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Removal of penicillin from wastewater: a short review

A.C. Mejía-López^a, J.J. Ramírez-García^a, M. Solache-Ríos^{b,*}

^aUniversidad Autónoma del Estado de México, Facultad de Química. Paseo Colón Esq, Paseo Tollocan S/N, C.P. 50120, Toluca, Edo. de Mex, México, emails: cecy_ppg17@hotmail.com (A.C. Mejía-López), jjramirezg@uaemex.mx (J.J. Ramírez-García)
^bDepartamento de Química, Instituto Nacional de Investigaciones Nucleares, Carretera México-Toluca S/N, La Marquesa, Ocoyoacac, Estado de México C. P. 52750, México, Tel. +52 5553297200; Fax: +52 5553297301;
email: marcos.solache@inin.gob.mx (M. Solache-Ríos)

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ABSTRACT

Wastewater treatment for the elimination of emerging pollutants such as penicillin, should be carried out in order to control the negative impact in the environment produced by these compounds, a particular characteristic they have is their high toxicity even at low concentrations, these pollutants are mainly found in wastewater. This review compiles and analyzes a list of recent papers for the removal of penicillin G from wastewater. The main techniques considered in this paper are: adsorption, advanced oxidation processes and some little studied on alternative treatments are considered, in this review the efficiency of removal, the characteristics, advantages and disadvantages for the removal of penicillin G has been highlighted, research carried out in the field of adsorption and advanced oxidation in recent years is detailed in order to open the way to novel studies that may allow a better perspective of the problem. This paper shows a general description of the state of art on the removal of penicillin G from water.

Keywords: Penicillin G; Removal; Emerging pollutants; Techniques

1. Introduction

Water is the most important resource that exists for life, only 2.5% of the total in the world is sweet [1]. Water degradation, also called water pollution can be defined as a disturbance in the natural conditions of the water, this may be due to the presence or absence of physical, chemical and/ or biological components inherent in each aquatic ecosystem [2] water pollution has been a problem during the past decades, because it prevents its reuse [3], some issues have been taken in order to make water resources sustainable [4,5].

Currently the main source of water pollution is derived from anthropogenic activities such as industrial, livestock and daily activities [2]. The great population growth has resulted from the creation of products and technologies, producing contamination in the water, this can be physical, chemical and/or biological [6], within these categories we can find the so-called emerging pollutants (EPs) which are compounds that already existed but that did not represent danger due to their low concentrations, or their toxic effects on the environment were unknown [7]; a very special feature of EPs is that they tend to be very soluble in water [8] and are continuously discharged into aquatic bodies, these compounds are commonly referred as pesticides, detergents, cosmetics, paints, drugs, among many other commonly used. Table 1 shows some EPs and its consequences on the ecosystem and health [9].

These substances are found in ecosystems in low concentrations, commonly in $\mu g/L$ or ng/L [19], unfortunately, their continuous discharge causes bioaccumulation, resulting in different toxicological affectations (Table 1).

^{*} Corresponding author.

Table 1 Effects of the EPs on living things

EPs	Туре	Effect	References
	Contraceptives and hormones	Feminization of fish	[10]
Description	Antibiotics	Microbial resistance	[11]
Drugs	Analgesics	Acute toxicity by bioaccumulation, damages the endocrine system	[12]
	Antidiabetic	Sterility, loss of reproductive capacity	[13]
		Exposure to phthalates leads to hormonal and metabolic disorders, as well as reproductive defects, can cause damage to the kidneys,	54.0
Industrial	Phthalates	thyroid and liver, contribute to liver and spleen cancer, can increase the number of inflammatory cells in the lungs and bronchial fluid, which can contribute to developing asthma	[14]
additives	Alkylphenols	Reproductive and developmental effects	[15]
	1,4-Dioxane	It increases the risk of cancer, causes changes in reproduction and has the ability to damage the liver and central nervous system	[16]
	Bisphenol A	Increased risk of cancer and apparent neurotoxicity	[17]
Surfactants	Anionic and non-anionic surfactants	Mimic natural hormones by interaction with the estrogen receptor	[18]

There have been several recommendations on environmental issues and conventions [3], such as the Stockholm Convention on Persistent Organic Pollutants [20] and the Rio Declaration on Environment and Development [21] where some criteria and possible EPs regulation have been declared. Unfortunately currently there is not any law or regulation that addresses the existing problem of emerging pollutants; some countries such as France and Germany have made laws on the proper use and disposal of waste in order to reduce pollution [5], in general the European Union should approve any chemical product that is used or marketed within the territory, to evaluate the environmental and toxicological risks that they could have [9,22], unfortunately in most countries worldwide there is not any regulation that prevents their continuous discharge, this is the result of a series of socioeconomic and political factors, especially in developing countries, where economic benefit is more attractive than environmental care, lack of regulations lead to bad social, industrial and environmental practices that harm ecosystems; therefore, it is necessary to carry out studies to evaluate economically viable treatments to remove these pollutants [10]. One of the advantages of reusing water is that it can reduce the amount of pollutants released [4].

When talking about EPs, special attention should be paid to drugs, since they are commonly employed for human or animal use, they serve to combat various diseases and ailments, the main route to entry into water bodies is through urine and excretions, because drugs are not adsorbed completely by the human body [11,23], for example antibiotics are absorbed from 30% to 90% by the human body; likewise considerable amounts of manufactured drugs are often poorly disposed [24].

Important issues, when talking about pharmacotoxicology, are the metabolites and degradation products of drugs that are usually found in the surface water and groundwater [25], due to infiltration by soils [2], currently there are studies showing that EPs may be found in drinking water for human consumption [26,27] causing a

persistent bioaccumulation, in such a way that affects the ecosystem and humans [6–8] Haga clic o pulse aquí para escribir texto. The entry of drugs into wastewater comes from various sources, however all come from untreated wastewater [10], some types of inputs of these substances have been observed, the first is during the discharge of industrial processes of pharmaceutical companies, caused by bad practices and disposal of pharmaceutical products; the second comes from residential areas as a result of the consumption and subsequent excretion of drugs [28]; different drugs have been found in water bodies such as: antibiotics, hormones, endocrine disruptors, antifungals, among many other compounds [23].

It has been observed that the use of antibiotics has accelerated the antibiotic resistant [25], microbial resistance can be natural (that is intrinsic to bacteria) or acquired (exposure of the bacteria to various genes) [29], this occurs by the indiscriminate and irresponsible use of some antimicrobial drugs [30]. The main problem is the production of resistant bacterial that generate diseases that are difficult to treat [31].

A particular case is observed in the penicillin G which was the first antibiotic discovered in 1928 by Alexander Fleming in a London laboratory [32], this compound has various properties (Table 2), it is absorbed between 15%-30% by the human body, which means that most of it is excreted from the body without being metabolized [33], in water bodies the presence of penicillin G has been found in concentrations of 0.93 µg/L, however, its degradation products have also been found in concentrations ranging from 0.41 to 1.36 µg/L [34]. Their inhibitory effect is conferred by the structure of the B-lactam that composes the penicillin (Fig. 1), this structure is also present in other commonly used antibiotics. Penicillin G is the most widely used antibiotic worldwide [35], due to its effects against gram-positive bacteria [36] that causes infectious diseases mainly in the nose, throat, respiratory tract, urinary tract and gynecological [37], therefore it is the antibiotic that has presented

Fig. 1. Molecular structure of penicillin G sodium obtained from PubChem.

more resistance by bacterial strains [38], and these infections increase the mortality and the cost in medical terms [39].

Penicillin G in an ecosystem can be found as benzylpenicillin or as the mixture of its degradation products, in the study of Li et al. [34], the amount of penicillin G was identify as penicilic, penicillic, penilelic, isopenilic acids and penicilloaldehyde, showing penicillin G is degraded by the natural conditions of an ecosystem, causing immediate and long-term damage to the living beings of such a system. The concentrations found were quantified in µg/L, it is a relatively low concentration, due to its bioaccumulation it is expected that the amounts found in animals exceed this amount.

For these reasons, several techniques have been used for the removal of penicillin G in aqueous systems, the objective of this article is to review current research on the elimination of antibiotics by various techniques, with the aim of showing the studies carried out, their results, as well as the viability of the processes. The study analyzes the new trends on the elimination of penicillin G, as well as the most basic methods for its treatment.

2. Methodology

Techniques for the removal of emerging contaminants is a topic of current interest, especially when talking about drugs such as penicillin G.

The Scopus database and ScienceDirect were used as a resource. The online searches were carried out with the help of the Google Scholar search engine, Snowball methods were used (which allowed the location of the oldest and most cited articles), together with the reference method cited. Search terms selected to identify relevant literature included: Emerging contaminants, penicillin G, removal of emerging contaminants, activated carbon, penicillin G sorption, zeolites, modified zeolites, removal of penicillin G with zeolites, advanced oxidation process, photocatalysis, photolysis, and removal of penicillin G by advanced reduction. The terms were also combined in several ways to obtain more defined and appropriate articles.

The articles obtained were analyzed considering: (1) the problem of emerging pollutants in wastewater (2) the use of different methods for the elimination of emerging contaminants and (3) analysis of treatment strategies for the removal of penicillin G. Most of the references cited were articles published between 2000 and 2022.

Table 2 Physico-chemical properties of penicillin G

Synonym	Benzylpenicillin sodium			
	Penicillin G sodium			
	Penicillin G sodium salt			
Molecular formula	$C_{16}H_{17}N_{2}NaO_{4}S$			
PM	356.4 g/mol			
State	Whitish crystalline solid			
Solubility in water	50 to 100 mg/mL at 25°C			
Melting point	209°C			
Density	1.41			
Information obtained from the National Center for				
Biotechnology Information [40]				

3. Removal by sorption

Sorbents are insoluble materials that can be natural, synthetic or modified, and usually have a great ability to retain different solutes, there are different sorbents that serve for the removal of emerging contaminants.

3.1. Aluminosilicates

Zeolites are crystalline whose structure is formed by three-dimensional tetrahedral units, in which a network of pores and cavities is generated with molecular dimensions between 3 to 10 angstroms [41], these materials have properties that make them unique, these are: molecular sieving, high thermal stability, acidity, sorption capacity, selectivity and ion exchange [42], which allows them to sip metal cations (including heavy metals), drugs, dyes, among other analytes [43].

The applications that have this type of materials are very varied, the literature reports that they have been used as molecular sieves, dehydrating agents, catalysts, CO₂ collectors [44], ion exchangers, [45] filters remediating pollution in the air, water purifiers and in general for the removal of contaminants from water [46].

Currently, a wide variety of articles are reported about their use for the treatment of contaminants, specifically several investigations have been carried out for the removal of drugs present in wastewater; Table 3 shows studies carried out for the removal of drugs with aluminosilicates. Table 3 shows a wide variety of studies, these investigations consider the use of natural zeolites and clays from deposits in various parts of the world, with different and sometimes modified properties that tend to improve the removal capabilities of drugs from wastewater [56].

Research for the removal of penicillin G with zeolites and clays has been a limited field. Current articles on the removal of penicillin G with aluminosilicates is very limited, this is probably due to their low selectivity [46], to improve their removal capacity and their selectivity,

Table 3 Drug removal with aluminosilicates

Adsorbate	Туре	Experimental conditions	Percentage of removal	Reference
Amoxicillin	Bentonite	pH 2-7, 0.1-3.5 g adsorbent, 30°C	88%	[47]
Ciprofloxacin	Bentonite	Batch: contact time 30 min, pH 4.5, 2.5 g/L bentonite	99%	[48]
Ibuprofen	Zeolite coated with magnetic nanoparticles	Batch: contact time, 300 min, 30°C, 200 rpm, pH 4.1, 1 g/L zeolite	98.75%	[49]
Naproxen	Zeolite coated with magnetic nanoparticles	Batch: contact time, 300 min, 30°C, 200 rpm, pH 4.1, 1 g/L zeolite	99.79%	[49]
Diclofenac	Zeolite coated with magnetic nanoparticles	Batch: contact time, 300 min, 30°C, 200 rpm, pH 4.1, 1 g/L zeolite	99.58%	[49]
Carbamazepine	Zeolite Y	Batch: contact time 24 h, pH 7, 23°C, 400 rpm, 7.13 µg/L	100%	[50]
Erythromycin	Zeolite Y	Batch: contact time 24 h, pH 7, 23°C, 400 rpm, 1.10 µg/L	100%	[50]
Levofloxacin	Zeolite Y	Batch: contact time 24 h, pH 7, 23°C, 400 rpm, 8.46 μg/L	96%	[50]
Tetracycline	Zeolite A with MCM-41	contact time: 100 min, 24°C, pH 7, 0.4 g/L adsorbent	99%	[51]
Tetracycline	13X zeolite modified with Cu(II) ions	Batch: contact time 116 min, pH 5.3, 0.4 g zeolite/L	86.18%	[52]
Azithromycin	Natural Slovak zeolites	Contact time: 30 min, pH 7, 10 g adsorbent	99.5%	[53]
Clarithromycin	Natural Slovak zeolites	Contact time: 30 min, pH 7, 10 g adsorbent	99.8%	[53]
Erythromycin	Natural Slovak zeolites	Contact time: 30 min, pH 7, 10 g adsorbent	98.5%	[53]
Acetaminophen	Mordenite	Computer simulation	-6%	
Atrazine	Mordenite	Computer simulation	43%	
Caffeine	Mordenite	Computer simulation	12%	
Carbamazepine	Mordenite	Computer simulation	40%	
DEET*	Mordenite	Computer simulation	97%	
Diazepam	Mordenite	Computer simulation	17%	[54,55]
Diclofenac	Mordenite	Computer simulation	-15%	
Dilantin	Mordenite	Computer simulation	14%	
Estrone	Mordenite	Computer simulation	100%	
Fluoxetine	Mordenite	Computer simulation	100%	
Gemfibrozil	Mordenite	Computer simulation	98%	
Hydrocodone	Mordenite	Computer simulation	23%	
lbuprofen	Mordenite	Computer simulation	98%	
Meprobamate	Mordenite	Computer simulation	97%	
Naproxen	Mordenite	Computer simulation	82%	
Oxybenzone	Mordenite	Computer simulation	99%	[54,55]
Pentoxifylline	Mordenite	Computer simulation	21%	
Sulfamethoxazole	Mordenite	Computer simulation	13%	
TCEP**	Mordenite	Computer simulation	21%	
Triclosan	Mordenite	Computer simulation	99%	

(Continued)

Table 3 Continued

Adsorbate	Туре	Experimental conditions	Percentage of removal	References
Trimethoprim	Mordenite	Computer simulation	46%	
Acetaminophen	Dealuminated Y	Computer simulation	-12%	
Atrazine	Dealuminated Y	Computer simulation	2%	
Caffeine	Dealuminated Y	Computer simulation	5%	
Carbamazepine	Dealuminated Y	Computer simulation	11%	[[] []
DEET*	Dealuminated Y	Computer simulation	6%	[54,55]
Diazepam	Dealuminated Y	Computer simulation	5%	
Diclofenac	Dealuminated Y	Computer simulation	-2%	
Dilantin	Dealuminated Y	Computer simulation	1%	
Estrone	Dealuminated Y	Computer simulation	35%	
Fluoxetine	Dealuminated Y	Computer simulation	98%	
Gemfibrozil	Dealuminated Y	Computer simulation	6%	
Hydrocodone	Dealuminated Y	Computer simulation	26%	
Ibuprofen	Dealuminated Y	Computer simulation	6%	
Meprobamate	Dealuminated Y	Computer simulation	7%	
Naproxen	Dealuminated Y	Computer simulation	2%	
Oxybenzone	Dealuminated Y	Computer simulation	47%	[54,55]
Pentoxifylline	Dealuminated Y	Computer simulation	3%	
Sulfamethox-	Dealuminated Y	Computer simulation	0%	
azole		-		
TCEP**	Dealuminated Y	Computer simulation	7%	
Triclosan	Dealuminated Y	Computer simulation	45%	
Trimethoprim	Dealuminated Y	Computer simulation	5%	

DEET* - N,N-diethyl-meta-toluamide;

TCEP** - Tri(2-chloroethyl) phosphate.

these materials have been modified with acidic agents, basic, cations and anions [59].

Modified montmorillonite with HDTMA has been used for the removal of penicillin G [57], montmorillonite which is a mineral of the clay family, its general formula is

$$M_{0.33}Al_2Si_4O_{10}(OH)_2 + nH_2O$$
 (1)

where M can be Na⁺, Ka⁺, Mg²⁺, Ca²⁺ [60], commonly found in sediments and soils. It can be used as an adsorbent material either directly or modified with one or more agents to improve its adsorption efficiency, as catalysts in chemical reactions and as oil bleachers [61,62].

Research locates montmorillonite as an adsorbent mainly for pesticides and heavy metals in water [63], there are currently few articles that use this clay for the removal of antibiotics, an example is the research of Nourmoradi et al. [57] where they modified the material with hexadecyltrimethylammonium (HDTMA), a removal of 83 mg of penicillin G per gram of clay was found.

Zeolites alone have the ability to sip metal cations, including heavy metals, drugs, and dyes, among other analytes [64]. The use of modified zeolites allow a greater selectivity for different solutes [65], the literature has reported the use of acidic agents, basic, cations, anions and surfactants for its modification [59], one investigation proposes

the use of a natural zeolite modified with $Ce(NO_3)_3$ [58], cerium has been placed as a relatively toxic metal for the environment, especially with its continuous discharge from various industrial processes [66], the modification with the HDTMA allowed a better removal of the analyte, the literature reports this surfactant as a good modifying agent for the removal of organic compounds such as dyes [67] and drugs [68].

Guocheng et al. [69] demonstrated the effects that antibiotics can have on clay soils or sediments, they concluded that montmorillonite can decrease or even deactivate the antibiotic effect of several compounds like ciprofloxacin and tetracycline, therefore, the research with this mineral is scarce.

Clays in general tend to be relatively inexpensive, they offer many advantages due to their ion exchange and adsorption capacities, these two characteristics are essential to manufacture materials that are specific for the removal of certain contaminants [46]. Modified zeolites are preferred due to their diversity of surface area, pore size and selectivity, which improves the adsorptive properties of the material. The final price of zeolite will depend on the chemical agents and the process used to modify them. The disadvantage is that penicillin would not be the only contaminant to be removed by the clay, but it would be a mixture of several substances lowering its removal efficiency.

3.2. Activated carbon

Activated carbon refers to a carbonaceous material of great porosity and activated with some chemical agent or by some physical technique [70], the carbon-rich material is commonly obtained by the pyrolysis of organic material or sludge resulting from water treatment plants [71].

This material has a myriad number of applications that include its use for pharmaceutical purposes as an antidote against poisoning [72], in creams for skin care and cleansing, and as an environmental pollution remediator [73].

There are many articles about its use for the treatment of pollutants, specifically several investigations have been carried out for the removal of drugs present in wastewater; Table 4 shows studies carried out for the removal of drugs with activated charcoal.

There are many articles where activated carbon presents high removal rates for various drugs, making it attractive for industries, however, when talking about the removal of penicillin G there are only a few articles about it. Some of these studies are shown in Table 5.

One of the most important advantages offered by activated carbon is that it can be extracted from almost any waste and give a reuse to a useless material, for example in the case of sorption with vid wood, vineyard wood that presents some fungal disease, these diseases can cause discoloration, necrosis and infection in leaves and stem, causing the death of plants [84], the material is carbonized and activated with different agents, and has been used for the removal of penicillin G.

Ania et al. [83] in their work entitled "Reactive adsorption of penicillin on activated carbons" published in 2011 said that one of the most important steps when removing penicillin G with any type of carbon is the activation where they highlight the use of basic and acidic activators, which generate a network of pores of large surface area favoring the removal of penicillin from wastewater.

Activated carbon has been one of the most widely used adsorbent materials over the years for the following reasons:

- (1) It is a relatively inexpensive material that can come from various sources such as: sewage sludge, fruit peels, and agricultural residues, among many other sources.
- (2) It has a large surface area and a very high microporosity, which makes it an extremely important material in adsorptive processes.

One of the points against this technique is its limitation for the adsorption of specific compounds, since having a large surface area and a high microporosity reduces its specificity for the removal of a particular pollutant.

3.3. Biosorption

Removal by biosorption refers to the removal of a pollutant by biological materials that are environmentally friendly, these adsorbents are economically viable due to their low costs, because they generate a little or no pollution and they are easy to handle [85]. This technique encompasses live sorbents such as fungi, algae, microorganisms, among many other types of biosorbents [86], over the

Table 4
Drug removal with activated charcoal

Adsorbate	Origin	Procedure	Adsorption capacity (mg/g)	Removal efficiency	Reference
Amoxicillin	Chicken feathers (keratin)	Carbonization (450°C-1 h), cooled and impregnated with ethanol and active with KOH (1:1-800°C-1 h)	102.8118	99.63%	[74]
Metronidazole	Siris seed	It was pyrolyzed, then activated with KOH (24 h) and irradiated with microwave waves (700 W–14 min)	191.31	NR	[75]
Tetracycline	Iris tectorum	Activated with H ₃ PO ₄ /Fe(NO ₃) ₃ (0.12:0.5) and microwaved (700 W–8 h)	588.33 mg/g	NR	[76]
Tetracycline Ciprofloxacin	Lignin	Carbonization (450°C–1 h), activated with H_3PO_4 (40%–1:2–12 h)	317.5121 318.1494	NR NR	[77]
Amoxicillin	Vine wood	Carbonization (600°C–2 h), activated with NaCl (3 M)	2.69	60%	[78]
Cephalexin		Carbonization (600°C–2 h), activated with NaOH 5% w/w	7.08	76%	
Tetracycline		Carbonization (600°C–2 h), activated with NaOH 5% w/w	1.98	88%	
Tetracycline Oxytetracycline	Activated carbon fibers	Microwave heated (600°C–15 min-N ₂)	312.5 312.5	22.70% 54.52%	[79]
Tetracycline Levofloxacin	Corn husk	Activation with FeCl ₃ (1:1–180 rpm–2 h–30°C) after pyrolysis was performed (300°C–1 h)	149.1 237.7	NR NR	[80]
Azithromycin	Azolla filiculoides	Batch: contact time 75 min, 60°C	164.2	98	[81]

years they have been used for the removal of metals, dyes, organic compounds and pharmaceuticals, the removal capacity of these analytes and a brief description of the procedure carried out is presented in Table 6.

In recent decades these methods have become more attractive for industries, especially those that produce pharmaceutical products, in the case of penicillin G, research is still scarce, articles focused on the elimination of penicillin G by means of biosorbents are shown in Table 7.

The use of penicillin G is promoted in the veterinary field so it is not strange to find this compound in water bodies [98]. The percentages of removal depend on the type of biosorption used, as well as the operating conditions; an advantage of this type of process is that the costs are relatively low compared to processes like advanced oxidation.

3.4. Other sorption materials

When talking about sorption of emerging compounds, the aforementioned materials are not the only existing ones, some good options are chitosan, carbon nanotubes, among some other potential sorbents. Table 8 shows some other adsorbents for the removal of penicillin G.

Table 5 Removal of penicillin G by activated charcoal

These materials have had a great use today, for example chitosan is a biopolymer that is currently located for the treatment of wastewater from industries such as pharmaceutical, cosmetic and food [103], research on removal of penicillin G with this material is scarce.

Carbon nanotubes have several layers of graphite that are classified according to the number of layers present in them, there are single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) [104], when in contact with a specific analyte (like penicillin G) functions as an adsorbent material.

There are other natural materials such as clays that can be used as sorbents for the removal of contaminants, kaolinite, ilite are commonly used due to their availability, stability and structural characteristics that facilitate the removal of this type of compounds [105], it is possible to apply them in studies for the removal of penicillin G.

4. Advanced oxidation techniques

Advanced oxidation techniques are processes that involve the formation of hydroxyl radicals (OH*) from water, hydrogen peroxide and catalysts supported on other

Origin	Procedure	Sorption capacity	Removal	Reference
		(mg/g)	efficiency	
Vine wood	Carbonization (600°C–2 h), without activation	NR	37.00%	
Vine wood	Carbonization (600°C-2 h), activated with KOH 5%w/w	NR	71.46	
Vine wood	Carbonization (600°C-2 h), activated with NaOH%w/w	8.41	73.94%	[70]
Vine wood	Carbonization (600°C-2 h), activated with ZnCl ₂ (1 M)	NR	68.79	[78]
Vine wood	Carbonization (600°C–2 h), activated with HNO ₃ (5 M)	NR	69.48	
Vine wood	Carbonization (600°C-2 h), activated with NaCl (3 M)	NR	70.56	
Activated carbon	NR	177	64.4	[82]
Activated carbon WVA 1100 (Westvaco, wood based, H ₃ PO ₄ activation)	Contact time 20 min, 25°C, pH 7	NR	NR	[83]

NR - Not reported.

Table 6
Removal of antibiotics by biosorption

Adsorbate	Biosorbent	Procedure	Adsorption capability	Degradation efficiency	Reference
Tetracycline	Green algae (Ulva lactuca)	The dried and crushed algae was used and an acid hydrolysis was performed	7.729 mg/L	79.3	[87]
Atrazine	Citricoccus sp.	The strain was identified and extracted using an EasyPure® Bacteria Genomic DNA, the gene was amplified by polymerase chain reaction	50 mg/L	NR	[88]
Ciproflox- acin	Termus sp.	Thermophilic bacteria were isolated, operating conditions 70°C and pH 6.5	57%	NR	[89]
Levofloxacin	Microalgae Chlorella vulgaris	The microalgae were contacted with levofloxacin for 11 d	12% (1 mg/L)	>90	[90]

Table 7
Removal of penicillin G by biosorbents

Biosorbent	Procedure	Initial penicillin G (g/L)	Degradation time (h)	Degradation efficiency	Reference
Paracoccus KDSPL-02	Batch: 30°C–35°C, pH 7–8, immobilized	1	4 h for 24 cycles	100%	[91]
Paracoccus KDSPL-03	Batch: 30°C-35°C, pH 7-8, immobilized	1.5	5 h for 24 cycles	100%	
Paracoccus KDSPL-04	Batch: 30°C-35°C, pH 7-8, immobilized	2	6 h for 20 cycles	100%	
Paracoccus KDSPL-05	Batch: 30°C–35°C, pH 7–8, free	1	12 h for 10 cycles	100%	
Paracoccus KDSPL-06	Batch: 30°C–35°C, pH 7–8, free	1.5	15 h for 10 cycles	100%	
Dried Rhizopus arrhizus	Batch: 35°C, pH 6	1	30 min	NR	[82]
Klebsiella pneumoniae Z-1	30°C, 121 rpm	0.3	24 h	>99%	[92]
Chamomile tea	pH 7 to 8	3	25 h	27%	[86]
Green tea	pH 7 to 9	3	26 h	<27%	
Mint tea	pH 7 to 10	3	27 h	<27%	
Phanerochaete chrysospor	ium	2	90–101 d	95.00%	[93]
Pseudomonas putida (fea	t)	0.003	40 d	36%	[94]
Daphnia magna		0.384	24 h	25%	[95]
Bacillus stearothermophil	1.5	50 min	70%-80%	[96]	
Lemna minor		0.2	75 min	94.60%	[97]

Table 8 Adsorbents for the removal of penicillin G

Material	Procedure	Adsorption capacity (mg/g)	Removal efficiency	Reference
Decaffeinated tea residues	Batch: contact time 40 min, pH 3	0.6719	39.3	[99]
Single-walled carbon nanotubes	Contact time: 105 min, 10°C, pH 5, 300 rpm	141	68.25%	[100]
Multi-walled carbon nanotubes	Contact time: 105 min, 10°C, pH 5, 300 rpm	119	56.37%	[100]
Chitosan extracted from Persian Gulf shrimp shell	Contact time: 10 min, pH 7	95.02	NR	[101]
Molecularly printed membranes	Incubation time 20 min	NR	NR	[102]

NR - Not reported.

materials, these techniques include photocatalytic oxidation, Fenton, ozonation, which aims to degrade or remove pollutants [106].

The hydroxyl radical has a great oxidizing power for organic matter, but at the same time the use of oxidizing agents that accelerate the degradation process is preferred, such as ozone (O₃), ultraviolet radiation (UV), hydrogen peroxide (H₂O₂), iron salts (Fe³⁺ and Fe²⁺) and catalysts such as titanium dioxide. There are two types of processes, photochemical and non-photochemical, this classification will depend on the participation of light during degradation or elimination [107].

Table 9 shows the studies found for the removal of drugs by means of advanced oxidation techniques:

It can be observed that at present there is a large number of articles that employ advanced oxidation processes as an alternative for the removal of drugs, their removal percentages are usually good (90%~99%), the articles for the elimination of penicillin G are few compared with other drugs, Table 10 shows the studies found for the removal of penicillin G (PG)

The removal efficiencies are high compared to other processes and techniques, the UV activation method showed that this process is a good option for the removal of penicillin G, unfortunately the costs at the industrial level are high compared to other processes.

The photocatalytic process has been accepted as a viable technique for the removal of organic compounds from

Table 9
Removal of antibiotics by advanced oxidation processes

Adsorbate	Technique	Procedure	Removal	Reference
Sulfadiazine	Photocatalysis	A TiO ₂ catalyst was used and a UV/Vis lamp was placed	100%	[108]
Trimethoprim		for 4 h at room temperature	>50%	
Amoxicillin			75%	
Enrofloxacin			50%	
Azithromycin			85%	
Carbamazepine	Ozonation	O_3 was used; $C_0 = 1.0 \text{ mg/L}$; $C_0 = 0.8 \text{ mg/L}$; Time = 10 min	95%	[109]
17β-Estradiol	Photocatalysis	A UV lamp (200 W) was used; $C_0 = 1 \mu \text{mol/L}$; $C_{\text{TiO2}} = 1 \text{ g/L}$	99%	[110]
Amoxicillin	UV/H ₂ O ₂	A UV lamp (254 W) was used; $C_0 = 0.5 \text{ mmol/L}$	3.93 mmol/L	[111]
Paracetamol	Ozonation	$C_0 = 5 \text{ mmol/L}; T = 25^{\circ}\text{C}; pH = 2$	100% and 30%	[112]
			mineralization	
Metronidazole	UV; Fenton; UV/H ₂ O ₂	$UV = 0-600 \text{ mJ/cm}^2$; $C_{H2O2} = 50 \text{ mg/L}$	20%	[113]

Table 10 Removal of penicillin G by advanced oxidation processes

Technique	Removal time	Removal efficiency	Reference
Persulfate UV activation	90 min	98.28%	[114]
Catalytic ozonation of penicillin G using natural zeolite loaded with cerium	15 min	99.5%	[58]
Sonophotocatalysis UV/WO ₃	120 min	91.30%	[115]
Sonophotocatalysis UV/ZnO	90 min	79.6	

water, because it is an environmentally friendly process, the disadvantage of this process is that there is the possibility of generating by-products or intermediates that could be more toxic, then it is advisable to couple photocatalysis with other techniques.

Oxidation processes have high yields, they are easy to use, but they can cause damage to the environment, as well as their costs are very high for industrial scales, currently this type of processes tend to be the favorites for the elimination of EPs due to their oxidizing power of organic matter.

5. Conclusions

Access to water has become a constant concern due to climate change, pollution and misuse. Currently, penicillin is still one of the most widely used antibiotics worldwide as a primary care drug in multiple diseases and ailments. This compound is difficult to degraded in the environment, causing an accumulation in ecosystems and resulting in the emergence of penicillin resistant strains, for this reason its consumption has been limited, as well as several pharmaceutical products. Scientists around the world have been concerned to solve this problem, they have developed a series of methods for the removal of this antibiotic from the environment, this review has shown the use of several materials for the treatment of EPs, being

the adsorption methods the most studied, the number of studies on the adsorption of penicillins with activated carbon from various origins is varied, the chemical and thermal modifications of the surface can turn them into multifunctional materials with both high and low yields, the removal depends on the amount of contaminants in the water to be treated, as well as the affinity of the adsorbent for the solute.

Advanced oxidation processes have been shown to have better results regardless of the process used, numerous studies show that the best bet is a degradation process for drugs, this is also demonstrated for the case of penicillin G where the percentages of removal were greater than 90%, this occurs due to the release of hydroxyl radicals that allow a rapid oxidation of organic matter, the main drawback with this technique are its high operating and maintenance costs, as well as its toxicity to the environment by the generation of hydroxyl radicals.

Finally, the lack of techniques such as coagulation, precipitation and integrated separation processes for the removal of penicillin G in wastewater was observed, so it is proposed to carry out studies in these areas to determine their advantages and disadvantages to remove drugs from water, currently there are some precedents for the use of these techniques for the removal of organic pollutants [116] therefore it is believed that under the ideal conditions the removal of penicillin G is possible.

Conflicts of interest

The authors declare that they have no conflicts of interest.

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