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Review

Magnetic adsorbents for removal of pharmaceuticals: A review of adsorption properties

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ABSTRACT

The global development of industry and agriculture around the world led to the contamination of various aquatic environments with pharmaceuticals. Even at low concentrations in water, these pollutants cause significant human health problems, adversely affect the quality of drinking water, and have a detrimental effect on the environment. The uncontrolled release of pharmaceuticals into aquatic ecosystems poses a real threat to all life on Earth and requires effective methods of removal. Adsorption is one of the best and most cost-effective ways to clean wastewater from micropollutants. Magnetic adsorbents attract considerable attention due to their outstanding magnetic properties, high surface reactivity, chemical stability, and the possibility of their modification and functionalization. The presence of various functional groups makes it possible to increase the adsorption efficiency. This article is a comprehensive review of studies on the use of various magnetic nanoparticles and composites for the removal of pharmaceuticals from aqueous environments through adsorption. The main attention is paid to two categories of pharmaceuticals: antibiotics (tetracycline, ciprofloxacin, levofloxacin, etc.) and nonsteroidal anti-inflammatory drugs (diclofenac, ibuprofen, etc.). The concentration of these pollutants in the European surface waters is provided. The main modes of interaction between the adsorbent (functionalized magnetic nanoparticles) and the adsorbate (pharmaceuticals) are discussed. The analyzed drugs are mainly adsorbed through electrostatic interactions, hydrogen bonds, π-π interaction, surface complexation, ion-exchange, etc. The effect of various parameters (pH, contact time, temperature, adsorbate concentration, adsorbent dose) on adsorption efficiency is summarized. The analysis shows that the adsorption behavior strongly depends on the solution pH, temperature, and the initial concentration of the pollutant. The functionalized magnetic nanoparticles have a good potential for pharmaceuticals removal from aqueous media. The perspectives and problems in magnetic adsorbents applications have been presented.

1. Introduction

The quality of natural waters is one of the determining factors of environmental safety and public health [1]. However, the pharmaceuticals' entry into water causes the deterioration of aquatic ecosystems. The pharmaceuticals' sources are hospital wastewaters, different medical facilities, and settlements (Fig. 1). These compounds are accumulating in bottom sediments, aquatic flora, and fauna, hurting the aquatic ecosystem and worsening its environmental safety [2].

Pharmaceuticals, having entered the reservoir, partially dissolve in water and partially sink to the bottom of the reservoir, where organic biomass of bottom sludge is formed, which is subjected to continuous decomposition by putrefactive bacteria and fungi [2]. During decomposition, organic substances intensively consume dissolved oxygen from water, releasing decomposition products. An excess of organic substances in a reservoir leads first to a violation of the biological balance, suppression of the biological self-cleaning of the reservoir, and then to a change in the type of pond or lake ecosystem [3]. This is why the wastewater must be thoroughly treated by different treatment methods.

The processes that are traditionally used for industrial wastewater treatment do not lead to the complete neutralization of toxic compounds contained in the wastewater. Pharmaceuticals, being stable and passing through several stages of purification, are not completely removed and accumulate in the environment [3]. An excessive concentration of these

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compounds in the environment leads to microflora and fauna damage. Another problem is that the growth of resistant bacteria takes place at low concentrations of pharmaceuticals in the environment [4]. This is why many researchers are focused on creating enhanced adsorbents for the removal of pharmaceuticals. During the last few years, research on the pharmaceuticals removal from wastewater using adsorption has gained much attention. Nowadays, the number of publications dedicated to the adsorption of pharmaceuticals/antibiotics is>5,800 documents in the Scopus database. Fig. 2 shows the number of articles for the 2012–2023 years.

A variety of nanomaterials is used as adsorbents for the extraction of pharmaceuticals from aquatic environments. A special place among the adsorbents for wastewater treatment is occupied by “green” adsorbents due to their low production cost, stability, better physicochemical properties, and high efficiency in the removal of pharmaceuticals [4]. The “green” biochar and activated charcoal were studied in pharmaceuticals adsorption by X. Zhu et al. [5]. A “green” synthesis was used by Magesh et al. [6] in the preparation of zinc oxide biosorbent impregnated with activated carbon for the removal of ciprofloxacin from aqueous solutions. The results showed the achievement of maximum removal of 99.8% [6]. In the study [7] a biosorbent made from acid-treated tamarind shells was used to remove ciprofloxacin from water and the removal efficiency was achieved at around 92%. Another “green” ceramic/organic xerogel adsorbent was synthesized by P. Arabkhani et al. [8] for the removal of antibiotics from water. Under optimized adsorption conditions, the removal efficiency was ca. 99, 99, 98, and 98% for amoxicillin, tetracycline, cephalexin, and penicillin G, respectively [8].

Among various adsorbents, magnetic oxide nanoparticles play a significant role in environmental restoration [9-11]. In most cases, they offer a large specific surface area. Iron oxide nanoparticles (maghemite γ-Fe_2O_3 or magnetite Fe_3O_4) and spinel ferrites are the most frequently studied magnetic nanoparticles [12-14]. Spinels are complex oxides with the general formula AB_2O_4, where A is Mg^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Be^{2+}, Co^{2+}, and B is Fe^{3+}, Al^{3+}, Cr^{3+}, Mn^{3+}, rarely Ti^{4+}, V^{3+} [15]. The spinel group also includes maghemite (γ-Fe_2O_3). Spinels are compounds with well-developed isomorphisms with a broad variety of A and B cations [16-18]. According to the cation distribution between the crystallographic positions, the spinel structures are classified as ***normal*** (M^{2+} cations are located in tetrahedral sites, and M^{3+} cations are in octahedra), ***inverted*** (M^{3+} cations are equally placed on both sites, while M^{2+} occupies only octahedral sites) and ***mixed*** spinels (both types of cations arbitrarily occupy tetrahedral and octahedral sites, and the cation distribution can be described as $(A_{1-x}B_x)[A_{x/2}B_{1-x/2}]_2O_4$, where x is the inversion degree. The normal spinel structure is inherent in $MgAl_2O_4$, $ZnFe_2O_4$, $FeAl_2O_4$, $(Mn, Fe)Al_2O_4$, etc. The inverted spinel structure is characteristic of Fe_3O_4, $MgFe_2O_4$, $CoFe_2O_4$, γ-Fe_2O_3, etc. Important in practical terms are magnetic ferrites with the general formula of MFe_2O_4, which are usually completely or partially inverted. The reason is that the Fe^{3+} ion with five d-electrons, according to the crystal field theory, has no preference for octahedral positions. Therefore, larger divalent ions occupy mainly octahedral positions, while Fe^{3+} ions are distributed in octahedral and tetrahedral positions leading to the inversion of the structure. It is worth noting that magnetite Fe_3O_4 is one of the best studied spinel magnetic adsorbents.

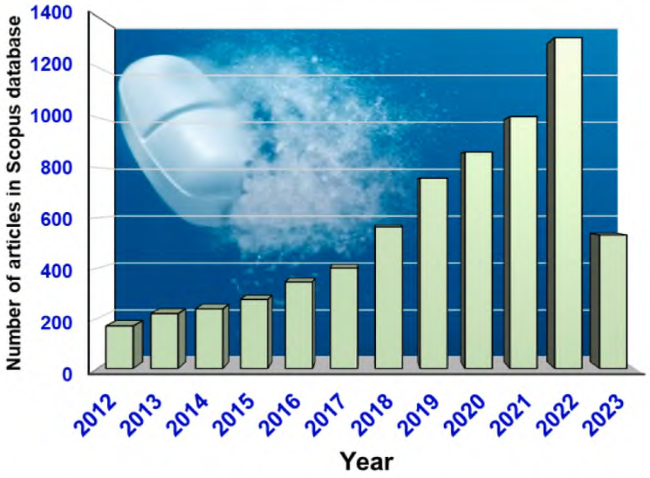

Fig. 2. The number of articles on “antibiotics adsorption”, indexed in the Scopus database (as of 03–04-2023).

The methods of synthesis significantly affect the adsorption capacity of magnetic adsorbents [19]. S.K. Paswan et al. [20] used the “bottom-up” and “top-down” classification for the synthesis of spinel adsorbents. In the “bottom-up” approach, materials are synthesized from smaller

Fig. 1. Ways of environmental pollution by pharmaceuticals.

units or molecules, which allows precise control over the size, shape, composition, and surface properties of the magnetic adsorbent [20]. “Top-down” approach involves the synthesis of materials through the decomposition of large structures into smaller particles or components [21]. “Bottom-up” methods include the co-precipitation method, sol–gel method, hydrothermal, solvothermal, microemulsion, etc. [20-22]. The top-down methods include mechanical milling and pulsed laser ablation [21]. In general, the choice of synthesis method will depend on the desired properties of the magnetic adsorbent, available equipment, cost, and scalability of the synthesis method.

The magnetic properties of ferrospinels are determined by the chemical composition and the distribution of cations within A- and B-sublattices. The different numbers of cations in A- and B-sublattices cause different net magnetic moments. Ferrites can be ferrimagnetic or antiferromagnetic. This is explained by the fact that the ions that are in the tetrahedral sites have antiparallel spins to the spins of the ions that occupy the octahedral sites. Thus the net magnetic moment is due to the antiferromagnetic order between the tetrahedral (A) and octahedral (B) magnetic moments [17].

Magnetic ferrite nanoparticles are widely used and demonstrate high activity in the removal of various types of environmental pollutants: metals and non-metals (Hg, Pb, Cr, Cu, U, Ni, As, etc.), dyes (Congo red, methylene blue, methyl violet, etc.), pharmaceuticals (tetracycline, ibuprofen, diclofenac, etc.) and other pollutants. Since the purification processes are carried out in an aqueous medium, an additional advantage of magnetic ferrite nanoparticles, in particular magnetite Fe_3O_4, are magnetic properties that allow its extraction from solution and separation with a magnet after the adsorption. Magnetic nanoparticles can be used as adsorbents alone, or as a magnetic core for complex composites or a matrix that can be further functionalized (Fig. 3). For example, functionalized magnetic nanoparticles have a big potential also in the adsorption of gases (hydrogen, H_2S, etc.) [23,24]. Fe_3O_4 NPs coated with silica and loaded with PdNPs demonstrated much higher H_2 consumption compared to palladium NPs alone [24]. In most cases, such magnetic adsorbents can be easily recovered. All magnetic sorbents demonstrate increased mechanical strength, high adsorption capacity concerning organic and inorganic pollutants, and high magnetic characteristics, which make it possible to subsequently collect the sorbent using permanent or electric magnets.

In this review, we decided to focus in detail on the adsorbents based on magnetic nanoparticles, which can be used to remove various pharmaceuticals from aquatic environments. In particular, attention is paid to two groups of pharmaceuticals – antibiotics and non-steroidal anti-inflammatory drugs that are most common and most dangerous for the environment. The physicochemical properties of adsorbents, including adsorption modes, are described in detail.

2. Distribution of pharmaceuticals in waters

Nowadays, >3000 active pharmaceuticals are known, which are used for the treatment of various diseases [29]. The most common classes of drugs involve antidepressants, antibiotics, anticonvulsants, hormones, beta-blockers, and anti-inflammatories. Pharmaceuticals as pollutants can be detected in soil, ground and surface waters, wastewater, tap water, and drinking water. They are considered micropollutants because they are present in the environment at very low concentrations [3]. They are difficult to detect, analyze and remove by existing wastewater treatment systems [30]. The presence of pharmaceuticals in the aquatic environment is a growing concern worldwide. Drinking water supplied to humans contains a large number of various drugs, including antibiotics, hormones, sedatives, anticonvulsants, and pain relievers [3]. There are various ways of getting such drugs into the water. In particular, when people take medicaments, the body absorbs a part of them. Non-absorbed pharmaceuticals (about 70%) are excreted

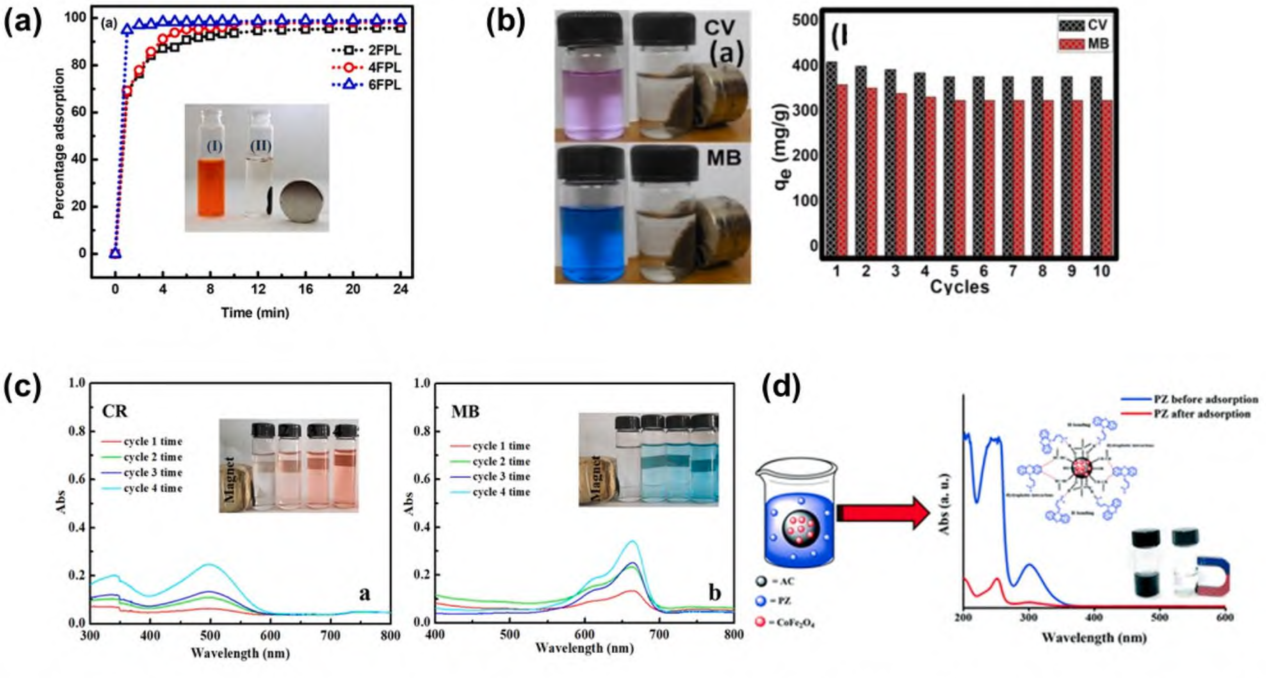

Fig. 3. (a) Polyethylene glycol-modified Fe_3O_4 combined with Mg–Al-layered double hydroxides for the removal of methyl orange from water. Reprinted with permission from [25]. Copyright 2020, American Chemical Society; (b) magnetic graphene oxide/chitin nanocomposites for adsorption of methylene blue and crystal violet from aqueous solutions separated by the external permanent magnet after the adsorption and its reproducibility. Reprinted with permission from [26]. Copyright 2020, American Chemical Society; (c) UV–vis spectra of Congo red and methylene blue after four removal cycles from tap water using novel core@double-shell three-layer adsorbent ($Fe_3O_4@SiO_2@Zn$–TDPAT) [TDPAT = 2,4,6-tris(3,5-dicarboxyl phenylamino)-1,3,5-triazine]. Reprinted with permission from [27]. Copyright 2019, American Chemical Society; (d) activated carbon (AC) modified with metal ferrite $CoFe_2O_4$ nanoparticles (AC–$CoFe_2O_4$) as a magnetic nano-adsorbent for promazine removal from wastewater. Reprinted with permission from [28]. Copyright 2022, Royal Society of Chemistry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

naturally, without changing their chemical composition, and are introduced to the sewer [2,29]. Wastewater undergoes traditional treatment and returns to rivers or lakes, the reservoirs of drinking water (Fig. 1). Table 1 shows the distribution of pharmaceuticals in various aquatic environments [31]. Fig. 4 shows the distribution of some representative examples of pharmaceuticals in European surface waters (data obtained from Refs. [32,33]). The municipal sewage treatment system is unable to completely remove the pharmaceuticals from the water. In addition, it has been found that adding chlorine and its compounds to water may increase the toxicity of some drugs [2].

A wide range of chemical and physical methods can be used to remove pharmaceuticals, for example, chemical oxidation and biodegradation (destructive methods), adsorption, liquid extraction, and membrane methods [3]. Adsorption processes are widely used in industry to remove organic impurities [34], like drugs [28,35-38], personal care products [39], petroleum products [40,41], surfactants [42], etc. The term 'adsorption' is usually used to describe the attachment of a molecule from a mobile phase to a solid surface. Adsorption is considered one of the most effective methods of drug removal from aquatic environments due to its convenience, easiness, and simplicity of implementation [30]. The adsorption can be affected by changing such parameters as temperature, concentration, and solution pH [43]. A good adsorbent should have a high adsorption capacity for the necessary components. The efficiency of the adsorbent also depends on its pore size and surface properties [30].

3. Modes of antibiotics adsorption

Understanding, which physicochemical processes taking place at the adsorbent surface (magnetic nanoparticles) are crucial for the adsorption of adsorbates (pharmaceuticals) is essential to design efficient adsorbents. The modes of pharmaceuticals' adsorption onto magnetic adsorbents can be governed by electrostatic or non-electrostatic interactions depending on the solution pH and the charge (or at least polarity) of the adsorbent and adsorbate. Electrostatic interactions come into play when the adsorbate is protonated or dissociated in an aqueous solution under experimental conditions. Other interactions include van der Waals forces, hydrogen bonds, π-π interactions, etc. [4].

The main modes of antibiotic adsorption are the following:

- the ***electrostatic interaction*** between the adsorbent surface and the adsorbate can be predicted by the charge of their oppositely charged functional groups [34]. The ionic charge varies depending on the dissociation constants (pK_a, pK_b), point of zero charge (pH_{PZC}), and solution pH. If the adsorbent surface and adsorbate molecules possess the same charge, then adsorption will decrease due to electrostatic repulsion between them [44]. If the charges are opposite, the electrostatic attraction occurs, and adsorption increases. Therefore, the surface charge of the adsorbent and adsorbate is the main factor affecting the adsorption efficiency [45];
- ***Van der Waals forces*** are arising between adsorbate molecules and the adsorbent surface. These relatively small forces of intermolecular interaction decrease very quickly with the increasing distance between the adsorbent and adsorbate molecules. At the magnetic nanocomposite surface, the adsorbate molecule is held by the force field of the surface for some time and then it can be desorbed [45]. There is a model of localized adsorption, according to which there are adsorption centers at the adsorbent surface, that is, certain areas where stronger adsorption occurs;
- ***hydrogen bonds*** arise due to the electrostatic attraction between the hydrogen from one molecule and an atom with a high electronegativity from another molecule [45]. Magnetic adsorbents contain a large number of oxygen-containing functional groups at their surface, such as –OH, –COOH, etc. [46]. These fragments can bind oxygen- or nitrogen-containing groups of pharmaceuticals with the formation of hydrogen bonds. The surface hydroxyl groups can be involved in binding various anionic species [47]. For example, the C=O and –NH functional groups in the magnetic adsorbent enhance chemisorption due to the formation of hydrogen bonds with the –COOH group in ciprofloxacin [48].
- the ***π-π interaction*** occurs between aromatic groups of adsorbent and adsorbate. The strength of the π-π bond is mostly influenced by the functional groups attached to the benzene ring of the adsorbent [45]. Functional groups of pharmaceuticals that have a strong electron-withdrawing capacity can act as π-acceptors, while, for example, OH-groups on benzene rings cause the adsorbent to act as a π-donor [49];
- ***surface complexation*** occurs when the molecules of pharmaceuticals form complexes with surface functional groups of magnetic adsorbents [50]. Surface functional groups of adsorbents can contain hydroxyl, carboxyl, amino, or thiol groups [51]. The formation of complexes may involve the formation of inner-sphere or outer-sphere complexes between the pharmaceutical molecule and iron ions coming from the magnetic adsorbent structure [46,52,53]. Inner-sphere complexes are arising when a direct chemical bond between the adsorbate (molecule of pharmaceutics) and the adsorbent surface is formed. Outer-sphere complexes are formed when the water molecules or hydroxyl groups are affiliating between the oppositely charged adsorbate (molecule of pharmaceutics) and the surface of the magnetic adsorbent. The formation of surface complexes is influenced by the solution pH, the solution ionic strength, the concentration of pharmaceuticals in the solution, and the physicochemical properties of the adsorbent.
- ***hydrophobic interactions*** occur when non-polar molecules or hydrophobic groups of pharmaceuticals interact with hydrophobic sites on the surface of the magnetic adsorbent. Such hydrophobic interaction is due to the desire of non-polar molecules or groups to minimize their contact with water. Such an adsorption mode is influenced by the concentration of the adsorbate in the solution, the density of hydrophobic groups, and the surface area of the adsorbent [54]. Hydrophobic interactions are observed mostly during the adsorption of pharmaceuticals, containing both hydrophilic and hydrophobic groups in their structure, e.g., ofloxacin, ciprofloxacin, norfloxacin, propranolol, clomipramine [55], or when the carbon-based [55,56] or polysaccharide-based [44] magnetic composites are used as adsorbents.
- ***ion exchange*** is observed when the ions that are already attracted to functional groups of the adsorbent surface can exchange with other ions present in the solution [45]. Magnetic adsorbents can be functionalized with ion-exchange sulfate, carboxylate, or amino groups that can attract and exchange ions from wastewater [57]. The selectivity of ion exchange depends on the specific functional group and ionic charge of the magnetic adsorbent, as well as on the concentration and charge of the ions in the solution [34]. The efficiency of the ion exchange process can be improved by optimizing the pH of the solution, temperature, and contact time of the adsorption. This mechanism is especially relevant for ionized antibiotics, which can

Table 1
Distribution of pharmaceuticals in different waters. Reprinted with permission from [31]. Copyright 2018, Elsevier.

Pharmaceuticals	Waters	Concentration ranges (μg mL^{-1})
Antibiotics	Waste & surface water	0.1–1.7
	Wastewater	0.4–1.84
	Drinking water	1.7
Antiphlogistics/anti-inflammatory	Wastewater	0.05–7.11
	Surface water	0.05–7.50
	Drinking water	1.0–10.0

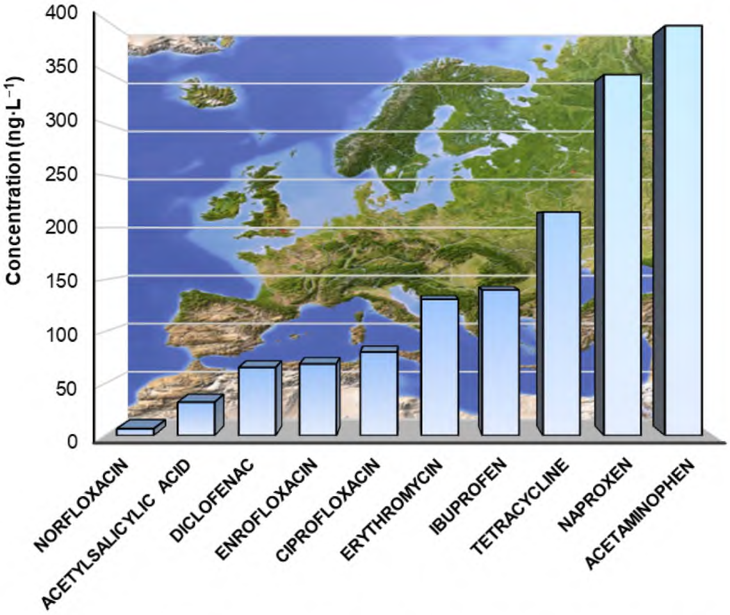

Fig. 4. The distribution of some representative examples of pharmaceuticals in European surface waters (the data obtained from Refs. [32,33]).

be protonated or deprotonated depending on the pH of the solution [34,58].

- the ***π-cation interaction*** involves an adsorption mechanism that can occur between aromatic groups of antibiotics (π-electron system of aromatic rings) and positively charged species such as metal ions or quaternary ammonium ions, presented on the surface of magnetic adsorbents. The strength of the π-cation interaction depends on the pharmaceutical structure, and cationic forms, as well as on the pH and ionic strength of the solution [59]. As an example, the interaction between the Fe atom of the spinel lattice and the aromatic π-electrons of an antibiotic molecule, for example, tetracycline, can be given [60].

Fig. 5 shows various types of interactions between magnetic adsorbents and pharmaceuticals.

The degree of pharmaceuticals' adsorption mainly depends on the surface charge of magnetic adsorbents, which, in turn, is affected by the pH of the solution. The adsorption can be controlled by measuring the point of zero charge (pH_{PZC}) of adsorbents. At $pH > pH_{PZC}$, the functional groups are deprotonated and the surface of the adsorbent is negatively charged, so the adsorbent successfully removes cationic adsorbates by electrostatic attraction from the aqueous solution. At $pH < pH_{PZC}$, the protonation of functional groups causes the positive charge of the adsorbent surface, so the adsorbent successfully removes the anionic adsorbates. Thus, it is possible to change the adsorption capacity of

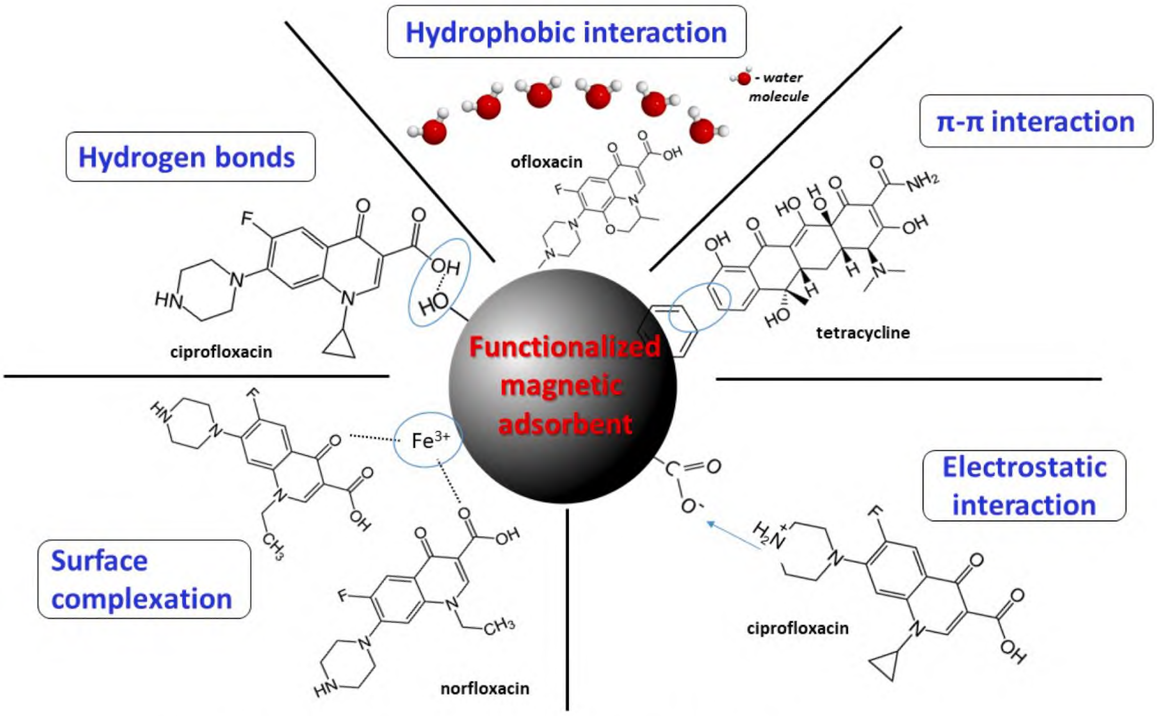

Fig. 5. Various types of adsorbent-adsorbate interactions at surfaces of magnetic adsorbents.

magnetic nanoparticles by changing the solution pH value [61]. For example, as investigated in the work [62], the adsorption capacity of magnetic graphene oxide adsorbent increases with the pH value increasing and the maximum adsorption was observed at pH 10. The increase in pH led to the deprotonation of –OH and –COOH groups of graphene sheets, making the surface charge more negative [62].

If pH > pK_a, the charge of the pharmaceutical is negative, and if pH < pK_a the charge of the pharmaceutical is positive. For example, the ***tetracyclines*** exist in three forms depending on the solution pH: in the cationic form at pH < 3.3, in the zwitterionic form at pH 3.3–7.7, and in the anionic form at pH > 7.7 [63]. During the adsorption of ***ciprofloxacin***, the carbonyl group is deprotonated at 5.9 (pK_{a1}), while the amine group is protonated at 8.9 (pK_{a2}) [54]. The removal of ciprofloxacin from aqueous solutions depending on the pH was carried out using granular iron hydroxide by M. Asadi-Ghalhari *et al.* [64]. The pH_{PZC} of the granular iron hydroxide is 7.5–8.2, therefore, at a pH below this range, the surface charge of the adsorbent is positive and the rate of ciprofloxacin removal increases, and at a pH above this point, the removal process is reduced. ***Levofloxacin*** exists in the cationic form at pH < 5 and in the anionic form at pH > 8.5. It can be adsorbed by a negatively charged adsorbent through the deprotonation of carboxyl groups or by a positively charged adsorbent through the protonation of an amino group. The efficiency of levofloxacin removal at low pH is lower than at high pH [65].

Usually, the adsorption is improved with increasing temperature, which is associated with an increase in the diffusion rate of dissoluble molecules. The adsorption process is often endothermic, but it can also be exothermic for a certain adsorbent, which is associated with weak interactions between the adsorbate and the surface-active groups of the adsorbent [44]. However, changes in the temperature during the adsorption process not only affect the rate of the pharmaceuticals diffusion through the outer surface of the adsorbent but also significantly affect the binding at surface active sites and the equilibrium adsorption capacity [66].

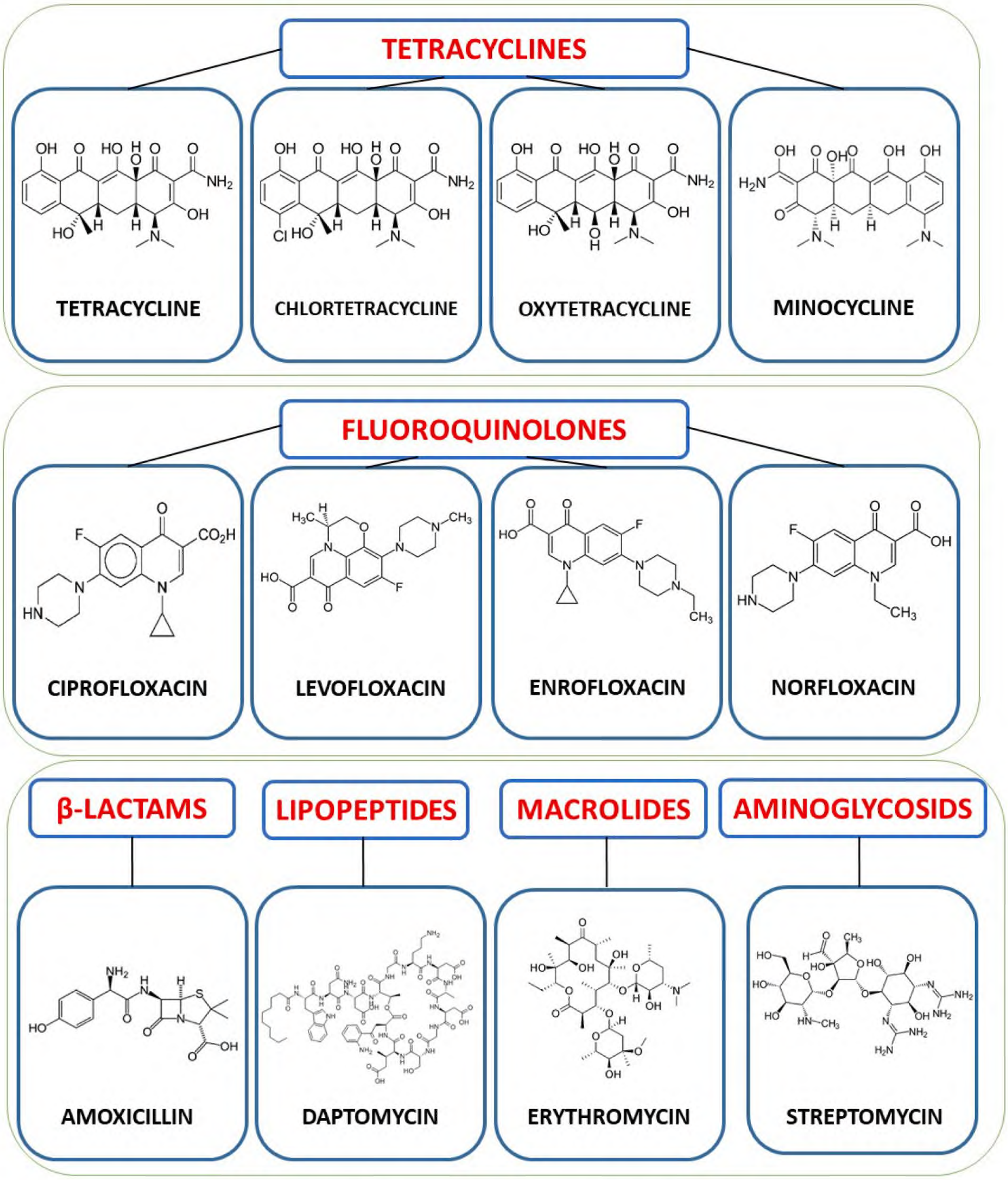

Fig. 6. Structures of the most common antibiotics.

4. Applications of magnetic nanoparticles for the adsorption of antibiotics

The key features of magnetic nanoparticles to be applied in the adsorption of pharmaceuticals are the following: high surface concentration of adsorption sites, high specific surface area, high chemical stability, adjustable particle size, magnetization, etc. To date, many studies have been conducted to demonstrate the effective use of magnetic oxide nanoparticles as adsorbents for the simple and rapid removal of different pharmaceuticals from wastewater: tetracycline [60,62,67-82], minocycline [83,84], ciprofloxacin [44,56,64,85-98], levofloxacin [65,99-104], enrofloxacin [94,105], norfloxacin [94,106,107], amoxicillin [87,108,109], daptomycin [110], erythromycin [73,87], streptomycin [73], cephalexin [111], metronidazole [112], sparfloxacin [86], cefotaxime [71], ceftriaxone [113], chloramphenicol [73], diclofenac [114-120], ibuprofen [69,117,120-125], acetylsalicylic acid [124,126], acetaminophen [123,126-129], ketoprofen [106,120,121], naproxen [117,120,122], atenolol [93], tamoxifen [130], gemfibrozil [93,117], etc. For example, P. Yadav *et al.* [131] synthesized Fe_3O_4-functionalized MIL101(Fe) chitosan composite beads for the removal of tetracycline, doxycycline, and ciprofloxacin from the aqueous medium (removal efficiency was over 99%). A. Parashar *et al.* [132] used magnetic iron oxide nanoparticles for effective removal (94.12–99.52%) of oxcarbazepine from wastewater.

Among more than ten classes of antibiotics, the tetracyclines, fluoroquinolones, aminoglycosides, β-lactams, and macrolides pose a

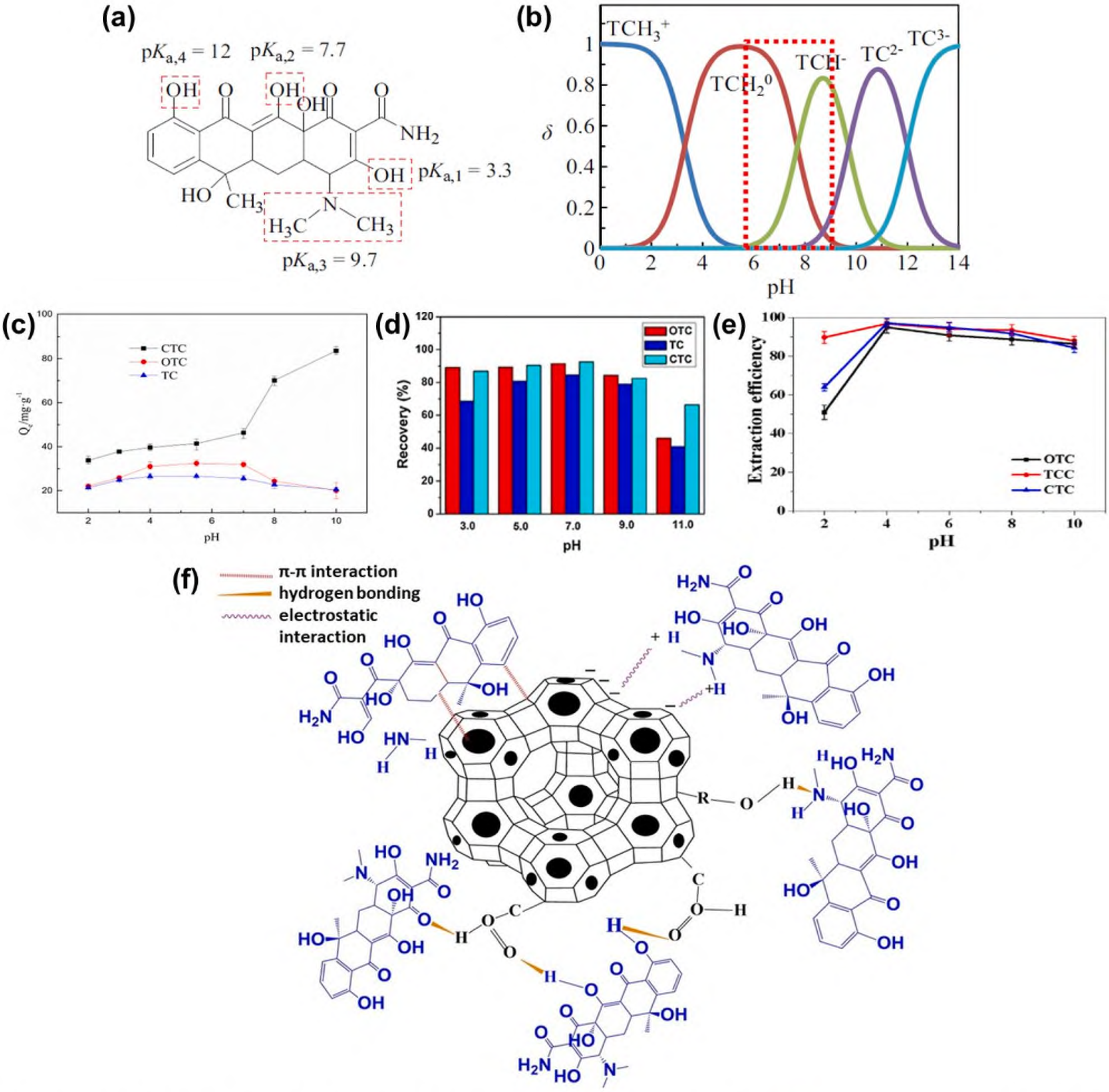

Fig. 7. (a) Chemical structure and (b) ionic species distribution of tetracycline. Reprinted with permission from [135]. Copyright 2018, Springer Nature; effect of pH on the extraction efficiency of three tetracyclines (OTC – oxytetracycline, TC – tetracycline, CTC – chlortetracycline) by: (c) MGO (MGO dosage = 2 mg, $[TCs]_0$ = 10 mg/L, V = 30 mL, T = 298 K and equilibrium time = 10 h). Reprinted with permission from [75]. Copyright 2019, Elsevier, (d) $Fe_3O_4@SiO_2@FeO$ (V = 10 mL, $[TCs]_0$ = 0.1 mg L^{-1}). Reprinted with permission from [77]. Copyright 2017, Elsevier, and (e) mNi@N-GrT (V = 10 mL, $[TCs]_0$ = 5 mg L^{-1}). Reprinted with permission from [78]. Copyright 2018, Elsevier; (f) modes of tetracycline adsorption using Fe_3O_4/clinoptilolite nanocomposite. Reprinted with permission from [80]. Copyright 2022, Elsevier.

significant risk to public health and the environment (Fig. 6). Antibiotics of these classes are most widely used both in medicine and in veterinary. Therefore, they are the most significant pollutants of surface water. Wide use of different antibiotics leads to the faster development of multiresistant pathogenic strains [29]. It is supposed that the increase in the resistance of pathogenic flora to antibiotics is a serious medical problem that poses a great danger to human health [29].

4.1. Adsorption of tetracyclines

Tetracyclines are one of the most widely used groups of broad-spectrum bacteriostatic antibiotics. The basis of its chemical structure is the octahydronaphthacene core [133]. Tetracycline, oxytetracycline, chlortetracycline, doxycycline, and methacycline are examples of tetracyclines. Tetracyclines are used in the form of bases or hydrochloride salts. Tetracyclines are amphoteric compounds with hydroxyl and dimethylamine functional groups. They can exist in ionized or non-ionized forms [134] depending on the pH: in the cationic form at pH < 3.3, in zwitterionic form at pH $= 3.3$–7.7, and in the anionic form at pH > 7.7 [63]. The molecular structure of tetracycline (Fig. 7a) has four functional groups that can dissociate and it can exhibit five dominant forms in water (Fig. 7b) [135]. These forms exhibit different physico-chemical and biological properties.

Many authors study the adsorption capacity of various magnetic nanoparticles, which can be used as highly effective adsorbents for the removal of tetracyclines from wastewater [60,62,67-69,75-82]. In their studies, scientists use nanoparticles of magnetic graphene oxide [62,69,75], goethite [76], Fe_3O_4 [70,72-74,77,80], $NiFe_2O_4$ [71], $MnFe_2O_4$ [79], etc. J. Miao *et al.* [75] have shown that the magnetic graphene oxide NPs demonstrate better adsorption of chlortetracycline in an alkaline medium, while the best adsorption of tetracycline and oxytetracycline has been observed at pH $= 3.3$ (Fig. 7c). L. Lian *et al.* [77] used the $Fe_3O_4@SiO_2@FeO$ nanocomposite for tetracycline adsorption and the effect of pH on adsorption capacity was studied (Fig. 7d). It was shown that the favorable adsorption efficiency was obtained in the pH range of 3 to 9, which may be related to the fact that $Fe_3O_4@SiO_2@FeO$ has a very low ζ-potential at this pH range. The electrostatic attraction between the negatively charged magnetic sorbent surface and tetracycline molecules occurs, so electron-donor groups of tetracycline can easily form stable metal-tetracycline complexes with Fe(II) on the sorbent surface [77]. Q. Wang *et al.* [78] studied tetracycline removal using an ultrathin magnetic nitrogen-doped graphene tube with nickel nanoparticles (mNi@N-GrT). It was concluded that the adsorption efficiency increased with pH increasing from 2 to 4 and did not change at pH above 4 (Fig. 7e). Humic acids can enhance the interaction between tetracycline and goethite at pH < 7 [76]. The presence of multivalent heavy metals such as Cu^{2+} can increase the adsorption of tetracycline on goethite through the formation of inner-sphere surface complexes. T. Ahamad *et al.* [79] synthesized the magnetic adsorbent using chitosan, diphenylurea, formaldehyde, and magnetic nanoparticles $MnFe_2O_4$ through the condensation polymerization route. The tetracyclines adsorption has been tested at pH from 2 to 10. It was established that the maximum removal efficiency was obtained at pH $= 6$, which is explained by the electrostatic attraction between the adsorbent and tetracycline molecules. The presence of acidic centers promotes the adsorption of tetracycline, as they can accept or donate protons depending on the solution pH [79]. A new magnetic adsorbent genipin-crosslinked chitosan/GO-SO_3H (GC/MGO-SO_3H) was successfully synthesized by Y. Liu *et al.* [69]. The maximum adsorption capacity towards tetracycline was obtained at pH $= 10$, as well as in the study [62], where magnetic graphene oxide was used as an adsorbent.

J. Miao *et al.* [75] synthesized the magnetic graphene oxide NPs and investigated that their maximum adsorption capacities towards chlortetracycline, oxytetracycline, and tetracycline hydrochloride were 304, 290, and 141 mg/g, respectively. L. Lian *et al.* [77] showed that the q_{max} of $Fe_3O_4@SiO_2@FeO$ was calculated to be 178, 129, and 133 mg/g according to the Langmuir model, for oxytetracycline, tetracycline, and chlortetracycline, respectively, while for the corresponding Fe_3O_4, it was only about 96, 48, and 82 mg/g. The enhanced q_{max} is because the FeO coating can provide additional Fe(II) and numerous adsorption centers [77]. T. Ahamad *et al.* [79] established that the maximum adsorption capacity of CDF@MF magnetic nanocomposite, which was fabricated using the condensation of the chitosan, formaldehyde, and diphenylurea in an acidic medium, for tetracyclines is 168 mg/g at room temperature and pH $= 6$. The π-π electron donor–acceptor interactions in aromatic magnetic adsorbent rings are responsible for enhanced tetracycline adsorption [79]. Y. Liu *et al.* [69] synthesized the magnetic genipin-crosslinked chitosan/GO-SO_3H. The maximum adsorption capacity of tetracycline increased from 473 to 556 mg/g when the temperature increased from 298 to 313 K. B. Yu *et al.* [62] studied the adsorption capacity of magnetic graphene oxide towards tetracycline and found it equal to 473 mg/g. M. Rouhani *et al.* [80] showed that the maximum adsorption capacity of Fe_3O_4/clinoptilolite nanocomposite was 181 mg/g, and the efficiency of tetracycline removal was 98.6% at pH $= 7$–8. The mechanism of adsorption has been explained due to van der Waals forces and the formation of hydrogen bonds between the polar tetracycline molecules and functional groups at the Fe_3O_4/clinoptilolite nanocomposite surface [80]. Fig. 7f shows the mechanism of tetracycline adsorption using Fe_3O_4/clinoptilolite adsorbent [80]. As can be seen the hydrogen bonds between H^+ from the surface functional groups of the Fe_3O_4/clinoptilolite nanocomposite and ions, originating from the polar tetracycline molecule, cause the formation of electrostatic repulsion. This results in reduced adsorption capacity of magnetic adsorbent under acidic conditions towards tetracycline molecules [80]. At a neutral pH of 7–8, the hydrogen bonds between tetracycline ions and OH groups at the nanocomposite surface turn into the main driving force for adsorption and leads to the highest removal efficiency [80]. All these results of adsorption studies indicate that magnetic oxide nanoparticles and nanocomposites are promising adsorbents for the tetracyclines removal from wastewater.

Minocycline is a tetracycline antibiotic used to treat many bacterial infections, including pneumonia. L. Lu *et al.* [84] obtained porous magnetic microspheres of $MgFe_2O_4/\gamma\text{-}Fe_2O_3$ which were investigated as new effective adsorbents for the minocycline removal from wastewater. The maximum adsorption capacity was 201 mg/g. The research results showed that the adsorption capacity increased with increasing temperature, which indicates the endothermic nature of adsorption [84]. In the antibiotic-adsorbent system, the complexes are formed between the functional groups of the antibiotic and the active centers of the adsorbent, which indicates chemisorption. $MgFe_2O_4/\gamma\text{-}Fe_2O_3$ adsorbents can be regenerated with methanol or NaOH solution and easily separated from aqueous solution due to their magnetic properties [84].

Table 2 provides an overview of the adsorption parameters for various magnetic adsorbents in tetracyclines removal from wastewater.

4.2. Adsorption of ciprofloxacin

Ciprofloxacin is an antibiotic of the fluoroquinolone class [136]. Ciprofloxacin exists in three forms in the solution: in the cationic form (with a protonated amino group at pH below 5.90 ± 0.15 [137]), in the anionic form (with a deprotonated carboxylic acid group at pH above 8.89 ± 0.11 [137]) and the zwitterionic form (Fig. 8a) [138]. According to [33], the average concentration of ciprofloxacin in the surface waters of Western Europe is 0.008 μg/L, and the maximum measured concentration is 13.6 μg/L. Many studies have been conducted to find effective magnetic adsorbents for ciprofloxacin removal from aquatic environments. The analysis of references showed that magnetic nanocomposites based on Fe_3O_4 [44,56,85-93,95-97], magnetic biochar [94], granular ferric hydroxide [64], magnetic chitosan grafted graphene oxide nanocomposite [98], etc. are most often used.

Fe_3O_4 nanoparticles are used as adsorbents for the removal of ciprofloxacin from wastewater [44,85-93,96,97]. S. Rakshit *et al.* [92]

Table 2
The adsorption parameters of different magnetic adsorbents in tetracyclines removal (PFO – pseudo-first-order kinetic model, PSO – pseudo-second-order kinetic model).

Adsorbent	Adsorbate	Adsorption model	Adsorption capacity (mg/g)	Optimum parameters					Removal efficiency (%)	References
				pH	Contact time (min)	Temperature (K)	Adsorbate concentration (mg/L)	Adsorbent dose		
Magnetic graphene oxide sponge (Fe_3O_4 + GO)	tetracycline	PSO, Temkin	473	10	18 h	328	400	5 mg	85	[62]
Magnetic graphene oxide	tetracycline	PSO, Freundlich	107	4–5	480	313	50	2 mg	N/A	[75]
Magnetic graphene oxide	chlortetracycline	PSO, Freundlich	162	4–5	480	313	50	2 mg	N/A	[75]
Magnetic graphene oxide	oxytetracycline	PSO, Freundlich	146	4–5	600	313	50	2 mg	N/A	[75]
γ-cyclodextrin-graphene oxide	tetracycline	PSO	365	8	30	298	400	1 g/L	91	[67]
γ-cyclodextrin-graphene oxide	chlortetracycline	PSO	375	8	30	298	400	1 g/L	94	[67]
Zeolite/Fe_3O_4	oxytetracycline	PSO, Langmuir	83	6	240	298	100	0.1 g	90.6	[68]
Magnetic genipin-crosslinked chitosan/graphene oxide-SO_3H composite	tetracycline	PSO, Langmuir	556	10	120	313	200	5 mg	85	[69]
Magnetic biochar/Fe_3O_4	tetracycline	PSO, Langmuir	112	6	60	298	30	20 mg	98.4	[70]
$NiFe_2O_4$–Covalent organic frameworks -chitosan-terephthalaldehyde nanocomposites film	tetracycline	PSO, Freundlich	389	8	40 h	293	100	170 mg/L	95	[71]
NH_2-Fe_3O_4/ $CuSiW_{12}$NP	tetracycline	PSO, Temkin	192	6.80	24 h	293	250	10 mg	88.6	[72]
Bovine serum albumin/Fe_3O_4	tetracycline	Langmuir	104	N/A	40	N/A	200	0.2 g	92	[73]
Fe_3O_4@ Polydopamine-SO_3H	tetracycline	PSO, Langmuir	139	4	1080	298	200	10 mg	N/A	[74]
Goethite (α-FeOOH)	tetracycline	PSO	N/A	3–10	24 h	298	50	0.02 g	N/A	[76]
Fe_3O_4@SiO_2@FeO	oxytetracycline	Langmuir	178	3–9	40	298	50	7.5 mg	91.7	[77]
Fe_3O_4@SiO_2@FeO	tetracycline	Langmuir	129	3–9	40	298	50	7.5 mg	97.3	[77]
Fe_3O_4@SiO_2@FeO	chlortetracycline	Langmuir	133	3–9	40	298	50	7.5 mg	93.5	[77]
$MnFe_2O_4$ (chitosandiphenylureaformaldehyde resin@MF)	tetracycline	PFO, Langmuir	168	6	60	298	100	0.01 mg	158	[79]
Fe_3O_4/Clinoptilolite	tetracycline	PFO, Freundlich	181	7.5	40	323	50	1.5 g/L	98.6	[80]
Iron oxide	tetracycline	PSO, Freundlich	0.78	10	360	318	25	30 g/L	97	[81]
Mn–Zn ferrite/biochar (MZF-BC)	tetracycline	PSO, Freundlich	142	3	240	N/A	50	10 mg	62	[82]
Magnetic-ordered mesoporous carbon materials	minocycline	PFO, Sips	193	8	10	293	1	1 mg	N/A	[83]
$MgFe_2O_4$/γ-Fe_2O_3	minocycline	PSO, Langmuir	119	N/A	48 h	298	100	25 mg	N/A	[84]

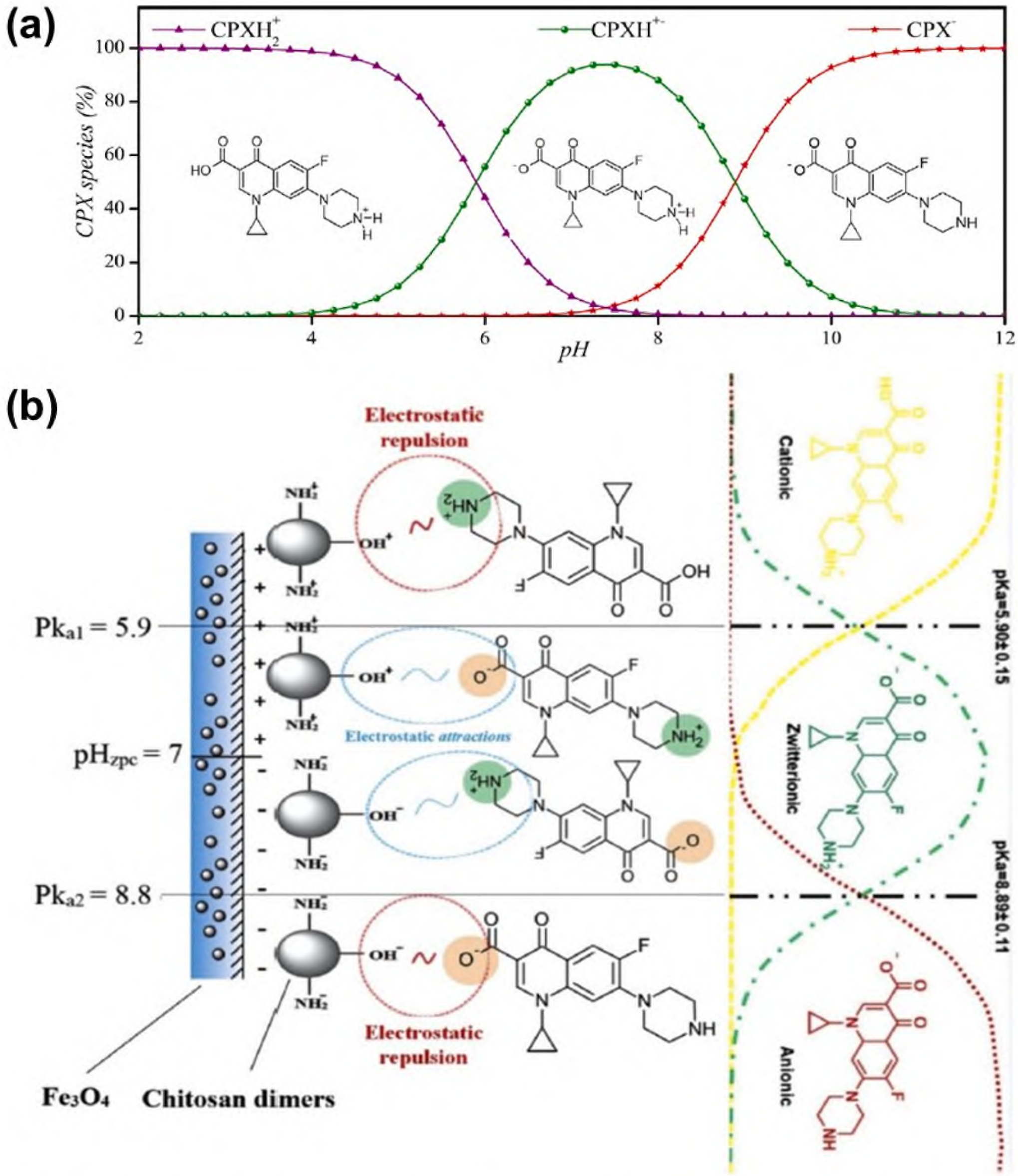

Fig. 8. (a) Distribution of ciprofloxacin forms as a function of pH. Reprinted with permission from [138]. Copyright 2015, Elsevier; (b) schematic illustration of the ciprofloxacin adsorption mechanism at different pH using chitosan nanocomposite (Fe-CS NC) supported by Fe_3O_4. Reprinted with permission from [44]. Copyright 2019, Elsevier.

evaluated the adsorption of ciprofloxacin on magnetic $Fe_3O_{4(s)}$ nanoparticles, which were obtained as a secondary corrosion product of iron nanoparticles. It was concluded that the adsorption of ciprofloxacin increased from 45% at pH = 3.44 to 80% at pH = 5.97. The results of in situ ATR-FTIR showed that coordination of ciprofloxacin on the magnetite surface with the involvement of functional carboxyl groups occurs [92]. H. Rasoulzadeh *et al.* [44] used chitosan nanocomposite (Fe-CS) supported by Fe_3O_4 for the removal of ciprofloxacin from aqueous solutions. The maximum removal efficiency and maximum adsorption capacity were 68% and 142 mg/g, respectively [44]. Fig. 8b shows the mechanism of ciprofloxacin adsorption using Fe-CS at different pH. As shown in Fig. 8b, the charge of functional groups depends on the solution pH. At $pH < 5.9$ and $pH > 8.9$, the same signs of surface charge of Fe-CS and CIP molecules caused electrostatic repulsion and reduced adsorption efficiency. However, at pH within the range of 5.9–8.9, the electrostatic attraction was responsible for the adsorption process.

Hydrophobic interactions between zwitterionic species of ciprofloxacin and the adsorbent at neutral pH can be another dominant mechanism of the adsorption process [44]. H. Mao *et al.* [89] investigated the adsorption capacity of magnetic Fe_3O_4-RM-NPs for the effective removal of ciprofloxacin from aqueous media. The highest removal rate of ciprofloxacin was achieved at pH = 6. This is explained by the fact that when the solution pH is below 5.9, the ciprofloxacin exists in the cationic form due to the protonation of the secondary amine on the piperazine group. When the solution pH is in the range of 6.1 to 8.7, the ciprofloxacin exists in a zwitterionic form. At a pH higher than 8.89, ciprofloxacin is available in the anionic form [89]. The results of the above studies show that Fe_3O_4 nanoparticles have great potential for the effective removal of ciprofloxacin from wastewater.

Table 3 provides an overview of the adsorption parameters of various magnetic adsorbents for the removal of ciprofloxacin from wastewater.

4.3. Adsorption of other antibiotics

Levofloxacin is a broad-spectrum antibiotic from the group of

Table 3
The adsorption parameters of different magnetic adsorbents in ciprofloxacin removal (PSO – pseudo-second-order kinetic model).

Adsorbent	Models of best fit	Adsorption capacity (mg/g)	Optimum parameters					Removal efficiency (%)	References
			pH	Contact time (min)	Temperature (K)	The concentration of adsorbate (mg/L)	Adsorbent dose		
Fe_3O_4-imprinted chitosan (Fe-CS)	PSO, Freundlich	143	6.5	300	298	8	1.4 g/L	68	[44]
Fe_3O_4	Langmuir	24	8	N/A	298	40	2.5 g/L	57	[85]
Fe_3O_4/graphene oxide/citrus peel-derived magnetic bio-nanocomposite (mGOCP)	PSO, Freundlich	283	6	72 h	298	160	0.02 g	N/A	[86]
Fe_3O_4/activated carbon/chitosan	PSO, Freundlich	90	N/A	120	298	15	1 mg	82	[87]
Magnetic alginate–Fe_3O_4 hydrogel fiber capable	N/A	12	3	24 h	N/A	10	0.1 g	61	[88]
Fe_3O_4/C	PSO, Langmuir	90	7	210	303	10	0.02 g	98	[89]
$K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5 – 0.95$) (KMS-1)/L-Cysteine/Fe_3O_4	PSO, Langmuir	181	6	80	298	50	135 mg/L	N/A	[90]
Humic acid (HA)-coated magnetic Fe_3O_4	PSO, Langmuir	102	8	40	298	15	1 mg	N/A	[91]
Levulinic acid (LA)-coated magnetic Fe_3O_4	PSO, Langmuir	54	12	60	298	15	1 mg	N/A	[91]
Fe_3O_4-coated polymer clay composite	Freundlich	39	7	720	303	1	1.5 g/L	95	[93]
Humic acid/magnetic biochar	PSO, Langmuir	3.76	10	480	298	10	2 g/L	87	[94]
Granular ferric hydroxide	Quadratic	N/A	7.5	27.5	N/A	6.05	1.39 g/L	42	[64]
Fe_3O_4-RM(red mud)-NPs	PSO, Freundlich	111	6	180	298	3	3 g/L	90	[96]
Fe_3O_4–MoO_3	PSO, Langmuir	39	7	150	333	10	5 mg	86	[97]
Fe_3O_4–MoO_3-Activated Carbon	PSO, Langmuir	45	7	150	333	10	5 mg	95.6	[97]
Magnetic chitosan grafted graphene oxide nanocomposite	PSO, Langmuir	283	5	480	298	20	10 mg	72	[98]

fluoroquinolones. Levofloxacin is active against gram-positive and gram-negative pathogens, including strains resistant to penicillins, cephalosporins, and/or aminoglycosides. The levofloxacin molecule exhibits two dissociation constant values ($pK_{a1} = 6.02$ and $pK_{a2} = 8.15$) and can be present in the cationic form (at $pH < 6.02$), in the zwitter-ionic form (at $6.02 < pH < 8.15$) or in the anionic form ($pH > 8.5$) (Fig. 9a) [65].

Various magnetic adsorbents are used for levofloxacin removal from water: $Fe_3O_4@SiO_2$ [99], Fe_3O_4–gINPs [104], $NiFe_2O_4$/biochar composites [101], biochar/$MgFe_2O_4$ [103], Ag_3PO_4/rGO/$CoFe_2O_4$ [102], magnetic carbon nanocomposite [100], etc. M.H. Al-Jabari *et al.* [99] studied the adsorption of levofloxacin at the surface of Fe_3O_4 and $Fe_3O_4@SiO_2$ nanoparticles. The maximum adsorption capacity of levofloxacin at the magnetic adsorbent ranged from 6.09 to 6.85 mg/g. The best removal efficiency was observed at pH 6.5 and achieved 80.2%. This is associated with the existence of levofloxacin in the neutral/zwitterion forms. The removal efficiency decreased with a decrease or increase in pH, which is related to the electrostatic repulsion of the same type of charges [99]. A. Ullah *et al.* [100] prepared a magnetic carbon nanocomposite from pineapple biomass and showed that its maximum adsorption towards levofloxacin was observed at pH = 7 and achieved 20.75 mg/g, which is associated with the cation exchange and a higher number of adsorption centers. Z. Xu *et al.* [101] used a manganese ferrite-modified biochar to remove levofloxacin. Hydrogen bonds influence the adsorption process. It was shown that oxygen-containing functional groups of the adsorbent can bind through the –OH and C=O groups of the levofloxacin molecule forming hydrogen bonds. Also, the presence of –OH and –COOH groups on the biochar surface contributed to the π-π and n-π electron-donor–acceptor interaction, increasing the adsorption efficiency [101]. B. Yao *et al.* [103] also used biochar in levofloxacin adsorption studies. The maximum adsorption capacity was 115 mg/g. The adsorption modes proposed by the authors are shown in Fig. 9b. As can be seen from Fig. 9b, the surface functional groups C=C, O–C=O, and M–O were involved in levofloxacin removal. In addition, the adsorption was enhanced by π-π electron-donor–acceptor interactions and H-bonds. The iron and magnesium atoms act as active adsorption centers, promoting levofloxacin adsorption [103].

Enrofloxacin is a fluoroquinolone antibiotic. The structure of enrofloxacin contains the dissociating groups –COOH and $–NH_n$, which indicates that enrofloxacin can exist in different forms depending on the solution pH (Fig. 9c) [139]. G. Peng *et al.* [105] studied the modes of enrofloxacin adsorption using Fe_3O_4/magnetic montmorillonite nanocomposite. The maximum adsorption capacity of 163 mg/g was achieved. Good adsorption properties were associated with electrostatic interaction.

R. Li *et al.* [140] synthesized a composite of manganese oxide based on magnetic biochar and untreated biochar for enrofloxacin removal. The maximum adsorption capacity of the magnetic nanocomposite was 7.19 mg/g. The adsorption capacity decreased with solution pH increasing (between 3.0 and 10.0) and with increasing ionic strength (0.001–0.1 M). Z. Gordi *et al.* [141] synthesized an adsorbent based on a mixture of magnetically functionalized graphene oxide and MOF for enrofloxacin removal. The maximum adsorption capacity was 345 mg/g. As the solution pH increased to 7.5, the efficiency of enrofloxacin removal increased, and above pH = 7.5, it decreased (pK_a values of carboxyl and amine groups are 5.88 and 7.74, respectively). The main adsorption mode was the electrostatic interaction. M. Zahoor *et al.* [142] used magnetic carbon nanocomposites to remove enrofloxacin from industrial wastewater. The maximum adsorption efficiency was observed at pH 6–8. The pH value affects the surface charge of the magnetic adsorbent and the dissociated form of enrofloxacin in the solution: the surfaces of the adsorbent and adsorbate have the same charge signs under acidic or alkaline conditions and electrostatic repulsion forces hinder the adsorption capacity.

Norfloxacin is a synthetic antibiotic belonging to the class of

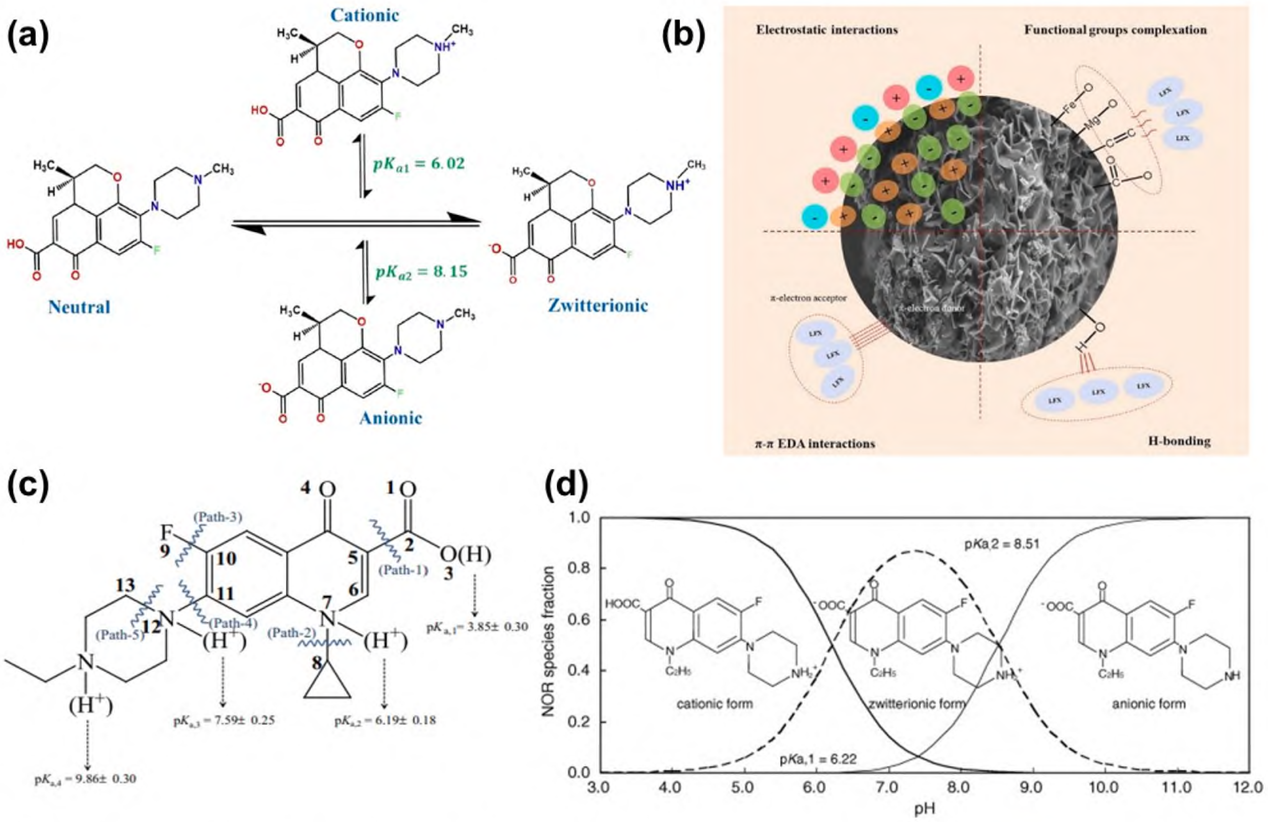

Fig. 9. (a) The cationic, anionic, and zwitterionic forms of levofloxacin at different pH. Reprinted with permission from [65]. Copyright 2021, Elsevier; (b) the possible adsorption modes of levofloxacin at biochar/$MgFe_2O_4$ magnetic composite. Reprinted with permission from [103]. Copyright 2021, Elsevier; (c) the formula of enrofloxacin (the dissociation may occur through the few pathways: path 1 is the cleavage of the C2–C5 bond, path 2 is the N7–C8 bond, path 3 is the F9–C10 bond, path 4 is the C11–N12 bond, and path 5 is the N12–C13 bond). Reprinted with permission from [139]. Copyright 2018, Springer Nature; (d) the molecular structure of norfloxacin and its ionic forms as a function of pH. Reprinted with permission from [143]. Copyright 2012, Elsevier.

fluoroquinolones. The dissociation constants pK_a of norfloxacin are 6.22 and 8.51. The cationic, zwitterionic, and anionic forms are shown in Fig. 9d [143]. According to [33] the average concentration of norfloxacin in surface waters of Western Europe is 0.009 μg/L, and the maximum measured concentration is 1.15 μg/L. Nowadays, the possibility of norfloxacin removal from wastewater is extensively studied, because it has a very harmful impact on the environment and human health. Much attention has been paid to the synthesis of new magnetic adsorbents [94,106,107], which would effectively remove norfloxacin from the aqueous environment. G. Peng *et al.* [106] synthesized a nitrogen-modified reduced graphene oxide incorporated into Fe_3O_4 magnetic nanoparticles (N-RGO/Fe_3O_4) as an adsorbent for norfloxacin removal. It was concluded that the maximum adsorption capacity was 158 mg/g. The mode of adsorption can be explained by the fact that norfloxacin has two proton-binding centers (carboxyl and piperazinyl groups) and they can exist in different forms depending on the solution pH. The cationic form is the dominant type at $pH < 6$, so the adsorption of norfloxacin is unfavorable in acidic solution due to electrostatic repulsion. When pH increases, the surface of the nanoadsorbent and the norfloxacin molecule gains opposite charges, so the adsorption increases [106]. M.M. Gaho *et al.* [107] synthesized the magnetic polymers – cross-linked Fe_3O_4 coated with oleic acid using methacrylic acid, ethylene glycoldimethacrylate, and 2,2-azobisisobutyronitrile. They showed high efficiency in norfloxacin removal from wastewater. The maximum adsorption capacity at 35 °C was 42 mg/g. The van der Waals forces and hydrogen bonds are mostly responsible for the adsorption of norfloxacin [107].

Amoxicillin is a broad-spectrum β-lactam antibiotic. Amoxicillin has amphoteric properties due to three main functional groups: $–NH_2$, –COOH, –OH [144]. It has three different acid dissociation constants: $pK_{a1} = 2.68$ (carboxyl group), $pK_{a2} = 7.49$ (amino group), and $pK_{a3} = 9.63$ (phenolic group) [145]. Therefore, amoxicillin can exist in an aqueous solution in four different forms ($Amox^+$, Amox, $Amox^-$, and $Amox^{2-}$) depending on the solution pH (Fig. 10a) [145]. M. Pooresmaeil *et al.* [108] synthesized a magnetic nanocomposite Fe_3O_4@Cd-MOF@CS for removing amoxicillin from wastewater. Fig. 10b shows the proposed modes of amoxicillin adsorption at the synthesized magnetic adsorbent. Fe_3O_4@Cd-MOF@CS has several types of functional groups that can participate in the adsorption of amoxicillin. Chitosan contains numerous hydroxyl and amine functional groups that can bind to the antibiotic through electrostatic attraction and hydrogen bonding. The Fe_3O_4@Cd-MOF composite contains a large number of aromatic rings, which provide the possibility of contaminant capture inside the cavities and, thus, additionally contribute to adsorption [108].

Daptomycin is an antibacterial drug of the cyclic lipopeptides class [146]. It has six ionizable residues [147], including three aspartic acids (Asp-3, Asp-7, and Asp-9), one methylglutamic acid (mGlu-12), one aliphatic amine (Orn-6), and one aromatic amine (Kyn-13) (Fig. 10c) [148]. It has four acidic groups (pK_a of 1.3, 3.8, 4.1, and 4.4) and two basic groups (pK_a of 1.3 and 10.7), resulting in a total molecular charge of −3 at neutral pH (the basic residue with a pK_a of 1.3 is not dissociated at neutral pH) [148]. T. Ai *et al.* [110] studied the adsorption of daptomycin at two magnetic ultrafine wood-based materials WSBC/Fe_3O_4 (willow sawdust) and PSBC/Fe_3O_4 (pine sawdust). The maximum adsorption capacity of daptomycin on WSBC/Fe_3O_4 and PSBC/Fe_3O_4 was 217 and 213 mg/g, respectively. The study of the adsorption mechanism indicates three stages of the adsorption process. The first step is the diffusion of daptomycin to the material surface, the second

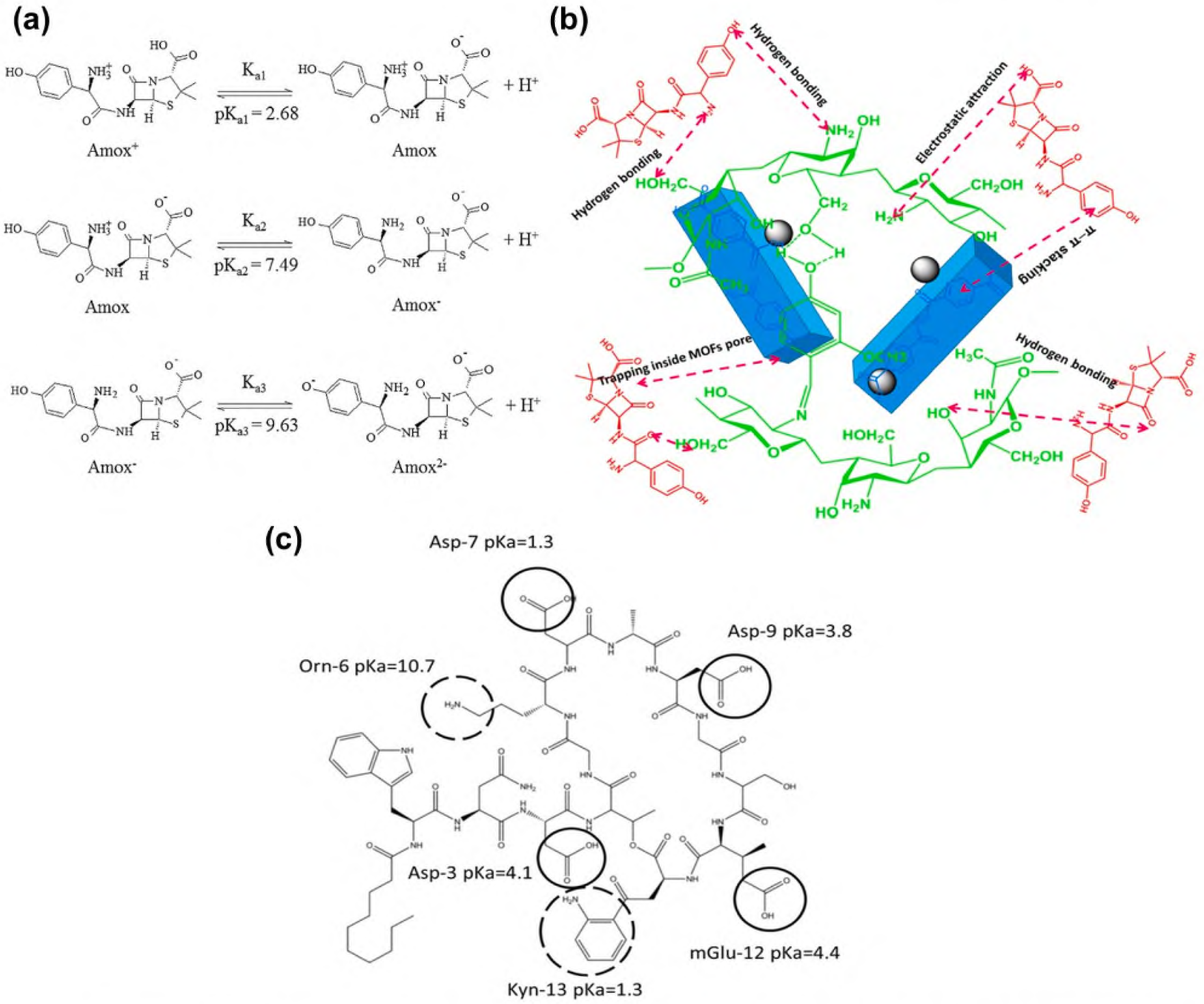

Fig. 10. (a) Different forms of amoxicillin and pK_a values. Reprinted with permission from [145]. Copyright 2016, Elsevier; (b) the proposed modes of amoxicillin binding by the Fe_3O_4@Cd-MOF@CS composite. Reprinted with permission from [108]. Copyright 2021, Elsevier; (c) the structure of daptomycin (acidic groups are surrounded by solid line circles, and basic groups are surrounded by dashed line circles: Asp – aspartic acid, mGlu – methylglutamic acid, Orn – ornithine, Kyn – kynurenine). Reprinted with permission from [148]. Copyright 2020, Springer Nature.

one involves penetration of the molecule into the porous structure of the adsorbent, where finally the equilibrium between adsorbed and non-adsorbed daptomycin is reached [110].

Table 4 provides an overview of the adsorption parameters for various magnetic adsorbents in different antibiotics removal from wastewater.

5. Applications of magnetic nanoparticles for the adsorption of non-steroidal drugs

Nonsteroidal anti-inflammatory drugs are a class of drugs that provide analgesic and antipyretic (antipyretic) effects and, when used in higher doses, can cause anti-inflammatory effects. The most famous representatives are diclofenac, ibuprofen, acetaminophen, ketoprofen, naproxen, acetylsalicylic acid (Fig. 11).

5.1. Adsorption of diclofenac

Diclofenac is used as a sodium salt. Diclofenac has poor biodegradability and low adsorbability. Diclofenac is widely used throughout the world and it is found in environmental waters. It was found that the average concentration of diclofenac in the surface waters of Western Europe is 0.020 μg/L, and the maximum measured concentration is 18.74 μg/L [33]. Therefore, the problem of purifying wastewater and drinking water from this pharmaceutical attracts particular attention. One of the methods of diclofenac removal from the aqueous environment is the use of adsorbents based on magnetic oxide nanoparticles [114-116].

Magnetic hybrid adsorbents Fe_3O_4@SiO_2/SiHTCC consisting of magnetite cores encapsulated in a silicon mesh containing quaternary chitosan were synthesized [114]. The ability of nanoparticles to adsorb diclofenac was evaluated in the pH range of 5–8 with a contact time of 5 h. The highest removal was achieved at pH = 6, which is associated with the anionic form of diclofenac ($–COO^-$). The maximum adsorption capacity was 240 mg/g. The mode of diclofenac adsorption is shown in Fig. 12a. The electrostatic interactions between the anionic form of the drug and the $–N^+(CH_3)_3$ groups of Fe_3O_4@SiO_2/SiHTCC particles is the main driving force of the adsorption process [114].

J.M.N. dos Santos *et al.* [115] used the $ZnFe_2O_4$/chitosan magnetic adsorbent capable of reducing the initial concentration of diclofenac from 50 to 12 mg/L within 20 min, at the initial pH of 4 and adsorbent dose of 0.2 g/L. It was associated with the ability of the amino groups of chitosan to protonation in an acidic medium. The maximum adsorption capacity was 188 mg/g [115]. X.X. Liang *et al.* [116] synthesized a

Table 4
Adsorption parameters of different magnetic adsorbents for other antibiotics (PFO – pseudo-first-order kinetic model, PSO – pseudo-second-order kinetic model).

Adsorbent	Adsorbate	Models of best fit	Adsorption capacity (mg/g)	Optimal parameters					Removal efficiency (%)	References
				pH	Contact time (min)	Temperature (K)	Antibiotic concentration (mg/L)	Adsorbent dose		
Fe_3O_4	levofloxacin	PSO, Langmuir	6.8	6.5	240	298	20	100 mg	80.2	[99]
Magnetic carbon nanocomposite	levofloxacin	PSO, Langmuir	21	7	60	298	40	0.04 g	N/A	[100]
$NiFe_2O_4$/biochar composites	levofloxacin	PSO, Langmuir	172	6	60 h	298	40	10 mg	N/A	[101]
Biochar/$MgFe_2O_4$	levofloxacin	PSO, Freundlich	115	5	240	298	100	0.3 g/L	N/A	[103]
Fe_3O_4–green iron NPs	levofloxacin	PSO, Freundlich	22.5	7	24 h	298	4	100 mg/L	86	[104]
Humic acid/magnetic biochar	enrofloxacin	PSO, Langmuir	4.03	10	480	298	10	2 g/L	85	[94]
Fe_3O_4/magnetic montmorillonite	enrofloxacin	PSO, Langmuir	163	6.85	60	298	30	0.1 g/L	90	[105]
Humic acid/magnetic biochar	norfloxacin	PSO, Langmuir	3.94	10	480	298	10	2 g/L	90	[94]
Nitrogen-doped reduced graphene oxide/Fe_3O_4 nanocomposite	norfloxacin	PSO, Langmuir	158	10	210	298	20	100 mg/L	61.2	[106]
Magnetic molecularly imprinted polymers	norfloxacin	PFO, Langmuir	42.3	6	30	308	30	1.5 mg	95	[107]
Fe_3O_4/activated carbon/chitosan	amoxicillin	PSO, Langmuir	526	N/A	120	298	60	1 mg	72	[87]
Magnetic cadmium-based MOFs modified with chitosan (Fe_3O_4@Cd-MOF@CS)	amoxicillin	PSO, Langmuir	103	8	240	298	200	50 mg	75	[108]
Magnetically modified graphene nanoplatelets	amoxicillin	PSO, Langmuir, Temkin	14.10	5	90	293	10	5 mg	84	[109]
Willow sawdust biochar/Fe_3O_4 Pine sawdust biochar/Fe_3O_4	daptomycin	PSO, Freundlich	217 213	4	240	298	25	0.025 g	N/A	[110]
Bovine serum albumin/Fe_3O_4	erythromycin	Langmuir	145	N/A	60	N/A	200	0.2 g	99	[73]
Fe_3O_4/activated carbon/chitosan	erythromycin	PSO, Langmuir	179	N/A	120	298	60	1 mg	54	[87]
Bovine serum albumin/Fe_3O_4	streptomycin	Langmuir	69	N/A	60	N/A	200	0.2 g	81.5	[73]
Amine-coated magnetic nanocomposite $NiFe_2O_4$@SiO_2	streptomycin	PSO, Langmuir	49	5	15	298	12	10 mg	70	[123]
Magnetic Fe_3O_4 NPs coated zeolite	cephalexin	PSO, Langmuir	25	7	120	293	40	0.6 g/L	93	[111]
Fe_3O_4-chitosan (CTS-MNPs)	metronidazole	PSO, Freundlich	97	3	90	318	10	2 g/L	99	[112]
Fe_3O_4/graphene oxide/citrus peel-derived magnetic bio-nanocomposite	sparfloxacin	PSO, Freundlich	502	6	72 h	298	360	0.02 g	N/A	[86]
$NiFe_2O_4$– Covalent organic frameworks -chitosan-terephthalaldehyde nanocomposites film	cefotaxime	PSO, Freundlich	309	4	40 h	293	100	170 mg/L	95	[71]
Activated carbon modified with magnetic Fe_3O_4 NPs	ceftriaxone	PSO, Langmuir	29	3.14	90	298	10	1.99 g/L	97	[113]
Bovine serum albumin/Fe_3O_4	chloramphenicol	Langmuir	148	N/A	50	N/A	200	0.2 g	96.4	[73]

magnetic composite based on amino-functional chitosan and Fe_3O_4 (ACS@Fe_3O_4) for diclofenac removal from water. The maximum adsorption capacity was 470 mg/g. It was shown that the amount of adsorbed diclofenac decreased with increasing pH due to repulsive electrostatic interactions between the negative surface charge of ACS@Fe_3O_4 and the negatively charged anionic form of diclofenac [116]. T.M. Salem Attia *et al.* [117] used zeolite-coated magnetic nanoparticles (γ-Fe_2O_3-zeolite) to remove diclofenac. Fast and high

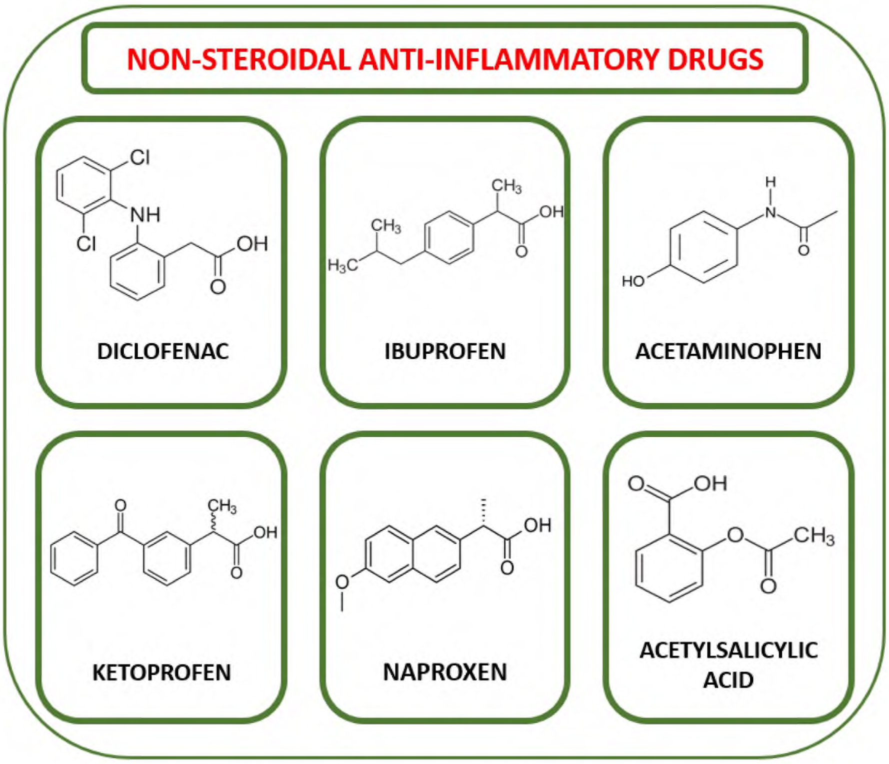

Fig. 11. Formulas of the common non-steroidal anti-inflammatory drugs.

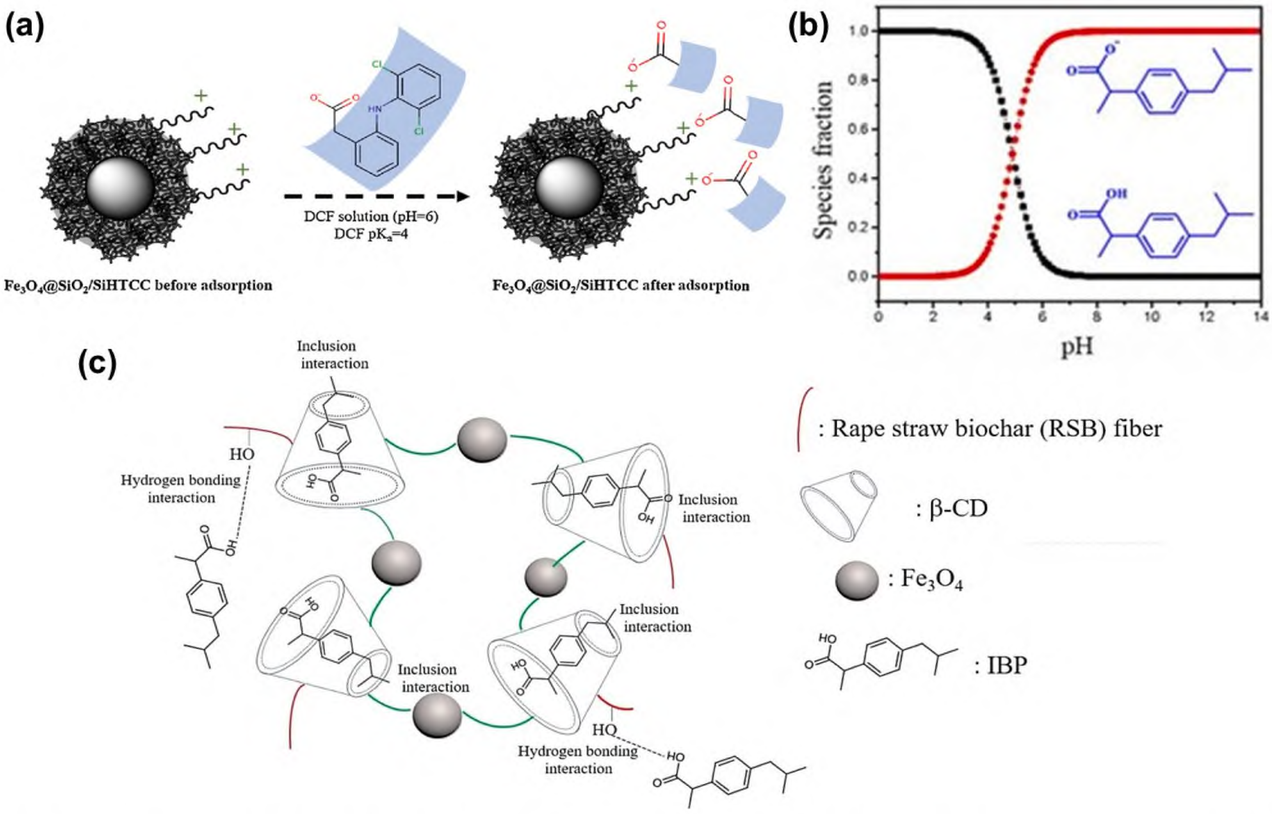

Fig. 12. (a) Schematic illustration of the mode of diclofenac adsorption at $Fe_3O_4@SiO_2/SiHTCC$ particles. Reprinted with permission from [114]. Copyright 2018, Elsevier; (b) distribution of neutral and ionic forms of ibuprofen at various pH. Reprinted with permission from [150]. Copyright 2020, The Author(s); (c) proposed mechanism of removal of ibuprofen by the rape straw biomass fiber and biochar/Fe_3O_4 /cyclodextrin adsorbent. Reprinted with permission from [125]. Copyright 2021, Elsevier.

adsorption of diclofenac is mainly explained by the presence of NH– and OH-groups in the diclofenac structure, so the adsorbent can adsorb a large amount of the drug (95%) in a very short time (10 min) (at adsorbent dose 1 g/L and diclofenac concentration of 0.1 mg/L) [117]. Table 5 provides an overview of the adsorption parameters for various magnetic adsorbents for diclofenac removal from wastewater.

5.2. *Adsorption of ibuprofen*

Ibuprofen is a derivative of phenylpropionic acid, which causes anti-inflammatory, analgesic, and antipyretic effects [149]. Fig. 12b shows the distribution of neutral and ionic forms of ibuprofen at various pH [150]. According to [33], the average concentration of ibuprofen in the surface waters of Western Europe is 0.097 μg/L, and the maximum measured concentration is 303 μg/L. Magnetic nanoparticles coated with zeolite (γ-Fe_2O_3-zeolite) were synthesized by T.M. Salem Attia *et al.* [117]. Zeolites are minerals with molecular-sized pores that can absorb and reliably retain various contaminants [151]. The ibuprofen removal efficiency was>95% within 10 min at an adsorbent dose of 1 g/L and ibuprofen concentration of 0.1 mg/L [117]. A.C. Fröhlich *et al.* [121] obtained $NiFe_2O_4$/activated carbon magnetic composite used for the ibuprofen adsorption. It was found that the adsorption was favorable under acidic conditions at 328 K. The maximum adsorption capacity was 261 mg/g. Y. Liu *et al.* [69] synthesized the magnetic genipin-crosslinked chitosan/graphene oxide-SO_3H (GC/MGO-SO_3H) as an adsorbent for ibuprofen removal. The maximum adsorption capacity increased from 113 to 138 mg/g at a temperature increased from 298 to 313 K.G. Wu *et al.* [125] synthesized a magnetic rape straw biomass fiber/β-Cyclodextrin/Fe_3O_4, which is a promising adsorbent for ibuprofen removal from wastewater (Fig. 12c). The mechanism of ibuprofen removal encompasses the formation of hydrogen bonds and electrostatic interactions. The synthesized adsorbent contains a large number of oxygen-containing groups (OH, C=O) on its surface, which can bind with ibuprofen through hydrogen bonds [125]. Table 6 provides an overview of the adsorption parameters of various magnetic adsorbents for the removal of ibuprofen from wastewater.

5.3. *Adsorption of other non-steroidal anti-inflammatory drugs*

Acetylsalicylic acid belongs to the group of non-steroidal anti-inflammatory drugs with analgesic, antipyretic, and anti-inflammatory properties. The average concentration of acetylsalicylic acid in the surface waters of Western Europe is 0.002 μg/L, and the maximum measured concentration is 0.36 μg/L [33]. A.S. Liyanage *et al.* [124] synthesized the magnetic Fe_3O_4/Douglas fir biochar adsorbents for acetylsalicylic acid removal from wastewater. The highest acetylsalicylic acid removal occurs at pH = 4–8 due to the electrostatic interaction between the positively charged adsorbent surface and the negatively charged adsorbate with carboxylate anions. E.A. Moacă *et al.* [126] used a magnetite-core active charcoal-shell matrix, Fe_3O_4@C, to remove acetylsalicylic acid from aqueous solutions. The maximum adsorption capacity of 234 mg/g was achieved. The magnetic matrix demonstrates two benefits: the easy magnetic separation from the liquid medium and the highly porous structure necessary for effective adsorption.

Acetaminophen is a widely used analgesic. The average concentration of acetaminophen in surface waters of Western Europe is 0.046 μg/L, and the maximum measured concentration is 230 μg/L [33]. S. C. Kollarahithlu *et al.* [123] used the amine-functionalized superparamagnetic silica nanocomposite for acetaminophen adsorption. Amino groups (–NH_2), which are present in the $NiFe_2O_4$@SiO_2@aminopropyltrimethoxysilane adsorbent, are easily protonated (–NH_3^+) and promote adsorption in an acidic medium (at pH from 4 to 6) through electrostatic interaction. This is explained by the formation of hydrogen bonds between the –OH group of acetaminophen and –NH_3^+ of the adsorbent [123]. R. Natarajan *et al.* [129] synthesized rhamnolipid-based chitosan magnetic nanosorbents for the removal of acetaminophen from aqueous solutions. The study showed the maximum removal of acetaminophen of 96.7%, the adsorption capacity was 96.3 mg/g at 60 min contact time, pH = 5, and temperature of 303 K.

Ketoprofen and naproxen are synthetic drugs that originate from propionic acid (according to their chemical structure) and belong to the group of non-steroidal anti-inflammatory drugs. The average concentration of naproxen in the surface waters of Western Europe is 0.057 μg/L, and the maximum measured concentration is 12.3 μg/L [33]. L. A. Al-Khateeb *et al.* [120] synthesized Fe_3O_4@graphene nanoplatelets nanocomposite for the removal of ketoprofen from wastewater. The adsorption capacity at a temperature of 296 K was 8.76 mg/g. The study showed that the π-π interaction is involved in the adsorption process between the π-electrons of the aromatic nanocomposite and the benzene rings of ketoprofen. Hydrogen bonds can also participate in adsorption through the interaction between the hydroxyl and carboxyl groups of the adsorbent and the carboxylic, nitrogen, and carbonyl groups of the adsorbate [120]. A. C. Fröhlich *et al.* [121] synthesized a $NiFe_2O_4$/activated carbon magnetic composite for the ketoprofen removal from an aqueous medium. The ketoprofen adsorption was favorable in acidic media at 328 K. The maximum adsorption capacity was 98 mg/g. L. A. Al-Khateeb *et al.* [120] used Fe_3O_4@graphene nanoplatelets nanocomposite for the removal of naproxen from wastewater. The adsorption capacity at a temperature of 296 K was 10.6 mg/g.

Table 7 provides an overview of the adsorption parameters of various magnetic adsorbents for nonsteroidal anti-inflammatory drugs removal

Table 5
Adsorption parameters of different magnetic adsorbents for diclofenac removal (PSO – pseudo-second-order kinetic model).

Adsorbent	Adsorption models	Adsorption capacity (mg/g)	Optimum parameters					Removal efficiency (%)	References
			pH	Contact time (min)	Temperature (K)	Concentration (mg/L)	Adsorbent dose		
Fe_3O_4@SiO_2/SiHTCC (N-(2-hydroxypropyl)-3-trimethylammonium chitosan chloride)	Langmuir	240	6	300	298	40	10 mg	60	[114]
$ZnFe_2O_4$/chitosan	PSO	188	4	20	298	50	0.2 g/L	75	[115]
Amino-functional chitosan@Fe_3O_4	PSO, Langmuir	469	4.5	60	303	1000	10 mg	91	[116]
Magnetic nanoparticles coated with zeolite	PSO, Freundlich	N/A	2	300	303	0.1	1 g/L	99.6	[117]
Cetyltrimethyl ammonium bromide-coated Fe_3O_4@decanoic acid	N/A	36	9	5	N/A	0.5	10 mg	75	[118]
Magnetic polydopamine-chitosan modified adsorbent	PSO	N/A	7	400	298	2	25 mg/mL	71	[119]
Fe_3O_4@graphene nanoplatelets nanocomposite	PSO	17	8	20	323	20	10 mg	81	[120]

Table 6
Adsorption parameters of different magnetic adsorbents for ibuprofen removal (PSO – pseudo-second-order kinetic model).

Adsorbent	Adsorption models	Adsorption capacity (mg/g)	Optimum parameters					Removal efficiency (%)	References
			pH	Contact time (min)	Temperature (K)	Concentration (mg/L)	Adsorbent dose		
Magnetic genipin-crosslinked chitosan/graphene oxide-SO_3H composite	PSO, Langmuir	138	6	120	308	10	5 mg	85	[69]
Magnetic nanoparticles coated with zeolite	PSO, Freundlich	N/A	2	300	303	0.1	1 g/L	99	[117]
Fe_3O_4@graphene nanoplatelets nanocomposite	PSO	9.24	8	20	323	20	10 mg	41	[120]
$NiFe_2O_4$/activated carbon	PSO, Sips	261	2	240	328	0–100	0.5 g/L	86.5	[121]
Amine-coated magnetic nanocomposite $NiFe_2O_4$@SiO_2	PSO, Langmuir	59	7	15	298	12	10 mg	97	[123]
Fe_3O_4/Douglas fir biochar	Langmuir	40	8	5	308	100	2.5 g/L	90	[124]
Rape straw biomass fiber/β-Cyclodextrin/Fe_3O_4	PSO, Freundlich	48	6	60	308	100	50 mg	90.3	[125]

from wastewater.

6. Perspectives

Research aimed at creating composite adsorbents with magnetic properties for water treatment is becoming more and more popular. The use of modification and functionalization of the surface of magnetic adsorbents allows creating the samples with unique properties. One of the main advantages of magnetically susceptible adsorbents, compared to ordinary (nonmagnetic) ones, is the possibility of controlling them by an external magnetic field. A magnetic field can penetrate various materials, including glass and polymers. Therefore, magnetic separation, as a non-contact and non-destructive technology, allows the removal of the used adsorbent, preventing water re-contamination with pharmaceuticals or other adsorbates. The effectiveness of magnetic separation is not affected by temperature, pH, or the concentration of the adsorbate in the

Table 7
Adsorption parameters of different magnetic adsorbents for non-steroidal anti-inflammatory drugs (PSO – pseudo-second-order kinetic model).

Adsorbent	Adsorbate	Adsorption models	Adsorption capacity (mg/g)	Optimum parameters					Removal efficiency (%)	References
				pH	Contact time (min)	Temperature (K)	Concentration (mg/L)	Adsorbent dose		
Fe_3O_4/Douglas fir biochar	acetylsalicylic acid	Langmuir	150	8	5	308	100	2.5 g/L	70	[124]
Fe_3O_4@C Matrix	acetylsalicylic acid	PSO, Freundlich	234	3	100	298	100	2 g/L	86	[126]
Amine-coated magnetic nanocomposite $NiFe_2O_4$@SiO_2	acetaminophen	PSO, Langmuir	58	6	15	298	12	10 mg	94	[123]
Magnetite nanoparticles modified β-cyclodextrin Polymer Coupled	acetaminophen	PSO, Langmuir	133	7	5	298	400	0.5 mg/L	75	[127]
Magnetic mesoporous silica microspheres	acetaminophen	PSO, Langmuir	311	5	30	303	150	1 g/L	97.4	[128]
Magnetic NPs coated with rhamnolipids (Rh-cMNP)	acetaminophen	PSO, Langmuir	96	5	60	303	60	20 mg	96.7	[129]
Fe_3O_4@C Matrix	acetaminophen (paracetamol)	PSO, Redlich–Peterson	142	3	60	298	50	2 g/L	97	[126]
Nitrogen-doped reduced graphene oxide/Fe_3O_4 nanocomposite	ketoprofen	PSO, Langmuir	468	7	210	298	20	100 mg/L	N/A	[106]
Fe_3O_4@graphene nanoplatelets nanocomposite	ketoprofen	PSO	12.2	8	20	323	20	10 mg	53.8	[120]
$NiFe_2O_4$/activated carbon	ketoprofen	PSO, Sips	98	2	240	328	0–100	0.5 g/L	86.5	[121]
Magnetic NPs coated with zeolite	naproxen	PSO, Freundlich	N/A	2	300	303	0.1	1 g/L	99.8	[117]
Fe_3O_4@graphene nanoplatelets nanocomposite	naproxen	PSO	13.1	8	20	323	20	10 mg	60.3	[120]

solution. Thus, magnetically controlled adsorbents can be used for the adsorption of heavy metals, and dyes, as well as for the purification of pharmaceutical effluents from antibiotics, drugs, etc. The use of such materials makes it possible to replace the mechanical separation stage, which is one of the most labor- and energy-consuming stages of this process. However, the development of the ideal treatment technology should be done in such a way that it could easily integrate with existing treatment facilities and should be a cost-effective and profitable process. Traditional adsorbents after their use in wastewater treatment create sludge, thus leading to secondary pollution. Instead, magnetic adsorbents do not cause this problem.

Water purification with magnetic nanoparticles is a rather complex procedure that presents some demands, in particular: low concentration of pollutants must be treated; extremely low concentration limits should be achieved after the process; nanoparticles cannot remain in purified water [152]. In addition, the magnetism of nanoparticles leads to a noticeable aggregation of particles and, consequently, a decrease in adsorption capacity, which complicates their reuse. Most of the analyzed studies were conducted using laboratory equipment, so more attention should be put to solve several problems such as analysis of the magnetic nanoparticles' productivity when they are used on an industrial scale; studying the process of continuous pharmaceuticals removal; investigation of the magnetic nanoparticles' toxicity after several cycles; the disposal of magnetic nanoparticles; assessment of the life cycle of magnetic nanoparticles; studying the impact of magnetic nanoparticles on the environment [153].

Adsorbents with magnetic properties are attractive not only because they are easily extracted from the treatment medium, but also due to the possibility of modulating the physicochemical characteristics of the adsorbent in the presence of an external magnetic field, created by both permanent magnet or electromagnetic field. In the second case, an additional effect of heating the magnetic adsorbent appears, which may enhance the adsorption of pollutants molecules. The applied magnetic field can cause changes in both the structure of the adsorbents (the so-called "magnetic memory effect") and adsorbed molecules. Adsorbates can change their dipole moment in the presence of a magnetic sorbent, thus causing additional agglomeration and stronger retention by the adsorbent surface. This phenomenon requires further research.

The regeneration of the magnetic adsorbents is an important aspect of their utilization and also should be taken into account. The regeneration depends on the type of magnetic adsorbent and the nature of the adsorbed pollutant. Regeneration involves removing contaminants from the surface of the adsorbent so that it can be reused. There are several methods of regeneration of magnetic adsorbents: thermal, chemical, biological, and magnetic. Thermal regeneration involves the heating of the adsorbent at a high temperature to remove adsorbed impurities. During the chemical regeneration, the adsorbent is treated with chemicals (e.g., HCl [44], CH_3OH [79], CH_3OH + NaOH [84], CH_3OH + CH_3COOH [94]), which desorb the impurities. During biological regeneration, the microorganisms destroy or remove pollutants onto the adsorbent surface. Another type of regeneration involves the use of a magnetic field to increase the mobility of adsorbed pollutants and enhance their desorption from the adsorbent surface [116]. After the regeneration, the adsorbent should be thoroughly rinsed to remove any remaining contaminants or regeneration agents. Therefore, proper regeneration and cleaning procedures are important to improve the performance of the magnetic adsorbent during repeated use [154].

Simultaneous adsorption of co-existing pharmaceuticals and selectivity of the adsorbents to specific pharmaceuticals are other important issues and challenges for the future development of the discussed technology [155]. The adsorption of co-existing pollutants should be performed by properly functionalized magnetic adsorbents to ensure the involvement of several types of adsorption modes [156,157]. The functional groups create new adsorption centers and can selectively/simultaneously adsorb different types of pharmaceuticals from the solution [124]. It is expected that the main modes of simultaneous adsorption will be electrostatic attraction and complex formation. Simultaneous removal of several pharmaceuticals from the solution can occur at different conditions (e.g., higher or lower pH or temperature) compared to separate removal of the same pharmaceuticals. *In-situ* experimental methods, as well as artificial intelligence and quantum chemical modeling, should be used for a deeper understanding of adsorption modes. Thus, extensive studies on the possibilities of real applications in water and wastewater treatment are crucial for the further development of prospective magnetic adsorbents.

7. Conclusions

The purpose of this review was to show the state of research on the removal of some most popular pharmaceuticals from an aqueous environment and to provide some suggestions for the enhancing adsorption effectiveness of magnetic adsorbents. Since pharmaceuticals have a significant toxic effect on the environment, and a detrimental effect on flora and fauna, therefore, the purification of wastewater from pharmaceuticals gains higher and higher priority among researchers around the world. Adsorption is considered the most common method of pharmaceuticals removal from water. This review presents the modes of adsorption of pharmaceuticals (in particular, antibiotics and non-steroidal anti-inflammatory drugs) from aqueous environments using various adsorbers with magnetic functionality. According to the analysis of articles, the high adsorption capacity of magnetic nanoparticles makes them prospective for large-scale use. The advantages of magnetic adsorbents encompass the possibility of separation from the aqueous medium using a magnetic field, the use of cheap precursors for synthesis, the high stability of these materials in water, the possibility of reuse, biocompatibility, simple synthesis methods, and the possibility of surface functionalization. Scientists from all over the world published a lot of works on the removal of pharmaceuticals, such as tetracycline, ciprofloxacin, levofloxacin, diclofenac, and ibuprofen. Among the magnetic adsorbents, Fe_3O_4-based nanoparticles are most often examined. The structures of magnetite or ferrites can be tuned with various cations, making it possible to increase the adsorption capacity, increase the amount of surface adsorption active sites and at the same time not to reduce significantly the magnetization of the adsorbent, which is important for separating the used adsorbent from the solution. The adsorption capacity of magnetic adsorbents ranges from tens to hundreds of mg/g. It can be increased in few times by creating composite magnetic adsorbents based on biochar, layered hydroxides, MOFs/COFs, graphene oxide, etc. The disadvantage of magnetic nano-adsorbents is their tendency to agglomeration, which can be simply resolved using coating/functionalization by different agents (amino acids, surfactants, silica, polymers (polyaniline, polystyrene, polypyrrole, etc.)). It is shown that the adsorption mode strongly depends on pH, temperature, adsorbent dose, and adsorbate concentration. We have discussed the correlations between molecular structures of pharmaceuticals and their existence in cationic, anionic, and zwitterionic forms depending on the pH of the aqueous solution. Analysis of the literature showed that the modes of pharmaceuticals adsorption on magnetic nanoadsorbents are mainly based on hydrophobic and electrostatic interactions, π-π interaction, surface complexations, ion exchange, as well as hydrogen bonds. This points to very limited possibilities to control the selectivity of the processes, e.g., aimed at the removal of only pharmaceuticals from water. Based on all these data, it is possible to assert the effective use of magnetic adsorbents for the removal of pharmaceuticals from aqueous environments.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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