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Occurrence and removal of pharmaceuticals from water using modified zeolites: a review

Isabela Arantes Ferreira*, Taynara Gomes Carreira, Alexandre Diório, Rosângela Bergamasco, Marcelo Fernandes Vieira

Department of Chemical Engineering, State University of Maringá, Colombo Avenue 5790, Building D-90, Maringá, Paraná 87020-900, Brazil, Phone: +055 (44) 3011-4778; emails: isarantes10@gmail.com (I.A. Ferreira), ra117927@uem.br (T.G. Carreira), adiorio2@uem.br (A. Diório), rbergamasco@uem.br (R. Bergamasco), mfvieira2@uem.br (M.F. Vieira)

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ABSTRACT

High consumption of pharmaceuticals has led to an increase in their discharge and detection in waters around the world. Most pharmaceutical compounds are not fully metabolized by the human body and end up in the environment, causing chronic contamination of aquatic species and posing an environmental and health threat. A low-cost and low-impact alternative for the removal of pharmaceuticals from water is their adsorption by modified zeolites. Herein is reported a review of the worldwide occurrence and removal by adsorption of these contaminants from water using modified zeolites. We found that pharmaceutical contamination of water is widespread and that adsorption by modified zeolites is a viable alternative with a satisfying removal efficiency for different pharmaceuticals.

Keywords: Adsorption; Advanced water treatment; Contaminants of emerging concerns; Pharmaceuticals

1. Introduction

The use of pharmaceuticals has been increasing worldwide, mainly due to population growth, wider access to healthcare and longer life expectancy [1,2]. They are used to control diseases in humans, animals and others [3], providing health and quality of life.

However, the high consumption and continuous introduction of these bioactive chemicals in wastewaters leads to chronic contamination of the soil, surface and ground waters at trace levels, which poses a threat to the flora and fauna and also affects human health [1,4,5]. Even after conventional wastewater treatment processes, a significant concentration of these compounds is not completely removed and remain in the environment in their original form or as by-products that are equally or more toxic [2,6,7].

Pharmaceuticals and their by-products are considered emerging pollutants due to the lack of reference limits, regulation and legislation on their environmental presence, even though studies conclude that most urban wastewaters are probably contaminated by them [7]. Among the most common pharmaceutical pollutants are antibiotics, anti-inflammatories, antidepressants, hormones and anticonvulsants [4].

The heterogeneous characteristics of pharmaceuticals, their persistence in the environment, low volatility, strong polarity, low mass concentration and biological accumulation are challenging aspects to their removal [5,8]. In this scenario, many advanced water treatment alternatives have been extensively studied as potential pharmaceuticals removal processes, such as biodegradation, electrocoagulation, conventional and advanced oxidation, irradiation, nanofiltration, reverse osmosis and adsorption processes [2].

* Corresponding author.

Adsorption techniques are simple, low cost, versatile, non-pollutant and do not generate by-products [9,10]; these characteristics make them an interesting, advanced treatment option and studies showed that adsorptive processes efficiently removed different classes of pharmaceuticals [11]. The most prominent, widely used and well-studied adsorbent is activated carbon; however, many other materials have also been proposed, such as clays, silica and zeolites [12,13].

Zeolites present high stability in different temperatures and in acidic conditions are efficient in selectively adsorbing organic micropollutants – such as pharmaceuticals – in competitive adsorption processes [11]. They are also cheap and available worldwide, making them an advantageous alternative to activated carbon, which is non-selective, costly to produce due to its high temperature synthesis, and has poor reactivation results [14,15].

However, in some cases, natural zeolites need to be modified to achieve better results under certain conditions. The removal of organic pollutants, for example, is limited for natural zeolites, once their small porous structure cannot adsorb the large organic molecules from pharmaceutical compounds [16]. Multiple modification processes have been studied to produce changes in the porous structure and surface chemistry, improving their characteristics and removal mechanisms for common pollutants [17].

In this context, the aim of this research is to provide a review of the state of the art of the use and efficiency of natural and modified zeolites in the removal of pharmaceuticals from water.

2. Methodology

To conduct this review, the terms "pharmaceutical", "removal", "water", "wastewater" and "modified zeolite" were searched in the ScienceDirect and Google Scholar databases. Only research papers were searched and then, pre-selected by their titles, abstracts and keywords. Over 600 articles were found and 35 were selected for this study. Selection was based on: date of publication (recent papers were prioritizes); occurrence location (including studies from different parts of the world); contaminant concentration; presence of experimental data; adsorption capacity; and removal efficiency.

3. Pharmaceuticals

Pharmaceuticals or drugs are defined as technically obtained or prepared products, containing one or more drugs and other substances, with a prophylactic, curative, palliative or diagnostic purpose [18]. They can be classified according to their biological activity and purpose [19]. The classes found in studies selected for this review were: (i) analgesics, (ii) antibiotics, (iii) anticonvulsants; (iv) antiseptics, (v) beta-blockers, (vi) keratolytics, (vii) lipid regulators, (viii) non-steroidal anti-inflammatory drugs (NSAIDs) and (ix) steroids.

3.1. Pharmacological classes

(i) Analgesics: commonly known as painkillers, used for relief of pain without sensory or conscience alterations [20], such as paracetamol and aspirin;

(ii) Antibiotics: antimicrobial compounds that kill or inhibit growth of bacterial and fungal pathogens, used in humans or as veterinary drugs, to reduce animal diseases and control zoonotic pathogens in animal products [21], such as penicillins and tetracyclines;

(iii) Anticonvulsants: also known as antiepileptic drugs, they are used in the treatment of seizures and epilepsy syndrome. Some common anticonvulsants are carbamazepine, phenytoin, phenobarbital, oxcarbazepine and valproic acid [22];

(iv) Antiseptics: antimicrobials that reduce infection, sepsis or putrefaction without damaging living tissue [23], for example, triclosan, an antiseptic used in personal care products such as soaps and cosmetics [24,25];

(v) Beta-blockers: used in treatment of hypertension and other cardiac conditions, like arrythmia, reducing mortality [26,27], for example, atenolol and propanolol;

(vi) Keratolytics: may be used topically in treatment of acne and psoriasis, releasing free-radical oxygen into the outer layers of the skin and causing shedding of these layers and oxidization of bacterial proteins in the sebaceous follicles [28,29]. One keratolytic agent, salicylic acid, can also be derived from acetylsalicylic acid (commonly known as aspirin), used as an analgesic and antipyretic drug [30,31];

(vii) Lipid regulators: traditionally, these drugs are used to lower lipid levels, for example, cholesterol, fatty acids and triglycerides, reducing cardiovascular conditions and improving health quality [32], such as simvastatin and gemfibrozil;

(viii) Non-steroidal anti-inflammatory drugs (NSAIDs): used in relief of pain, fever and inflammation [33]. They are the most prescribed and taken class of drugs in the world [34]. Examples are ibuprofen, diclofenac and naproxen;

(ix) Steroids: steroids are hormones that regulate vital biological functions; steroid-based drugs are employed in the treatment of many different conditions, like rheumatoid arthritis, heart diseases, inflammations, allergic reactions, cancer, metabolic diseases and, specially, in contraception in the form of estrogen [35].

3.2. Environmental concerns

For the past decades, the presence of pharmaceuticals in the environment has been extensively studied and verified, with studies from around the world detecting water contamination by different drugs in every continent, including Antarctica [36].

The biggest concern is in the fact that these contaminants are released continuously, leading to accumulation and chronic exposure of aquatic biota [37]. Some aquatic species may be exposed for their entire life cycles, causing chronic effects that lead to subtle changes over time, highlighting the importance of evaluating the toxicity of biologically active micropollutants such as pharmaceuticals [19,38].

Pharmaceuticals may enter the environment through many different routes and sources, such as: pharmaceutical industrial effluents, hospital and domestic waste, landfill effluents and excretion by animals after veterinary administration [19]. They can also reach drinking

water through the contamination of soil, surface water and groundwater [39].

Drugs are not fully metabolized by the human body, being excreted through feces and urine into the wastewater in their original form or as metabolites [39]. Studies found that up to 75% of antibiotics [40] and 85% of diclofenac [38] consumed are excreted unchanged, in their active forms. The presence of antibiotics in the environment, for example, may select resistant bacteria and cause the spread of drug-resistant pathogens, with wastewater treatment plants being appointed as hotspots for selection of antibiotic resistance genes in aquatic bacteria [41,42]. Antibiotics may also affect the microbes in wastewater plants, causing the inhibition of wastewater bacteria and hindering organic matter degradation, nitrification and denitrification [43].

Paracetamol, also known as acetaminophen, is known to be responsible for oxidative stress in plants and animals, also affecting their histological development, tissue regeneration, embryogenesis and development, metabolism, and neurotoxicity and behavior [44].

Salicylic acid is the compound most frequently detected and presents the highest concentration in Canadian Sewage Treatment Plants Effluents and surface waters [45]. Studies have shown that salicylic acid may be toxic for aquatic organisms, causing oxidative stress impacts in freshwater species and increase of metabolic capacity in *M. galloprovincialis* [46,47].

Ethinylestradiol, a synthetic estrogen, has been detected in the environment since the 1990s and is widespread in waters [19]. This steroid is considered an endocrine disruptor and known to be one of the main compounds that affect different species when present in the environment [48,49]. Studies have shown that ethinylestradiol affects the reproduction of wild fish, with its chronic contamination of water causing feminization of male fish even at low concentrations, which impacts directly the sustainability of its population [50].

As for the NSAID diclofenac (which is also one of the most found pharmaceuticals in water), a study has found that prolonged exposure even to lower concentrations causes its accumulation in the liver, kidneys, gills and muscles of fish, therefore leading to a decrease in their health [37]. For diclofenac, the lowest observed effect concentration causing fish toxicity was circa 10 mg/L, which is in the range of wastewater concentrations [38].

Regarding beta-blockers, Maszkowska et al. [51] have evaluated the acute ecotoxicology of propranolol, metoprolol and nadolol in non-target organisms, finding that the first two can be considered harmful. According to the study, metropolol and propanolol diminished 50% of green algae (*S. vacuolatus*) growth at a concentration of, respectively, 76 and 24 mg/L. However, the risk the compounds pose is diminished due to environment concentrations being significantly lower than those the study has found [51]. It is important to note, however, that this study did not evaluate chronic contamination or mixture of substances, which the authors consider important factors to determine their toxic potential.

Carbamazepine, a frequently detected anticonvulsant, has known effects on embryo development and behaviour of larvae of zebrafish, inducing developmental toxicity in concentrations from 1 to 5 μg/L [52].

Triclosan is also one of the pharmaceutical contaminants most frequently detected, with its toxicity causing a major impact on aquatic environments and species, along with exposing humans to potentially dangerous levels of contamination [25]. Studies have shown that exposure to triclosan may compromise endocrine function, thyroid issues and antibiotic resistance in animal models in concentrations as low as 0.15 μg/L [25,53].

A study has shown that lipid regulator gemfibrozil inhibits gamete fertilization and causes a decrease in larvae survival of marine species at environmental levels, impacting their early stages and affecting coastal ecosystems [54].

3.3. Presence in surface waters

The occurrence of pharmaceuticals in surface waters around the world from 2017 to 2023 was reviewed and displayed in Fig. 1. The most studied pharmacological class are antibiotics (50 occurrences), and the most frequently detected drugs were carbamazepine (28 occurrences), paracetamol (25 occurrences) and atenolol (22 occurrences). The results are presented in Table 1.

4. Zeolites

Zeolites are hydrated, crystalline aluminosilicates, with orderly microporous structures that allow exchange of guest species [66]. They are composed of framework structures containing TO_4 tetrahedral units (T = Si, Al) connected by O atoms [67]. They can be natural or synthetized and can also be modified.

4.1. Natural zeolites (NZ)

Zeolites are natural minerals found all over the world, in sedimentary deposits, usually of volcanic origin [68]. About 45 types of natural zeolites with varying chemical properties have been discovered, the most widely used ones being clinoptilolite and mordenite [69].

Natural zeolites are applied in environmental remediation largely due to their ability of exchanging cations; their use in the removal of water and wastewater pollutants, like ammonium (NH_4^+), heavy metal cations (Cs^+, Pb^{2+}) and other toxic cations is well known and studied [17,68].

4.2. Modified zeolites

Zeolite modification methods can be categorized into physical, chemical and composite. Physical modifications include thermal and ultrasonic modification methods, which can improve ion-exchange capacity, elimination of pore impurities, increase and uniformization of pore size and increase in surface area [17,70].

Chemical modifications include acid, alkali, salt, cationic surfactant and rare earth methods [17]. Acid modification seeks to replace Ca^{2+} and Mg^{2+} zeolite ions with H^+ in order to increase surface area and porosity, working best on pollutants such as ammonia and uranium [17,71]. Alkali modification, in turn, acts through two mechanisms: reducing Si/Al from zeolite for uniform pore sizes and electrostatic interaction to form covalent bonds, being a good alternative on the removal of organic pollutants [72,73].

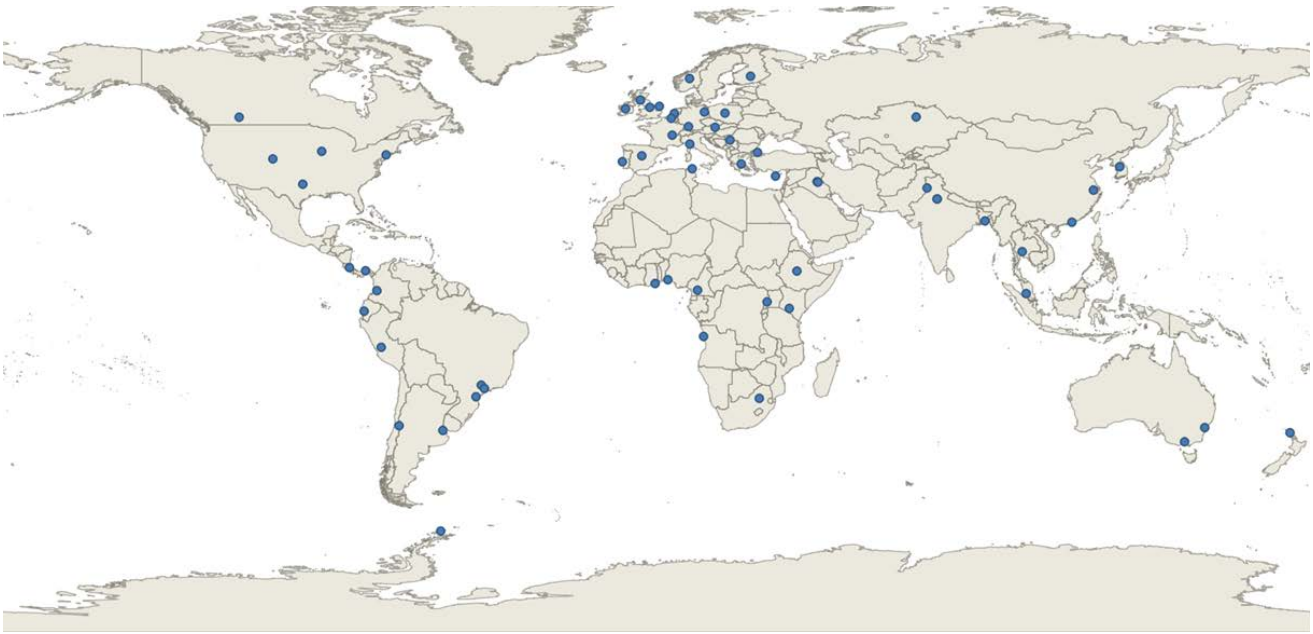

Fig. 1. Occurrence of pharmaceuticals in surface waters around the world.

Table 1
Occurrence of pharmaceuticals on surface waters around the world

Pharmacological class	Environmental effects	Pharmaceutical	Mean concentration (ng/L)	Occurrence	Country	References
		Paracetamol	19,280	Curitiba	Brazil	[55]
		Paracetamol	9,622	Buenos Aires	Argentina	[56]
		Paracetamol	506.0	Lagos	Nigeria	[57]
		Paracetamol	243.0	River Dee	Scotland	[58]
		Paracetamol	30.0	Itirapina	Brazil	[59]
		Paracetamol	10.1	Tai Lake Basin	China	[60]
		Paracetamol	79.4	Laguna Rusia	Antarctica	[36]
		Paracetamol	8,690	Odo-Iya Alaro River	Nigeria	[36]
		Paracetamol	182	Kordjor River	Ghana	[36]
		Paracetamol	4,290	Pienaars River	South Africa	[36]
	- Oxidative stress in plants and animals	Paracetamol	392	Medjerda River	Tunisia	[36]
		Paracetamol	619	Catinton River	Angola	[36]
Analgesics	- Alterations in biochemical, metabolic and cellular processes	Paracetamol	13,600	Bulbula River	Ethiopia	[36]
		Paracetamol	5,120	Mfoundi	Cameroon	[36]
		Paracetamol	159	Ishim River	Kazakhstan	[36]
		Paracetamol	121	South Platte	USA	[36]
		Paracetamol	148	Wagner Creek	USA	[36]
		Paracetamol	109	East River	USA	[36]
		Paracetamol	535	Bow River	Canada	[36]
		Paracetamol	46	Nepean River	Australia	[36]
		Paracetamol	111	Torrens River	Australia	[36]
		Paracetamol	70.8	Waitangi River	New Zealand	[36]
		Paracetamol	2,410	Cauca River	Colombia	[36]
		Paracetamol	2,090	Abajo River	Panama	[36]
		Paracetamol	4,580	Daule River	Ecuador	[36]

Table 1 (Continued)

Table 1

Pharmacological class	Environmental effects	Pharmaceutical	Mean concentration (ng/L)	Occurrence	Country	References
Antibiotics	- Selection of resistant bacteria - Spread of drug-resistant pathogens	Cephalexin	308.0	N/A	Finland	[61]
		Cephalexin	203.3	N/A	Finland	[56]
		Cephalexin	87.6	N/A	Ireland	[56]
		Cephalexin	66.4	N/A	Ireland	[56]
		Cephalexin	66.3	N/A	Cyprus	[56]
		Cephalexin	65.2	N/A	Spain	[56]
		Cephalexin	65.0	N/A	Cyprus	[56]
		Cephalexin	60.7	N/A	Norway	[56]
		Cephalexin	38.4	N/A	Portugal	[56]
		Chloramphenicol	23.1	Gombak River	Malaysia	[62]
		Chloramphenicol	22.9	Selangor River	Malaysia	[57]
		Chloramphenicol	16.6	Lui River	Malaysia	[57]
		Chloramphenicol	2.1	Tai Lake Basin	China	[60]
		Clindamycin	239.0	Vistula River	Poland	[63]
		Clindamycin	110.7	N/A	Germany	[56]
		Clindamycin	101.4	N/A	Spain	[56]
		Clindamycin	97.1	N/A	Norway	[56]
		Clindamycin	94.2	N/A	Finland	[56]
		Clindamycin	88.8	N/A	Finland	[56]
		Clindamycin	86.6	N/A	Portugal	[56]
		Clindamycin	59.1	N/A	Ireland	[56]
		Clindamycin	42.5	N/A	Ireland	[56]
		Clindamycin	31.5	N/A	Portugal	[56]
		Clindamycin	27.8	N/A	Cyprus	[56]
		Clindamycin	8.5	N/A	Portugal	[56]
		Clindamycin	6.5	N/A	Cyprus	[56]
		Clindamycin	2.6	Tai Lake Basin	China	[60]
		Enrofloxacin	69.4	N/A	Spain	[56]
		Enrofloxacin	175	Langat River	Malaysia	[36]
		Enrofloxacin	18.5	Ravi River	Pakistan	[36]
		Enrofloxacin	451	Wadi River	Palestine	[36]
		Enrofloxacin	244	Trancão River	Portugal	[36]
		Enrofloxacin	113	Ardieres River	France	[36]
		Enrofloxacin	122	Kargotis River	Cyprus	[36]
		Enrofloxacin	186	Muddy Creek	USA	[36]
		Enrofloxacin	163	Maipo	Chile	[36]
		Enrofloxacin	141	Matanza-Riachuelo River	Argentina	[36]
		Tetracycline	231.2	N/A	Portugal	[56]
		Tetracycline	194.2	N/A	Ireland	[56]
		Tetracycline	179.2	N/A	Norway	[56]
		Tetracycline	165.7	N/A	Portugal	[56]
		Tetracycline	147.5	N/A	Portugal	[56]
		Tetracycline	141.0	N/A	Ireland	[56]
		Tetracycline	70.6	N/A	Finland	[56]
		Tetracycline	36.9	N/A	Cyprus	[56]
		Tetracycline	24.5	N/A	Cyprus	[56]
		Tetracycline	16.8	N/A	Finland	[56]
		Tetracycline	15.4	N/A	Germany	[56]
		Tetracycline	21.4	Chaohu Lake	China	[64]
		Tetracycline		Langat River	Malaysia	

Table 1 (Continued)

Table 1

Pharmacological class	Environmental effects	Pharmaceutical	Mean concentration (ng/L)	Occurrence	Country	References
		Carbamazepine	232.0	Jundiaí River Basin	Brazil	[11]
		Carbamazepine	99.0	Buenos Aires	Argentina	[56]
		Carbamazepine	66.0	River Dee	Scotland	[58]
		Carbamazepine	22.2	Danube River	Serbia	[65]
		Carbamazepine	9.0	Lagos	Nigeria	[57]
		Carbamazepine	5.2	Tai Lake Basin	China	[60]
		Carbamazepine	23.7	Toronto	Canada	[36]
		Carbamazepine	33.3	Puerto Vallarta	Mexico	[36]
		Carbamazepine	189	South Platte	USA	[36]
		Carbamazepine	219	Muddy Creek	USA	[36]
		Carbamazepine	202	Trinity	USA	[36]
		Carbamazepine	26.7	Calgary	Canada	[36]
		Carbamazepine	159	Torres River	Costa Rica	[36]
	Disturbs growth and	Carbamazepine	84.1	Sydney	Australia	[36]
Anticonvulsants	development of fish	Carbamazepine	21.9	Melbourne	Australia	[36]
	embryos and larvae	Carbamazepine	81.6	Natal	Brazil	[36]
		Carbamazepine	113	Matanza-Riachuelo River	Argentina	[36]
		Carbamazepine	1,090	Santiago	Chile	[36]
		Carbamazepine	92.6	Guayaquil	Ecuador	[36]
		Carbamazepine	409	Lagos	Nigeria	[36]
		Carbamazepine	103	Accra	Ghana	[36]
		Carbamazepine	883	Nairobi	Kenya	[36]
		Carbamazepine	405	Pienaars River	South Africa	[36]
		Carbamazepine	99.6	Addis Ababa	Ethiopia	[36]
		Carbamazepine	156	Ravi River	Pakistan	[36]
		Carbamazepine	206	Delhi	India	[36]
		Carbamazepine	140	Bangkok	Thailand	[36]
		Carbamazepine	48.7	Seoul	South Korea	[36]
	- Affects endocrine and	Triclosan	71.0	Vistula River	Poland	[63]
	thyroid function in	Triclosan	29.1	Jundiaí River Basin	Brazil	[11]
Antiseptics	animals	Triclosan	10.6	Lui River	Malaysia	[62]
	- Promotes antibiotic resistance					
		Atenolol	431.0	Jundiaí River Basin	Brazil	[11]
		Atenolol	427.0	Buenos Aires	Argentina	[56]
		Atenolol	329	Lagos	Nigeria	[36]
		Atenolol	139	Accra	Ghana	[36]
		Atenolol	200	Nairobi	Kenya	[36]
		Atenolol	625	Pienaars River	South Africa	[36]
		Atenolol	184	Luanda	Angola	[36]
		Atenolol	222	Addis Ababa	Ethiopia	[36]
Beta-blockers	Decrease in algae reproduction	Atenolol	209	Tigris River	Iraq	[36]
		Atenolol	258	Langat River	Malaysia	[36]
		Atenolol	1,430	Ravi River	Pakistan	[36]
		Atenolol	1,160.9	Hyderabad	India	[36]
		Atenolol	134	Kai Tak River	Hong Kong	[36]
		Atenolol	45.7	Han River	South Korea	[36]
		Atenolol	158	Vecht River	Netherlands	[36]
		Atenolol	1,090	Torres River	Costa Rica	[36]
		Atenolol	85.1	Trinity	USA	[36]

Table 1 (Continued)

Table 1

Pharmacological class	Environmental effects	Pharmaceutical	Mean concentration (ng/L)	Occurrence	Country	References
Beta-blockers	Decrease in algae reproduction	Atenolol	197	Muddy Creek	USA	[36]
		Atenolol	78.1	South Platte	USA	[36]
		Atenolol	34.1	Don River	Canada	[36]
		Atenolol	47.9	Abajo River	Panama	[36]
		Atenolol	417	Santiago	Chile	[36]
		Atenolol	64.6	Huancayo	Peru	[36]
		Propranolol	29.6	Jundiaí River Basin	Brazil	[11]
		Propranolol	3.5	Tai Lake Basin	China	[60]
		Propranolol	21.0	Buenos Aires	Argentina	[56]
		Propranolol	31.7	Ravi River	Pakistan	[36]
		Propranolol	20.6	Yamuna River	India	[36]
		Propranolol	30.8	Kai Tak River	Hong Kong	[36]
		Propranolol	21.8	Wadi River	Palestine	[36]
		Propranolol	49.6	Danube River	Austria	[36]
		Propranolol	145	Senne River	Belgium	[36]
		Propranolol	184	Foss River	England	[36]
		Propranolol	45.5	Vecht River	Netherlands	[36]
		Propranolol	397	Clyde River	Scotland	[36]
		Propranolol	69.1	Manzanares River	Spain	[36]
		Propranolol	125	Ammer River	Germany	[36]
		Propranolol	47.7	Aire River	England	[36]
		Propranolol	78.2	South Platte	USA	[36]
		Propranolol	85.7	Muddy Creek	USA	[36]
		Propranolol	43.1	Trinity	USA	[36]
Keratolytic agents	- Toxic for aquatic organisms - Disrupts metabolism	Salicylic acid	333.0	Buenos Aires	Argentina	[51]
Lipid regulators	Affects reproduction in some animals	Gemfibrozil	158.0	Lagos	Nigeria	[52]
NSAIDs	Accumulation in internal organs of some animals	Diclofenac	284.0	Buenos Aires	Argentina	[51]
		Diclofenac	214.0	Jundiaí River Basin	Brazil	[11]
		Diclofenac	132.0	River Dee	Scotland	[53]
		Diclofenac	4.8	Gombak River	Malaysia	[57]
		Diclofenac	4.3	Selangor River	Malaysia	[57]
		Diclofenac	2.8	Lui River	Malaysia	[57]
		Diclofenac acid	22.7	Tai Lake Basin	China	[55]
		Diclofenac sodium	20.0	Itirapina	Brazil	[59]
		Ibuprofen	4,705.0	Buenos Aires	Argentina	[51]
		Ibuprofen	298.0	Lagos	Nigeria	[52]
		Ibuprofen	250.0	Jundiaí River Basin	Brazil	[11]
		Ibuprofen	144.0	River Dee	Scotland	[53]
		Ibuprofen	60.1	Danube River	Serbia	[65]
		Ibuprofen	10.0	Itirapina	Brazil	[54]
		Naproxen	400.0	Buenos Aires	Argentina	[51]
		Naproxen	82.8	Jundiaí River Basin	Brazil	[11]
		Naproxen	102	Odo-Iya Alaro River	Nigeria	[36]
		Naproxen	91.2	Nairobi	Kenya	[36]
		Naproxen	102	Rwizi River	Uganda	[36]
		Naproxen	778	Khal River	Bangladesh	[36]

Table 1 (Continued)

Table 1

Pharmacological class	Environmental effects	Pharmaceutical	Mean concentration (ng/L)	Occurrence	Country	References
NSAIDs	Accumulation in internal organs of some animals	Naproxen	221	Diyala River	Iraq	[36]
		Naproxen	43.2	Nepean River	Australia	[36]
		Naproxen	896	Bapu Ghat River	India	[36]
		Naproxen	206	Kai Tak River	Hong Kong	[36]
		Naproxen	588	Ergene River	Turkey	[36]
		Naproxen	92.5	Han River	South Korea	[36]
		Naproxen	1,340	Danube River	Austria	[36]
		Naproxen	344	Spree River	Germany	[36]
		Naproxen	104	Asopos River	Greece	[36]
		Naproxen	703	Senne River	Belgium	[36]
		Naproxen	627	South Platte	USA	[36]
		Naproxen	715	Trinity River	USA	[36]
		Naproxen	10.0	Itirapina	Brazil	[54]

N/A: not available.

Similarly to acid and alkali modifications, salt modifications act by exchanging Ca^{2+} and Mg^{2+} in zeolites and provoking electrostatic interactions, being used in the removal of ammonia and metallic ions [74]. Cationic surfactants act by cations exchange and hydrophobic alkyl chains, increasing anion removal and being applied to the adsorption of antimonate and EDTA [75,76]. Zeolite modification through hydrothermal treatment in the presence of surfactant CTAB (hexadecyltrimethylammonium bromide; $CH_3(CH_2)_{15}N(Br)(CH_3)_3$) is an appropriate strategy aiming pharmaceuticals adsorption [77].

Lastly, rare earth modifications use the cation exchange, hydroxides surface formation, electrostatic interaction and ligand exchange reaction mechanisms to improve removal of ammonia and phosphorus [17].

Other types of modification methods usually include association with nanoparticles [78], enzymes [79] or catalysts, aiming to increase sorption or provide other removal mechanisms such as photocatalysis [80].

5. Use of modified zeolites in the removal of pharmaceuticals

Recent studies regarding the use of modified zeolites in the adsorption of different pharmaceutical compounds have been researched and summarized in Tables 2 and 3. Table 2 refers to modifications aimed at improving adsorption, whereas Table 3 includes modifications for photocatalytic and adsorption purposes.

5.1. Modifications for adsorption purposes

In this category, modification by cationic surfactants is the most frequent among researched studies, with 17 occurrences by itself or associated with other modifications (Table 2). Adsorption results for cationic surfactant modified zeolites (MZ) are efficient in the removal of dicloxacillin (96.52% RE) [81], triclosan (96% RE and q_e = 46.95 mg/g) [15] and ethynylstradiol (96.87% RE). However, it is observed that adsorption capacities for cationic surfactants tend to be smaller than for other studied modifications.

Studies with MZ coated with magnetic nanoparticles reached outstandingly high removal efficiencies (98.75%–99.79%) for NSAIDs and gemfibrozil, proving to be another interesting alternative. The highest adsorption capacity among the researched studies is, however, for MoS_2 nanoparticles MZ, reaching a staggering q_e = 396.70 mg/g for the adsorption of tetracycline [82], much higher than those found by any other of the selected studies.

5.2. Modifications for adsorption and photocatalysis purposes

As seen in Table 3, all the researched works on MZ with catalysts used antibiotics as their contaminants, the most frequent being amoxicillin and tetracycline (3 occurrences each). Results obtained in these studies show high removal efficiencies (>93%), due to the association of two removal processes (photocatalysis and adsorption).

Fe-doped MZ were the most frequent modification for photocatalysis purposes, with 4 occurrences. The association of a crystallization process, cationic surfactant modification and $FeCl_3$ impregnation obtained an outstanding q_e = 526.32 mg/g and RE = 98.7% for the removal of tetracycline, presenting the best results out of all studied modifications [95]. Another study reached a q_e = 200.00 mg/g and RE = 100% for tetracycline using only $FeCl_3$, another impressive result [96]. RE = 100% was also obtained through $FeCl_3$ modification by another study, for both tetracycline and amoxicillin [97].

5.3. Regeneration studies

One of the main concerns regarding adsorption as a water treatment method is the management and disposal of saturated adsorbents, which may compromise the sustainability and economic viability of the contaminant removal process [100]. Adsorbent regeneration is a way of reutilizing the adsorbent material by degrading or removing the

Table 2
Modified zeolites for adsorption purposes and adsorption capacity for different pharmaceuticals

Pharmacological class	Pharmaceutical	Type of zeolite modification	Removal efficiency (RE)	Max. adsorption capacity (q_e) (mg/g)	References
Analgesics	Paracetamol	Cationic surfactant - hexadecyltrimethylammonium (HDTMA)	N/A	0.8488	[83]
Antibiotics	Ceftriaxone	Cationic surfactant - HDTMA	N/A	0.0076	[73]
	Cephalexin	Coating by MnO_2 nanoparticles	89%	24.50	[66]
	Chloramphenicol	Cationic surfactant - ionic liquids	N/A	<2.5	[84]
	Clindamycin	Cationic surfactant - HDTMA	N/A	1.68	[85]
	Dicloxacillin	Cationic surfactant - HDTMA	96.52%	1.072	[81]
	Tetracycline	Acid impregnation by HNO_3	90%	N/A	[86]
	Tetracycline	Cationic surfactant (unspecified)	65%	N/A	[87]
	Tetracycline	MoS_2 nanoparticles	N/A	396.70	[82]
Anticonvulsants	Carbamazepine	Cationic surfactant - hexadecyltrimethylammonium bromide (HDTMA-Br)	N/A	0.17	[88]
Antiseptics	Triclosan	Cationic surfactant - cetylpyridinium bromide	96%	46.95	[15]
Beta-blockers	Atenolol	Alkali treatment by NaOH + acid treatment by H_2O:HCl	N/A	N/A	[89]
	Propranolol hydrochloride	Cationic surfactant (DDBA)	47.40%	N/A	[90]
	Propranolol hydrochloride	Cationic surfactant (DDBA) - pre-treatment with HCl	48.40%	N/A	[90]
	Propranolol hydrochloride	Cationic surfactant (DDAB) - pre-treatment with NaCl	65.50%	N/A	[90]
Keratolitic agents	Salicylic acid	Incorporation of transition metal (Co^{2+}, Ni^{2+} or Cu^{2+}) + cetylpyridinium chloride	N/A	3.9	[91]
	Salicylic acid	Alkali treatment by NaOH + acid treatment by H_2O:HCl	N/A	N/A	[89]
	Salicylic acid	Cationic surfactant - HDTMA	N/A	N/A	[92]
Lipid regulator	Gemfibrozil	Coating with magnetic nanoparticles	99.13%	N/A	[78]
NSAIDs	Diclofenac	Cationic surfactant - HDTMA	N/A	N/A	[84]
	Diclofenac sodium	Alkali treatment by NaOH + acid treatment by H_2O:HCl	N/A	N/A	[89]
	Diclofenac sodium	Cationic surfactant - cetylpyridinium chloride	N/A	N/A	[93]
	Diclofenac sodium	Coating with magnetic nanoparticles	99.58%	N/A	[78]
	Ibuprofen	Coating with magnetic nanoparticles	98.75%	N/A	[92]
	Ibuprofen sodium	Cationic surfactant - HDTMA	N/A	N/A	[92]
	Naproxen	Coating with magnetic nanoparticles	99.79%	N/A	[88]
Steroids	Ethinylestradiol	Pre-treatment with NaCl + cationic surfactant (HDTMA)	96.87%	0.71	[94]

N/A: not available.

contaminant, thus increasing their applicability and reducing the quantities in which they are produced and disposed of [101].

Out of all researched studies, only a few present results and discussions on the reusability of MZ after the adsorption of pharmaceuticals. Maraschi et al. [80] (fluoroquinolone adsorption on TiO_2 MZ) conducted three regeneration cycles using 5 h of solar light irradiation for desorption, observing no loss in both adsorption capacity and photocatalytic activity.

Guo et al. (tetracycline adsorption on $FeCl_3$ and nanoparticles impregnated MZ) have found that, after 5 regeneration cycles using 0.01 M NaOH solution as eluent for desorption, removal efficiency stayed above 80% [95].

Changduang et al. [97] ($FeCl_3$ impregnation) found that after 5 regeneration cycles, the removal efficiency of

Table 3
Modified zeolites for adsorption and photocatalysis purposes and adsorption capacity for different pharmaceuticals

Pharmacological class	Pharmaceutical	Type of zeolite modification	Removal efficiency (RE)	Max. adsorption capacity (q_e) (mg/g)	References
Antibiotics	Amoxicillin	$FeCl_3$	100%	N/A	[97]
	Amoxicillin	MgO	97.9%	N/A	[98]
	Amoxicillin	Sea salt impregnation	93%	N/A	[99]
	Enrofloxacin	TiO_2	98%	24.1	[80]
	Marbofloxacin	TiO_2	96%	23.1	[77]
	Tetracycline	$FeCl_3$	100%	N/A	[97]
	Tetracycline	Impregnation assisted one-step crystallization - NaOH, $NaAlO_2$ and $Na_2SiO_3{\cdot}9H_2O$ and cetyltrimethylammonium bromide + $FeCl_3$	98.7%	526.32	[95]
	Tetracycline	$FeCl_3$	100%	200.00	[96]

N/A: not available.

amoxicillin and tetracycline dropped from 100% to, respectively, 68.5% and 65.7%. Liu et al. [82] (tetracycline adsorption on MoS_2 MZ) observed a 25% drop in adsorption capacity after 5 regeneration cycles.

The studies show an efficient regeneration of MZ and maintenance of a high contaminant removal efficiency after the adsorption–desorption and photocatalysis cycles. This suggests, once again, that MZ are a promising adsorbent with good economic applicability, especially when associated with photocatalysis.

6. Conclusion

This paper aims to provide a summary of current literature regarding water contamination by pharmaceuticals, the risks they may cause and MZ as sustainable alternatives for removing the drugs from the environment. Through the researched studies, we can conclude that the water contamination by pharmaceuticals is chronic and widespread, and thus researchers have proposed many techniques to remove these pharmaceuticals. The analyzed studies in this paper showed that MZ proved to be efficient in removing some of the most found drugs in the environment, especially when associated with photocatalysis, and have the potential to be a low cost, green, viable treatment option.

For future studies, the investigation of adsorption of pharmaceuticals mixtures into MZ can be done. Since pharmaceuticals do not occur separately in the environment, investigating how mixtures affect the adsorption process by competitive adsorption would be a step closer to possible real-world applications in contaminated waters. Also, most of the researched studies worked with higher concentrations than those usually found in the environment (in the order of ng/L), leading to higher adsorption and removal rates. Thus, future research may study trace contamination levels and examine how they affect the adsorption process with MZ.

Another suggestion is testing pharmaceutical adsorption onto MZ in fixed bed columns, since most studies have only conducted batch experiments. Studies on the cost-benefit of zeolite modifications vs. their *in natura* versions, comparing parameters such as adsorption capacity, removal rate, environmental impact and production costs would be interesting for determining real-world application of MZ in water treatment.

Author credit statements

Isabela A. Ferreira: writing original draft, review and editing, conceptualization, methodology; Taynara Gomes Carreira: writing original draft, review and editing; Alexandre Diório: review and editing, data curation, methodology; Rosângela Bergamasco: review, supervision; Marcelo F. Vieira: review and editing, data curation, supervision, visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationship that could have appeared to influence this work.

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