CLEISEANO EMANUEL DA SILVA PANIAGUA
(ORGANIZADOR)

Collection:

APPLIED CHEMICAL ENGINEERING

Atena Editora
Ano 2022

CLEISEANO EMANUEL DA SILVA PANIAGUA
(ORGANIZADOR)

Collection:

APPLIED CHEMICAL ENGINEERING

Atena Editora
Ano 2022

Editora chefe
Profª Drª Antonella Carvalho de Oliveira
Editora executiva
Natalia Oliveira
Assistente editorial
Flávia Roberta Barão
Bibliotecária
Janaina Ramos
Projeto gráfico
Camila Alves de Cremo
Daphynny Pamplona
Gabriel Motomu Teshima
Luiza Alves Batista
Natália Sandrini de Azevedo
Imagens da capa
iStock
Edição de arte
Luiza Alves Batista

Atena Editora
Ano 2022

Atena
Editora
Ano 2022

Collection: applied chemical engineering

Diagramação: Daphynny Pamplona
Correção: Yaiddy Paola Martinez
Indexação: Amanda Kelly da Costa Veiga
Revisão: Os autores
Organizador: Cleiseano Emanuel da Silva Paniagua

Dados Internacionais de Catalogação na Publicação (CIP)

C697 Collection: applied chemical engineering / Organizador Cleiseano Emanuel da Silva Paniagua. – Ponta Grossa - PR: Atena, 2022.

Formato: PDF
Requisitos de sistema: Adobe Acrobat Reader
Modo de acesso: World Wide Web
Inclui bibliografia
ISBN 978-65-5983-856-1
DOI: https://doi.org/10.22533/at.ed.561223101

1. Chemical engineering. I. Paniagua, Cleiseano Emanuel da Silva (Organizador). II. Título.

CDD 660

Elaborado por Bibliotecária Janaina Ramos – CRB-8/9166

Atena Editora
Ponta Grossa – Paraná – Brasil
Telefone: +55 (42) 3323-5493
www.atenaeditora.com.br
contato@atenaeditora.com.br

Atena Editora
Ano 2022

DECLARAÇÃO DOS AUTORES

Os autores desta obra: 1. Atestam não possuir qualquer interesse comercial que constitua um conflito de interesses em relação ao artigo científico publicado; 2. Declaram que participaram ativamente da construção dos respectivos manuscritos, preferencialmente na: a) Concepção do estudo, e/ou aquisição de dados, e/ou análise e interpretação de dados; b) Elaboração do artigo ou revisão com vistas a tornar o material intelectualmente relevante; c) Aprovação final do manuscrito para submissão.; 3. Certificam que os artigos científicos publicados estão completamente isentos de dados e/ou resultados fraudulentos; 4. Confirmam a citação e a referência correta de todos os dados e de interpretações de dados de outras pesquisas; 5. Reconhecem terem informado todas as fontes de financiamento recebidas para a consecução da pesquisa; 6. Autorizam a edição da obra, que incluem os registros de ficha catalográfica, ISBN, DOI e demais indexadores, projeto visual e criação de capa, diagramação de miolo, assim como lançamento e divulgação da mesma conforme critérios da Atena Editora.

DECLARAÇÃO DA EDITORA

A Atena Editora declara, para os devidos fins de direito, que: 1. A presente publicação constitui apenas transferência temporária dos direitos autorais, direito sobre a publicação, inclusive não constitui responsabilidade solidária na criação dos manuscritos publicados, nos termos previstos na Lei sobre direitos autorais (Lei 9610/98), no art. 184 do Código Penal e no art. 927 do Código Civil; 2. Autoriza e incentiva os autores a assinarem contratos com repositórios institucionais, com fins exclusivos de divulgação da obra, desde que com o devido reconhecimento de autoria e edição e sem qualquer finalidade comercial; 3. Todos os e-book são *open access, desta forma* não os comercializa em seu site, sites parceiros, plataformas de *e-commerce,* ou qualquer outro meio virtual ou físico, portanto, está isenta de repasses de direitos autorais aos autores; 4. Todos os membros do conselho editorial são doutores e vinculados a instituições de ensino superior públicas, conforme recomendação da CAPES para obtenção do Qualis livro; 5. Não cede, comercializa ou autoriza a utilização dos nomes e e-mails dos autores, bem como nenhum outro dado dos mesmos, para qualquer finalidade que não o escopo da divulgação desta obra.

Atena
Editora
Ano 2022

APRESENTAÇÃO

The e-book: “Collection: Applied chemical engineering” consists of ten book chapters that were organized and divided into four thematic units, namely: *i*) natural products: extraction and purification of active principles; *ii*) development of new materials: study, comparison, different properties and applications; *iii*) use of analytical instruments for food quality control and; *iv*) development and application of bioadsorbents and advanced treatment technologies to remove contaminants from aquatic matrices.

The first theme presents two studies that evaluated the extraction of essential oil from the Baru species plant (*Dipteryxalata Vog*.) with nematicidal activity in combating *Meloidogyne javanica*. The second work evaluated triterpene purification processes from plant bioactives of Amazonian species. The second theme consists of three book chapters aimed at the study and comparison of natural, glass and mixed fibers for future applications; preparation of graphene oxides for production as composites in the form Cu/TiO_2/rGO and estimates of thermodynamic properties of esters used in the production of biodiesel using a Gaussian software associated with the Constantinou and Gani group method.

The third thematic unit consists of two works, one using the UV-Vis spectrophotometry technique to quantify the metallic ions of cadmium, copper, chromium, mercury, nickel and lead in cheeses produced by hand on rural properties; the second work evaluated the Kombucha probiotic and its importance in fermented foods. Finally, the fourth and last theme consists of three works with different approaches. The first deals with the possible environmental impacts that can be caused to water and soil as a result of exposure to Fracking gas present in Mexico. The second presents the study of the adsorption capacity from the biomass generated by the Andiroba species (*Carapaguianensis Aubl.)* in the removal of copper ions present in wastewater from industrial activities. The third chapter presents the study of the influence of the complexity of different aqueous matrices on the degradation of a mixture of drugs using the solar photolysis processes, TiO_2/Solar and its combination with the addition of H_2O_2. This process constitutes one of the advanced treatment technologies to be made feasible on a large scale as a complementary step to conventional water and sewage treatment processes.

In this perspective, Atena Editora has been working with the aim of stimulating and encouraging both Brazilian researchers and those from other countries to publish their work with quality assurance and excellence in the form of books, book chapters and articles that are available in the Editora’s website and other digital platforms with free access.

Cleiseano Emanuel da Silva Paniagua

SUMÁRIO

CAPÍTULO 10

INFLUENCE OF MATRIX COMPOSITION ON THE DEGRADATION OF A PHARMACEUTICALS MIXTURE THROUGH HETEROGENEOUS PHOTOLYSIS AND PHOTOCATALYSIS UNDER SOLAR RADIATION PROCESSES

Data de aceite: 01/01/2022

Cleiseano Emanuel da Silva Paniagua
PhD in Chemistry from the Federal University of Uberlândia, Brazil
Post-doctoral student in Chemistry at the Federal University of Uberlândia/MG
Student of the specialization course in Science and Mathematics Teaching, Federal Institute of Triângulo Mineiro - Campus Uberlândia /MG
http://lattes.cnpq.br/12970002659897780
https://orcid.org/0000-0003-3587-486X

ABSTRACT: The degradation of a mixture of the pharmaceuticals gemfibrozil (GEM), hydrochlorothiazide (HCTZ) and naproxen (NAP) were evaluated by different processes and in different aqueous matrices: deionized water (DW), river water (RW) and effluent from a Treatment Plant Sewage (STP eflluent). The experimental conditions were previously optimized, being: [TiO_2]=150 mg/L (DW and RW) and 450 mg/L (STP eflluent); pH=5.8 (DW and RW) and 7.7 (STP eflluent) and [H_2O_2]=6.0 mg/L (with replacement every 20 min of reaction). Photolysis presented a degradation efficiency of 44% (DW and RW) and 76% (STP eflluent) after an energy dose of 448 and 524kJ/m^2, respectively. The TiO_2/solar process increased the degradation to 87% (DW), 84% (RW) and 97% (STP eflluent). In the TiO_2/H_2O_2/solar process, the degradation efficiency reached 99% (DW) with 317kJ/m^2, for RW the percentage of degradation was below the detection limit of the pharmaceuticals after 448 kJ/m^2. Mineralization and acute toxicity to *Vibrio fischeri* bacterium were determined at the beginning and end of each process used. The initial STP eflluent matrix showed 14% mineralization and 50% toxicity. Already the matrices of DW and RW, presented toxicity less than 4%. In all matrices, mineralization and acute toxicity increase from the process of photolysis to that of photocatalysis. For the STP eflluent matrix, 52% of mineralization and 71% of toxicity was obtained. For the DW and RW matrices, the TiO_2/H_2O_2/Solar process showed the best efficiency among the evaluated processes, obtaining a mineralization of 84% (DW) and 72% (RW) and a toxicity of 83% (DW) and total (RW). The final consumption of H_2O_2 was quantified and presented, respectively, 73 and 79mg/L for DW and RW. Therefore, the TiO_2/Solar process had a high potential to be used as a complementary step to conventional processes for treating both water for drinking purposes and for sewage.

KEYWORDS: *Vibrio fischeri* bacterium, heterogeneous photocatalysis, mineralization and toxicity.

1 | INTRODUCTION

Water constitutes a mineral resource of great importance, representing 75% of the body mass of the vast majority of living organisms. It actively participates in almost all biological processes for the maintenance of vital functions of living beings. Although 75% of the Earth's surface is constituted by water, the fraction that corresponds to fresh water is about 2.5%, of which 68.9% are present in the form of glaciers;

29.9% in groundwater; 0.9% in soils and only 0.3% in the form of surface water (rivers and lakes) that are destined for public supply (ÁLVAREZ- RUIZ; PICÓ, 2020; BOGER et al., 2021; MENG et al., 2021).

However, more than two decades ago, substances were detected and quantified at trace levels (*μ*g to ng/L) based on the improvement and development of analytical techniques, such as High Performance Liquid Chromatography coupled with Mass Spectrometry (HPLC - MS) which made it possible to determine substances that were until then "invisible" in different aquatic compartments, which began to indicate that even present in low concentrations, they have ecotoxicological properties and represent a risk to the different organizations existing in the most diverse ecosystems and aquatic biotas, being called Contaminants of Emerging Concern (CEC) that belong to a variety of classes, including: *i*) pharmaceuticals; *ii*) pesticides; *iii*) brominated flame retardants; *iv*) dyes and preservatives; *v*) hormones; *vi*) personal care products; *vii*) microplastics among others (CARTAXO et al., 2020; PIVETTA et al., 2020; STARLING; AMORIM; LEÃO, 2019), as shown in Figure 1.

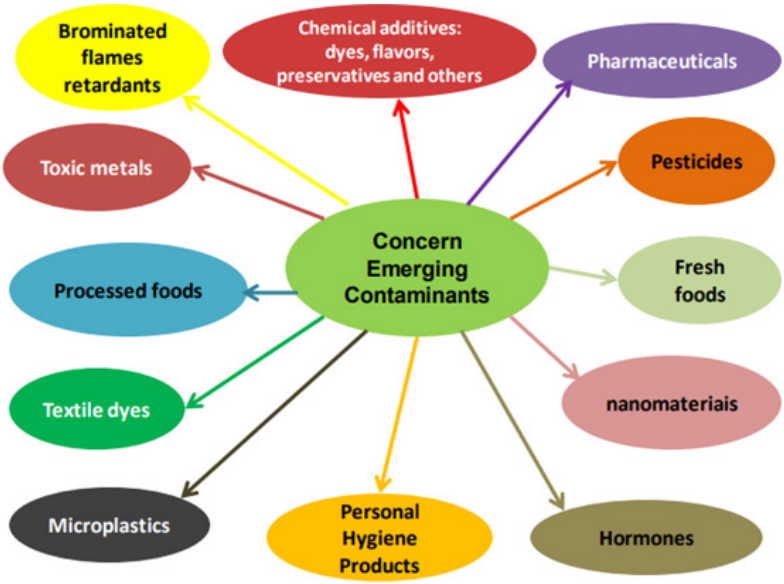

Figure 1: Classes of Contaminants of Emerging Concern

Source: The author (2021).

Among the CEC, there are pharmaceuticals, substances developed to be persistent and can be absorbed and metabolized by the body in order to meet a specific therapeutic purpose. However, most of these compounds are excreted unchanged (between 50 and 90% of the active principle) by organisms. In addition, the pharmaceuticals can reach

the different aquatic reservoirs through household sewage, disposal in the garbage that goes to dumps or landfills, discharge into industrial sewage treatment stations and animal medicine that undergo conventional sewage treatment processes and are released into surface waters (ARSAND et al., 2020; OLIVEIRA et al., 2020; VERAS et al., 2019), can be represented in Figure 2.

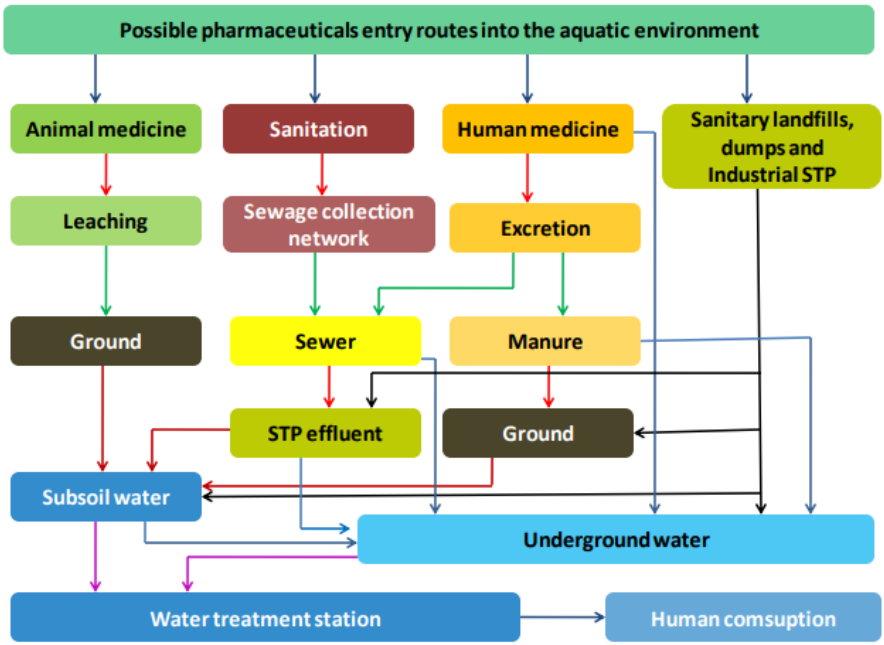

Figure 2: representation of possible entry routes of pharmaceuticals in aquatic environments.

Source: The author (2021).

Conventional water and sewage treatment processes were designed to reduce: *i*) organic load; *ii*) color and turbidity and; *iii*) microorganisms with pathogenic properties. Therefore, studies with the aim of promoting the removal of specific target compounds have been carried out with a view to presenting high efficiency, lower cost, possibility of reusing effluents for non-potable purposes and that are ecologically correct (ARSAND et al., 2020; OLIVEIRA et al., 2020; PANIAGUA et al., 2020).

Among the various techniques that have been investigated are the Advanced Oxidative Processes (AOPs) that can be used as a complementary step to conventional treatment processes. AOPs are processes based on the generation of hydroxyl (HO•) and sulfate ($SO_4^{\cdot-}$) radicals, which have high values of standard reduction potentials (E^o= +2.6-3.1V), capable of promoting oxidation and conversion of organic matter, depending on operating conditions, into CO_2 and H_2O (ARSAND et al., 2020; OLIVEIRA et al., 2020).

Paiva et al. (2018) evaluated the efficiency of the modified photo-Fenton process

(FeOx/H_2O_2/UV-A) in the degradation of the same drug mixture in surface water. Under the best optimized conditions (pH = 6.2; [FeOX] = 54 μmol/L at a ratio of 1:9; [H_2O_2] = 4.0 mg/L and 15 min of artificial irradiation), the degradation efficiency was below the Limit of pharmaceuticals detection (0.0033µmol/L for NAP and 0.01 µmol/L for GEM and HCTZ) which guaranteed to reach values above 99% removal. On the other hand Paniagua et al. (2019 and 2020) evaluated the efficiency of the photoassisted peroxidation process (H_2O_2/UV-C) and heterogeneous photocatalysis (TiO_2/UV-A) in surface water. Under the best conditions for H_2O_2/UV-C (pH=6.2; [H_2O_2]= 4.0 mg/L and 30 min of irradiation) a degradation efficiency above 99% was obtained, as it was below the LD of the pharmaceuticals. For the TiO_2/UV-A process (pH=6.2; [TiO_2]=150mg/L; [H_2O_2]=6.0 mg/L and 120 min of treatment) the efficiency was 87%. The authors also evaluated the efficiency of these AOPs in the STP effluent matrix and, under the best conditions optimized for H_2O_2/UV-C (pH=7.7; [H_2O_2]= 64 mg/L; 30 min of irradiation) the efficiency was of 93%. On the other hand, the TiO_2/UV-A process (pH = 7.7; [TiO_2] = 450 mg/L; 240 min of irradiation) the efficiency was 90% (PANIAGUA et al., 2019 e 2020).

However, no work was found in the literature that reported evaluating the degradation efficiency of target compounds using solar radiation combined with the heterogeneous photocatalysis process in different aqueous matrices (DW, RW and STP effluent) and how these can interfere with degradation efficiency. Therefore, the present work evaluated the influence of matrix composition (DW, RW and STP effluent) on the degradation efficiency of a mixture of the pharmaceuticals GEM, HCTZ and NAP by heterogeneous photolysis and photocatalysis processes (TiO_2 and TiO_2/H_2O_2) under solar radiation.

2 | MATERIALS AND METHODS

2.1 Reagents

All solutions were prepared in DW and with analytical-grade reagents. GEM, HCTZ, and NAP standards, each with a certified purity higher than 99 wt %, were acquired from Sigma-Aldrich. High-performance liquid chromatograph (HPLC) analyses were performed using HPLC-grade methanol (J. T. Baker). NH_4VO_3 from Vetec was used as received. The remaining reagents employed in this work, which weretitanium dioxide P25 (Degussa/Evonick), $C_4K_2O_9Ti{\cdot}2H_2O$, H_2O_2 (30 wt %), Na_2SO_3, all from Synth, were used without further purification.

2.2 Sampling of River Water (RW) and Sewage Treatment Plant (STP) effluent

In order to evaluate the efficiency of the heterogeneous photocatalytic process and its matrix effects on the degradation of GEM, HCTZ, and NAP, samples of RW and STP effluents were collected in municipal wastewater treatment plants. The collection took place in the autumn and spring of 2017. The sampling of RW was performed from a river used to

supply water to the city of Uberlândia, Brazil (18° 55′08 ″S, 48° 16′37 ″W). The sampling of STP effluent was carried out after complete treatment in the municipal wastewater, which consists of steps of: *i*) removal of coarse solids and sand; *ii*) use of upflow anaerobic reactors; and *iii*) use of a FlotFlux® channel based on sequential application of coagulation-flocculation-flotation. The RW and STP effluent samples were stored at 4°C for two to three weeks while conducting the photodegradation experiments. The physical-chemical characterization of these samples is shown in Table S1.

Parameter	RW	STP[1]	STP[2]
Alkalinity as $CaCO_3$ (mg L^{-1})	22[a]	269[a]	176[a]
Conductivity (µS cm^{-1})	7.2[a]	846[a]	563[a]
BOD_5 (mg L^{-1})	3.7[b]	95[b]	49[b]
COD (mg L^{-1})	13[a]	202[a]	127[a]
DTC (mg L^{-1})	14[a]	87[a]	62[a]
DIC (mg L^{-1})	7.3[a]	49[a]	37[a]
DOC (mg L^{-1})	6.7[a]	38[a]	25[a]
pH	5.8[a]	7.7[a]	7.4[a]
Total dissolved solids (mg L^{-1})	<10[b]	27[b]	36[b]
Turbidity (nephelometric units)	5.8[b]	5.5[b]	4.3[b]
Chloride (mg L^{-1})	1.4[b]	174[b]	89[b]
Total sulphate (mg L^{-1})	0.8[b]	36[b]	47[b]
*Dissolved iron (mg L^{-1})	0.5[a]	0.5[a]	0.2[a]
Phosphorus (mg L^{-1})	<0.05[b]	0.9[b]	1.4[b]
Ammoniacal nitrogen (mg L^{-1})	<0.2[b]	32[b]	41[b]

Table S1. Physical-chemical characterization of the RW and STP effluent.

[a]Measured in our laboratory.

[b]Data furnished by the Department of Water and Sewage in Uberlândia (DMAE).

*Dissolved Fe without acid digestion.

BOD_5 = biochemical oxygen demand after five days

COD = chemical oxygen demand

DTC = dissolved total carbon

DIC = dissolved inorganic carbon

DOC = dissolved organic carbon

STP[1] = sample collected in September 2017

STP[2] = sample collected in December 2017.

2.3 Preparation of the pharmaceuticals mixture stock solution

A stock solution of the pharmaceuticals (18 mmol/L) in HPLC grade methanol was prepared. By diluting the stock solution, fortification was made in aqueous matrices to result in the desired concentration of target compounds (1.8 μmol/L of each compound), which corresponds to common concentrations of 451 μg/L of GEM, 536 μg/ L of HCTZ and 413 μg/L of NAP.

2.4 Photodegradation experiments

The concentrations of GEM, HCTZ, and NAP were determined using an LC-6AD chromatograph (Shimadzu) containing a ultraviolet-diode-array detector (model SPD-M20A, Shimadzu) and a Phenomenex C-18 column (Luna, 5 μm, 250 × 4.6 mm), as described by Paiva et al. (2018).

H_2O_2 was spectrophotometrically quantified by the titanium oxalate method when H_2O_2 concentrations below 50 mg L^{-1} were used and the metavanadate method (NOGUEIRA; OLIVEIRA; PARTELINE, 2005). was used when monitoring H_2O_2 concentrations that were greater than 50 mg L^{-1}. Mineralization was determined using carbon analyzer equipment (Shimadzu TOC VCPN model) with automatic injection (ASI-V model).

Acute toxicity was assessed by measuring the bioluminescence emission of the bacteria *V. fischeri* after 30 min of exposure to the non-treated and treated solutions obtained during the heterogeneous photocatalysis process (after adjustment of the salinity to 2%), and it was compared with a solution of 2% NaCl, used as a control, as described by the Brazilian norm (NBR 15411-3:2012 method) A solution of 13.4 mg L^{-1} of Cr^{6+} was employed as a positive toxicant control. A thermoblock was used to maintain the temperature at 15 °C. In addition, the residual H_2O_2 present in the DW and RW samples was removed by the addition of 150 µL of 2.0 g L^{-1} bovine catalase, followed by stirring for 30 s (PANIAGUA et al., 2019 and 2020).

3 | RESULTS AND DISCUSSION

Solar radiation was measured as a function of the accumulated energy dose (W/m^2) obtained as a function of the time used in artificial radiation (UV-A), with an average irradiance of 32.2 ± 0.5 W/m^2 in 300 min. being determined. The time of solar irradiation necessary to obtain the same dose of energy in relation to the artificial one was greater at all time intervals, with samples being collected to monitor the degradation of the drug mixture (Figure 3), removal of dissolved organic carbon (Figure 4), the acute toxicity to Vibrio fischeri bacteria (Figure 5) and peroxide consumption (Figure 6) as presented and discussed below.

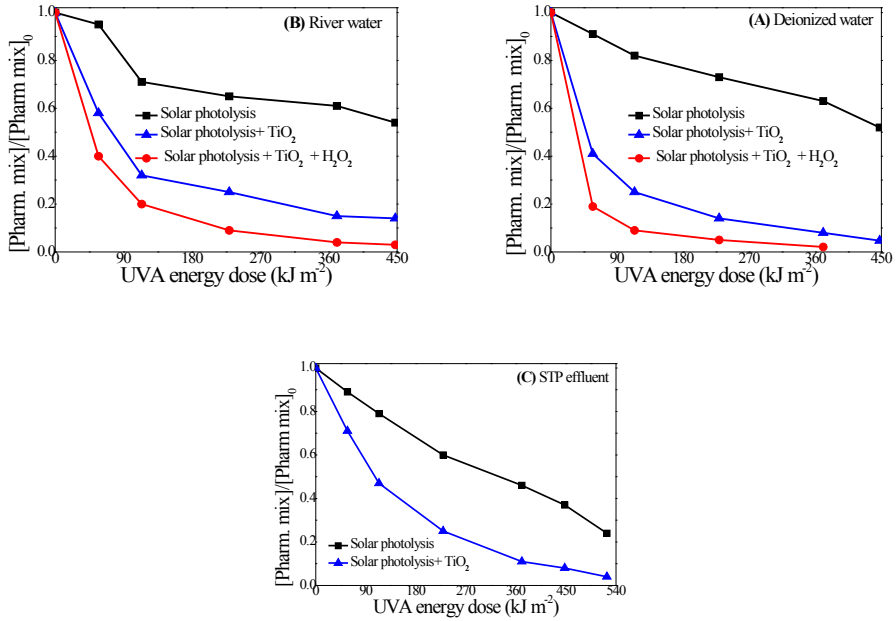

Figure 3: Degradation profile obtained in solar radiation under the best conditions optimized in artificial radiation by the UV-A photolysis processes, and TiO_2/UV-A and TiO_2/H_2O_2/UV-A in the degradation of pharmaceuticals mix. Initial conditions:[Pharmaceuticals] = 1.80 **µ**mol/L; pH = 5.8 (DW and RW) and 7,7 (STP effluent); [H_2O_2] = 6.0 mg/L (DW and RW); [TiO_2] = 150.0 mg/L(DW and RW) e 450 mg/L (STP effluent).

Source: Paniagua (2018).

After the application of a dose of 448 KJ/m², solar photolysis showed a degradation efficiency of 44% for DW. By combining solar radiation with the photocatalyst, an efficiency of 87% was achieved and after the combination of H_2O_2 6.0 mg/L (with replacement every 20 min) the TiO_2/Solar process raised the efficiency to 99%, in a lower dose of energy (371KJ/m²) in relation to that previously used. For the RW matrix, solar photolysis showed 43% degradation over a longer period of time (285 min) in order to reach the same dose of energy in relation to DW. When applying the TiO_2/Solar process, the degradation increases to 84% and achieves a degradation efficiency below the Detection Limit of the pharmaceuticals when combining with H_2O_2 (6.0 mg/L) under the same energy dose. As for the STP effluent matrix, it was necessary to use both a higher energy dose (524 kJ/m²) and a longer treatment time (360min) in order to obtain a degradation efficiency of 76% through radiation solar. When using the TiO_2/Solar process, there was an increase in degradation (97%) under a lower energy dose (448 kJ/m²) which was exactly the same dose in relation to the DW and RW matrices. The composition of the matrix directly influences the efficiency of degradation of target compounds due to the increase in the organic load and anions that compete for hydroxyl radicals, decreasing their availability and consequently affecting

the efficiency of the catalyst against the target compounds, which can be attributed to: *i*) reduction in the amount of photoenergy that is transferred to the medium due to the greater turbidity provided by the particles of the catalyst, which has an inhibiting effect on light penetration, due to the decrease in the amount of photons that will be effectively transferred (KOLTISAKIDOU et al. , 2017) and *ii*) there may be aggregation of suspended catalyst particles, reducing the surface area that contains the active sites (KOLTISAKIDOU et al., 2017).

The determination of COD was carried out by collecting initial samples from all evaluated matrices and after applying 448 kJ/m² (DW and RW) and 524kJ/m² (STP effluent) of accumulated energy dose, resulting in the data presented and discussed in Figure 4.

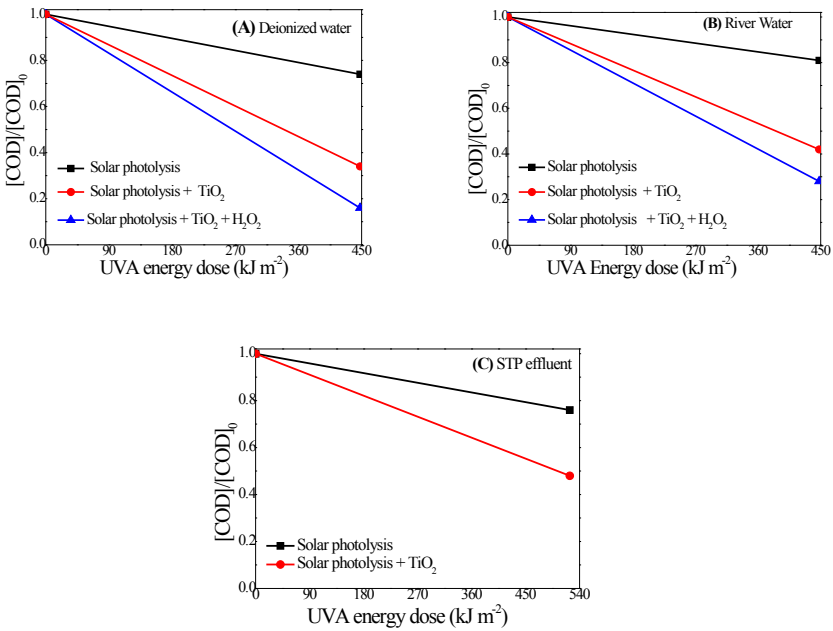

Figure 4: Removal of COD obtained by solar radiation under the best conditions optimized by artificial radiation by TiO_2/H_2O_2/Solarphotolysis processes in the degradation of pharmaceuticals : Initial conditions: [Pharmaceuticals] = 1.80 µmol/L; pH = 5.8 (DW and RW) and 7.7 (STP effluent); [H_2O_2] = 6.0 mg/L (DW and RW); [TiO_2] = 150 mg/L (DW and RW) and 450 mg/L (STP effluent).

Source: Paniagua (2018).

For the DW matrix (Figure 4A), solar photolysis provided 26% mineralization after an energy dose of 448kJ/m². Combining solar radiation with TiO_2 mineralization increased to 66%, reaching 84% by adding 6.0 mg/L of H_2O_2 (with replacement every 20 min). In the river water matrix (Figure 4B), the isolated use of solar photolysis presented a mineralization of 19%, when using the photocatalyst activated by solar photolysis, the removal of DOC

increased to 58%, reaching 72% when associated the TiO_2/Solar process with 6.0 mg/L of H_2O_2 (with replacement every 20 min). There is a reduction in the removal of COD in all evaluated processes in relation to the DW matrix, which can be explained by the existence of organic matter that compete for hydroxyl radicals and/or by the saturation of adsorption sites on the surface of the photocatalyst, implying in reducing the availability of sites leading to reduced degradation efficiency of target compounds (DUTA; ANDRONIC; ENESCA, 2018; SAGI et al., 2018). On the other hand, the STP effluent matrix (Figure 4C) showed a COD removal of 14% in the initial sample, increasing to 24% after the application of 524 KJ/m2 in 360 min of treatment. Under the same energy dose, by combining solar radiation with the photocatalyst, the degradation efficiency reached 52%.

Given these results, it is observed that the increased complexity of the matrix results in less removal of COD from the target compounds, which can be attributed to: *i*) higher concentration of organic matter that increases the opacity of the solution, making light penetration more difficult. which implies in the reduction of COD removal (CERIANI et al., 2018; YOON et al., 2018); *ii*) the reduction in the number of free hydroxyl radicals, since most of them reacted with the organic matter from the matrices (KOLTSAKIDOU et al., 2017).

In order to assess the evolution of acute toxicity by reducing the luminescence of the *Vibrio fischeri* bacterium. Therefore, initial samples were collected in all matrices and in different doses of accumulated energy: 57, 114, 229, 371, 448 and 524 kJ/m^2, and the last dose was applied only to the STP effluent matrix, the results obtained are shown in Figure 5.

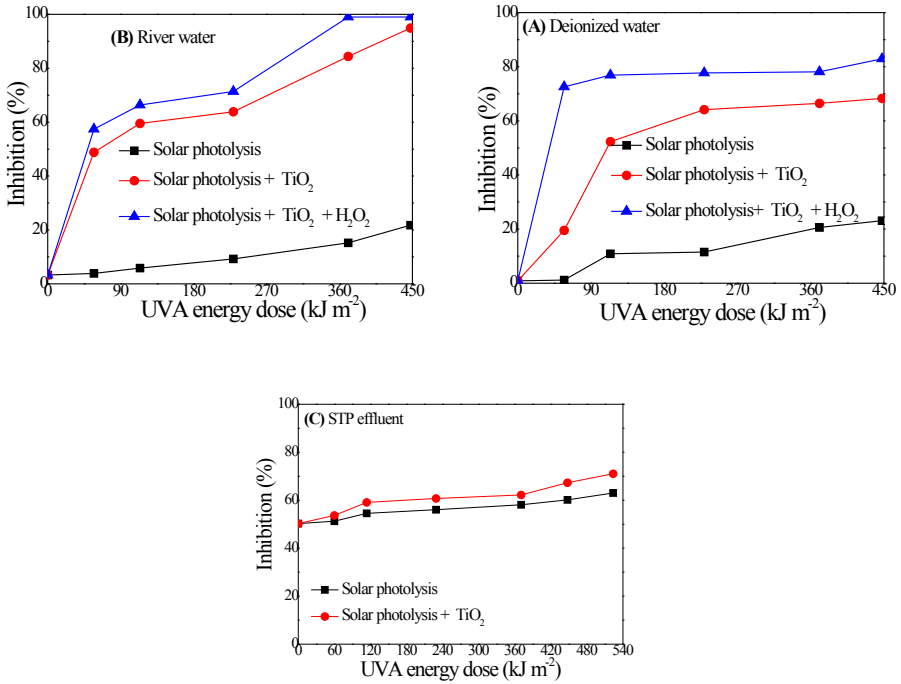

Figure 5: Inhibition of *V. fischeri* bacterium in different matrices under the best optimized conditions in UV-A photolysis and TiO_2/H_2O_2/UV-A in the degradation of pharmaceuticals: Initial conditions: [Pharmaceuticals] = 1.80 µmol/L; pH = 5.8 (DW and RW) e 7.7 (STP effluent); [H_2O_2] = 6.0 mg/L(DW and RW); [TiO_2] = 150 mg/L(DW and RW) e 450 mg/L(STP effluent).

Source: Paniagua (2018).

The DW matrix (Figure 5A) showed an initial inhibition of 1% and increased to 23% after the application of an energy dose of 448 kJ/m² from solar photolysis. Applying the TiO_2/Solar process, the inhibition of luminescence increased to 68%, reaching 83% when combining the TiO_2/Solar process with 6.0 mg/L H_2O_2 (with replacement every 20 min of reaction). For the RW matrix (Figure 5B) the initial inhibition was 3.3% which increased to 25% after the application of an energy dose of 448 kJ/m² by solar photolysis. By combining solar radiation with the photocatalyst, the luminescence inhibition for *Vibrio fischeri* reaches 95% and is total after the association of the TiO_2/Solar process with H_2O_2 (6.0 mg/L), requiring replacement every 20 min of reaction. As for the STP effluent matrix (Figure 5C), the initial toxicity of the *in natura* sample is 50%, which increases to 63% after the application of 524 kJ/m² of energy dose from solar radiation. When solar photolysis is combined with TiO_2 there is an increase to 71% in the inhibition of bioluminescence generated by the *Vibrio fischeri* bacterium. The toxicity quantified *in natura* matrices comes from organic substances that degrade, causing the generation of more toxic by-products than those originally present in the matrices (GORENOGLU et al., 2018; TURKAY et al., 2018).

For the DW and RW matrices, the addition of H_2O_2 at 6.0 mg/L (with replacement every 20 min), influenced the increase in degradation efficiency, the removal of COD and greater toxicity to the *Vibrio fischeri* bacterium (ABBAS et al., 2018). Therefore, it is necessary to quantify the concentration of H_2O_2 that was used until the end of the oxidation process, as shown in Figure 6.

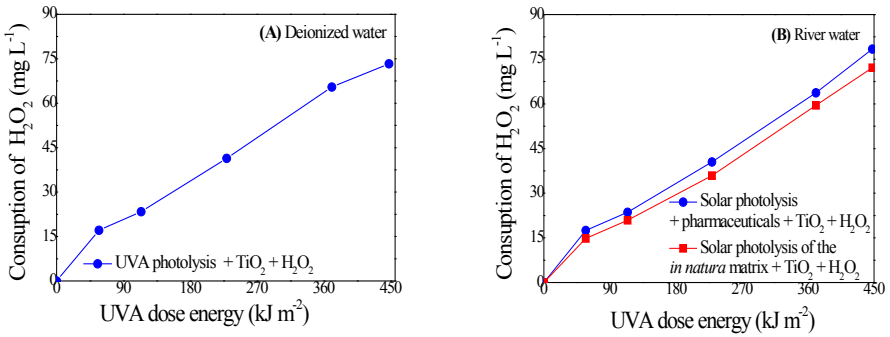

Figure 6: Consumption of H_2O_2 in the TiO_2/H_2O_2/Solar process pharmaceuticals degradation: (A) Deionized Water and (B) River Water. Initial conditions: [Pharmaceuticals] = 1.80 µmol/L; [H_2O_2] = 6.0 mg/L; pH = 5.8 and [TiO_2] = 150 mg/L.

Source: Paniagua (2018).

In the DW matrix (Figure 6A), the consumption of H_2O_2 reached 73 mg/L after the application of an energy dose of 448 kJ/m². In RW (Figure 6B), the consumption of H_2O_2, *in natura* matrix, was 72 mg/L after 448kJ/m² of energy in a time of 300 min of reaction. When the drug mixture was added to the AR matrix, the peroxide consumption increased to 79 mg/L (10% more), and this increase can be attributed to organic matter from the pharmaceuticals mixture.

4 | CONCLUSIONS

Combining solar radiation with TiO_2 resulted in greater degradation efficiency for the drug mixture in all evaluated matrices. When adding H_2O_2 to the TiO_2/Solar process, there is both an increase in degradation efficiency and a reduction in treatment time in DW and RW matrices. On the other hand, the increase in matrix complexity acts to reduce degradation efficiency, requiring a higher concentration of photocatalyst (450 mg/L) associated with a higher dose of energy (524kJ/m²) to be applied.

Mineralization, in the form of COD, resulted in values above 60% for all evaluated matrices, which confirms that high degradation efficiency does not result in similar percentages for COD removal. The evaluation of acute toxicity with the bacterium *Vibrio fischeri* showed high inhibition of luminescence for the DW matrix, since it presents an

organic load from the by-products obtained after the degradation of the target compounds. However, the same behavior could not be observed for the RW and STP effluent matrices, as they have organic matter in their composition and are capable of generating greater toxicity before and after the pharmaceuticals mixture degradation process.

Therefore, the TiO_2/Solar process has great potential to be used as a complementary step to conventional treatment processes, in order to remove compounds of a specific nature such as those evaluated in this work.

REFERENCES

ABBAS, M. et al. *Vibrio fischeri* bioluminescence inhibition assay for ecotoxicity assessment: A review. **Science of The Total Environment**, v. 626, p. 1295- 1309, 2018. https://doi.org/10.1016/j.j.scitotenv.2018.01.066.

ÁLVAREZ-RUIZ, R.; PICÓ, Y. Analysis of emerging and related pollutants in aquatic biota. **Trends in Environmental Analytical Chemistry**, v. 25, p. e00082, 2020. https://doi.org/10.1016/j.teac.2020.e00082

ARSAND, J. B. et al. Presence of antibiotic resistance genes and its association with antibiotic occurrence in Dilúvio River in southern Brazil.**Science of the Total Environment**, v. 738, p. 139781, 2020.https://doi.org/10.1016/j.scitotenv.2020.139781

BOGER, B. et al. Occurrence of antibiotics and antibiotic resistant bacterium in subtropical urban Rivers in Brazil. **Journal of Hazardous Materials**, v. 402, p.123448, 2021. https://doi.org/10.1016/j.jhazmat.2020.123448

CARTAXO, A. S. B. et al. Emerging contaminants in Waters intended for human consumption: occurrence, implications and treatment technologies. **Brazilian Journal of Development**, v. 6, n. 8, p.61814-61827, 2020.https://doi.org/10.34117/bjdv6n8-559.

CERIANI, E. et al. Complete mineralization of organic pollutants in water by treatment with air non-thermal plasma.**Chemical Engineering Journal**, v. 337, p. 567-575, 2018.https://doi.org/10.1016/j.cej.2017.12.107

DUTA, A.; ANDRONIC, L.; ENESCA, A. The influence of low irradiace and electrolytes on the mineralization efficiency of organic pollutants using the Vis-active photocatalytic tandem $CuInS_2/TiO_2/SnO_2$. **Catalysis Today**, v. 300, p. 18-27, 2018.http://dx.doi.org/10.1016/j.cattod.2017.03.018

FERNANDES, M. J. et al. Antibiotics and antidepressants occurence in surface Waters and sediments collected in the north of Portugal. **Chemosphere**, v. 239,p.124729, 2020. https://doi.org/10.1016/j.chemosphere.2019.124729

GORENOGLU, E. et al. Effect of triclosan and its photolysis products on marine bacterium *V. fischeri* and freshwater alga *R. subcapitata*.**Journal of Environmental Management**, v. 211, p. 218-224, 2018. https://doi.org/10.1016/j.jenvman.2018.01.056

KOLTISAKIDOU, A. et al. Cytarabine degradation by simulated solar assisted photocatalysis using TiO_2. **Chemical Engineering Journal**, v. 316, p.823-831, 2017.https://doi.org/10.1016/j.cej.2017.01.132

MENG, Y. et al.A review on analytical methods for pharmaceutical and personal care products and their transformation products. **Journal of Environmental Science**, v. 101, p. 260-281, 2021.https://doi.org/10.1016/j.jes.2020.08.025

NOGUEIRA, R. F. P.; OLIVEIRA, M. C.; PATERLINI, W. C. Simple and fast spectrophotometric determination of H_2O_2 in photo-Fenton reactions using metavanadate. **Talanta**, v. 66, p. 86-91, 2005. https://doi.org/10.1016/j.talanta.2004.10.001

OLIVEIRA, M. et al. Pharmaceuticals residues and xenobiotics contaminants: occurrence, analytical techniques and sustainable alternatives for wastewater treatment. **Science of the Total Environment**, v. 705, p. 135568, 2020.https://doi.org/10.1016/j.scitotenv.2019.135568

PAIVA, V. A. B. et al., Simultaneous degradation of pharmaceuticals by classic and modified photo-Fenton process. **Journal of Environmental Chemical Engineering**, v. 6, p. 1086-1092, 2018. https://doi.org/10.1016/j.jece.2018.01.013

PANIAGUA, C. E. S. **Simultaneous degradation of the pharmaceuticals gemfibrozil, hydrochlorothiazide and naproxen by the processes TiO_2/UV-A, TiO_2/H_2O_2/UV-A and H_2O_2/UV-C in different aqueous matrices.** 2018. 159 f. Thesis (Doctorate in Chemistry) - Institute of Chemistry, Federal University of Uberlândia, Uberlândia, 2018. http://dx.doi.org/10.14393/ufu.te.2018.799

PANIAGUA, C. E. S. et al. Simultaneous degradation of the pharmaceuticals gemfibrozil, hydrochlorothiazide and naproxen and toxicity changes during UV-C and UV-C/H_2O_2 processes in different aqueous matrixes. **Journal of Environmental Chemical Engineering**, v.7, p.1-7, 2019. https://doi.org/10.1016/j.jece.2019.103164

PANIAGUA, C. E. S. et al. Matrix Effects on the Degradation of Gemfibrozil, Hydrochlorothiazide, and Naproxen by Heterogeneous Photocatalysis. **Journal Brazilian Chemical Society**, v. 31, n.6, p. 1161-1169, 2020. http://dx.doi.org/10.21577/0103-5053.20200002

PIVETTA, R. C. et al. Tracking the occurrence of psychotropic pharmaceuticals in Brazilian wastewater treatment plants and surface water, with assessment of environmental risks. **Science of the Total Environment**, v.727, p.138661, 2020.https://doi.org/10.1016/j.scitotenv.2020.138661

SÁGI, G. et al. The impact of H_2O_2 and the role of mineralization in biodegradation or ecotoxicity assessment of advanced oxidation processes. **Radiation Physics and Chemistry**, v. 144, p.361-366, 2018.http://dx.doi.org/10.1016/j.radphyschem.2017.09.023

STARLING, M. C. V. M.; AMORIM, C. C.; LEÃO, M. M. D. Occurrence, control and fate of contaminants of emerging concern in environmental compartments in Brazil. **Journal of Hazardous Materials**, v. 372, p. 17-36, 2019.https://doi.org/10.1016/j.jhazmat.2018.04.043

TURKAY, O. et al. Electro-oxidation of cytostatic drugs: Experimental and theoretical identification of by-products and evaluation of ecotoxicological effects. **Chemical Engineering Journal**, v. 334, p. 1820-1827, 2018.https://doi.org/10.1016/j.cej.2017.11.105

VERAS, T. B. et al. Analysis of the presence of anti-inflammatories drugs in surface water: A case study in Beberibe river – PE, Brazil. **Chemosphere**, v.222, p. 961-969, 2019.https://doi.org/10.1016/j.chemosphere.2019.01.167

YOON, G. et al. Selection criteria for oxidation method in total organic carbon measurement. **Chemosphere**, v. 199, p. 453-458, 2018. https://doi.org/10.1016/j.chemosphere.2018.02.074.

SOBRE O ORGANIZADOR

CLEISEANO EMANUEL DA SILVA PANIAGUA - Technician in Chemistry from the Professional College of Uberlândia (2008), Bachelor of Chemistry from the Federal University of Uberlândia (2010), Degree in Chemistry from the University of Uberaba (2011) and in Biological Sciences from the Faculdade Única (2021). Specialist in Teaching Methodology of Chemistry and Teaching in Higher Education at Faculdade JK Serrana in Brasília (2012), specialist in Teaching Science and Mathematics at Instituto Federal do Triângulo Mineiro (2021). Master in Chemistry from the Federal University of Uberlândia (2015), with emphasis on development of bioadsorbent to remove As (V), Sb (III) and Se (IV) ions in different aquatic matrices. PhD in Chemistry from the Federal University of Uberlândia (2018), with emphasis on Advanced Oxidative Processes [heterogeneous photocatalysis (TiO_2/UV-A and TiO_2/Solar)] and H_2O_2/UV-C for removal of contaminants of emerging cocern (CEC) in different aquatic matrices. She carried out her first Post-Doctoral internship (from May 2019 to June 2021) at the Federal University of Uberlândia with an emphasis on the application of new oxidizing agents using solar radiation to remove CEC in effluents from a sewage treatment plant. He is currently carrying out his second Postdoctoral Internship (July 2021 - current) at UFU in the same line of research. Degree in Physics at Faculdade Única (September 2021 to November 2022), studying *lato sensu* postgraduate studies in Advanced Instrumental Analysis at Unileyva College. He has 11 years of experience as a chemistry technician at the Federal Institute of Goiás, having acted as responsible for the analysis of physical-chemical and biological parameters of water and effluents from a sewage treatment plant. It operates in the following lines of research: (*i*) Development of new methodologies for the treatment and recovery of chemical waste generated in the laboratories of teaching and research institutions; (*ii*) CEC monitoring studies; (*iii*) Development of new advanced technologies for CEC removal in different aquatic matrices; (*iv*) Application of advanced oxidative processes (H_2O_2/UV-C, TiO_2/UV-A and photo-Fenton and others) to remove CEC in effluents from a sewage treatment plant for reuse purposes; (*v*) Study and development of new bioadsorbents for environmental remediation of CEC in different aquatic matrices; (*vi*) Environmental Education and; (*vii*) literacy and scientific processes in the area of Science of Nature, especially biology and chemistry.

ÍNDICE REMISSIVO

www.atenaeditora.com.br
contato@atenaeditora.com.br
@atenaeditora
www.facebook.com/atenaeditora.com.br

Collection:

APPLIED CHEMICAL ENGINEERING

Atena Editora
Ano 2022

www.atenaeditora.com.br
contato@atenaeditora.com.br
@atenaeditora
www.facebook.com/atenaeditora.com.br

Collection:

APPLIED CHEMICAL ENGINEERING

Atena Editora
Ano 2022