Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1051121

57 (2016) 12842–12860
June

Taylor & Francis
Taylor & Francis Group

A review on removal of pharmaceuticals from water by adsorption

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Received 7 December 2013; Accepted 6 May 2015

ABSTRACT

Pharmaceuticals and personal care products are recognized as emerging pollutants in water resources. Various treatment options have been investigated for the removal of pharmaceuticals that include both conventional (e.g., biodegradation, adsorption, activated sludge) and advanced (e.g., membrane, microfiltration, ozonation) processes. This article reviews literature for adsorptive removal of pharmaceuticals from water sources. Adsorbents from various origins were reviewed for their capacity to remove pharmaceuticals from water. These adsorbents include carbonaceous materials, clay minerals, siliceous adsorbents, and polymeric materials. The adsorption capacity of adsorbents to adsorb pharmaceuticals from water is discussed in this study. The review discusses the mechanism for adsorption of pharmaceuticals onto adsorbents as well. Finally, effectiveness of processing parameters during adsorption processes is presented.

Keywords: Adsorption; Pharmaceuticals; Water treatment; Adsorption capacity; Adsorbents

1. Introduction

Extensive use of pharmaceuticals in health care has injected considerable amount of these substances to environment in unutilized or metabolized form [1]. Table 1 shows some frequently detected pharmaceuticals in effluents of wastewater and surface water. The presence of pharmaceuticals in aquatic environment is recognized as a potential toxicological pollution [2–6]. Due to their persistence in aquatic environment, pharmaceuticals pose long-term risks to aquatic life and their dependents through endocrine disruption and development of resistant bacterial strains. Fat-soluble steroids accumulate in fish or other aquatic species and are transported to human body [7–10].

Previously, researchers have reviewed pollution and fate of pharmaceuticals in receiving waters [2,11–21]. Halling-Sørensen et al. [2] reviewed the pollution of groundwater, river water, ocean, and soil by pharmaceuticals and their biodegradation in soil sediments, sewage sludge, and soil. Some of the pharmaceuticals were found readily degradable while others were persistent. Biodegradation was useful to lower concentration of pharmaceuticals in receiving waters. Pharmaceuticals degradation was high in sediments or sludge than receiving water. Soils containing micro-organisms or heat labile substances were better medium for degradation of pharmaceuticals than

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Table 1
Occurrence of commonly detected pharmaceuticals in different water sources

Pharmaceutical	Water source	Concentration (ng/L)	Ref.
Amoxicillin	Hospital effluents	900	[41]
	WWTP influents	9.94×10^3	[41]
Ampicillin	Industrial effluents	5.8×10^3	[42]
Atenolol	River	250–600	[43]
Bezafibrate	WWTP influents	0.3–87	[44]
Caffeine	Urban effluents	23–776	[45]
	Surface water	2.9–194	[45]
	WWTP influents	2,448–4,865	[46]
	River	38–250	[43]
Carbamazepine	WWTP influents	33–1,318	[44]
	Urban effluents	73–729	[45]
	Surface water	4.5–61	[45]
	WWTP influents	24–50	[46]
	River	56–160	[43]
Cefaclor	WWTP influents	6.15×10^3	[41]
Cefazolin	Industrial effluents	4.2×10^3	[42]
Cefotaxime	Industrial effluents	4.2×10^3	[42]
Cephalexin	Hospital effluents	1×10^4	[41]
	WWTP influents	6.4×10^4	[41]
	Industrial effluents	3.1×10^3	[42]
Ciprofloxacin	WWTP influents	27–514	[44]
	WWTP influents	11–63	[46]
	Hospital effluents	1.5×10^4	[41]
	WWTP influents	1.1×10^3	[41]
Clarithromycin	WWTP influents	nd-724	[46]
Clofibric acid	WWTP influents	nd-82	[44]
	Liao River	18	[33]
Demethyl diazepam	WWTP influents	nd-62	[44]
Diclofenac	Urban effluents	8.8–127	[45]
	Surface water	1.1–6.8	[45]
	WWTP influents	9–13	[46]
	River	21–98	[43]
	Liao River	717	[33]
Dilantin	Urban effluents	8.8–181	[45]
	Surface water	1.1–8.9	[45]
Enrofloxacin	Hospital effluents	100	[27]
Erythromycin	WWTP influents	9–353	[44]
	Urban effluents	8.9–294	[45]
	Surface water	1.8–4.8	[45]
Gemfibrozil	WWTP influents	181–451	[46]
Ibuprofen	Liao River	246	[33]
	Urban effluents	10–137	[45]
	Surface water	11–38	[45]
	River	35–270	[43]
Iopromide	Urban effluents	1,170–4,030	[45]
	Surface water	20–361	[45]
	River	780–8,100	[43]
Lincomycin	WWTP influents	11–629	[44]
	Hospital effluents	1.7×10^3	[41]
	Industrial effluents	1.1×10^5	[42]
Metronidazole	Industrial effluents	7.8×10^3	[42]
Nalidixic acid	Industrial effluents	6.7×10^3	[42]

(*Continued*)

Table 1 (*Continued*)

Pharmaceutical	Water source	Concentration (ng/L)	Ref.
Naproxen	Urban effluents	20–483	[45]
	Surface water	1.8–18	[45]
	River	81–360	[43]
Norfloxacin	Hospital effluents	200	[41]
Ofloxacin	WWTP influents	150–1,081	[44]
	Industrial effluents	1.3×10^3	[42]
Oxytetracycline	Industrial effluents	1.5×10^4	[42]
Salicylic acid	WWTP influents	433–8,036	[46]
	Liao River	295	[33]
Spiramycin	WWTP influents	11–129	[44]
Sulfadiazine	Industrial effluents	353	[42]
Sulfamethoxazole	WWTP influents	46–253	[44]
	Urban effluents	3.8–407	[45]
	Surface water	1.7–36	[45]
	WWTP influents	13–261	[46]
	River	9–190	[43]
	Hospital effluents	300	[41]
	WWTP influents	3×10^3	[41]
	Industrial effluents	5.8×10^3	[42]
Sulfanilamide	Industrial effluents	207	[42]
Sulfathiazole	Industrial effluents	9.6×10^3	[42]
Tetracycline	Industrial effluents	1.5×10^3	[42]
Trimethoprim	Urban effluents	10–188	[45]
	Surface water	3.2–53.	[45]
	River	11–94	[43]
	Hospital effluents	300	[41]
	WWTP influents	4.3×10^3	[41]

sediments or sludge. Jones et al. [11] reviewed that the presence of pharmaceuticals in water was not an immediate threat to aquatic life and emphasized on setting permissible limits for concentration of pharmaceuticals in wastewater. The authors did not recommend advanced technologies to treat pharmaceuticals at effluent treatment plants. Heberer [17] reviewed the fate of pharmaceuticals and reported trace level presence of pharmaceuticals in drinking water supplies. The author observed that polar pharmaceuticals were detected in underground waters while non-polar were less detectable. Deblonde et al. [13] reported the presence of more than 50 pharmaceuticals in influents of wastewater treatment plants in range 0.007–56.63 g/L. Removal of pharmaceuticals in effluents showed 20–30% removal of beta blockers, anti-inflammatory, and analgesics and 50% removal of antibiotics. Caffeine was not removed by conventional treatment. The authors suggested the advancement in existing technology to reduce load of pharmaceuticals in aquatic environment. Liu and Wong [21] reported a comprehensive review on pharmaceutical contamination in China and emphasized that precautionary measures should be taken to inhibit flow of pharmaceutical loads to waters, soil, human, and wild animals. The review also covered the toxic effects of pharmaceuticals on algae and goldfish.

Relatively, lesser number of review articles are available on remediation of pharmaceuticals from water through advanced oxidation process [22–24], photo degradation [25], sorption in soil [18], electrochemical degradation [26,27], and absorption by aquatic plants [28]. Rivera-Utrilla et al. [24] reviewed the removal of pharmaceuticals from water through activated carbon, advanced oxidation technologies using ozone, UV radiation, gamma radiations, and electrooxidation. In adsorption, carbon activated by phosphorous oxyacids showed high adsorption capacity (345 mg/g) for pharmaceuticals. Advanced oxidation treatments were found effective in removing pharmaceuticals from solution. Removal efficiency for various pharmaceuticals was 70–100% using gamma radiations; 40–99% using ozone-based advanced oxidation; and 20–100% using UV radiations. Sirés and Brillas [26] reviewed the removal of pharmaceuticals using electrochemical oxidation, Fenton-based electrochemical oxidation, and photoelectrocatalysis. The authors found that Fenton-based electrochemical oxidation has

been dominantly investigated for the removal of pharmaceuticals from synthetic wastewater. UV radiation was recommended for refractory carboxylic acids produced as secondary by-product during decomposition of pharmaceuticals. Zhang et al. [28] reviewed the removal of pharmaceuticals through aquatic plant-based systems with focus on constructed wetlands. The authors found that refractory pharmaceuticals such as caffeine and clofibric acid to biodegradation could be effectively removed through phytodegradation. The authors also found that constructed wetlands possess great potential to remove hydrophobic pharmaceuticals such as tonalide and galaxolide. The design and operation of constructed wetlands such as flow pass, batch, or continuous operation and the presence of vegetation influenced the uptake of pharmaceuticals in constructed wetlands. Feng et al. [27] reviewed the removal of anti-inflammatory and analgesic pharmaceuticals by electrochemical oxidation. The authors complained low efficiency of wastewater treatment plants to remove pharmaceuticals and emphasized the possibility of electrochemical-based advanced oxidation technology to treat emerging micro pollutants. Ikehata et al. [23] reviewed the removal of pharmaceuticals through ozonation and advanced oxidation and recommended ozonation and advanced oxidation as one suitable option to biologically persistent pharmaceuticals. It was found that simple ozonation was sufficient to remove pharmaceuticals containing active functional groups, like non-aromatic carbon–carbon rings containing double bonds, amines and activated aromatics rings such as in diclofenac, and carbamazepine and 17b-estradiol. Fenton and photo-Fenton-based advanced oxidation was required for the removal of stable pharmaceuticals like clofibric acid, ibuprofen, and diazepam. The authors emphasized the need to identify secondary by-products from oxidation process since these may be toxic or persistent.

A comprehensive review on removal of pharmaceuticals through adsorption is missing from literature and may be useful for those interested in removal of pharmaceuticals through adsorption. Adsorption is a well-researched technique for the removal of organic compounds such as dyes [29–31] and harmful synthetic chemicals [32–36]. Recognition of adsorption technique lies in low initial investment, simpler reactor/absorber design, operational simplicity, and unselective nature. Various low-cost adsorbents such as natural materials, agricultural and industrial wastes, municipal, and animal husbandry wastes have been investigated for the removal of organic compounds from water. Many of these were proposed as adsorbents for purification of water from dyes and synthetic organic chemicals. Adsorptive removal of pharmaceuticals from water sources has been the subject of research interest over the last two decades. Many studies have assessed the capability of adsorption processes in removing pharmaceuticals from water [31,37–40]. Accordingly, it is observed that hydrophobic pharmaceuticals possess high affinity for adsorbent surface while those of hydrophilic nature are not adsorbed easily. Further studies would be helpful to understand properly the adsorption mechanism for pharmaceuticals and their equilibrium adsorption capacity of adsorbents. The scope of this article is the removal of pharmaceuticals from water on adsorbents. The adsorption capacity of various adsorbents such as activated carbon, clays, silica, and polymer adsorbents is discussed. The effect of pH, concentration of pharmaceuticals, ionic strength, and co-sorption on adsorption is described in this review.

2. Sorption capacity

Sorption capacity is the maximum amount of solute adsorb onto an adsorbent under equilibrium conditions. Sorption capacity depends upon many factors such as source of origin, BET surface area, surface properties, type of solute, and pore structure. Chemical properties such as acidic or basic character, point of zero charge, and functional groups are influential factors. Other parameters include the size of the solute molecules, and types of interactions among species whether physical or electrostatic (electron transfer).

2.1. Carbonaceous sorbents

Carbonaceous adsorbents are usually the first choice of researchers for purification of water from harmful chemicals and metals. These are activated carbon materials, charcoal, activated sludge, and graphite. Their porous structure with BET surface area up to 2,100 m^2/g makes and possesses adsorption capacities for organic and non-organic chemicals in liquid or gaseous phases. Their parent source material can be coal, peat, lignite, and coconut shells, etc.

Activated carbon is the dominantly studied sorbent for the removal of pharmaceuticals from water mainly due to its high surface area and easier availability in the market. Sorption capacity of commercial activated carbon (CAC) is listed in Table 2 for different pharmaceuticals. Table 2 indicates that adsorption capacity of activated carbon is dependent upon the type of solute (pharmaceutical). For example, CAC (BET = 1,225 m^2/g), adsorbed 338, 328, and 394 mg/g of tinidazole, metronidazole, and ronidazole, respectively, under the

Table 2
Sorption capacity of carbonaceous sorbents for different types of pharmaceuticals

Pharmaceutical	Adsorbents	Dose (g/L)	pH	T (°C)	BET (m^2/g)	Capacity (mg/g)	Ref.
Amoxicillin	AC	–	4.98	30	1092.9	221.8	[49]
Carbamazepine	MWNT10	0.025	7.0	23	357	7,910	[50]
	MWNT100	0.05	7.0	23	58	41.1	[50]
Dimetridazole	CAC	1	7	25	1,225	280	[47]
	CAC	1	7	25	1,301	186	[47]
	PCAC	1	7	25	848	287	[47]
Ibuprofen	CP-K_2CO_3	0.7	2–4	30	891	145.2	[51]
	CP-steam	0.7	2–4	30	1,060	393.4	[51]
Metronidazole	CAC	1	7	25	1,225	328	[47]
	CAC	1	7	25	1,301	213	[47]
	PCAC	1	7	25	848	287	[47]
	AC	0.08	7	25	851	144.9	[48]
	AC	0.08	7	25	851	93.20	[48]
	AC	0.08	7	25	851	132	[48]
Norfloxacin	C-CNTs	0.2	–	25	–	51.1	[33]
	H-CNTs	0.2	–	25	–	75.3	[33]
	G-CNTs	0.166	–	25	–	56.8	[33]
	AC	0.133	–	25	–	106.5	[33]
Oxytetracycline	MWNT10	0.025	7.0	23	357	190.2	[50]
	MWNT100	0.05	7.0	23	58	30.4	[50]
Penicillin G	AC	1	6	25	–	315	[52]
	AC	1	6	25	1,000	290	[52]
	R. Arrhizus	1.02	6	35	–	375	[52]
	AS	0.96	6	35	–	459	[52]
	AC	0.95	6	35	1,000	330	[52]
Phenothiazine	Charcoal	0.1	–	25	1,014	162	[53]
Ronidazole	CAC	1	7	25	1,225	394	[47]
	CAC	1	7	25	1,301	164	[47]
	PCAC	1	7	25	848	378	[47]
Sulfamethoxazole	P-SWNT	0.25	5.9	–	410.7	144	[54]
	K-SWNT	0.25	5.9		652.8	328	[54]
	P-MWNT	0.25	5.9	–	157	32	[54]
	K-MWNT	0.25	5.9		422	209	[54]
	AC	0.08	7	–	851	185	[48]
	AC	0.08	7	–	851	156	[48]
	AC	0.08	7	–	851	170	[48]
	H-CNT	–	3.7	25	228	100	[34]
Tetracycline	PCAC	–	–	–	624	439	[54]
	SWNT	–	5.2	–	244	370	[54]
	MWNT	–	5.2	–	44	148	[54]
	Graphite	–	5.2	–	2.2	4.5	[54]
	P-SWNT	0.25	5.9	25	410.7	334	[54]
	K-SWNT	0.25	5.9	25	652.8	726	[54]
	P-MWNT	0.25	5.9	25	157	98	[54]
	K-MWNT	0.25	5.9	25	422	398	[54]
Tinidazole	CAC	1	7	25	1,225	338	[47]
	CAC	1	7	25	1,301	385	[47]
	PCAC	1	7	25	848	256	[47]
Tylosin	P-SWNT	0.25	5.9	–	410.7	261	[54]
	K-SWNT	0.25	5.9	–	652.8	466	[54]
	P-MWNT	0.25	5.9	–	157	77	[54]
	K-MWNT	0.25	5.9	–	422	270	[54]

same operating conditions [47]. Similarly, another CAC (BET = 885 m^2/g) adsorbed 144.9 mg/g of metronidazole and 185 mg/g of sulfamethoxazole [48]. Comparing these two examples, the role of surface area seems quite evident as CAC (1,225 m^2/g) adsorbed almost double amount of metronidazole compared to CAC (885 m^2/g).

Activated carbon is usually synthesized from a wide variety of precursor materials and preparation procedures. Different biomass types have been used in preparation of activated carbon such as palm shell [55], sawdust [56], coconut husk [55], rice husk [57], wheat bran [58], and walnut wood [59]. Physical and chemical properties of activated carbon are dependent upon their precursor biomass and preparation procedure. Few other carbonaceous materials such as carbon nano tubes (CNTs) and graphitic carbons are investigated to remove pharmaceuticals. Graphitic carbons are less efficient due to their low porosity and are usually used for comparison purposes only [54]. On the other hand, CNTs have shown considerable adsorption capacity for selected pharmaceuticals. It is also observed that SWNT is more efficient adsorbent than MWNT. The efficiency of SWNT probably is due to exposed surface area and easily accessible pores compared to MWNT. A study [54] found the adsorption capacity order for tetracycline (TCH) as SWNT > MWNT > AC > graphite. Low adsorption capacity for MWNT was due to molecular sieving effect as bulky TCH compound failed to seep through inner pores. On the other hand, poor adsorption onto graphite was associated with its low surface area. This example shows that size of the adsorbing molecules and accessibility of pores may be the two deciding factors for the estimation of adsorption capacity.

Modification of normal CNTs sometimes gives better adsorption efficiencies. CNTs have been graphitized, hydrolyzed, or carboxylized [33,34], and etched with KOH (K-CNTs) [54,60]. Ji et al. [60] observed that etching of CNTs with KOH enhanced its adsorption capacity dramatically for three antibiotics (sulfamethoxazole, tysolin, and TCH). For example, amount of sulfamethoxazole adsorbed onto KOH-modified SWNT (K-SWNT) was 56% more than unetched SWNT and 84% in case of KOH-modified MWNT (K-MWNT). Similarly, 54 and 84% enhancement was observed for TCH in case of K-SWNT and K-MWNT. Etching process increased the surface area of CNTs that might be the main reason for improved performance of etched CNTs.

Activated carbons are recognized as better adsorbents for the removal of antibiotics compared to CNTs. High adsorption capacity for activated carbons may be due to their porous nature and disorganized pore structures. In a study by Wang et al. [33], activated carbon adsorbed almost twice the amount of norfloxacin adsorbed onto modified CNT. Similarly, adsorption capacity order for naphthalene (organic chemical) was AC > SWNT > MWNT > graphite [54]. Surface area of activated carbon used in their study was approximately twofold compared to that of SWNT and fourfold compared to MWNT. However, average pore diameter of activated carbon was five times less than MWNT and half of SWNT. Naphthalene is a small size molecule, so size exclusion effect will be minimal, and adsorption capacity will mainly depend on surface area. However, size exclusion may be important in case of bulky molecules. In case of large size molecules, performance of CNTs might improve due to their large pore diameter as discussed previously in case of TCH [54]. For bulky molecules, mesoporous activated carbons will be better option for adsorption studies. Activated carbon was observed to be efficient adsorbent for the removal of pharmaceuticals or antibiotics among all carbonaceous adsorbents reviewed in this section. Surface area and pore diameter seem like two major factors. CNTs showed better performance for bulky molecules compared to activated carbon. Modified CNTs look like better adsorbents than their precursors. Surface area was increased by modification, which increased adsorption capacity. For commercial purposes, activated carbons are usually preferred due to low cost. Mesoporous activated carbons might be more suitable for the removal of sized pharmaceutical compounds from water.

2.2. Clays

Clays are aluminosilicate minerals that are colloidal fractions of sediments, rocks, and water. These clays are composed of quartz, metals, silicates, and carbonates and exit in layered structures of sediments, rocks, carbonates, or silicates. These make up cation and anions on their surface such as H^+, K^+, SO_4^{2-}, NO^{3-}, Ca^{2+}, and Mg^{2+}. Clays have found many applications in removal of pharmaceuticals due to their ability to exchange ions with acidic or basis pharmaceutical compounds. Clays scavenge naturally the organic, inorganic pollutants present in liquid or gaseous form. These are cheap, abundantly available, and require less processing cost as adsorbents. Clays are excellent adsorbents due to their large surface area, mechanical stability, layered structure, and high capacity to exchange ions.

Clays are popular low-cost adsorbents for the removal of pollutants. Clays possess high surface area and are available abundantly in different parts of

world. Clays are approximately 20 times cheaper than CAC [32,61]. Clays have been applied for the removal of methylene blue [32], phenolic compounds [62,63], and heavy metals [64]. Major portion of clays composed of soil, rock, sediments, and clay minerals having colloidal particle size <2 μm. Clay minerals itself are mixture of carbonates, silica, metal oxides, and metal ions (Mg^{2+}, K^{+}, NH_4^{+}, Na^{+}, PO_4^{3-}, NO_3^{-}) [64]. Heterogeneity in surface properties of clays, their ability to scavenge external pollutants in ion exchange mechanism and porous structure make clays suitable for adsorption applications. Adsorption capacity of clays usually depends upon their chemical and porous characteristics [65,66].

Relatively fewer studies have been conducted for the removal of pharmaceuticals using clays. These might not be limited to nitroimidazoles [47], NSAIDs [67], TCHs [68–71], macrolides [72], B-lactums [49]. Ion exchange may be a dominant binding mechanism since clays carry sufficient amount 284 of metal ions, silicates, and carbonates. Clays possess low affinity for non-polar or aromatic pharmaceuticals and are expected to adsorb sufficient quantities of polar pharmaceuticals [73]. The role of pH is crucial during adsorption, since the majority of pharmaceuticals carry more than one ionic state. For example, ciprofloxacin exists in zwitterionic form in between $pK_a = 1$ (pH 6.0) and $pK_a = 2$ (pH 8.8). Wu et al. [74] observed that amount of ciprofloxacin adsorbed onto montmorillonite clay was nearly constant for pH range 3–8 and decreased sharply at $pK_a \sim 2$. Ciprofloxacin possesses polar characteristics in acidic and zwitterions pH range that might have encouraged its adsorption onto montmorillonite via cation-exchange mechanism. On the other hand, ciprofloxacin exists as non-polar compound at high pH (>8.8) that decreases its adsorption on montmorillonite.

Table 3 demonstrates that clays possess sufficient affinity for pharmaceutical compounds. Zhang et al. [73] studied the effect of modified smectite clays on the removal of carbamazepine and found adsorption capacity order as: TMPA-smectite > HDTMA smectite > NH4-smectite > K-smectite > Ca-smectite > PTMA-smectite. They linked high adsorption capacity of TMPA-smectite to π–π interactions between phenyl ring in TMPA and conjugate aromatic moiety in carbamazepine. Putra et al. [49] suggested bentonite as an alternative adsorbent for wastewater applications in Indonesian region. Chang et al. [75] observed high affinity of rectorite clays for TCH with 140 mg/g of adsorption capacity. Chang et al. [76] and Turku et al. [77] observed the order for adsorption capacity for TCH on swelling clays as Na-montmorillonite > Ca-montmorillonite > rectorite in pH range 2–4. According to authors, efficiency of specific clay is the function of its ability to absorb TCH into the intercalated interlayer. Akçay et al. [67] found that adsorption mechanism of flurbiprofen onto TBAM was both physical and chemical. They reported exothermic nature of adsorption process due to negative values of Gibbs free energy, enthalpy, and entropy. Similarly, Bekci et al. [78] found that adsorption of trimethoprim (TRM) antibiotic onto montmorillonite KSF clay was spontaneous and exothermic. They attributed ion exchange capability of montmorillonite KSF clays for its high adsorption capacity.

2.3. Silica-based sorbents

Silica-based sorbents have been applied for the removal of pharmaceuticals. Silica sorbents have high BET surface area, porous texture, and mechanical stability. These are cheap and abundantly available. These have investigated for the removal of various pollutants such as dyes, hazardous metals, and organic pollutants, due to their high adsorption capacities.

Coarse clay fraction present in soil contains sufficient quantity of silica components. Silica and its allied adsorbents have been used in adsorption applications. Their extensive applications are due to their large surface area, stability under extreme conditions, regular porous matrix structure, fast adsorption kinetics, and easier regeneration [82,83]. Pharmaceuticals that have been investigated using silica-based adsorbents are carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, cloprop, norfloxacin, ciprofloxacin, and TCH [38,77,84,85]. Mesoporous silica is of particular interest as its pore size is large enough to absorb bulky size molecules of pharmaceuticals. On the other hand, small pore dimensions as in case of microporous silica reduce sorption capacity [86]. Size exclusion is one major factor for poor performance of microporous silica. Pore size limitations are especially true for physical sorption of pharmaceuticals species. However, H-bonding or cation exchange among functional groups of pharmaceuticals and silanol groups on silica surface [77] will boost sorption capacity of adsorbents. Impregnation of metal oxides or other functional groups onto silica is expected to boost its adsorption capacity for polar pharmaceuticals [84]. Table 4 lists the adsorption capacity of some silica-based adsorbents.

Synthesized mesoporous silica (SBA) is a well-ordered porous structure that can be prepared according to the procedure given elsewhere [88] and is quite effective in sorption of pharmaceuticals or other organic compounds. SBA contains mesopores size up

Table 3
Sorption capacity of mineral clays for the removal of pharmaceuticals

	Adsorbents	Dose (g/L)	pH	T (°C)	BET (m^2/g)	Capacity (mg/g)	Ref.
Amoxicillin	Bentonite clay	–	2.3	30	91.6	53.9	[49]
Chlortetracycline	Na-montmorillonite	–	5.5	25	623	79	[69]
	Na-kaolinite	–	5.5	25	25	26.7	[69]
Flumequine polymer	Kaolinitic clay	2.5	4.5	25	14	3.12	[79]
Flurbiprofen	Organophilic montmorillonite clay	4	–	25	18	240	[67]
Oxytetracycline	Na-montmorillonite	–	5.5	25	623	33	[69]
	Na-kaolinite	–	5.5	25	25	15.18	[69]
Tetracycline	Na-montmorillonite	–	5.5	25	623	49.7	[69]
	Na-kaolinite	–	5.5	25	25	29	[69]
	Na-montmorillonite clay mineral	5	4.5	25	725	423	[76]
	Ca-montmorillonite clay mineral	5	4.5	25	717	342	[76]
	Rectorite clay	5	4.5	25	363	135	[75]
	Rectorite clay	5	11	25	363	40	[75]
	Kaolinite	–	4	25	13.1	3.8	[80]
	Mesoporous silica	–	6	23	700	44.4	[77]
	Montmorillonite	0.45	3	20	607	421	[81]
	Ca saturated clay	10	7	24	–	11.3	[71]
	K-clay-HS complex	10	7	24	–	11.1	[71]
	Montmorillonite	6.6	5.5	25	–	86.6	[70]
	Montmorillonite	6.6	5.5	25	–	78.5	[70]
Tylosin	Montmorillonite clay	–	8	–	–	68	[72]
	Bentonite clay	–	6.1	–	–	188	[72]
	Illite	–	8	–	–	24	[72]
	Kaolinite	–	8	–	–	6.8	[72]

Table 4
Adsorption capacity of silica-based sorbents for different pharmaceuticals

Pharmaceutical	Adsorbents	Dose (g/L)	pH	T (°C)	BET (m^2/g)	Capacity (mg/g)	Ref.
Carbamazepine	Mesoporous silica SBA-15	2	5	25	737	160	[38]
Clofibric acid	Mesoporous silica SBA-15	2	5	25	737	70	[38]
Ibuprofen	Mesoporous silica SBA-15	2	5	25	737	410	[38]
Ofloxacin	Mesoporous SiO_2	–	7.2	25	700	429	[87]
	Nonporous SiO_2	–	7.2	25	7.5	2.1	[87]
	Nonporous SiO_2	–	7.2	25	37	18.7	[87]
Tetracycline	Mesoporous silica	–	6	23	700	44.4	[77]

to 300 Å that provides sufficient space for bulky size molecules of pharmaceuticals such as carbamazepine, TCH, and adsorptive removal >80% of initial concentration [38]. Surface modification as described earlier might enhance adsorptive properties of SBA as observed in Vu et al. [84]. Fe-modified SBA adsorbed >20% extra amount of TCH comparative to non-modified one. However, it is also notable that impregnation of reactive species onto SBA will decrease overall surface area. Overall, mesoporosity is one important factor for better adsorption of pharmaceuticals onto silica or its allied adsorbents.

2.4. Polymeric sorbents

Polymeric sorbents have lower adsorption capacity when compared with activated carbon or mesoporous sorbents but these possess certain advantages. Polymeric materials have potential applications in water treatment area as a replacement of activated

carbon due to their mechanical strength and large surface area [89]. Polymeric sorbents have high mechanical strength, uniform pore size distribution, and ability to regenerate easily under mild conditions. Polymeric sorbents are resistant to fouling and are long lasting up to 2,000 regeneration cycles [90] unlike activated carbon that requires regeneration on regular basis.

Polymer sorbents can be modified as ionic or hydrophobic to suit for the removal of polar and non-polar pharmaceuticals from water [37,91]. Polymeric sorbents are classified based on the charge properties as neutral, ionic, or hydrophobic. It is true that charge matching of adsorbate and adsorbent is necessary for efficient adsorption. Zwitterionic cephalosporin C absorbed more on neutral polymeric adsorbent than to polar counterparts [92]. Non-ionic polymeric sorbents of sulphonated polystyrene origin (SP207, SP850, and XAD-2) adsorbed sufficient quantity of cephalosporin C in zwitterionic pH range (pH 5.3) [93]. In zwitterionic region, cephalosporin resembles more like a neutral organic compound since net charge is zero. The percentage of interactive sorption is minimal among aromatic rings of cephalosporin C and polymeric sorbent and physical sorption dominates. The pore sizes and surface area of the sorbents will be of significant importance in such type of adsorptions. Second classification can be based on polymerization nature such as aromatic or aliphatic. Adsorption capability of an individual polymeric sorbent will depend on these surface properties and chemical nature. Ring-structured sorbents, for example, will have more affinity for aromatic rings on the pharmaceuticals and lesser to the ionized points. Inverse is true for aliphatic-type sorbents. Affinity for cephalosporin C can be 17 times higher onto aromatic ring-structured polymeric sorbent XAD-16 comparative to an aliphatic polymeric sorbent as in [92]. Similarly, they reported that more amount of penicillin V and TCH was adsorbed onto aromatic sorbent (Amberlite XAD-16) than to aliphatic ester sorbent (Amberlite XAD-7).

The adsorption capacity of polymeric sorbents for the removal of pharmaceuticals is given in Table 5. Researchers have investigated removal capability of polymeric sorbents. Lee et al. [93] reported that approximately 990 mg/g cephalosporin C adsorbed onto resin Amberlite XAD-16. They found that external mass transfer rates and intraparticle diffusion controlled the overall sorption mechanism in a fixed bed of XAD-16 resin. Ramos et al. [36] found that non-ionic polymer XAD-16 adsorbed 253 mg/g of cephalosporin C at equilibrium concentration of 1.0 g/L and approximately 990 mg/g at equilibrium concentration of 3.0 g/L. They also found that XAD-16 resin was regenerated by passing methanol in a fixed bed reactor. Robberson et al. [37] reported that adsorption of nalidixic acid onto cationic or neutral polymeric resins was dependent on pH of solution. For $pH < pK_a$, maximum amount was adsorbed onto neutral polymers through hydrophobic interactions. Cationic polymers adsorbed more of nalidixic acid comparatively for $pH > pK_a$ values through anion–cation exchange mechanisms.

Matching of characteristics polymers resins and pharmaceutical compound is necessary for effective adsorption. Two essential factors include (i) aromatic or aliphatic structure of pharmaceuticals and (ii) neutral, ionic, or zwitterionic nature of pharmaceuticals. It is crucial that adsorbent and adsorbate should be of similar nature for efficient adsorption. Hydrophobic pharmaceuticals match neutral polymers and ionized pharmaceuticals match ionic polymers. Similarly, pharmaceuticals containing aromatic ring match aromatic polymers.

2.5. Miscellaneous sorbents

Various adsorbents materials have been investigated for the removal of pharmaceuticals as an alternative to conventional adsorbents. These include oxidized cellulose [97], goethite [98], biofilms [99], activated sludge [100], aluminum oxide [101–103], organic materials (compost, humic acid, and manure) [104], iron oxides [102,103,105], manganese oxides [105], zero valent iron nano-particles [106], activated charcoal [53] nickel(II) grafted MCM-41 [107], and chitosan particles [108]. Adsorption capacity of these adsorbents is given in Table 6.

3. Effect of parameters on adsorption

3.1. Effect of pH

The pH of solution imparts significant influence on sorption of pharmaceuticals especially in case of interactive sorption. Investigations have shown that it is difficult to obtain a constant adsorption capacity over the entire pH range irrespective of the nature of adsorbent. It is necessary to determine an optimum pH for a specified adsorption process. Fig. 1 gives information about the adsorption of three pharmaceuticals (TRM, ciprofloxacin, and TCH) onto montmorillonite clay. Montmorillonite clays possess negatively charge over pH range of 2–12 [110]. Decrease in adsorption of ciprofloxacin and TCH corresponds to their net electrostatic charge. For example, ciprofloxacin molecule became negatively charged for pH >8.8. Adsorption of ciprofloxacin decreased on

Table 5
Sorption capacity of polymeric sorbets for the removal of pharmaceuticals

Pharmaceutical	Adsorbents	Dose (g/L)	pH	T (°C)	BET (m^2/g)	Capacity (mg/g)	Ref.
Cephalexin	Amberlite XAD-16 polymer	30	3	25	800	116	[94]
	Amberlite XAD-4 polymer	30	3	25	725	357	[94]
Cephalosporin C	SP850, a macroreticular resin	–	2.7	25	1,000	541	[93]
Erythromycin	Amberlite XAD-4	0.002	–	30	725	358	[95]
	Amberlite XAD-7	0.002	–	30	450	505	[96]
	Amberlite XAD-16	0.002	–	30	>800	131	[96]
Nalidixic acid	Polystyrene–divinylbenzene, X16	–	–	–	20	800	[37]
	Phenol–formaldehyde, X761	–	–	–	15	200	[37]
Penicillin V	Polymer Amberlite XAD-16	–	2.7	25	904	1,401	[92]

Table 6
Adsorption capacity of various sorbents for pharmaceutical compounds

Pharmaceutical	Adsorbents	Dose (g/L)	pH	T (°C)	BET (m^2/g)	Capacity (mg/g)	Ref.
Enrofloxacin	Natural zeolite	10	7	–	–	19.3	[109]
	Natural zeolite	10	7	–	–	17	[109]
Ciprofloxacin	Hydrous oxides of Al (HAO)	–	7.8	25	386	13.6	[103]
Norfloxacin	Alumina pure	10	6.8	22–25	155	6.4	[86]
	Alumina gel	10	6.6	22–25	300	<1	[86]
	Porapak P (organic medium)	10	6.0	22–25	100–200	<1	[86]
Diclofenac sodium	MZ-300% CPC	4	7.4	–	68.6	48.5	[110]
	MZ-200% CPC	4	7.4	–	68.6	41	[110]
	MZ-100%CPC	4	7.4	–	68.6	21	[110]
Cephalexin	Cellulose oxide	–	3.5	25	14.8	79	[97]
Ampicillin	Cellulose oxide	–	3.5	25	14.8	139	[97]
Tryptophan	Cellulose oxide	–	3.5	25	14.8	122	[97]
Fluoroquinolone	Goethite	5	5	–	159	49.6	[98]

negatively charged montmorillonite surface in basic solution. Similarly, adsorption of TCH follows the order: acidic > zwitterionic > basic that showed adsorption very much depends upon electrostatic interaction between TCH molecule and negatively charge montmorillonite clay [81]. Bekci et al. [78] used slightly acidic montmorillonite KSF clay at pH ~ 3.31 in solutions. Positively charged clay surface possesses strong affinity for ionized form of TRM for pH < 5.03, so adsorption was efficient in this pH range. As pH-increased >5.03, TRM became neutral and showed least affinity onto montmorillonite KSF. Dutta et al. [94] found that adsorption of cephalosporin C and even an amino acid onto a non-ionic polymeric sorbent (XAD-16) was maximum at their respective isoelectric points. At isoelectric points, compounds exhibit non-ionic character, so adsorption onto a non-ionic surface was higher. It is clear from the discussion that matching of electrostatic charges is necessary for effective adsorption of pharmaceuticals onto clays. Interactions among water and pharmaceuticals are another factor that depends upon pH. For example, penicillin V contains a carboxylic group attached to its β-lactum ring. This carboxylic group exists in protonated form (–COOH) at low pH values and deprotonated (–COO) at high pH values. Protonated form has low solubility in water and thus easily removable from water. The contrary for deprotonated form [92]. Similarly, Dutta et al. [94] found that adsorption of cephalexin and cefadroxil antibiotics onto non-ionic polymers (XAD-4, XAD-16, XAD-2, XAD-7) decreased as a function of pH. This illustrated that any sort of interactions other than adsorbent/adsorbate interactions decreases overall adsorption. Thus, it can be extracted from the discussion that pairing of ionic properties of both adsorbent and pharmaceutical compound is necessary. Neutral pharmaceuticals adsorb easily onto non-ionic sorbents. In that case, surface

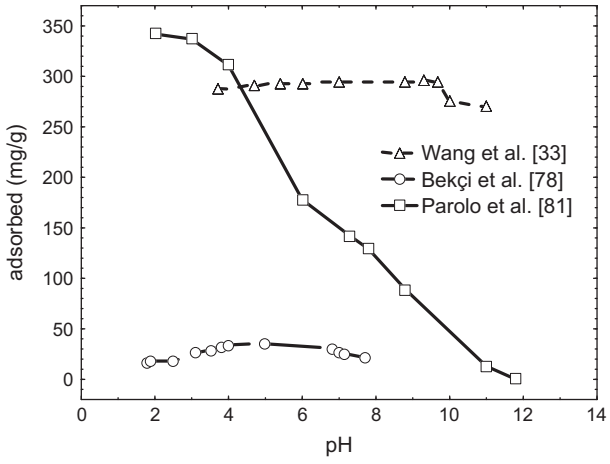

Fig. 1. Effect of pH of solution on equilibrium adsorbed amount of three antibiotics on montmorillonite clay: ciprofloxacin [33], trimethoprim [78], and tetracycline [81].

area and pore size may have a role to measure adsorption capacity. Interactive sorption depends more upon electrostatic forces for effective adsorption. Furthermore, estimation of an optimum pH of solution is necessary for ionized pharmaceuticals, and for charge surfaces containing surface interacting groups.

3.2. Adsorbent dosage

Investigations have shown that percentage removal of pharmaceuticals increased as a function of adsorbent dosage [38,111,112]. This increase was often attributed to the extra availability of vacant sites at higher dosages. It has been reported that adsorption of pharmaceuticals rarely reached a saturation value [96]; therefore, further increase in adsorbent dosage may not be of measureable significance. It is true that increase in dosage level leads to extra removal of pharmaceuticals. However, amount of pharmaceutical adsorbed per unit mass of dosage (i.e., mg pharmaceutical/g dose) gives better indication of adsorption capacity for any specific adsorbent. Infect, it was observed that ratio amount of pharmaceutical adsorbed to dosage decreased as a function of adsorbent dose. Ribeiro and Ribeiro [96] performed experiment for sorption of erythromycin onto polymeric sorbents XAD-4, XAD-7, and XAD-16. They found adsorbents reach their saturation values at 5, 10, 2.5 g/L dosages for XAD-16, XAD-4, and XAD-7, respectively. They also found that by increasing dosages to 10 g/L removal of erythromycin did not extend to an appreciable degree. Therefore, it may be necessary to analyze the adsorption efficiency per unit mass of dosage. Excess usage of adsorbent may increase overall cost of the operation especially in case of synthesized adsorbents such as polymeric resins and activated carbons. Kim et al. [5] demonstrated that adsorption of trimethoprim onto activated carbon reached a saturation value for 1.0 g/L of adsorbent and further increase in dosage level did not worth adsorption capacity of activated carbon. It is recommended to measure optimum dosage of adsorbent for a given concentration of pharmaceutical compound.

3.3. Concentration of pharmaceuticals

Adsorption capacity and rate of adsorption are very much dependent upon initial concentration of pharmaceuticals. Initial concentration minimizes mass transfer resistance by supplying necessary driving force. In general, initial concentration boosts adsorption of pharmaceuticals irrespective of the nature of adsorbent surface such as microporous, mesoporous, negatively or positively charge surface. The concentration increases the accessibility of pores for adsorbate molecules and increases interactions at solid–liquid interface. Relatively few studies considered the initial concentration as a parameter for assessment of adsorption capacity. Aksu and Tunç [52] observed increase in adsorption capacity of three sorbents (activated carbon, activated sludge, and *Rhizopus arrhizus*) by increasing initial concentration of penicillin G from 50 to 1,000 mg/L. Similarly, adsorption capacity of activated carbon was increased from 20.3 to 42.7 mg/g by increasing TCH concentration from 20 to 300 mg/L [113]. Tian et al. [114] found that amount of levofloxacin adsorbed onto polyacrylonitrile (PAN) filters at initial concentration of 100 mg/L was much more than 5 mg/L. Xu et al. [115] reported that adsorption capacity of imprinted polymer and functionalized imprinted polymer increased as a function of norfloxacin concentration. According to this discussion, the amount of pharmaceuticals adsorbed onto polymer increases as a function of initial concentration irrespective of the adsorbent nature. However, there must be a saturation limit for a specific adsorbent. Saturation level of an adsorbent can be easily estimated from equilibrium adsorption concentration. Equilibrium adsorption concentration gives more elaborated picture of the effect of concentration.

3.4. Ionic strength

Ionic strength is a measure of the degree of anionic or cationic species present in solution. Pharmaceuticals usually contain multifunctional groups in their structure with certain degree of ionization potential. Two

functional groups are present in structure of sulfonamides (acidic amide and amino group) and three in case of TCH (β-di-ketone, dimethylamine, and tricarbonyl) [116]. Cephalosporins exhibit values of pK_a 1–3 in solutions [117] that is an indication of the presence of multiple functional groups in their structure. Ionic strength and ionization of pharmaceuticals are inter-related and can be followed easily from pH speciation curves. Cephapirin sodium salt (CHP) exists in cationic (CHP^+), zwitterionic (CHP°), and anionic (CHP^-) forms for <2.5, 2.5–5.44, and >5.44 values of pH, respectively [118]. Thus, the portion of ionic or neutral states of individual molecules will depend upon the ionic strength of solution. It can be recommended at the stage that maximum concentration of pharmaceutical should be in one of above-mentioned states for efficient adsorption, i.e., cationic, anionic, or zwitterionic. It is because adsorbents surfaces are usually neutral, anionic, or cationic and are designed to accept oppositely charged species of solute molecules. Therefore, matching of ionization states of solute and adsorbent is necessary for efficient adsorption.

Qtaitat [119] found that increasing ionic strength of solution with NaCl solution from 0.01 to 0.1 decreased adsorption of TRM onto montmorillonite. Montmorillonite clays are usually negatively charged [74,81]. Increase in concentration of Na^+ in solution stabilized TRM^+ molecules to their neutral state TRM°, which decreased cation-exchange interactions between TRM^+ and montmorillonite. Bekci et al. [78] also observed that increase in ionic strength of solution with NaCl ions decreased adsorption of TRM onto montmorillonite KSF clay. Parolo et al. [81] plotted −Log NaCl (electrolyte concentration) vs. amount of TCH adsorbed onto negatively charged montmorillonite clays. The authors have found adsorption of TCH decreased as a function of NaCl concentration at pH values of 4 and 7. In general, concentration of TCH^+ 500 ions was much higher at pH 4 compared to that at pH 7. Therefore, the suppression of cationic TCH^+ to neutral TCH at pH 4 was high. This might be the reason for rapid rate of decrease in adsorbed amount of TCH at pH 4. Similar decrease in adsorption of TCH was observed as a function of ionic strength of solution onto a negatively charged silica surface as discussed in [77]. Ji et al. [54] reported negligible effects of ionic strength on adsorption of two sulfonamides (sulfapyridine and sulfamethoxazole) onto activated carbon and graphite. Addition of NaCl as an ionic source slightly increased sulfonamides while that of $CaCl_2$ decreased their uptake. Activated carbon and graphite are different adsorbents than montmorillonite clay. Activated carbon or graphite materials used in their study contained low concentration of surface-active groups and were relatively neutral in nature. In their investigated pH range (pH 6), pH speciation for sulfamethoxazole is near zwitterionic and that for sulfapyridine lies in zwitterionic region completely. In such a case, when pH is around the zwitterionic or anionic region of solute, the role of ionic strength may be insignificant.

3.5. Temperature

Temperature is also an important parameter for adsorption process. High temperature normally increases molecular activity at boundary layer interface, which may increase the rate of diffusion of solute molecules. Such an adsorption process is usually endothermic. However, literature shows that adsorption behavior of solute onto a specific adsorbent might also be exothermic in nature [120]. In such cases, probably, adsorbent capacity decreases for particular solute due to weakness of interactive forces between surface-active groups at adsorbent surface and that of solute species [121].

Turku et al. [77] found decrease in adsorption of TCH onto negatively charged silica adsorbent as a function of temperature. Aksu and Tunç [52] reported that at low initial concentrations ($C_0 = 100$ mg/L), increase in temperature did not influence uptake of penicillin G onto three carbonaceous adsorbents (activated carbon, *Rhizopus arrhizus,* and activated sludge). However, for $C_0 = 1{,}000$ mg/L, adsorption capacity increased for 25–35˚C and then decreased sharply for >35˚C. Bekci et al. [78] reported that adsorption of TRM onto negatively charged montmorillonite KSF decreased considerably by increasing temperature of solution (303–318 K). Akçay et al. [67] found that adsorption of flurbiprofen antibiotic decreased as a function of temperature from 25 to 40˚C. Mestre et al. [51] reported little significance of temperature during adsorption of ibuprofen onto activated carbon. Similarly, change in temperature did not influence the adsorption capacity of zeolite for enrofloxacin [109]. Ribeiro and Ribeiro [96] also found that adsorption capacity of anionic and neutral resins (XAD-4, XAD-16, XAD-7) for erythromycin remained almost constant in 25–50˚C temperature range. Temperature plays role to (i) modify molecular activity at solid liquid interface, (ii) interrupt the interactions among the functional groups of solute and adsorbent species, and (iii) modify the nature of adsorbent. For point (iii), little information is available in literature about the effect of temperature in modifying the structural properties of the adsorbent. Probably, temperature has almost no effect on modifying nature of adsorbents and or their porous

nature. However, temperature has moderate effect on defining the interactions among the solute and adsorbent species. It might be positive if the interactions among species are endothermic and negative in case of exothermic interactions. Point (i) shows that temperature always enhances probably of adsorption of solute onto adsorbents irrespective of their characteristics. Therefore, positive effect of temperature on adsorption may be due to endothermic interactions and enhancement in molecular interactions. In case of negative effect of temperature, exothermic interactions play dominant role. According to this discussion, temperature influences adsorption in case of charged adsorbents and ionized solute molecules. Temperature variations may not affect adsorption of non-polar pharmaceutical compounds onto neutral adsorbents.

3.6. Cosorption

Wang et al. [70] investigated the effect of the presence of Cu(II) ions for adsorption of TCH onto montmorillonite. They found adsorption of TCH onto montmorillonite increased significantly in the presence of Cu(II) ions. They associated enhancement in sorption to the strong affinity of montmorillonite clay for TCH–Cu(II) ionic complex [60]. Zeta potential of TCH decreased in the presence of Cu(II) that is a clear indication of the strong interactions among TCH and Cu(II) ions. Therefore, TCH–Cu(II) formed a complex that probably possessed a net positive charge overall and has increased overall adsorption onto montmorillonite. Jia et al. [122] also found increased sorption of TCH onto two soil clays in the presence of Cu(II) ions. Ötker [109] observed increased in adsorption of enrofloxacin onto natural zeolite in the presence of ammonium ions. Adsorption capacity of natural zeolite increased from 19.3 to 65.7 mg/L in the presence of ammoniacal nitrogen (NH_4-N) from 0 to 100 mg/L. Yu et al. [123] reported that the presence of natural organic matter in the background solution substantially reduced the sorption capacity of activated carbon during the uptake of naproxen and carbamazepine. Similarly, reduction in sorption capacity of activated carbon was observed in the presence of background natural organic matter in case of 2-methylisoborneol (not a pharmaceutical compound) [124].

4. Brief discussion on mechanism of adsorption of pharmaceuticals onto adsorbents

4.1. Silanol functional groups

Bui and Choi [38] reported that adsorption of pharmaceuticals (carbamazepine, clofibric acid, diclofenac, ibuprofen, and ketoprofen) was strongly dependent on pH of the solution. The adsorption was attributed to the several function groups of silica surface (SiOH, Si O···H···O Si, $SiOH_2^+$, SiO^-). The possible interaction between hydroxyl (–COOH) group of pharmaceutical and silanol (SiOH) groups from silica is given in Eq. (1), where B is the remaining part of pharmaceutical compound such as in case of diclofenac [125]. Eq. (2) represents the hydrogen bonding interaction between silanol and hydroxyl groups. Hydrogen bonding interaction might be easier due to low activation energy compared to ligand exchange reaction. Ligand exchange reaction is stronger.

$$\equiv \text{Si–OH} + \text{COOH–B} \rightarrow \equiv \text{Si–OOC–B} + H_2O \quad (1)$$

$$\equiv \text{Si–OH} + \text{COOH–B} \rightarrow \equiv \text{Si–O}\cdots\text{H}\cdots\text{OOC} - \text{B} + H^+ \quad (2)$$

Goyne et al. [87] associated sorption of ofloxacin to SiO_2 through cationic ligand exchange and cationic bridging mechanism (Eq. (3)) via piperazinyl group of ofloxacin and silanol group in silica. Where ofx and ofx^+ are ofloxacin and its protonated forms, respectively.

$$\equiv \text{Si–OH} + ofx^+ \rightleftharpoons \equiv \text{Si–O} - of\ x\ + H^+ \quad (3)$$

whereas the ligand exchange mechanisms in case of Al_2O_3 proceeded through carboxylate/ketonic group.

$$\equiv \text{Al–OH} + of\ x \rightleftharpoons \equiv \text{Al–}of\ x^+ + OH^- \quad (4)$$

Carbonaceous materials contain surface-active groups such as silanol groups for cationic exchange mechanism and carboxylate group (–COOH) for ligand exchange mechanism. These groups have significant contribution toward adsorption ability of adsorbents. Functional groups on activated carbon type materials can be phenolics, carboxyl, and lactone [6,49]. These functional groups are consisted of acidic and basic groups mainly which affect the surface charges and adsorption properties of activated carbon. Adsorption on activated carbon therefore not only relies upon its pore structure as the change of surface charges is also a crucial factor affecting the adsorption capacity.

4.2. Carbonyl functional groups

Pharmaceuticals also bind to the adsorbent surfaces through carbonyl group (C=O). The role of C=O

group during adsorption process is measureable by band shifts in IR spectroscopy [75,118]. The absorption spectrum for C=O shifts to lower or higher frequency when C=O group interacts with cations on adsorbent surface. This band shift in IR spectrum was observed for oxytetracycline adsorption onto montmorillonite clay lowering from 1,685 to 1,665 cm^{-1} 167 [33]. In another study, C=O band for flurbiprofen antibiotic shifted from 1,700 to 1,708 cm^{-1} 168 after adsorption onto TBAM [67]. The C=O group usually binds to the charged surface through cationic mechanism or through H atom bonded with OH group of water attached to cations on adsorbent surface [126]. Deprotonated OH group seems to have higher affinity for C=O than to protonated one. This was observed for feldspar or quartz surfaces that their deprotonated hydroxyl group attached easily to C=O group of cephapirin antibiotic than to protonated form of hydroxyl group [118].

4.3. Ion exchange

Binding of pharmaceuticals onto adsorbent might be due to ion exchange via protonation. Exchange of ions between adsorbent and pharmaceutical compound leads strong affinity among species. In fact, in many studies, the ion exchange has been assumed as binding mechanism among sorbent and pharmaceuticals species especially for clay type adsorbents [33,49,74,79,126–128]. Ion exchange mechanism can be due to the presence of permanent charged species such as in montmorillonite clays [68]. It can also be due to induced protonation of species in clays by changing pH values like in kaolinite as proposed in [80]. According to, Na^+ cation was exchanged during transfer of TCH onto kaolinite surface. Similarly, for bentonite clays, adsorption of amoxicillin was associated to the degree of protonation for cation-exchange mechanism as shown in Eq. (3) [49]. Carboxylic group of flumequine was adsorbed onto positively charged edges of kaolinite surface via a similar mechanism as in Eq. (3) [79]. Moreover, it was also observed in [79], that overall amount of flumequine adsorbed onto kaolinite was decreased by increasing pH of solution. This may show that degree of protonation or deprotonation of species is one important factor for adsorption via ion exchange mechanism.

4.4. Dissociative sorption

Dissociative adsorption is normally associated with fragmentation of solute molecules. All of the fragments attach to the adsorbent surface [129]. Ania et al. [130] reported that penicillin dissociated into secondary products during adsorption onto activated carbon and that intermediates adsorbed onto the adsorbent. Penicillin initially decomposed to primary intermediate (penicillenic acid). Penicillenic acid decomposed further into secondary intermediates (penillic acids and penilloic acids). Spectrophotometric absorbance was criteria to measure adsorbed amount of penicillenic acids (320 nm), penillic acids (233 nm), and penilloic acids (285 nm). Zhang and Huang [98] found that all of fluoroquinolones (ciprofloxacin, enrofloxacin, norfloxacin, ofloxacin, and lomefloxacin) were dissociated except flumequine during their adsorption onto goethite. Approximately 60% of ciprofloxacin was oxidized into intermediates products in ~400 h and that of 70% of norfloxacin in 300-h duration. However, they did not report the decomposition kinetics of products other than ciprofloxacin or norfloxacin. They proposed interesting interactions between fluoroquinolones and goethite. Carboxylic group present in the fluoroquinolones was assumed to adsorb onto goethite surface while piperazinyl ring was oxidized to intermediates. Dissociative adsorption is common in case of solute species that contains easily oxidizable functional groups. Adsorbent characteristics are also essential in defining the nature and extent of dissociation during the adsorption process. However, we could not see any cumulative or recessive effect of dissociation on adsorption efficiency. In case of adsorption rate >> dissociation rate of a solute specie, the uptake can be considered as purely adsorptive. This is true especially when adsorption study is performed over short time duration.

5. Summary

Pharmaceuticals adsorb onto a specific adsorbent surface through physically controlled mechanism or interactive mechanism. Physical attachment is a less susceptible pathway that may occur in cases of less polar pharmaceuticals onto non-polar adsorbents such as carbon nanotubes, graphitic carbon, and mineral free clays. Physical sorption of the pharmaceuticals is dependent upon mesoporous surface area of adsorbent. Interactive sorption is a dominant pathway for adsorption of pharmaceutical compounds. This is because pharmaceuticals contain various active sites such as functional groups (–COOH, –OH, $–NH_2$, –CHO, =O, C=O, –NH, $=SO_2$) and other electrostatic points containing heterogeneous atoms (–F, –Cl, etc.). Adsorption of a particular pharmaceutical may occur via interactive mechanism such as van der Waals forces, electrostatic interactions, protonation, ion exchange, dipole–dipole interactions, H-bonding, and

complex-formation. The interactive sorption is the interaction of functional groups of adsorbent and pharmaceutical species. Carboxylic group (–COOH) shows more affinity toward polar silanol groups (–SiOH) on adsorbent surface. Carbonyl group (C=O) can attach easily with –OH surface group of adsorbent via cationic or H-bonding mechanism. From the reviewed literatures, sorption capacity was found to be dependent upon BET surface area of the adsorbents. Among carbonaceous adsorbents, CAC was found a better adsorbent for pharmaceutical compounds than graphitic carbon, carbon nanotubes. It has also been reported that modified carbon nanotubes adsorbed more pharmaceuticals compared to their original source. Suitable modification can be acid/base treatment, carboxylation, or hydroxylation of carbonaceous source. These modifications increase the probability of interactive sorption. Clays are other attractive alternative to carbonaceous adsorbents, since these are naturally occurring materials and are available at low cost. Adsorption capacity of clays is relatively lower than carbonaceous materials due to their lower BET surface area. Montmorillonite clays possessed high adsorption capacity compared to kaolinite, rectorite, and bentonite. Surface modification is usually not recommended for clay type sorbents since clay minerals itself are mixtures of carbonates, silica, metal oxides, and metal ions (Mg^{2+}, K^{+}, NH_4^{+}, Na^{+}, PO_4^{3-}, NO_3^{-}). Polymeric materials have been recommended in literature as alternative adsorbents due to their regeneration ability. Polymeric materials are suitable adsorbents for hydrophobic pharmaceutical compounds. Among silica-based adsorbents, mesoporous silica possessed high capacity for adsorption of pharmaceuticals. Non-porous and microporous silica were rather ineffective in removing bulky-sized pharmaceuticals. Adsorption of pharmaceuticals depends very much upon operating parameters such as ionic strength, pH, adsorbent dosage, initial concentration, temperature, and effect of the presence of secondary solute component. Pharmaceuticals contain multifunctional groups in their structure with certain ionization potential and can exist in cationic, anionic, or neutral form depending upon ionic strength of solution. To achieve higher degree of adsorption, it is necessary to confine pharmaceutical compound in one of three forms since the adsorbent with opposite charge characteristics will be helpful for effective removal. Temperature may enhance or restrict adsorption of pharmaceuticals onto an adsorbent depending upon the endothermic or exothermic nature of sorption. Finally, the effect of secondary solute presence on adsorption is of empirical in nature and may require further investigation.

References

[1] P. Drillia, S.N. Dokianakis, M.S. Fountoulakis, M. Kornaros, K. Stamatelatou, G. Lyberatos, On the occasional biodegradation of pharmaceuticals in the activated sludge process: The example of the antibiotic sulfamethoxazole, J. Hazard. Mater. 122 (2005) 259–265.

[2] B. Halling-Sørensen, S. Nors Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lützhøft, S.E. Jørgensen, Occurrence, fate and effects of pharmaceutical substances in the environment—A review, Chemosphere 36 (1998) 357–393.

[3] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environ. Health Perspect. 107 (1999) 907–938.

[4] K. Kümmerer, Drugs in the environment: Emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources—A review, Chemosphere 45 (2001) 957–969.

[5] S.H. Kim, H.K. Shon, H.H. Ngo, Adsorption characteristics of antibiotics trimethoprim on powdered and granular activated carbon, J. Ind. Eng. Chem. 16 (2010) 344–349.

[6] P. Pocostales, P. Álvarez, F.J. Beltrán, Catalytic ozonation promoted by alumina-based catalysts for the removal of some pharmaceutical compounds from water, Chem. Eng. J. 168 (2011) 1289–1295.

[7] S. Esplugas, D.M. Bila, L.G.T. Krause, M. Dezotti, Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents, J. Hazard. Mater. 149 (2007) 631–642.

[8] N. Nakada, H. Shinohara, A. Murata, K. Kiri, S. Managaki, N. Sato, H. Takada, Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant, Water Res. 41 (2007) 4373–4382.

[9] M. Carballa, G. Manterola, L. Larrea, T. Ternes, F. Omil, J.M. Lema, Influence of ozone pre-treatment on sludge anaerobic digestion: Removal of pharmaceutical and personal care products, Chemosphere 67 (2007) 1444–1452.

[10] J. Akhtar, N.S. Amin, A. Aris, Combined adsorption and catalytic ozonation for removal of sulfamethoxazole using Fe_2O_3/CeO_2 loaded activated carbon, Chem. Eng. J. 170 (2011) 136–144.

[11] O.A. Jones, J.N. Lester, N. Voulvoulis, Pharmaceuticals: A threat to drinking water? Trends Biotechnol. 23 (2005) 163–167.

[12] R. Pal, M. Megharaj, K.P. Kirkbride, R. Naidu, Illicit drugs and the environment—A review, Sci. Total Environ. 463–464 (2013) 1079–1092.

[13] T. Deblonde, C. Cossu-Leguille, P. Hartemann, Emerging pollutants in wastewater: A review of the literature, Int. J. Hyg. Environ. Health 214 (2011) 442–448.

[14] D. Fatta-Kassinos, K. Kümmerer, pharmaceuticals in the environment: Sources, fate, effects and risks, Environ. Sci. Pollut. Res. 17 (2010) 519–521.

[15] R. Gunnarsdóttir, P.D. Jenssen, P. Erland Jensen, A. Villumsen, R. Kallenborn, A review of wastewater handling in the Arctic with special reference to pharmaceuticals and personal care products (PPCPs) and microbial pollution, Ecol. Eng. 50 (2013) 76–85.
[16] A. Azizullah, M.N.K. Khattak, P. Richter, D.-P. Häder, Water pollution in Pakistan and its impact on public health—A review, Environ. Int. 37 (2011) 479–497.
[17] T. Heberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data, Toxicol. Lett. 131 (2002) 5–17.
[18] J. Tolls, Sorption of veterinary pharmaceuticals in soils: A review, Environ. Sci. Technol. 35 (2001) 3397–3406.
[19] C. Ort, M.G. Lawrence, J. Rieckermann, A. Joss, Sampling for pharmaceuticals and personal care products (PPCPs) and illicit drugs in wastewater systems: Are your conclusions valid? A critical review, Environ. Sci. Technol. 44 (2010) 6024–6035.
[20] S. Kaplan, Review: Pharmacological pollution in water, Crit. Rev. Environ. Sci. Technol. 43 (2012) 1074–1116.
[21] J.-L. Liu, M.-H. Wong, Pharmaceuticals and personal care products (PPCPs): A review on environmental contamination in China, Environ. Int. 59 (2013) 208–224.
[22] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402–417.
[23] K. Ikehata, N. Jodeiri Naghashkar, M. Gamal El-Din, Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: A review, Ozone: Sci. Eng. 28 (2006) 353–414
[24] J. Rivera-Utrilla, M. Sánchez-Polo, M.Á. Ferro-García, G. Prados-Joya, R. Ocampo-Pérez, Pharmaceuticals as emerging contaminants and their removal from water. A review, Chemosphere 93 (2013) 1268–1287.
[25] A. Boreen, W. Arnold, K. McNeill, Photodegradation of pharmaceuticals in the aquatic environment: A review, Aquat. Sci. 65 (2003) 320–341.
[26] I. Sirés, E. Brillas, Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review, Environ. Int. 40 (2012) 212–229.
[27] L. Feng, E.D. van Hullebusch, 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. 228 (2013) 944–964.
[28] D. Zhang, R.M. Gersberg, W.J. Ng, S.K. Tan, Removal of pharmaceuticals and personal care products in aquatic plant-based systems: A review, Environ. Pollut. 184 (2014) 620–639.
[29] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal—A review, J. Environ. Manage. 90 (2009) 2313–2342.
[30] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, Bioresour. Technol. 97 (2006) 1061–1085.
[31] L. Huang, Y. Sun, W. Wang, Q. Yue, T. Yang, Comparative study on characterization of activated carbons prepared by microwave and conventional heating methods and application in removal of oxytetracycline (OTC), Chem. Eng. J. 171 (2011) 1446–1453.
[32] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: A review, J. Hazard. Mater. 177 (2010) 70–80.
[33] C.-J. Wang, Z. Li, W.-T. Jiang, J.-S. Jean, C.-C. Liu, Cation exchange interaction between antibiotic ciprofloxacin and montmorillonite, J. Hazard. Mater. 183 (2010) 309–314.
[34] S. Zhang, T. Shao, S.S.K. Bekaroglu, T. Karanfil, Adsorption of synthetic organic chemicals by carbon nanotubes: Effects of background solution chemistry, Water Res. 44 (2010) 2067–2074.
[35] B. Pavoni, D. Drusian, A. Giacometti, M. Zanette, Assessment of organic chlorinated compound removal from aqueous matrices by adsorption on activated carbon, Water Res. 40 (2006) 3571–3579.
[36] A.M. Ramos, M. Otero, A.E. Rodrigues, Recovery of Vitamin B12 and cephalosporin-C from aqueous solutions by adsorption on non-ionic polymeric adsorbents, Sep. Purif. Technol. 38 (2004) 85–98.
[37] K.A. Robberson, A.B. Waghe, D.A. Sabatini, E.C. Butler, Adsorption of the quinolone antibiotic nalidixic acid onto anion-exchange and neutral polymers, Chemosphere 63 (2006) 934–941.
[38] T.X. Bui, H. Choi, Adsorptive removal of selected pharmaceuticals by mesoporous silica SBA-15, J. Hazard. Mater. 168 (2009) 602–608.
[39] I. Cabrita, B. Ruiz, A.S. Mestre, I.M. Fonseca, A.P. Carvalho, C.O. Ania, Removal of an analgesic using activated carbons prepared from urban and industrial residues, Chem. Eng. J. 163 (2010) 249–255.
[40] W. Liu, J. Zhang, C. Zhang, L. Ren, Sorption of norfloxacin by lotus stalk-based activated carbon and iron-doped activated alumina: Mechanisms, isotherms and kinetics, Chem. Eng. J. 171 (2011) 431–438.
[41] A.J. Watkinson, E.J. Murby, D.W. Kolpin, S.D. Costanzo, The occurrence of antibiotics in an urban watershed: From wastewater to drinking water, Sci. Total Environ. 407 (2009) 2711–2723.
[42] A.Y.-C. Lin, T.-H. Yu, C.-F. Lin, Pharmaceutical contamination in residential, industrial, and agricultural waste streams: Risk to aqueous environments in Taiwan, Chemosphere 74 (2008) 131–141.
[43] Y. Yoon, J. Ryu, J. Oh, B.-G. Choi, S.A. Snyder, Occurrence of endocrine disrupting compounds, pharmaceuticals, and personal care products in the Han River (Seoul, South Korea), Sci. Total Environ. 408 (2010) 636–643.
[44] S. Castiglioni, R. Bagnati, R. Fanelli, F. Pomati, D. Calamari, E. Zuccato, Removal of pharmaceuticals in sewage treatment plants in Italy, Environ. Sci. Technol. 40 (2005) 357–363.
[45] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters, Water Res. 41 (2007) 1013–1021.
[46] A.L. Spongberg, J.D. Witter, Pharmaceutical compounds in the wastewater process stream in Northwest Ohio, Sci. Total Environ. 397 (2008) 148–157.

[47] J. Rivera-Utrilla, G. Prados-Joya, 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. 170 (2009) 298–305.
[48] E. Çalışkan, S. Göktürk, Adsorption characteristics of sulfamethoxazole and metronidazole on activated carbon, Sep. Sci. Technol. 45 (2010) 244–255.
[49] E.K. Putra, R. Pranowo, J. Sunarso, N. Indraswati, S. Ismadji, Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics, Water Res. 43 (2009) 2419–2430.
[50] P. Oleszczuk, B. Pan, B. Xing, Adsorption and desorption of oxytetracycline and carbamazepine by multiwalled carbon nanotubes, Environ. Sci. Technol. 43 (2009) 9167–9173.
[51] A.S. Mestre, J. Pires, J.M.F. Nogueira, A.P. Carvalho, Activated carbons for the adsorption of ibuprofen, Carbon 45 (2007) 1979–1988.
[52] Z. Aksu, Ö. Tunç, Application of biosorption for penicillin G removal: Comparison with activated carbon, Proc. Biochem. 40 (2005) 831–847.
[53] N. Erdinç, S. Göktürk, M. Tunçay, A study on the adsorption characteristics of an amphiphilic phenothiazine drug on activated charcoal in the presence of surfactants, Colloids Surf. B 75 (2010) 194–203.
[54] L. Ji, W. Chen, S. Zheng, Z. Xu, D. Zhu, Adsorption of sulfonamide antibiotics to multiwalled carbon nanotubes, Langmuir 25 (2009) 11608–11613.
[55] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye using activated carbon prepared from oil palm shell: Batch and fixed bed studies, Desalination 225 (2008) 13–28.
[56] B.H. Hameed, A.L. Ahmad, K.N.A. Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, Dyes Pigm. 75 (2007) 143–149.
[57] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—A comparative study, Dyes Pigm. 51 (2001) 25–40.
[58] A. Özer, G. Dursun, Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon, J. Hazard. Mater. 146 (2007) 262–269.
[59] V. Gómez-Serrano, E.M. Cuerda-Correa, M.C. Fernández-González, M.F. Alexandre-Franco, A. Macías-García, Preparation of activated carbons from walnut wood: A study of microporosity and fractal dimension, Smart Mater. Struct. 14 (2005) 363–368.
[60] L. Ji, Y. Shao, Z. Xu, S. Zheng, D. Zhu, Adsorption of monoaromatic compounds and pharmaceutical antibiotics on carbon nanotubes activated by KOH etching, Environ. Sci. Technol. 44 (2010) 6429–6436.
[61] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review, J. Hazard. Mater. 97 (2003) 219–243.
[62] S.-H. Lin, R.-S. Juang, Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review, J. Environ. Manage. 90 (2009) 1336–1349.
[63] M. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: A review, Adv. Colloid Interface Sci. 143 (2008) 48–67.
[64] K.G. Bhattacharyya, S.S. Gupta, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review, Adv. Colloid Interface Sci. 140 (2008) 114–131.
[65] M. Akçay, Characterization and determination of the thermodynamic and kinetic properties of p-CP adsorption onto organophilic bentonite from aqueous solution, J. Colloid Interface Sci. 280 (2004) 299–304.
[66] M. Akçay, Characterization and adsorption properties of tetrabutylammonium montmorillonite (TBAM) clay: Thermodynamic and kinetic calculations, J. Colloid Interface Sci. 296 (2006) 16–21.
[67] G. Akçay, E. Kılınç, M. Akçay, The equilibrium and kinetics studies of flurbiprofen adsorption onto tetrabutylammonium montmorillonite (TBAM), Colloids Surf. A 335 (2009) 189–193.
[68] H.-S. Chang, K.-H. Choo, B. Lee, S.-J. Choi, The methods of identification, analysis, and removal of endocrine disrupting compounds (EDCs) in water, J. Hazard. Mater. 172 (2009) 1–12.
[69] R.A. Figueroa, A. Leonard, A.A. MacKay, Modeling tetracycline antibiotic sorption to clays, Environ. Sci. Technol. 38 (2003) 476–483.
[70] Y.-J. Wang, D.-A. Jia, 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. 42 (2008) 3254–3259.
[71] J.R.V. Pils, D.A. Laird, Sorption of tetracycline and chlortetracycline on K- and Ca-Saturated soil clays, humic substances, and Clay−humic complexes, Environ. Sci. Technol. 41 (2007) 1928–1933.
[72] M. Bewick, The adsorption and release of tylosin by clays and soils, Plant Soil 51 (1979) 363–372.
[73] W. Zhang, Y. Ding, S.A. Boyd, B.J. Teppen, H. Li, Sorption and desorption of carbamazepine from water by smectite clays, Chemosphere 81 (2010) 954–960.
[74] Q. Wu, Z. Li, H. Hong, K. Yin, L. Tie, Adsorption and intercalation of ciprofloxacin on montmorillonite, Appl. Clay Sci. 50 (2010) 204–211.
[75] P.-H. Chang, J.-S. Jean, W.-T. Jiang, Z. Li, Mechanism of tetracycline sorption on rectorite, Colloids Surf. A 339 (2009) 94–99.
[76] P.-H. Chang, Z. Li, W.-T. Jiang, J.-S. Jean, Adsorption and intercalation of tetracycline by swelling clay minerals, Appl. Clay Sci. 46 (2009) 27–36.
[77] I. Turku, T. Sainio, E. Paatero, Thermodynamics of tetracycline adsorption on silica, Environ. Chem. Lett. 5 (2007) 225–228.
[78] Z. Bekci, Y. Seki, M.K. Yurdakoc, Equilibrium studies for trimethoprim adsorption on montmorillonite KSF, J. Hazard. Mater. 133 (2006) 233–242.
[79] R.K. Khandal, J.C. Thoisy-Dur, M. Terce, Adsorption characteristics of flumequine on kaolinitic clay, Geoderma 50 (1991) 95–107.
[80] Z. Li, L. Schulz, C. Ackley, N. Fenske, Adsorption of tetracycline on kaolinite with pH-dependent surface charges, J. Colloid Interface Sci. 351 (2010) 254–260.
[81] M.E. Parolo, M.C. Savini, J.M. Vallés, M.T. Baschini, M.J. Avena, Tetracycline adsorption on montmorillonite: pH and ionic strength effects, Appl. Clay Sci. 40 (2008) 179–186.

[82] X. Xue, F. Li, Removal of Cu(II) from aqueous solution by adsorption onto functionalized SBA-16 mesoporous silica, Microporous Mesoporous Mater. 116 (2008) 116–122.
[83] J. Qiu, Z. Wang, H. Li, L. Xu, J. Peng, M. Zhai, C. Yang, J. Li, G. Wei, Adsorption of Cr(VI) using silica-based adsorbent prepared by radiation-induced grafting, J. Hazard. Mater. 166 (2009) 270–276.
[84] B. Vu, E. Shin, O. Snisarenko, W. Jeong, H. Lee, Removal of the antibiotic tetracycline by Fe-impregnated SBA-15, Korean J. Chem. Eng. 27 (2010) 116–120.
[85] P. Patiparn, S. Thitikamon, Removal of ciprofloxazin and carbamazepine by adsorption on functionalized mesoporous silicates, World Acad. Sci. Eng. Technol. 69 (2010) 546–550.
[86] O. Lorphensri, J. Intravijit, D.A. Sabatini, T.C.G. Kibbey, K. Osathaphan, C. Saiwan, Sorption of acetaminophen, 17α-ethynyl estradiol, nalidixic acid, and norfloxacin to silica, alumina, and a hydrophobic medium, Water Res. 40 (2006) 1481–1491.
[87] K.W. Goyne, J. Chorover, J.D. Kubicki, A.R. Zimmerman, S.L. Brantley, Sorption of the antibiotic ofloxacin to mesoporous and nonporous alumina and silica, J. Colloid Interface Sci. 283 (2005) 160–170.
[88] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, Science 279 (1998) 548–552.
[89] B. Pan, B. Pan, W. Zhang, L. Lv, Q. Zhang, S. Zheng, Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters, Chem. Eng. J. 151 (2009) 19–29.
[90] Z. Xu, Q. Zhang, H.H.P. Fang, Applications of porous resin sorbents in industrial wastewater treatment and resource recovery, Crit. Rev. Environ. Sci. Technol. 33 (2003) 363–389.
[91] M. Scordino, A. Di Mauro, A. Passerini, E. Maccarone, Adsorption of flavonoids on resins: Hesperidin, J. Agric. Food Chem. 51 (2003) 6998–7004.
[92] M.V. Chaubal, G.F. Payne, C.H. Reynolds, R.L. Albright, Equilibria for the adsorption of antibiotics onto neutral polymeric sorbents: Experimental and modeling studies, Biotechnol. Bioeng. 47 (1995) 215–226.
[93] J.W. Lee, H.C. Park, H. Moon, Adsorption and desorption of cephalosporin c on nonionic polymeric sorbents, Sep. Purif. Technol. 12 (1997) 1–11.
[94] M. Dutta, N.N. Dutta, K.G. Bhattacharya, Aqueous phase adsorption of certain beta-lactam antibiotics onto polymeric resins and activated carbon, Sep. Purif. Technol. 16 (1999) 213–224.
[95] M.L. Ribeiro, I.C. Ribeiro, Modelling the adsorption kinetics of erythromycin onto neutral and anionic resins, Bioprocess Biosyst. Eng. 26 (2003) 49–55.
[96] M.L. Ribeiro, I.C. Ribeiro, Modelling the adsorption kinetics of erythromycin onto neutral and anionic resins, Bioprocess Biosyst. Eng. 26 (2003) 49–55.
[97] D.S. Zimnitsky, T.L. Yurkshtovich, P.M. Bychkovsky, Adsorption of zwitterionic drugs on oxidized cellulose from aqueous and water/alcohol solutions, J. Phys. Chem. B 108 (2004) 17812–17817.
[98] H. Zhang, C.-H. Huang, Adsorption and oxidation of fluoroquinolone antibacterial agents and structurally related amines with goethite, Chemosphere 66 (2007) 1502–1512.
[99] D.B. Wunder, V.A. Bosscher, R.C. Cok, R.M. Hozalski, Sorption of antibiotics to biofilm, Water Res. 45 (2011) 2270–2280.
[100] T. Urase, T. Kikuta, Separate estimation of adsorption and degradation of pharmaceutical substances and estrogens in the activated sludge process, Water Res. 39 (2005) 1289–1300.
[101] W.-R. Chen, C.-H. Huang, Adsorption and transformation of tetracycline antibiotics with aluminum oxide, Chemosphere 79 (2010) 779–785.
[102] C. Gu, K.G. Karthikeyan, Sorption of the antimicrobial ciprofloxacin to aluminum and iron hydrous oxides, Environ. Sci. Technol. 39 (2005) 9166–9173.
[103] C. Gu, K.G. Karthikeyan, Interaction of tetracycline with aluminum and iron hydrous oxides, Environ. Sci. Technol. 39 (2005) 2660–2667.
[104] M. Kahle, C. Stamm, Sorption of the veterinary antimicrobial sulfathiazole to organic materials of different origin, Environ. Sci. Technol. 41 (2006) 132–138.
[105] J. Feitosa-Felizzola, K. Hanna, S. Chiron, Adsorption and transformation of selected human-used macrolide antibacterial agents with iron(III) and manganese (IV) oxides, Environ. Pollut. 157 (2009) 1317–1322.
[106] Z. Fang, J. Chen, X. Qiu, X. Qiu, W. Cheng, L. Zhu, Effective removal of antibiotic metronidazole from water by nanoscale zero-valent iron particles, Desalination 268 (2011) 60–67.
[107] S.M. Rivera-Jiménez, A.J. Hernández-Maldonado, Nickel(II) grafted MCM-41: A novel sorbent for the removal of Naproxen from water, Microporous Mesoporous Mater. 116 (2008) 246–252.
[108] A.L.P.F. Caroni, C.R.M. de Lima, M.R. Pereira, J.L.C. Fonseca, The kinetics of adsorption of tetracycline on chitosan particles, J. Colloid Interface Sci. 340 (2009) 182–191.
[109] H.M. Ötker, I. Akmehmet-BalcIoglu, Adsorption and degradation of enrofloxacin, a veterinary antibiotic on natural zeolite, J. Hazard. Mater. 122 (2005) 251–258.
[110] D. Krajišnik, A. Daković, M. Milojević, A. Malenović, M. Kragović, D.B. Bogdanović, V. Dondur, J. Milić, Properties of diclofenac sodium sorption onto natural zeolite modified with cetylpyridinium chloride, Colloids Surf. B 83 (2011) 165–172.
[111] I. Vergili, H. Barlas, Removal of selected pharmaceutical compounds from water by an organic polymer resin, J. Sci. Ind. Res. 68 (2009) 417–425.
[112] A. Rossner, S.A. Snyder, D.R.U. Knappe, Removal of emerging contaminants of concern by alternative adsorbents, Water Res. 43 (2009) 3787–3796.
[113] G. Li, H. Li, Y. Li, J. Chen, M. Zhu, X.Zhang, Adsorption of tetracycline by activated carbon fiber, Fourth International Conference on Bioinformatics and Biomedical Engineering, Chengdu, 2010, pp. 1–4.
[114] Q. Tian, C.D. Gomersall, A. Wong, P. Leung, G. Choi, G.M. Joynt, P. Tan, J. Lipman, Effect of drug concentration on adsorption of levofloxacin by polyacrylonitrile haemofilters, Int. J. Antimicrob. Agents 28 (2006) 147–150.

[115] Z. Xu, D. Kuang, L. Liu, Q. Deng, Selective adsorption of norfloxacin in aqueous media by an imprinted polymer based on hydrophobic and electrostatic interactions, J. Pharm. Biomed. Anal. 45 (2007) 54–61.
[116] K.-J. Choi, H.-J. Son, S.-H. Kim, Ionic treatment for removal of sulfonamide and tetracycline classes of antibiotic, Sci. Total Environ. 387 (2007) 247–256.
[117] S.R. El-Shaboury, G.A. Saleh, F.A. Mohamed, A.H. Rageh, Analysis of cephalosporin antibiotics, J. Pharm. Biomed. Anal. 45 (2007) 1–19.
[118] J.W. Peterson, R.S. Burkhart, D.C. Shaw, A.B. Schuiling, M.J. Haserodt, M.D. Seymour, Experimental determination of ampicillin adsorption to nanometer-size Al_2O_3 in water, Chemosphere 80 (2010) 1268–1273.
[119] M.A. Qtaitat, Study of the interaction of trimethoprim-montmorillonite by infrared spectroscopy, Spectrochim. Acta Part A 60 (2004) 673–678.
[120] Z. Zawani, C.A. Luqman, S.Y.C. Thomas, Equilibrium, kinetics and thermodynamic studies: Adsorption of remazol black 5 on the palm kernel shell activated carbon (PKS-AC), Eur. J. Sci. Res. 37 (2009) 67–76.
[121] Z.A. Al-Anber, M.A.S. Al-Anber, Thermodynamics and kinetic studies of iron(III) adsorption by olive cake in a batch system, J. Mex. Chem. Soc. 52 (2008) 108–115
[122] D.-A. Jia, D.-M. Zhou, Y.-J. Wang, H.-W. Zhu, J.-L. Chen, Adsorption and cosorption of Cu(II) and tetracycline on two soils with different characteristics, Geoderma 146 (2008) 224–230.
[123] Z. Yu, S. Peldszus, P.M. Huck, Adsorption characteristics of selected pharmaceuticals and an endocrine disrupting compound—Naproxen, carbamazepine and nonylphenol—On activated carbon, Water Res. 42 (2008) 2873–2882.
[124] C. Hepplewhite, G. Newcombe, D.R. Knappe, NOM and MIB, who wins in the competition for activated carbon adsorption sites? Water Sci. Technol. 49 (2004) 257–265.
[125] N. Suriyanon, P. Punyapalakul, C. Ngamcharussrivichai, Mechanistic study of diclofenac and carbamazepine adsorption on functionalized silica-based porous materials, Chem. Eng. J. 214 (2013) 208–218.
[126] P. Kulshrestha, R.F. Giese, D.S. Aga, Investigating the molecular interactions of oxytetracycline in clay and organic matter: Insights on factors affecting its mobility in soil, Environ. Sci. Technol. 38 (2004) 4097–4105.
[127] G. Li, H. Li, Y. Li, J. Chen, M. Zhu, X. Zhang, Adsorption of tetracycline by activated carbon fiber, Fourth International Conference on Bioinformatics and Biomedical Engineering, Chengdu, China, 2010.
[128] J. Gao, J.A. Pedersen, Adsorption of sulfonamide antimicrobial agents to clay minerals, Environ. Sci. Technol. 39 (2005) 9509–9516.
[129] Iupac, Dissociative Adsorption (1997). Available from: <http://old.iupac.org/goldbook/D01803.pdf>.
[130] C. Ania, J. Pelayo, T. Bandosz, Reactive adsorption of penicillin on activated carbons, Adsorption 17 (2011) 421–429.