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COMPARISON OF METHODS FOR ANTIBIOTIC COMPOUNDS REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract

This article presents an in-depth exploration of diverse methodologies for the separation and removal of various classes of antibiotics from water and aqueous solutions. Focusing on recent advancements, the study offers a comprehensive overview of active substances and novel combinations employed in the removal processes. Notably, the role of adsorbents is discussed, emphasizing their high porosity that enables efficient absorption of substantial contaminant doses. Additionally, the financial benefits of employing photocatalysts in contaminant degradation are highlighted, with an emphasis on the growing body of research in this area. The historical significance of exchange resin as one of the pioneering removal methods is acknowledged, alongside a more contemporary examination of electrochemical approaches specifically tailored to the structural and ionic characteristics of antibiotics. Serving as a valuable guide, this article addresses the advantages and considerations associated with diverse methods of separating antibiotics from aqueous solutions, providing insights into emerging technologies and facilitating informed decision-making in environmental remediation efforts.

Key words*: antibiotics, adsorption, exchange resin, photocatalysis.*

INTRODUCTION

The most frequently detected organic micropollutants in wastewater are pharmaceutically active compounds, either individually or in combination, utilized as medications to treat various diseases (Natarajan et al., 2022). Hospital wastewater stands out as a significant source of antibiotic pollution due to the release of drugs and their metabolites into the environment through the excretion of treated patients (Shen et al., 2022; Sanguanpak et al., 2022). The active substances from medications become part of the ecosystem, affecting the metabolism of wildlife. Even though drinking water treatment plants treat surface water, recent research indicates the presence of traces left behind by the process.

The pharmaceutical compounds are discharged into the environment in their original or metabolized forms (Rusu et al., 2021), often leading to adverse effects as their toxic potency can exceed that of the parent substance (Figure 1). The accumulation of antibiotics in the environment can contribute to the emergence of antibiotic-resistant bacteria, thereby fostering resistance to drugs in microorganisms. Additionally, this accumulation can result in endocrine disruption, genotoxicity, aquatic toxicity, and the proliferation of pathogenic bacteria resistant to antibiotics. The crucial aspect of separating antibiotics from wastewater primarily revolves around halting or diminishing the process of bacterial antibiotic resistance (Sanguanpak et al., 2022).

Lipophilic molecules reach the adipose tissue of surrounding animals from the water, including the meat intended for human consumption, thus amplifying bacterial resistance to antibiotics. Chloramphenicol and tetracyclines have been identified in significant concentrations, up to 10 mg per 1 kg of vegetables such as tomatoes, cucumbers, lettuce, and carrots, becoming components of the human diet (Wang et al., 2011).

This article will explore several methods for separating drugs from water, each with its own application in nature, while detailing their respective advantages and disadvantages. Many of these methods are particularly effective for removing water-soluble compounds, which are challenging to eliminate from wastewater.

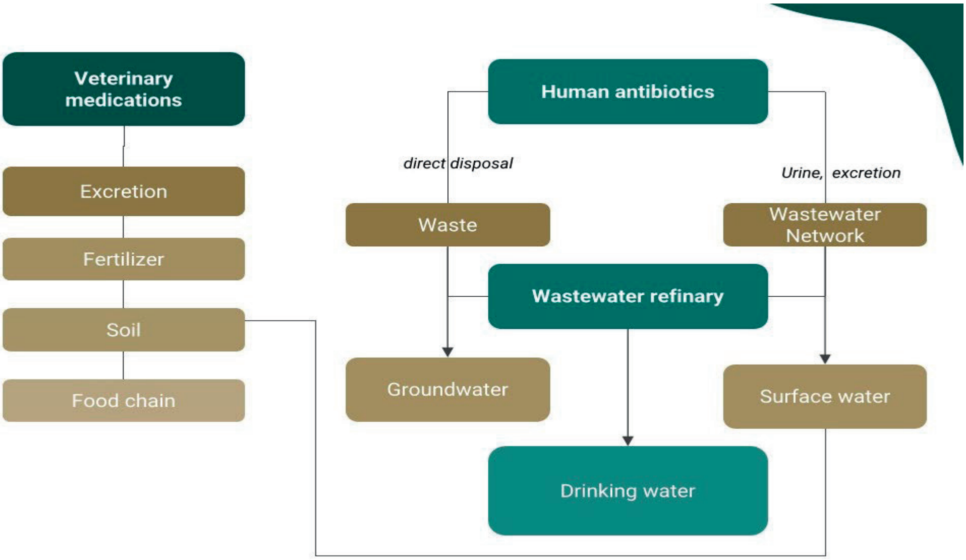

Figure 1. Sources of contamination

While resin exchange, adsorption, photocatalysis, and electrochemical oxidation have shown promising results individually, it is likely that a combination of these techniques will offer the most effective solution for separating a mixture of drugs with diverse chemical structures from aqueous environments.

MATERIALS AND METHODS

Methods for removal antibiotic compounds

The methods that can be used for removal of organic compounds from wastewaters are presented in Figure 2 (Derakhshan et al., 2018; Favier et al., 2023). There are three types of traditional wastewater treatment methods: chemical, physical, and biological.

The chemical processes include neutralization, oxidation, reduction, electrolysis, ion exchange, and catalysis. Two types of properties are associated with chemical wastewater treatment that are considered advantageous: the properties of the reaction products between treated chemicals and contaminants, refer to to their volatility, solubility, or other properties related to their inability to remain in suspension and/or water stream; and the chemical characteristics of the pollutants, associated to their ability to interact or react with chemicals designed to treat pollutants. The biological treatments typically are realized with bacteria, nematodes, or other microscopic organisms, that break down the organic pollutants in wastewater. Using regular cellular processes, converting the biodegradable organic contaminants into simple substances and additional biomass (Phoon et al., 2020; Roșu et al., 2022). Anaerobic digestion, aerated lagoons, activated sludge, fungal treatment, trickling filters, and stabilization are the components of the biological approach. Physical methods of treating wastewater involve removing pollutants through the application of physical barriers and forces found in nature, such as gravity, electrical attraction, and van der Waals forces. The chemical structure of the polluting chemicals is typically not altered by physical treatment. There are, however, some exceptions where the physical state is altered, such as scattered compounds that may have led to agglomeration, as is commonly observed in the filtration and vaporization stages. The physical methods include the following processes: sedimentation, coagulation, membrane treatment, adsorption, distillation, and filtration.

The rate of hydrolysis is crucial for determining how long antibiotics would survive in the environment. Certain organic molecules, such amides and esters, can undergo substantial breakdown in the environment through a process of hydrolysis.

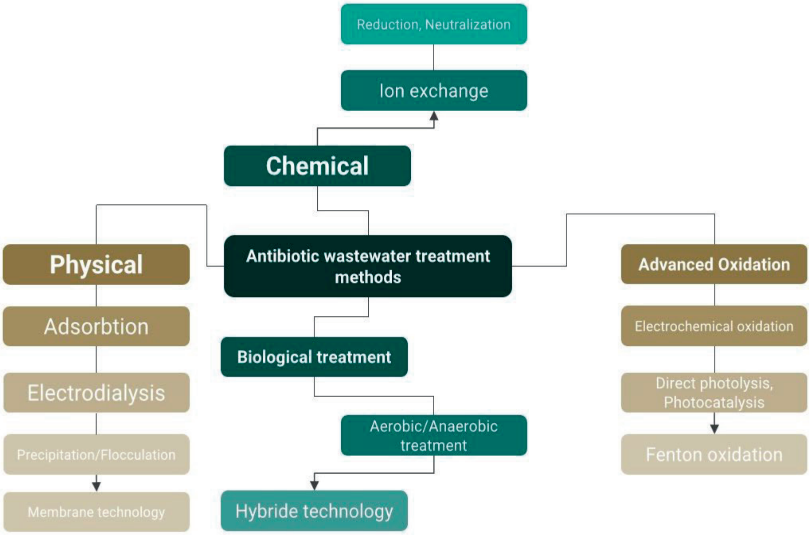

Figure 2. Methods for removing antibiotic substances

Because of their strong polarity, antibiotics containing amides and esters functional groups may be less bio-accumulative (Lin et al., 2007). The most significant environmental variables that affect the rate of hydrolysis are pH and temperature; for example, the rate of hydrolysis usually increases with temperature, on the other hand ionic strength influences hydrolysis.

The adsorption method stands out as a widely used, cost-effective, and non-toxic approach with high regeneration rates for adsorbents. In the process of adsorbing pharmaceutical substances, interactions between the adsorbent and the active compound span various types, including physical bonds, weak chemical bonds, electrostatic interactions, or donor-acceptor interactions.

The selection of a polymer matrix or an ion-exchange column depends on the specific chemical structure of the active substance and its functional groups. To enhance the creation of new active sites, elevate degradation efficiency through accelerated electron transfer, and modify electron density, some research incorporated nitrogen atoms into geopolymers by doping them with nitric acid during polymerization (Huang et al., 2023).

Adsorption can be categorized into physical physisorption, driven by weak intermolecular forces, and chemical chemisorption, involving stronger chemical bond formation such as electrostatic attraction, ion exchange, van der Waals forces, and hydrogen bonding (Sanguanpak et al., 2022).

Adsorption mechanisms encompass physical adsorption, involving various intermolecular forces like hydrogen bonding and van der Waals forces, and chemisorption, characterized by stronger chemical bond formation such as electrostatic attraction, ion exchange, and hydrogen bonding (Figure 3).

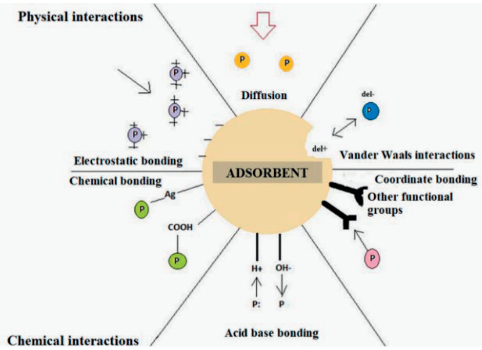

Figure 3. Adsorption mechanism

Other contributing factors include hydrophobic effects, electrostatic interactions, and covalent interactions, including electron acceptor-donor interactions.

Electrostatic repulsion between negatively charged groups from adsorbent and anionic groups from drugs can hinder effective adsorption. pH plays a crucial role in effective adsorption; when the solution pH is below the pharmaceutical's pKa value, the drug remains ionized, facilitating greater adsorption onto negatively charged adsorbents through electrostatic linkage (Natarajan et al., 2022).

The characteristics of an adsorbent are crucial for adsorption processes include porosity, high surface area, and functional groups, particularly hydroxyl and amino groups, which facilitate excellent adsorption capabilities. Research have endeavoured to enhance the porosity of adsorbent by employing surface modifiers, including surfactants like cetyltrimethyl-ammonium bromide and sodium dodecyl sulphate, or foaming agents such as hydrogen peroxide and aluminium. This effort aims to facilitate their application as adsorbents for the removal of different types of pollutants (Youssef et al., 2023).

Enhancing the specific surface area of the adsorbent promotes interaction between active adsorption sites and the molecules being adsorbed. This is facilitated by interconnected pores of varying sizes and shapes, providing a larger accessible surface area for molecule adsorption. Materials characterized by fine-grained microstructures, high densities, and low porosities exhibited greater strength compared to those with larger pores and lower densities.

Adsorbents offer various advantages such as stability, affordability, environmental friendliness, ease of preparation, high mechanical strength, durability, mesoporous structure, ion-exchange capacity, physicochemical stability, high durability, acid resistance, good thermal resistance, thermal stability, high mechanical properties, low CO_2 emissions, low energy consumption compared to other separation processes (Youssef et al., 2023). Utilizing adsorption methods a remarkable removal efficiency of 95-100% was achieved for the antibiotic Ciprofloxacin (Natarajan et al., 2022).

Resin exchange is commonly employed in separating antibiotics, while for pharmaceutical adsorption, a different mechanism known as ion exchange can be used. This process involves the exchange of ions between pharmaceutical compounds and protons located on specific oxygen-containing functional groups within the polymer, such as carboxyl and hydroxyl groups. The pH of the solution plays a main role in this interaction by influencing the quantities of different charged species present (e.g., cations, anions, and neutrals) and their sorptive interactions with the oppositely charged sorbents for ionizable pollutants. Surface complex and electrostatic interactions also impact the adsorption process, particularly in carbon adsorption. Interestingly, the internal charges of the adsorbent material may have a greater impact on adsorption capacity than the surface charges of the adsorbed material. For example, a decrease in the isoelectric point (the pH at which the surface carries no net electrical charge) of the adsorbent's surface from 6 to 4.8 leads to increased electrostatic interactions between the adsorbent and ions.

Resin can also be tailored to encapsulate specific substances or pollutants by analyzing their chemical structure, acting as a framework for a particular template molecule based on its size, shape, and arrangement of functional groups (known as MIPs - molecularly imprinted polymers) (Mokhtari et al., 2022; Mlunguza et al., 2019). These are created using a combination of monomers, crosslinkers, surfactants, solvents, and templates. While they demonstrate a strong foundation in isolating the targeted molecule, their limitation arises when dealing with complex mixtures of antibiotics in water (Mokhtari et al., 2022). In order to delineate the sources of pharmaceutical substances in the environment, MIPs have been developed not only for molecules dissolved in water but also for samples such as human plasma and urine (e.g., albendazole), as well as for determining antibiotics in milk (Liu et al., 2022).

Advanced oxidation process (AOP) is highly efficient in eliminating antibiotics by generating potent oxidizing agents, such as hydroxyl radicals. These radicals dismantle the chemical structure of pharmaceutical substances, yielding non-toxic intermediate products (Carbuloni et al., 2020). Since most pharmaceutical products have a limited biodegradability, the widely utilized wastewater treatment methods are insufficient to fully remove pharmaceutical products from the environment. AOPs are classified into two categories: photochemical

AOPs (such as photolysis, photocatalysis, and photo-Fenton) and non-photochemical AOPs (such as ozonation, Fenton, and electrolysis). Generally speaking, organic pollutants interact with hydroxyl radicals this would result in the formation of a peroxyl radical, which would then react with oxygen molecules to produce a variety of oxidation products.

Photocatalysis offers advantages like cost reduction, increased efficacy, and enhanced degradation of active substances (Apostolescu et al., 2023). During advanced oxidation, activated species, primarily hydroxyl radicals, disintegrate pharmaceutical substances into less toxic intermediates or completely oxidize them to CO_2 and H_2O. Titanium dioxide (TiO_2), often immobilized in polymers due to the difficulty of separating fine TiO_2 from wastewater, serves as the most utilized catalyst (Nutescu et al., 2023; Sescu et al., 2018).

(1) Pharmaceutical ingredient + hν → $e^- + h^+$
(2) $H_2O \rightarrow OH^- + H^+$
(3) O_2 *(adsorbed)* + $e^- \rightarrow O_2^{*-}$
(4) $O_2^{*-} + e^- \rightarrow HOO^*$
(5) $2HOO^* + O_2 \rightarrow H_2O_2$
(6) $H_2O_2 \rightarrow 2OH^*$
(7) $h^+ + OH^- \rightarrow OH^*$
(8) $h^+ + H_2O \rightarrow OH^* + H^+$
(9) OH^* + RH → Less toxic compound
(10) Intermediate compound → $H_2O + H_2$

Hydroxyl radicals are the predominant oxidizing agents in advanced oxidation processes (Huang et al., 2023). Adsorbents with higher TiO_2 concentrations can bolster active site availability and reactive species production, primarily hydroxyl radicals. However, the presence of organic or inorganic matter in wastewater can hinder oxidant efficiency by attenuating UV light intensity, diminishing photocatalytic degradation performance. Various mechanisms such as size exclusion, molecular sieving, hydrophobic interaction, electrostatic interaction, and adsorption also contribute to pollutant removal.

To enhance the photocatalytic effect, some studies have explored combining TiO_2 (known for its high chemical stability and low cost) with ZrO_2 (characterized by its non-toxicity, reusability, and thermal stability). This combination offers advantages such as improved textural and structural properties, a higher surface area, smaller particle size, increased anatase phase, and variation in energy band gap (Carbuloni et al., 2020). In any research focusing on the separation and degradation of pharmaceutical substances into intermediary compounds, it is crucial to assess the toxicity of the final molecules (Saravanan et al., 2022). Some studies have utilized *Lactuca sativa* seeds as phototoxicity bioindicators (Carbuloni et al., 2020) or enzymes derived from living organisms and fungal cultures for this purpose (Mlunguza et al., 2019). Mangan-ion-based photocatalysis can effectively manipulate the energy and electronic bands of the catalyst (Wenjing et al., 2023), a process that leads to the removal of up to 88.7% of tetracyclines from water.

In addition to photocatalysis, the oxidation process can also occur electrochemically, with efficiency being enhanced by the use of hydrogen peroxide (Wenjing et al., 2023). Parameters influencing the removal efficiency of antibiotics include the initial concentration of the organic substance, the type of electrolyte, the electrodes used, the electrical intensity applied, and the pH of the solution. Sulfamethoxazole is one of the pharmaceutical substances destroyed in studies through the electrochemical process. Generally, the mechanism of photocatalytic semiconductor unfolds in five main stages: reactant transfer, reactant adsorption, reaction unfolding in the adsorbed phase, product desorption, and removal of products from the intermediate zone.

Membrane treatment was recognized as the key technology for the separation of pollutants. Wu et al. synthesized PVC membrane for UF of antibiotics and the retention can be up to 80% in 2016 (Wu et al., 2016). Weng and co-workers have conducted antibiotics separation by using zwitterionic polyamide NF membranes with the highest antibiotics' retention of 96.5% (Weng et al., 2016).

Studies on ***electrochemical separation*** techniques for removing molecules from wastewater, such as electrochemical oxidation, electrocoagulation, and electro-flotation, have shown promising results in degrading organic compounds. Electrochemical oxidation can be categorized as direct, where the pollutant is degraded on the anode surface through direct oxidation with the presence of Na_2SO_4, or indirect, where mineralization occurs with oxidants generated indirectly in the solution, often in the presence of sodium hypochlorite or potassium hypochlorite. Various anode materials are utilized in electrochemical degradation, including platinum, TiO_2, graphite, activated carbon, and combinations like Sn/Sb/Ni, which offer advantages such as low voltage operation, short reaction time, complete mineralization, and sometimes require no pH adjustments (Kurt et al., 2021).

Key aspects of the electrochemical degradation process/experiment include the choice of anode materials, generation of indirect oxidants (e.g., chloride or hypochlorite ions), distance between the anode and cathode, and the electrolyte used to increase conductivity (e.g., NaCl, Na_2SO_4, KCl). Electrooxidation can often be optimized at neutral pH values, which is both easier for researchers and more cost-effective to operate. The degradation time of molecules is strongly influenced by the type of oxidation process (direct or indirect), the choice of anode material, and the pH of the solution.

Comparative methods: alone or in combination

Advantages and disadvantages of each presented method are presented in Table 1 (Phoon et al., 2020).

In recent studies, research has focused on investigating combinations of antibiotics in aqueous solutions using adsorbents doped with TiO_2 required for photocatalysis. A study conducted a combined approach of adsorption and photocatalysis to separate six antibiotics (amoxicillin, ciprofloxacin, norfloxacin, sulfamethoxazole, tetracycline, trimethoprim) from wastewater (Natarajan et al., 2022).

Table 1. Advantages and disadvantages of methods for antibiotics removal

Treatment process	Main advantages	Main disadvantages
Photocatalysis	Good stability of photocatalyst; high activity and non-toxicity; efficient recovery and recyclability of photocatalyst; low cost, fully destroy the organic pollutant.	Fast electron-hole recombination; poor efficiency for high concentrations; toxic by-products
Fenton	In-situ production of reactive radicals; without sludge; rapid degradation	Formation of unknown by-products; technical constraints; ferrous sludge produced; high concentration of anions.
Ozonation	Destroy antibiotics in a very short period (240–300 s)	
Electrochemical oxidation	Zero-sludge; unselective or selective function of the electrochemical cell	Expensive
Wet oxidation	Converted insoluble organic material into soluble compounds; for effluent too toxic for biological treatment	High pressure and energy conditions; pH dependence; No full mineralization.
Adsorption	High effective process; good ability to separate different contaminants; simple equipment.	Non-selective methods; high cost of regeneration; influenced by pH; further process after adsorption (regeneration).
Membrane technology	Large range of applications; high selectivity; simple and efficient; no chemicals required	High energy requirements and operation and maintenance costs; limited flow rates; the high cost of investment; fouling effect needs a further process for elimination.
Anaerobic treatment	Produces methane as a by-product; Lower biomass yield.	High energy consumption and operating cost; not digest all type of antibiotics.
Aerobic treatment	Higher loading rate; high performance	High energy consumption and operating cost; not digest all type of antibiotics.

A porous material composite membrane, consisting of a semi-crystalline aluminosilicate membrane with two layers, each containing metakaolin, an alkaline activator, and air foam was used. The porous support layer, negatively charged with hydrophobic properties, incorporated aluminium powder, while the dense coating layer contained TiO_2 nanoparticles, rendering it dense with voids and cracks. TiO_2 acted as a filler, densifying the microstructure. This membrane exhibited characteristics of both amorphous gel phase and nanocrystalline zeolite. The maximum degradation achieved was 40% at a TiO_2 concentration of 6% (Natarajan et al., 2022). This study exemplifies effective research into separating a combination of antibiotics using adsorption and photocatalysis, resulting in enhanced drug degradation in wastewater.

Rimoldi et al. synthesized TiO_2/WO_3 for tetracycline (TC) removal using UV lamp (Rimoldi et al., 2018), Ahmadi et al. investigated TC degradation with UV-C lamps (Ahmadi et al., 2017). Wang et al. evaluated the effectiveness of TC degradation with ZnO under UV irradiation (Wang et al., 2016). Certain studies on photocatalytic TC degradation under UV light have demonstrated good performance; Xu et al. used carbon quantum dots and $ZnIn_2S_4$ composites was removed more than 80% of TC in 30 minutes (Xu et al., 2018). Acosta et al. reported to have produced active carbon with the TC adsorption capacity of 312 mg/g (Acosta et al., 2016). Besides AC, some other adsorbent materials also have a good performance in TC removal such as, the graphene oxide (GO) that was prepared by Gao et al. in 2012, can achieve 313 mg/g of adsorption capacity (Gao et al., 2012). Zhao et al. (2017) proposed that, the ionic strength of water bodies could affect the adsorption performance.

In an effort to increase the efficacy of wastewater treatment, hybrid systems that combine membrane technology and photocatalysis have drawn interest recently (Sarasidis et al., 2017). The photocatalytic membrane reactor is a type of integrated hybrid system that may be classified into two types: one where the catalyst is dispersed in the wastewater medium and the other where it is immobilized on or in the membrane surface.

CONCLUSIONS

In conclusion, this article offers a comprehensive analysis of various methodologies employed for the separation and removal of antibiotics from water and aqueous solutions. Recent advancements in the field are thoroughly explored, providing insights into active substances and innovative combinations utilized in the removal processes. The pivotal role of adsorbents is underscored, emphasizing their high porosity and efficient absorption capabilities for substantial contaminant doses. Furthermore, the financial advantages of employing photocatalysts in contaminant degradation are highlighted, reflecting the growing body of research in this domain. Acknowledging the historical significance of exchange resin as a pioneering removal method, the article also delves into more contemporary electrochemical approaches tailored to the structural and ionic characteristics of antibiotics. By offering a valuable guide, this paper addresses the advantages and considerations associated with diverse methods of separating antibiotics from aqueous solutions, thereby providing insights into emerging technologies and facilitating informed decision-making in environmental remediation efforts.

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