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REVIEW ARTICLE

Adsorption behavior of antibiotic in soil environment: a critical review

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Abstract Antibiotics are used widely in human and veterinary medicine, and are ubiquitous in environment matrices worldwide. Due to their consumption, excretion, and persistence, antibiotics are disseminated mostly via direct and indirect emissions such as excrements, sewage irrigation, and sludge compost and enter the soil and impact negatively the natural ecosystem of soil. Most antibiotics are amphiphilic or amphoteric and ionize. A non-polar core combined with polar functional moieties makes up numerous antibiotic molecules. Because of various molecule structures, physicochemical properties vary widely among antibiotic compounds. Sorption is an important process for the environment behaviors and fate of antibiotics in soil environment. The adsorption process has decisive role for the environmental behaviors and the ultimate fates of antibiotics in soil. Multiply physicochemical properties of antibiotics induce the large variations of their adsorption behaviors. In addition, factors of soil environment such as the pH, ionic strength, metal ions, and organic matter content also strongly impact the adsorption processes of antibiotics. Review about adsorption of antibiotics on soil can provide a fresh insight into understanding the antibiotic-soil interactions. Therefore, literatures about the adsorption mechanisms of antibiotics in soil environment and the effects of environment factors on adsorption behaviors of antibiotics in soil are reviewed and discussed systematically in this review.

Keywords adsorption, antibiotics, environment factors, soil

1 Introduction

Antibiotics have been used in large quantities for several decades as human and veterinary medicine and husbandry growth promoters. They are highly effective and bioactive substances. Occurrence and fate of antibiotics in environment have drawn great attention of researchers all over the world in recent years [1,2]. Currently, they were frequently detected in municipal wastewater, surface water, ground water, soils and sediments [3–5]. Although the concentration of antibiotics residue in the environment is low [4,6,7], they are considered to be emerging pollutants because antibiotics and their transformation products may result in the development/maintenance/transfer/spread of antibiotics resistant bacteria and antibiotics resistance genes in the long-term and have long-term risks to human and ecological health [8,9]. Long-term exposure to low and sub-toxic concentrations of antibiotics could change microbial ecology, promote the development and spread of antibiotic-resistance, provoke toxic effects on aquatic species, and even present unexpected effects on human health via food chain [5,10].

Antibiotics enter soil and other environmental matrixes after their consumption, excretion, and persistence. Soil acts as a source of antibiotic contaminants for the aqueous environment due to surface runoff and leaching [11]. Study revealed the presence of antibiotics in soil, vegetable, and cereals with concentrations ranging from a few $\mu g \cdot kg^{-1}$ up to $g \cdot kg^{-1}$ [12]. The high polarity and non-volatile nature of most antibiotics prevent their escape from soil [13]. Both the physicochemical properties (including molecular structure, size, shape, solubility, and hydrophobicity) of antibiotics and the basic characteristics (type, texture, pH, and organic matter content) of soil strongly affect the behaviors and fates of antibiotics in soil [14]. Most of important, antibiotics are responsible for the production of resistant microorganisms, causing serious problems of public health, namely difficulties in treating pathologies and imbalance of microbial ecosystems [15].

Among various technologies for antibiotics removal,

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adsorption has been regarded as one of the most prevalent methods [16–19]. Adsorption processes have decisive role for the environmental behaviors and the ultimate fates of antibiotics. In recent years, some review articles about the input, occurrence, and effects of antibiotics in the environment [14,20], about the analytical methodologies for determination of antibiotics [21], and about the oxidation technologies for the removal of antibiotics [22,23] have been published. Though many studies have been conducted to investigate the adsorption and desorption of antibiotics on soils, a review article concerning the adsorption behaviors of antibiotics in soil environment hasn't been found until now.

Therefore, on the basis of summary about the generally physicochemical properties of antibiotics and their sources in soil; information about the adsorption mechanisms of antibiotics in soil has been reviewed; and environmental factors impacting the adsorption behaviors of antibiotics in soil environment have been systematically discussed and evaluated in this review.

2 Basic properties of antibiotics and their sources in soil

2.1 Basic properties of antibiotics

Antibiotics define a multitude of heterogeneous compounds that are classified by different fields of usage and different structural classes. And these antibiotic compounds show different molecular structures and diverse physicochemical properties [24]. Most antibiotics show apparent tendencies to ionize and show multivalence with the medium pH changing. They generally contain a multitude of ionic functional groups and multiple acid dissociation constants (pK_a). The values of pK_a are associated with the different functional groups of the compounds. Most antibiotics show positive, neutral, and negative valences along with the pH of solution changing. An overview of the selected classes of representative antibiotics and their basic physicochemical properties are list in Table 1.

Table 1 Basically physicochemical properties of selected classes of antibiotics

selected classes	representative compounds	core structure	basic properties
aminoglycosides	apramycin	comprised of two or more amino sugars joined by a glycoside linkage to a hexose nucleus of the drug. The structure of these antibiotics is derived from these two molecules.	MM: 332.4–615.6 ($g \cdot mol^{-1}$)
	gentamycin		WS: 10–500 ($g \cdot L^{-1}$)
	kanamycin		log K_{OW}: -8.1 – -0.8
	neomycin		pKa: 6.9–8.5
	sisomycin		HC: 8.5×10^{-12}–4.1×10^{-12}
	spectinomycin		
	streptomycin		
β-lactams	amoxicillin	comprised of a thiazolidine ring connected to a β-lactam ring, to which a side chain is attached.	MM: 334.4–470.3 ($g \cdot mol^{-1}$)
	ampicillin		WS: 22–10100 ($mg \cdot L^{-1}$)
	azlocillin		log K_{OW}: 0.9–2.9
	benzylpenicillin		pKa: 2.7
	carbenicillin		HC: 2.5×10^{-19}–1.2×10^{-12}
	cefazolin		
	cefuroxim		
	cefotaxim		
	cefprozil		
	cloxacilin		
	dicloxacilin		
	flucloxacillin		
	meropenem		
	methicillin		
	mezlocillin		
	nafcillin		
	oxacillin		
	piperacillin		
	phenoxymethylcillin		
	penicillin G		

(*Continued*)

selected classes	representative compounds	core structure	basic properties
glycopeptides	vancomycin	comprised of carbohydrate moieties (glycans) covalently attached to the side chains of an amino acid.	MM: 1450.7 $(\mathrm{g\cdot mol^{-1}})$ WS: >100 $(\mathrm{mg\cdot L^{-1}})$ not soluble in octanol *pKa*: 5.0 HC: negligible
macrolides	azithromycin clarithromycin erythromycin roxithromycin spiramycin tylosin vancomycin	comprised of highly substituted monocyclic lactone with one or more saccharides glycosidically attached to hydroxyl groups. The lactone rings are usually 12, 14 or 16-membered.	MM: 687.9–916.1 $(\mathrm{g\cdot mol^{-1}})$ WS: 0.45–15 $(\mathrm{mg\cdot L^{-1}})$ log K_{OW}: 1.6–3.1 *pKa*: 7.7–8.9 HC: 7.8×10^{-36}–2.0×10^{-26}
fluorquinolones	ciprofloxacin enrofloxacin, flumequin, sarafloxacin	containing two fused rings with a carboxylic acid and a ketone group.	MM: 229.5–417.6 $(\mathrm{g\cdot mol^{-1}})$ WS: 3.2–17790 $(\mathrm{mg\cdot L^{-1}})$ log Kow: -1.0–1.6 *pKa*: 8.6 HC: 5.2×10^{-17}–3.2×10^{-8}
sulphonamides	sulphanilamide sulphadimethoxine sulphadimidine sulphamethoxazole sulphapyridine sulphathiazole	characterized by sulfonyl group connected to an amine group.	MM: 172.2–300.3 $(\mathrm{g\cdot mol^{-1}})$ WS: 7.5–1500 $(\mathrm{mg\cdot L^{-1}})$ log K_{OW}: -0.1–1.7 *pKa*: 2~3; 4.5–10.6 HC: 1.3×10^{-12}–1.8×10^{-8}
tetracyclines	chlortetracycline doxycycline oxytetracycline tetracycline doxycycline erythro-mycin A	containing an octrahydronaphtacene ring skeleton, consisting of 4 fused rings.	MM: 444.5–527.6 $(\mathrm{g\cdot mol^{-1}})$ WS: 203–52000 $(\mathrm{mg\cdot L^{-1}})$ log K_{OW}: -1.3–0.05 *pKa*: 3.3; 7.7; 9.3 HC: 1.7×10^{-23}–4.8×10^{-23}

Notes: MM, molar mass; WS, water solubility; HC, Henry's constant

Aminoglycosides are a class of basic, strongly polar polycationic compounds. Their molecular structures contain two or more amino sugars that are glycosidically bound to aminocyclitol. Aminoglycosides are soluble in water, mostly hydrophilic, and susceptible to photodegradation.

β-lactams antibiotics mainly include sub-classes of penicillins and cephalosporins. The effect of penicillins is directly connected to the β-lactam ring that is easily cleaved in acidic and basic media. Cephalosporins are derivatives of 7-amino-cephalosporanic acid, condensed with a six-membered heterocycle in contrast to the five-membered hetero-cycle of penicillins.

Tetracyclines (TCs) are polyketides and amphoteric compounds, comprised of a naphthacene ring structure, and relatively stable in acids [25]. TCs can form chelate complexes with divalent metal ions and β-diketones and can strongly bind to proteins and silanolic groups [22]. Most TCs are sparingly water soluble, while the solubility of the corresponding hydrochlorides is much higher. The TCs can effectively absorb light and thus, are susceptible to photodegradation [23].

Sulfonamides (SAs) are relatively insoluble in water, and show the tendency of protonation of the amino group at pH 2–3 and deprotonation of the $R_1SO_2NHR_2$ moiety at pH 5–11 [28]. In general, SAs are the amphoteric compounds and behave as weak acids and form salts in strongly acidic or basic solutions. Mostly, SAs, substituted at the amino-N, have greatly reduced antibacterial activity.

Macrolides are defined as lactone structures with cycles of more than 10 C-atoms. These compounds are weak bases and are unstable in acids. Different derivatives of macrolides have different solubility.

Most fluorquinolones (FQs), such as quinolones, show high chemical stability. This class of antibiotics is insensitive to hydrolysis. Their antibiotic potency depends mostly on the aromatic fluorine substituent at the C-6 position [29].

2.2 Sources and concentration of antibiotics in soil environment

In recent years, the contamination of soil environment by antibiotics increased with their wide use [30]. Antibiotics can be introduced into soil by a diversity of input sources. First, antibiotics can be directly discharged into the soil. In addition, a considerable quantity of antibiotics also can be indirectly introduced into the soil. For example, veterinary antibiotics can be introduced into soil through use of livestock wastes as fertilizers [6,14]. Human antibiotics are discharged into the sewer network and reach the wastewater treatment plants (WWTPs) with the excretion (urine and faeces) emissions. Most of WWTPs are not designed to remove highly polar micropollutants like antibiotics [31–35]. Consequently, these pollutants can be transported to surface water and reach groundwater after leaching. Ultimately, the contaminated water can enter the soil environment by irrigation. Antibiotics can also be discharged into soil through land application of sludge produced by WWTPs or landfill.

Some studies found the detectable contents of antibiotics in the manure, excretion, and fertilized soil. For example, manure samples from pigs contained 3.5 $mg \cdot kg^{-1}$ of SAs and 4 $mg \cdot kg^{-1}$ of TCs [36–38]. Residual concentrations of antibiotics in agricultural soils ranged from 450 to 900 $\mu g \cdot kg^{-1}$ for TCs [39], from 13 to 67 $\mu g \cdot kg^{-1}$ for macrolides and from 6 to 52 $\mu g \cdot kg^{-1}$ for FQs [40]. In soils under conventional land farming fertilized with manure and monitored for two years, average concentrations of up to 199 $\mu g \cdot kg^{-1}$ tetracycline, 7 $\mu g \cdot kg^{-1}$ chlortetracycline [37], and 11 $\mu g \cdot kg^{-1}$ sulfadimidine [36] were detected. Veterinary antibiotics existed in the soil from organic vegetable farmland fertilized with livestock wastes in Tianjin [41], with concentrations up to 2683 $ng \cdot g^{-1}$ (dw). Tetracycline has been detected in liquid manure-treated agriculture field at concentrations of about 10 $\mu g \cdot kg^{-1}$ [42], and a monitoring program in the United States directed at waters that are suspected to be contaminated with antibiotics used in husbandry detected trimethoprim and sulfamethoxazole in 30% of the samples [43]. Therefore, the question arises of what happens with the antibiotics once they have reached the soil.

3 Adsorption mechanisms of antibiotics in soil environment

Investigation of antibiotics adsorption on soils is of great importance, because such a process is closely associated with the ecotoxicity, degradation, transportation, and bioaccumulation of antibiotics in soil. A larger effort has been made to understand the adsorption mechanisms of antibiotics to natural soils [44–47]. Important findings from these studies showed that the adsorption of antibiotics is strongly influenced by basic physicochemical properties of soils such as the constituents, pH, ionic environment, texture, and organic matter (OM). In addition, the amphiphilic and amphoteric properties of antibiotics and their steric configuration also have a strong impaction on their adsorption on soil. However, all the physicochemical properties of antibiotics are mainly induced by their molecule structures.

Physicochemical properties vary widely among compounds of antibiotics from their various structural classes. Some antibiotics are hydrophobic or non-polar, whereas others are highlywater soluble or dissociated depending on the pH values for soils. Therefore, these various environment factors and compounds properties induce large differences for the adsorption behaviors and capacities of antibiotics. The adsorption capacity of organic chemicals between the water phase and a solid-phase sorbent, such as soil or sediment, is represented by the sorption coefficient (K_d, $K_d = C_S/C_W$, Cs and C_W represents the concentration of a compound in the sorbent phase ($mg \cdot kg^{-1}$) and in the water ($mg \cdot L^{-1}$) at equilibrium, respectively.). In this review, literature data about the adsorption of selected antibiotics on soils and the K_d values of them are collected (Table 2). The K_d values of fluoroquinolones and tetracyclines are much higher than those of other pharmaceuticals, which suggest that ciprofloxacin,

Table 2 Literature data of sorption coefficients of antibiotics in soil

selected classes	representative compounds	sorbents	conditions	K_d /($L \cdot kg^{-1}$)
fluoroquinolones	enrofloxacin	three kinds of sandy loam soils; pH: 4.9,5.3,7.5;	24 h; (20±1)°C	260–5610 [48]
	ciprofloxacin	one kind of sandy loam soil; pH: 5.3;	24 h; (20±1)°C	430 [48]
sulfonamides	sulfamethazine	two kinds of soil; pH: 7.5,7.2	14 h; 0.01 $mol \cdot L^{-1}$ $CaCl_2$	4.2–6.8 [49]
tetracyclines	oxytetracycline	three kinds of sandy loam soils; pH: 6.1,5.6,6.3;	24 h; 0.01 $mol \cdot L^{-1}$ $CaCl_2$	420–1030 [50]
		one kind of wood soil; pH: 5.3 one kind of plain soil: pH: 6.0	72 h; 10 $mmol \cdot L^{-1}$ PIPES buffer solution, 1.5 $mmol \cdot L^{-1}$ NaN_3	351.9–3910 152.6–1308 [51]
	tetracycline	one kind of organic matter-rich soil; pH: 4.6, 6.1	24 h; 0.01 $mol \cdot L^{-1}$ $CaCl_2$	1140–1620 [52]
macrolides	tylosin	three kinds of sandy loam soils; pH: 6.1,5.6,6.3	24 h; 0.01 $mol \cdot L^{-1}$ $CaCl_2$	8.3–128 [50]
	abamectin		24 h; 0.01 $mol \cdot L^{-1}$ $CaCl_2$	7–134 [53]

norfloxacin, and enrofloxacinare liable to accumulate in the surface soil and show low mobility in soil. Macrolides are easy to adsorb on soils with high mineral contents such as Fe, Al, and Mn, and show low migration tendencies, for example, only about 13% tylosin is desorbed from soil [50,54]. Desorption rate of oxytetracycline is only 0.5%–2.3% in soil collected from cropland field [50]. However, the K_d values of sulfonamides are much lower, which shows strong mobility in soil [49]. Therefore, different kinds of antibiotics indicate different distribution and behaviors in natural soil.

For different antibiotics, their structures and functional groups may be the main factors affecting their adsorption behaviors. The strong polarity and much ionic groups of the molecules for quinolones and tetracyclines are the main factors inducing their high adsorption levels. The ciprofloxacin molecules contain one –COOH, one –C = O, one $–CONH_2$, and one $–N(CH_3)_2$, which contribute to its strong adsorption to soil. The –COOH group also has big contribution to the adsorption of quinolone to soil [54]. The adsorption capacities of quinolone antibiotics containing the –COOH group including enrofloxacin, ciprofloxacin, and ofloxacin were comparable in the same kind of soil; and the adsorption capacity of enrofloxacin without the –COOH group was reduced by two orders of magnitude [48]. Quinolones adsorbed on the negative adsorption sites on the surface of soil by the bond bridge between –COOH and cations [48]. Study showed that ciprofloxacin adsorbed on soil by the action of bidentate coordination between the hydroxyl oxygen of –COOH and oxygen atoms of –C = O and the surface of HFO [56].

Tetracycline antibiotics can adsorb on soils by the electrostatic interaction between the positive-charged group ($–NH(CH_3)_2$) and the negative-charged adsorption site, or by the ion-exchange interaction between the positive-charged groups and the cations adhering to the surface of soil [57]. The –OH and –CONH groups of the molecule for tetracycline can adsorb on the negative-charged adsorption sites of soil by the bond bridge of the multivalence metal ions [58,59], and also can adsorb on the surface of metal oxides by the surface complexation with metal ions. The molecules of tetracycline antibiotics contained a number of polar functional groups. These groups also can interact with the polar portion of soil by hydrogen bonding [60]. Therefore, the combined actions of multiple functional groups induce fairly high adsorption capacities of tetracycline and quinolone.

Though macrolides contained the similar functional groups as tetracycline, they showed lower adsorption capacities than tetracycline, which might be induced by the reasons that macrolides had less quantities of –OH and –C = O per unit mass than that of tetracycline. Previous study revealed that electrostatic actions strongly impacted on the adsorption of macrolides, in addition, hydrogen bond interactions of polar portion in humic acid also contributed its adsorption [61].

Sulfonamide antibiotics only have aniline and amide groups, thus they show weak adsorption on soil. Bond bridge interactions including between the H_2O molecule and the phenylamino group and between the cationic ions and the acylamino group, contributed to the adsorption of zero valence sulfonamide to montmorillonite. During its adsorption processes, cation exchange also contributes to adsorption of cationic sulfonamide species on montmorillonite, and the nature of the sulfonamide R-group influenced the degree of adsorption of cationic and neutral species [62]. Cationic sulfathiazole interacted with organic matter by cation exchange; and zero-valence sulfathiazole interacted with aromatic groups of organic matter by the actions of hydrogen bonding and Van der Waals' force [63]. Phenoloxidases or metal oxides can oxidize phenol derivatives of organic matters, and generates electron deficiency sites. Nucleophilic addition occurring between the free amino nitrogen of sulfonamide and the electron deficiency sites of organic matter can result in the adsorption of sulfonamide to organic matter [64].

4 Effect of environmental factors on adsorption of antibiotics on soils

Beside the effects of the basic properties of antibiotics on their adsorption, various physicochemical properties of soil including OM content, type and amount of clay content, ion exchange capacity, and pH also strongly impact the adsorption of antibiotics on soil.

4.1 Effect of pH

Different types of soils show various acid or base properties. Antibiotic compounds can exist as cations, zwitterions, and anions at environmentally relevant pH values and display pH dependent adsorption on soils [45,51]. The adsorption of antibiotics is strongly controlled by the properties of numerous compounds to ionize depending on the medium pH [65]. For example, octanol/water coefficients of ionizing compounds change considerably in a pH range around the acid dissociation constant [66]. The maximum sorption capacity of montmorillonite for tetracycline decreased as pH increased from 1.5 to 11.0 [67]. The adsorption of tetracycline to montmorillonite and kaolinite decreased with pH increasing from 4 to 9 [57].

Here, oxytetracyline (OTC) is taken as the example to verify the impaction of pH on OTC adsorption. OTC showed different valence of OTC^+, OTC^0, and OTC^- in the solution with different range values of $pH < 3.6$, $3.6 < pH < 7.5$, and $pH > 7.5$, respectively. When the surface of pure clays contains large quantities of exchangeable cations, pH can alter the number of OTC^+. Therefore, adsorption capacities of OTC improve with cation exchange interaction enhancing [48,57,62]. However, OTC excludes with metal oxides because the same charge is indicated on their surface under the acidic and base conditions, which induce the low adsorption capacities of OTC to the metal oxides [51,54,68]. Organic matter contains some kinds of function group, especially some protonation of function groups affected by pH, therefore, OTC can interact with OM by hydrogen bonding when the pH is low. OTC (OTC^+ or OTC^-) interacts with the –COO– group by electrostatic action and is adsorbed by OM, when the group numbers of –COO– increase with the pH values improving and the protonation enhancing [58,60].

For other antibiotics, the effects of pH are also apparent. The adsorption coefficients of SAs increase from < 1 up to 30 when the soil pH decrease from 8 to 4 [12,69]. Correspondingly, the adsorption of tetracycline to humic substances and clay minerals is apparently influenced by the pH of medium [52,70]. Chelate complexes of tetracyclines preferentially involve the tautomeric C-11-C-12 β-diketone system that is formed under base conditions from the keto-enol molecule, whereas the dimethylamino group at C-4 position becomes increasingly involved with decreasing pH [71]. The adsorption of oxytetracycline to humic acid varies significantly with pH [70].

Adsorption of sulfamethazine was strongly impacted by the pH of soil, with higher K_d values for soils with high organic carbon and lower K_d values as the pH increased [72], which showed that hydrophobic sorption was probably involved for $pH < 7.4$ due to the non-ionized form of sulfamethazine while surface sorption was probably involved for $pH > 7.4$ due to the ionized form of sulfamethazine. Adsorption of sulfonamide antimicrobial on clay minerals also exhibited pronounced pH dependence consistent with sorbate speciation and clay properties [62]. Sulfonamide antimicrobials did not intercalate into montmorillonite, and surface charge density influenced sorption by determining adsorption domain size, therefore, adsorption of uncharged sulfamethazine to montmorillonite was relatively insensitive to pH.

4.2 Effect of ion strength

Coexisting ions have an important effect on the antibiotics adsorption. Ionic strength can promote or inhibit the adsorption of antibiotics by inorganic minerals. Monovalent metallic ions (Na^+, K^+) can compete with cationic/zero-valence antibiotics for adsorption sites, which impact heavily the adsorption of antibiotics. When ion strength increased from $0.02\ mol \cdot L^{-1}$ to $0.18\ mol \cdot L^{-1}$, the distribution coefficients between humic acid and water for clarithromycin reduced about 90% [61]. Adsorption of tetracycline on humic acid and hydrated aluminum-iron oxides markedly decreased [56,60].

Multivalence metal ions (including Ca^{2+}, Mg^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}) also impact heavily the adsorption behaviors of antibiotics. These ions can compete with cationic/zero-valence antibiotics for adsorption sites with low pH, thus they restrain adsorption. These multivalence metal ions can contact with the negative-charged part of antibiotic and the negative-charged sorption sites on the surface of solid by covalent bonding action, and form the three-phase complexation of antibiotic-metal ion-adsorbate, thus improve adsorption of antibiotic [73]. Sorption behaviors of quinolone in the dissolved organic matter (DOM) solutions were by the action of ionize bond bridging [74]. Divalent calcium and copper ions significantly improve the adsorption of tetracycline on montmorillonite and humic acid [57,58,71,75].

Oxytetracycline adsorption was 2.5 times greater when Ca^{2+} was showed in solution containing clay minerals as compared to Na^+ [52], because TCs formed reversible complexes with multivalent cations [59].The adsorption of tetracyclines onmontmorillonite and kaolinite decreased with ionic strength increasing [57].Adsorption of uncharged sulfamethazine to montmorillonite was insensitive to pH and ionic strength, while that to kaolinite was highly sensitive to ionic strength [62].

4.3 Effect of organic matter

Organic matter is one the main active component in the nature soil. The quantity and the composition of SOM strongly impact the adsorption of antibiotics to soil. A major effect of the OM is its direct competition for the available adsorption surface/sites. Organic matter contains large numbers of the functional group of –COO– which provides some adsorption sites for positive-charged antibiotic ions [61]. Thus, antibiotics would be adsorbed by the polar functional group of OM with the hydrogen-bond interaction [60] or by the bond bridge with metal ions [58]. The adsorption of antibiotics like FQs and SAs to faeces that are rich for the OM content is strong [76]. The distribution coefficients of oxytetracycline and tylosin are smaller in manure than that in soils [71]. However, the content of OM is generally low in the nature soil; moreover, OM can shield the sorption sites on the surface of clay minerals, which induce the adsorption reduction of antibiotics to soil. Therefore, OM is not always the main contributor for antibiotics adsorption to soil.

Though the content of dissolved organic matter (DOM) is much low in soil, it contains multiple kinds of reactive function groups such as carboxyl, hydroxyl, and carbonyl. Some previous studies verified that DOM in soil significantly impacts the adsorption and mobility of organic chemicals in soil. For example, when the DOM content is little in soil, it promotes the adsorption of antibiotics on montmorillonite by coadsorption [77]. The much stronger sorption of TCs to DOM stresses that adsorption is not attributable to hydrophobic partitioning, but ionic interactions and hydrogen bond [36]. DOM promotes the dissolve of antibiotics with its content increasing, which induces desorption of antibiotics [77]. The distribution coefficient ($K_{d,\ DOM}$) of organic chemicals between DOM and water was used by some studies to represent their distribution extent toward DOM under the distribution equilibrium conditions. The $K_{d,\ DOM}$ values for association of quinoloneis in the range of 100–53000 $\mathrm{L\cdot kg^{-1}}$ [78]. The $K_{d,\ DOM}$ values for tetracycline tohumic acid is in the range of 1500–2000 $\mathrm{L\cdot kg^{-1}}$ [52]. These results verified that DOM played an important role for the distribution behaviors of antibiotics in soil environment.

4.4 Comprehensive effects of soil properties

The adsorption behaviors of the same antibiotic compound showed big differences in different type of soil. The study about adsorption of different antibiotic compounds on different soil showed that distribution coefficients (K_d) determined by a batch equilibrium method varied between 0.5 and 0.7 for metronidazole, 0.7 and 1.7 for olaquindox, and 8 and 128 for tylosin [50]. The adsorption of tylosin seems to be only significantly correlated with the clay content of soil, and no other significant interactions were observed. Oxytetracycline was particularly strongly sorbed in all soils investigated, with the K_d values between 417 in sand soil and 1026 in sandy loam, and no significant desorption was observed.

Oxytetracycline zwitterions adsorbed to a greater extent than ciprofloxacin zwitterions on soil with moderate-to-low effective cation exchange capacities (ECEC $<$ 10 $\mathrm{cmolc\cdot kg^{-1}}$) because adjacent pairs of hydroxyl groups on the oxytetracycline molecule (absent in ciprofloxacin) facilitated greater surface complexation to soil metal oxides and aluminosilicate edge sites [79]. However, ciprofloxacin adsorbed to a higher extent than oxytetracycline on soils with “high” ECEC values ($>$ 10 $\mathrm{cmolc\cdot kg^{-1}}$) [79], which indicated that both positive charge localization on the cationic amine and the extent of charge delocalization to the heterocyclic ring influenced molecular orientation within the montmorillonite interlayers, van der Waals force interactions, and the potential for adsorption. The adsorption of compounds structurally similar to oxytetracycline revealed that greater positive charge localization on the cationic amine facilitated sorption to montmorillonite, whereas other substituted anionic and cationic groups on a zwitterionic molecule resulted in unfavorable coulombic interactions between the anionic moiety and the negatively charged surface and hindered sorption. Thus, greater ciprofloxacin zwitterion adsorption to the ‘high’ ECEC soils resulted from greater distance between the anionic and cationic groups, which maximized columbic attraction to the surface.

Adsorption of tylosin and oxytetracyclineon soils was significantly correlated with the contents of clay, OM, and Fe oxides [80]. The basic physicochemical characteristic of soil is correlated with the adsorption constant of oxytetracycline, tylosin, and sulfachlorpyridazine concluded from the sorption experiment using 11 kinds of soils [81]. The sorption experiment of oxytetracycline by 30 kinds of soils with largely different properties was conducted; the results showed that the grain size and the contents of CEC and metal oxides have an important effect on the adsorption of antibiotic [46]. The CEC of soil is one of the important factors impacting adsorption of antibiotics to soils [45].

In addition, the interactions among different components of soil also impacted adsorption of organic chemicals. The adsorption capacity of compound induced by clay minerals and humic acid for tetracycline was lower than that of each of these two components [47]. Interactions between the charges and functional groups of OM and the charged sites on surface of minerals reduce the amount of adsorption sites. In addition, organic matter hinders the entry of tetracycline into the minerals. However, when a chernozem was dispersed and separated into particle size fractions, the adsorption of SAs to the clay size fraction with stable organo-mineral complexes was about two times greater than to the sand size fraction, which was characterized by particulate OM of plant origin [82].The adsorption of tetracycline and chlortetracycline on clays, humic substances, and clay-humic complexes derived from two agricultural soils was studied [47]. The results from this study showed that strongest sorption was observed for clays, followed by humic substances, and then clay-humic. Decreased sorption with increasing pH suggests that cation bridging and cation exchange contribute to sorption. Tetracycline and chlortetracycline were sorbed in the interlayers of smectites and that the presence of humic substances reduced interlayer sorption of tetracyclines by smectites in clay-humic. Therefore, organic-mineral complexes effectively change the adsorption capacities of some antibiotics.

5 Conclusions

The presence and fate of antibiotics in environmental matrices have received a special attention by the scientific community. Some antibiotics compounds are persistent and resistant in the environment. Even at low concentration levels, in which they are detected, they can produce harmful effects either in aquatic or terrestrial ecosystems. For these reasons, removal processes have been studied to solve environmental contamination issues. Adsorption, as a useful tool for controlling the extent of antibiotic pollution, is used widely at present. The adsorption mechanisms of antibiotics are very complex. Antibiotics, a class of ionized and polarable organic chemicals, exist in ionic or molecule forms and easily dissolve in water, which includes the complex of their adsorption by soil and sediment. Antibiotics can sorb by soil with intermolecular forces such as hydrogen bond and Van der Waals' force, or with multiple interactions such as cation exchange, electrostatic, bond-bridge, coordination, and complexion. Moreover, some factors such as pH, ion strength, and metal ions all strongly impact on their adsorption on soil. Therefore, adsorption of antibiotic by soil is very complex process. In the present studies on adsorption of antibiotics by soil, sorbents are single, and experiment conditions are very different from real environment of soil. Therefore, systematic investigations on the sorption mechanisms and laws of antibiotics in the in situ or more immediate the natural environment of soil is very imperative in the future. More experiments are needed to reveal the joint influences of the physicochemical properties of soil, the coaction of various pollutants, and the correlations between the antibiotic structures and the adsorption/migration capacities.

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