The Application of Zeolites and Mesoporous Silica Materials

Subjects: Environmental Sciences

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Zeolites and mesoporous silica materials are effective adsorbents that can be useful for the removal of various pharmaceuticals including non-steroidal anti-inflammatory drugs and antibiotics from low-quality water. This paper summarizes the properties and basic characteristics of zeolites and mesoporous silica materials and reviews the recent studies on the efficacy of the adsorption of selected non-steroidal medicinal products and antibiotics by these adsorbents to assess the potential opportunities and challenges of using them in water treatment. It was found that the adsorption capacity of sorbents with high silica content is related to their surface hydrophobicity (hydrophilicity) and structural features, such as micropore volume and pore size, as well as the properties of the studied medicinal products.

zeolites | mesoporous sorbents | wastewater purification | drug analysis

1. Introduction

Pharmaceuticals are substances with a high biological activity, which are introduced into the body in a strictly defined dose to achieve a desired (therapeutic or preventive) effect. They are exposed to the environment in many ways, the most important being excretion by humans and animals and inappropriate disposal of drugs. These compounds are excreted from the body in the form of parent compounds or as metabolites formed in the first and second phase of biotransformation [1][2][3]. Many pharmaceutically active compounds were already detected in water in the 1980s. Bush (1997) grouped these therapeutic substances into the following classes: (a) anti-inflammatory agents and analgesics, (b) antibiotics, (c) antiepileptics, (d) antidepressants, (e) lipid-lowering agents, (f) antihistamines, (g) β-blockers, and (h) other substances [3][4].

Pharmaceuticals that are most frequently detected, including antibiotics, anti-inflammatory drugs, and analgesics, have become a growing environmental concern worldwide [5][6]. They occur mainly in the aquatic environments, such as surface and underground waters, water reservoirs, effluents and influents of sewage treatment plants, and drinking water [7][8][9][10][11][12][13]. Medicines are found in trace concentrations up to 100 μg L^{-1} in wastewater resulting from drug production [14]. Drugs are found in the environment because these pollutants cannot be completely removed in sewage treatment plants [15], and thus persist without undergoing degradation [16]. Incomplete elimination of pharmaceuticals was also observed in drinking water treatment plants [17][18]. This paper focuses on two groups of pharmaceuticals—non-steroidal anti-inflammatory drugs (NSAIDs) and antibiotics—as they are the most widely used medicinal products worldwide. NSAIDs (diclofenac, ibuprofen, ketoprofen, and naproxen) were chosen owing to their large-scale use and widespread distribution in surface waters and

wastewater, which is confirmed by numerous scientific studies [19][20][21]. In turn, the antibiotics discussed in this article (erythromycin, sulfamethoxazole, tetracycline, and trimethoprim) were selected as they are included in the World Health Organization's List of Essential Medicines [22] and are also used widely as antimicrobial substances against bacteria [20][23][24]. Of the NSAIDs of interest, only ibuprofen is on the WHO list. **Figure 1**a–d presents the concentrations of selected drugs from the group of NSAIDs and antibiotics found in the aquatic environment based on data from the analyzed studies.

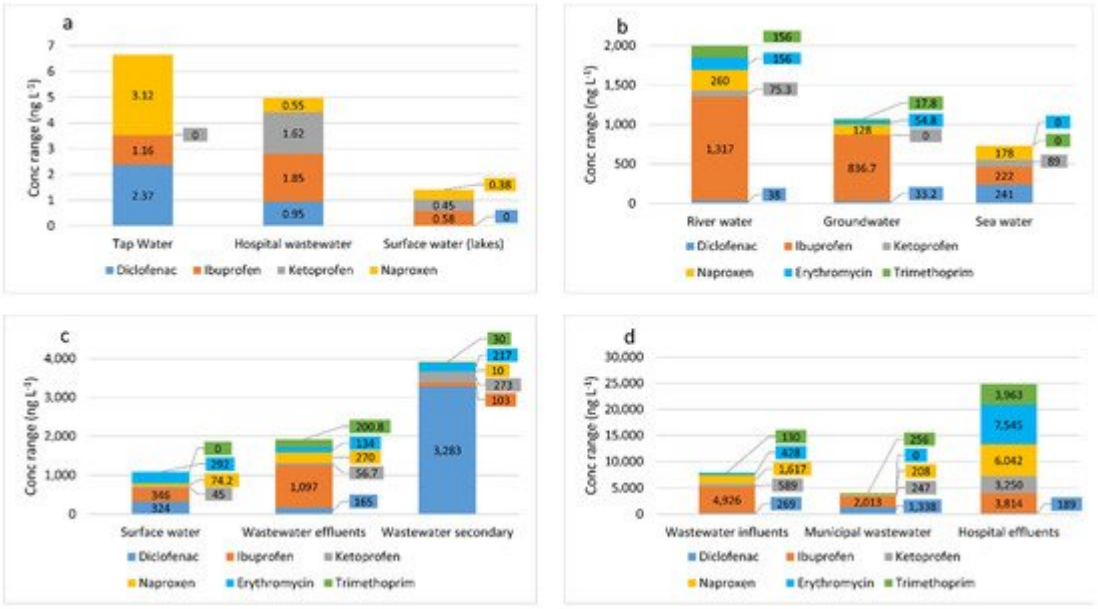

Figure 1. Concentrations of some pharmaceuticals (antibiotics, anti-inflammatory drugs, and analgesics) recorded in the world in selected water types: (**a**) tap water [25], hospital wastewater, and surface water (lakes) [26]; (**b**) river water, groundwater [27], and seawater [28]; (**c**) surface water [29], wastewater effluents, and wastewater secondary [27][30]; and (**d**) wastewater influents [30], municipal wastewater [29], and hospital effluents [30].

Based on the data from **Figure 1**a–d, it can be stated that antibiotic concentrations were highest in hospital effluents, wastewater effluents, and river water. In three types of water (tap water, hospital wastewater, surface water (lakes)) presented in **Figure 1**a, erythromycin and trimethoprim were not detected. The highest concentrations of diclofenac, ibuprofen, and ketoprofen were found in wastewater influents, municipal wastewater, and hospital effluents. Thus, it can be concluded that the drug concentrations in different types of waters and wastewater are found in the following order: hospital effluents > wastewater influents > municipal wastewater > secondary wastewater > river water > wastewater effluents > groundwater > surface water > seawater > tap water > hospital wastewater > surface water (lakes). Owing to human activity, pharmaceuticals are detected in various types of water and wastewater on each continent, including the North Scandinavian water environment [31]. The strategy for their removal can be the same everywhere, as long as the concentrations are at a similar level. The most easily removable drugs are mainly those belonging to the group of non-steroidal analgesics and anti-inflammatory drugs, including ibuprofen, ketoprofen, and naproxen. On the other hand, the elimination of pharmaceuticals such as diclofenac from wastewater is difficult.

Pharmaceuticals are chemically stable. However, owing to physicochemical and biotic factors [32], they undergo biodegradation, conjugation, deconstruction, and sorption. Therefore, the knowledge of these processes is necessary to predict the environmental fate of medicinal substances [13]. The high stability of drugs is related to their relatively high durability under environmental conditions. In contrast, some pharmaceutical metabolites resulting from oxidation, reduction, and/or hydrolysis are more susceptible to further transformations, and thus are less stable in the aquatic environment [33]. The transformations of pharmaceuticals taking place in the aquatic environment are not thoroughly studied so far [34][35][36]. Pharmaceuticals undergo many reactions and changes, the first of which dilutes the drugs when they reach the surface water and water reservoirs [37], while chemical reactions may partially or completely change the original pharmaceuticals (parent compounds) [1]. The products resulting from the transformation of pharmaceutical compounds are sometimes more stable than the parent compounds and may be more or less toxic. Moreover, pharmaceuticals may undergo biotic (aerobic and anaerobic) and abiotic (chemical) reactions in the environment [15][38]. Most often, pharmaceuticals are trapped in sewage sludge, but their original molecular structures are preserved. This is generally observed in the case of lipophilic and difficult-to-degrade substances. Pharmaceuticals also possibly transform into hydrophilic compounds, which remain stable. Such hydrophilic products pass through sewage treatment plants and reach the flowing surface waters (rivers) and still surface waters (water reservoirs and lakes) [5]. It has been shown that pharmaceuticals exhibit a very wide range of removal rates without any logical scheme, even if they belong to the same therapeutic groups [39]. **Figure 2** presents the approximate nonmetabolized fractions of selected pharmaceuticals from the NSAID group and that of antibiotics entering wastewater after ingestion and human metabolism. The *x*-axis excretion percentage represents unmetabolized or partially metabolized pharmaceuticals that are eliminated as the original active ingredient.

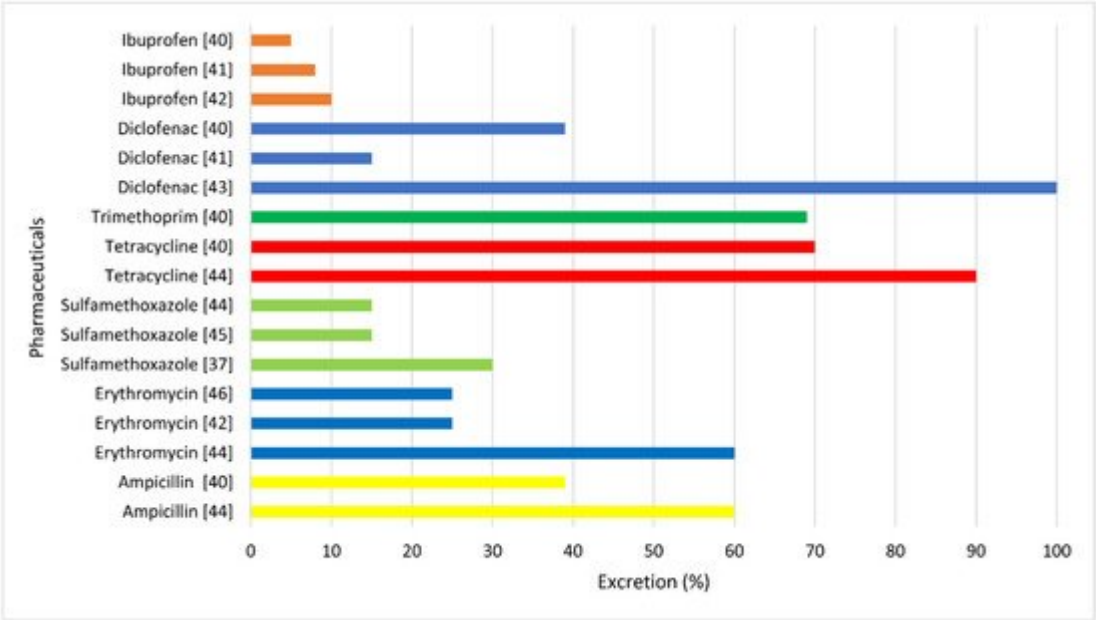

Figure 2. Typical pharmaceuticals and their approximate nonmetabolized fractions entering sewage after being ingested and subjected to human metabolism: ibuprofen [40][41][42]; diclofenac [40][41][43]; trimethoprim [40]; tetracycline [40][44]; sulfamethoxazole [37][44][45]; erythromycin [42][46]; and amplicillin [40][44].

Pharmaceuticals enter the environment mainly by water transport and further spread into the environment through the food chain [7]. The side effects of these substances are still unknown and have not been tested. Pharmaceuticals can affect aquatic ecosystems, but the extent of this damage is not clear [5][47]. Some studies have already reported that these compounds pose both acute and chronic threats to flora and fauna. It has been proven that diclofenac has a negative effect on vultures, causing a decline in their population [48]. In turn, Schwaiger et al. [49] and Triebskorn et al. [50] indicated that exposure of rainbow trout to diclofenac results in damage to internal organs. Sulfamethaxazole has also been shown to affect the germination of rice and oats [51].

Because of the above-described consequences, it is necessary to optimize and improve the technologies currently used for the treatment of wastewater and surface water in order to eliminate pharmaceutical residues from them. Because the biological and physical removal efficiency of these residues is not very high, there is a need to search for other more effective cleaning methods. Chemical (e.g., ozonation and oxidation) and physicochemical processes (e.g., adsorption, membrane filtration, and coagulation) are commonly used for the removal of medicines from aqueous solutions [52][53][54]. Some of the pharmaceutical substances in the suspension go to both primary and secondary sediments. Among the proposed physicochemical processes, adsorption is the most preferred method for removing pharmaceutical residues [55], which works based on the principle of remediation [3]. The advantages of adsorption are that it allows obtaining high-quality treated wastewater, it is easy and cheap to operate, and it does not result in the production of undesirable by-products [56][57]. It can be used for the treatment of various types of water and wastewater, including those with a high content of organic compounds, which cannot be removed by other methods [58] Adsorption of drugs with the use of porous materials, mainly activated carbon, is known as one of the most effective processes for removing these groups of pharmaceuticals, and is thus widely used. Powdered active carbon is often used in adsorption processes [59][60]. It contains numerous pores of different sizes and has different functional groups on its surface. However, its disadvantage is the difficulty associated with the regeneration of the used adsorbent and the low-selective adsorption of organic adsorbents, especially at low concentrations. Activated charcoal adsorbs a wide spectrum of medicines, especially hydrophobic compounds, owing to its well-developed pore structure, large surface area, and high degree of fragmentation. On the other hand, hydrophilic drugs are inefficiently removed [17][18][61]. A disadvantage encountered with the use of activated charcoal is that the working capacity of the material is significantly reduced if natural organic matter is present, as well as regeneration of the used adsorbent. Regenerative processes significantly affect the pore structure and chemical properties of functional groups in activated carbon, thereby reducing their adsorption efficiency in relation to the removed pharmaceuticals. Thermal regeneration of activated carbon can also cause carbon losses of up to 10% of its mass, which results in the need to purchase new activated carbon. As an alternative, zeolites and mesoporous silica materials can be used. These are characterized by the need for shorter contact time, lower desorption percentage, and better structural stability (which allows regeneration at high temperature) compared with activated carbon, all of which justify their use. This paper presents the general characteristics of zeolites and mesoporous silica materials and an authoritative review of data from research publications, which have not been discussed before in other studies. While individual publications contain results describing the removal efficiency of a selected pharmaceutical (belonging to one of the two groups analyzed), there is no study providing a comparative summary of removal efficiencies and conditions of the experiments conducted for several compounds

from a given group and several zeolite sorbents or mesoporous materials. Therefore, efforts have been made to include in this paper the data on the efficiency of zeolites and mesoporous materials to remove the two most common groups of pharmaceuticals—antibiotics and non-steroid pharmaceuticals—from water. The paper reviews the literature on the physicochemical properties of selected zeolites (natural, synthetic, and high silica) and mesoporous silica materials—Mobil Composition of Matter (MCM-41) and Santa Barbara Amorphous (SBA-15)—and their relation to the adsorption of selected antibiotics and non-steroid pharmaceuticals. The zeolites and mesoporous silica materials described in this paper were chosen for this review because of their high availability in the market and their proven effectiveness in removing antibiotics and non-steroidal drugs from aqueous solutions. Zeolites have been shown to have the potential to be successfully used for the adsorption of sulfamethoxazole from water [62]. The adsorption efficiency of zeolites and mesoporous silica materials was characterized taking into account their properties and the diversity of the two analyzed groups of drugs. The paper also discusses the potential possibilities and challenges related to the use of zeolites and mesoporous silica materials in water treatment. The review serves two purposes. Firstly, it allows determining the sorption capacity (described in the literature of zeolites and two mesoporous silica materials) of MCM-41 and SBA-15 in relation to the drugs dissolved in water. Additionally, it can be used to analyze their effectiveness of drug removal and potential use in wastewater treatment and groundwater remediation. Secondly, it allows determining the structural features of the analyzed adsorbent materials, which influence their adsorption of drugs from aqueous solutions. All the collected information may be of help to select materials for water treatment in the future.

2. Physicochemical Properties of Zeolites and Mesoporous Silica Materials

2.1. Zeolites

The Swedish mineralogist F. Crondtedt used the name zeolite for the first time in 1756. While analyzing the newly discovered mineral, he noticed that it was losing water when heated. In Greek, the word zeolite means “boiling stone” [63]. During the time of their discovery, zeolites were considered as a separate group of minerals [64]. They are defined as tectosilicates, which are inorganic polymers having a three-dimensional structure, and are made up of SiO_4 tetraeders, some of which can be replaced by AlO_4 [65][66][67]. A characteristic feature of zeolites is the crystalline structure voids in the form of chambers and channels [68]. The size of zeolites ranges from 3 to 30 Å [69].

Depending on the proportion of silica and aluminium (Si/Al ratio), the properties of zeolites can vary. High-silicon zeolites with a high Si/Al ratio of up to several thousands are produced industrially [70][71]. The hydrophobicity of these zeolites is a beneficial property that facilitates the adsorption of pharmaceuticals from aqueous solutions [72].

The structural features of high-silica zeolites are determined mainly by their framework. A framework type represents the unique channel and frame structure and has the greatest impact on the effectiveness of pharmaceutical adsorption. Mordenite (MOR), faujasite (FAU), and MFI are the type of zeolites selected for this review because they are the most commercially available and have already been tested for the removal of

antibiotics and non-steroidal drugs from aqueous solutions. Their structural characteristics are summarized in **Table 1**.

Table 1. Key properties of three commonly used frameworks of zeolites.

Frame-Work Type	Ring Number and Pore Opening Size [73]		Framework Density [73]	Accessible Area Maximum [74]	Maximum Diameter of a Sphere [74]
	(Å × Å)	(Å × Å)	(T-Atoms per 1000 Å)	(m^2 g^{-1})	(Å)
FAU	12 ring 7.4 × 7.4	-	12.7	1211.42	11.24
MOR	12 ring 6.5 × 7.4	8 ring 2.6 × 5.7	17.2	1010.22	6.70
MFI	10 ring 5.1 × 5.5	10 ring 5.3 × 5.6	17.9	834.41	6.36

All the selected framework types are characterized by a large surface area (from 834 to 1211 m^2 g^{-1}) for adsorption. The skeleton density of zeolites is related to their pore volume—zeolites with a lower skeleton density have a larger pore volume [75]. The pore volume of zeolites, which is inversely proportional to skeletal structure density, increases in the following order: FAU > MOR > MFI (**Table 1**).

Zeolites can also be divided according to their origin into two groups: natural and synthetic. The changes and geological processes taking place in the rocks under hydrothermal conditions favor the formation of natural zeolites. Zeolite deposits occurring in the form of geological deposits, which are profitable for extraction and processing, are found only for some types, such as clinoptilolite, MOR, philipsite, and chabasite. Synthetic zeolites can also be obtained by chemical synthesis. The synthesis of these zeolites is usually carried out under hydrothermal conditions in an alkaline environment [76]. Clay minerals, minerals from the silica group, and by-products of coal combustion (e.g., fly ash) can be used as raw materials for chemical synthesis. The synthesis process changes the chemical and mineral composition and structure of the raw material, consequently giving rise to a zeolite material with new physicochemical properties [77]. **Table 2** presents a summary of publications describing the synthesis of selected synthetic zeolites (Na-A, Na-P1, and Na-X) from fly ashes.

Table 2. Selected publications on the synthesis of synthetic zeolites Na-A, Na-P1, and Na-X from fly ashes.

Type of Zeolite	Conditions of Synthesis			NaOH/Fly Ash Ratio	Reference
	NaOH [M]	T [°C]	t [h]		
Na-A	0.5–3.5	60	10–48	0.5–3.5	[78]
	2.0	100	2	0.8	[79]
	2.2	85	12	0.23	[80]

Type of Zeolite	Conditions of Synthesis			NaOH/Fly Ash Ratio	Reference
	NaOH [M]	T [°C]	t [h]		
	2.0–5.0	100–150	0.5–6	0.5–1.6	[81]
	2.8–5.0	25	48	0.28–0.5	[82]
	2.0	90–150	12	-	[83]
Na-P1	3.0	103	12	0.5	[84]
	1.0–3.0	90	21	0.4–1.2	[85]
	0.5–5.0	150–200	3–48	-	[86]
	3.0	125	8	-	[87]
	0.4–0.5	120	3–24	0.08–0.64	[88]
	3.0	125	9	0.96	[86]
	1.16	80–320	6	0.28	[89]
	1.0	105	24	0.8	[90]
	-	100	12–48	1.0	[91]
	3.0	90	24–72	0.3	[92]
Na-X	3.0	75	24	2.4	[90]
	-	10	120	-	[93]
	3.0	[95] 75	24	0.33	[65]

eral hours [94]

s that the

to natural ones [96]. A cost-effective structural modification is performed before natural zeolites are applied in industries. Moreover, synthetic zeolites are characterized by better texture and adsorption properties compared with natural zeolites. This is because the conditions of the synthesis process can be controlled to obtain zeolite materials with the optimal structure for selected applications. Chemical synthesis of zeolites involves great cost; therefore, the substrates used for synthesis should be cheap mineral or waste materials [97]. Furthermore, zeolites obtained from the conversion of fly ash are characterized by a low production cost, durability, chemical inertia, nonflammability, and developed specific surface area, which are important features found in top-class adsorbents. Another area where zeolites can be applied is to remove pharmaceuticals from water [98][99]. The following subsections present the role and effectiveness of selected zeolites: Zeolite Socony Mobil 5 (ZSM-5); natural Jordanian zeolite (intermediate silica); MOR zeolites with a SiO_2/Al_2O_3 of 18 (MOR18), 200 (MOR200), 240 (MOR240), and 400 (MOR400); modified MOR with an SiO_2/Al_2O_3 ratio of 18 and 240 (TMOR18, TMOR240); magnetic nanoparticles-coated zeolite (MNCZ); zeolite Y; MOR; Slovak natural zeolites from Košice, Slovakia (Zeocem); and FAU-type zeolites (FAU-1, FAU-2). These zeolites were selected thanks to their proven effectiveness in removing antibiotics and non-steroidal drugs from aqueous solutions in studies published to date.

References

1. Kümmerer, K. The presence of pharmaceuticals in the environment due to human use—Present knowledge and future challenges. J. Environ. Manag. 2009, 90, 2354–2366.
2. Rivera-Utrilla, J.; Sanchez-Polo, M.; García Maria Ángeles, F.; Prados-Joya, G.; Perez, R.O. Pharmaceuticals as emerging contaminants and their removal from water. A review. Chemosphere 2013, 93, 1268–1287.
3. Rivera-Utrilla, J.; Gómez-Pacheco, C.V.; Sanchez-Polo, M.; Peñalver, J.J.L.; Perez, R.O. Tetracycline removal from water by adsorption/bioadsorption on activated carbons and sludge-derived adsorbents. J. Environ. Manag. 2013, 131, 16–24.
4. Bush, K. Antimicrobial agents. Curr. Opin. Chem. Biol. 1997, 1, 169–175.
5. Halling-Sørensen, B.; Nielsen, S.N.; Lanzky, P.; Ingerslev, F.; Lützhøft, H.H.; Jørgensen, S. Occurrence, fate and effects of pharmaceutical substances in the environment- A review. Chemosphere 1998, 36, 357–393.
6. Hernando, M.D.; Mezcua, M.; Alba, A.R.F.; Barceló, D. Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. Talanta 2006, 69, 334–342.
7. Fent, K.; Weston, A.; Caminada, D. Ecotoxicology of human pharmaceuticals. Aquat. Toxicol. 2006, 76, 122–159.
8. Nikolaou, A.; Meric, S.; Fatta, D. Occurrence patterns of pharmaceuticals in water and wastewater environments. Anal. Bioanal. Chem. 2007, 387, 1225–1234.
9. Schafhauser, B.H.; Kristofco, L.; de Oliveira, C.M.R.; Brooks, B.W. Global review and analysis of erythromycin in the environment: Occurrence, bioaccumulation and antibiotic resistance hazards. Environ. Pollut. 2018, 238, 440–451.
10. Balakrishna, K.; Rath, A.; Praveenkumarreddy, Y.; Guruge, K.S.; Subedi, B. A review of the occurrence of pharmaceuticals and personal care products in Indian water bodies. Ecotoxicol. Environ. Saf. 2017, 137, 113–120.
11. Der Beek, T.A.; Weber, F.-A.; Bergmann, A.; Hickmann, S.; Ebert, I.; Hein, A.; Küster, A. Pharmaceuticals in the environment-Global occurrences and perspectives. Environ. Toxicol. Chem. 2016, 35, 823–835.
12. Heberer, T. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data. Toxicol. Lett. 2002, 131, 5–17.
13. Heberer, T. Tracking persistent pharmaceutical residues from municipal sewage to drinking water. J. Hydrol. 2002, 266, 175–189.

14. Larsson, D.J.; de Pedro, C.; Paxeus, N. Effluent from drug manufactures contains extremely high levels of pharmaceuticals. J. Hazard. Mater. 2007, 148, 751–755.
15. Castiglioni, S.; Bagnati, R.; Fanelli, R.; Pomati, F.; Calamari, D.; Zuccato, E. Removal of Pharmaceuticals in Sewage Treatment Plants in Italy. Environ. Sci. Technol. 2006, 40, 357–363.
16. Tixier, C.; Singer, H.P.; Oellers, S.; Müller, S.R. Occurrence and Fate of Carbamazepine, Clofibric Acid, Diclofenac, Ibuprofen, Ketoprofen, and Naproxen in Surface Waters. Environ. Sci. Technol. 2003, 37, 1061–1068.
17. Ternes, T.A.; Meisenheimer, M.; McDowell, D.; Sacher, F.; Brauch, H.-J.; Haist-Gulde, B.; Preuss, G.; Wilme, U.; Zulei-Seibert, N. Removal of Pharmaceuticals during Drinking Water Treatment. Environ. Sci. Technol. 2002, 36, 3855–3863.
18. Westerhoff, P.; Yoon, Y.; Snyder, S.; Wert, E. Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes. Environ. Sci. Technol. 2005, 39, 6649–6663.
19. Daughton, C.G.; Ternes, T.A. Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environ. Health Perspect. 1999, 107, 907–938.
20. Benotti, M.J.; Trenholm, R.A.; Vanderford, B.J.; Holady, J.C.; Stanford, B.D.; Snyder, S. Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water. Environ. Sci. Technol. 2009, 43, 597–603.
21. Mhuka, V.; Dube, S.; Nindi, M.M. Occurrence of pharmaceutical and personal care products (PPCPs) in wastewater and receiving waters in South Africa using LC-OrbitrapTM MS. Emerg. Contam. 2020, 6, 250–258.
22. WHO. WHO Model Lists of Essential Medicines; WHO: Geneva, Switzerland, 2020.
23. Yang, S.; Carlson, K. Evolution of antibiotic occurrence in a river through pristine, urban and agricultural landscapes. Water Res. 2003, 37, 4645–4656.
24. Kulkarni, P.; Olson, N.D.; Raspanti, G.A.; Goldstein, R.E.R.; Gibbs, S.G.; Sapkota, A.; Sapkota, A.R. Antibiotic Concentrations Decrease during Wastewater Treatment but Persist at Low Levels in Reclaimed Water. Int. J. Environ. Res. Public Health 2017, 14, 668.
25. Cai, M.-Q.; Wang, R.; Feng, L.; Zhang, L.-Q. Determination of selected pharmaceuticals in tap water and drinking water treatment plant by high-performance liquid chromatography-triple quadrupole mass spectrometer in Beijing, China. Environ. Sci. Pollut. Res. 2015, 22, 1854–1867.
26. Tran, N.H.; Urase, T.; Ta, T.T. A Preliminary Study on the Occurrence of Pharmaceutically Active Compounds in Hospital Wastewater and Surface Water in Hanoi, Vietnam. CLEAN Soil Air Water 2014, 42, 267–275.

27. Paíga, P.; Santos, L.; Ramos, S.; Jorge, S.; Silva, J.G.; Delerue-Matos, C. Presence of pharmaceuticals in the Lis river (Portugal): Sources, fate and seasonal variation. Sci. Total. Environ. 2016, 573, 164–177.
28. Lolić, A.; Paíga, P.; Santos, L.H.; Ramos, S.; Correia, M.; Delerue-Matos, C. Assessment of non-steroidal anti-inflammatory and analgesic pharmaceuticals in seawaters of North of Portugal: Occurrence and environmental risk. Sci. Total. Environ. 2015, 508, 240–250.
29. Petrovic, M.; Skrbic, B.; Živančev, J.; Climent, L.F.; Barceló, D. Determination of 81 pharmaceutical drugs by high performance liquid chromatography coupled to mass spectrometry with hybrid triple quadrupole–linear ion trap in different types of water in Serbia. Sci. Total. Environ. 2014, 468–469, 415–428.
30. Santos, L.; Gros, M.; Rodriguez-Mozaz, S.; Delerue-Matos, C.; Pena, A.; Barceló, D.; Montenegro, M. Contribution of hospital effluents to the load of pharmaceuticals in urban wastewaters: Identification of ecologically relevant pharmaceuticals. Sci. Total. Environ. 2013, 461–462, 302–316.
31. Kallenborn, R.; Fick, J.; Lindberg, R.; Moe, M.; Nielsen, K.M.; Tysklind, M.; Vasskog, T. Pharmaceutical Residues in Northern European Environments: Consequences and Perspectives. In Pharmaceuticals in the Environment; Springer: Berlin/Heidelberg, Germany, 2008; pp. 61–74.
32. Khetan, S.K.; Collins, T.J. Human pharmaceuticals in the aquatic environment: A challenge to green chemisty. Chem. Rev. 2007, 107, 2319–2364.
33. Löffler, D.; Römbke, J.; Meller, M.; Ternes, T.A. Environmental Fate of Pharmaceuticals in Water/Sediment Systems. Environ. Sci. Technol. 2005, 39, 5209–5218.
34. Li, W. Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. Environ. Pollut. 2014, 187, 193–201.
35. Lapworth, D.; Baran, N.; Stuart, M.; Ward, R. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ. Pollut. 2012, 163, 287–303.
36. Pal, A.; Gin, K.Y.-H.; Lin, A.; Reinhard, M. Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects. Sci. Total. Environ. 2010, 408, 6062–6069.
37. Mompelat, S.; Le Bot, B.; Thomas, O. Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. Environ. Int. 2009, 35, 803–814.
38. Joss, A.; Keller, E.; Alder, A.C.; Göbel, A.; McArdell, C.S.; Ternes, T.; Siegrist, H. Removal of pharmaceuticals and fragrances in biological wastewater treatment. Water Res. 2005, 39, 3139–3152.

39. Jelic, A.; Gros, M.; Ginebreda, A.; Cespedes-Sánchez, R.; Ventura, F.; Petrovic, M.; Barceló, D. Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. Water Res. 2011, 45, 1165–1176.
40. Jjemba, P.K. Excretion and ecotoxicity of pharmaceutical and personal care products in the environment. Ecotoxicol. Environ. Saf. 2006, 63, 113–130.
41. Ternes, T.A. Occurrence of drugs in German sewage treatment plants and rivers. Water Res. 1998, 32, 3245–3260.
42. Bound, J.P.; Voulvoulis, N. Household Disposal of Pharmaceuticals as a Pathway for Aquatic Contamination in the United Kingdom. Environ. Health Perspect. 2005, 113, 1705–1711.
43. Carlsson, C.; Johansson, A.K.; Alvan, G.; Bergman, K.; Kühler, T. Are pharmaceuticals potent environmental pollutants?: Part I: Environmental risk assessments of selected active pharmaceutical ingredients. Sci. Total Environ. 2006, 364, 67–87.
44. Hirsch, R.; Ternes, T.; Haberer, K.; Kratz, K.-L. Occurrence of antibiotics in the aquatic environment. Sci. Total. Environ. 1999, 225, 109–118.
45. Costanzo, S.D.; Murby, J.; Bates, J. Ecosystem response to antibiotics entering the aquatic environment. Mar. Pollut. Bull. 2005, 51, 218–223.
46. Huschek, G.; Hansen, P.D.; Maurer, H.H.; Krengel, D.; Kayser, A. Environmental risk assesssment of medicinal products for human use according to European Commission recommendations. Environ. Toxicol. 2004, 19, 226–240.
47. Petrie, B.; Barden, R.; Kasprzyk-Hordern, B. A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring. Water Res. 2015, 72, 3–27.
48. Oaks, J.L.; Gilbert, M.; Virani, M.Z.; Watson, R.T.; Meteyer, C.U.; Rideout, B.A.; Shivaprasad, H.L.; Ahmed, S.; Chaudhry, M.J.I.; Arshad, M.; et al. Diclofenac residues as the cause of vulture population decline in Pakistan. Nature 2004, 427, 630–633.
49. Schwaiger, J.; Ferling, H.; Mallow, U.; Wintermayr, H.; Negele, R. Toxic effects of the non-steroidal anti-inflammatory drug diclofenac: Part I: Histopathological alterations and bioaccumulation in rainbow trout. Aquat. Toxicol. 2004, 68, 141–150.
50. Triebskorn, R.; Casper, H.; Scheil, V.; Schwaiger, J. Ultrastructural effects of pharmaceuticals (carbamazepine, clofibric acid, metoprolol, diclofenac) in rainbow trout (Oncorhynchus mykiss) and common carp (Cyprinus carpio). Anal. Bioanal. Chem. 2007, 387, 1405–1416.
51. Liu, F.; Ying, G.-G.; Tao, R.; Zhao, J.-L.; Yang, J.-F.; Zhao, L.-F. Effects of six selected antibiotics on plant growth and soil microbial and enzymatic activities. Environ. Pollut. 2009, 157, 1636–1642.

52. Coelho, A.D.; Sans, C.; Agüera, A.; Gómez, M.J.; Esplugas, S.; Dezotti, M. Effects of ozone pre-treatment on diclofenac: Intermediates, biodegradability and toxicity assessment. Sci. Total. Environ. 2009, 407, 3572–3578.
53. Gebhardt, W.; Schröder, H.F. Liquid chromatography–(tandem) mass spectrometry for the follow-up of the elimination of persistent pharmaceuticals during wastewater treatment applying biological wastewater treatment and advanced oxidation. J. Chromatogr. A 2007, 1160, 34–43.
54. Suarez, S.; Lema, J.; Omil, F. Pre-treatment of hospital wastewater by coagulation–flocculation and flotation. Bioresour. Technol. 2009, 100, 2138–2146.
55. Bui, T.X.; Choi, H. Adsorptive removal of selected pharmaceuticals by mesoporous silica SBA-15. J. Hazard. Mater. 2009, 168, 602–608.
56. Al-Ghouti, M.A.; Khraisheh, M.A.; Ahmad, M.N.; Allen, S. Adsorption behaviour of methylene blue onto Jordanian diatomite: A kinetic study. J. Hazard. Mater. 2009, 165, 589–598.
57. Brown, P.A.; Brown, J.M.; Allen, S.J. The application of kudzu as a medium for the adsorption of heavy metals from dilute aqueous wastestreams. Bioresour. Technol. 2001, 78, 195–201.
58. Homem, V.; Santos, L. Degradation and removal methods of antibiotics from aqueous matrices—A review. J. Environ. Manag. 2011, 92, 2304–2347.
59. El Qada, E.N.; Allen, S.J.; Walker, G.M. Adsorption of basic dyes from aqueous solution onto activated carbons. Chem. Eng. J. 2008, 135, 174–184.
60. El Qada, E.N.; Allen, S.J.; Walker, G. Adsorption of Methylene Blue onto activated carbon produced from steam activated bituminous coal: A study of equilibrium adsorption isotherm. Chem. Eng. J. 2006, 124, 103–110.
61. Vieno, N.M.; Härkki, H.; Tuhkanen, T.; Kronberg, L. Occurrence of Pharmaceuticals in River Water and Their Elimination in a Pilot-Scale Drinking Water Treatment Plant. Environ. Sci. Technol. 2007, 41, 5077–5084.
62. de Sousa, D.N.R.; Insa, S.; Mozeto, A.A.; Petrovic, M.; Chaves, T.F.; Fadini, P.S. Equilibrium and kinetic studies of the adsorption of antibiotics from aqueous solutions onto powdered zeolites. Chemosphere 2018, 205, 137–146.
63. Masters, A.F.; Maschmeyer, T. Zeolites—From curiosity to cornerstone. Microporous Mesoporous Mater. 2011, 142, 423–438.
64. Valdés, M.G.; Pérez-Cordoves, A.; Díaz-García, M. Zeolites and zeolite-based materials in analytical chemistry. TrAC Trends Anal. Chem. 2006, 25, 24–30.
65. Franus, W.; Wdowin, M.; Franus, M. Synthesis and characterization of zeolites prepared from industrial fly ash. Environ. Monit. Assess. 2014, 186, 5721–5729.

66. Franus, M.; Wdowin, M.; Bandura, L.; Franus, W. Removal of environmental pollutions using zeolites from fly ash: A review. Fresenius Environ. Bull. 2015, 24, 854–866.
67. Niwa, M.; Katada, N.; Okumura, K. Introduction to Zeolite Science and Catalysis. In Superconductivity; Springer Science and Business Media LLC: Berlin/Heidelberg, Germany, 2010; Volume 141, pp. 1–8.
68. Li, Y.; Yu, J. New Stories of Zeolite Structures: Their Descriptions, Determinations, Predictions, and Evaluations. Chem. Rev. 2014, 114, 7268–7316.
69. Weitkamp, J. Zeolites and catalysis. Solid State Ion. 2000, 131, 175–188.
70. Burton, A. Recent trends in the synthesis of high-silica zeolites. Catal. Rev. 2018, 60, 132–175.
71. Burton, A.W.; Zones, S.I.; Elomari, S. The chemistry of phase selectivity in the synthesis of high-silica zeolites. Curr. Opin. Colloid Interface Sci. 2005, 10, 211–219.
72. Maesen, T. The zeolite scene—An overview. In Studies in Surface Science and Catalysis; Elsevier Inc.: Amsterdam, The Netherlands, 2007; Volume 168, pp. 1–12. ISBN 0444530630.
73. Baerlocher, C.; McCusker, L.B.; Olson, D.H. Atlas of Zeolite Framework Types, 6th ed.; Elsevier: Amsterdam, The Netherlands, 2007; Available online: https://www.elsevier.com/books/atlas-of-zeolite-framework-types/baerlocher/978-0-444-53064-6 (accessed on 24 September 2020).
74. Foster, M.; Rivin, I.; Treacy, M.; Friedrichs, O.D. A geometric solution to the largest-free-sphere problem in zeolite frameworks. Microporous Mesoporous Mater. 2006, 90, 32–38.
75. Meier, W.M.; Baerlocher, C. Zeolite type frameworks: Connectivities, configurations and conformations. In Structures and Structure Determination; Springer: Berlin/Heidelberg, Germany, 1999; pp. 141–161.
76. Feng, S.-H.; Li, G.-H. Hydrothermal and Solvothermal Syntheses. In Modern Inorganic Synthetic Chemistry; Elsevier BV: Amsterdam, The Netherlands, 2017; pp. 73–104.
77. Wang, Y.U.J.; Jia, D.E.A.N.; Rui-Juan, S.U.N.; Hao-Wen, Z.H.U.; Zhou, D.M. Adsorption and cosorption of tetracycline and copper(ll) on montmorillonite as affected by solution pH. Environ. Sci. Technol. 2008, 42, 3254–3259.
78. Miyake, M.; Tamura, C.; Matsuda, M. Resource Recovery of Waste Incineration Fly Ash: Synthesis of Zeolites A and P. J. Am. Ceram. Soc. 2004, 85, 1873–1875.
79. Hui, K.S.; Chao, C. Effects of step-change of synthesis temperature on synthesis of zeolite 4A from coal fly ash. Microporous Mesoporous Mater. 2006, 88, 145–151.
80. Tanaka, H.; Fujii, A. Effect of stirring on the dissolution of coal fly ash and synthesis of pure-form Na-A and -X zeolites by two-step process. Adv. Powder Technol. 2009, 20, 473–479.

81. Nascimento, M.; Soares, P.S.M.; Souza, V.P. Adsorption of heavy metal cations using coal fly ash modified by hydrothermal method. Fuel 2009, 88, 1714–1719.
82. Ma, W.; Brown, P.W.; Komarneni, S. Characterization and cation exchange properties of zeolite synthesized from fly ashes. J. Mater. Res. 1998, 13, 3–7.
83. Steenbruggen, G.; Hollman, G. The synthesis of zeolites from fly ash and the properties of the zeolite products. J. Geochem. Explor. 1998, 62, 305–309.
84. Park, M.; Choi, C.L.; Lim, W.T.; Kim, M.C.; Choi, J.; Heo, N.H. Molten-salt method for the synthesis of zeolitic materials: I. Zeolite formation in alkaline molten-salt system. Microporous Mesoporous Mater. 2000, 37, 81–89.
85. Woolard, C.D.; Petrus, K.; van der Horst, M. The use of a modified fly ash as an adsorbent for lead. Water SA 2000, 26, 531–536.
86. Querol, X.; Moreno, N.; Umana, J.; Juan, R.; Hernandez, S.; Pereira, C.F.; Ayora, C.; Janssen, M.; Garcia-Martinez, J.; Linares-Solano, A.; et al. Application of zeolitic material synthesised from fly ash to the decontamination of waste water and flue gas. J. Chem. Technol. Biotechnol. 2002, 77, 292–298.
87. Moreno, N.; Querol, X.; Plana, F.; Andres, J.M.; Janssen, M.; Nugteren, H. Pure zeolite synthesis from silica extracted from coal fly ashes. J. Chem. Technol. Biotechnol. 2002, 77, 274–279.
88. Murayama, N.; Yamamoto, H.; Shibata, J. Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. Int. J. Miner. Process. 2002, 64, 1–17.
89. Adamczyk, Z.; Bialecka, B. Hydrothermal synthesis of zeolites from Polish coal fly ash. Pol. J. Environ. Stud. 2005, 14, 713–719.
90. Derkowski, A.; Franus, W.; Beran, E.; Czímerová, A. Properties and potential applications of zeolitic materials produced from fly ash using simple method of synthesis. Powder Technol. 2006, 166, 47–54.
91. Musyoka, N.M.; Petrik, L.F.; Balfour, G.; Gitari, W.M.; Hums, E. Synthesis of hydroxy sodalite from coal fly ash using waste industrial brine solution. J. Environ. Sci. Health Part A 2011, 46, 1699–1707.
92. Srinivasan, A.; Grutzeck, M.W. The Adsorption of SO2by Zeolites Synthesized from Fly Ash. Environ. Sci. Technol. 1999, 33, 1464–1469.
93. Sakthivel, T.; Reid, D.L.; Goldstein, I.; Hench, L.; Seal, S. Hydrophobic High Surface Area Zeolites Derived from Fly Ash for Oil Spill Remediation. Environ. Sci. Technol. 2013, 47, 5843–5850.
94. Bukhari, S.S.; Behin, J.; Kazemian, H.; Rohani, S. Conversion of coal fly ash to zeolite utilizing microwave and ultrasound energies: A review. Fuel 2015, 140, 250–266.

95. Franus, W.; Wdowin, M. Wykorzystanie popiołów lotnych klasy F do produkcji materiału zeolitowego na skalę półtechniczną. Polityka Energ. 2011, 14, 79–91.
96. Cordoves, A.; Valdés, M.; Fernández, J.C.; Luis, G.; García-Calzón, J.; García, M.E. Characterization of the binding site affinity distribution of a surfactant-modified clinoptilolite. Microporous Mesoporous Mater. 2008, 109, 33–48.
97. Jha, B.; Singh, D.N. ChemInform Abstract: A Review on Synthesis, Characterization and Industrial Applications of Flyash Zeolites. TrAC Trends Anal. Chem. 2012, 33, 65–132.
98. Martucci, A.; Pasti, L.; Marchetti, N.; Cavazzini, A.; Dondi, F.; Alberti, A. Adsorption of pharmaceuticals from aqueous solutions on synthetic zeolites. Microporous Mesoporous Mater. 2012, 148, 174–183.
99. de Ridder, D.; Verberk, J.; Heijman, B.; Amy, G.; van Dijk, J. Zeolites for nitrosamine and pharmaceutical removal from demineralised and surface water: Mechanisms and efficacy. Sep. Purif. Technol. 2012, 89, 71–77.