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REMOVAL OF ANTIBIOTIC EMERGING POLLUTANTS: AN OVERVIEW

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ABSTRACT

In recent decades the presence of pollutants has grown considerably around the world, along with the scarcity of fresh water. One of the environmental problems that has intensified lately is the presence of antibiotic resistant strains and the appearance of resistant genes due to the misuse and high worldwide consumption of this type of pharmaceutical products. Therefore, the number of investigations has been intensified to address these great problems that can affect public health and cause great economic losses around the world. For this reason, in this review, different antibiotics removal techniques in water have been compiled and analyzed critically.

Keywords: Emerging Pollutants; Removal; Antibiotics; Adsorption, Polymers.

1. INTRODUCTION

Water is one of the most vital resources and is indispensable to life, but, due to the global increase in technology, population, pollution, and the general lack of this resource, water conservation has become a problem at the world level, and combatting this problem [1, 2] has become a robust challenge. As a result of environmental pollution, so-called emerging pollutants (EPs) have arisen, which are of either natural or synthetic origin, are found in concentrations ranging from parts per billion to parts per million, and have the capacity to have serious effects on human health and aquatic ecosystems [3, 4]. EPs occur in aquatic ecosystems due to different sources of exposure, such as pharmaceuticals, endocrine disruptors, plastics, personal care products, pesticides, and fire retardants [2]. Pharmaceuticals play an important role in our daily lives, as they are used to minimize the impact of diseases, viruses, etc.[5, 6]

Exposure to antibiotics in aquatic systems has generated the development of antibiotic-resistant strains and genes. One example of this type of emerging antibiotic-based contaminant is tetracycline occurring at concentrations ranging from 10 to 100 µg L$^{-1,}$ which causes algae and nematode depletion in inland aquatic systems. From all the problems caused by the presence of antibiotics in aqueous systems, different methods can be described, such as electrochemical methods, biological methods, adsorption methods, membrane processes, and chemical oxidation processes [7, 8]. However, one of the most latent problems in most of the processes used to address these issues is the associated cost. Adsorption methods have great advantages, such as low costs and high efficiencies [9, 10]. There has been a significant increase in recent years with reference to publications reporting this problem from 2010 to 2021, and there has been an increase in research based on the removal of antibiotics and emerging contaminants (see Fig.1).

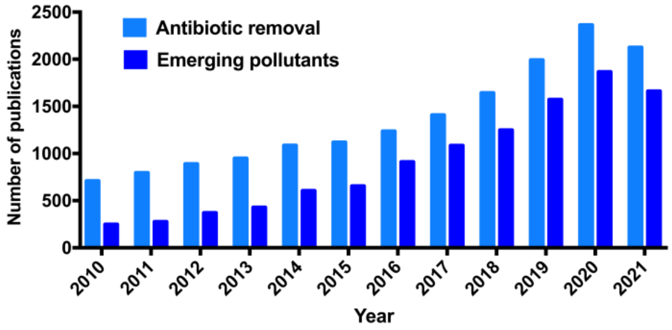

Figure 1. Annual publication report on the removal of antibiotics and emerging pollutants for the period 2010 to 2021. Data from Scopus and Web of Science on September 27, 2021.

This review aims to provide an update on the application of different techniques and a variety of materials reported in the scientific literature on the elimination of emerging pharmaceutical contaminants such as antibiotics, which generate resistant bacterial strains and public health problems worldwide.

2. GENERAL ASPECTS OF ANTIBIOTICS

Antibiotics are chemical compounds of natural and synthetic origin that have been present for several decades and are used to control (bacteriostatic) or kill (bactericides) a wide variety of infectious diseases, both in human and veterinary medicine [11-14].

Antibiotics are classified (see Table 1) into β-lactams, macrolides, quinolones, tetracyclines, and aminoglycosides, among several others [15]; their classification lies in their mechanism of action, molecular structure, spectrum of activity, etc., in combatting different types of bacteria [16]. Penicillins and cephalosporins interrupt the formation of the bacterial cell wall, while macrolides and aminoglycosides are responsible for "destroying" the synthesis of proteins; fluoroquinolones directly interfere with bacterial DNA synthesis, and tetracyclines inhibit bacterial protein synthesis [17, 18]. Antibiotics are a great help in combating a wide range of infectious diseases.

Antibiotics belonging to the family of β-lactams are highly used a worldwide, so their potential importance is considered and found within this classification (penicillin's, amoxicillin, ampicillin, flucloxacillin). These antibiotics act by killing bacteria by inhibiting cell wall formation [18, 19].

Tetracyclines are antibiotics originally derived from several streptomycin species corresponding to metabolism by products[12, 20] and have characteristics that allow them to act on receptors via different cellular properties. Chemically, tetracyclines are composed of a 4-ring skeleton (see Fig. 2) that confers rigidity. Fuoco (2012)[21] reported that tetracyclines inhibit protein synthesis in bacteria by the amino group at position C4 (antibacterial activity) and ketophenolic tautomers at positions C1 and C3 of ring A [22].

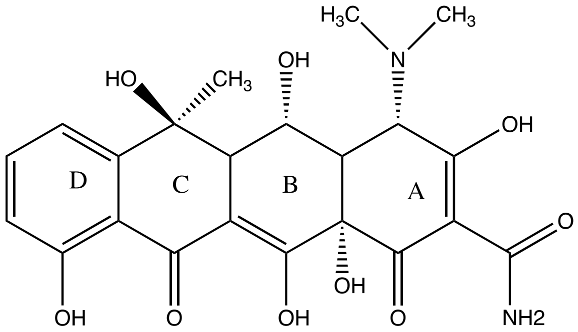

Fig. 2. Chemical structure of oxytetracycline (OTC). Adapted image from paper by B.L. Rivas et al. 2020[22].

Quinolones are broad-spectrum bactericidal antibiotics that belong to the antibiotic group that is responsible for preventing bacteria from multiplying by inhibiting DNA girasa [15]. Quinolones kill bacteria quickly, although, in turn, they gain resistance through mutations or the altered expression of target proteins [23]. Therefore, there are reports about the effects of quinolones and other antibiotics on drinking water [24].

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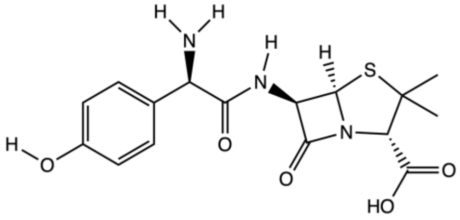
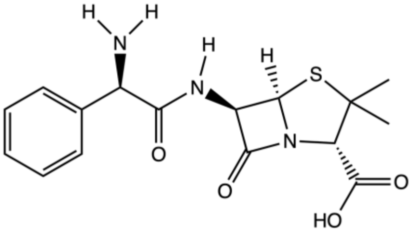
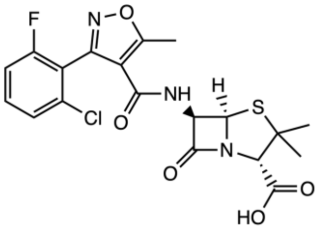
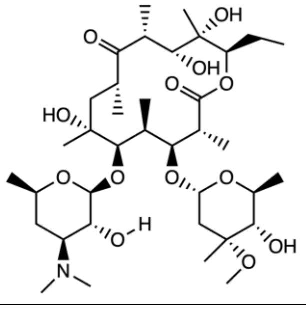
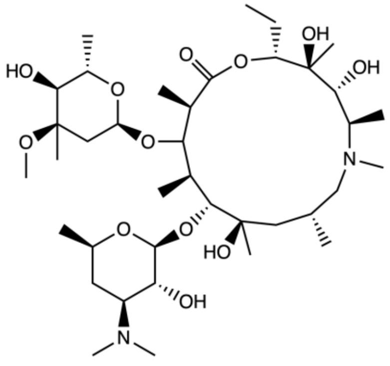
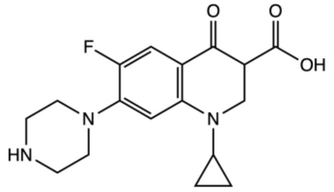
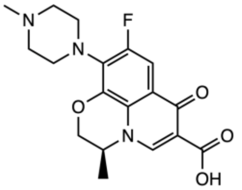
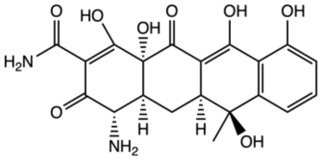
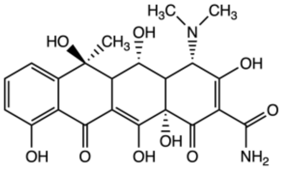
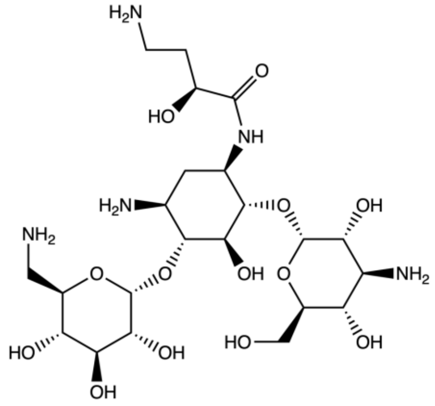
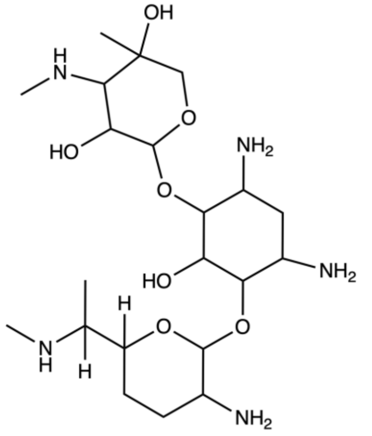
Russell (2004) reported that macrolides are thus classified because, in their molecular structure, they contain large lactone rings linked through glycosidic bonds to amino sugars. These macrolides are prepared from the bacterium Streptomyces. This type of antibiotic is bacteriostatic and interferes with the production of the binding of bacterial proteins 50S , and it is quite effective against pneumonia, influenza, etc .[17].

Finally, aminoglycosides (molecular structures containing amino sugars) are responsible for obstructing the synthesis of bacterial proteins essential for the growth of bacteria. These antibiotics act mainly in the digestive tract, fighting enteric infections [14, 15, 17, 25]. Many antibiotics, such as tetracyclines, sulfonamides, and quinolones, are widely used for the treatment of many infectious diseases. However, tetracycline is an antibiotic that is excreted from the body through the urine and feces, with approximately 90% of the main compound ending up in bodies of water[26].

The increase in the human population has contributed to the increase in the use of antibiotics. Between 2000 and 2015, the number of strains increased by over 65%, and most have the ability to generate highly resistant strains in the environment, so it is feared that the high presence of these compounds in different bodies of water may be an important pollution factor, as well as causing various diseases in both humans and animals [27, 28]. This is mainly because, with the increase in world population, agricultural practices and industrialization are increasing in parallel and directly increasing the demand for water, which is related to the presence of resistant microorganisms because wastewater treatment plants perform little or no elimination of these pollutants [28].

Table 1. Main groups of antibiotics found in aquatic systems.

Group	Antibiotic	MW (g/mol)	Molecular Structure
ß-Lactams	Amoxicillin	365.4	
	Ampicillin	394.4	
	Flucoxacillin	453.9	
Macrolides	Erythromycin	733.9	
	Azithromycin	748.9	

Quinolones	Ciprofloxacin	331.4	
	Levofloxacin	361.4	
Tetracyclines	Tetracycline	444.4	
	Oxytetracycline	460.4	
Aminoglycosides	Amikacin	585.6	
	Gentamicin	477.6	

3. ANTIBIOTICS REMOVAL

Antibiotics are known to combat the presence of diseases caused by bacteria worldwide. However, these pollutants have become a worldwide problem in recent years due to their presence in aqueous systems and are considered emerging pollutants, like many other organic pollutants. Because of this, many organic compounds have been considered highly hazardous because they can cause serious problems in both humans and in various ecosystems[29]. Among the many polluting compounds, pesticides, industrial waste, household waste, dyes, antibiotics, analgesics, endocrine disruptors, etc., are present in wastewater, groundwater, drinking water, and even in the soil [30-32]. The presence of pharmaceutical products is considered a danger that affects ecosystems due to accumulation, affecting microorganisms and causing the appearance of resistant bacterial strains [32, 33], which create problems for human and animal health [34, 35].

The generation of antibiotic resistance occurs because bacteria manage to decrease or eliminate the effectiveness of antibiotics that prevent certain infectious diseases [16]. To reduce the problem of the presence of antibiotics in environmental systems, a wide variety of techniques have been reported that can range from biological [36], chemical, physical [37], or a combination of these to eliminate or reduce the concentration, that do not affect environmental systems. Processes such as advanced oxidation and adsorption are used to safely and effectively remove compounds. The latter are the most economical, easy to obtain, and have a high percentage of reuse [34, 37].

3.1. Removal by Advanced Oxidation Processes (AOP)

There are processes that use technologies to degrade and mineralize recalcitrant organic matter found in different bodies of water by reacting with hydroxyl radicals [38]. They are known as advanced oxidation processes, and they use oxidants (such as the aforementioned hydroxyl radical) that are responsible for decreasing the levels of chemical oxygen demand (COD)/biological oxygen demand (BOD) by separating the oxidizable organic and inorganic components. AOP is considered an alternative to traditional methods and that makes it possible to increase the degradability of contaminants in waste water and the inactivation of pathogenic organisms [39, 40].

These processes are particularly used in the treatment of wastewater containing toxic, recalcitrant compounds and pharmaceutical residues, among others [41-43]. These compounds involve the formation of hydroxyl radicals (OH), which are very reactive and nonselective substances with oxidation potentials greater than those of the most common oxidants (ozone, chlorine, etc.) with values of Eo =2.8 V and are able to react with almost all classes of organic compounds [44, 45]. Hydroxyl radicals are continuously produced chemically, photochemically, and electrochemically, among other ways.

Specifically, AOPs are responsible for oxidizing contaminants through hydrogen sequestration or electrophilic addition to double bonds that generate free organic radicals and react with oxygen molecules by forming peroxy radicals, which initiate oxidative degradation reactions and lead to the mineralization of contaminants. It should be mentioned that the formation of radicals reacts very quickly in aromatic compounds and more slowly in aliphatics, attacking the ortho and para positions of one of the electrodonator substituents (activating group)[46].

It is important to consider that there are a number of processesin AOPs, such as ozonization, Fenton, photolysis, and photocatalysis [45, 47]. Each of the above processes is used for the treatment of polluted water due to the constant threats of human, urban, industrial, and agricultural activities that use a wide range of polluting products, such as industrial chemicals, pesticides, pharmaceutical compounds, etc. [48] Among the pollutants mentioned, it is important to mention those groups of recalcitrant compounds, such as antibiotics, which are compounds that are difficult to degrade due to the complexity of their structures [49, 50] and contact with the environment, can constitute a high risk because they may cause resistance incertain bacterial strains [48].

Thus, to achieve a good response to advanced oxidation processes, it is important to consider that the efficacy of OH radicals makes them the best oxidant after fluorine[51, 52]. Table 2 summarizes a series of reactions that allow us to determine reduction potentials.

Table 2. Reduction potential in aqueous media of the most used oxidant agents

Oxidizing	Reduction reaction	E°/V
Fluorine	$F_2(g) + 2H^+ + 2e^- \rightarrow 2HF$	3.05
	$F_2(g) + 2e^- \rightarrow 2F^-$	
Hydroxyl radical	$OH + H+ + e^- \rightarrow H_2O$	2.80
Ferrate	$FeO_{42}^- + 8H+ + 3e^- \rightarrow Fe_3+ + 4H_2O$	2.20
Ozone	$O_3(g) + 2H+ + 2e^- \rightarrow O_2(g) + H_2O$	2.08
Hydrogen peroxide	$H_2O_2 + 2H+ + 2e^- \rightarrow 2H_2O$	1.76
Permanganate (b)	$MnO_4^- + 8H+ + 5e^- \rightarrow Mn_2+ + 4H_2O$	1.51
Permanganate (a)	$MnO_4^- + 4H+ + 3e^- \rightarrow MnO_2(s) + 2H_2O$	1.67
Chlorine	$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36

3.1.1 Ozonization:

Ozonization is an advanced oxidation process that uses ozone as a strong oxidizing reagent, reacts with different organic substances and can occur by selective electrochemical attack on unsaturated bonds and aromatic compounds or by the indirect reaction of free radicals occurring during oxidation processes [45]. Some authors, such as Zhu et al. (2017) applied his treatment to wastewater and observed that compounds of higher molecular weight were dissociated into other small molecules [53]. Ozonization processes, due to their high oxidizing capacity, are a method used to degrade microorganisms from water. However, it has been reported that this type of treatment is limited due to slow kinetics and the formation of reaction intermediates that may be more toxic than the original compound [45, 54].

Because of this, catalytic ozonization is one of the techniques that can be used to improve the degradation yields of compounds that are less sensitive to molecular ozone [55, 56]. The ozonization process should be considered to have several advantages, including easy installation, little mounting space, a constant volume of effluent, and a lack of sludge formation. Ozone is generated in situ, and the remnants of ozone are removed because they decompose into oxygen[51, 57].

3.1.2 Fenton

The Fenton reaction corresponds to one of the most studied advanced oxidation processes; here, iron is the catalyst, and hydrogen peroxide (Equation 1) corresponds to the oxidant [58-60] and aims at the production of hydroxyl radicals, which are highly reactive, making them feasible to use them in the degradation of a diversity of organic compounds [61].

$$Fe^{2+}+H_2O_2\rightarrow Fe^{3+}+{}^{\bullet}OH+OH^- \quad (Eq.\ 1)$$

$$Fe^{3+}+H_2O_2\rightarrow Fe^{2+}+HO^{\bullet}_2+H^+ \quad (Eq.\ 2)$$

According to Babuponnusami and Muthukumar (2012) [62], the process is carried out in different stages consisting of pH adjustment, oxidation, neutralization, and coagulation/precipitation. In reported studies, it has been observed that at very low pH (2.5), ferrous complexes and the inhibition of the reaction between Fe^{2+} are formed [63]. In addition, at pH > 5, the ferric complexes formed can inhibit the reaction, obtaining that the optimal value of the medium is approximately 2.8 to 3.0 and that the reaction is propagated by a catalytic behavior $Fe^{3+/}Fe^{2+}$ (Eq. 2).

One of the limitations of the Fenton process is the constant supply of reagent (H_2O_2)[45, 63], so one of the alternatives is the use of the Fenton process with UV radiation, called photofenton. This process has applications in various areas, such as sewage, sludge, and/or soil. Table 3 shows the efficiency of the removal by Fenton processes of antibiotics present in wastewater and the inactivation of pathogenic organisms[64]. Thus, Elmolla et al. (2010) studied the use of artificial neural networks (ANNs) to predict and simulate the degradation of antibiotics such as amoxicillin, ampicillin, and cloxacillin in aqueous solutions considering it in terms of COD elimination by the Fenton process, where it was determined that there was a high effect on the degradation of antibiotics in terms of DOC elimination[40].

Michael et al. (2012) [36] reported a method of degradation of antibiotics (ofloxacin and trimethoprim) at low concentrations (1 mg L^{-1}) in household effluents through the solar-powered Fenton process (solar photo Fenton), wherein low concentrations of iron and hydrogen peroxide ($[Fe^{+2}]_0$ =5 mg L^{-1}, $[H_2O_2]_0$ =75 mg L^{-1}) were considered and demonstrated to be an effective method for the removal of these antibiotics. Fiorentino et al. (2019) evaluated the effect of antibiotic resistance by treating wastewater with the Fenton process (see Table 3), and 7 of the 10 detected antibiotics (azithromycin, ciprofloxacin, clarithromycin, erythromycin, lincomycin, levofloxacin, enrofloxacin, doxycycline, clindamycin, and metronidazole) were effectively eliminated (among 60–100%) using iron and hydrogen peroxide ($[Fe^{2+}]_0$ = 5mg L^{-1}, $[H_2O_2]0$ =50 mg L^{-1}) [65].

Table 3: Removal efficiency of antibiotics in water by the Fenton process

Antibiotic	Operation Conditions	Maximum removal efficiency	Reference
Ciprofloxacin (CPR)	H_2O_2 = 20 - 84 mM Fe^{2+} = 5 - 21 mM pH= 5	74%	[51]
Ciprofloxacin (CPR)	H_2O_2 = 26 - 51 mM Fe^{2+} = 5 - 10 mM pH= 3	76%	[51]
Ciprofloxacin (CPR)	H_2O_2 = 50 mM Fe^{2+} = 5 mM pH= 2.8	100%	[65]
Ciprofloxacin (CPR)	H_2O_2 = 12 mM Fe^{2+} = 1,75 g L^{-1} pH= 3.0	89%	[66]
Doxycycline (DXY)	H_2O_2 = 2.9 - 26.5 mM Fe^{2+} = 0.09 - 2.1 mM pH= 5.0	100%	[51]
Doxycycline (DXY)	H_2O_2 = 50 mM Fe^{2+} = 5 mM pH= 2.8	100%	[65]
Levofloxacine (LVF)	H_2O_2 = 0.375 - 1.5 mM Fe^{2+} = 0.0375 - 0.15 mM pH= 3	100%	[51]
Levofloxacine (LVF)	H_2O_2 = 50 mM Fe^{2+} = 5 mM pH= 2.8	61%	[65]
Trimethoprim (TRM)	H_2O_2 = 0.5 - 4 mM Fe^{2+} = 0.025 - 0.2 mM pH= 3	100% in ultrapure water 36% in synthetic wastewater	[51]

3.1.3 Photolysis

In addition to ozonization and Fenton reactions, photolysis is also considered to be an advanced oxidation process, which consists of the breakdown of bonds by radiant energy. The reaction carried out in photolysis processes is defined by the interaction of one or more photons with a "target molecule". It is important to consider that reactions, specifically the formation of radicals, are affected by environmental conditions such as pH, temperature, and hydrogen peroxide concentration [67]. To obtain radicals such as superoxide, ozone, and hydrogen peroxide, electron transfer from the excited state of the organic compound to molecular oxygen must occur due to the homolysis of the weak bonds or other wise [51, 68]. Two types of photolysis can be distinguished:

1. Photolysis of O_3 (O_3/UV): This type of photolysis in aqueous medium starts its decomposition by the formation of hydroxyl radicals, so UV allows an increase in the process of the degradation of polluting compounds by the formation of radicals. However, problems arise in ozonization processes due to the limitations of UV irradiation [69].
2. Photolysis of H_2O_2 (H_2O_2/UV): This type of photolysis has a low extinction of UV rays, so there is lower removal efficiency. Epold et al. (2012) reported photolysis (and other methods of AOPs) as a process for the degradation of ibuprofen (IBP) and sulfamethoxazole (SMX) in different aqueous matrices, where most of the removal of SMX was achieved with UV photolysis, and the most rapid removal of IBP was achieved with H_2O_2/UV [39]. Likewise, Rodríguez-Chueca et al. (2019) performed wastewater treatments using different types of AOPs for the removal of more than 53 antibiotics, among which are macrolides (azithromycin: through 100%), fluoroquinolones (ciprofloxacin and ofloxacin: through 100%), sulfonamides (sulfadiazine 95% sulfamethoxazole 50%), lincosamides, and nitromidazole (metronidazole 90%), among others, and these removal methods via AOPs were successful as evidenced by good removal [70].

3.1.4. Photocatalysis

In general, photocatalysis corresponds to an ecological and successful method that involves the absorption of light by a catalyst, that is, it is a process of the acceleration of a photoreaction in the presence of a catalyst. In this photocatalytic oxidation process, organic pollutants are destroyed in the presence of different types of semiconductor photocatalysts, like TiO_2, ZnO, WO_3, SnO_2, and V_2O_3 [51, 71, 72], that allow for the conversion of photonic energy into chemical energy [73]. Likewise, Pham T. D. et al. (2020) reported two types of catalysis that allow for the removal of organic pollutants: heterogeneous and homogeneous catalysis. These processes are part of the advanced catalytic oxidation processes [45].

Heterogeneous catalysis is a process of photocatalysis in which the liquid phase can be distinguished, which is where the contaminants are located while the catalyst is in the solid phase [74, 75]. Among the photocatalysts used, titanium dioxide is the most common because of its characteristics of stability and low cost [76, 77].

Homogeneous catalysis states that homogeneous catalysis processes are involved in catalytic ozonation, and the most frequently used catalysts are transition metals such as Cr(II), Cu(II), Fe(II), Fe(III) among others, due to the interaction they have with them [45].

The removal of antibiotics by photocatalysis using TiO_2 is the most common method; however, these AOPs help to remove different types of organic compounds. Pragada and A. K Thalla (2021) studied the degradation of triclosan in gray water treatments that are discharged from an anaerobic-aerobic treatment system using a solar photocatalytic reactor, where they obtained an 83.27% triclosan removal efficiency at the laboratory scale [78]. We also present other studies in which the elimination of levofloxacin occurs through photocatalysis and ozonation processes, in which removal corresponding to 59% and 70% was measured [79]. Guo et al. (2017) reported the degradation and mineralization of amoxicillin in aqueous suspensions, where the TiO_2 catalyst allowed for the removal and mineralization of 93%[80]. Another example of ozonization-photocatalysis was reported [77]to have benefits such as disinfection and the removal of recalcitrant contaminants from wastewater.

3.2 Removal by Adsorption Processes

Adsorption processes are mass transfer processes wherein gas or solute sorption phenomena occur over liquid or solid surfaces and are used in the purification of wastewater for the elimination of different types of compounds, whether organic or inorganic, that are not biodegradable [81]. Therefore, adsorption processes are considered the most promising in terms of efficiency, simplicity, and economy [41]. In recent years, the application of materials for the adsorption of antibiotics has increased considerably due to the interactions carried out between the adsorbate molecules and the functional groups or specific surface of the adsorbent. At present, a large amount of materials used in antibiotic adsorption processes have been reported among these materials, nonpolymeric materials are highlighted and used frequently by the scientific community, as they are materials based on activated carbon, such as clay and ceramic, biochar and metal-organic frameworks (MOFs), and polymer-based materials.

3.2.1 Activated Carbon

Activated carbon corresponds to one of the adsorbents most commonly used for the removal of organic pollutants as inorganic on an industrial scale due to its extensive characteristics and applications, as it may be used in the form of dust, impregnated or granulated, and each shape has a specific purpose [43, 82, 83]. The high adsorption power is due to the variety of porous networks, such as micro (small pore diameter ≤ 2 nm), meso (pores with ranges between 2 nm to 50 nm) , and macropore networks (pores in a range > 50 nm). The microporous structure gives a large surface area to the material, while the mesopores allow for the adsorption of molecules, and the macropores function as transport channels that finally reach the micropores. Thus, activated carbon-based materials have the ability to be used as universal adsorbents [33, 84], as well as for water and air purification at an industrial scale [83, 84].

The production of activated carbon is generally divided into two stages corresponding to the pyrolysis of the precursor, which can be charcoal, wood, etc., followed by activation producing porosity [84]. It should be noted that activated carbons are generally hydrophobic, which confers the presence of polar groups, allows them to better interact with the contaminant and varies the experimental parameters, such as pH, ionic Strength, and temperature [33]. Some works in the literature have reported in recent years on the removal of pharmaceutical pollutants such as antibiotics. Wan et al. studied magnetic activated carbon for the removal of the sulfonamide antibiotic, as this adsorption method is performed by coupling a pretreatment and treatment assisted by glucose and iron sludge and showed good results when removing sulfonamide via adsorption; however, it was determined that this process is highly pH dependent, and it has been determined that the pH values increase from 5 to 9 in concentrations of 40 to 50 mg g^{-1}[85]. Berges et al. 2020 described the removal of antibiotics in water through the adsorption process and determined theremoval of four antibiotics present in the fluoroquinolone families (enrofloxacin approximately 50%), beta lactams (amoxicillin approximately 41%), trimethoprim (trimethoprim approximately 50%), and sulfonamides (sulfadiazine 67%); in addition, it was determined that sulfonamides and trimethoprim have a high affinity for activated carbon, which facilitates their adsorption [86].

3.2.2 Clays

Clays are hydrated aluminosilicate minerals that are highly available in nature, can be found in a high degree of purity, and that, due to their physicochemical properties, can adsorb organic species [87]. This type of material is highly abundant in soil and sediments, allowing the removal of different organic compounds [88], so these materials are important because they influence the transport of pollutants through the environment (Wu et al. 2013)[89]. One of the advantages of using clay materials in removal processes is that it is an economical material with a high capacity to remove organic and inorganic pollutants [90]. One of its important characteristics, in addition to being one of the more abundant adsorbents in nature, is that it has a high ion exchange capacity, high specific surface area, and good colloidal dispersion, making these materials good for the treatment of wastewater containing organic and inorganic compounds, among others [91-93].

Different studies have been based on the chemical modification of clays to increase adsorption capacity by increasing the content of total organic carbon and surface load, which allows for better and greater elimination of organic pollutants [89, 94]. However, activated carbon is still used in greater quantities than are these minerals, due to its significant use in the removal of organic and inorganic compounds. Activated carbon presents a great disadvantage since clay minerals, such as kaolinite and montmorillonite, are much more economical, thus environmental remediation via activated carbon is greatly limited. Based on this, a series of studies have shown that these minerals have a high affinity for emerging antibiotic-type contaminants, such as tetracyclines [95-97], ciprofloxacin [89, 98-100], and sulfonamide [101], among others. Maged et al. (2020) reported the removal of tetracyclines through the use of the thermal activation of bentonite because it has better properties than does natural bentonite; it was determined that the adsorption of the monolayer measured by the Langmuir model was 156.7 and 388.1 mg g^{-1} for natural bentonite and heat-activated bentonite, respectively [92].

However, as we have already mentioned on several occasions, antibiotic resistance is a global problem, so the use of these clays is of major interest due to their high availability and low cost. Gulen and Demircivi (2020) exposed the clays while controlling the contact time, pH of the solution, and temperature and achieved the removal of ciprofloxacin in aqueous solutions using montmorillonite (MMT), obtaining maximum adsorption results close to 98% at pH 7[99]. Likewise, Wabel et al. (2020) reported the removal of chlorotetracycline from contaminated water bodies using natural clays, and they determined that, at a pH range ranging from 3.5 to 5.5, the maximum removal reached 98.80–99.05% due to the high amounts of esmectite and kaolinite present in the clay used by the authors [102]. Ashiq et al. (2021) studied kaolinite and kaolinite modified as adsorbents for the removal of oxytetracycline in aqueous media, and the study considered the effect of pH, ionic strength, initial concentration, and contact time of oxytetracycline adsorption, obtaining a maximum adsorption of 60.5% at pH 6 with the modified kaolinite [103].

3.2.3 Biochar

Biochar is a carbon-rich material that has high porosity and specific large surfaces and is synthesized from the biomass pyrolysis of plant and animal origin[69, 104]. Ahmad et al. 2014[69] reported a series of definitions for biochar based on several authors, among whom we found Lehmann and Joseph (2009)[105], who defined biochar as "a carbon (C)-rich product when biomass such as wood, manure or leaves is heated in a closed container with little or no unavailable air". Shackley et al. (2012)[106] defined biochar as "the porous carbonaceous solid produced by the thermochemical conversion of organic materials in an oxygen depleted atmosphere that has physicochemical properties suitable for safe and long-term storage of carbon in the environment." Verheijen et al. (2010)[107] defined biochar as "biomass that has been pyrolyzed in a zero or low oxygen environment applied to soil at a specific site that is expected to sustainably sequester C and concurrently improve soil functions under current and future management, while avoiding short-and long-term detrimental effects to the wider environment as well as to human and animal health". This is how this material has begun to be used as an effective and cost-effective adsorbent for the removal of organic and inorganic pollutants [104, 108], carbon sequestration, and the recycling of agricultural waste and byproducts. In addition, water retention in soils containing biochar increased by 18%, while nutrient-leaching decreased [109]. According to Premarathna et al. (2019), the high efficiency of biochar is related to features such as surface area, pore size, and ion exchange capacity [104].

In terms of its physico-chemical characteristics, biochar has a pH ranging from neutral to alkaline, but biochar with acidic pH has also been recorded. These pH values depend mainly on the material from which they are made [110]. On the other hand, this material is highly effective for the removal of organic pollutants such as tetracyclines, as it is more economical than methods such as ozone oxidation and photocatalytic degradation, among others. Therefore, biochar seems to be a very good alternative in terms of adsorption properties, profitability, and easy operation [111]. Different investigations have been reported using biochar as an antibiotic removal material [108], such as tetracyclines [104], sulfadiazine [112, 113], sulfamethoxazole, sulfametazine [112], and sulfonamide [114].

Cheng et al. (2020) reported the use of biochar derived from grapefruit husk; it obtained a fairly effective removal of sulfamethoxazole, sulfadiazine, and sulfamethazine in ranges of 82.44–88.15%, 53.40–77.53%, and 61.12–80.68%, respectively [112]. On the other hand, Jiang et al. (2018) studied the removal of antibiotics and heavy metals using biochar derived from pig manure digestate (MDS) due to its high number of functional groups available. The author reported that this biochar had the capacity to remove 83.98% As(III), 83.76% sulfadimidine, and 77.34% tisoline [115].

3.3 Removal process by polymeric materials

Among the different removal methods reported in the literature [116-118], adsorption is one of the methods with high yields in the elimination of emerging antibiotic-type contaminants and one that is being used in conjunction with other elimination methodologies. This is mainly due to its low cost, easy application, and simple design, factors that make it promising in the elimination of antibiotics in aqueous solutions. There are currently a variety of adsorbents used in removal studies, including adsorbents to inorganic material bases such as clay, metals, and oxides, carbon adsorbents, etc. [92, 119, 120]. However, polymer applications have become a major source of solutions to the problem of organic pollutants [121]. Due to their great versatility, polymeric materials are used for antibiotic removal, mainly due to the great variety of functional groups present in their chains that are responsible for the interactions in the removal processes. Table 4 shows the main functional groups present in different polymer matrices, which have the ability to interact with different antibiotics [122]. Different polymeric materials used in recent years in antibiotic removal studies have been reported in the literature; within this type of material, we can find hydrogels, composite polymers, nanocomposites, and water-soluble polymers and membranes (see Fig. 3A).

Table 4. Different polymer matrices containing functional groups with antibiotic interaction capability.

Polymer	**Available functional group**	**Reference**
Poly(acrylamide)	$–OH$, $N–H$, $–COOH$, $–CONH_2$	[123]
Polyvinyl alcohol/chitosan	$–OH$, $–CH_3$, $–C–O–C$, $–NH_2$	[124]
Lignin-*g*-poly(acrylic acid)	$–OH$, $–C–O$, $–C–O–C$	[125]
Chitosan alkylated	$– [N+(CH_3)_3]$, $–NH_2$, $–OH$	[126]
Poly[3-(methacryloylamino) propyl] dimethyl (3-sulfopropyl) ammonium hydroxide-*co*-sodium 4-styrenesulfonate]	$– [N^+(CH_3)_3]$, aromatic rings, RSO_3^-, $N–H$, $–C = O$	[127]

It should be noted that the great versatility of polymeric materials allows for a variety of different interactions with antibiotics, which will depend on the functional groups and structures present in both the adsorbent and the adsorbate. These interactions are the main mechanisms in retention processes, including i) electrostatic interactions, the main retention mechanism in most materials reported in the literature; ii) hydrophobic interactions; iii) hydrogen bonds; iv)π-π interactions; and v) the morphology of the materials. In specific cases, the pore content [22, 128-131] would also be considered. Fig. 3B shows the main mechanisms of the retention processes.

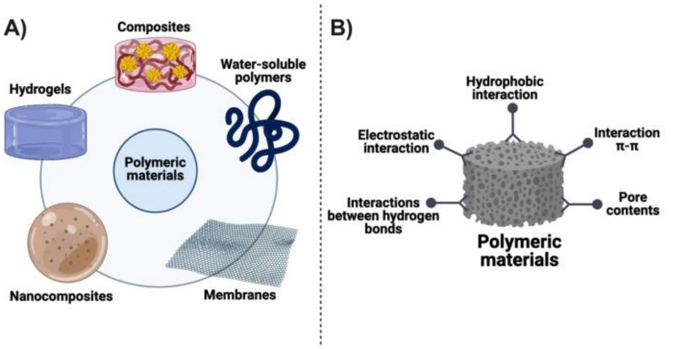


Fig. 3 A) Different polymeric materials used in the removal of antibiotics and B) main factors in the mechanisms of the elimination of antibiotics. Representation made by information from Urbano et al. [131] and Rivas et al. [22].

3.3.1 Hydrogels

Hydrogels (HGs) have been widely used in different research fields, including agriculture, food additives, biomedical applications, and drug administration; however, in recent years, they have also been widely used in environmental applications as adsorbent materials [122]. HGs are based on the formation of three-dimensional polymer networks that have the capacity to swell with high water contents, a property that makes HGs unique. These materials are characterized by their flexibility and biocompatibility, which make them excellent candidates in different fields of applied sciences and, specifically, as adsorbent materials [132, 133]. To obtain HGs, a main monomer reagent, a crosslinking reagent, and an initiator are all required. Some monomers and polymers used to obtain HGs are shown in Fig.4. It should be noted that hydrogels can have a wide variety of properties according to different factors, as can the cross-linking, which can be via ionic transient bonds, hydrogen and hydrophobic bridges, or permanent covalent bonds. Additionally, the technique of obtention, which can vary in polymerization, mass, reticulation, and reverse suspension [122, 134]. Some applications of hydrogels in the elimination of antibiotics are summarized below.

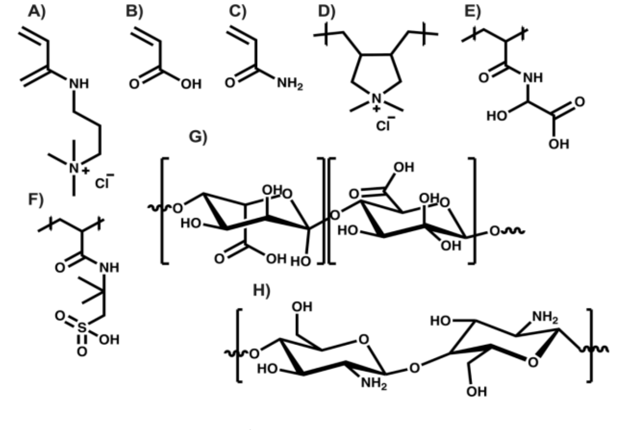


Fig. 4. Chemical structures of monomers and synthetic and natural polymers to obtain hydrogels. A) 3-Acrylamidopropyl-trimethylammonium chloride, B) acrylic acid, C) acrylamide, D) poly(diallyldimethylammonium chloride), E) poly(2-acrylamidoglycolic acid), F) poly(2-acrylamido-2-methyl-1-propansulfonic acid, G) alginic acid, and H) chitosan. The structures were drawn using ChemDraw Professional 16.0

Addolmaleik et al. investigated the removal of tetracycline by hydrogels of chitosan and polyalcohol-electrolyzed nanofibers obtained by cross-linking with glutaraldehyde. The hydrogel obtained had a maximum adsorption capacity of 102 mg g^{-1} with adsorbent doses ranging between 0.05 and 0.25 g in 20 mL of solution and concentrations between 50 and 250 mg L^{-1}. The experimental results were adjusted to Langmuir isotherms and presented optimal values of the adsorption of tetracycline with adsorbent doses of 0.25 g and 100 mg L^{-1}tetracycline [135]. Ranjibari et al. removed tetracycline from chitosan pearls conjugated with tricaprilamine chloride, a cationic surfactant (aliquat-336).In this study, adsorption processes were performed in the pH 5–11 range, obtaining a maximum adsorption capacity of 22.42 mg g^{-1} at 45 °C and adjusting to Langmuir isotherms. Similarly, the interactions that govern the absorption processes in this study were through hydrogen bond interactions, π -ion interactions, and π/xH interactions[136]. Wang et al. investigated the use of chitosan-derived granular hydrogels with 3D structures grafted with acrylic acid as a monomer for the efficient adsorption of fluoroquinolone-type antibiotics in aqueous solutions. In this study, adsorption parameters such as pH, contact time, concentration, and ionic force were investigated. The hydrogels obtained showed porous 3D structures and ionizable groups due to the grafting of acrylic acid. The maximum adsorption of 267.7 mg g^{-1} ciprofloxacin and 387.7 mg g^{-1} enrofloxacin was observed at pH 3. Additionally, load-discharge cycles were tested, obtaining adsorption capacities higher than 85% after the fifth cycle, which confers hydrogel capabilities in the elimination of fluoroquinolone-type antibiotics [137].

Li et al. investigated the use of double-stranded hydrogel beads from sodium alginate and *K*-carrageenan ionic reticulation with capabilities in the removal of ciprofloxacin, where the obtained hydrogel beads exhibited an adsorption capacity of 245 mg g^{-1} and minor swelling compared with single-network hydrogel beads. The hydrogel beads were prepared using different polymer concentrations, which were added to calcium chloride solutions with constant agitation and with the help of a peristaltic pump for a period of 12 h to complete the gelling processes. Fig. 5 shows the procedure for the synthesis of the hydrogels. With respect to the adsorption nature, hydrogel beads have physical and chemical adsorption, where it is believed that electrostatic interactions play an important role, as well as hydrogen bonds in adsorption processes [133].

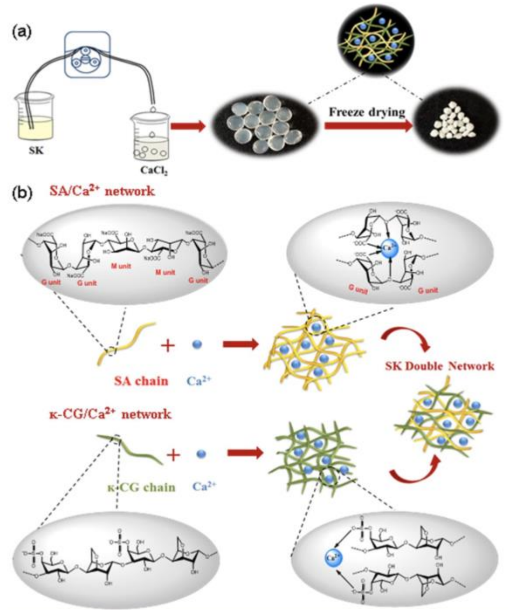


Fig. 5. Schematic diagram of the synthesis process: a) cross-linked hydrogel beads and b) interactions present between alginate ions and carrageen anions. (Li et al. 2019)[133].

3.3.2 Polymer composites and nanocomposites

Composite polymers and nanocomposites have been used in a variety of applications. Such materials are formed by combining two materials with different structures to obtain a final product with properties superior to the initial materials and obtained from phase dispersions that may be homogeneous or heterogeneous [138, 139]. The conformations of these materials are usually formed by two components consisting of a matrix (polymer) and a reinforcement (metal, ceramics, plastics, etc.)[140, 141]. Although these materials have similar procurement characteristics, since they are formed by a matrix and a filling, they exhibit differences based on the dimensions of the filling. The concept of polymeric nanocomposites implies that the filler must have at least a nanometric range (10^{-9} m) in some of its dimensions [142], and we find different nanometric scale fillers, such as OD particles (fullerenes), 1D (nanofibers), 2D (montmorillonite clays), and 3D (nanodiamonds)[143]. The advantages of using nanofillers at the nanoscale are the improvement of mechanical, physical, and specific area properties compared with regular composite polymers, where these characteristics have earned great interest in the scientific community and in environmental applications [144, 145]. In general, nanocomposite polymeric materials are unmatched materials with different fillers and provide high yields for a number of applications. Fig. 6 shows the methods for obtaining polymeric nanocomposites through, i) polymer-nanoparticle mixtures, ii) polymer-polymer mixture precursors of nanoparticles and subsequently obtained through in situ precipitation or nucleation initiators and processes, and iii) by the in situ polymerization between monomers and nanoparticles [146].

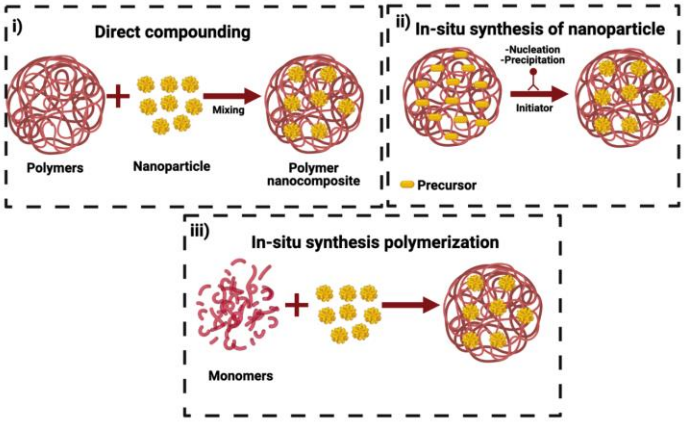


Fig. 6. Synthesis methods for polymer nanocomposites. Representation made by information from Zhang et al.[33]

Examples of the application of composite polymers in the removal of antibiotics used in recent years are described below. Yaqubi et al. investigated the removal of tetracycline and amoxicillin in aqueous solutions by fixed bed columns with chitosan-carbon beads. The adsorption capacity ranged from 12 to 250 mg g^{-1} under optimal experimental conditions. The kinetic studies were adjusted to pseudo first-order models due to the characteristics of the material and the characteristics of the filling with a specific surface of approximately 375 mg g^{-1}, as well as influenced by the presence of carboxyl and hydroxyl groups that facilitated interaction with antibiotics. However, the authors require more in-depth trials with reference to experimental conditions such as pH, antibiotic concentration temperature, adsorbent dose, and influence of the size of composite beads, important factors in adsorption processes [147].

Afzal et al. investigated the adsorption of ciprofloxacin with hydrogel beads from chitosan/biocarbon. The composite polymers obtained had adsorption capacities of 36.72 mg g^{-1} and 25.73 mg g^{-1} after six regeneration cycles, and the high removal capacities were influenced by mixed mechanisms through electron donor-acceptor interactions, hydrogen bonds, and hydrophobic interactions. Another contribution that the authors present is that the nanocomposite polymer is an economic and environmentally friendly adsorbent [148]. Sun et al. used double net hydrogel beads from sodium alginate and graphene functionalized with amino groups to eliminate ciprofloxacin in aqueous solutions. The removal studies were carried out in batch experiments in 30 mL containers, approximately 10 hydrogel beads (between 137–157 mg) and 20 mL of antibiotic. The maximum holding capacity was 301 mg g^{-1}. The effects related to the variation of the ionic force were evaluated, presenting retention greater than 90%. The associated retention mechanisms are mainly influenced by physisorption processes, van der Waals forces, and chemo processes attributed to interactions between composite pearls and antibiotics. These interactions are due to the presence of hydroxyl, carboxylic acid, and epoxy groups of graphene and hydroxyl and carboxylate alginate groups that interact with those of the antibiotic. In addition, interactions are co-assisted by hydroxyl groups of graphene sheets acting as electron donors, while benzene with the fluorine atom and the heterocyclic ring of the antibiotic act as electron acceptors. Given the diversity of interactions, this material is a suitable candidate for the removal of this type of antibiotic [149]. Yadav et al. investigated magnetic polymer compounds of β-cyclodextrin/activated carbon/sodium alginate in the elimination of norfloxacin and ciprofloxacin in aqueous solutions. The composite obtained showed adsorption capacities of 2.55 mg g^{-1} and 3.123 mg g^{-1} for norfloxacin and ciprofloxacin, respectively. The adsorption models that conformed to the experimental data were Langmuir and Temkin models, while at the kinetic level, the kinetic model of pseudo second order was adjusted. With respect to regeneration possibilities, they have high adsorption capacity with load-discharge cycles and the advantages of easy separation from contact solutions without loss of mass by the compounds [150]. Cantero-Lopez et al., obtained a biocomposite from the vinyl monomer 2-metacroyloxyethyltrimethylammonium chloride (ClAETA) in the presence of nanofibrillated cellulose (CNF) for the removal of the emerging contaminant sodium nafcillin monohydrate (NFX). Obtaining the highest adsorption capacity of 45 mg g at a ratio of P(PClAETA)1-12-2CNF% in only 180 min and at a concentration of 200 mg L at pH 6.0 due to speciation of the antibiotic molecule [151].

Moreover, the application of polymeric nanocomposites as mentioned above has been expanded in recent years, and some relevant work in the removal of antibiotics of high veterinary and human health demand is described below. Wang et al. investigated nanocomposite pearls obtained from cellulose and humic acid to improve the retention performance of ciprofloxacin in water. This nanocomposite reached a maximum adsorption capacity of 10.87 mg g^{-1} in batch experiments. The whole process was carried out by chemically controlled monolayer adsorption due to ion exchange provided by the hydroxyl groups of the nanocomposite and amino groups of ciprofloxacin [152]. Zheng et al. synthesized nanocomposites from magnetic carboxymethyl cellulose grafted as sodium poly(*p*-styrenesulfonate) along with Fe_3O_4 magnetic nanoparticles with an approximate diameter of 50 nm, exhibiting an excellent adsorption capacity of 527.93 mg g^{-1} for ciprofloxacin. The absorption mechanism used by these materials was through $\pi - \pi$ interactions, hydrogen bonds, and cation exchange. Moreover, regeneration values greater than 80% were obtained in reuse processes [153]. Li et al. investigated the ability to remove tetracycline from chitosan nanocomposites and magnetic nanoparticles reticulated with terephthal dehyde. Studies have shown that the material has a maximum adsorption capacity of 288.5 mg g^{-1} at pH 8.0. With respect to the material obtained, interactions were shown due to the hydroxyl groups, chitosan, and phenyl amino cross-linking that assisted the adsorption processes; with respect to the mechanism, cationic exchange has been shown to play a fundamental role in tetracycline retention, as well as in the formation of hydrogen bonds and π - π interactions [154] (see Fig. 7).

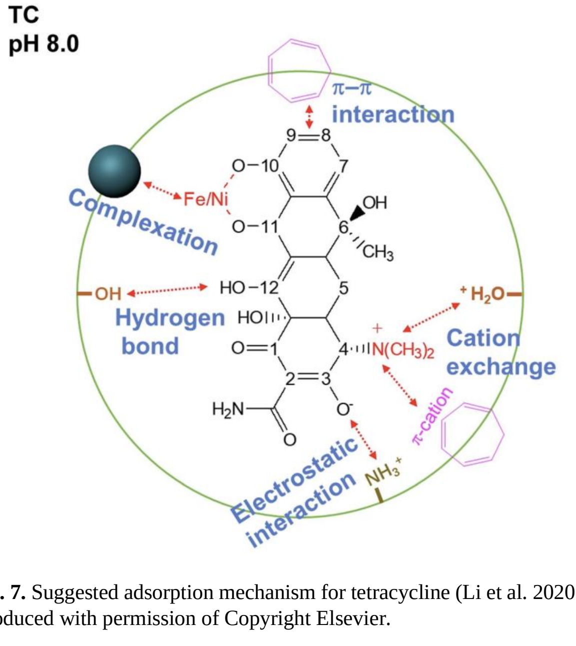


Fig. 7. Suggested adsorption mechanism for tetracycline (Li et al. 2020)[154]. Reproduced with permission of Copyright Elsevier.

Mohamammadi Nodeh et al. investigated the removal of ciprofloxacin by means of magnetic nanocomposites based on graphene oxide and polyaniline. For this study, the authors evaluated the capacity of ciprofloxacin removal by means of different studies, such as studies on pH, adsorbent dose, contact times, antibiotic concentration, and temperature. The most relevant results in this study noted that the maximum retention capacity was carried out at pH 6, a dose of 20 mg, and a contact time of 30 min at room temperature. Moreover, the authors suggest that the adsorption of ciprofloxacin occurs by processes of adsorption in multiple layers due to the characteristics of the material, which is attributed to its maximum adsorption capacity of 106.38 mg g^{-1} [155]. Ma et al. used nanocomposite hydrogels from carbon/graphene oxide/sodium alginate nanotubes for the removal of ciprofloxacin in aqueous solutions. Nanocomposite hydrogels were prepared from nanotubes and graphene oxide with alginate to improve the properties of traditional absorbents and to obtain compound hydrogels with a triple network. These hydrogels can use their three-dimensional networks to improve antibiotic adsorption capacity compared to traditionally obtained hydrogels and two-network hydrogels. The selection of ciprofloxacin was due to its ability to interfere in the photosynthetic processes of plants and in the obstruction of morphological processes and the appearance of abnormal genotoxicity in them [156]. The adsorption capacity for different materials ranged from 107 to 181 mg g^{-1}, and adsorption mechanisms are based on $\pi - \pi$ interactions present in the triple-grid structure of nanocomposites, as well as the presence of aromatic rings of the analyte and the nanocomposite, which is similar to adsorption by electrostatic interactions between the functional groups of the antibiotic and the electrical charges generated on the surface of graphene oxide [157].

Another material to consider that has been used in recent years are nanoclays, given their handling facilities, low costs, high abundance in nature, high specific surface and ion exchange, which have made them optimal filler materials in different polymer matrices [158]. Thakur et al. investigated the removal of ampicillin in water, a type of antibiotic highly used in both human and veterinary medicine that possesses a β-lactam ring. The nanocomposites were prepared using xanthan/poly (itaconic acid)/bentonite gum and co aided by microwave radiation, which helped with both the thermal treatment and the catalysis of the reaction process. It should be noted that these nanocomposites were used as APS initiators and MBA was used as the cross-linker reagent. The nanocomposite obtained demonstrated the high adsorption capacity of ampicillin [159]. Ma et al. used carboxymethyl chitosan and montmorillonite nanocomposites for tetracycline removal, showing that antibiotic adsorption depends mainly on antibiotic speciation and solution pH. It was found that using the materials obtained, the removal was carried out in a period of 2 h for tetracycline and chlortetracycline, obtaining maximum adsorption capacities of 187.6 and 271.7 mg g^{-1}, respectively, and was an optimal material in the removal of antibiotics from the tetracycline family [160].

3.3.3 Membranes and water-soluble polymers

Membrane processes have been widely used in the removal of both organic and inorganic contaminants; however, in recent years, they have been highly used for the removal of pharmaceutical compounds in wastewater [161]. The use of different types of membrane technologies in these specific applications is reported, among which the membranes of nanofiltration, ultrafiltration, microfiltration, and direct osmosis are highlighted [161].

- Nanofiltration: This is a type of separation in which water passes through a semipermeable membrane, together with a pressure gradient, and adsorption is based on the electrical constants of the analyte and membranes [162, 163]. The advantage of nanofiltration is that it allows for greater permeate flow and high rejection properties, while its disadvantages are greater transmembrane pressure and susceptibility to fouling [164, 165].
- Ultrafiltration: This type of technology can work under different pressure conditions and thus improve the conditions of interaction between the solute and solution, which allows for working at low transmembrane pressures and helps to separate many types of biological compounds [166, 167]. Ultrafiltration processes depend on the composition, operating parameters, and characteristics of the membrane. One of the advantages is the higher recovery rates of low-molecular-weight molecules [168, 169].
- Microfiltration: One of the characteristics of microfiltration is that is has high flows and lower irreversible dirt values, characteristics that have been used in many research laboratories [170, 171]. This type of membrane can be used in pre-coagulation processes, as it helps to reduce the process of fouling and embedding on the surface of membranes [172].
- Forward osmosis: This type of technology has received great attention due to its low energy costs and low fouling [173, 174]. The process is carried out by means of an osmotic impulse, which consists of the movement of solutions across the permeable membrane from a solution with lower osmotic pressure to a solution with higher potential [175].

Examples of some work involving the use of membrane technologies are as follows: in the case of direct osmosis, Pan et al. used direct osmosis membranes as recovery technology and in the separation of tetracyclines in wastewater, obtaining rejections greater than 90% in all pH ranges at high concentrations of tetracycline and water flows of 20 Lm^{-2} h^{-1}. The authors concluded that the acidic medium favors the processes of tetracycline elimination due to the speciation of the antibiotic molecule and the properties of the membranes that are favored. This membrane showed rejection percentages higher than 90 % after several operating cycles [176]. Homayoonfal et al. separated amoxicillin from pharmaceutical solutions by using polysulfone/polyacrylic acid ultrafiltration membranes. In this work, membranes of different pore sizes were prepared through phase reversal processes by adding layers of polyacrylic acid by means of UV-induced grafts on the surface of the polysulfone membrane. Amoxicillin separation efficiency was achieved at an optimal pH of 9.0 and a retention of 91% with a flow rate of 108.3 Lm^{-2} h^{-1}, where the retention capacity was due to the nature of the speciation that has a polyacrylic acid layer and the surface activity obtained in the process of grafting into the ultrafiltration membrane [177]. Dolar et al. investigated the application of different membranes of direct osmosis, such as LFC-1 and XLE, and nanofiltration (NF90, NF270, NF) in the removal of antibiotics of veterinary origin, such as ciprofloxacin and other types of antibiotics, obtaining high retention levels greater than 95% for direct osmosis membranes. However, nanofiltration membranes showed retention percentages ranging from 15% to 100%, attributing each retention to the molecular mass of antibiotics [178, 179].

Table 5 shows the removal efficiencies using membrane technologies of three representative antibiotics commonly found in aquatic systems.

Table 5. Comparison of the antibiotic removal efficiency of antibiotics of veterinary and human interest using membrane technologies

Antibiotic	Removal efficiency (%)				
	Microfiltration	Nanofiltration	Ultrafiltration	Osmotic	Reference
Amoxicillin	-	99.09	-	90.57	[180, 181]
Oxytetracycline	100	99.8	41–52	98	[182]
Ciprofloxacin	-	98.9	70–80	97.2–100	[183]

There are applications of water-soluble polymers coupled to ultrafiltration membranes, such as the liquid-phase polymer-based retention (LPR) technique, which is a membrane and polymer-based technique that presents a series of advantages with respect to other adsorption systems. This technique uses different water−soluble polymers (WSPs) obtained by different synthetic routes. Functional homos and copolymers or polyelectrolyte polymers are usually obtained by radical polymerization [184]. Polyelectrolytes are identified as having groups with permanent charges or charges that vary according to pH (see Fig. 8), and these meet specific functions depending on the contaminant to be removed [185]. This technique is a very attractive alternative for the elimination of antibiotics for the treatment of aqueous effluents due to its simplicity of operation and relatively low energy consumption. In addition, the LPR technique presents a series of advantages in comparison with other separation systems because the process is carried out in a homogeneous medium, eliminating the diffusion problems in the adsorbent particles and avoiding the ass-transfer restrictions of the interface, as it is also possible to cause the selective interaction of the polymer with certain species of interest [186, 187].

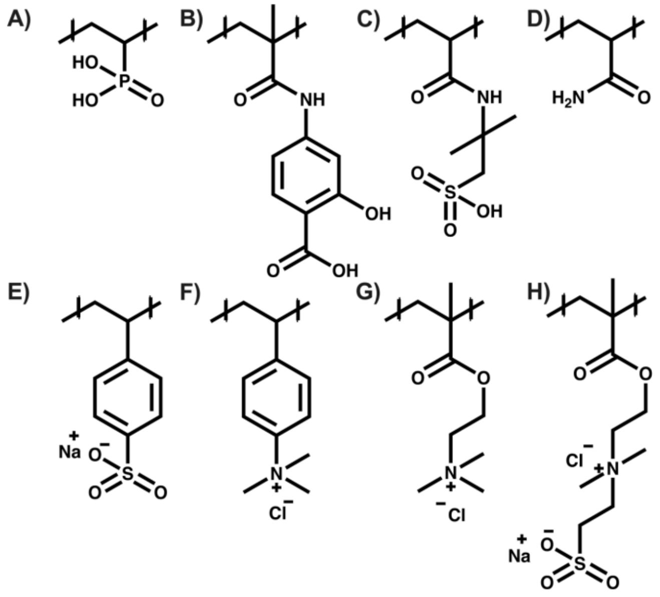


Fig. 8. Examples of water–soluble polymers used for the removal using the LPR technique[184, 185], A) Poly(vinylphosphonic acid), B) Poly(N-methacryloyl-4-aminosalicylic acid), C) Poly(2-acrylamido-2-methyl-1-propanesulfonic acid), D) Poly(acrylamide), E) Poly(sodium 4-styrenesulfonate), F) Poly(ar-vinyl benzyl) trimethylammonium chloride, G) Poly[2-(methacryloyloxy) ethyl] trimethylammonium chloride, and H) Poly[3-(methacryloylamino) propyl] dimethyl(3-sulfopropyl) ammonium hydroxide. The structures were drawn using ChemDraw Professional 16.0

The LPR technique is a hybrid method of membrane separation which combines ultrafiltration membranes with water-soluble polymers in order to separate low-molecular-weight species dissolved in aqueous solution. The system consisted primarily of an ultrafiltration cell with a magnetic stirrer containing a membrane filter, a reservoir, a selector, and compressed nitrogen gas as a pressure source [188]. The LPR technique can be applied by two methods: the washing or elution method (with the ionic strength kept constant or not).

These are the most-used method to study the metal ion retention properties of a water-soluble polymer and can be considered as a discontinuous separation process because the separation mechanism steps occur at different times and in sequential form and the enrichment or concentration of methods which is a continuous separation process wherein separation mechanism steps occur at the same time. Additionally, the technique can be performed at constant or variable ionic strength and is commonly used to determine the maximum retention capacity of polymers [185] (see Fig. 9).

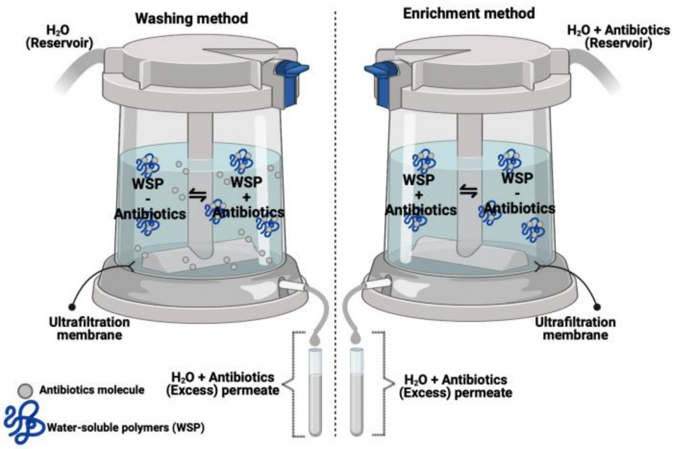


Fig. 9. Methods of application of the LPR technique. Representation made by information from Palacio et al. [189].

The studies carried out using this technique have been addressed mainly to remove inorganic contaminants, elimination of metals in water such as molybdenum, vanadium, chromium, copper, boron, cadmium, nickel, cobalt, and lead, and also some organic compounds such as dyes [187, 190, 191]. To date, few investigations have been carried out for the removal of antibiotics. For example, Palacio et al. investigated the ability to remove chitosan alkylated with quaternary ammonia groups using the LPR technique in the removal of tetracycline, amoxicillin and ciprofloxacin in aqueous solutions. For this, the solubility of chitosan was evaluated at different pH and found to be soluble throughout the pH range compared to unmodified chitosan. In the removal studies the maximum adsorption was obtained at pH higher than that 9.0 with removal percentage greater than 70% and obtaining maximum retention capacity of 185.6, 420.2 and 632.8 mg g^{-1} for ciprofloxacin, amoxicillin and tetracycline respectively. Retention capacity is associated with speciation, variations in antibiotic loads and the variety of interactions depending on the functional groups and structures of the antibiotics that interact with the modified chitosan [192]. In other studies, Palacio et al. (2018 and 2020) investigated the retention capacity of ciprofloxacin and tetracycline using three synthetic polyelectrolyte copolymers with different (positive: negative) charge ratios (1:2, 2:1, and 1:1) in order to assess the effects of charges of polyelectrolyte copolymers. The copolymers were obtained by radical polymerization and using ammonium persulfate initiator, and spectroscopically characterized by ^{1}H-NMR. The results obtained through NMR were known as the load distribution of the copolymers by measuring the reactivity walls using the Kelen-Tüdös and Fineman-Ross method. The retention percentages obtained were greater than 80 % for the three copolymers at pH 5.0 for ciprofloxacin and for tetracycline at pH 11.0 and 3.0 according to the charge ratios of the copolymers. The maximum retention capacity varied between 176.8 to 7131.2 mg g^{-1} for tetracycline and 478.1 to 571.4 mg g^{-1} for ciprofloxacin. In conclusion of the work described above, it can be said that the LPR technique is a friendly, effective and easy to use option as preliminary stages in the degradation processes of this type of contaminants [186, 189].

It should be noted that in the literature it is very little reported with reference to this hybridized removal technique that combines the presence of water-soluble polymers with ultrafiltration membranes for their application in the removal of emerging contaminants such as antibiotics, highlighting its easy handling, low energy costs, high reusability when purchased with other antibiotic removal techniques.

CONCLUSIONS AND OUTLOOK

This review is fundamentally based on analysis of an emerging contaminant type such as antibiotics, that are capable of producing resistant bacterial strains and generating antibiotic-resistant genes in such a way that they could cause public health problems worldwide. It should be noted that emerging antibiotic-type contaminants may be present in quantities ranging from ng L^{-1} to mg L^{-1}. However, at the current level of disposal technologies, there are still great challenges to evaluating selectivity and specificity in the removal of pollutants at very low concentrations. Currently, a variety of technologies aimed at minimizing the impact of these antibiotic pollutants, that combat the presence of pathogens, face a major challenge in removing them from water. Therefore, forces must be gathered to combine technologies that can remove and minimize the impacts caused by these pollutants in the long and short term. Where, LPR is a low-cost hybrid technique, easy to handle and respectful of the environment, since soluble biopolymers can be coupled to remove these contaminants from water. It should be noted that All the techniques analyzed are useful to achieve this important challenge. However, there is still an important challenge to improve the efficiency, selectivity and reuse of adsorbents, but also the application of combined techniques such as the case of LPR.

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