Aseel M. Aljeboree et al /J. Pharm. Sci. & Res. Vol. 10(9), 2018, 2252-2257

ISSN:0975-1459
Journal of Pharmaceutical Sciences and Research
www.jpsr.pharmainfo.in

Adsorption of Pharmaceuticals as emerging contaminants from aqueous solutions on to friendly surfaces such as activated carbon: A review

Aseel M. Aljeboree[1] **Abass Noor Alshirifi**[2]
[1]*College of science for women-Chemistry Department/Babylon university*
[2]*College of science -Chemistry Department/Babylon university*

Abstract

Antibiotics, an important type of pharmaceutical pollutant, have attracted many researchers to the study of their removal from aqueous solutions. Pharmaceuticals, which are frequently detected in natural and wastewater bodies as well as drinking water have attracted considerable attention, because they do not readily biodegrade and may persist and remain toxic. As a result, pharmaceutical residues pose on-going and potential health and environmental risks. Activated carbon (AC) has been widely used as highly effective adsorbent for antibiotics because of its large specific surface area, high porosity, and favorable pore size distribution. In this article, the adsorption performance of AC towards major type of antibiotics such as tetracyclines,. According to collected data, maximum adsorption capacities of 477.1 mg/g were reported for tetracyclines ,. AC adsorption demonstrated superior performance for drugs, thus being efficient technology for treatment of these pollutants.

Keyword : Pharmaceuticals ,Removal , Adsorption , Wastewater , Tetracycline, Antibiotics , Active carbon

INTRODUCTION:

Pharmaceuticals as emerging pollutants have become a major concern because of their low biodegradability, high persistence, and facile bioaccumulation[1]. Pharmaceuticals or drugs are extensively consumed to improve the health statuses of humans and animals[2] Common drugs are antibiotics, analgesics, anti-inflammatory agents, lipid regulators, hormones, and β-blockers [3] These biologically active chemicals appear in effluents of hospitals, drug factories, and landfills [4, 5]. In recent years, pharmaceuticals and personal care products (PPCPs) have been widely used in all aspects of life and their presence in the environment has aroused dramatic attention [6], since a lot of effluents from urban wastewater treatment plants are contaminated with PPCPs residues [7]. As a general consensus, the existence of PPCPs can not only affect drinking water quality, but also exist a potential risk for ecosystem and human health in a long term [8]. In particular, tetracycline (TC), the second highest antibiotics in production and use, which belongs to one kind of PPCPs, is universally used as human and veterinary medicines to treat diseases and promote growth [9]. However, it is non-biodegradable and has toxicity [10] , and in some cases the TC concentrations in surface soil and surface water were detected to be as high as 86–199 μg/kg and 0.07–1.34 μg/L, respectively [11, 12]. Obviously, it is imperative to develop efficient methods to remove TC.

Several methods, including electrocoagulation [13] ,biodegradation[14] , ultrafiltration membrane [15] ,ozonation [16], , and adsorption[17], used to process pharmaceuticals. some these methods, adsorption is the simple , inexpensive, and more versatile technique for removel these pollutants [18], biochar [19], Activated carbon [20], zeolite [21], mesoporous silica [22], carbon nanotubes (CNTs) [23]. clays [24], chitosan [25], . biomass wastes [26], resin [26] . and graphene oxide [27] , magnetic resin [28] , alkali bio-char [29], HCl-modified zeolite [30], MCM-41 impregnated with , La-impregnated MCM-41 materials[31] [32], anaerobic granular sludge[33] , graphene oxide functionalized magnetic particles[34] , NaOH-activated sludge, Sorbet commercial activated carbons, merck commercial activated carbons[35] , bamboo charcoal[36, 37] activated carbon fiber modified by microwave[38, 39] , , illite[40] , , multi-walled carbon nanotubes , nitrifying granular [41] clays, humic substances, and clay-humic complexes [42], marine sediments [43], mesoporous BiOI microspheres [44], the red soil (RS, UdicFerrosols) [45], palygorskite [46], ITAC-Fe [47], .The fundamental feature of using activated carbon to removel pharmaceuticals is that it does not output poisonous or pharmacologically active products. According to the literature, activated carbons generally elucidate a high ability to absorbs pharmaceuticals [48],[49],[50] [51, 52],[53],[54] . conducted an inclusive study on the adsorption of antibiotics (nitroimidazoles) on various types of activated carbons, finding an increase in the adsorption rate with a decrease in the percentage of oxygen and an increase in the hydrophobicity of the carbon. generally, hydrophobic interactions seem to govern the adsorption kinetics. Nitroimidazole adsorption was largely determined by the chemical properties of the carbon.

TETRACYCLINE

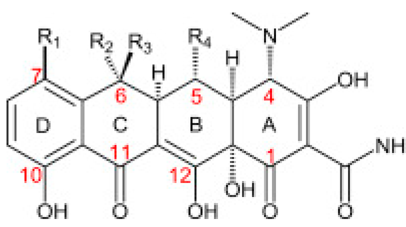
Antibacterial substances secluded from *Streptomyces aureofaciens* are called tetracycline antibiotics (TCs); TCs inhibit Gram-positive and Gram-negative bacteria, mycoplasmas ,chlamydiae, protozoan parasites and, rickettsiae [55]. As a typical PPCP (pharmaceutical and personal care product), TCs mainly contain, oxytetracycline ,tetracycline and chlortetracycline . TCs are widely used in the treatment of stock farming and animal diseases, and its incomplete metabolization in animals and humans has resulted in a significant number of residues in the aqueous environment[56] . These residues exert adverse effects on aquatic ecosystems, not only resulting in the generation of a variety of resistant bacteria[55] but also affecting the aquatic animal life[57]. Additionally, these residues pose a potential threat to human health through drinking water, the food chain, etc. The structure of TCs and the pKa corresponding to the different deprotonations are shown in Table 1[58]. Obviously, the pH plays a crucial role in the removal process of TCs.

Pharmaceutical pollutants

Pharmaceuticals or drugs are extensively consumed to improve the health statuses of humans and animals [59, 60].

Antibiotics are commonly used pharmaceuticals that protect humans and animals against diseases and infection caused by bacteria[61] These chemicals pollutant also used to get better the animals and growth of plants [62] The most important antibiotics are penicillins, tetracyclines (TCs) ,sulfonamides, quinolones and macrolides [63] The continual existence of antibiotics in aquatic systems continually produces harmful bacteria[5, 64] .

Table 1. The structure and main physicochemical properties of tetracycline.

Molecular structure	Name	R_1	R_2	R_3	R_4	$pK_{a1,2,3}$
	Minocycline	$N(CH_3)_2$	H	H	H	2.8, 7.8, 9.3
	Epitetracycline, Tetracycline	H	CH_3	OH	H	3.3, 7.8, 9.6
	Chlortetracycline	Cl	CH_3	OH	H	3.3, 7.5, 9.3
	Meclocycline	Cl	O	=	OH	4.1, 6.9, 9.6
	Demeclocycline	Cl	H	OH	H	3.4, 7.4, 9.4
	Doxycycline	H	H	CH_3	OH	3.0, 8.0, 9.2
	Oxytetracycline	H	CH_3	OH	OH	3.2, 7.5, 8.9

Anti-inflammatory agents and Analgesics are drugs utilized to relieve pain and block inflammation. The most known analgesics are aspirin and acetaminophen [65] naproxen (NA) ,diclofenac ,ketoprofen, and Ibuprofen (IB), are common anti-inflammatory agents. Drugs belonging to the class of anti-inflammatory agents and analgesics are classified as hazardous pollutant because of their immutability in aqueous solutions [66] .

Hormones are very important drugs given their wide use and hazardous effect on humans and animals. estrogens type of Common natural hormones [67] such as estriol along with its derivatives, whereas the synthetic counterpart is 17α-ethinylestradiol [68], Therefore, estrogens have been categorized as abundant pollutants. Their presence in wastewaters poses a significant hazard to ecosystems[69] .

β-Blockers are extensively utilized drugs for treating cardiovascular diseases, such as hypertension and angina . These drugs include propranolol atenolol and metoprolol (MTP) [70]. MTP is a widely consumed drug [71] and its metabolism in the human body produces metoprolol acid and other derivatives that comprise about 85% of the urinary content. Metoprolol acid constitutes the main component of the MTP metabolite and can be produced from MTP by biodegradation [72].

Lipid regulators represent important drugs that impede cardiovascular disease progression and reduce cholesterol concentrations to prevent heart diseases [73], These drugs mainly consist of statins and fibrates. The first group of lipid regulators is rarely present in the environment because metabolites are the main source of statins [74], By contrast, the second group decreases the amount of cholesterol by impeding lipoprotein formation. Clofibric acid and its derivatives are among the fibrates most frequently detected in waters [75].

Pharmaceutically active compounds (PhACs),

They are among water pollutants that have been frequently detected in the effluents of wastewater treatment plants (WWTPs) [76] PhACs are widely used as prescription or non-prescription medicines and after their usage, they find their way into wastewater through urine and feces either as intact substances or metabolites [77], It is a matter of concern that WWTPs are not able to efficiently remove these pollutants due to their persistent nature, resulting in their discharge into surface water [78]. Due to the persistence and high lipid solubility of some of the organic pollutants, they can bioaccumulate in the fatty tissues of living organisms [79]. Recently, some evidences have been found that a few pharmaceutical compounds can mobilize towards the food chain, and hence their concentration is increased[80] The presence of PhACs in waterways may lead to several issues in the environment, such as male fish feminization as a result of exposure to steroidal hormones and development of antibiotic-resistant genes due to released non-metabolized antibiotics into water [81].

The worldwide annual consumption of PhACs is estimated to be 100,000 tons or more and the trend is increasing due to the diseases and aging population [82], For instance, about 877 tons of diclofenac, listed as 12th best-selling generics in the world[83] ,and 942 tons of carbamazepine, listed as 8th bestselling psychiatric drugs worldwide [84], were sold in 2007 in 76 countries. A significant portion of these PhACs are released into the environment in intact or metabolized form. The increasing concern over the accumulation of micropollutants in the aquatic media triggered many research works to evaluate their biodegradation in wastewater treatment systems [85]. The results implied that unlike traditional wastewater treatment processes, such as conventional activated sludge, recently-developed methods for wastewater treatment including membrane separation, advanced oxidation processes (AOPs) and adsorption onto activated carbon, are able to achieve high efficiency for PhACs removal[86-88]. However, still, challenges remained with these technologies including the formation of more toxic by-products during AOPs [89], the disposal of the concentrated stream in membrane separation [90] and the regeneration of absorbents [91] Therefore, development of effective treatment processes to remove PhACs from wastewater is always of high importance. In Table 2, the information about physicochemical properties of the most studied compounds has been presented as they are helpful in the prediction of the efficiency of enzymatic treatment. In the following sections, removal efficiencies of PhACs by different forms of the enzyme (whole-cell culture, crude extracts and immobilized) are also discussed.

Activated carbon

Activated carbon, a widely used adsorbent in industrial processes, is composed of a microporous, homogenous structure with high surface area and shows radiation stability. The process for producing high-efficiency activated carbon is not completely investigated in developing countries. Furthermore, there are many problems with the regeneration of used activated carbon. Nowadays, there is a great interest in finding inexpensive and effective alternatives to the existing commercial activated carbon [92].

Active carbons can be produced from a variety of carbonaceous materials, by chemical or physical activation. It is well known that their structural properties (external surface area ,micropore volume, and pore size distribution) depend on the carbonization and the activation processes. [93]. The costs of commercial activated carbon very expensive compared costs of activated carbon prepared from biomaterials are very low compared to the costs of commercial activated carbon very expensive . Waste materials that have been successfully used to manufacture activated carbon in the recent past include bagasse , coir pith[94] apricot stones (ASAC) [95], pine cone ,[96]coconut shell [92].sunflower seed hull [97], pine-fruit shell [98] hazelnut husks, rice hulls, oil palm shell [99], and Coconut husk[100]

Table 2. Physical-chemical properties and therapeutic functions of selected pharmaceuticals [101, 102]

Compound	Acronym	Molecular formula	Molecular weight (g/mol)	Water solubility (mg/L)	Classification	Log K_{ow}	pKa
Tetracycline	TC	$C_{22}H_{24}N_2O_8$	444.435	231	Antibiotic	−1.37	3.3
Chlortetracycline	CTC	$C_{22}H_{23}ClN_2O_8$	478.882	8.6	Antibiotic	−0.68	P_1 = 3.30 P_2 = 7.55 P_3 = 9.33
Doxycycline	DC	$C_{22}H_{24}N_2O_8$	444.43	630	Antibiotic	3.5	P_1 = 3.4 P_2 = 7.7 P_3 = 9.7
Oxytetracycline	OTC	$C_{22}H_{24}N_2O_9$	460.434	313	Antibiotic	−0.90	P_1 = 3.3 P_2 = 7.3 P_3 = 9.1
Ciprofloxacine	CPF	$C_{17}H_{18}FN_3O_3$	331.346	30000	Antibiotic	0.28	6.09
Enrofloxacin	EFC	$C_{19}H_{22}FN_3O_3$	359.4	146	Antibiotic	3.48	P_1 = 5.94 P_2 = 8.70
Sulfamethoxazole	SMX	$C_{10}H_{11}N_3O_3S$	253.3	610	Antibiotic	0.89	P_1 = 1.7 P_2 = 5.6
Sulfamonomethoxine	SMM	$C_{11}H_{12}N_4O_3S$	280.302	10000	Antibiotic	−0.04	5.9
Sulfapyridine	SPY	$C_{11}H_{11}N_3O_2S$	249.29	268	Antibiotic	0.35	8.43
Norfloxacin	NOR	$C_{16}H_{18}FN_3O_3$	319.331	178000	Antibiotic	0.46	P_1 = 6.34 P_2 = 8.75
Oseltamivir	OST	$C_{16}H_{28}N_2O_4$	312.40	1600	Antiviral	0.95	7.7
Propranolol	PPL	$C_{16}H_{21}NO_2$	259.34	61.7	Beta-blocker	3.48	9.6
Sulfadimethoxine	SDM	$C_{12}H_{14}N_4O_4S$	310.33	343	Antibacterial	1.63	5.9

Table 3. Summary of studies describing the adsorption of Tetracyclines by activated carbon and its composites. The maximum adsorption capacity and specific experimental conditions such as temperature and pH are listed.

Material	Treatment	Specific surface area (m^2 g^{-1})	Tetracycline species	Qe (mg g^{-1})	Temp./pH	Ref.
Activated carbons (ACs) by KOH activation	KOH to TPC weight ratios (*W*) between 0.5 and 6, and activation temperatures from 600 to 800 °C	814	Tetracycline	312	300 K/4.35	[103]
The Nano porous activated carbon was prepared from the carbonaceous material	prepared from apricot shell by chemical activation using phosphoric acid	0.05 -0.25	Tetracycline	76.97	393K/ 6.5	[104]
Activated carbon (AC) prepared from apricot shell	The adsorbent was produced via a chemical activation method using phosphoric acid heated in an air oven at 100 °C for 24 h	307.6	Tetracycline	308.33	303K/6.5	[105]
Agave americana fibres (A) and mimosa Tannin (T) were used as precursors of activated carbons (ACs).	hydrothermal carbonisation (HTC) step prior to pyrolysis	1200	Tetracycline	80	298K/7	[106]
new activated carbon form cotton cloth residues	prepared by chemical activation in the presence of phosphoric acid and pyrolysis at 600 °C	1175	Tetracycline	109	293K/6.2	[107]
Activated Carbon The wood biochar was obtained by pyrolysis of a softwood	thermally treated at 600–800 °C in the air/nitrogen atmosphere	316	Tetracycline	120	77k/6.5	[108]
NaOH-activated carbon produced from macadamia nut shells	Kept at 500 °C for 120 min under N2atmosphere, mixed with NaOH under	1524	Tetracycline	455.33	298 /8.74	[109]
Activated carbon prepared from lignin	Exposed to H_3PO_4solution for 12 h and dried at 450 °C for 1 h	931.53	Tetracycline	317.5121	293 K/5.50	[110]
Activated Carbon Fiber	Heated in a microwave oven under 600 °C and maintained for 15 min under N_2 atmosphere	1153.25	Tetracycline	312.5,	293 K/2	[111]
Activated Carbons from Agricultural Residues	Heated at 10 °C min^{-1} up to 850 °C under N_2atmosphere	821	Tetracycline	308.8	293 K/4	[112]
Commercial activated carbon	Compared the behavior of commercial activated carbons and sludge-derived materials	1200	Tetracycline,	471.1,	298 K/4-5	[113]

The adsorption removal of antibiotics by activated carbon

Adsorption removal of tetracycline

AC has been used as an adsorbent because of its high surface area and its excellent adsorption capacity for a broad range of contaminants . The development of activated carbon could be summarized in two aspects: improving the adsorption capability by doping active carbon with other inorganic substances to activate them in different ways and searching for cheap raw materials and optimal activation methods. Related research is listed in Table 3.

L. Huang the found prepared ferric nitrate-doped activated carbons from Iris tectorum, SEM photographs of ITAC (Iris tectorum with H_3PO_4) and ITAC-Fe (the mixture of H_3PO_4 and ferric nitrate). The adsorption of TC exhibited strong pH-dependent behavior, and the adsorption capacity decreased rapidly with increasing solution pH. The maximum adsorption capacity of TC is 769 mg/g. [111]

Martins, pezoti et al. they found The activated carbon (AC) with macadamia nut shells used as precursors showed a good yield (19.79%) and high surface area (1524 $m^2\ g^{-1}$) for tetracycline; it also demonstrated a considerable adsorption capacity (455.33 mg g^{-1}). [109] .

Zhang, Zuo et al. they found Tetracycline (TC) was cost-effectively removed by coupling of flow-through electro-Fenton (EF) and in-situ regenerative active carbon felt (ACF) adsorption system, which used a modified graphite felt as the cathode. It proved the coupling process achieved a higher removal efficiency (5–44%) than single flow-through EF system and kept stable performance in 600 min treatment. [114]

Muthanna J.Ahmed et.al., they found Activated carbon (AC) because of its high porosity, large specific surface area, and favorable pore size distribution. using as highly effective adsorbent for antibiotics the adsorption performance of AC towards three major types of antibiotics such as quinolones ,tetracyclines and penicillins maximum adsorption capacities of 638.6 ,1340.8 and 570.4 mg/g were reported for quinolones ,tetracyclines, , and penicillins, respectively [115].

YajunChen et.al., they found rice husk ash (RHA) , agricultural waste, has the possibility to be an applicable alternative adsorbent for the removal of tetracycline (TC) from aqueous solution. study are the effect of adsorption time, solution pH, initial concentration of TC, and temperature .[116]

Chen, Wang et al. they found adsorption capacity of RHA natural adsorbate and cheap for the removal of TC from aqueous solution. The adsorption capacity increases from 1.51 to 3.41 mg/g and the removal efficiency decreases 60.93% to 34.40%, when the initial concentration of TC solution increases from 5 mg/L to 20 mg/L[116]

Mojtaba HedayatiMarzbali et.al., hey found removal of Tetracycline (TC) from aqueous solution using activated carbon (AC) prepared from apricot shell by activation phosphoric acid. The , total pore volume ,average pore diameter, and specific surface area were , 0.191 cm3 g^{-1}, and 1.957 nm,307.6 m2 g^{-1} respectively. The effect of contact time ,adsorbent dosage, initial TC concentration , initial pH of the solution on TC and temperature adsorption was studied [105]

R.Acosta et.al., they found TPC-ACs were successfully tested for tetracycline (TC) abatement. The adsorption equilibrium was reached after 15 h at 25 °C, TC adsorption was found a spontaneous process. TPC-ACs maximum TC adsorption of 312 mg g−1, higher than that of the (CAC) used as a reference .[117]

Rivera-Utrilla, et al. they found commercial activated carbons studied have a high TC adsorption capacity (65–471 mg/g). At the study pH (pH 4–5), the capacity of carbons to adsorb TC is directly related to the density of delocalized π electrons in both the graphene layers of the carbon and the TC aromatic ring. [113]

Rivera-Utrilla et al. (2013b) They found analyzed the adsorption demeanor of TC and OTC on commercial carbon CAC. The experimental equilibrium data of both antibiotics were provided by Freundlich with R^2 of 0.9851 and 0.9782 compared to 0.9999 and 0.9991 by Langmuir isotherms. For the Langmuir isotherm, the values of qmax were 413.2 and 471.1 mg/g for OTC and TC, respectively. [113]

CONCLUSIONS AND FUTURE PERSPECTIVES

environmental pollution is increasingly serious With the rapid development of human society and the economy,, but on the other hand, people are increasingly concerned about their health . Antibiotics in wastewater , groundwater, effluent, seawater pose and tap water, possible menace to human validity . From the original activated carbon to the latest graphene, carbon-based materials play decisive roles in the practicability of removing antibiotics. . Activated carbon has been commercially used in wastewater treatment plants ,

Although an increasing number of studies included the adsorption of pharmaceuticals on ACs from agro-industrial wastes, there are still several points which need more attention, such as modification of adsorbent to enhancement adsorption capacity, utilization of composite adsorbents, multi-component adsorption, treatment of real effluents, fixed-bed studies, and enhancement of regeneration. Furthermore, studies should also be extended to pilot and full scale to evaluate the potential use of ACs at the industrial level

REFERENCES

1. Zhang, S., et al., *Adsorption of pharmaceuticals on chitosan-based magnetic composite particles with core-brush topology*. Chemical Engineering Journal. **304**: p. 325-334.
2. Cecconet, D., et al., *Biological combination processes for efficient removal of pharmaceutically active compounds from wastewater: A review and future perspectives*. Journal of Environmental Chemical Engineering. **5**(4): p. 3590-3603.
3. Taheran, M., et al., *Membrane processes for removal of pharmaceutically active compounds (PhACs) from water and wastewaters*. Science of The Total Environment. **547**: p. 60-77.
4. Ashfaq, M., et al., *Ecological risk assessment of pharmaceuticals in the receiving environment of pharmaceutical wastewater in Pakistan*. Ecotoxicology and Environmental Safety. **136**: p. 31-39.
5. Aseel Musthaq Aljeboree, A.N.A., *Colorimetric Determination of phenylephrine hydrochloride drug Using 4-Aminoantipyrine: Stability and higher sensitivity*. J. Pharm. Sci. & Res. , 2018. **10**(7): p. 1774-1779.
6. J. Radjenovic, M.P., F. Ventura, D. BarcelÓ, *Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatmentWater Res.*, . 2008. **42** p. pp. 3601-3610.

7. F. Ferrag-Siagh, F.F., I. Soutrel, H. Ait-Amar, H. Djelal, A. Amrane, *Tetracycline degradation and mineralization by the coupling of an electro-Fenton pretreatment and a biological process*J. Chem. Technol. Biot., 2013. **88** p. pp. 1380-1386.

8. I. Sires, E.B., *Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies:*. a review Environ. Int, 2012. **40**: p. pp. 212-229.
9. Y. Wang, H.Z., J. Zhang, C. Lu, Q. Huang, J. Wu, F. Li, *Degradation of tetracycline in aqueous media by ozonation in an internal loop-lift reactor*. J. Hazard. Mater, 2011. **192**: p. pp. 35-43.
10. V.L. Cunningham, D.J.C.C., R.E. Hannah, *Environmental risk assessment of paroxetine*. Environ. Sci. Technol., 2004. **38** p. pp. 3351-3359.
11. KASIM H. KADHIM, A.N.A.a.A.S.A., ***Separation and Preconcentration for Determination of Ultra Trace of Chromium(III) and Zinc(II) Using Spectrofluorimetry Techniques***. *Asian Journal of Chemistry, 2014*. **26**: p. *139-142*.
12. L.L. Ji, Y.Q.W., S.R. Zheng, D.Q. Zhu, *Adsorption of tetracycline and sulfamethoxazole on crop residue-derived ashes: Implication for the relative importance of black carbon to soil sorption*. Environ. Sci. Technol., 2011. **45**: p. pp. 5580-5586.
13. Nariyan, E., A. Aghababaei, and M. Sillanpí¤í¤, *Removal of pharmaceutical from water with an electrocoagulation process; effect of various parameters and studies of isotherm and kinetic*. Separation and Purification Technology. **188**: p. 266-281.
14. Zhou, H., et al., *Enhancement with physicochemical and biological treatments in the removal of pharmaceutically active compounds during sewage sludge*

anaerobic digestion processes. Chemical Engineering Journal. **316**: p. 361-369.

15. Sheng, C., et al., *Removal of Trace Pharmaceuticals from Water using coagulation and powdered activated carbon as pretreatment to ultrafiltration membrane system.* Science of The Total Environment. **550**: p. 1075-1083.
16. Gomes, J.o., et al., *Application of ozonation for pharmaceuticals and personal care products removal from water.* Science of The Total Environment. **586**: p. 265-283.
17. Marques, S.C.R., et al., *Pharmaceuticals removal by activated carbons: Role of morphology on cyclic thermal regeneration.* Chemical Engineering Journal. **321**: p. 233-244.
18. Moro, T.R., et al., *Adsorption of pharmaceuticals in water through lignocellulosic fibers synergism.* Chemosphere. **171**: p. 57-65.
19. Lin, L., W. Jiang, and P. Xu, *Comparative study on pharmaceuticals adsorption in reclaimed water desalination concentrate using biochar: Impact of salts and organic matter.* Science of The Total Environment. **601-602**: p. 857-864.
20. Calisto, V.n., et al., *Single and multi-component adsorption of psychiatric pharmaceuticals onto alternative and commercial carbons.* Journal of Environmental Management. **192**: p. 15-24.
21. Sun, K., et al., *Sorption and retention of diclofenac on zeolite in the presence of cationic surfactant.* Journal of Hazardous Materials. **323**: p. 584-592.
22. Liang, Z., et al., *Adsorption of quinolone antibiotics in spherical mesoporous silica: Effects of the retained template and its alkyl chain length.* Journal of Hazardous Materials. **305**: p. 8-14.
23. Zhao, H., et al., *Adsorption behavior and mechanism of chloramphenicols, sulfonamides, and non-antibiotic pharmaceuticals on multi-walled carbon nanotubes.* Journal of Hazardous Materials. **310**: p. 235-245.
24. Dordio, A.V., et al., *Mechanisms of removal of three widespread pharmaceuticals by two clay materials.* Journal of Hazardous Materials. **323**: p. 575-583.
25. Kyzas, G.Z., D.N. Bikiaris, and D.A. Lambropoulou, *Effect of humic acid on pharmaceuticals adsorption using sulfonic acid grafted chitosan.* Journal of Molecular Liquids. **230**: p. 1-5.
26. Zhou, Y., L. Zhang, and Z. Cheng, *Removal of organic pollutants from aqueous solution using agricultural wastes: A review.* Journal of Molecular Liquids. **212**: p. 739-762.
27. Shan, D., et al., *Preparation of porous graphene oxide by chemically intercalating a rigid molecule for enhanced removal of typical pharmaceuticals.* Carbon. **119**: p. 101-109.
28. Q. Zhou, Z.L., C. Shuang, A. Li, M. Zhang, M. Wang, *Efficient removal of tetracycline by reusable magnetic microspheres with a high surface area*

Chem. Eng. J.,, 2012. **210**: p. pp. 350-356,.

29. P. Liu, W.J.L., H. Jiang, J.J. Chen, W.W. Li, H.Q. Yu, *Modification of bio-char derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution.* Bioresour. Technol., 2012. **121**: p. pp. 235-240.
30. Y.L. Zou, H.H., M. Chu, J.W. Lin, D.Q. Yin, Y.N. Li, *Adsorption research of tetracycline from water by HCl-modified zeolite.* Adv. Mater. Res., 2012. **573-574**: p. pp. 43-47, .
31. B.K. Vu, O.S., H.S. Lee, E.W. Shin, *Adsorption of tetracycline on La-impregnated MCM-41 materials.* Environ. Tech., 2010. **31**(3): p. pp. 233-241.
32. Y. Gao, Y.L., L. Zhang, H. Huang, J.J. Hu, S.M. Shah, X.G. Su, *Adsorption and removal of tetracycline antibiotics from aqueous solution by graphene oxide.* J. Colloid Interface Sci, 2012. **368** (1): p. pp. 540-546,.
33. K. Li, F.J., Y. Liu, Z. Tong, X. Zhan, Z. Hu, *Adsorption removal of tetracycline from aqueous solution by an aerobic granular sludge: equilibrium and kinetic studies.* Water Sci. Technol., 2013. **67**(7): p. pp. 1490-1496.
34. Y. Lin, S.X., J. Li, *Fast and highly efficient tetracyclines removal from environmental waters by graphene oxide functionalized magnetic particles* Chem. Eng. J., 2013. **225**: p. pp. 679-685,.
35. J. Rivera-Utrilla, C.V.G.-P., M. Sánchez-Polo, J.J. López-Peñalver, R. Ocampo-Pérez, *Tetracycline removal from water by adsorption/bioadsorption on activated carbons and sludge-derived adsorbents.* J. Environ. Manage., 2013. **131**: p. pp. 16-24,.
36. P. Liao, Z.Z., J. Dai, X. Wu, W. Zhang, K. Wang, S. Yuan, *Adsorption of tetracycline and chloramphenicol in aqueous solutions by bamboo charcoal: a batch and fixed-bed column study.* Chem. Eng. J., 2013. **228**: p. pp. 496-505.
37. L. Zhang, X.Y.S., X.Y. Liu, L.J. Yang, F. Pan, J. Lv, *Studies on the removal of tetracycline by multi-walled carbon nanotubes.* Chem. Eng. J., 2011. **178**: p. pp. 26-33, .
38. L. Huang, C.S., B. Zhang, S. Niu, B. Gao, *Characterization of activated carbon fiber by microwave heating and the adsorption of tetracycline antibiotics.* Sep. Sci. Technol., 2013. **48**(9): p. pp. 1356-1363,.
39. P. Liao, Z.Z., J. Dai, X. Wu, W. Zhang, K. Wang, S. Yuan, *Adsorption of tetracycline and chloramphenicol in aqueous solutions by bamboo charcoal: a batch and fixed-bed column study.* Chem. Eng. J.,, (2013. **228**: p. pp. 496-505,.
40. P. Chang, Z.L., J. Jean, W. Jiang, C. Wang, K. Lin, *Adsorption of tetracycline on 2:1 layered non-swelling clay mineral illite.* Appl. Clay Sci.,, 2012. **67-68**: p. pp. 158-163.
41. Y.J. Shi, X.H.W., Z. Qi, M.H. Diao, M.M. Gao, S.F. Xing, S.G. Wang, X.C. Zhao, *Sorption and biodegradation of tetracycline by nitrifying granules and the toxicity of tetracycline on granules.* J. Hazard. Mater.,, 2011. **191**(1-3): p. pp. 103-109.
42. J.R.V. Pils, D.A.L., *Sorption of tetracycline and chlortetracycline on K- and Ca-saturated soil clays, humic substances, and clay-humic complexes.* Environ. Sci. Technol.,, 2007. **41**(6): p. pp. 1928-1933.
43. X.R. Xu, X.Y.L., *Sorption and desorption of antibiotic tetracycline on marine sediments.* Chemosphere, 2010. **78**(4): p. pp. 430-436.
44. R. Hao, X.X., X. Zuo, J. Nan, W. Zhang, *Efficient adsorption and visible-light photocatalytic degradation of tetracycline hydrochloride using mesoporous BiOI microspheres.* J. Hazard. Mater.,, 2012. **209-210**: p. pp. 137-145,.
45. Y. Wang, R.S., A. Xiao, S. Wang, D. Zhou, *Phosphate affects the adsorption of tetracycline on two soils with different characteristics.* Geoderma, , 2010. **156**(3-4): p. pp. 237-242.
46. P.H. Chang, Z.H.L., T.L. Yu, S. Munkhbayer, T.H. Kuo, Y.C. Hung, J.S. Jean, K.H. Lin, *Sorptive removal of tetracycline from water by palygorskite.* J. Hazard. Mater. , 2009. **165** (1-3): p. pp. 148-155, .
47. G. Li, D.Z., M. Wang, J. Huang, L. Huang, *Preparation of activated carbons from Iris tectorum employing ferric nitrate as dopant for removal of tetracycline from aqueous solutions.* Ecotoxicol. Environ. Saf. , 2013. **98**: p. pp. 273-282, .
48. Dutta, M., N.N. Dutta, and K.G. Bhattacharya, *Aqueous phase adsorption of certain beta-lactam antibiotics onto polymeric resins and activated carbon.* Separation and Purification Technology, 1999. **16**(3): p. 213-224.
49. Fuerhacker, M., A. Dأ¼rauer, and A. Jungbauer, *Adsorption isotherms of 17²خ-estradiol on granular activated carbon (GAC).* Chemosphere, 2001. **44**(7): p. 1573-1579.
50. Adams et al. and Y.W. C. Adams, K. Loftin, M. Meyer, *Removal of antibiotics from surface and distilled water in conventional water treatment processes.* J. Environ. Eng., 2002. **128**: p. pp. 253-260.
51. Snyder, S.A., et al., *Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals.* Desalination, 2007. **202**(1): p. 156-181.
52. Simazaki et al. and J.F. D. Simazaki, S. Manabe, M. Matsuda, M. Asami, S. Kunikane, *Removal of selected pharmaceuticals by chlorination, coagulation-sedimentation and powdered activated carbon treatment*

35. Water Sci. Technol.,, 2008. **58**: p. pp. 1129-1135.

53. Choi et al., a. and S.G.K. K.J. Choi, S.H. Kim, *Removal of antibiotics by coagulation and granular activated carbon filtration.* J. Hazard. Mater, 2008. **151**: p. pp. 38-43.
54. Rivera-Utrilla et al. and G.P.-J. J. Rivera-Utrilla, M. Sánchez-Polo, M.A. Ferro-García, I. Bautista-Toledo, *Removal of nitroimidazole antibiotics from aqueous solution by adsorption/bioadsorption on activated carbon.* J. Hazard. Mater.,, 2009. **170**: p. pp. 298-305.
55. M. Gossen, H.B., *Tight control of gene expression in mammalian cells by tetracycline-responsive promoters*Proc. Natl. Acad. Sci, 1992. **89** p. 5547-5551.

56. Y.-J. Wang, D.-A.J., R.-J. Sun, H.-W. Zhu, D.-M. Zhou, *Adsorption and cosorption of tetracycline and copper (II) on montmorillonite as affected by solution pH*Environ. Sci. Technol, 2008. **42**: p. 3254-3259.

57. Kأ¼mmerer, K., *Antibiotics in the aquatic environment â€“ A review â€“ Part I.* Chemosphere, 2009. **75**(4): p. 417-434.
58. L.c.H. Santos, D.a.n., A. Pena, M.C.O.B. Montenegro, P. Solich, L. Nov¢kov¢, *Fast and sensitive UHPLC methods with fluorescence and tandem mass spectrometry detection for the determination of tetracycline antibiotics in surface waters*J. Chromatogr. B,, 2013. **927**: p. 201-208.

59. D. Cecconet, D.M., A. Callegari, A.G. Capodaglio, *Biological combination processes for efficient removal of pharmaceutically active compounds from wastewater: a review and future perspectives.* J. Environ. Chem. Eng.,, 2017. **5**: p. 3590-3603.
60. S. Klatte, H.-C.S., M. Hempel, *Pharmaceuticals in the environment - A short review on options to minimize the exposure of humans, animals and ecosystems.* Sustain. Chem. Pharm., , 2017. **5** p. 61-66.
61. Y. Yang, Y.S.O., K.-H. Kim, E.E. Kwon, Y.F. Tsang, *Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: a review.* Sci. Total Environ., , 2017. **596-597**: p. 303-320.
62. F. Yu, Y.L., S. Han, J. Ma, *Adsorptive removal of antibiotics from aqueous solution using carbon materials.* Chemosphere, , 2016 **153**: p. 365-385.
63. A. Puckowski, K.M., P. Łukaszewicz, M. Boreck, M. Caban, et al., *Bioaccumulation and analytics of pharmaceutical residues in the environment: a review.* J. Pharm. Biomed. Anal., , 2016 **127** p. 232-255.
64. R. Acosta, V.F., A. Martinez de Yuso, D. Nabarlatz, A. Celzard, *Tetracycline adsorption onto activated carbons produced by KOH activation of tyre pyrolysis char.* Chemosphere, 2016. **149** p. 168-176.
65. L. Feng, E.D.v.H., M.A. Rodrigo, G. Esposito, M.A. Oturan, *Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review.* Chem. Eng. J., , 2013. **228** p. 944-964.
66. Close and B.S. B. Tiwari, Y. Ouarda, P. Drogui, R.D. Tyagi, G. Buelna, *Review on fate and mechanism of removal of pharmaceutical pollutants from wastewater using biological approach.* Bioresour. Technol., , 2017. **224**: p. pp. 1-12.

67. Li, W.C., *Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil.* Environ. Pollut.,, 2014. **187**: p. 193-201.
68. Y. Yang, Y.S.O., K.-H. Kim, E.E. Kwon, Y.F. Tsang, *Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: a review.* Sci. Total Environ., 2017. **596-597**: p. 303-320.
69. B. Tiwari, B.S., Y. Ouarda, P. Drogui, R.D. Tyagi, G. Buelna, *Review on fate and mechanism of removal of pharmaceutical pollutants from wastewater using biological approach.* Bioresour. Technol., 2017. **224**: p. 1-12.
70. Y. Yang, Y.S.O., K.-H. Kim, E.E. Kwon, Y.F. Tsang, *Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: a review.* Sci. Total Environ., 2017. **596-597** p. 303-320.
71. Z. Dong, D.B.S., R.E. Moran, J.P. Shine, *Prioritizing environmental risk of prescription pharmaceuticals.* Regul. Toxicol. Pharmacol, 2013. **65**: p. 60-67.
72. E.N. Evgenidou, I.K.K., D.A. Lambropoulou, *Occurrence and removal of transformation products of PPCPs and illicit drugs in wastewaters: a review.* Sci. Total Environ., 2015. **505** p. 905-926.
73. A.B. Caracciolo, E.T., P. Grenni *Pharmaceuticals in the environment: biodegradation and effects on natural microbial communities. A review.* J. Pharm. Biomed. Anal.,, 2015. **106**: p. 25-36.
74. E. Gracia-Lor, J.V.S., R. Serrano, F. Hernández *Occurrence and removal of pharmaceuticals in wastewater treatment plants at the Spanish Mediterranean area of Valencia*Chemosphere,, 2012. **87**: p. 453-462.

75. L. Patrolecco, N.A., P. Grenni, A. Tolomei, A.B. Caracciolo, et al., *Simultaneous determination of human pharmaceuticals in water samples by solid phase extraction and HPLC with UV-Fluorescence detection.* Microchem. J.,, 2013. **107**: p. 165-171.
76. E. Marco-Urrea, M.P.-T., T. Vicent, G. Caminal, *Ability of white-rot fungi to remove selected pharmaceuticals and identification of degradation products of ibuprofen by Trametes versicolor.* Chemosphere,, 2009. **74** p. 765-772.
77. M. Naghdi, M.T., S.K. Brar, A. Kermanshahi-pour, M. Verma, R. Surampalli, *Immobilized laccase on oxygen functionalized nanobiochars through mineral acids treatment for removal of carbamazepine.* Sci. Total Environ., 2017.
78. J. Lienert, K.G., B.I. Escher, *Screening method for ecotoxicological hazard assessment of 42 pharmaceuticals considering human metabolism and excretory routes.* Environ. Sci. Technol., , 2007. **41**: p. 4471-4478.
79. Burkhardt-Holm, P., *Linking water quality to human health and environment: the fate of micropollutants.* Inst. Water Policy Natl. Univ. Singap., 2011: p. 1-62.
80. A. Lagesson, J.F., T. Brodin, J. Fick, M. Jonsson, P. Byström, J. Klaminder and p. (), *Bioaccumulation of five pharmaceuticals at multiple trophic levels in an aquatic food web - insights from a field experiment*Sci. Total Environ.,, 2016. **568**: p. 208-215.

81. S.O. De García, G.P.P., P.A. García-Encina, R.I. Mata and *Ranking of concern, based on environmental indexes, for pharmaceutical and personal care products: an application to the Spanish case.* J. Environ. Manag., 2013. **129**: p. 384-397.
82. Kümmerer, K., *Pharmaceuticals in the Environment-a Brief Summary, Pharmaceuticals in the Environment.* Springer, 2008: p. 3-21.
83. L. Lonappan, S.K.B., R.K. Das, M. Verma, R.Y. Surampalli, *Diclofenac and its transformation products: environmental occurrence and toxicity-A review.* Environ. Int, 2016. **96**: p. 127-138.

84. D.P. Mohapatra, S.K.B., R.D. Tyagi, P. Picard, R.Y. Surampalli, *Carbamazepine in municipal wastewater and wastewater sludge: ultrafast quantification by laser diode thermal desorption-atmospheric pressure chemical ionization coupled with tandem mass spectrometry* Talanta, 2012. **99** (247-255).
85. P.E. Stackelberg, J.G., E.T. Furlong, M.T. Meyer, S.D. Zaugg, R.L. Lippincott *Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds.* Sci. Total Environ., 2007. **377**: p. 255-272.
86. K. Ikehata, N.J.N., M. Gamal El-Din *Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: a review.* Ozone Sci. Eng.,, 2006. **28**: p. 353-414.
87. J. Radjenović, M.P., F. Ventura, D. Barceló, *Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment.* Water Res.,, 2008. **42**: p. 3601-3610.
88. N. Tadkaew, F.I.H., J.A. McDonald, S.J. Khan, L.D. Nghiem *Removal of trace organics by MBR treatment: the role of molecular properties.* Water Res., 2011. **45**: p. 2439-2451.
89. T. Kosjek, H.R.A., B. Kompare, A. Ledin, E. Heath, *Fate of carbamazepine during water treatment.* Environ. Sci. Technol.,, 2009. **43**: p. 6256-6261.
90. P. Westerhoff, H.M., D. Minakata, J. Crittenden, *Oxidation of organics in retentates from reverse osmosis wastewater reuse facilities.* Water Res., 2009. **43** p. 3992-3998.
91. Bathen, D., *Physical waves in adsorption technology-an overview.* Sep. Purif. Technol.,, 2003. **33**: p. 163-177.
92. Aseel M Aljeboree, A.N.A., Ayad F Alkaim, *Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon.* Arabian journal of chemistry, 2017. **10**: p. 3381-3393.
93. Daguerre, E., A. Guillot, and F. Stoeckli, *Activated carbons prepared from thermally and chemically treated petroleum and coal tar pitches.* Carbon, 2001. **39**(8): p. 1279-1285.
94. Tsai, W.T., Chang, C.Y., Lin, M.C., Chien, S.F., Sun, H.F., Hsieh, and M.F., *Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl2 activation.* Chemosphere, 2001. **45**: p. 51-58.
95. A F Alkaim, M.B.A., *Adsorption of basic yellow dye from aqueous solutions by Activated carbon derived from waste apricot stones (ASAC): Equilibrium, and thermodynamic aspects.* international journal of chemical sciences, 2013. **11**(2): p. 797-814.
96. Ghaedi, M., Sadeghian, B., Pebdani, A.A., Sahraei, R., Daneshfar, A., Duran, C., *Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon.* Chem. Eng. J., 2012. **187**: p. 133-141.
97. ALJEBORI, A.M.K.A., ABBAS NOOR, *Effect of Different Parameters on the Adsorption of Textile Dye Maxilon Blue GRL from Aqueous Solution by Using White Marble.* Asian Journal of Chemistry, 2012. **24**(12): p. 5813-5816.
98. Royer, B., Cardoso, N.F., Lima, E.C., Vaghetti, J.P., Simon, N.M., Calvete, T., Veses, R.C., *Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions: kinetic and equilibrium study.* J. Hazard. Mater, 2009. **164**: p. 1213-1222.
99. Tan, I.W., Ahmad, A.L., Hameed, B.H., *Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies.* . Desalination, 2008. **225**: p. 13-28.
100. Aseel M Aljeboree, A.F.A., Ammar H Al-Dujaili, *Adsorption isotherm, kinetic modeling and thermodynamics of crystal violet dye on coconut husk-based activated carbon.* Desalination and Water Treatment, 2015. **53**(13): p. 3656-3667.
101. L.D. Nghiem, P.J.C., C. Espendiller, *Mechanisms underlying the effects of membrane fouling on the nanofiltration of trace organic contaminants.* Desalination,, 2010. **250**: p. 682-687.
102. M. Taheran, S.K.B., M. Verma, R.Y. Surampalli, T.C. Zhang, J.R. Valéro, *Membrane processes for removal of pharmaceutically active compounds (PhACs) from water and wastewaters.* Sci. Total Environ.,, 2016. **547**: p. 60-77.
103. Acosta, R., et al., *Tetracycline adsorption onto activated carbons produced by KOH activation of tyre pyrolysis char.* Chemosphere, 2016. **149**: p. 168-176.
104. Marzbali, M.H. and M. Esmaieli, *Fixed bed adsorption of tetracycline on a mesoporous activated carbon: Experimental study and neuro-fuzzy modeling.* Journal of Applied Research and Technology. **15**(5): p. 454-463.
105. Marzbali, M.H., et al., *Tetracycline adsorption by H3PO4-activated carbon produced from apricot nut shells: A batch study.* Process Safety and Environmental Protection. **102**: p. 700-709.
106. Selmi, T., et al., *Tetracycline removal with activated carbons produced by hydrothermal carbonisation of Agave americana fibres and mimosa tannin.* Industrial Crops and Products. **115**: p. 146-157.
107. Boudrahem, N., et al., *Single and mixture adsorption of clofibric acid, tetracycline and paracetamol onto Activated carbon developed from cotton cloth residue.* Process Safety and Environmental Protection. **111**: p. 544-559.
108. Zhu, X., et al., *Thermal treatment of biochar in the air/nitrogen atmosphere for developed mesoporosity and enhanced adsorption to tetracycline.* Bioresource Technology. **263**: p. 475-482.
109. Martins, A.C., et al., *Removal of tetracycline by NaOH-activated carbon produced from macadamia nut shells: Kinetic and equilibrium studies.* Chemical Engineering Journal. **260**: p. 291-299.
110. L. Huang, M.W., C. Shi, J. Huang, B. Zhang, *Adsorption of tetracycline and ciprofloxacin on activated carbon prepared from lignin with H3PO4 activation.* Desalination Water Treat, 2014. **52** p. 2678-2687.

111. L. Huang, C.S., B. Zhang, S. Niu, B. Gao, *Characterization of activated carbon fiber by microwave heating and the adsorption of tetracycline antibiotics*Sep. Sci. Technol., 2013. **48** p. 1356-1363.

112. Torres-Pʃ©rez, J., C. Gʃ©rente, and Y. Andrʃ¨s, *Sustainable Activated Carbons from Agricultural Residues Dedicated to Antibiotic Removal by Adsorption.* Chinese Journal of Chemical Engineering. **20**(3): p. 524-529.
113. Rivera-Utrilla, J., et al., *Tetracycline removal from water by adsorption/bioadsorption on activated carbons and sludge-derived adsorbents.* Journal of Environmental Management. **131**: p. 16-24.
114. Zhang, Y., et al., *Removal of tetracycline by coupling of flow-through electro-Fenton and in-situ regenerative active carbon felt adsorption.* Chemical Engineering Journal. **335**: p. 685-692.
115. J.Ahmed, M., *Adsorption of quinolone, tetracycline, and penicillin antibiotics from aqueous solution using activated carbons: Review.* Environmental Toxicology and Pharmacology, 2017. **50**: p. Pages 1-10.
116. Y. Zhao, W.Z., H. Chen, Q. Luo, *Anodic oxidation of hydrazine at carbon nanotube powder microelectrode and its detection.* Talanta, 2002. **58**: p. 529-534.
117. Acosta, R., et al., *Tetracycline adsorption onto activated carbons produced by KOH activation of tyre pyrolysis char.* Chemosphere. **149**: p. 168-176.