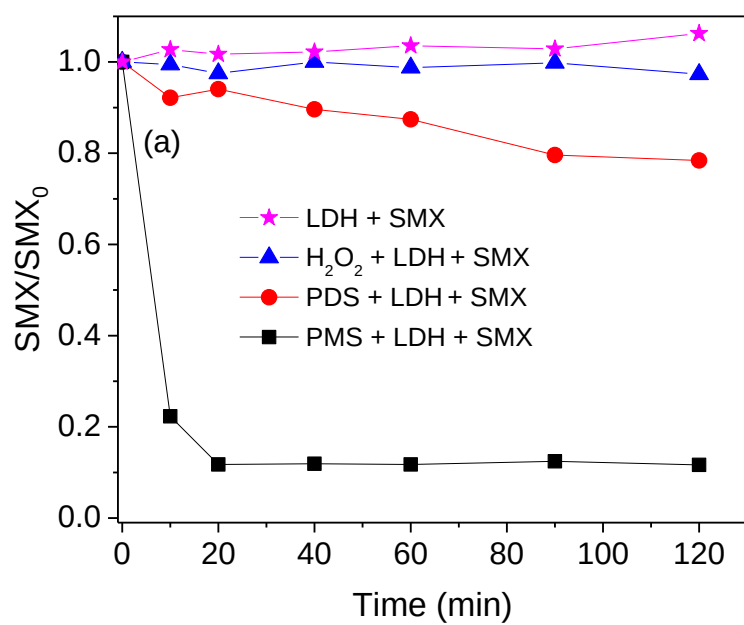
The initial pH of the SMX solution was 6.7, decreased to pH 3 after adding PMS, and remained constant during 120 min of reaction (Figure 4.S1b). One of the advantages of applying PMS direct oxidation is that the system can be operated efficiently over a wide pH range (pH = 3 - 11) [30,31].

Although the three peroxides investigated are similar in structure with O–O bond (Figure 4. S2), PMS differentiates from the other peroxides since it decomposes spontaneously in water (Eq. 4.1) with subsequent self-oxidation (Eq. 4.2). In this step, ¹O₂ can be generated, which contributed for the increase of SMX oxidation (Figure 4.S1) [32,33].



Previous similar studies have reported the removal of SMX, sulfadiazine, sulfamerazine, sulfamethazine, sulfatiazol and sulfanilamide using PMS direct oxidation[31,33,34]. However, the inefficiency of direct oxidation of phenol, atrazine, and benzoic acid with PMS revealed its selectivity towards some contaminants such as sulfonamides.

After addition of 0.5 g L⁻¹ LDH, PMS was activated and rapidly oxidized SMX (89% after 20 min) (Figure 4.1a), with a total consumption of PMS in the first 20 - 40 min of reaction (Figure 4.1b). On the other side, LDH/PDS and LDH/H₂O₂ resulted in much lower degradation. This behavior is related to the asymmetry of these peroxides. While PMS (⁻O₃SO-OH) is asymmetric with a dipolar structure (Figure 4.S2), PDS (⁻O₃SO-OSO₃⁻) and H₂O₂ present symmetrical structures and therefore were more difficult to be activated and generate reactive oxygen species than PMS. Furthermore, the bond energy of PDS (140 kJ mol⁻¹) is lower than that of H₂O₂ (213.3 kJ mol⁻¹). This can be an advantage in the LDH/PDS compared to LDH/H₂O₂ system (Figure 4.1a). No reference value of bond energy is available for PMS [14,32].



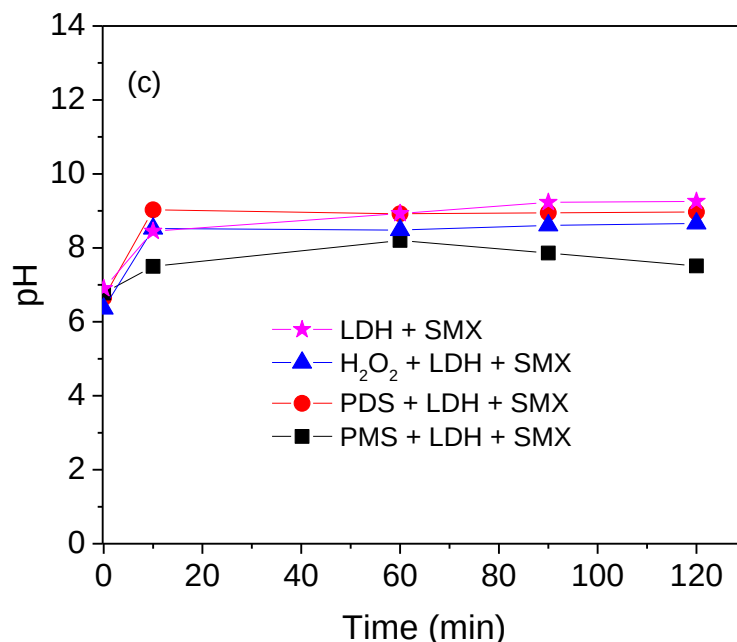


Figure 4.1 Evaluation of LDH catalytic activity (a), consumption of oxidizing agent (b), and increases of pH in deionized water (c) in SMX degradation using 1 mM H₂O₂, PDS and PMS. Conditions: 500 µg L⁻¹ SMX; 0.5 g L⁻¹ LDH.

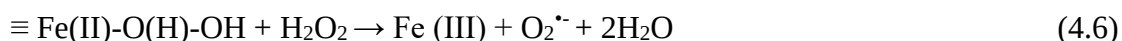
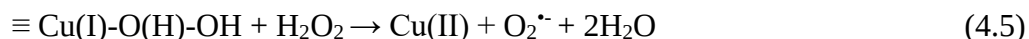
Control experiments in the dark indicated that there was no SMX adsorption on the catalyst surface (Figure 4.1a).

In LDH/PDS system, only 22% of SMX were removed with 3% PDS consumption (Figure 4.1b). The calculated stoichiometric efficiency (amount of SMX degraded in relation to PDS consumed on a molar basis) was 0.36%. Low stoichiometric efficiencies for PDS consumption can be justified due to the low initial concentration of SMX besides the small amount of Cu(II) and Fe(III) present in the catalyst. Furthermore, the SMX degradation efficiency in PDS activated systems was dependent on PDS concentration and pH.

The degradation of SMX in LDH/H₂O₂ system after 120 min was only 3% (Figure 4.1a), which is 4.4 times lower than the direct oxidation with H₂O₂ (13.3%), however with total consumption of the 1 mM H₂O₂ initially present (Figure 4.S1). Increasing H₂O₂ concentration from 1 mM to 4 mM in the presence of 0.5 g L⁻¹ increased SMX degradation by about 20% (Figure 4.S3). However, further increase to 10 mM did not further improve removal rate, indicating adsorption or complexation between LDH and H₂O₂. The formation of a complex between the transition metals of LDH and H₂O₂, as depicted in Eq. 4.3 and 4.4 and as previously reported by Goldstein et al. (1993) [35], might account for the high consumption of H₂O₂ in the absence of SMX.

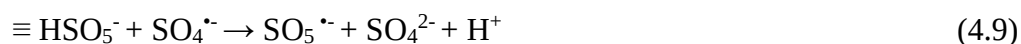


Consequently, Cu(I)-O(H)-OH and Fe(II)-O(H)-OH could be generated on the surface of the LDH but were most likely non-reactive with SMX. In addition, the reaction of these complexes formed with H₂O₂ can generate the O₂^{•-} (Eq. 4.5 and 4.6), resulting in less efficient degradation than with HO[•] [36–38].



When LDH is dispersed in water, the hydroxyl groups present in the vertices of the octahedrons structure can act as Bronsted-Lowry bases accepting protons, with the formation of hydroxyl groups in the solution, resulting in the increase of solution pH in the first 10 min of the reaction and maintained at 7.7 ± 0.3 with PMS, 9.0 ± 0.1 with PDS and 8.6 ± 0.1 with H₂O₂ until the end of the experiments (120 min) (Figure 4.1c). These pH values are close to the values of urban wastewaters, which is advantageous in wastewater treatment applications, since it demands no pH adjustment reducing the treatment costs.

As shown in the equations 4.7 - 4.10, the possible radical generation mechanisms in the LDH/PMS system influenced the SMX degradation efficiency (Figure 4.1a) and confirms that activation of PMS with LDH promotes high degradation kinetics, due to the generation of the two types of radicals, SO₄^{•-}, and HO[•] [17].



According to our investigations, LDH/PMS was the best system to be used for SMX removal in the investigated systems, with total consumption under neutral conditions within 20 min of reaction. Furthermore, the self-oxidation of PMS (Eq. 4.2) also has a contribution to the activated process and can reduce costs for the application.

4.3.2 Application of LDH/PDS, LDH/PMS and LDH/H₂O₂ systems for the degradation of SMX in wastewater

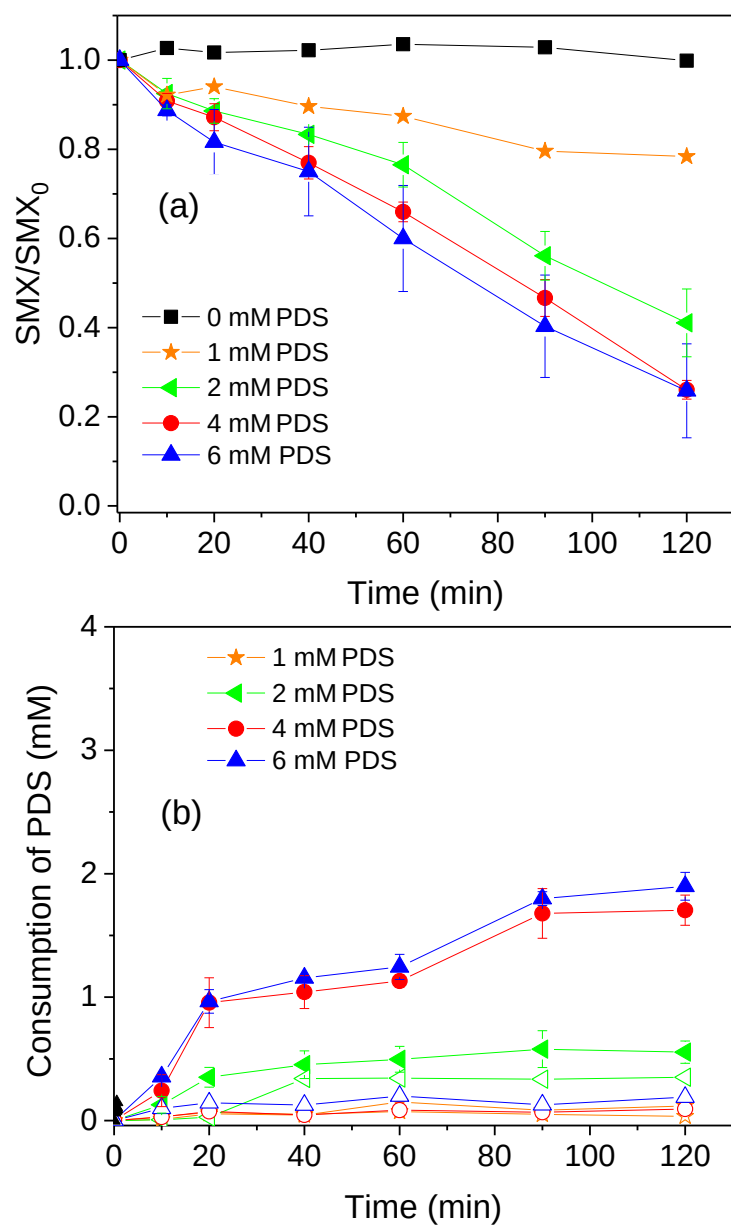
The application of the investigated systems to pharmaceutical removal in wastewater requires the evaluation of the effect of the concentration of catalyst and oxidizing agent. For this purpose, LDH/PDS was chosen because PDS has some advantages over PMS, such as lower price and greater stability that facilitates transport [39]. Furthermore, in the initial studies of this work, PMS showed too fast degradation kinetics, making the evaluation difficult, and H₂O₂ was inefficient for SMX degradation (see Figure 4.1a).

As shown in Figure 4.2a, the presence of PDS was necessary to promote SMX degradation, which resulted in 74% after 120 min when increasing its concentration from 0 mM to 6 mM. However, as no significant difference was observed using 4 and 6 mM PDS, 4 mM PDS was chosen to be used in further experiments.

Notably, no consumption of PDS occurred in the absence of SMX (Figure 4.2b open symbols) using 1, 2, 4 and 6 mM PDS, indicating that no complexation or adsorption between PDS and LDH. After the interaction of LDH with PDS, reactive species such as SO₄^{•-} can be generated. However, in the absence of SMX to be oxidized, these radicals recombine regenerating PDS (Eq. 4.11), which explains the absence of significant consumption of PDS in reaction medium [40].



Only 10% SMX were degraded directly by PDS (Figure 4.2c). However, SMX degradation was improved to 59% after 120 min in the presence of 0.3 g L⁻¹ LDH, which increased to 74% when LDH concentration was increased to 0.5 g L⁻¹ with no further enhancement from 0.5 to 0.8 g L⁻¹. The concentration of 0.5 g L⁻¹ LDH was therefore selected for further experiments.



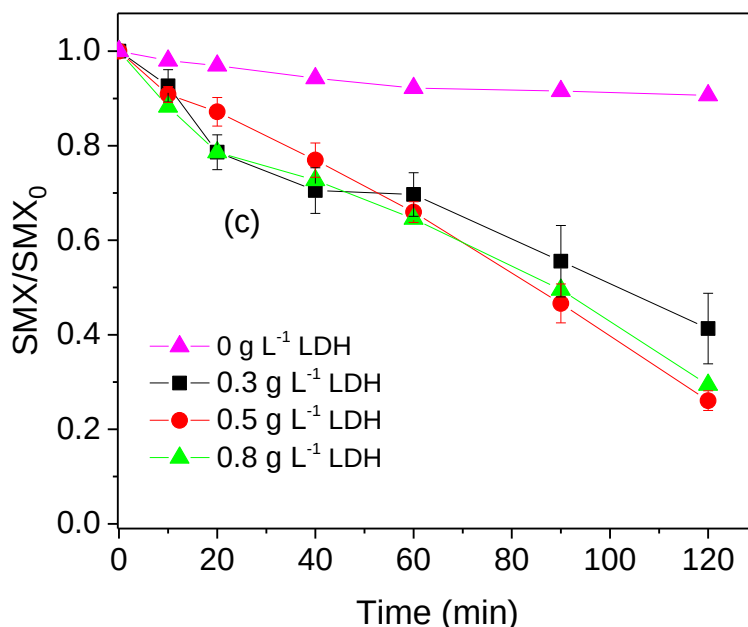
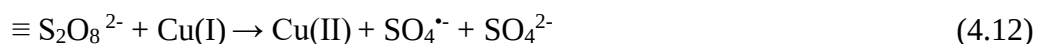


Figure 4.2 Effect of PDS concentration on SMX degradation (a), consumption of PDS in the presence (solid symbols) and in the absence of SMX (open symbols) (b), and effect of LDH concentration on SMX degradation (c). Conditions: pH = 9.0 ± 0.1; 500 µg L⁻¹ SMX; 0.5 g L⁻¹ LDH and 4 mM PDS.

The presence of Cu(I) and Fe(II) species in the LDH structure was identified by XPS (Costa-Serge et al., 2022) [20], which contributed to decomposition of PDS (S₂O₈²⁻) and generation of HO• and SO₄•⁻ (Eq. 4.12 – 4.14) and subsequent SMX oxidation [11,13]. Figure 4.S2 represents the structure of the different oxidizing agents and indicates how the generation of SO₄•⁻, SO₄²⁻ and HO• occurs due to the cleavage of the O-O bond when PDS can receive an electron from Cu(I) and Fe(II) (Eq. 4.12 and 4.13). Furthermore, under neutral conditions, SO₄•⁻ slowly hydrolysis to generate HO• (Eq. 4.14).



The Cu(II)/Cu(I) redox pair ($E^0 = 0.17 \text{ V}$ in aqueous solution) is much lower than the redox potential of PDS ($E^0 = 2.01 \text{ V}$) and therefore, in the system with PDS the redox cycle Cu(II)/Cu(I) is thermodynamically unfavorable [41], indicating the advantage of the CuMgFe-B(OH)₄, which has Cu(I) in its composition. The activation of PDS by Cu(II) needs to be further investigated, particularly in heterogeneous catalysis.

After defining the concentration of oxidant (4 mM) and catalyst (0.5 g L^{-1}) in the LDH/PDS system, the effect of the three oxidants for the removal of SMX in STWW was compared in the absence and presence of LDH.

The direct oxidation of SMX in wastewater using 4 mM H_2O_2 , PDS or PMS showed that PMS was the only oxidant leading to full oxidation of SMX after 40 min (see Figure 4.3a) consuming 37.5% of initial PMS amount (Figure 4.S4 a), similarly to the observed in deionized water (Figure 4.S1). The efficiency of SMX direct oxidation with PMS in STWW is due to the self-oxidation of PMS which generates singlet oxygen (Eq. 4.2), as discussed in the section 4.3.1.

However, it was observed that the degradation of SMX in STWW was accelerated with all oxidizing agents when LDH was introduced (Fig. 4.3 b). In the case of LDH/PMS, SMX was below detection limit ($8.76 \mu\text{g L}^{-1}$) after only 20 min revealing the excellent activity of the catalyst for the generation of reactive oxygen species (Eq. 4.7 – 4.10) while consuming 3 mM PMS (Figure 4.S4 b). In contrast, in LDH/PDS, a non-radical mechanism of SMX degradation was prevailing as will be discussed later (Figure 4.4 and 4.5).

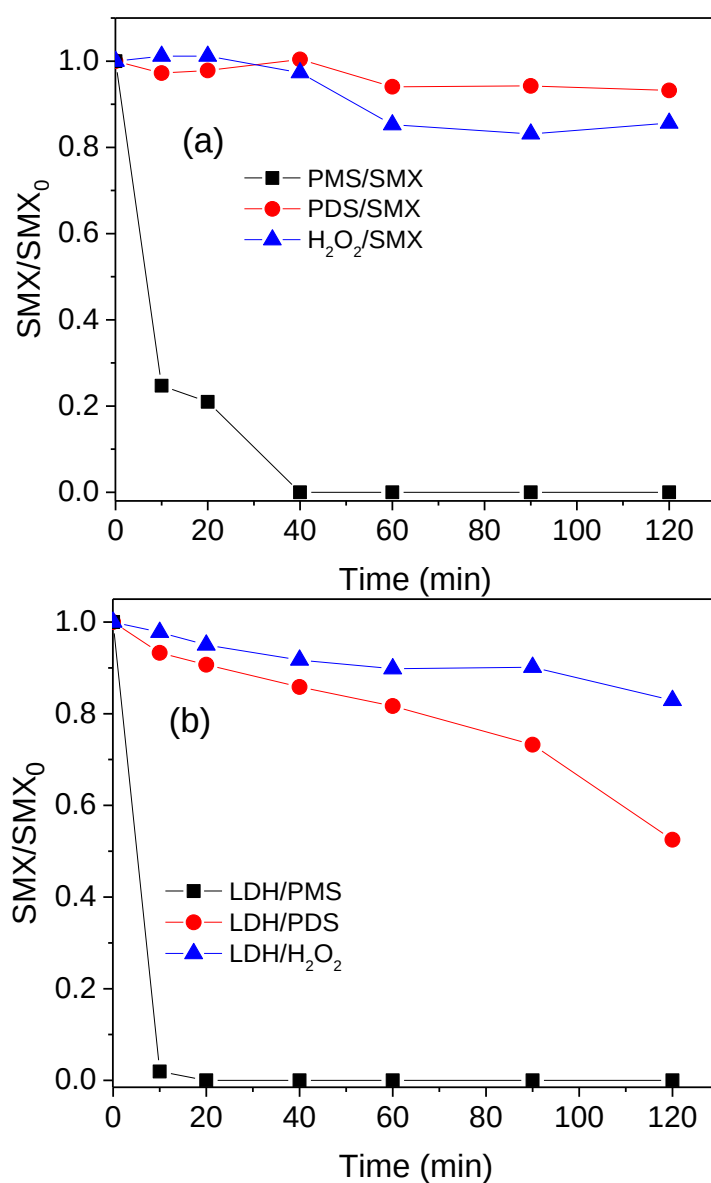


Figure 4.3 Direct SMX oxidation with PDS, PMS and H₂O₂ in STWW (a) and in SMX degradation in LDH/PDS, LDH/PMS and LDH/H₂O₂ systems in STWW (b). Conditions: pH = 7.5; 500 µg L⁻¹ SMX, 0.5 g L⁻¹ LDH; 4 mM of PDS, PMS and H₂O₂.

In the LDH/PDS system, after 120 min, 50% of SMX was removed in STWW, while only 18% SMX removal was obtained in LDH/H₂O₂ system with 44% consumption (Figure S4 b) due to the formation of a complex between LDH and H₂O₂ with subsequent formation of superoxide radical (Eq. 4.3 – 4.6).

The experiments in STWW were performed with an oxidizing agent concentration four times higher than the experiments in purified water (Figure 4.1a) with similar catalytic decomposition by LDH: PMS > PDS > H₂O₂. This indicates the higher effectiveness of the

system with PMS, which after activation by LDH simultaneously generates the two radicals $\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$ (Eq. 4.7 and 4.8) compared to PDS and H_2O_2 systems.

In addition, these results are in good agreement with other studies, which showed that $\text{HO}^{\bullet}$ are most probably eliminated by the organic matter in the effluent and $\text{SO}_4^{\bullet-}$ radicals have a slightly higher redox potential (2.5 – 3.1V) compared to $\text{HO}^{\bullet}$ (1.8 – 2.7) resulting in higher reaction rate constants with contaminants rich in electrons [17,42,43].

According to these results, LDH can promote efficient activation of PMS, being considered the most promising system among those investigated for the removal of SMX from STWW.

4.3.3 Mechanism of SMX transformation using LDH/PDS, LDH/ H_2O_2 , LDH/PMS, and PMS alone

SMX transformation pathways in all investigated systems (see Figure 4.4) were elucidated on the basis of the identification of transformation products (TPs) (see Figure 4.S5 and Figure 4.S6). A suspect screening approach in LC-HRMS was adopted based on a database composed of a list of possible TPs already identified in the literature in different oxidative treatment processes. Their molecular formula and exact mass are reported in Table 4.S2. Potential TPs with intensities lower than 1×10^4 cps, with a signal to noise ratios lower than 10, isotopic ratio higher than 10%, and mass accuracy errors higher than 5 ppm were discarded.

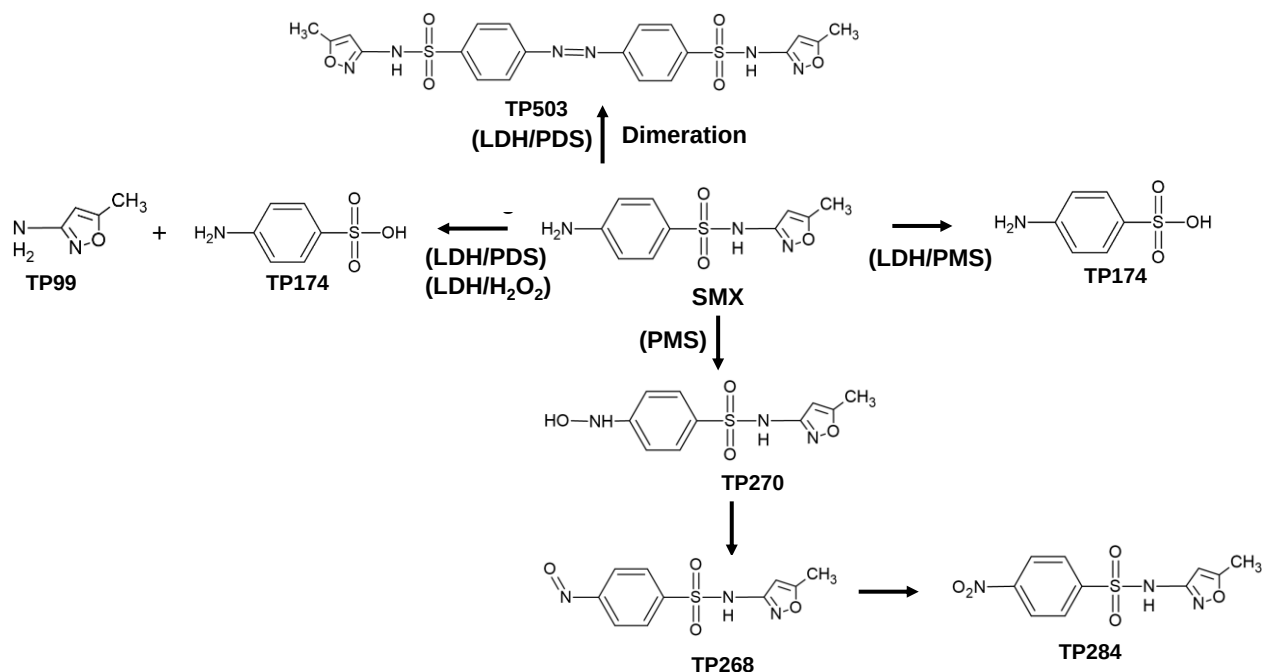


Figure 4.4 Proposed transformation pathways of SMX in LDH/PMS, LDH/PDS, LDH/H₂O₂ and direct oxidation of PMS systems.

Dimerization, cleavage of sulfonamide bond and oxidation reactions dominated the transformation of SMX, which could indicate that different reactive species contributed to the degradation mechanism (Figure 4.4).

To understand the role of reactive oxygen species in SMX degradation mechanisms, the reactions between scavengers and radicals were investigated in the LDH/PDS system (Figure 4.5). The scavengers used were methanol, with a second order kinetic constant $k(\text{HO}^\bullet) = 9.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and $k(\text{SO}_4^{\bullet-}) = 2.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, p-benzoquinone (BQ) ($k(\text{HO}_2^\bullet/\text{O}_2^{\bullet-}) = 2.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), nitrobenzene (NB) ($k(\text{HO}^\bullet) = 3.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and furfuryl alcohol (FFA) ($k(^1\text{O}_2) = 1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) (Appiani et al., 2017; Li et al., 2021).

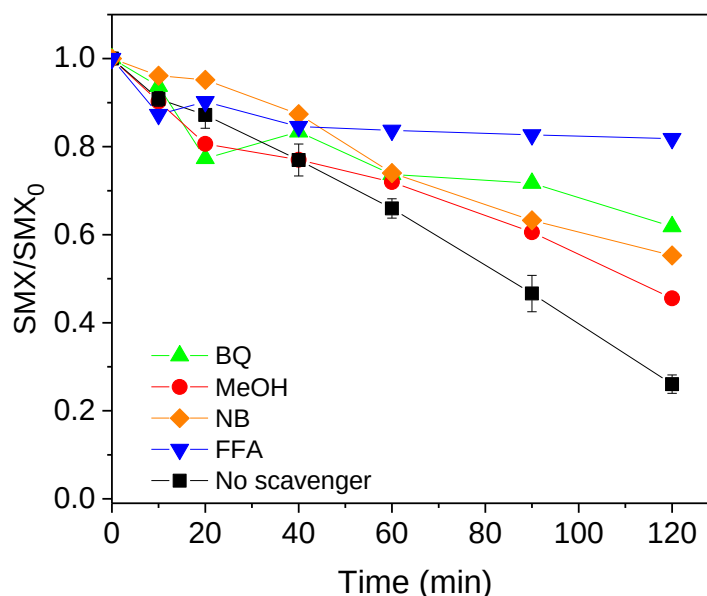
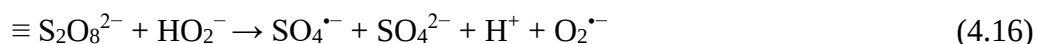
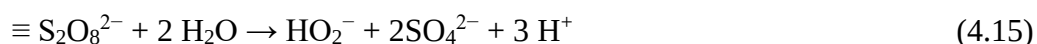


Figure 4.5 Effects of different radical scavengers using 200 mg L⁻¹ BQ, MeOH, NB and FFA on SMX degradation in LDH/PDS system. Conditions: 500 µg L⁻¹ SMX; 4 mM PDS and 0.5 g L⁻¹ LDH.

The SMX degradation was strongly inhibited in the presence of FFA (Figure 4.5), showing a decrease in the reaction rate constant from $k = 0.0095 \text{ min}^{-1}$ to $k = 0.0022 \text{ min}^{-1}$, and indicating the contribution of $^1\text{O}_2$ species. In addition, a significant inhibition of SMX degradation was observed using BQ ($k = 0.0042 \text{ min}^{-1}$), indicating some contribution of $\text{O}_2^{\bullet-}$ on SMX removal.

The results obtained with the different scavengers lead to the conclusion that in the LDH/PDS system, the relative significance of the reactive species followed the sequence: $^1\text{O}_2 > \text{HO}_2^{\bullet}/\text{O}_2^{\bullet-} > \text{HO}^{\bullet} > \text{SO}_4^{\bullet-}$ with radical and non-radical processes.

Interestingly, the $\text{O}_2^{\bullet-}$ can lead to the formation of $^1\text{O}_2$ (Eq. 4.15 – 4.17) during catalytic activation of PDS and contributed to the SMX degradation:



The $^1\text{O}_2$ has specific reactivity against SMX leading to TP228, TP202, TP176 and TP162 (see Table 4.S2 and Al-Nu'airat et al., 2021[44]; Yin et al., 2019 [45]). However, none of these TPs could not be detected, suggesting their adsorption on catalyst surface or concentration bellow detection limit.

SMX dimerization (TP503) was identified only in LDH/PDS system. The formation of dimers in heterogeneous Fenton-like oxidation processes has been related to high valence

metals such as Cu(III) and Fe(IV) [13,41]. More specifically, in Fenton chemistry, the formation of Fe(IV) species has been recognized, which might account for the formation of SMX dimers, as previously reported [46].

A possible mechanism might be the formation of an electrostatic interaction between oxygen atoms in PDS and Fe(III) in the surface of LDH following by one electron transfer process to generate Fe(IV) (see Eq. 4.18)



As shown in Figure 4.6, the Raman spectrum of the catalyst after the reaction with PDS shows a peak at 617 cm^{-1} , characteristic of Cu-O stretching vibration of a metastable Cu(III) (Eq. 4.12 and 4.19) [47]. This peak is absent in the spectrum of PDS alone and in the spectrum of LDH before the reaction confirming the presence of Cu(III) on LDH surface that contributes to the transformation of SMX with dimer generation in the LDH/PDS system (Figure 4.4).

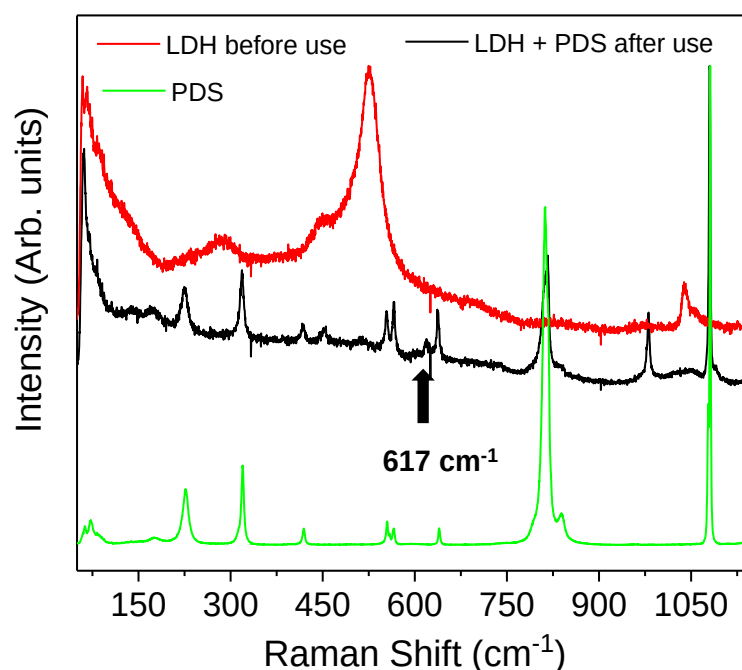


Figure 4.6 Raman spectrum of PDS, LDH before and after reaction with PDS, without SMX.

Another transformation pathway in LDH/PDS system was the cleavage of the sulfonamide bond, leading to TP174 and TP99. These two TPs were also detected in LDH/H₂O₂ while in LDH/PMS system, only TP174 was identified, most likely due to an oxidation of TP99.

Direct oxidation of SMX by PMS was responsible for the oxidation of the amino group (-NH₂-SMX) and the formation of hydroxylamine (-NHOH-SMX), TP270 and then to nitro derivatives of SMX, TP268 (-NO-SMX) and TP284 (-NO₂-SMX), which were identified and confirmed by the comparison with the analytical standards available. All these TPs detected during direct oxidation of SMX exhibit stronger toxicity than the original compound [48,49].

The formation of toxic compounds due to the direct oxidation of SMX by PMS occurs at the N atom bounded to the benzene ring [33]. Ji et al., 2018 [11] reported this mechanism of SMX transformation into toxic degradation products after direct oxidation with PMS occurred via the formation of a transition state complex between the oxygen atom of the PMS peroxide bond and the nitrogen atom of the SMX. Therefore, the transfer of electrons from SMX to PMS led to the formation of the intermediate TP270, followed by oxidation and formation of the respective nitro derivatives of SMX.

Monitoring the generation of nitro compounds during the application of AOPs is essential, especially when nitrite or nitrate ions are released from the oxidative degradation of N-containing pollutants, which facilitates the formation of nitroproducts [50].

In the LDH/PMS system, only one degradation product was identified, and no toxic nitro degradation products were detected (Figure 4.4) since LDH interacts with PMS, and after catalytic decomposition, the generation of reactive species occurs (Eq. 4.7 – 4.10) avoiding the formation of toxic intermediate derived from the interaction of SMX with PMS alone.

In conclusion, although PMS alone shows high efficiency in removing SMX (Figure 4. 3 a), the presence of LDH is very important to avoid the formation of compounds more harmful than SMX besides of accelerating the degradation (Figure 4. 3 b).

4.3.4 Application of LDH/PDS and LDH/PMS to the removal of a mixture of antibiotics in urban wastewater

To investigate the application of LDH/PDS and LDH/PMS systems in the removal of antibiotics from STWW effluents, antibiotics of four different classes frequently detected in surface waters were investigated: AMX, CFX, CIP and SMX.

Firstly, direct oxidation by PDS and PMS (absence of LDH), and adsorption onto the catalyst (absence of oxidant) were investigated in purified water. Direct oxidation by PMS achieved 98%, 71%, 45% and 87% abatement of SMX, CIP, CFX and AMX after 120 min, respectively. Lower direct oxidation was observed with PDS, between 10.4% and 23.9% for SMX and CFX, respectively, but achieved 89.8% in the case of AMX, probably due to a significant contribution of hydrolysis.

The antibiotics adsorbed very differently on LDH surface. Complete removal of CFX after 120 min was observed, while only 28% of CIP, 58% of AMX and negligible adsorption were observed in the case of SMX after the same time (Figure 4. 7). The complete removal of CFX is possibly due to the formation of a complex between Cu(II) and CFX as previously reported [13,51]. Furthermore, complexation of β -Lactams with Cu(II) could also contribute to the removal of AMX by LDH only.

Addition of PDS (LDH/PDS system) improved the removal of SMX, CIP and AMX, achieving 28%, 85% and 71%, respectively, while a slight decrease of CFX to 93% was observed in relation to adsorption in the absence of LDH. The addition of PDS may have occupied some sites on the surface of the catalyst, which reduced the complexation with CFX, and consequently the removal.

On the other hand, LDH/PMS promoted highest degradation rates, achieving total removal of CIP and CFX, and more than 90% of SMX and AMX after 120 min, with total consumption of PMS (Figure 4. S7 a). These results indicate the efficiency of LDH to activate PMS and consequent degradation of the antibiotics simultaneously.

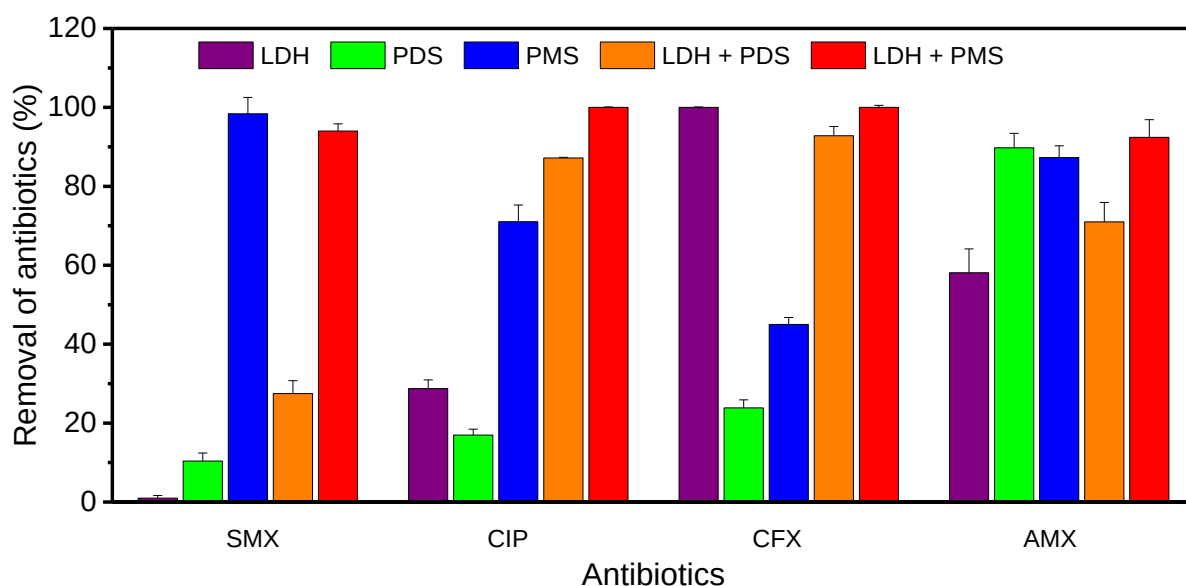


Figure 4.7 Effect of the adsorption, direct oxidation by PDS and PMS and catalytic degradation with LDH/PMS and LDH/PDS for removing SMX, AMX, CFX and CIP in deionized water after 120 min of the reaction. Conditions: 2.0 mg L⁻¹ of SMX, CIP, AMX and CFX; 0.5 g L⁻¹ LDH; 4 mM of PDS and PMS; pH 8.31 ± 0.20 for LDH/PDS and 5.74 ± 0.18 for LDH/PMS.

In the simultaneous degradation of antibiotics, the system LDH/PDS can operate even at mildly basic conditions (Figure 4. S7 b) with 1.84 mM of PDS consumption (Figure 4. S7 a),

with similar pH variation as shown in the Figure 4. 1 c, which is an advantage attributed to the catalyst as previously discussed [24][20].

Although systems with PMS are more efficient than PDS, some well-known disadvantages of using PMS for simultaneous disinfection and contaminants removal are its higher cost compared with PDS and its instability, which implies in difficulty of storage over a long period [52].

To further verify whether LDH is a promising catalyst for the treatment of urban wastewater with mixed antibiotics, the LDH/PDS system was applied to STWW treatment, resulting in efficient degradation of CFX and AMX, while SMX and CIP presents higher stability and resistance to degradation (Table 4.1).

Table 4.1 Efficiency of LDH/PDS systems for the simultaneous degradation of SMX, CIP, CFX and AMX in STWW. Conditions: pH = 7.5; 250 $\mu\text{g L}^{-1}$ of SMX, CIP, CFX and AMX, 0.5 g L^{-1} LDH; 4 mM PDS

Antibiotic	Antibiotic removal in wastewater (%)
SMX	27 $\pm$ 2
CIP	52 $\pm$ 3
CFX	98 $\pm$ 1
AMX	100 $\pm$ 2

Based on the above findings, there are important novelties when applying LDH with different oxidizing agents in heterogeneous Fenton processes for organic micropollutants removal from urban wastewater. The similar results in deionized water (see Figure 4. 7) and STWW (Table 4. 1) demonstrated the potential of using LDH in the investigated processes.

To assess the efficiency of the degradation process, the chemical constituents of the effluent need to be considered, such as inorganic anions that can act as radical scavengers, especially if they are present in concentrations higher than target contaminants [53].

Despite the high concentrations of the anions present in the effluent SO_4^{2-} , NO_3^- , Cl^- , HCO_3^- , and organic carbon (Table 4.S1) their presence did not contribute for the inhibition of the degradation process in radical scavenging reactions as verified by the results in Table 4.1, suggesting that high valence species such as Cu(III) may be involved in the degradation process.

4.3.5 Application to urban wastewater disinfection

The capacity of the investigated oxidative systems for secondary treated urban wastewater disinfection was evaluated in the dark and at room temperature considering the inactivation of the gram-negative *E. coli* and gram-positive *Enterococcus*, which were selected since both strains are indicators of the occurrence of pathogenic bacteria [54].

Many studies have reported the use of copper in bacterial inactivation, which mechanism is based on the attack of the reactive species to the bacterial cell wall [55] leading to cell lysis and death [56,57]

As shown in Figure 4. 8, the initial abundances of *E. coli* and *Enterococcus* in secondary-treated urban wastewater were $5.25 \pm 0.13 \log_{10}$ MPN/100 mL and $4.45 \pm 0.15 \log_{10}$ MPN/100 mL, respectively.

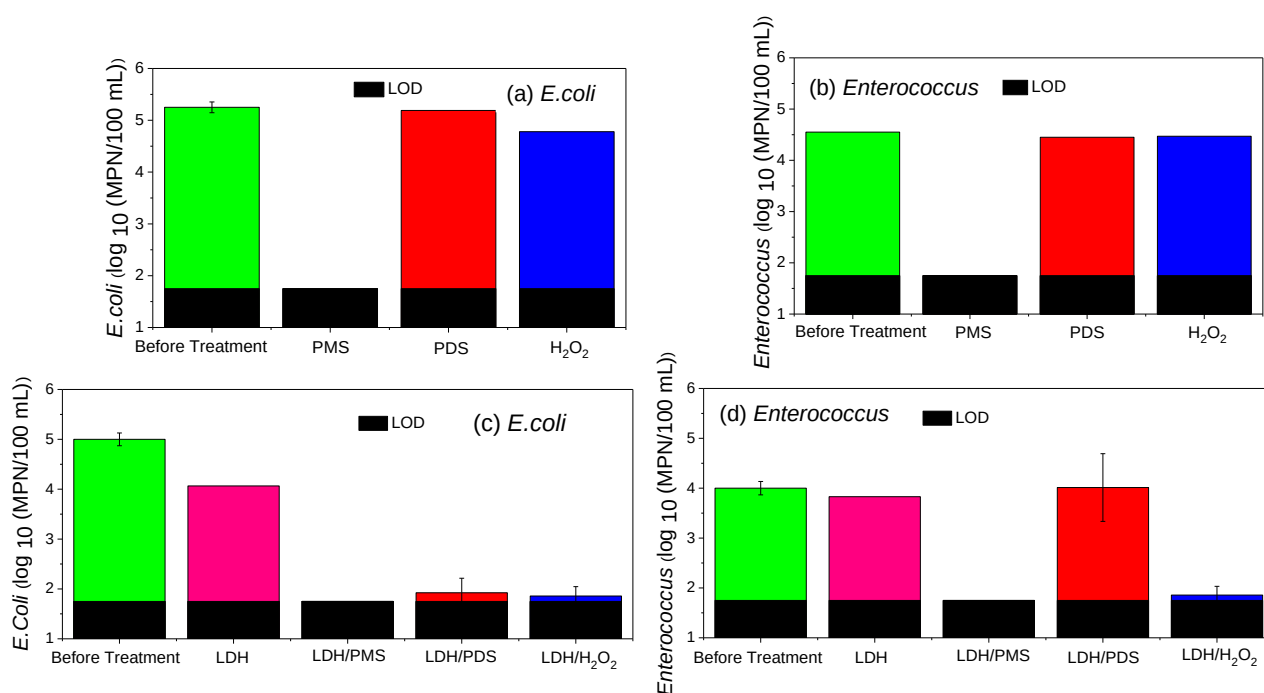


Figure 4.8 Inactivation profiles of *E. Coli* (a) and *Enterococcus* (b) in secondary treated urban wastewater before and after treatment in direct oxidation with PMS, PDS and H₂O₂ and with different systems LDH, LDH/PMS, LDH/PDS and LDH/H₂O₂ (c and d). Conditions: 0.5 g L⁻¹ LDH, 4 mM of PMS, PDS and H₂O₂.

No significant reduction of *E. coli* and *Enterococcus* was observed after 120 min treatment by direct oxidation with PDS and H₂O₂ (Figure 4. 8 a and b). However, PMS alone resulted in complete inactivation of *E. coli* and *Enterococcus* after 120 min ($<1.75 \log_{10}$ MPN/100 mL) confirming its effectiveness as disinfecting agent as reported in previous studies [58,59].

This very good result could be explained by the self-oxidation of PMS (Eq. 4.1 and 4.2) that can generate the singlet oxygen causing disturbance of membrane permeability, resulting in malfunction of cell metabolism and cell inactivation, indicating that systems with singlet oxygen generation are promising to promote wastewater disinfection[60,61].

LDH/H₂O₂ system showed high efficiency for disinfection achieving 92% inactivation of *E. coli* and 93% of *Enterococcus*. This could be due to the formation of the complexes between LDH and H₂O₂ (Eq. 4.3 and 4.4) and the subsequent formation of superoxide radical (Eq.4.5 and 4.6), which although did not show reactivity for SMX removal, showed positive effect on the inactivation of pathogens.

Differently, LDH/PDS system achieved 91% inactivation of *E. coli* after 120 min, but failed to inactivate *Enterococcus*. Inactivation of *Enterococcus* is more difficult, as it is a gram positive bacteria with a relatively thick cell wall and dense layer (20–80 nm) composed of phosphoric acid (10%) and peptidoglycan (90%), more resistant to disinfectants compared to gram negative bacteria that present a thinner cell wall (10–15 nm) composed of lipopolysaccharide (10–15%), phospholipid/ lipoprotein (60%), and peptidoglycan (10–20%) [17].

Consequently, the sequence of efficiency for bacterial disinfection was the following: LDH/PMS = PMS alone > LDH/H₂O₂ > LDH/PDS.

4.3.6 Catalyst stability

For a catalyst to find application in wastewater treatment, it is essential to confirm its stability. The stability of LDH was evaluated by the determination of the concentrations of the total soluble iron, copper and magnesium ions after the experiments when using 0.5 g L⁻¹ LDH. No significant leaching of Fe and Cu was observed in LDH/H₂O₂ and LDH/PDS systems, with total iron and copper concentrations below detection limit (<0.01 mg L⁻¹) after 120 min of reaction. However, in the LDH/PMS system, copper concentration achieved 4.58 mg L⁻¹ indicating the effect of PMS on HDL stability. All systems investigated showed some Mg leaching, achieving 2.99 mg L⁻¹ with HDL alone, 5.15 mg L⁻¹ with LDH/H₂O₂, 16.92 mg L⁻¹ with LDH/PDS and 51.40 mg L⁻¹ with LDH/PMS. Although magnesium ions play no role in degradation reactions, it indicates some instability of the HDL with PMS, suggesting a minor contribution of the proton of the PMS structure (Figure 4. S2).

Possible structural changes of the LDH during the Fenton reaction were evaluated by analyzing the catalyst after reaction using XRD, XPS and SEM analysis in LDH/PDS, LDH/PMS and LDH/H₂O₂ (Figure 4.S8 – 4.S10).

The X-ray diffractograms (Figure 4.S8) of the catalyst revealed three equidistant peaks, (003), (006), and (009), corresponding to the stacking of the lamellae, characteristic of the LDH structure [24,62,63]. The preservation of the LDH structure after use, without any phase segregation confirms catalyst stability in the three systems investigated.

SEM analyzes of LDH after use in the reaction show that no important changes in the morphology after treatment with H_2O_2 occurred (Figure 4. S9). However, some agglomeration of the particles was observed after treatment with PDS and PMS (Figure 4. S9 c and d), which can be attributed to more aggressive redox reactions, which apparently leads to slight corrosion on the LDH surface with a slight magnesium leaching as already mentioned.

XPS analyzes was applied to identify the bonding states of Cu and Fe surface species in the CuMgFe-B(OH)_4 after use with H_2O_2 , PDS and PMS (Figure 4. S10). The three fitted components of the Cu $2p_{3/2}$ spectra at 932.2 eV, 933.7 eV, and 934.8 eV were assigned to Cu(I), (Cu_2O) and Cu(II) (CuO and Cu(OH)_2) species, respectively. The Fe $2p_{3/2}$ high-resolution spectra were deconvoluted into four components at 709.5 eV, 711.1 eV, 712.3 eV, and 714.3 eV, associated to the presence of Fe(II) (FeO), Fe(III) (Fe_2O_3 and FeOOH), and an Fe(III) shake-up satellite. Cu(I) and Fe(II) species is observed in LDH spectra evidencing the presence of these species on the LDH surface. The reduction of iron and copper due to the presence of boron species on the surface of CuMgFe-B(OH)_4 was demonstrated in our previous study [20]. The presence of these reduced species during the catalytic decomposition of H_2O_2 , PDS and PMS, increased the generation of reactive species for degradation of contaminants and disinfection of STWW, as previously discussed.

4.4 Conclusions

This research aimed at evaluating the performances of CuMgFe-B(OH)_4 -LDH with H_2O_2 , PDS and PMS for the simultaneous degradation of antibiotics and pathogens inactivation in urban wastewater. Although PMS alone promoted selected antibiotics oxidation and bacterial disinfection to almost a similar extent than the LDH/PMS system, PMS alone led to the formation of toxic SMX intermediates such as the nitroso and nitro derivatives. The LDH/ H_2O_2 system was not effective for degradation of antibiotics, but promoted significant disinfection of urban wastewater, mainly the inactivation of the resistant *Enterococcus*. In the LDH/PDS system, a non-radical based oxidation was evidenced by the lack of detection of nitroso- and nitro-SMX, by radical scavenger testing and by the formation of a SMX dimer which was

ascribed to be due to the reactivity of Cu(III). This system was effective in degrading different antibiotics and also in eliminating *E. coli*, but not *Enterococcus* in urban wastewater. As a whole, CuMgFe-B(OH)₄ LDH is a promising catalyst for detoxification and disinfection of urban wastewater.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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Supplementary Material

Simultaneous disinfection of urban wastewater and antibiotics degradation mediated by CuMgFe-B(OH)₄ layered double hydroxide with different oxidizing agents

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Table 4.S1 Physical-chemical properties of the investigated secondary treated urban wastewater after filtration on 0.45 µm cellulose filter.

Parameter	Value
*EC (mS/cm)	1.6 ± 0.4
pH	7.5 ± 0.1
*TSS (mg/L)	8.2 ± 2.6
*TOC (mg/L)	12.6 ± 5
HCO ₃ ⁻ (mg/L)	514.3
Cl ⁻ (mg/L)	195.3
NO ₃ ⁻ (mg/L)	13.0 ± 1.5
NH ₄ ⁺ (mg/L)	0.5
SO ₄ ²⁻ (mg/L)	58.9
Cu (µg/L)	3.75

*Total Suspended Solids (TSS), *Chemical Oxygen Demand (COD), *Electrical Conductivity (EC).

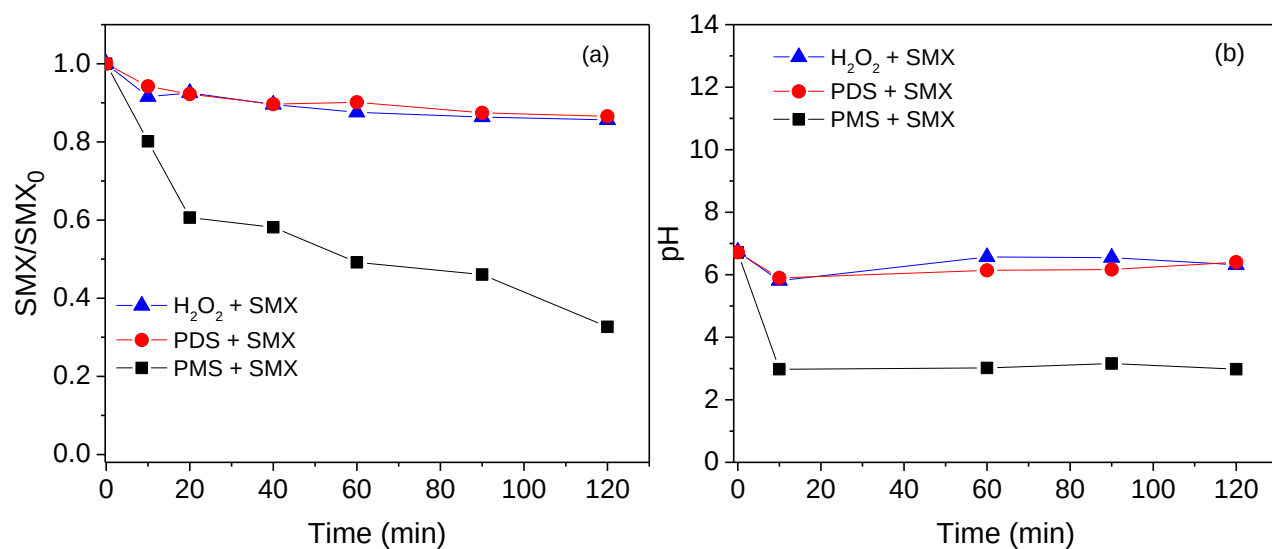


Figure 4.S1 Direct oxidation of SMX (a) and pH variation (b) without LDH with the oxidants PDS, PMS and H_2O_2 . Conditions: 500 $\mu\text{g L}^{-1}$ of SMX; 1 mM of H_2O_2 , PMS and PDS.

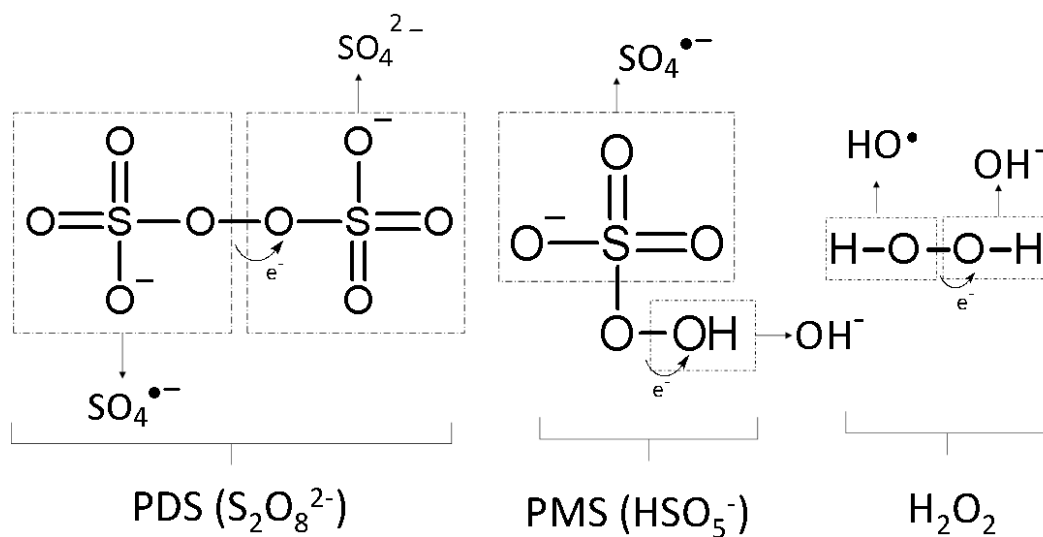


Figure 4.S2 Chemical structure and activation mechanisms through electron transferring processes of PDS, PMS and H_2O_2 .

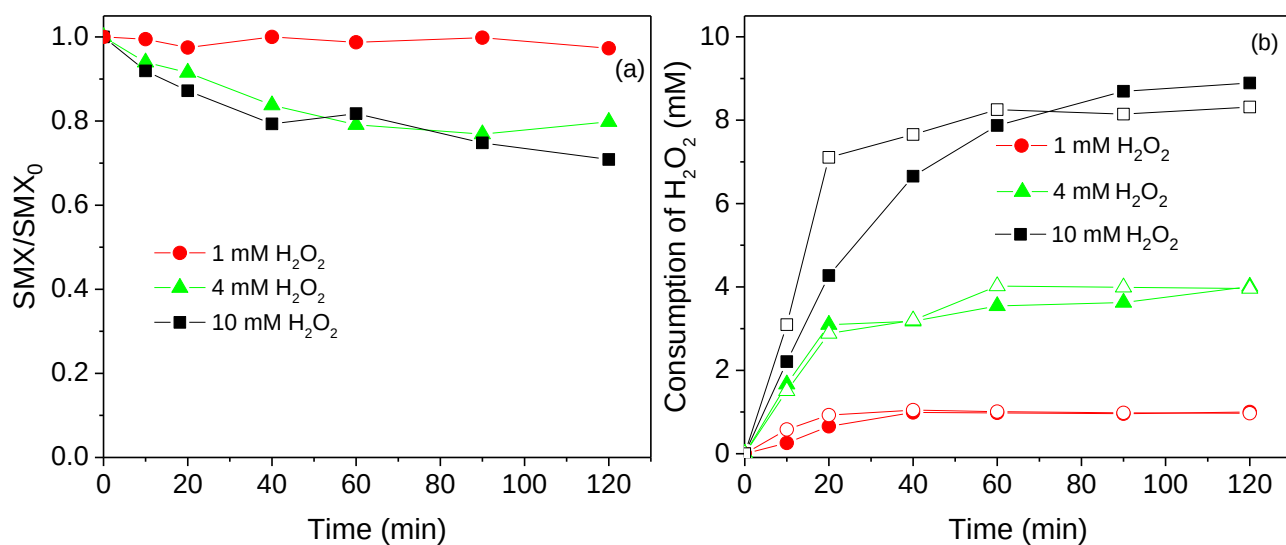


Figure 4.S3 Effect of H_2O_2 concentration on SMX degradation in the presence of LDH (a) and H_2O_2 consumption (b). Solid symbols: consumption in the presence of SMX and open symbols: consumption in the absence of SMX. Conditions: $500 \mu\text{g L}^{-1}$ of SMX; 0.5 g L^{-1} of LDH.

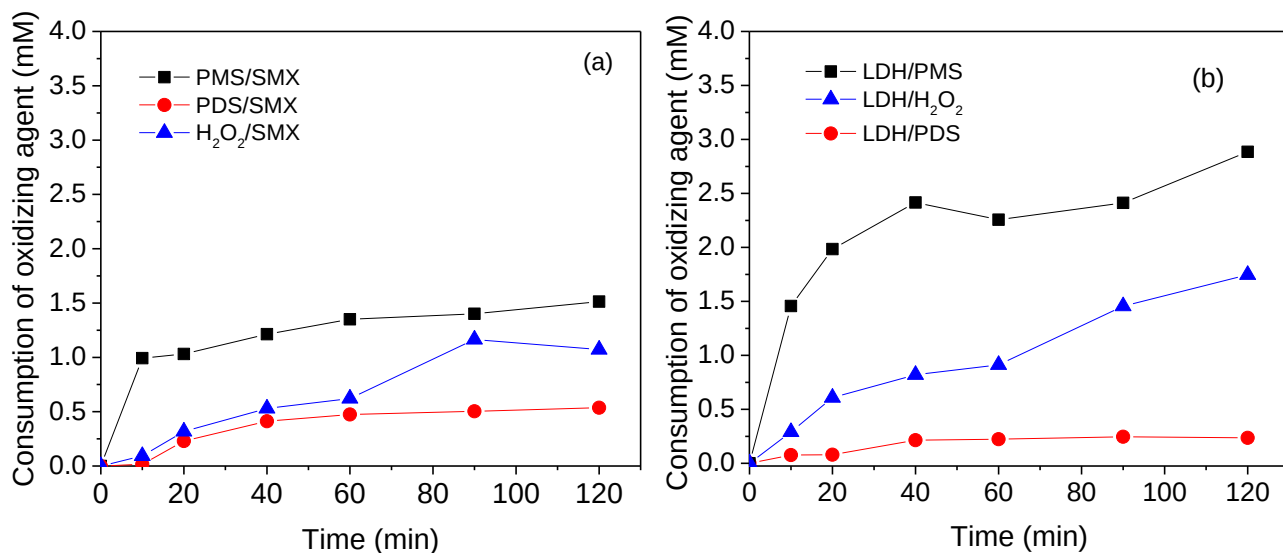
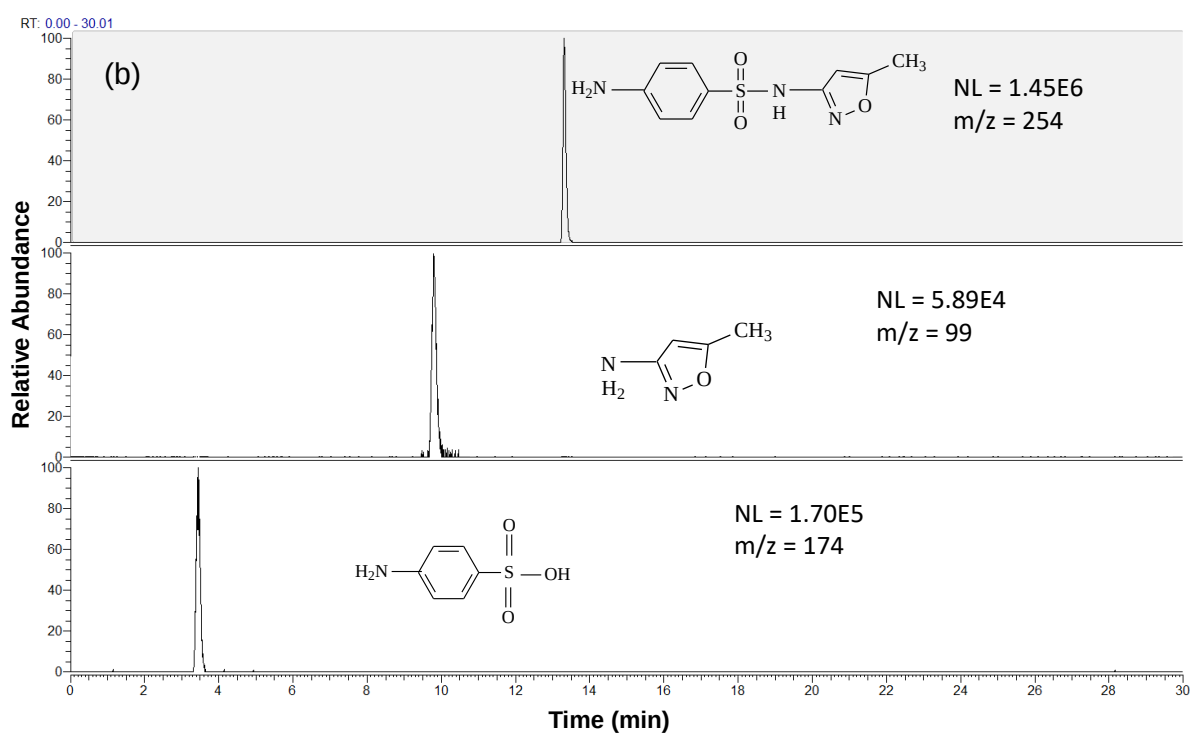
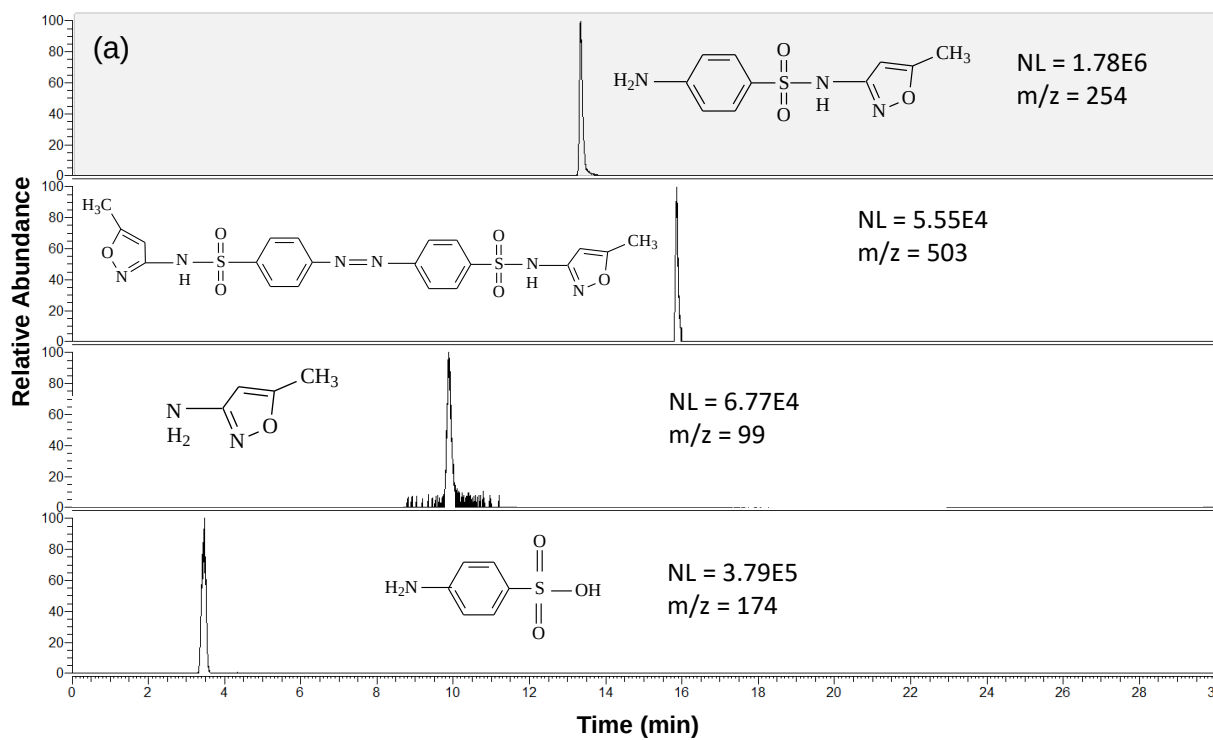


Figure 4.S4 Consumption of oxidizing agent in direct SMX oxidation of PMS, PDS and H_2O_2 (a) and in LDH/PDS, LDH/PMS and LDH/ H_2O_2 systems in STWW (b). Conditions: $\text{pH} = 7.5$; $500 \mu\text{g L}^{-1}$ SMX, 0.5 g L^{-1} LDH; 4 mM of PDS, PMS and H_2O_2 .

Table 4.S2 List of previously identified transformation products of sulfamethoxazole (SMX) under different oxidative systems according to the literature [1 – 4].

Compound	Formula	Monoisotopic mass	[M + H] ⁺
SMX	C ₁₀ H ₁₁ N ₃ O ₃ S	253.0516	254.0594
TP256	C ₉ H ₉ N ₃ O ₄ S	255.0308	256.0386
TP270	C ₁₀ H ₁₁ N ₃ O ₄ S	269.0465	270.0543
TP284	C ₁₀ H ₉ N ₃ O ₅ S	283.0257	284.0335
TP503	C ₂₀ H ₁₈ N ₆ O ₆ S ₂	502.0724	503.0802
TP519	C ₂₀ H ₁₈ N ₆ O ₇ S ₂	518.0673	519.0751
TP99	C ₄ H ₆ N ₂ O	98.0475	99.0553
TP174	C ₆ H ₇ NO ₃ S	173.0141	174.0219
TP215	C ₈ H ₁₀ N ₂ O ₃ S	214.0407	215.0485
TP296	C ₁₂ H ₁₃ N ₃ O ₄ S	295.0621	296.0699
TP312	C ₁₂ H ₁₃ N ₃ O ₅ S	311.0570	312.0648
TP268	C ₁₀ H ₉ N ₃ O ₄ S	267.0308	268.0386
TP255	C ₁₀ H ₁₀ N ₂ O ₄ S	254.0356	255.0434
TP228	C ₉ H ₁₂ N ₂ O ₃ S	228.0641	229.0641
TP202	C ₇ H ₁₀ N ₂ O ₃ S	202.0484	203.0484
TP176	C ₅ H ₈ N ₂ O ₃ S	176.0328	177.0328
TP162	C ₄ H ₆ N ₂ O ₃ S	162.0171	163.0171
TP239	C ₁₀ H ₁₀ N ₂ O ₃ S	238.0407	239.0485
TP221	C ₁₀ H ₈ N ₂ O ₂ S	220.0301	221.0379
TP179	C ₈ H ₆ N ₂ OS	178.0195	179.0273
TP176	C ₄ H ₄ N ₂ O ₄ S	175.9886	176.9964
TP149	C ₂ HN ₂ O ₄ S	148.9652	149.9730



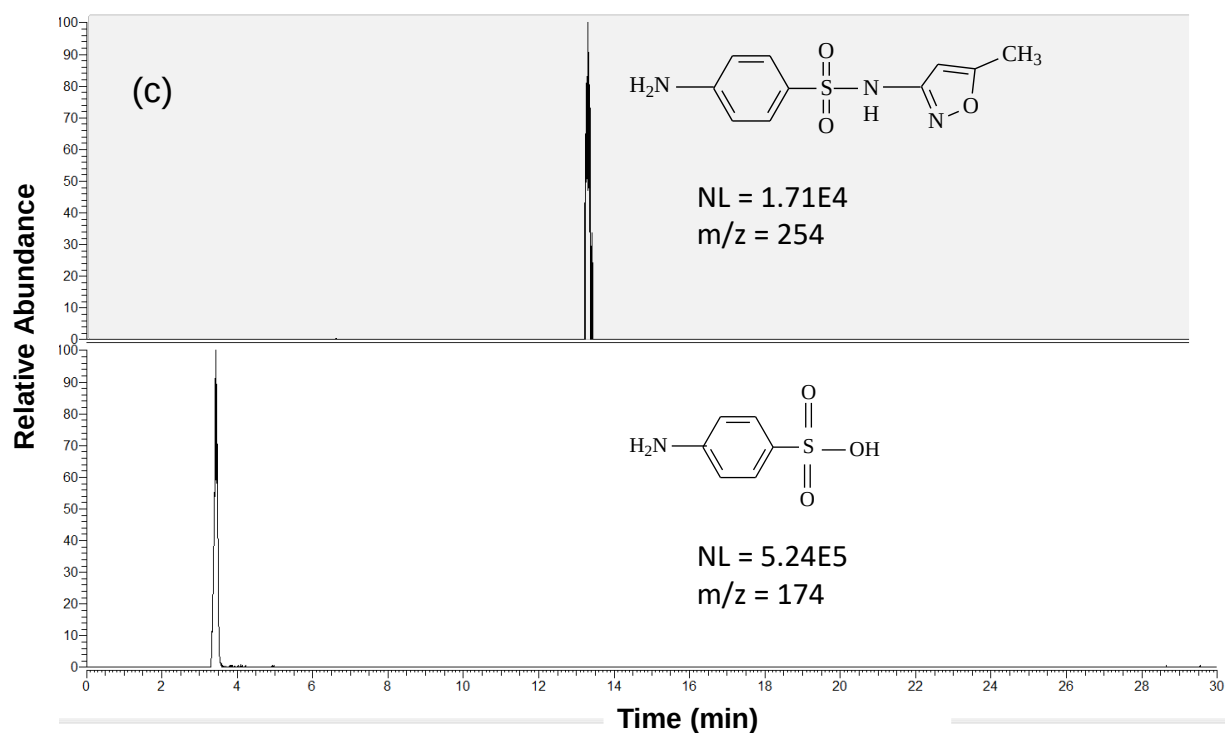


Figure 4.S5 Extracted Ion Chromatograms (EIC) of detected SMX transformation products in the system LDH/PDS (a), LDH/H₂O₂ (b) and LDH/PMS (c).

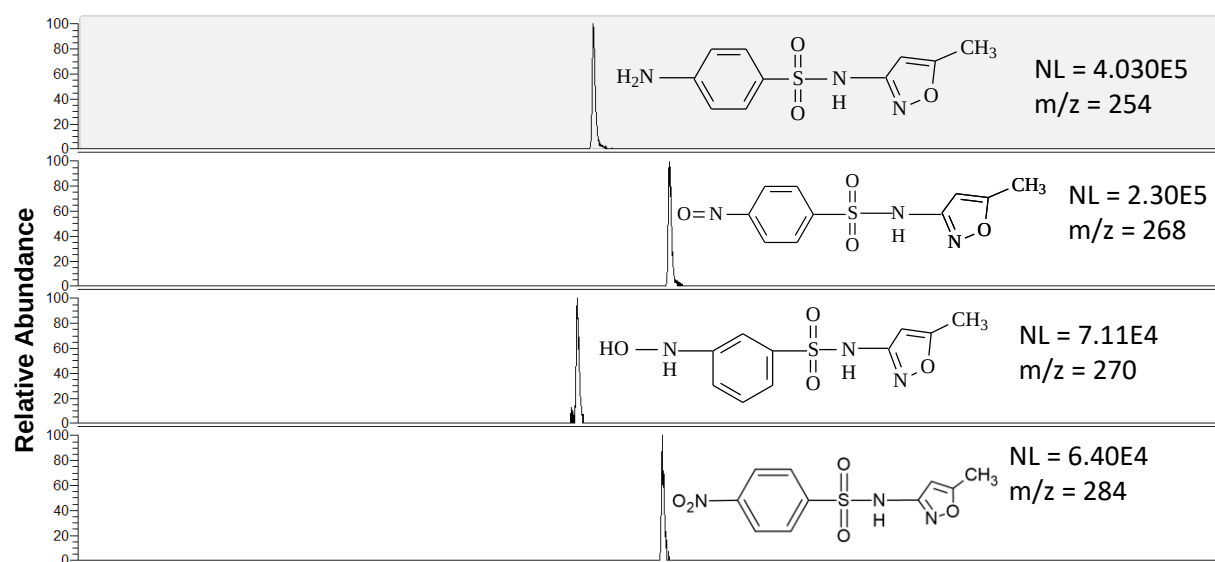


Figure 4.S6 Extracted Ion Chromatograms (EIC) of detected SMX transformation products under direct PMS oxidation.

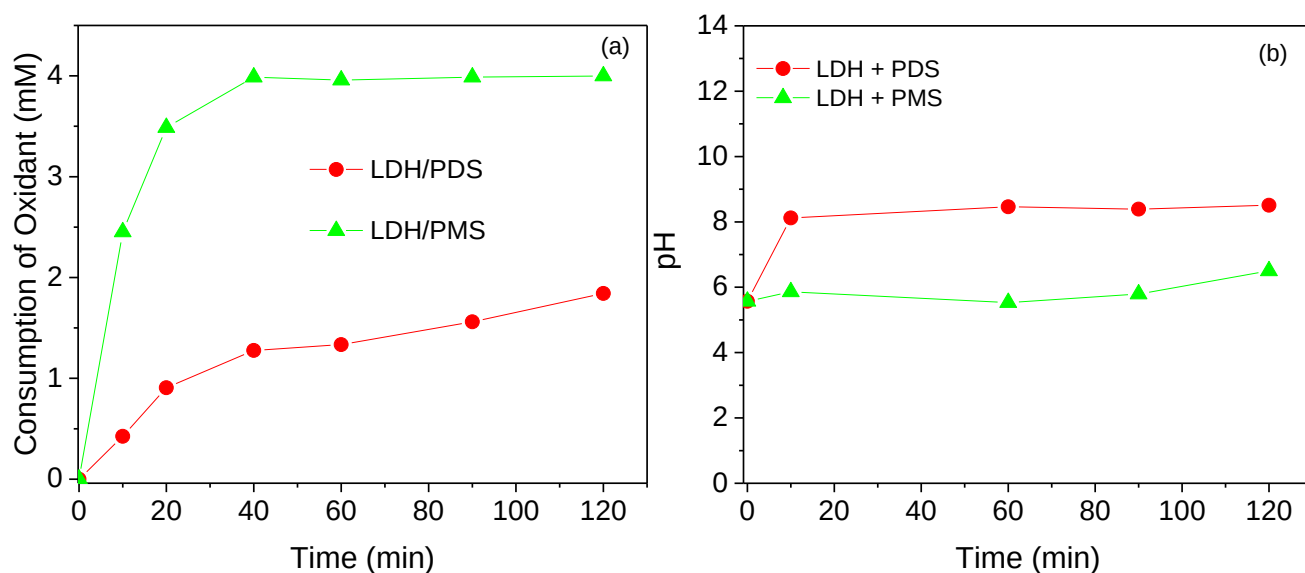


Figure 4.S7 Consumption of PDS and PMS (a) and pH variation(b) in the LDH/PDS and LDH/PMS systems on the degradation of mixed compounds of the contaminants SMX, CIP, CFX and AMX. Conditions: 2.0 mg L⁻¹ of SMX, CIP, AMX and CFX, 0.5 g L⁻¹ CuMgFe-B(OH)₄, 4 Mm of PDS and PMS.

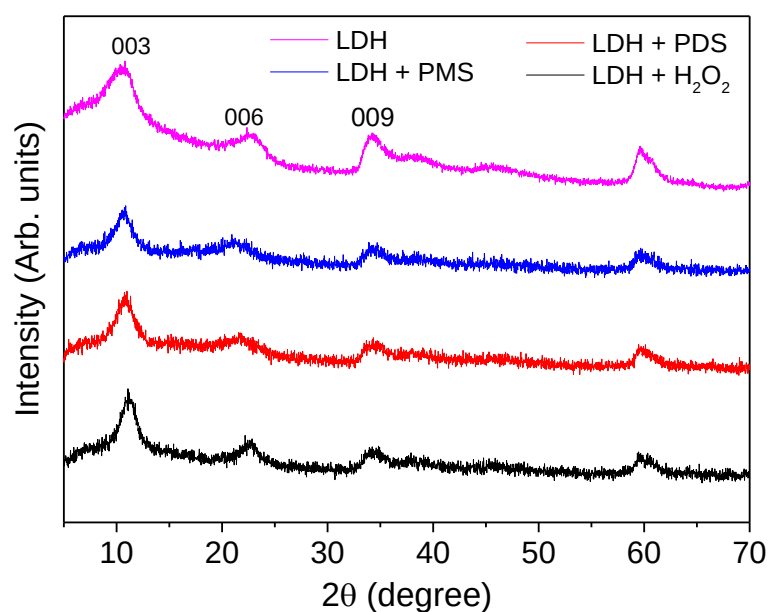


Figure 4.S8 X-ray diffractograms of the LDH catalyst after Fenton process with LDH/PMS, LDH/PDS and LDH/H₂O₂.

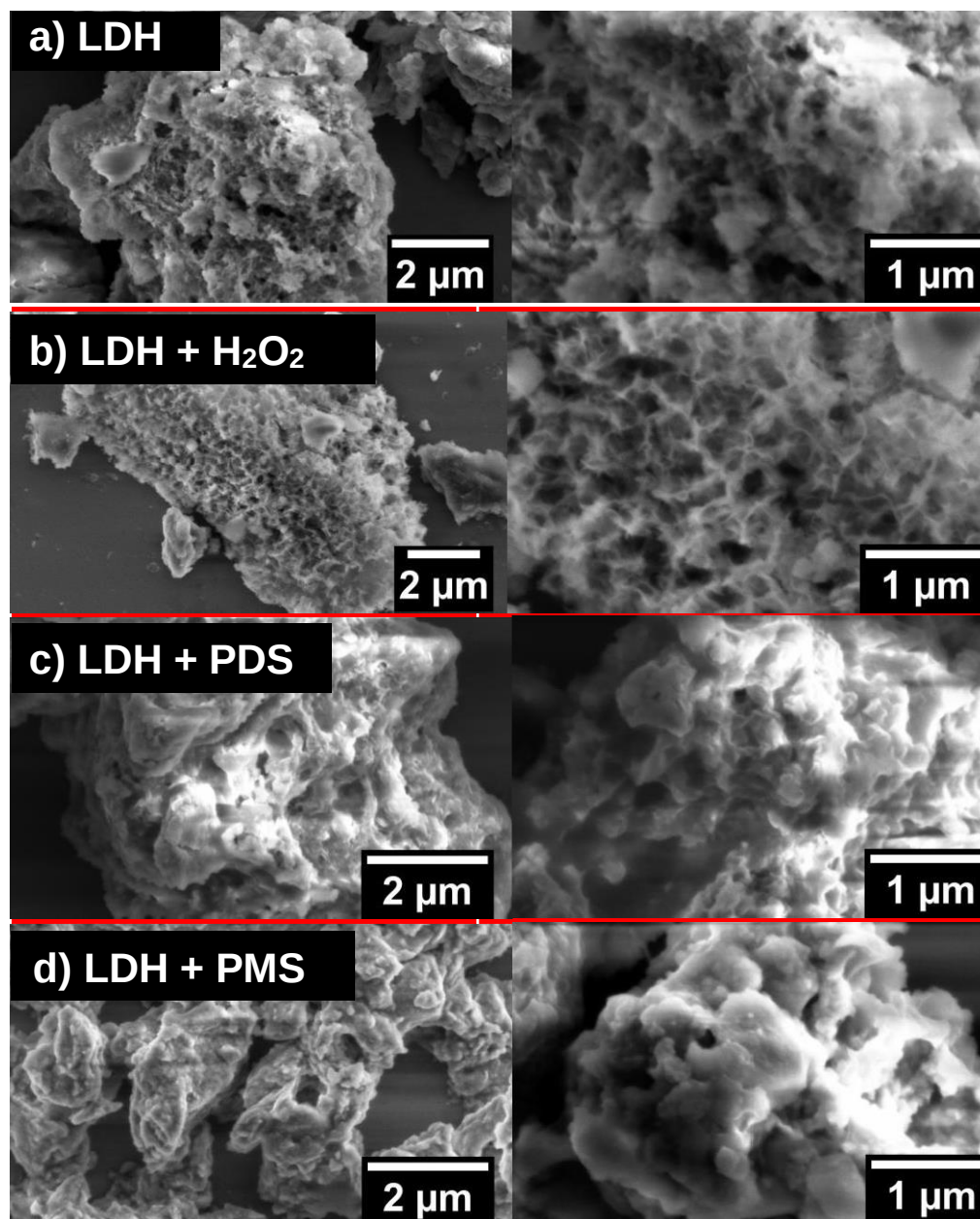


Figure 4.S9 SEM images of the LDH before (a) and after treatment with H₂O₂ (b), PDS (c) and PMS (d) at two different magnifications.

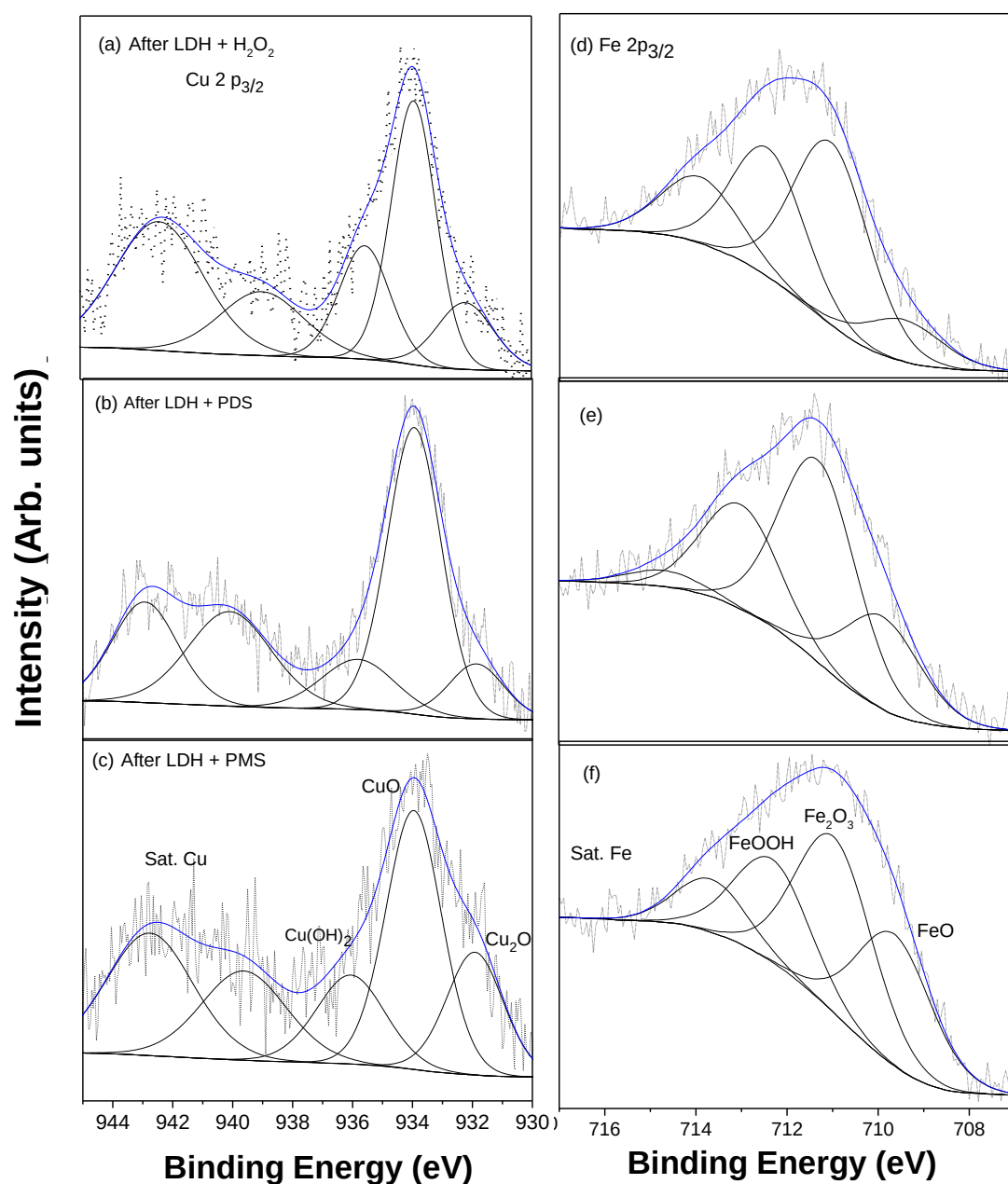


Figure 4.S10 XPS high resolution spectra of Cu 2p_{3/2} (a), (b), (c), and Fe 2p_{3/2} spectra (d), (e), (f), (g) of CuMgFe-B(OH)₄ after reaction with H₂O₂, PDS and PMS.

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5 GENERAL CONCLUSION

The main goal of this Ph. D thesis was to synthesize, characterize and study the mechanism involved in heterogeneous Fenton processes and in sulfate radical- AOP mediated by LDHs of the pyroaurite-type (CuMgFe-LDH) for pharmaceuticals degradation and disinfection of secondary treated urban wastewater (STWW).

The effect of the incorporation of copper in the lamellar structure of MgFe-CO₃ was investigated for STZ removal in the Fenton processes. The connection between the characterization of copper LDH and the degradation experiments confirm that the presence of copper was important for the complete removal of STZ under the conditions used. The results showed that complete STZ removal was achieved after 90 min of reaction using 4 mmol L⁻¹ of H₂O₂ and 0.5 g L⁻¹ CuMgFe-CO₃, at pH 7.5, under Vis-LED irradiation and good stability even after four cycles use.

The effect of the interlamellar anions B(OH)₄⁻, CO₃²⁻, SO₄²⁻ and NO₃⁻ on the efficiency of CuMgFe-LDH as a catalyst for the Fenton and photo-Fenton processes, evaluated by degradation of 5-FU, showed that the degradation was very influenced by the interlamellar anion with notorious superiority of borate anion.

For the first time in the literature, it was proposed a mechanism on the surface of LDH with borate anion indicating that the presence of borate can modify the surface charge and facilitate the reduction of Cu(II) and Fe(III) species on the CuMgFe-B(OH)₄ surface, improving the degradation efficiency in relation to other anions, especially in the dark reaction. 5-FU was completely degraded under solar radiation after 20 min, and after 40 min in the dark, with good efficiency and stability. Furthermore, the CuMgFe-B(OH)₄ presented high stability after 4 cycles of use.

Although CuMgFe-B(OH)₄ showed higher efficiency, the CuMgFe-CO₃, CuMgFe-NO₃ and CuMgFe-SO₄ are also promising, especially under solar radiation. However, it is important to highlight that the high efficiency of CuMgFe-B(OH)₄ in the dark reveals its potential for application at a lower cost without the need for irradiation.

The activation of PMS, PDS and H₂O₂ by CuMgFe-B(OH)₄ showed that the best investigated system was the LDH/PMS, which provided more than 90% removal of all antibiotics after 120 min and complete inactivation of the pathogens using 0.5 g L⁻¹ of LDH and 4 mmol L⁻¹ of PMS. Despite some studies reporting the efficiency of PMS alone in the removal of pharmaceutical contaminants from wastewater, many authors also reported some disadvantages in the application of this system, such as the formation of toxic degradation by-

products. This study showed that after the insertion of LDH into the LDH/PMS system, toxic degradation products of SMX were not identified, indicating the importance of the LDH in the system.

In disinfection experiments, both LDH-activated PMS and PMS alone promoted the inactivation of *Escherichia coli* and *Enterococcus faecalis*. The LDH/PDS and LDH/H₂O₂ systems showed lower efficiency than LDH/PMS for antibiotics removal and disinfection.

As a conclusion, this research showed that the catalytic activity of borate-LDH is better in sulfate radical reactions with PMS and PDS than in the classical Fenton processes with H₂O₂, due to the possibility of the generation of both types of radicals in these systems (SO₄^{•-} and HO[•]) and the longer half-life time of SO₄^{•-} compared to the HO[•] under neutral conditions.

All the LDHs synthesized in this work shown to be very stable, with excellent performance in neutral conditions. This can be very crucial for Fenton applications.

However, it is important to mention that LDHs are unstable at pH < 4, which is not a problem for the practical applications since the pH of urban wastewater is around 7.5.

As future perspectives of this work, LDH pellets could be synthesized and incorporated into continuous flow columns for the simultaneous degradation of contaminants and inactivation of pathogens to allow for a large-scale application. It would also be interesting to investigate the synergism of LDH with other catalysts forming composites for heterogeneous Fenton applications.

Other interesting parameters to be investigated are: LDHs synthesis with other cations and proportions of metallic ions and whether different rates of addition of cations during the coprecipitation process can affect the catalytic properties of these materials.

6 RESUMO EXPANDIDO DA TESE EM PORTUGUÊS

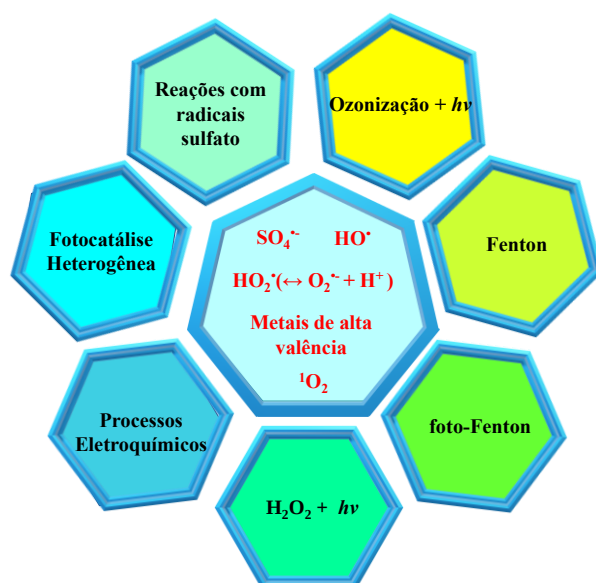
Esta seção apresenta resumidamente os principais resultados desta tese de doutorado.

Tendo em vista que a ineficiência do tratamento convencional de águas residuais urbanas para a remoção de contaminantes emergentes e inativação de patógenos afeta negativamente a qualidade da água e pode contribuir para a transmissão de doenças infecciosas, ameaçando a saúde humana e o meio ambiente, estratégias de tratamento eficientes e de baixo custo precisam ser colocadas em prática.

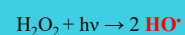
Dentre as tecnologias eficientes para o tratamento adequado de efluentes, tem-se os Processos Oxidativos Avançados (POAs), devido à capacidade de produzir espécies reativas, principalmente radicais hidroxila ($\text{HO}^\bullet$), que apresentam alto potencial padrão de redução ($E^\circ = 2,8 \text{ V}$) e baixa seletividade para a oxidação de contaminantes orgânicos, podendo levar à mineralização dos compostos orgânicos a CO_2 , H_2O e sais inorgânicos. Além disso, essas espécies reativas podem reagir com a parede celular de bactérias atingindo enzimas e substâncias intracelulares, levando à inativação de patógenos.

Nas últimas décadas, os POA têm sido investigados visando sua aplicação isolada ou combinada a outros processos de tratamento de águas e efluentes. Além do $\text{HO}^\bullet$, outras espécies reativas podem ser geradas como $\text{SO}_4^{\bullet-}$, $\text{HO}_2^\bullet$, $\text{O}_2^{\bullet-}$, metais de alta valência e $^1\text{O}_2$. Diferentes agentes oxidantes e várias combinações podem ser usadas para produzir essas espécies reativas.

A Figura 1 apresenta os POAs mais aplicados para o tratamento de efluentes.



Ozonização + $h\nu$: $\text{O}_3 + h\nu + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$

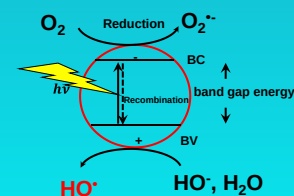


Fenton: $\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{HO}^\bullet + \text{HO}^\bullet$

foto-Fenton: $\text{Fe(OH)}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{HO}^\bullet$

$\text{H}_2\text{O}_2 + h\nu$: $\text{H}_2\text{O}_2 + h\nu \rightarrow 2 \text{HO}^\bullet$

Fotocatálise Heterogênea:



Reações com $\text{Fe}^{2+} + \text{HSO}_5^- \rightarrow \text{Fe}^{3+} + \text{SO}_4^{\bullet-} + \text{OH}^-$

Radicais sulfato: $\text{Fe}^{2+} + \text{HSO}_5^- \rightarrow \text{Fe}^{3+} + \text{HO}^\bullet + \text{SO}_4^{2-}$

$\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{\bullet-} + \text{SO}_4^{2-}$

Figura 1 Representação dos principais POAs aplicados no tratamento de água residual.

Os oxidantes mais utilizados em POA para remediação ambiental são H_2O_2 , persulfato (PDS) e peroximonosulfato (PMS). Conforme demonstrado na Figura 2, esses oxidantes apresentam o grupo peroxo (ligação O-O), e após a decomposição catalítica por metais e transferência eletrônica tem-se a geração de radicais.

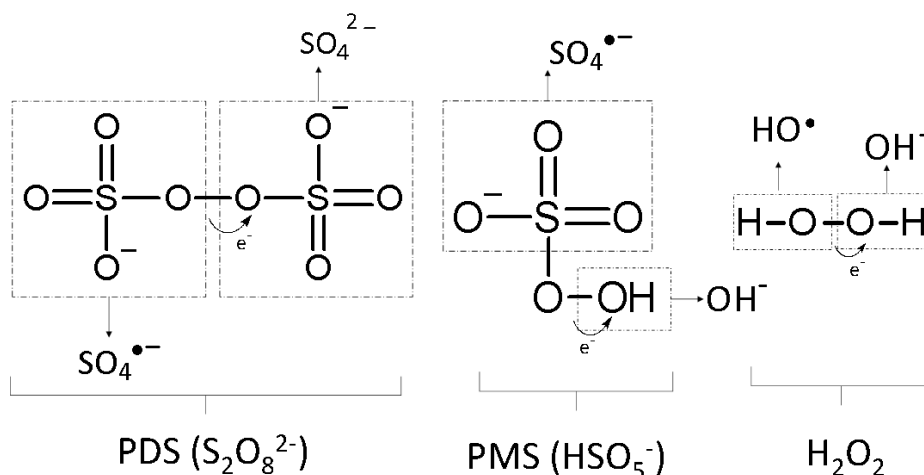


Figura 2 Estrutura química e mecanismos de ativação através de processos de transferência de elétrons de PDS, PMS e H_2O_2 .

A Tabela 1 mostra que esses três oxidantes têm propriedades diferentes e também que o PMS ativado pode gerar ambos os tipos de radicais, $\text{SO}_4^{\bullet-}$ e $\text{HO}^{\bullet}$. No entanto, é um oxidante mais caro.

Tabela 1 Propriedades e custo dos oxidantes H_2O_2 , PMS e PDS aplicados em POAs.

Oxidante	E^0 (V)	Principais	Solubilidade	USD Kg ⁻¹
		espécies geradas	em água em 25 °C (g L ⁻¹)	
H_2O_2	1,77	$\text{HO}^{\bullet}$	Solúvel	1,5
PDS	2,01	$\text{SO}_4^{\bullet-}$	730	0,74
PMS	1,82	$\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$	298	2,2

A vantagem de usar H_2O_2 é sua total solubilidade em água em comparação com PDS e PMS. A aplicação de PDS também é interessante por ser a opção mais econômica dentre estes agentes oxidantes.

Dentre os POAs, tem-se o processo Fenton heterogêneo que utiliza partículas de catalisador na fase sólida para ativar oxidantes e pode ser interessante para aplicações operacionais de larga escala, principalmente quando combinado com a radiação solar. Estudos comprovaram a eficiência deste processo na remoção de várias classes de fármacos como antibióticos, antidepressivos, anticancerosos, hormônios como os estrogênios, anti-inflamatórios e outros.

Estudos recentes têm relatado a aplicação de diferentes tipos de catalisadores no processo Fenton heterogêneo. Minerais de ferro como magnetita, hematita, ferridrita, goethita, lepidocrocita e maghemita apresentam baixa toxicidade e são os catalisadores mais comumente empregados em Fenton.

Além disso, vários minerais de ferro podem ser incorporados em vários materiais de suporte, como zeólitos, estruturas metal-orgânicas (MOFs), argilas, óxido de grafeno (GO) e sílica para aumentar a estabilidade térmica, resistência a solventes orgânicos e resistência mecânica. Além do ferro, outros cátions que participam das reações de Fenton como Cu, Ce, Mn, Cr, Co e Ru podem ser incorporados a esses materiais para acelerar o processo de degradação.

Apesar das inúmeras vantagens reportadas no emprego destes catalisadores no processo Fenton heterogêneo, a significativa lixiviação dos metais, a baixa eficiência no reuso do catalisador e a necessidade de ajuste do pH, foram algumas das limitações reportadas, as quais prejudicam a atividade catalítica destes materiais.

Entretanto, estas limitações podem ser contornadas com aplicação de Hidróxidos Duplos Lamelares (HDLs), uma vez que a atividade catalítica desses materiais pode ser melhorada variando tanto os cátions quanto os ânions interlamelares na estrutura do catalisador.

Devido às suas características estruturais únicas, as lamelas 2D podem incorporar diferentes metais, o que resulta em um alto sinergismo entre os cátions. Outras vantagens deste catalisador incluem dispersão em nível atômico de cátions estruturais, baixa toxicidade, alta porosidade, estabilidade térmica/química, baixa lixiviação de metais e simplicidade de síntese em escala de laboratório, o que é interessante para suas aplicações práticas. Essas características diferenciam os HDLs dos catalisadores comumente reportados.

Para entender a estrutura de um HDL é conveniente usar a estrutura da brucita $[\text{Mg}(\text{OH})_2]$, onde os cátions M^{2+} estão nos centros dos octaedros com seis grupos hidroxila (OH^-) nos vértices, enquanto cada OH^- é circundado por três cátions metálicos e eles são apontados para os cantos e formam os empilhamentos das lamelas (Figura 3).

A transformação da brucita em HDL ocorre devido à substituição do cátion divalente (M^{2+}) pelo cátion trivalente (M^{3+}) na estrutura (Figura 3), resultando em uma carga residual positiva que requer a presença de um ânion interlamelar com carga compatível para contrabalançar as cargas na estrutura.

Esse processo gera uma expansão no empilhamento das lamelas (Figura 3), formando o HDL, que é representado pela fórmula geral: $[M(II)_{(1-x)}M(III)_x(OH)_2] (A^n)_{x/n} \cdot mH_2O$. O valor de x representa a razão molar de $M(III)/(M(II) + M(III))$. Neste caso, a faixa de $0,2 \leq x \leq 0,33$ é geralmente reconhecida como adequada para HDL.

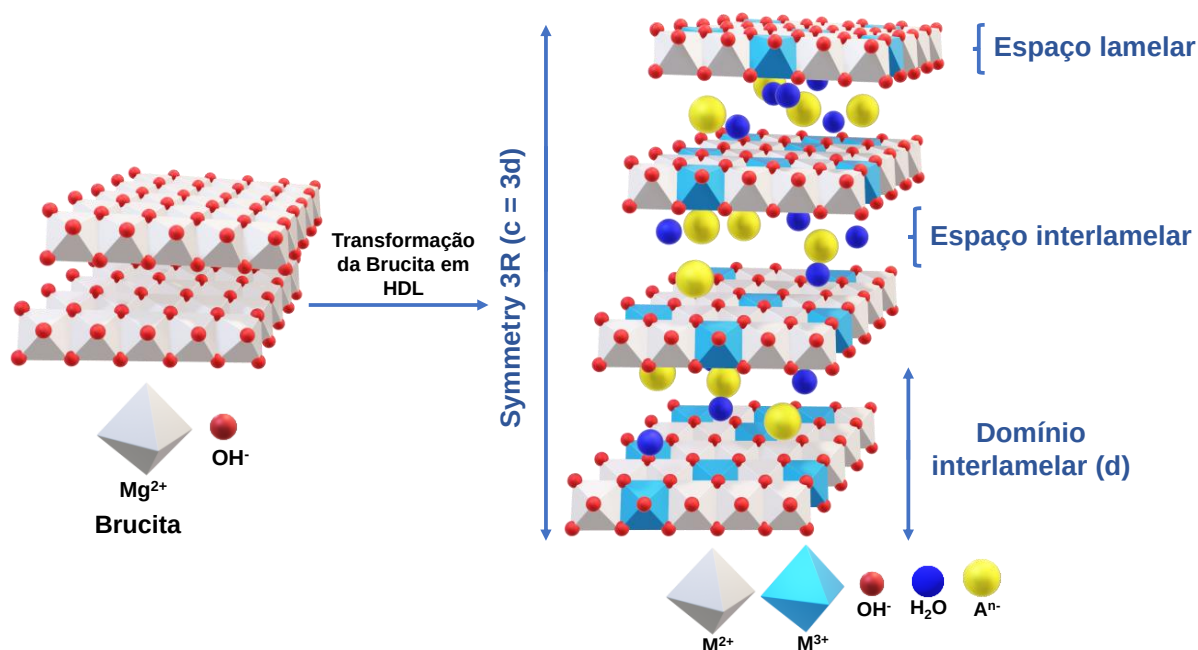


Figura 3 Transformação da brucita em HDL.

A incorporação de metais que participam das reações de Fenton como por exemplo Fe, Cu, Ce, Mn, Cr, Co e Ru, e diferentes ânions interlamelares como: as Cl^- , Br^- , I^- , CO_3^{2-} , NO_3^- , ClO_4^- , SO_4^{2-} , $S_2O_3^{2-}$, $NiCl_4^{2-}$, $CoCl_4^{2-}$ e $Fe(CN)_6^{3-}$ possibilita o emprego destes materiais como catalisadores em processo Fenton heterogêneo.

O objetivo geral desta tese foi avaliar a influência do cobre, diferentes ânions e diferentes oxidantes na atividade catalítica de HDL para a degradação de fármacos e inativação de patógenos via processo Fenton heterogêneo aplicado em efluente após passar por uma estação de tratamento de esgoto (ETE).

Desta forma, os experimentos foram realizados em água deionizada e em efluente urbano. Todos os catalisadores foram sintetizados pelo método de co-precipitação a $pH = 11$

(constante) e os experimentos de degradação foram realizados em diferentes condições experimentais, conforme será discutido a seguir.

Inicialmente foi avaliada a atividade catalítica em processo Fenton heterogêneo de um (HDL) de MgFe-CO_3 com e sem a inserção de cobre na estrutura, utilizando H_2O_2 como oxidante para a remoção do antibiótico sulfatiazol (STZ) em água. Foi adicionado 7% cobre (com relação ao número total de mols de Mg e Fe). Os dois catalisadores apresentaram difratogramas de raios X semelhantes, com planos basais correspondentes aos empilhamentos das lamelas: (003), (006) e (009), característico da estrutura HDL (Figura 4).

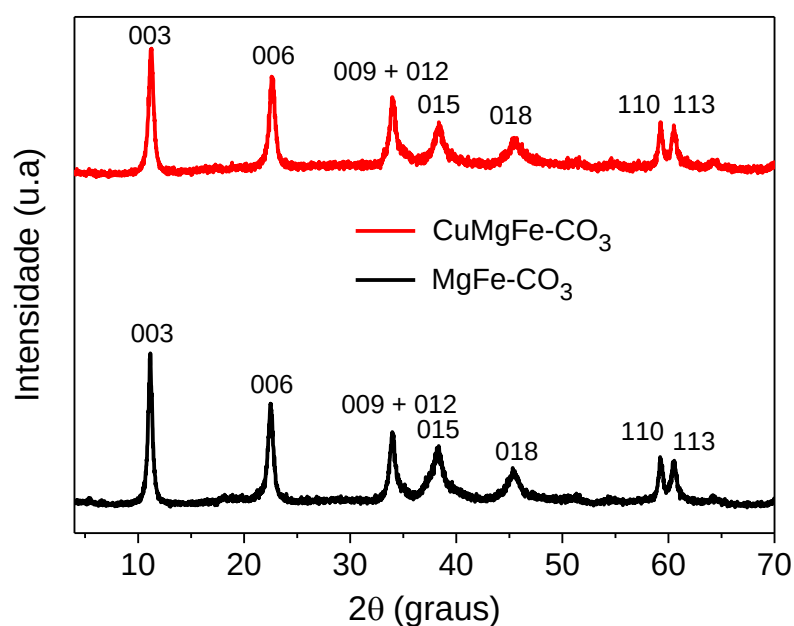
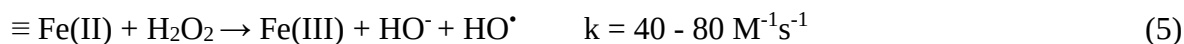
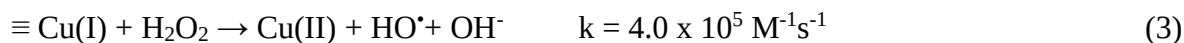
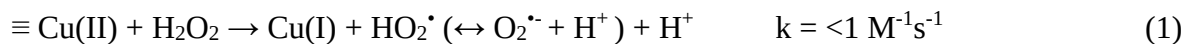


Figura 4 Difratogramas de raios-X de MgFe-CO_3 e CuMgFe-CO_3 .

A inserção de cobre aumentou a área específica do catalisador, de 42 para 91 $\text{m}^2 \text{g}^{-1}$, o que melhorou as propriedades catalíticas do material devido ao aumento da quantidade de sítios ativos disponíveis para as reações de Fenton.

Para avaliar o efeito da inserção de cobre na estrutura do HDL, estudos cinéticos de degradação em diferentes concentrações do catalisador (0,2 – 1,0 g L^{-1}) e de H_2O_2 (0 – 6 mmol L^{-1}) foram realizados. O HDL CuMgFe-CO_3 apresentou melhor atividade catalítica do que o HDL sem cobre nas diferentes condições investigadas. Isso pode ser explicado devido a incorporação de cobre no HDL favorecer a transferência de elétrons de H_2O_2 para o Cu(II) , o que reflete no aumento da taxa de formação $\text{HO}_2^*/\text{O}_2^{\cdot-}$ e levando à redução de Cu(II) a Cu(I) , acelerando a degradação devido à reação mais rápida de Cu(I) com H_2O_2 (Eq. 1-3), quando comparada com Fe(II) e H_2O_2 no clássico processo Fenton (Eq. 4 e 5).



As melhores concentrações de HDL e H_2O_2 nos experimentos com o HDL de cobre foram $0,5 \text{ g L}^{-1}$ e 4 mmol L^{-1} , respectivamente. Nestas condições e sob irradiação LED- Vis ($1,3 \text{ W}$; $460 \pm 20 \text{ nm}$), a concentração de STZ diminuiu para níveis indetectáveis após 90 min, enquanto que com MgFe-CO_3 $1,0 \text{ g L}^{-1}$ de catalisador foi necessário para atingir total remoção de STZ após 120 min, conforme representado na Figura 5.

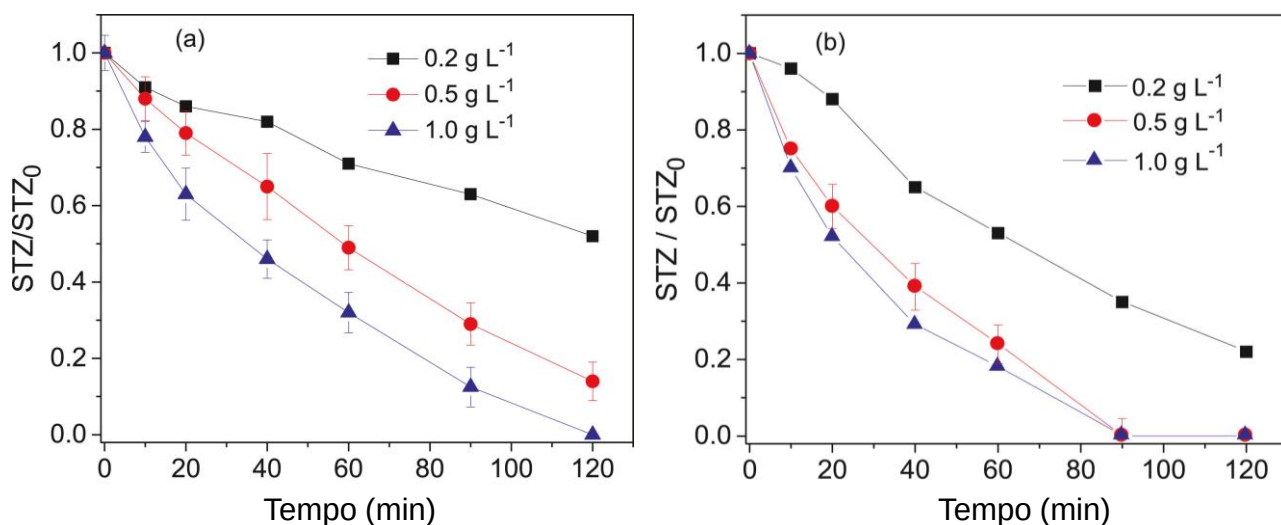


Figura 5 Efeito da concentração de HDL na degradação de STZ. Condições: pH 7,5; $150 \mu\text{g L}^{-1}$ STZ; $4 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$; Irradiação Vis-LED, (a) MgFe-CO_3 e (b) CuMgFe-CO_3 .

Os experimentos no escuro e na ausência de H_2O_2 não mostraram capacidade de adsorção de STZ por HDL. Da mesma forma, a fotólise de H_2O_2 resultou em apenas 10% de remoção de STZ, enquanto nenhuma remoção significativa foi observada somente com aplicação de irradiação com LED visível.

Uma propriedade interessante destes materiais é a capacidade de funcionarem em meio neutro e manterem o pH da solução após a inserção do HDL. Experimentos para avaliar o aumento do pH nas suspensões em água com os catalisadores foram realizados com $0,5 \text{ g L}^{-1}$ do HDL com cobre e sem cobre. O pH natural da solução STZ foi de 5,6.

É possível observar na Figura 6, um rápido aumento para pH 7,5 no sistema com CuMgFe-CO_3 e pH 7,2 no sistema com MgFe-CO_3 no primeiro minuto de reação, seguido de

estabilização em torno de pH 7,8 até o final do experimento. Este aumento no pH foi devido aos grupos hidroxila presentes na estrutura do catalisador, que neutralizaram a solução. Embora esse pH não seja ideal para a reação de Fenton, o material não é estável em $\text{pH} < 4$ e interessante o aumento do pH ocorreu mesmo com a acidificação prévia da solução.

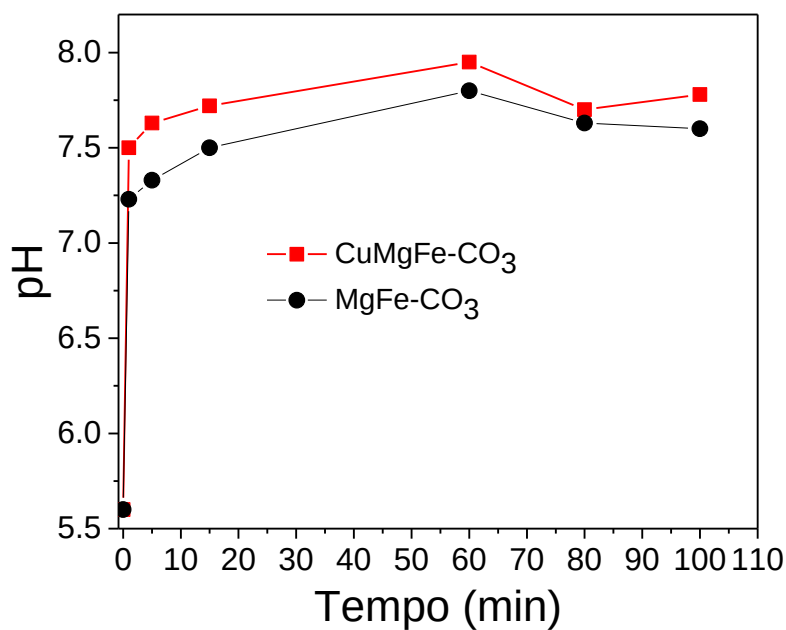


Figura 6 Aumento do pH em suspensões aquosas de $0,5 \text{ g L}^{-1}$ MgFe-CO_3 e CuMgFe-CO_3 .

Para melhor entendimento do mecanismo de degradação do antibiótico com o HDL com cobre e sem cobre, o papel das espécies reativas de oxigênio no mecanismo de degradação foi investigado pela adição com álcool terc-butílico (TBA) e p-benzoquinona (BQ), sequestradores de radicais $\text{HO}^\bullet$ e $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$, respectivamente (Figura 7). Além disso análises de XPS foram usadas para identificar os estados de ligação das espécies de Cu e Fe na superfície do catalisador com cobre, antes e depois de quatro ciclos de degradação de Fenton (Figura 8).

É possível observar na Figura 7, que para ambos os catalisadores, na ausência dos sequestradores, 90% de degradação de STZ foi obtida após 120 min, seguindo um modelo de reação de primeira ordem com uma constante de velocidade (k) de $0,019 \text{ min}^{-1}$. No entanto na presença de TBA e o HDL com cobre, a degradação de STZ foi mais reprimida do que com o HDL sem cobre e atingiu apenas 19% de degradação ($k = 0,002 \text{ min}^{-1}$) enquanto que 48% de degradação foi atingida com o HDL sem cobre ($k = 0,006 \text{ min}^{-1}$). Da mesma forma, na presença de BQ, a degradação atingiu 30% ($k = 0,004 \text{ min}^{-1}$) e 69% ($k = 0,010 \text{ min}^{-1}$) usando o HDL sem e com cobre, respectivamente.

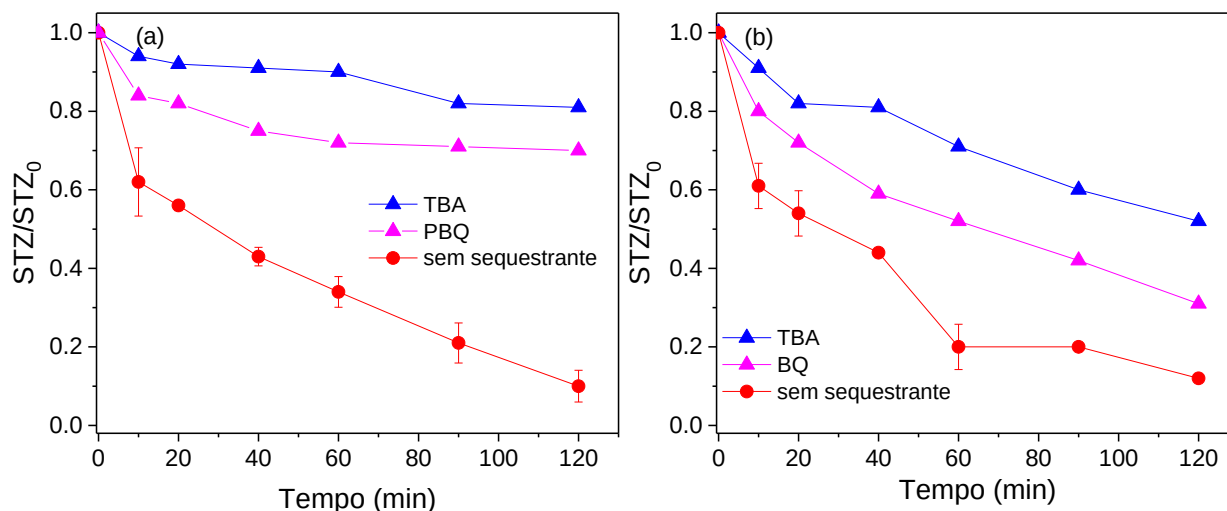


Figura 7 Influência da presença de TBA e BQ na degradação de STZ no escuro com (a) MgFe-CO_3 ($1,0 \text{ g L}^{-1}$) e (b) CuMgFe-CO_3 ($0,5 \text{ g L}^{-1}$). Condições: pH 7,5; $150 \mu\text{g L}^{-1}$ STZ; $4 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$; 100 mmol L^{-1} TBA; 1 mmol L^{-1} de BQ.

Conforme demonstrado na Figura 7 os radicais $\text{HO}^\bullet$ e $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$, têm um papel importante no mecanismo de oxidação de STZ, sendo o radical hidroxila a principal espécie oxidativa, uma vez que a degradação foi mais afetada na presença de sequestrante deste radical.

Os espectros de XPS de alta resolução de Fe $2p_{3/2}$ foram deconvoluídos em quatro componentes em 709,5, 711,1, 712,3 e 514,3 eV, relacionados à presença de Fe(II), Fe(III) (Fe_2O_3 e FeOOH) e um satélite “shake-up” de Fe(III), respectivamente. A comparação dos espectros mostrou que os sítios de ferro permaneceram inalterados após o processo de degradação. Desconsiderando os satélites “shake-up” de Cu (II) em energias de ligação mais altas dos espectros de Cu $2p_{3/2}$, os três componentes em 932,2, 933,7 e 934,8 eV podem ser atribuídos às espécies Cu(I) e Cu(II) (CuO e Cu(OH)_2), respectivamente (Figura 8).

É importante ressaltar que é bastante comum observar nos espectros de XPS a presença de um componente fraco atribuído à redução de espécies provenientes dos sais precursores, como por exemplo, a presença de Cu(I) em amostras preparadas com precursores de Cu(II), o que pode ser explicado devido a uma possível redução parcial de Cu(II) induzida por raios X.

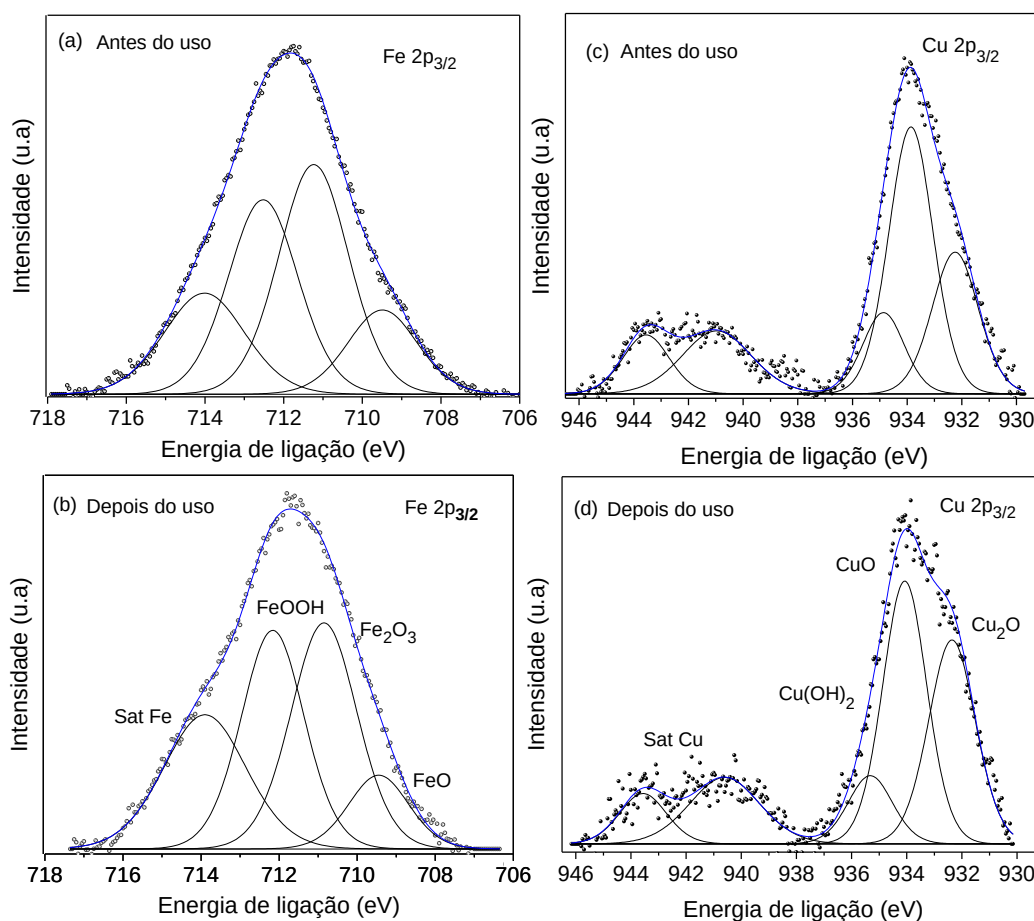


Figura 8 XPS Fe 2p_{3/2} (a, b) e Cu 2p_{3/2} (c, d) espectros de CuMgFe-CO₃, antes (a, c) e após (b, d) quatro ciclos de uso no processo Fenton.

O aumento observado de Cu(I) após quatro ciclos de processo sugere a redução de Cu(II) durante a decomposição catalítica de H₂O₂ (Eq. 1). A presença de sítios de Cu(I) na superfície da estrutura do HDL é importante, pois pode contribuir significativamente para a geração de radicais hidroxila conforme a Eq.3, contribuindo para a eficiência do processo de degradação.

O reuso do catalisador é fundamental de ser investigado. Neste sentido, experimentos de degradação de STZ foram realizados durante quatro ciclos de 120 min do processo Fenton no escuro e os resultados mostraram que a atividade catalítica do CuMgFe-CO₃ diminuiu apenas 10% após o quarto ciclo, indicando uma boa estabilidade do catalisador.

Nesta etapa foi possível concluir que a inserção de cobre na superfície do catalisador foi muito importante para o processo de degradação de STZ via reações de Fenton. A formação de pares redox Cu(II)/Cu(I) e Fe(III)/Fe(II) propiciaram a decomposição efetiva de H₂O₂ para formar HO[•] e HO₂[•] /O₂^{•-}, resultando em degradação aprimorada de STZ, em comparação com o HDL sem cobre.

O foco principal dos estudos sobre o uso de HDLs do tipo piroaurita nas reações de Fenton reportados na literatura, tem sido avaliar os efeitos de diferentes cátions nas lamelas, como Mn, Fe, Cu e Co, sem considerar o efeito do ânion interlamelar, que também pode influenciar a atividade catalítica.

Com base na capacidade do ânion ser trocado, a seguinte ordem de estabilidade já foi relatada para a intercalação do ânion no espaço interlamelar no HDL: $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$. Essa sequência foi proposta levando em consideração a densidade de carga do ânion, que geralmente, quanto maior a densidade de carga, maior a interação eletrostática com as lamelas, o que contribui para a tendência de serem intercalados no espaço interlamelar.

Sendo assim, para avaliar se o ânion interlamelar na estrutura do HDL poderia causar algum efeito positivo na atividade catalítica do material, decidiu-se sintetizar HDLs de CuMgFe, com variação dos ânions: CO_3^{2-} , SO_4^{2-} , B(OH)_4^- e NO_3^- .

Em particular, o ânion B(OH)_4^- foi selecionado para ser intercalado no HDL, uma vez que estudos recentes descreveram a influência de espécies de boro na alteração da densidade de carga superficial, e consequentemente aumentando a cinética de reação de Fenton.

Os difratogramas de raios-X (Figura 9) mostram três picos principais (003), (006) e (009) atribuídos à estrutura lamelar e aos planos de empilhamento, característicos da estrutura do HDL. Além disso é possível observar que esses materiais possuem pureza de fase e cristalinidade.

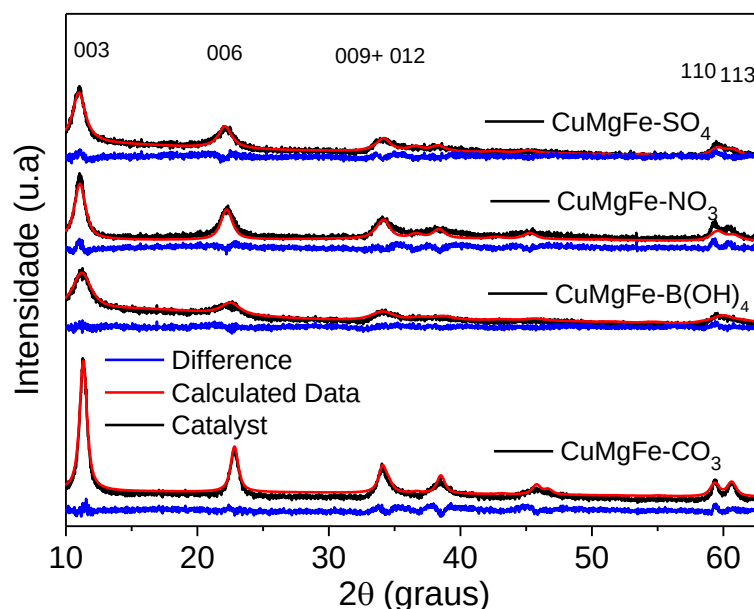


Figura 9 Difrátogramas de raios-X com refinamento Rietveld de CuMgFe-SO₄, CuMgFe-NO₃, CuMgFe-B(OH)₄ e CuMgFe-CO₃.

A Tabela 2 mostra que o ânion interlamelar afeta principalmente o tamanho de cristalito e a área específica dos catalisadores.

Tabela 2 Efeito de diferentes ânions no espaçamento basal (d_{003}), tamanho médio do cristalito na direção c e área específica para o CuMgFe-CO₃ (CO₃²⁻), CuMgFe-B(OH)₄ (B(OH)₄⁻), CuMgFe-NO₃ (NO₃⁻) e CuMgFe-SO₄ (SO₄²⁻).

Parâmetros	CO ₃ ²⁻	B(OH) ₄ ⁻	NO ₃ ⁻	SO ₄ ²⁻
d₀₀₃ (nm)	0,78	0,79	0,80	0,81
Tamanho de cristalito na direção c (nm)	11,8	4,7	7,7	6,7
Área específica (m² g⁻¹)	68	17	10	25

Essas modificações estão relacionadas às diferenças de densidade de carga e tamanho de SO₄²⁻, NO₃⁻, B(OH)₄⁻ e CO₃²⁻ que interferem na estabilização da estrutura dos HDLs. Conforme mostrado na Tabela 2, o tamanho de cristalito e a área específica são menores para CuMgFe-B(OH)₄, CuMgFe-NO₃, CuMgFe-SO₄ do que para CuMgFe-CO₃, o que reflete a menor capacidade de estabilização da estrutura do HDL com esses ânions em comparação ao CO₃²⁻.

Os resultados de morfologia destes catalisadores ajudam a explicar os resultados da Tabela 2 e fazer uma relação com a facilidade de intercalação do ânion interlamelar. É possível observar nas imagens de microscopia eletrônica de varredura (MEV) (Figura 10), uma morfologia diferente para CuMgFe-B(OH)₄ (quando comparado aos demais HDLs), com formato irregular e partículas menores. Essas estruturas do tipo “stone-like” levam a um menor empacotamento das plaquetas o que justifica a menor área e tamanho de cristalito, e consequentemente o fato deste ânion apresentar menor capacidade de estabilizar a estrutura do HDL, quando comparado com os outros HDLs sintetizados.

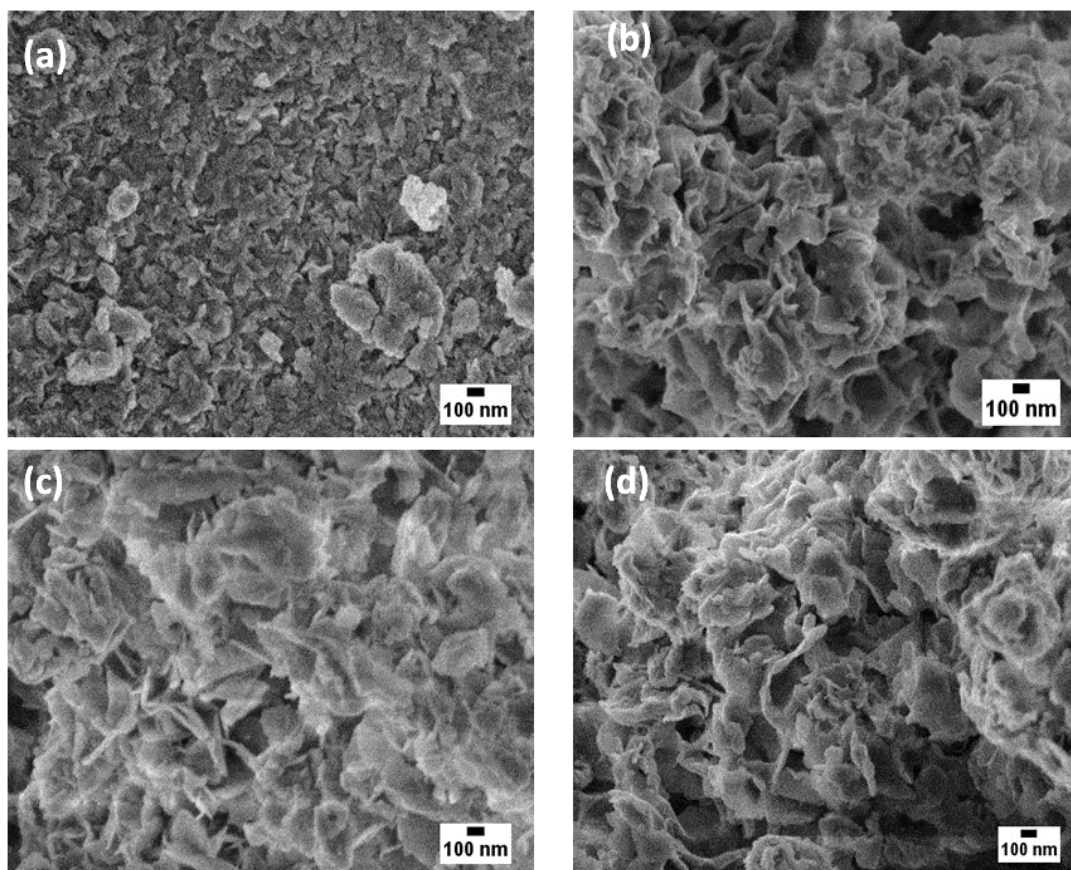


Figura 10 Imagens de MEV dos materiais sintetizados a) CuMgFe-B(OH)_4 , b) CuMgFe-SO_4 , c) CuMgFe-CO_3 , and d) CuMgFe-NO_3 .

Diferentemente, CuMgFe-CO_3 apresenta plaquetas maiores com morfologia do tipo rosa de areia o que resulta em maior estabilização na formação do hidróxido duplo e por isso apresenta maior capacidade de ser intercalado.

Os espectros de XPS de alta resolução de B 1s, C 1s, N 1s e S 2p mostram que os ânions B(OH)_4^- , CO_3^{2-} , NO_3^- e SO_4^{2-} foram intercalados no espaço interlamelar dos respectivos HDLs (Figura 11).

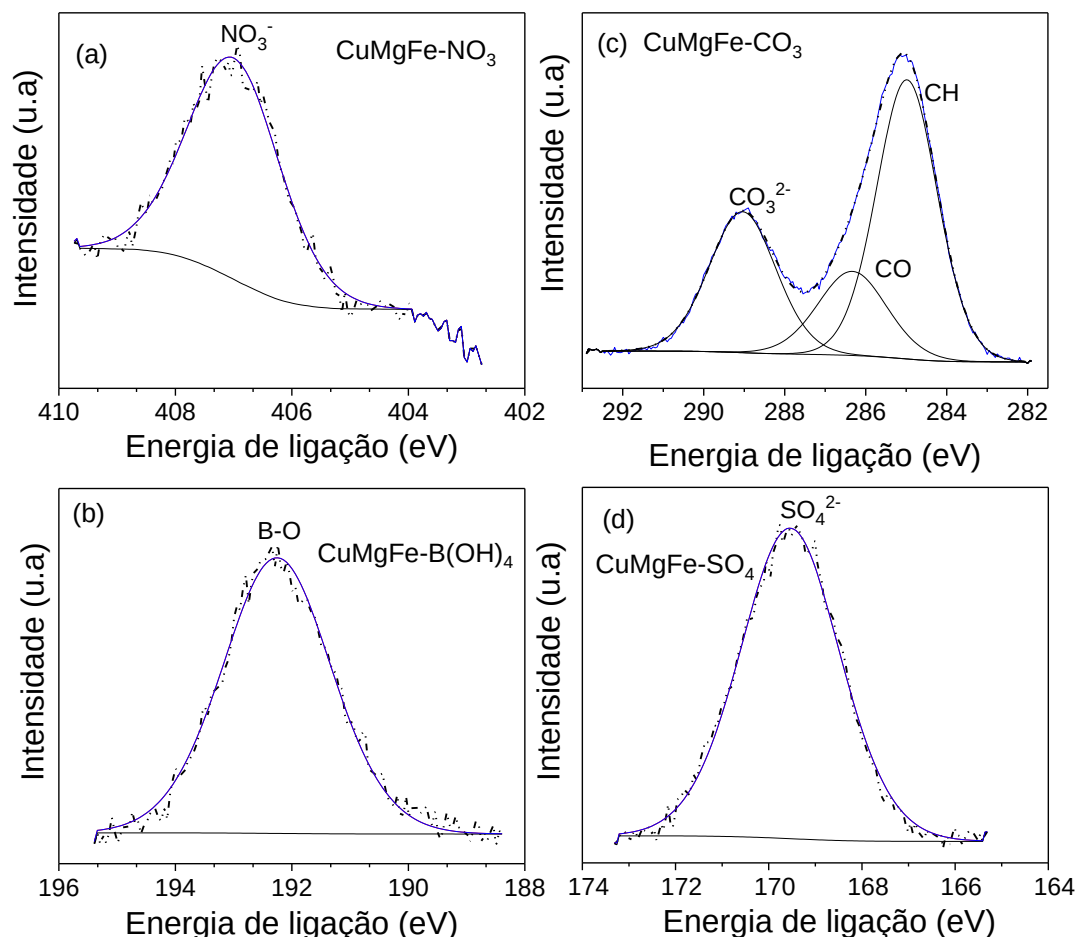


Figura 11 Espectros de XPS de alta resolução de N 1s (a), B 1s (b), C 1s (c) e S 2p (d) dos HDLs sintetizados.

O espectro de N 1s na Figura 12a apresentam um único pico em 407,07 eV, relacionado ao NO_3^- e nas Figuras 9c e d, o componente carbonato em 289,1 eV se sobrepõe com uma pequena contribuição de carboxil -CO característico do CuMgFe-CO_3 . O pico em 169,8 eV do espectro S 2p indica que o enxofre está na forma de sulfato (SO_4^{2-}) no caso de CuMgFe-SO_4 .

O sinal localizado em 192,3 eV está associado às ligações BO. Tendo em vista que o ânion interlamelar na estrutura do HDL está situado nas galerias interlamelares juntamente com as moléculas de água, é difícil confirmar o tipo de espécie de boro presente na superfície do catalisador. Para confirmar a presença do ânion B(OH)_4^- , os espectros de FTIR de CuMgFe-B(OH)_4 mostraram uma banda de baixa intensidade em 680 cm^{-1} , atribuída a vibrações assimétricas de B-O e uma banda adicional em $1200 - 1000\text{ cm}^{-1}$ de B-OH (Figura 12). Esses resultados aliados aos de XPS permitem inferir que as ligações B-O e B-OH estão presentes no espaço interlamelar de CuMgFe-B(OH)_4 , o que pode influenciar as características estruturais e melhorar a atividade do catalisador.

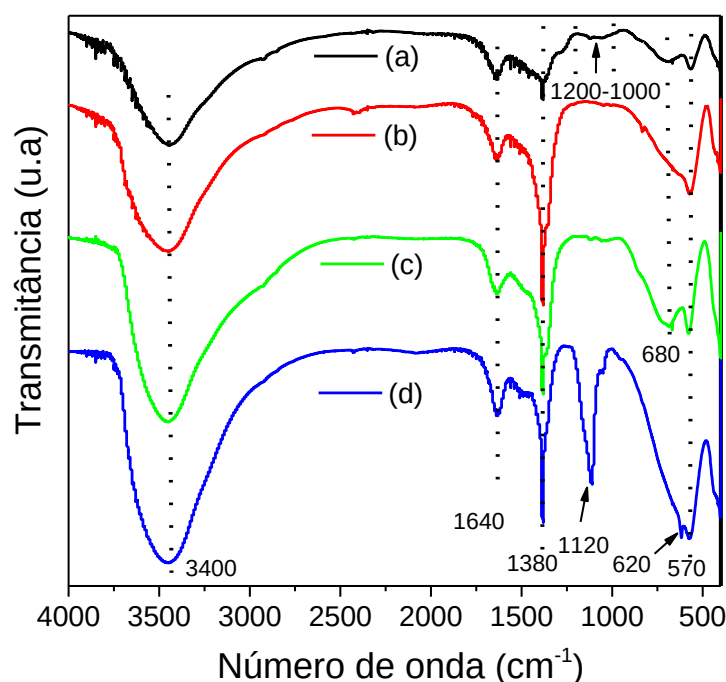


Figura 12 Espectros de FTIR de (a) CuMgFe-B(OH)_4 , (b) CuMgFe-NO_3 , (c) CuMgFe-CO_3 e (d) CuMgFe-SO_4 .

Além disso, os espectros de FTIR dos catalisadores mostram uma banda larga na faixa de 3750 cm^{-1} a 3250 cm^{-1} corresponde ao alongamento dos grupos hidroxila das moléculas de água presentes no espaço interlamelar na estrutura dos HDLs. Além disso, a banda centrada em 1640 cm^{-1} é atribuída a modos OH^- de vibrações de moléculas de água em diferentes catalisadores. A banda em 570 cm^{-1} corresponde às vibrações de estiramento da ligação de oxigênio com o metal (MO , $\text{M} = \text{Mg, Fe e Cu}$).

Conforme mostrado acima, os resultados da caracterização de CuMgFe-B(OH)_4 permitem propor um mecanismo para explicar a possibilidade de reduções parciais de ferro e cobre na superfície do catalisador causadas pela presença de ácido bórico. O modelo (Figura 13) foi proposto para o cobre, devido já ter sido reportado um mecanismo semelhante para o ferro com goethitas modificadas com ácido bórico.

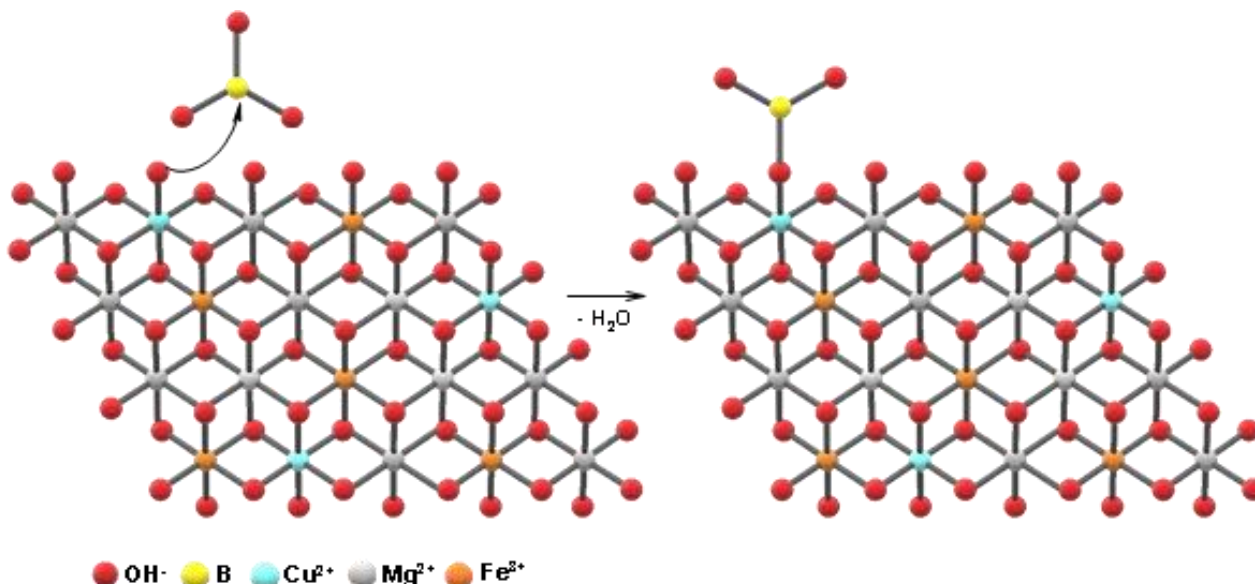


Figura 13 Reação de superfície proposta entre CuMgFe-B(OH)_4 e B(OH)_3 .

Com base nas condições de síntese e no valor de $\text{pK}_a = 9,2$, o ácido bórico e o ânion borato podem estar presentes na superfície do catalisador.



A concentração teórica de B(OH)_4^- é de $7,5 \times 10^{-3} \text{ mol L}^{-1}$ em solução aquosa durante a preparação de CuMgFe-B(OH)_4 . Tendo em vista que mecanismos de reação na superfície de catalisadores com o ânion B(OH)_4^- são menos estáveis, o reagente dominante pode ser B(OH)_3 cuja reação na superfície do HDL ocorre com formação de uma estrutura de estado de transição e eliminação de uma molécula de água (Figura 13).

O fortalecimento da ligação entre o boro e o oxigênio do grupo hidroxila presente na superfície do HDL auxilia na estabilidade da ligação de hidrogênio entre o grupo hidroxila do ácido bórico e o hidrogênio do grupo hidroxila presente em CuMgFe-B(OH)_4 (Figura 13). Após a remoção da molécula de água e complexação do ácido bórico na superfície do HDL, pode ocorrer redução de Cu(II) e Fe(III) na superfície do HDL. O mecanismo proposto mostra que B(OH)_3 pode atuar como promotor da transferência de elétrons na superfície de CuMgFe-B(OH)_4 , modificando a densidade eletrônica e resultando na presença de Fe(II) e também na elevada quantidade de Cu(I) conforme verificado na análise por XPS (Figura 14).

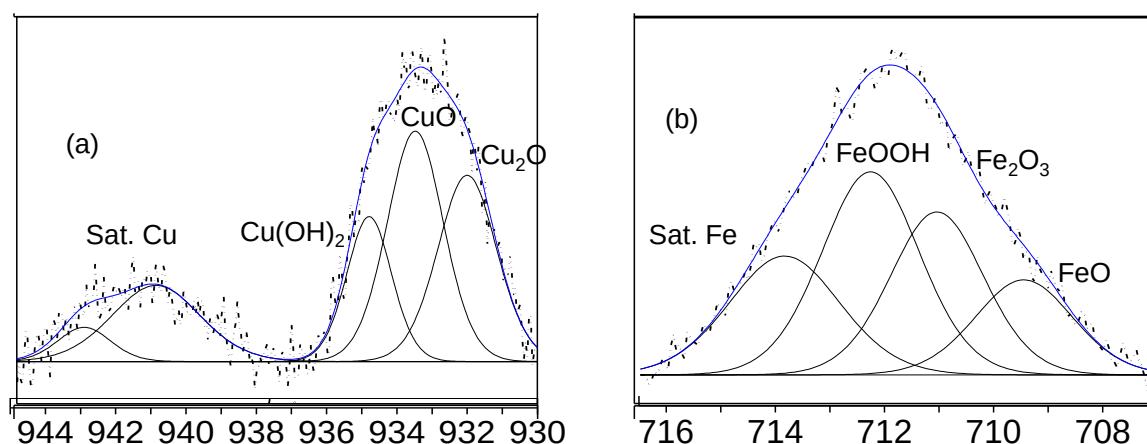


Figura 14 Espectros XPS de alta resolução de Cu $2p_{3/2}$ (a), Fe $2p_{3/2}$ (b) de CuMgFe-B(OH)_4 .

Para avaliar o efeito dos diferentes ânions interlamelares na estrutura dos HDLs, os diferentes materiais foram aplicados tanto no escuro como sob irradiação solar na degradação do 5-FU.

Inicialmente, para avaliar a adsorção do contaminante na superfície do catalisador e uma possível contribuição do processo fotocatalítico sob radiação solar sem H_2O_2 , experimentos controles foram realizados na ausência de H_2O_2 no escuro e sob radiação solar. Os resultados não mostraram adsorção significativa de 5-FU em HDLs no escuro ou degradação fotocatalítica de 5-FU sob radiação solar até 120 min.

Seguidamente o efeito do ânion interlamelar foi investigado na degradação de 5-FU e na presença de H_2O_2 (Figura 15). Notavelmente, o HDL contendo ânion borato (CuMgFe-B(OH)_4) promoveu uma taxa de degradação significativamente maior de 5-FU em comparação com outros HDLs, atingindo a degradação total de 5-FU após 40 min e seguindo uma cinética de pseudo-primeira ordem com uma constante de taxa de reação $k = 0,133 \text{ min}^{-1}$ ($R^2 = 0,997$). O segundo HDL mais eficiente foi CuMgFe-NO_3 , que promoveu a degradação total do 5-FU após 120 min com $k = 0,017 \text{ min}^{-1}$ ($R^2 = 0,997$). É interessante notar que a eficiência do HDL contendo carbonato e sulfato como ânion interlamelar foi muito semelhante, alcançando cerca de 70% de degradação de 5-FU no escuro após 120 min com $k = 0,009 \text{ min}^{-1}$ ($R^2 = 0,990$) e $k = 0,010 \text{ min}^{-1}$ ($R^2 = 0,999$), respectivamente.

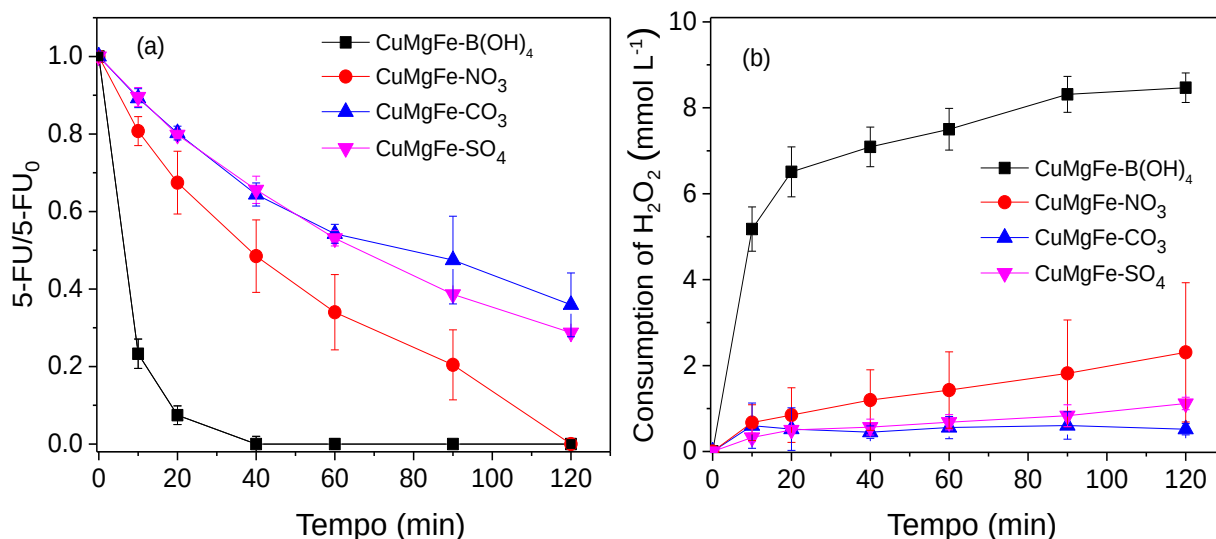


Figura 15 Influência do ânion interlamelar na degradação de 5-FU no escuro (a) e consumo de H_2O_2 (b). Condições iniciais: 5-FU = 200 $\mu g L^{-1}$, LDHs = 0,5 g L^{-1} e H_2O_2 = 10 mmol L^{-1} .

Esses resultados permitem propor uma sequência de eficiência catalítica para a degradação de 5-FU no escuro usando os HDLs investigados: $CuMgFe-B(OH)_4 > CuMgFe-NO_3 > CuMgFe-SO_4 > CuMgFe-CO_3$.

A alta atividade catalítica observada com $CuMgFe-B(OH)_4$ pode ser explicada pelas espécies de boro inseridas no espaço interlamelar, que podem modificar a densidade de eletrônica na superfície do material e facilitar as reduções de Fe(III) e Cu(II) melhorando a cinética de degradação (Eq.1-5). A quantidade significativa de Cu(I) na superfície de $CuMgFe-B(OH)_4$ indicada pela análise XPS (Figura 16) desempenha um papel importante na geração de radicais hidroxila (Eq. 1 e 3) e, conseqüentemente, na remoção do contaminante no escuro.

Ao realizar as reações sob irradiação solar, a eficiência de degradação foi melhorada com todos os catalisadores estudados em comparação com o escuro (Figura 16). Após 90 min (dose UV = 240,50 kJ m^{-2}), a degradação completa do 5-FU foi observada em todos os sistemas investigados e nenhuma diferença significativa foi observada para os materiais $CuMgFe-NO_3$, $CuMgFe-CO_3$ e $CuMgFe-SO_4$. Sob irradiação solar, $CuMgFe-B(OH)_4$ também apresentou a melhor atividade alcançando degradação completa com dose de energia cinco vezes menor (48,52 kJ m^{-2} , 20 min) e maior consumo de H_2O_2 (Figura 16 b) em relação aos outros catalisadores, confirmando a superioridade do HDL de borato na degradação em processo foto-Fenton. Entretanto, o notório aumento da degradação de 5-FU com outros HDLs reforça o papel da fotorredução de Fe(III) e Cu(II), conseguida sob irradiação solar, o que contribui também no caso do $CuMgFe-B(OH)_4$, porém em menor grau considerando o papel do borato.

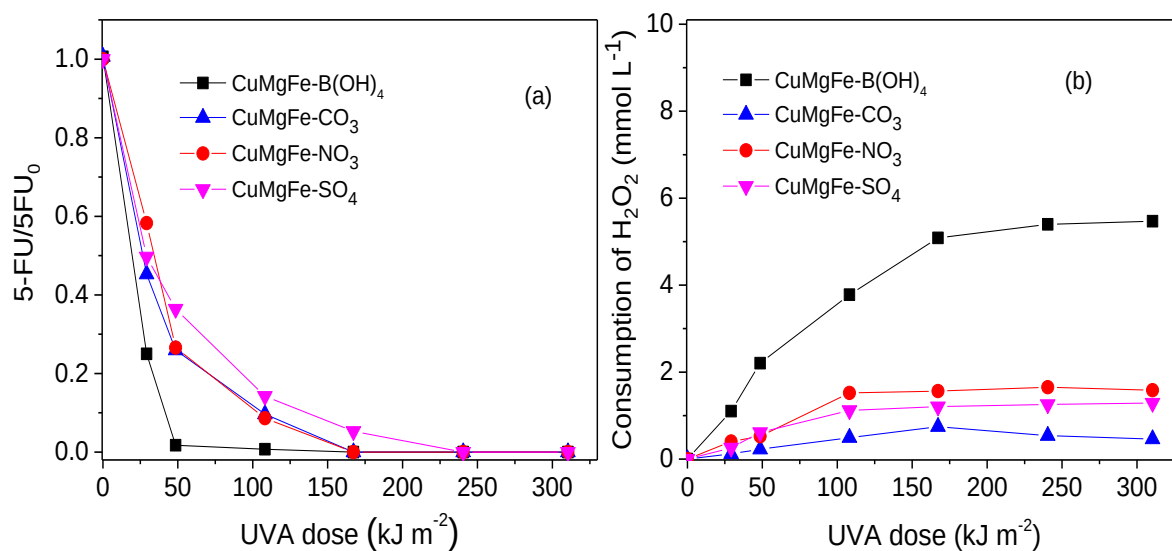


Figura 16 Influência do ânion interlamelar na degradação do 5-FU sob radiação solar (a) e consumo de H₂O₂ (b). Condições iniciais: 5-FU = 200 µg L⁻¹, LDHs = 0,5 g L⁻¹ e H₂O₂ = 10 mmol L⁻¹.

A estabilidade da atividade catalítica de CuMgFe-B(OH)₄ em processo Fenton foi avaliada após quatro ciclos de 120 min. Os resultados mostraram que o material manteve a atividade catalítica durante quatro ciclos resultando na remoção total de 5-FU após 90 min.

As possíveis modificações causadas pelo borato na estrutura do material podem manter a atividade catalítica após o uso do catalisador, o que evidencia ainda mais as propriedades catalíticas deste HDL. A atividade catalítica também foi mantida nos experimentos realizados em efluente urbano, embora tenha sido observada forte inibição da degradação neste caso devido ao efeito de matriz, resultando em 38% de degradação do 5-FU no efluente após 120 min.

A matéria orgânica natural e o carbonato são sequestrantes comuns de espécies reativas de oxigênio, que reduzem a eficiência da degradação. No entanto, a atividade catalítica de CuMgFe-B(OH)₄ foi mantida mesmo em uma amostra tão complexa. Portanto, é possível concluir que CuMgFe-B(OH)₄ tem potencial para aplicação para a remoção de contaminantes de corpos d'água no escuro e sob radiação solar, em pH ao redor da neutralidade.

A ativação de PMS, PDS e H₂O₂ por CuMgFe-B(OH)₄ foi investigada para a degradação de antibióticos frequentemente detectados em efluentes (SMX, CIP, CFX e AMX) e para a desinfecção bacteriana (*Escherichia coli* e *Enterococcus*) por processo Fenton heterogêneo. O processo de degradação foi realizado em água deionizada e em efluente após passar por uma estação de tratamento de esgoto.

O sistema HDL/PDS foi escolhido para avaliação das melhores concentrações de agente oxidante e HDL empregadas no processo.

Conforme mostrado na Figura 17, a presença de PDS foi necessária para promover a degradação de SMX, que resultou em 74% após 120 min ao aumentar sua concentração de 0 mmol L⁻¹ para 6 mmol L⁻¹. No entanto, como nenhuma diferença significativa foi observada usando 4 e 6 mmol L⁻¹ PDS, 4 mmol L⁻¹ PDS foi escolhido para ser usado em experimentos posteriores.

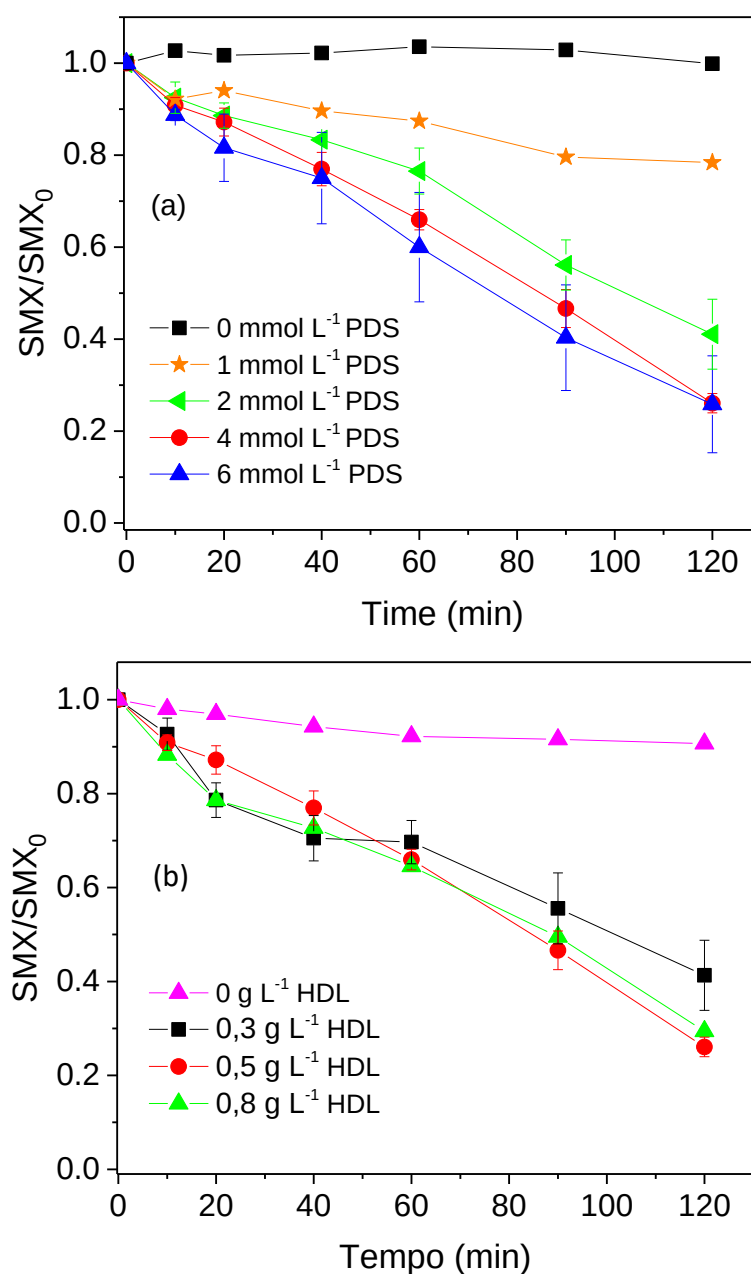
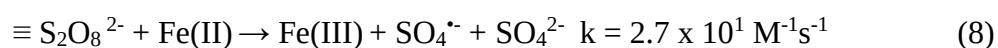


Figura 17 Efeito da concentração de PDS (a) e HDL (b) na degradação de SMX. Condições: pH = $8,7 \pm 0,8$; 500 $\mu\text{g L}^{-1}$ SMX; 0,5 g L⁻¹ LDH e 4 mmol L⁻¹ PDS.

A degradação de SMX foi melhorada para 59% após 120 min na presença de 0,3 g L⁻¹ de HDL, que aumentou para 74% quando a concentração de HDL foi aumentada para 0,5 g L⁻¹ sem aumento adicional de 0,5 para 0,8 g L⁻¹. A concentração de 0,5 g L⁻¹ de HDL foi, portanto, selecionada para experimentos posteriores.

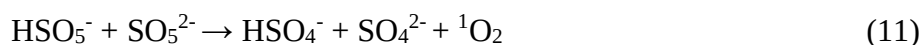
Conforme resultados de XPS (Figura 14), a presença das espécies Cu(I) e Fe(II) na estrutura do HDL foi identificada e contribuiu para a decomposição do PDS e geração de HO[•] e SO₄^{•-} (Eq. 7-9), e subsequente oxidação de SMX.



O potencial do par redox Cu(II)/Cu(I) ($E^0 = 0,17 \text{ V}$ em solução aquosa) é muito menor que o potencial redox do PDS ($E^0 = 2,01 \text{ V}$) e, portanto, no sistema com PDS a redução de Cu(II) é termodinamicamente desfavorável, indicando a vantagem do CuMgFe-B(OH)₄, que possui Cu(I) em sua composição. A ativação de PDS por Cu(II) precisa ser melhor investigada, particularmente em catálise heterogênea.

Após definir a concentração de oxidante (4 mmol L⁻¹) e catalisador (0,5 g L⁻¹) no sistema HDL/PDS, comparou-se o efeito dos três oxidantes na remoção de SMX em efluente urbano na ausência e presença de HDL.

A oxidação direta de SMX em águas residuais usando 4 mmol L⁻¹ H₂O₂, PDS ou PMS mostrou que o PMS foi o único oxidante que promoveu a oxidação completa de SMX após 40 min (Figura 16a). A alta eficiência da oxidação direta do SMX com PMS em efluente urbano se deve à auto-oxidação do PMS que gera oxigênio singlete (Eq. 10 e 11).



A Figura 18 mostra que a degradação de SMX em efluente urbano foi acelerada com todos os agentes oxidantes quando o HDL foi introduzido. No caso de HDL/PMS, SMX ficou abaixo do limite de detecção (8,76 µg L⁻¹) após 20 min de reação revelando a excelente atividade do catalisador para a geração de espécies reativas de oxigênio (Eq. 12-15) enquanto consumia 3 mmol L⁻¹. Em contraste, em LDH/PDS, prevalece um mecanismo não radicalar de degradação de SMX que será discutido mais adiante.

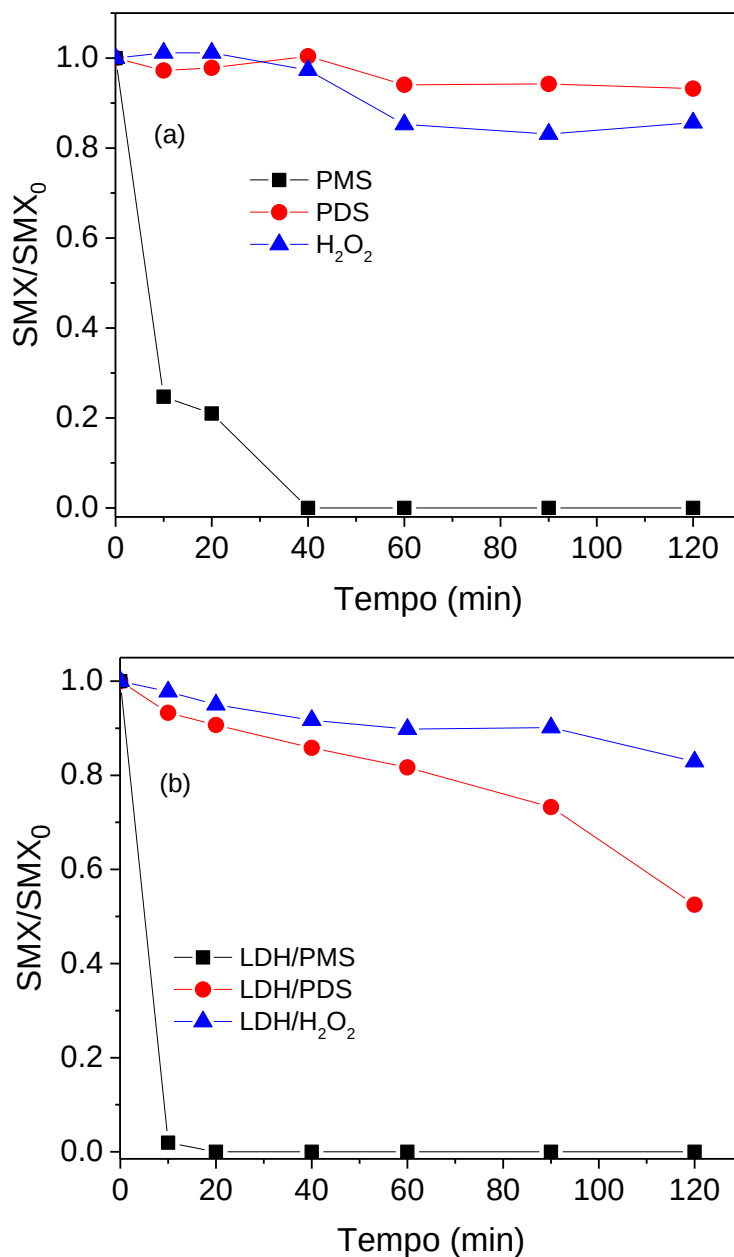
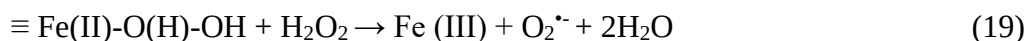
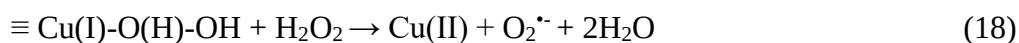


Figura 18 Oxidação direta de SMX com PDS, PMS e H₂O₂ a) e degradação de SMX em sistemas HDL/PDS, HDL/PMS e HDL/H₂O₂ (b) em efluente urbano pré-tratado. Condições: pH = 7,5; 500 µg L⁻¹ SMX, 0,5 g L⁻¹ HDL; 4 mmol L⁻¹ de PDS, PMS e H₂O₂.

No sistema HDL/PDS, após 120 min, 50% de SMX foram removidos em efluente urbano, enquanto apenas 18% de remoção de SMX foram obtidos no sistema HDL/H₂O₂ com

44% de consumo de H_2O_2 , devido à formação de um complexo entre HDL e H_2O_2 (Eq. 16 e 17), os quais posteriormente levam a formação do $\text{O}_2^{\cdot-}$ (Eq. 18 e 19), que não é eficiente para a remoção de SMX.



Os resultados indicam maior eficácia do sistema com PMS, que após ativação por HDL pode ter gerado simultaneamente os dois tipos de radicais $\text{SO}_4^{\cdot-}$ e $\text{HO}^{\cdot}$ (Eq. 12-15) em relação aos sistemas PDS e H_2O_2 .

As vias de transformação de SMX em todos os sistemas investigados foram elucidadas com base na identificação de produtos de degradação utilizando cromatografia líquida acoplada à espectrometria de massa de alta resolução (ver Figura 19).

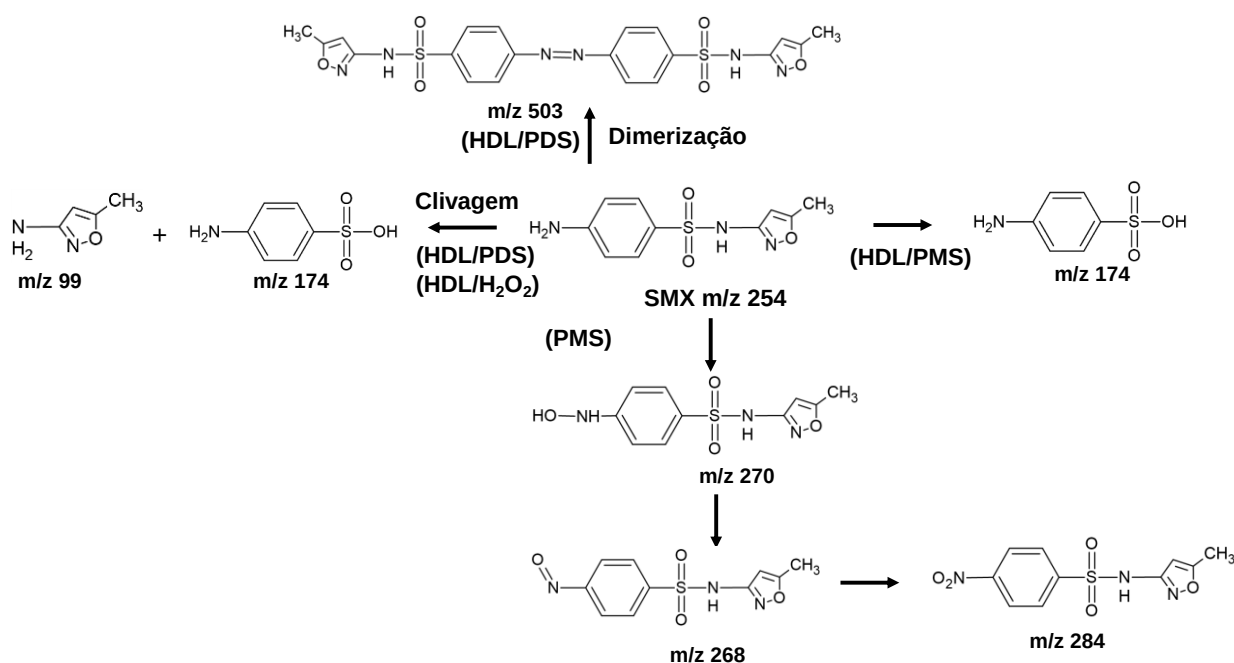


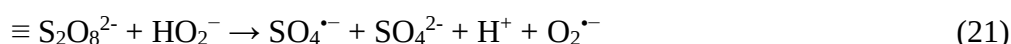
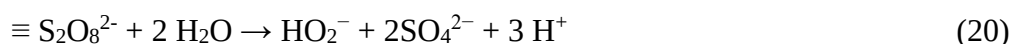
Figura 19 Proposta de produtos de degradação para SMX em sistemas HDL/PMS, HDL/PDS, HDL/H₂O₂ e oxidação direta de sistemas PMS.

Dimerização, clivagem da ligação sulfonamida e reações de oxidação dominaram a transformação de SMX, o que pode indicar que diferentes espécies reativas contribuíram para o mecanismo de degradação (Figura 19).

Para entender o papel das espécies reativas de oxigênio no mecanismo de degradação do SMX, o efeito dos sequestrantes na degradação foi investigado no sistema HDL/PDS (Figura 20). Os sequestrantes utilizados foram metanol, com uma constante cinética de segunda ordem $k(\text{HO}^\bullet) = 9,7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ e $k(\text{SO}_4^{\bullet-}) = 2,5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, p-benzoquinona (BQ) ($k(\text{HO}_2^\bullet/\text{O}_2^{\bullet-}) = 2,9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), nitrobenzeno (NB) ($k(\text{HO}^\bullet) = 3,2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) e álcool furfurílico (FFA) ($k(^1\text{O}_2) = 1,2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$).

FFA mostrou inibição significativa da degradação de SMX, indicando a contribuição de $^1\text{O}_2$ na degradação.

O $\text{O}_2^{\bullet-}$ pode levar à formação de $^1\text{O}_2$ (Eq. 20-22) durante a ativação catalítica do PDS e desta forma contribuir para a degradação do SMX:



Os resultados obtidos com os diferentes sequestrantes permitem concluir que no sistema HDL/PDS, as espécies reativas predominantes seguem a sequência: $^1\text{O}_2 > \text{HO}_2^\bullet/\text{O}_2^{\bullet-} > \text{HO}^\bullet > \text{SO}_4^{\bullet-}$.

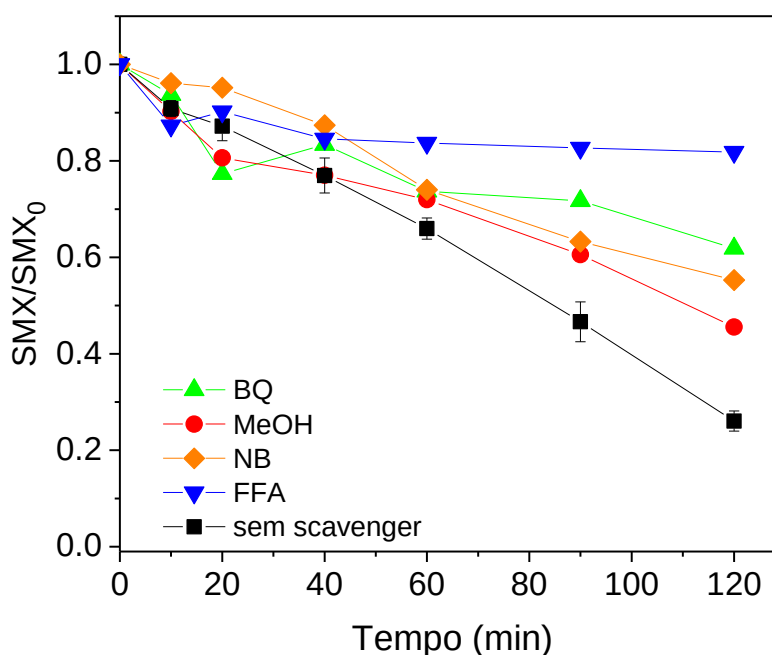


Figura 20 Efeito dos diferentes sequestradores de radicais usando 200 mg L^{-1} BQ, MeOH, NB e FFA na degradação de SMX no sistema HDL/PDS. Condições: $500 \text{ } \mu\text{g L}^{-1}$ SMX; PDS 4 mmol L^{-1} e LDH $0,5 \text{ g L}^{-1}$.

A dimerização de SMX (m/z 503) foi identificada apenas no sistema HDL/PDS. A formação de dímeros em processos de oxidação heterogênea do tipo Fenton tem sido

relacionada a metais de alta valência como Cu(III) e Fe(IV). De acordo com os resultados das Figuras 19 e 20, os radicais podem desempenhar uma menor influência na degradação do SMX no sistema HDL/PDS.

Outra via de transformação no sistema HDL/PDS foi a quebra da ligação sulfonamida, levando a m/z 174 e m/z 99. Esses dois produtos também foram detectados com HDL/H₂O₂, enquanto no sistema HDL/PMS, apenas o m/z 174 foi identificado, provavelmente devido a uma oxidação do m/z 99.

A oxidação direta de SMX por PMS foi responsável pela oxidação do grupo amino (-NH₂-SMX) e a formação de hidroxilamina (-NHOH-SMX), m/z 270 e depois a derivados nitro de SMX, m/z 268 (-NO-SMX) e m/z 284 (-NO₂-SMX), que foram identificados e confirmados pela comparação com os padrões analíticos disponíveis. Todos esses produtos detectados durante a oxidação direta do SMX exibem maior toxicidade do que o composto original. A formação de compostos tóxicos devido à oxidação direta de SMX por PMS ocorre no átomo N ligado ao anel benzeno devido à formação de um complexo de estado de transição entre o átomo de oxigênio da ligação -O-O- de PMS e o átomo de N do SMX.

Portanto, os resultados deste trabalho indicam que a transferência de elétrons de SMX para PMS levou à formação do intermediário m/z 270, seguido de oxidação e formação dos respectivos derivados nitro de SMX (m/z 268 e m/z 284).

No sistema HDL/PMS, apenas um produto de degradação foi detectado. Interessantemente neste sistema, nenhum produto de degradação nitro tóxico foi detectado porque o HDL pode interagir com o PMS e após a decomposição catalítica gerar espécies reativas (Eq. 12-15) evitando a formação de complexos de estado de transição entre o átomo de oxigênio do PMS e o átomo de nitrogênio do SMX que levam à formação de compostos tóxicos conforme reportado anteriormente.

Para investigar a aplicação dos sistemas HDL/PDS e HDL/PMS na remoção de antibióticos em mistura, foram investigados antibióticos de quatro classes diferentes: AMX (penicilina), CFX (cefalosporina), CIP (quinolonas) e SMX (sulfonamida), que foram selecionados por serem os antibióticos mais frequentemente detectados em efluentes de estação de tratamento de esgoto, cujas diferentes estruturas químicas levam a diferentes comportamentos nos sistemas oxidativos investigados.

Os experimentos para avaliar a adsorção dos fármacos na superfície do catalisador mostraram que após 120 min ocorre remoção completa de CFX, enquanto ocorreu apenas adsorção parcial de CIP (28%) e AMX (58%), e insignificante no caso de SMX (Figura 21).

A formação de um complexo entre Cu(II) e CFX já foi relatada na literatura sugerindo que um complexo com HDL possa ter sido formado com CFX. Também foi relatado que a complexação de β -lactâmicos com Cu(II) pode levar à sua degradação.

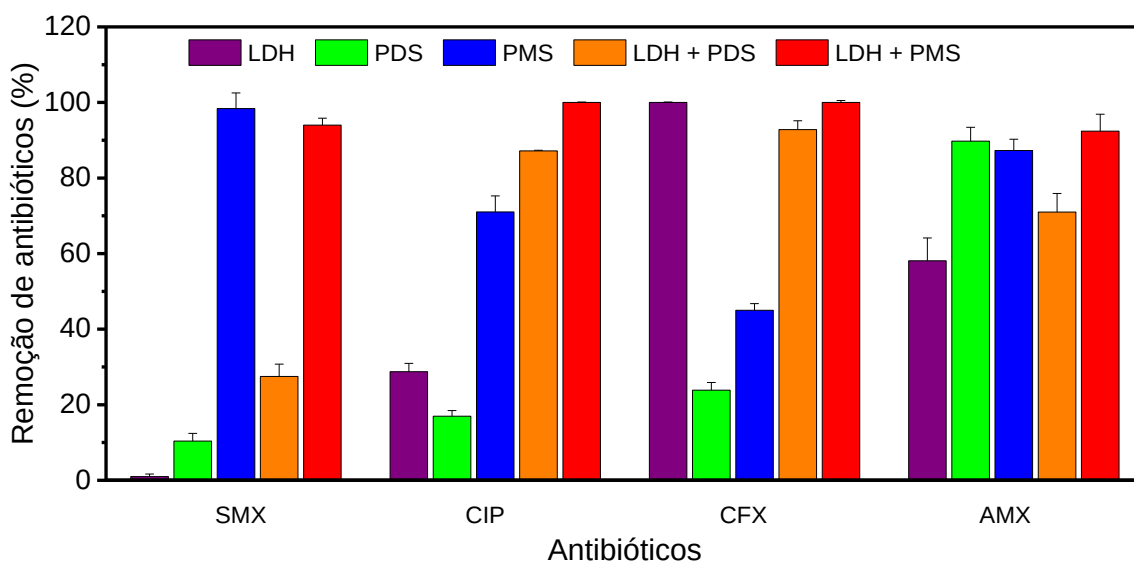


Figura 21 Efeito da adsorção, oxidação direta por PDS e PMS e degradação catalítica com HDL/PMS e HDL/PDS para remoção de SMX, AMX, CFX e CIP em água deionizada após 120 min de reação. Condições: $2.000 \mu\text{g L}^{-1}$ de SMX, CIP, AMX e CFX; $0,5 \text{ g L}^{-1}$ de HDL; 4 mmol L^{-1} de PDS e PMS; pH $8,31 \pm 0,20$ para HDL/PDS e $5,74 \pm 0,18$ para HDL/PMS.

Conforme mostrado na Figura 21, PDS apresentou oxidação direta mais pronunciada para AMX, com 89% de remoção após 120 min. A oxidação direta de antibióticos por PMS também foi possível com 98%, 71%, 45% e 87% para SMX, CIP, CFX e AMX, respectivamente, após 120 min. No entanto, o sistema HDL/PDS resultou em menor degradação de todos os antibióticos quando comparado com HDL/PMS, variando de 27,5% (SMX) a 93% (CFX). A remoção de CFX no sistema LDH/PDS diminuiu 7% quando comparada ao sistema na ausência de PDS. A adição de PDS pode ter ocupado alguns sítios na superfície do catalisador, o que reduziu a complexação com CFX.

No entanto, HDL/PMS promoveu maiores taxas de degradação atingindo remoção total de CIP e CFX e mais de 90% de SMX e AMX após 120 min. Esses resultados indicam que a eficiência da degradação simultânea dos antibióticos seguiu a ordem: HDL/PMS > PMS > HDL/PDS.

Embora os sistemas com PMS sejam mais eficientes que o PDS, algumas desvantagens bem conhecidas do uso do PMS para desinfecção e remoção de contaminantes são seu maior

custo em comparação com PDS e H_2O_2 e sua instabilidade, o que implica em dificuldade de armazenamento por um longo período.

Para verificar se o HDL é um catalisador promissor para o tratamento de águas residuais urbanas contendo antibióticos, o sistema HDL/PDS foi aplicado ao efluente urbano após passar por tratamento de esgoto convencional, resultando em degradação eficiente de CFX (98%) e AMX (100%), enquanto CIP apresenta maior estabilidade e resistência à degradação atingindo 52% de degradação (Tabela 3).

Tabela 3 Eficiência do sistema HDL/PDS para degradação simultânea de SMX, CIP, CFX e AMX em efluente urbano após passar por tratamento de esgoto convencional. Condições: pH = 7,5; 250 $\mu\text{g L}^{-1}$ de SMX, CIP, CFX e AMX, 0,5 g L^{-1} HDL; 4 mmol L^{-1} de PDS.

Antibióticos	Remoção de antibióticos em efluente (%)
SMX	27 ± 2
CIP	52 ± 3
CFX	98 ± 1
AMX	100 ± 2

Os resultados semelhantes em água deionizada (ver Figura 22) e efluente urbano (Tabela 3) demonstraram o potencial do uso de HDL nos processos investigados.

A capacidade dos sistemas heterogêneos investigados para desinfecção do efluente urbano foi avaliada no escuro e à temperatura ambiente considerando a inativação de *Escherichia coli* (*E.coli*) e *Enterococcus faecalis*.

Conforme mostrado na Figura 22, as abundâncias iniciais de *E. coli* e *Enterococcus* em águas residuais urbanas após tratamento secundário foram de $5,25 \pm 0,13 \log_{10} \text{NPM}/100 \text{ mL}$ e $4,45 \pm 0,15 \log_{10} \text{NMP}/100 \text{ mL}$, respectivamente.

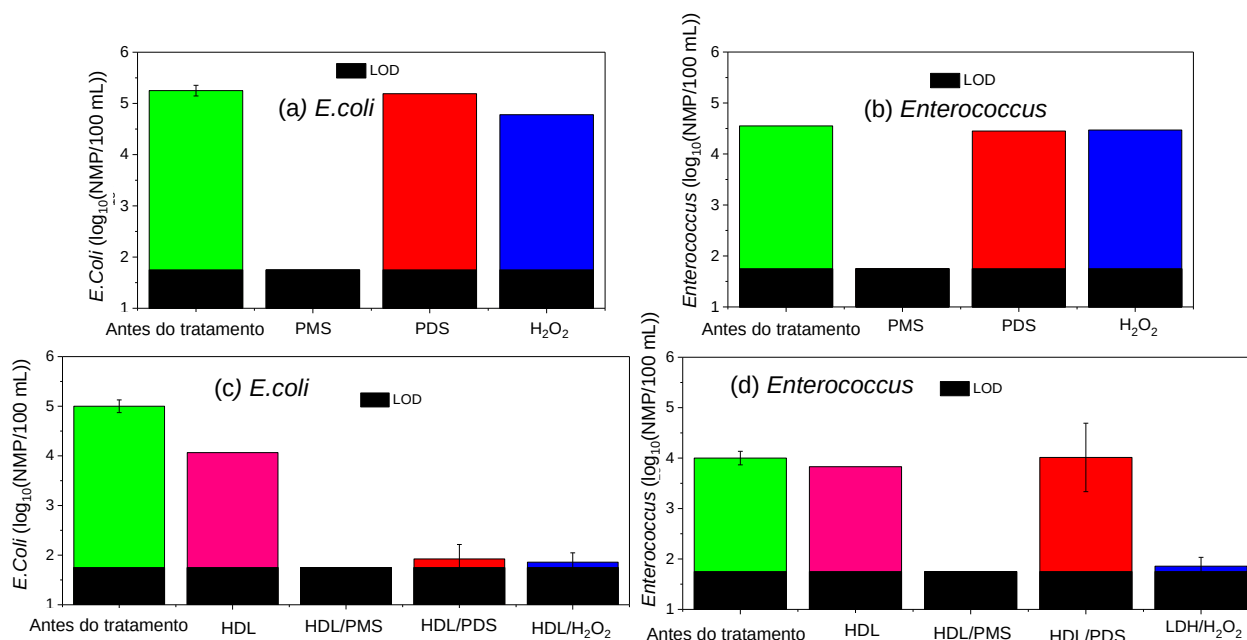


Figura 22 Perfis de inativação de *E. Coli* (a) e *Enterococcus* (b) no efluente urbano pré-tratado antes e após tratamento em oxidação direta com PMS, PDS e H_2O_2 e com diferentes sistemas HDL, HDL/PMS, HDL/PDS e HDL/ H_2O_2 (c e d). Condições: $0,5 \text{ g L}^{-1}$ HDL, 4 mmol L^{-1} de PMS, PDS e H_2O_2 .

Nenhuma inativação significativa de *E. coli* e *Enterococcus* foi observada após 120 min de tratamento por oxidação direta com PDS e H_2O_2 . No entanto, o PMS sozinho resultou na inativação completa de *Escherichia coli* e *Enterococcus* após 120 min ($<1,75 \log_{10} \text{ NMP/100 mL}$), confirmando sua eficácia como agente desinfetante conforme já relatado em estudos anteriores.

Este resultado pode ser explicado pela auto-oxidação do PMS (Eq. 10 e 11) que pode gerar o $^1O_2$ causando distúrbio da permeabilidade da membrana, resultando em mau funcionamento do metabolismo celular e inativação celular, indicando que os sistemas com geração de $^1O_2$ são promissores para promover a desinfecção de águas residuais.

O sistema HDL/ H_2O_2 apresentou alta eficiência de desinfecção atingindo 92% de inativação de *Escherichia coli* e 93% de *Enterococcus*. Isso pode ser devido à formação de complexos de superfície entre HDL e H_2O_2 (Eq. 16 e 17), que levam a formação do $O_2^{\cdot -}$ (Eq. 18 e 19), que embora não tenham mostrado reatividade para a remoção de SMX, apresentaram efeito positivo na inativação de patógenos.

Diferentemente, o sistema HDL/PDS alcançou 91% de inativação de *Escherichia coli* após 120 min, mas falhou em inativar *Enterococcus*. A inativação de *Enterococcus* é mais difícil, pois é uma bactéria gram positiva com parede celular relativamente espessa e camada densa (20–80 nm) composta de ácido fosfórico (10%) e peptidoglicano (90%), mais resistente

a desinfetantes em comparação com bactérias gram negativas, que apresentam uma parede celular mais fina (10–15 nm) composta por lipopolissacarídeo (10–15%), fosfolípido/lipoproteína (60%) e peptidoglicano (10–20%).

Consequentemente, a sequência de eficiência para desinfecção bacteriana foi a seguinte: HDL/PMS = PMS sozinho > HDL/H₂O₂ > HDL/PDS.

Em conclusão, os resultados apresentados nesta tese mostram que HDLs com cobre podem funcionar eficientemente como catalisadores no processo Fenton heterogêneo. O HDL com borato como ânion interlamelar apresentou melhor performance catalítica devido induzir reduções de Cu(II) e Fe(III) na superfície do catalisador acelerando o processo Fenton. A combinação de CuMgFe-B(OH)₄ para a decomposição catalítica de H₂O₂, PDS e PMS mostrou que diferentes tipos de espécies reativas podem ser geradas em cada sistema e que a eficiência de degradação depende das características das estruturais dos contaminantes. A alta estabilidade dos HDLs e a eficiência de remoção de contaminantes e inativação de patógenos em condições de neutralidade torna estes materiais potenciais candidatos para aplicações práticas no tratamento de efluente.

ATTACHMENTS

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Fenton-like degradation of sulfathiazole using copper-modified MgFe-CO₃ layered double hydroxide

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Effect of the interlamellar anion on CuMgFe-LDH in solar photo-Fenton and Fenton-like degradation of the anticancer drug 5-fluorouracil

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