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IMPLEMENTATION OF A PHOTOCATALYTIC SOLAR CELL FOR THE DEGRADATION OF EMERGING POLLUTANTS OF PHARMACEUTICAL ORIGIN

Implementación de una celda solar fotocatalítica para la degradación de contaminantes emergentes de origen farmaceútico

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Key words: photocatalysis, acetylsalicylic acid, trimethoprim, ranitidine.

ABSTRACT

Emerging pollutants of pharmaceutical origin have a continuous entry into the aquatic environment in very low concentrations and can alter the organism of living beings. The main characteristics of these pollutants are their high stability and persistence in water, which can generate bioaccumulation, endocrine disruption, and bacterial resistance. These pollutants are excreted without metabolizing after their application, reaching wastewater and subsequently surface water because the methods used to eliminate them (biological treatments) are not efficient. A photocatalytic system is a great alternative to degrade emerging pollutants of pharmaceutical origin. Therefore, the implementation of a photocatalytic solar cell turns out to be a low-cost, efficient, and environmentally friendly solution. Acetylsalicylic acid, trimethoprim, and ranitidine were selected to simulate wastewater with emerging pollutants at a concentration of 1 g/L. They were subjected to a solar cell to carry out their degradation by photocatalysis, using TiO_2 as a photocatalyst. The evaluation was carried out by analytical methods: UV-Vis spectrophotometry, chemical oxygen demand (COD) and total organic carbon (TOC). Acetylsalicylic acid was the drug that degraded the most, decreasing its COD from 152.6 to 10.4 mg/L at the end of treatment, while TOC started at 118.6 mg/L and ended at 1.4 mg/L. Trimethoprim turned out to be the drug with the least decrease in COD and TOC. Finally, it can be concluded that the coupling of solar energy to the photocatalysis process was satisfactory,, obtaining a technology of low cost and less impact.

Palabras clave: fotocatálisis, ácido acetilsalicílico, trimetoprima, ranitidina.

RESUMEN

Los contaminantes emergentes de origen farmacéutico ingresan de manera continua al medio acuático en concentraciones muy bajas y pueden alterar el organismo de los seres vivos. Algunas de las principales características de estos contaminantes son su alta estabilidad y persistencia en el medio acuoso, lo que puede generar bioacumulación, disrupción endocrina y resistencia bacteriana. Estos contaminantes se excretan sin metabolizar después de su aplicación, llegando al agua residual y posteriormente al agua superficial debido a que los métodos empleados para eliminarlos (tratamientos biológicos) no son eficientes. Un sistema fotocatalítico representa una alternativa para degradar contaminantes emergentes de origen farmacéutico. Por ello, la implementación de una celda solar fotocatalítica resulta ser una solución de bajo costo, eficiente y amigable con el ambiente. Se seleccionó ácido acetilsalicílico, trimetoprima y ranitidina para simular agua residual con contaminantes emergentes a una concentración de 1 g/L. Los efluentes sintéticos fueron sometidos a la celda solar para realizar la degradación de los contaminantes mediante fotocatálisis, utilizando TiO_2 como fotocatalizador. La evaluación se realizó mediante los métodos analíticos: espectrofotometría UV-Vis, demanda química de oxígeno (DQO) y carbono orgánico total (COT). El ácido acetilsalicílico fue el fármaco que tuvo mayor degradación, disminuyendo su DQO de 152.6 a 10.4 mg/L al final del tratamiento, mientras que el COT comenzó en 118.6 mg/L y finalizo en 1.4 mg/L. La trimetoprima resultó ser el fármaco con la menor disminución de DQO y COT. Por último, se puede concluir que el acoplamiento de la energía solar al proceso de fotocatálisis fue satisfactorio, obteniéndose una tecnología de bajo costo y de menor impacto.

INTRODUCTION

Humanity's life expectancy and quality of life has now increased considerably, mainly due to scientific advances and technological development. The involvement of chemicals in man's daily life has facilitated the realization of his various activities, for example, pharmaceuticals have provided greater longevity, fuels have allowed greater efficiency in transport and textile dyes are used to dye garments, etc. However, the growing population, rapid industrialization and mismanagement of these chemicals have made them a major environmental problem as they begin to harm natural resources. Aquatic contamination is associated with pollutants derived from anthropogenic activities, whose wastewater carries in addition to various pathogens, a wide variety of organic and inorganic substances such as oils, surfactants, textile dyes, phenols, heavy metals and a wide range of emerging contaminants, being the latter are the subject of interest of this research.

An emerging pollutant is an environmentally detected substance that is not currently included in environmental monitoring programs and may be a candidate for future legislation due to its adverse effects and/or persistence (Norman Network 2016). These contaminants are classified into: personal care products (Montes-Grajales et al. 2017, Gogoi et al. 2018), UV filters (Baron et al. 2013, Ribeiro et al. 2017), endocrine disruptors (Vilela et al. 2018), hydrocarbons (Starling et al. 2018, Tursi et al. 2018), illicit drugs (Pal et al. 2013, Cosenza et al. 2018), food additives (Postigo et al. 2015), metabolites (Delarco 2008, Narváez-Valderrama et al. 2012), fire retardants (Peng et al. 2017), pesticides (Pal et al. 2014) and pharmaceutical products (Quijano Prieto 2016, Rodriguez-Narváez et al. 2017).

The most important environmental effects of emerging pollutants refer to bioaccumulation and biomagnification, persistence, toxicity, endocrine disruption potential, carcinogenic effects, mutagenic and teratogenic effects (Guillén et al. 2012). Some others may be harmful to both humans and aquatic organisms, causing disorders such as endocrine disruptive effects, estrogenic or hormonal disruption, fetal malformation or even DNA damage (Fawell and Ong 2012). Routes of human exposure include ingestion, inhalation, and dermal contact through food and water (Pease and Gentry 2016).

The presence of emerging pharmaceutical pollutants in drinking water has raised significant concerns regarding the risk of estrogenic and/or other potentially adverse effects on living beings, including humans (Liu et al. 2015). Approximately 3000 different substances can be used as pharmaceutical ingredients, analgesics, antibiotics, antidiabetics, beta-blockers, contraceptives, antidepressants, among others.

Of these, only a subset has been investigated for its impact on the environment (Rodríguez-Narváez et al. 2017). The main concern regarding antibiotics is the development of bacterial resistance after release to the environment (Petit et al. 2015, Xu et al. 2015, Zhang et al. 2015), in addition to the detrimental effect on the biodegradation of plant materials, which alters the first food chain in aquatic ecosystems (Richardson and Ternes 2014). The constant use of pharmaceutical products increases their presence in surface water, groundwater, wastewater, and stormwater runoff in urban areas (Campanha et al. 2015, Diamond et al. 2015, Lambert and Skelly 2016, McGrane 2016).

The excessive use or discharge/elimination of emerging pollutants of pharmaceutical origin in the environment or their handling without due precautions are polluting aquatic bodies and generating dangerous and adverse effects on the ecosystem. Therefore, the removal of organic pollutants from wastewater has been a great challenge. Various efforts have been made to eliminate/degrade organic contaminations from water (Gusain et al. 2019). In general, physical, chemical, and biological treatments are used to eliminate and minimize organic pollutants and their degraded products from the aquatic environment. These methods are used independently or in conjunction with other methods to detoxify contaminated wastewater. Some of the commonly used methods to decontaminate water are adsorption, membrane filtration, biological degradation, photocatalytic degradation, liquid-liquid extraction, nanofiltration, oxidation, reverse osmosis, UV irradiation, etc. (Shao et al. 2018, Luo et al. 2019, Patel et al. 2019, Rasheed et al. 2019, Ferreiro et al. 2020). Although these methods are effective for the elimination of emerging pollutants (including those of pharmaceutical origin) they still have their own deficiencies, such as secondary contamination, large investment in equipment, high energy consumption and the production of more toxic by-products (Nidheesh and Gandhimathi 2012, Zhang et al. 2019).

Advanced oxidation processes (AOP) use semiconductors that effectively degrade a wide variety of organic pollutants. In addition, it has advantages such as high treatment efficiency, simple process equipment, easy operating conditions and lack of secondary contaminants (Choi et al. 2017, Luo et al. 2019), being the most promising technology in the topic of emerging pollutants of pharmaceutical origin (Deng et al. 2020). Photocatalysis is an AOP that is based on photoactivation of photocatalysts with incident photons emitted by a radiation source (sunlight or artificial light). Radiation activates the photocatalyst and causes pairs of electro "hollows", which produce free radicals such as the hydroxyl radical when in contact with load carriers. Radicals are transient compounds that directly attack organic and inorganic pollutants present in water (Bustillo-Lecompte 2020). The use of different materials for semiconductor manufacturing has been demonstrated in many ways; in addition, the number of chemical elements implemented in semiconductors in recent decades has increased from 11 to more than 60 (Borgues et al. 2016). Among the most used semiconductors is TiO_2, being the photocatalyst with less environmental impact due to its different properties such as a chemical structure of high stability, biocompatibility, low-cost production, and physical, optical, electrical, and photocatalytic properties (Bai et al. 2012, Li et al. 2016).

Finally, this research has as its main objective the implementation of a photocatalytic solar cell, which can achieve the efficient degradation of emerging pollutants of pharmaceutical origin. The cell is intended to activate the semiconductor using solar energy, matching or improving the degradation efficiency of currently used biological methods. The operation of the photocatalytic solar cell will also be achieved, obtaining an efficient reactor for degrading emerging pollutants, with less environmental impact (compared to the impacts of chemical methods) and low-cost due to the incorporation of solar energy.

MATERIALS AND METHODS

Selection of emerging pollutants of pharmaceutical origin

Solutions with emerging contaminants were prepared for similar wastewater. The drugs were subjected to degradation in their commercial form, that is, as tablets and with excipients. The contaminants used were: Acetylsalicylic acid (500 mg of acetylsalicylic acid, 50 mg of caffeine, excipients corn starch and cellulose powder, BAYER brand), trimethoprim (160 mg of trimethoprim, 800 mg of sulfamethoxazole, sodium carboxymethyl starch excipients, polyvinylpyrrolidone K30, docusate sodium, magnesium stearate [Septrin Forte]), stearate, Septrin Forte brand) ranitidine (300 mg ranitidine, 0.400 mg soy lecithin, microcrystalline cellulose excipients, croscarmellose sodium, hydrated colloidal silica, magnesium stearate, polyvinyl alcohol, titanium dioxide, talc, xanthan gum [Toriol]). According to the research of Weber et al. (2014) trimethoprim was reported in wastewater from 29 countries whereof, being an antibiotic, can generate resistance in bacterial strains (Kemper 2008). For its part, acetylsalicylic acid was reported in waters of 13 countries.

This compound can cause non-intended physiological responses in organisms such as accumulation in tissues, reproductive damage, behavioral changes, among others (Casallas and Franco 2019).

Ranitidine has also been detected in surface waters (Elías et al. 2019) as a typical precursor for nitrosamine dimethylamine, an extremely potent human carcinogen. During chlorination, ranitidine has a higher conversion rate (approximately 90 %) (Shen and Andrews 2011), so its elimination in water bodies is essential to avoid damages to human health.

Table I shows the main characteristics of the compounds to be used. Being in the form of tablets, each of the drugs was crushed in a mortar and then dissolved in water. The concentration used was 1 g/L with a pH of 7, in order to establish similar conditions to wastewater coming out of the treatment plants, which generally have a neutral pH and high drug concentrations.

Photocatalytic solar cell

The degradation of emerging pollutants of pharmaceutical origin was carried out by heterogeneous photocatalysis. The reactor used to carry out the activity was a photocatalytic solar cell, which directs solar energy to the semiconductor to increase its degradation efficiency.

The photocatalytic solar cell (**Fig. 1**) has as its main base a cell/container where the wastewater to be treated is concentrated; the photocatalytic activity develops in the borosilicate coil located in the upper part of the cell; the semiconductor is impregnated in the coil walls. Another essential component is the solar collector, which is an aluminum plate in the shape of a parabolic mirror, whose function is to redirect the solar rays so that they concentrate on the semiconductor and maintain a higher degradation efficiency. The submersible water pump keeps the water recirculating throughout the system.

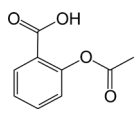
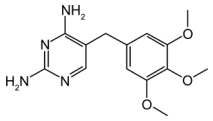
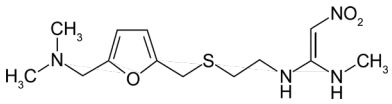
Because the cell works with solar energy, we explored the grounds of the Escuela Nacional de Ciencias Biológicas (National School of Biological Sciences) of the Instituto Politécnico Nacional (National Polytechnic Institute, IPN) to find the area with the highest solar radiation or the most appropriate light intensity.

During the survey, an HER-410 luxmeter (Steren) was used to measure the intensity of the light.

Semiconductor impregnation

The semiconductor used to carry out the photocatalysis process was TiO_2 (JT Barker 4162-01,

TABLE I. PROPERTIES OF EMERGING POLLUTANTS OF PHARMACEUTICAL ORIGIN.

	Properties/drug	Acetylsalicylic acid	Trimethoprim	Ranitidine
Chemical characteristics	Formula	$C_9H_8O_4$	$C_{14}H_{18}N_4O_3$	$C_{13}H_{22}N_4O_3S$
	Chemical structure			
	IUPAC name	Acid 2-(acetyloxy)-benzoic	5-(dimethoxybenzyl) pirimidin-2,4-diamine	(E)-N-(2-((5-((dimethylaminomethyl) furan-2-yl) methylthio) ethyl)-N'-methyl-2-nitroethane-1,1-diamine
Physical properties	Molecular weight (g/mol)	180.10	290.32	314.40
	Density (g/mL)	1.40	1.075	1.07
	Water solubility (mg/mL)	1.00	12.10	660
Pharmacokinetics	Bioavailability (%)	Quick and complete	90-100	> 39-88
	Protein union (%)	99.6	42-46	11.12
	Metabolism	Hepatic	Hepatic	Hepatic

Prepared from data from Katzung et al. (2007) and Dzeshk et al. (2017).

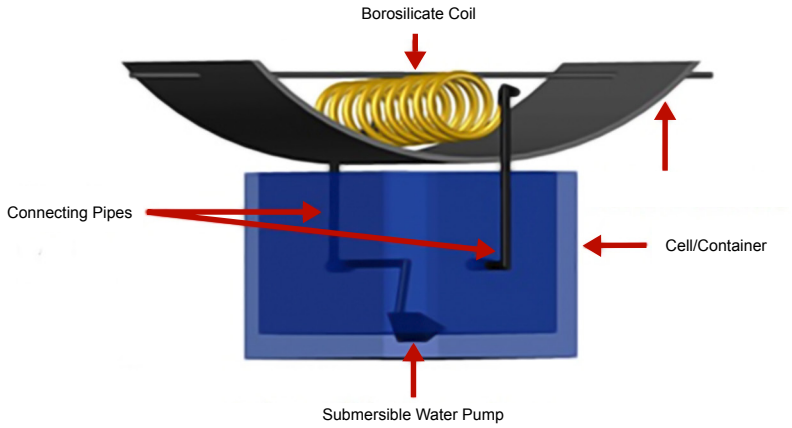


Fig. 1. Photocatalytic solar cell configuration.

analytical grade) because it has certain advantages as a photocatalyst: it has a band gap of 3.2 eV, it is not toxic, it is low cost and has long-term photostability (Chong et al. 2010). TiO_2 is a semiconductor mostly used for photocatalysis (Alexandrino et al. 2017).

The method used to deposit the photocatalyst on the support was chemical impregnation, which was carried out according to Arango-Parado et al. (2009): TiO_2 was deposited on the walls of the borosilicate support, which had a serpentine shape. First, the coil was washed with a solution of 15 mL of acetone and another solution of 15 mL of ethanol, then the drying was carried out at 50 °C. Then, a 100 mL solution of 0.01 M TiO2 (Sigma-Aldrich, particle size, reagent grade) was prepared and the coil recirculated for 120 min. Further on, the support was taken to the drying oven, where it was dried at 50 °C for 4 h (Arango-Parrado et al. 2009).

Photocatalytic activity

The photocatalytic activity in the solar cell was carried out for a total time of 120 min. The reaction period was established from 12:00 to 14:00, which according to the UV Index reported by the government of Mexico City is the interval in which there is greater solar radiation during the day.

Once the solar cell was installed in the area with the highest radiation, 2 L of solution were deposited in the cell/container and the pump was turned on so that the water could begin to recirculate. The sampling was carried out every 30 min, for this, 50 mL vials were used which were filled in the effluent after the borosilicate coil. Once the sample was obtained, it was taken to the laboratory and refrigerated. Subsequently, the different analytical methods were carried out.

Evaluation of photocatalytic solar cell

The evaluation of the efficiency of the solar cell was carried out using the analytical methods of UV-Vis spectrophotometry, chemical oxygen demand (COD) and total organic carbon (TOC).

A Beckman model DU 700 UV-Vis spectrophotometers was used, where the samples were read in an interval of 400-600 nm, to know the photocatalytic activity of TiO_2 in the visible region.

COD is the amount of oxygen required to chemically oxidize organic matter into carbon dioxide and water. It represents a measure of all organic and inorganic matter solubilized and/or suspended that can be chemically oxidized (Ramírez-Burgos et al. 2008). The method to determine COD is in accordance with the NMX-AA-030/1-SCFI-2012 standard (SE 2012).

The TOC for its part is the amount of carbon attached to an organic compound and is frequently used as a non-specific indicator of water quality. It is measured by the amount of carbon dioxide that is generated by oxidizing organic matter under special conditions.

The method used in the determination of total organic carbon was carried out in accordance with the US-EPA 415.3 standard.

The COD and TOC analytical methods were performed at the Laboratorio Central de Instrumentación (Central Instrumentation Laboratory) of the IPN, which is a laboratory accredited by the Entidad Mexicana de Acreditación (Mexican Certification Entity) (Nº AG-063-007/06). It is also certified by the Red Nacional de Laboratorios Ambientales (National Network of Environmental Laboratories) DF/Mex/Qro/ (REDLA 031/ AAR/).

RESULTS AND DISCUSSIONS

Photocatalytic solar cell operation

The design of the photocatalytic solar cell was functional throughout the experiment. There were no operating problems that could obstruct the photocatalysis process. The solar collector managed to keep the semiconductor irradiated during the time exposed, which gave rise to a greater photocatalytic activity. At the end of the experimental phase, the coil was again subjected to UV lamps to verify that TiO_2 was still impregnated in its walls, having favorable results.

During the time in which each of the drugs was subjected to degradation, the data of the UV index (from the government of Mexico City) and the illuminance were measured by means of a luxmeter. Both parameters were recorded at the time of measuring each of the samples. The results obtained are shown in **Table II**.

Table II shows that both the UV index and illuminance maintained high values during the degradation of pollutants. The only drug that obtained low solar irradiation was acetylsalicylic acid in minute 120 of reaction. These data establish that the semiconductor had sufficient solar radiation to achieve adequate degradation.

UV-Vis spectrophotometry

For each one of the samples that were subjected to the UV-Vis spectrometer, a spectrophotometric bar was made at wavelengths between 400 and 600 nm. **Table III** shows the absorbances obtained at 400, 500 and 600 nm, because at these wavelengths they achieved the highest expression (**Table III**).

Acetylsalicylic acid maintained a constant decrease in its absorbance during the reaction time. At 30 and 60 minutes it reported the same absorbance. After 30 minutes of exposure in the photocatalytic solar cell, its absorbance decreased more than 50 (± 2) %. At the end of the treatment, a reduction of 76.75 (± 1) % of the initial absorbance was obtained. Trimethoprim and ranitidine had a similar behavior during treatment. Its absorbance decreased at 30 minutes of reaction, increased at 60 minutes, and

TABLE II. RECORD OF THE UV INDEX (UVI) AND ILLUMINANCE (LX^{100}) REPORTED DURING THE DEGRADATION MONITORING OF EMERGING POLLUTANTS OF PHARMACEUTICAL ORIGIN.

Time (Min).	Acetylsalicylic acid		Trimethoprim		Ranitidine	
	UVI	Lx^{100}	UVI	Lx^{100}	UVI	Lx^{100}
0	12	1168	12	1200	13	1030
30	13	1179	11	1110	13	1200
60	10	816	12	1206	13	1054
120	5	500	11	1140	13	1138

TABLE III. RECORD OF THE ABSORBANCES OBTAINED BY THE UV-VIS SPECTROPHOTOMETER DURING THE DEGRADATION MONITORING OF EMERGING POLLUTANTS OF PHARMACEUTICAL ORIGIN.

	Acetylsalicylic acid			Trimethoprim			Ranitidine		
Time (min)/λ	400	500	600	400	500	600	400	500	600
0	0.093	0.085	0.081	0.056	0.032	0.024	0.085	0.053	0.053
30	0.029	0.024	0.019	0.046	0.021	0.015	0.041	0.030	0.023
60	0.029	0.024	0.020	0.051	0.026	0.015	0.048	0.034	0.030
90	0.027	0.024	0.018	0.055	0.030	0.018	0.040	0.023	0.021
120	0.024	0.021	0.017	0.049	0.028	0.017	0.030	0.018	0.020

* All values have a standard error of ± 0.002.

finally tended to decrease at 90 and 120 minutes. Trimethoprim ended the treatment with a 15 % decrease in absorbance, while ranitidine reduced it by 64.59 (± 2) %.

Chemical oxygen demand

Figure 2 shows the COD of the three drugs subjected to degradation. Acetylsalicylic acid had a progressive decline over time, while the other two drugs behaved similarly. Acetylsalicylic acid started with a concentration of 152.6 mg/L of, which decreased gradually until the end of the treatment, leaving a final COD of 50.3 mg/L.

Trimethoprim maintained an initial COD concentration of 136.8 mg/L, after 30 minutes of exposure it increased its concentration to 142.5 mg/L; at minute 60, its concentration was 116.4 mg/L, which increased to 121.7 mg/L at minute 90. The treatment ended with a final COD of 96.4 mg/L.

Ranitidine maintained the same behavior as trimethoprim, increasing its concentrations at minutes 30 and 90. This last drug decreased its COD by 36.86 % at the end of the photocatalysis treatment, being the drug that showed greater persistence in the treated water. Ranitidine started with a COD of 148.4 mg/L and ended with a concentration of 93.7 mg/L.

Total organic carbon

Finally, the data from the TOC method were obtained. **Figure 3** shows the behavior of each of the exposed drugs.

The three drugs exposed in the photocatalytic solar cell showed a tendency to progressively decrease over time, with acetylsalicylic acid being the pollutant that maintained a greater decrease in TOC.

Acetylsalicylic acid decreased its TOC concentration by 81.96 % starting with 118.6 mg/L and ending with a concentration of 21.4 mg/L. It decreased gradually to 112.7 mg/L and the treatment ended with 17.7 mg/L of TOC.

Like the two previous drugs, ranitidine significantly decreased its TOC concentrations (47.4 %), starting with 119.2 mg/L and at the end of the treatment it retained 62.8 mg/L.

Of the three emerging pollutants of pharmaceutical origin that were subjected to degradation in the photocatalytic solar cell, acetylsalicylic acid was the drug that presented the greatest degradation according to the different analytical methods discussed. Both in UV-Vis spectrophotometry and in the COD and TOC tests, acetylsalicylic acid showed a decrease of more than 50 %, with TOC being the parameter where a higher percentage was reflected.

Trimethoprim and ranitidine maintained the same behavior in UV-Vis spectrophotometry and COD, increasing their concentration in a time interval of 30-90 min and decreasing at the end of the treatment. The increase in the concentrations of these two drugs may be due to their structural forms (**Table I**). These compounds have a greater number of bonds and functional groups that, when subjected to the oxidation process, begin to regroup, origina-

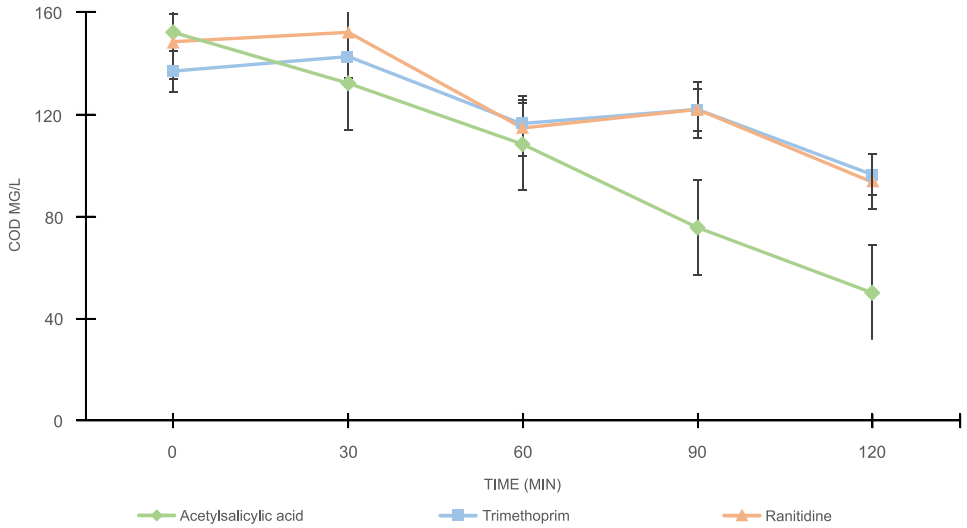


Fig 2 . Chemical oxygen demand (COD) of emerging pollutants of pharmaceutical origin subjected to degradation.

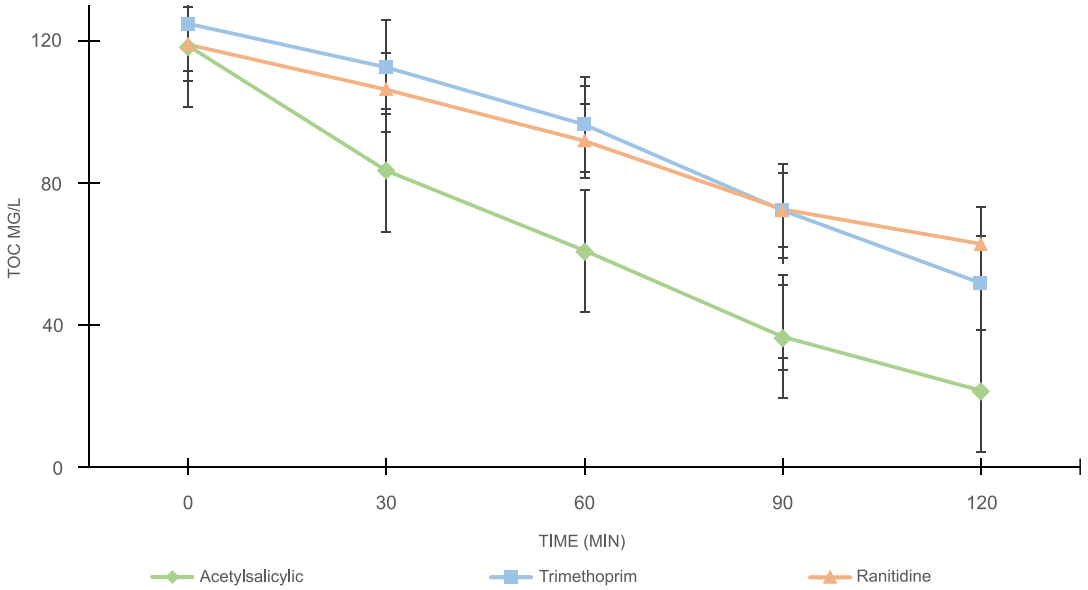


Fig. 3. Total organic carbon (TOC) of emerging pollutants of pharmaceutical origin subjected to degradation.

ting new compounds that can increase absorbance by some time in treatment. However, as time passes, these new compounds undergo constant degradation until they achieve complete mineralization.

Although trimethoprim and ranitidine were expressed in a similar way, ranitidine was the drug that showed the highest persistence in water in all the analyzes performed.

Analyzing the previous results, it is reported that the proposed photocatalytic system presented a higher percentage of removal of emerging pollutants than physical treatments, such as flotation and coagulation (20 % efficiency according to Westerhoff et al. [2005] and Alexandrino et al. [2017]). Regarding biological treatments, the photocatalytic solar cell achieved a similar efficiency. The above-mentioned provides us with an alternative to the treatment of these pollutants, which is the implementation of the solar cell as a tertiary treatment, after the biological treatment. Although the photocatalytic solar cell did not achieve the complete degradation of emerging pollutants, it was shown that it is functional and that it can be an innovative reactor and competitive with the treatment methods that currently exist.

It should be noted that the photocatalytic activity took place in the visible region and not in the UV region, which is where it presents a high efficiency. According to Borges et al. 2016 and Chen et al. (2010),TiO_2, due to the width of its forbidden band only absorbs UV energy, taking advantage of only 5 % of the solar spectrum. Finally, this research proposes the study of techniques or materials that achieve the improvement of TiO_2 to obtain the maximum benefit of the visible region and solar energy. Some of the alternatives to achieve greater efficiency of the TiO_2 photocatalyst are metallic doping, non-metallic doping, and organometallic sensitization.

CONCLUSIONS

Once the experimental design is completed and the results discussed, it can be concluded that:

The photocatalytic solar cell managed to couple solar energy to the photocatalysis process, being a promising technology in the degradation of emerging pollutants.

The semiconductor used is better required to increase the efficiency of the system.

The photocatalytic solar cell can be implemented as a tertiary treatment of currently used biological methods.

Acetylsalicylic acid was the drug that presented the greatest degradation according to all the methods used.

Of the three exposed drugs, ranitidine was the one that expressed the highest persistence in water.

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