

Iron-based materials for the adsorption and photocatalytic degradation of pharmaceutical drugs: A comprehensive review of the mechanism pathway

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ABSTRACT

Adsorption and photocatalytic degradation techniques for removing various contaminants have received broad consideration and acceptance due to their advantages over conventional wastewater treatment techniques. Iron-based materials are among several groups of adsorbents, and photocatalysts that have proven to be effective in pharmaceuticals-based pollutants removal from wastewater. Pharmaceutical drug removal is accompanied by several mechanisms, so there is a deep need for a better understanding of the complexity and development of wastewater treatment using iron-based materials. Therefore, this review examined the mechanism of adsorption and photocatalysis degradation of pharmaceuticals in aqueous solutions by iron-based materials. The adsorption of pharmaceutical drugs was found to be influenced by changes in the solution pH. The mechanism of removal of these contaminants by iron-based materials through adsorption occurred via electrostatic, π - π , and hydrogen bond interactions among others. In the case of photocatalysis, the first mechanism occurred through the formation the hydroxyl radicals due to highly reactive species (electrons and holes) that partook in the reaction processes, while the second mechanism is related to the formation of hydrogen peroxide, H_2O_2 , by photo-generated electrons in the conduction band and with the well-known photo dissolution of iron oxide leading to free Fe^{2+} and Fe^{3+} ions. The overall idea of this review is to provide useful information on the mechanisms of adsorption and photocatalytic degradation of pharmaceutical contaminants using iron-based materials. The review summarizes the current understanding and the advances in the pharmaceutical-bearing effluent treatment using nanostructured adsorbents and photocatalysts, including future developments for a cleaner and safer environment.

1. Introduction

Water pollution has led to various diseases that have resulted in severe health issues and increased mortality of humans and aquatic life. Therefore, to solve the problems that emanated from wastewater contamination, pharmaceutical industries came up with different classes of drugs that could improve the deteriorating health conditions of the affected population [1,2]. Meanwhile, the untreated discharge of effluents from pharmaceutical industries, hospitals, and sewers, has increased the contamination of surface and groundwater [3–5]. More so, the incomplete metabolism of pharmaceutical drugs in the body system,

which led to their release into the environment through excretion, has also added to the contamination load. The unregulated presence of antibiotics in the environment has made bacteria build resistance against these drugs [6,7], making them less effective when administered to humans and livestock [8,9], and creating one of the most relevant concerns in public health worldwide.

Discharge of pharmaceutical drugs (antibiotics, anti-inflammatory drugs) into surface and groundwater or soil has also made clean water to be contaminated, leading to the death of some important bacteria in the environment [6,10–13]. The challenges that contaminants pose to the ecosystems and therefore to the services they provide, have

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motivated a number of studies focusing on their removal. Aside from this, there are different guidelines regarding the discharge of industrial effluents into water [14–16]. Since some pharmaceutical drugs are usually found in trace amounts and cannot be degraded easily by microorganisms, different techniques have been developed for their removal from wastewater before their discharge into the environment. Wastewater treatment plants provide in general insufficient elimination of pharmaceutical-based pollutants in aquatic reservoirs, which leads to their widespread in the environment. Among many techniques, adsorption and photocatalytic degradation are claimed to be environmentally and economically effective. Thus, from 2011 to 2020 > 65,000 and 50,000 scientific articles containing adsorption and photocatalysis, respectively, were published (Scopus source). The percentage of the overall publications related to adsorption and photocatalysis keeps increasing annually (Fig. 1).

These two groups of techniques in some cases complement each other, which is why before the commencement of the photocatalytic degradation experiment, the vessels containing the materials (adsorbent/photocatalyst) and the solutions to be adsorbed/degraded are kept without irradiation of light. The role that adsorbents and photocatalysts play in the removal/degradation processes cannot be overemphasized. So then, the materials that would be used as adsorbents and photocatalysts should not be toxic to the environment, chemically stable, photoactive (in the case of photocatalytic degradation), and economically attractive [17].

Different materials have been used for treatment of pharmaceutical drugs in wastewater. Among them are bismuth tungstate (Bi_2WO_6), metal-organic frameworks, TiO_2 - carbon dots, and biopolymer composites among others [18–21]. A recent review reported the applicability of cerium oxides, due to its abundant oxygen vacancies and high oxygen storage capacity, as photocatalyst for the treatment of wastewater containing pharmaceutical drug [22]. Iron-based materials are another interesting material of choice for adsorption and photocatalytic degradation of different pharmaceutical drugs. As a ubiquitous and abundant element with unique chemical properties, iron has an important role in a number of reactions of great importance in natural environments and wastewater treatments.

1.1. Purpose of this review

Although there have been some published review articles on the adsorption/photocatalytic degradation of various types of contaminants, the mechanisms taking place during the antibiotic adsorption/degradation on iron-based materials have not been adequately reported and reviewed. Considering the limited information on the mechanism of interaction of iron-based material with contaminants, Chunming [23] suggested that the focus of future review papers should be tailored toward this. A review work by Aragaw et al., [24] on the iron-based nanoparticle for the removal of contaminants generalized the removal mechanisms basically as adsorption and photocatalytic degradation, while a full understanding of the interaction between contaminants and

the iron-based materials was not provided. The review paper by Seef Saadi Fiyadh et al. [25], on the use of carbon nanotubes for the adsorption of heavy metals, failed to enlighten on the mechanism of adsorption, meanwhile, the authors mentioned chemisorption mechanism which was related to the model that was proposed by Elovich. However, the adsorption mechanism of contaminants cannot only be based on adsorption isotherms or kinetic models, since there is information on the adsorption mechanism which isotherms and kinetic model will not be able to fully provide. Given this, this review seeks to comprehensively study the adsorption and photocatalytic degradation mechanism of some selected contaminants that are reported in the literature, highlighting the characterization techniques that were used to elucidate them.

This review critically analyzed water remediation from pharmaceutical pollutants within the application of iron-oxide-based materials and adsorption/photocatalytic degradation mechanisms. In the addition to profound information, an in-depth explanation of the mechanism pathway was provided. A deep understanding of these mechanisms is more than an issue of basic knowledge but may also give insights into the possible improvements in the performance of materials selected and bring resilience to the process application. The influences of some environment factors were also discussed. Future developments needed for pharmaceuticals-free water and a safe environment have also been explored. We believe this will help the readers in appreciating and applying the benefits of the review in their further studies.

1.2. Iron-based materials

Iron is one of the most abundant elements on earth and is being widely used for remediation [26] in naturally occurring or man-made processes. As the literature proves, iron oxides are the most cost-effective semiconducting materials, capable of absorbing a wide range of visible light due to the values of their bandgap [27]. Examples of iron oxides, hydroxides, and oxy-hydroxides [28] include goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), akaganeite ($\beta\text{-FeOOH}$), ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), hematite (Fe_2O_3), magnetite (Fe_3O_4), among others. They are naturally available and have also been widely synthesized in the laboratory.

Among many iron-based materials, spinel ferrites are one of the most intensively studied and applied for removing pollutants from wastewater. They exist as garnet ($\text{M}_3\text{Fe}_5\text{O}_{12}$), hexagonal ($\text{MFe}_{12}\text{O}_{19}$), and spinel (MFe_2O_4) structures, where M represents (Mn, Fe, Co, Ni, Cu, and Zn) [29]. The two metallic cations, Fe and M are positioned in the tetrahedron or octahedron of the crystallographic sites and coordinated to oxygen atoms; spinel could be in form of normal or inverse spinel (As shown in Fig. 2a) [30]. The occupation of Fe and M in each of the crystallographic sites determines the formation of different forms of spinel ferrite. It is called normal spinel whenever the M cations occupy the tetrahedral sites while Fe cations - octahedral sites. However, it becomes inverse spinel when tetrahedral sites are fully occupied by Fe cations, and the octahedral sites are occupied evenly by the two cations

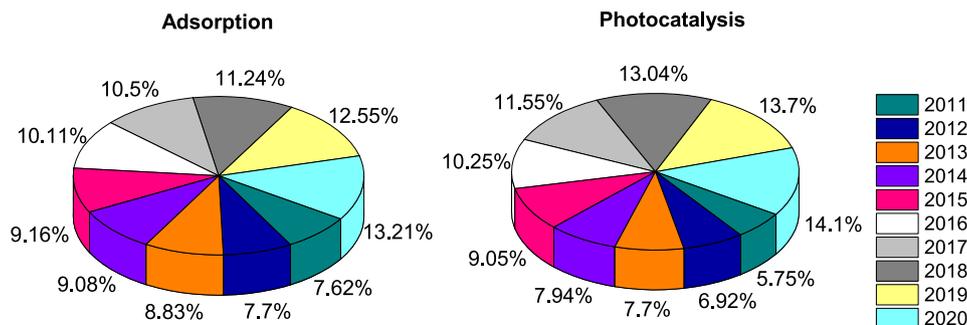


Fig. 1. Diagram presenting the statistical data on publications on adsorption and photocatalysis from 2011 until 2020 (Scopus source).

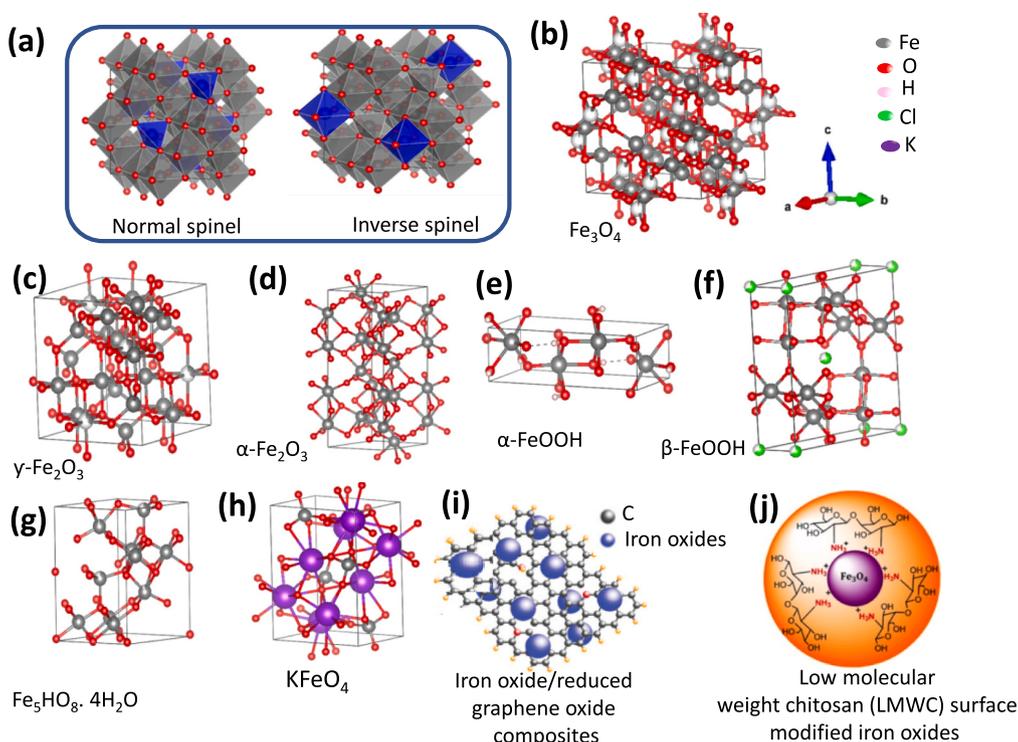


Fig. 2. The crystallographic unit cell of (a) normal and inverse spinel, (b) magnetite (Fe_3O_4), (c) hematite ($\alpha\text{-Fe}_2\text{O}_3$), (d) maghemite ($\gamma\text{-Fe}_2\text{O}_3$), (e) goethite ($\alpha\text{-FeOOH}$), (f) akaganeite ($\beta\text{-FeOOH}$), (g) ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), (h) potassium ferrate (KFeO_4); (i) the composite of iron oxide/reduced graphene oxide, [70], Reproduced with permission, copyright 2013, Wiley; (j) surface modification of iron oxides by low molecular weight chitosan, [71], Reproduced with permission, copyright 2017, Elsevier.

[31]. Both structures are chemically stable. Their magnetic properties make separating them possible with external magnets from aqueous solutions after the adsorption/(photo)catalysis process. The application of cobalt ferrite (CoFe_2O_4) as the catalyst, with a highly active surface for the activation of hydrogen peroxides to degrade doxycycline has been reported by Hong and coworkers [32]. The addition of 1.2 g L^{-1} of the spinel ferrite (CoFe_2O_4) with 10 mM of H_2O_2 resulted in the degradation of 92 % of doxycycline. Two different types of drugs (dipyron and diclofenac) were removed from the aqueous solution by nickel ferrite as studied by Springer et al., (2018) [33]. The study carried out at pH 5.8, showed that 31.2 and 16.8 mg g^{-1} of dipyron and diclofenac were respectively removed by NiFe_2O_4 . This shows the application of spinel ferrites as catalysts and adsorbents.

Magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$) with their crystallographic unit cell are shown in Fig. 2b, c, and d respectively. These various phases have been reported to remove pharmaceutical drugs from aqueous solutions through adsorption/photocatalytic degradation.

Magnetite is an example of inverse spinel ferrite. It differs from other iron oxides in that it contains both Fe(III) and Fe(II) in its crystal structure [28]. All the tetrahedral sites are occupied by Fe(III), while the octahedral sites are occupied equally by Fe(II) and Fe(III) [34,35]. Its magnetic properties have increased its usage for different applications such as drug delivery, water treatment, and so on. Its potential to remove doxycycline at various solution pH, contact time, etc., was studied by Ghaemi and Absalan [36]. This study reported a maximum adsorption capacity of 61.35 mg g^{-1} at pH 3 and 5 min contact time. It was noted that Fe_3O_4 could be reused for three cycles while the adsorption capacity was still maintained.

Hematite is thermodynamically more stable than every other iron (oxyhydr)oxides under atmospheric conditions. Among the few things to know about hematite is that it is also referred to as iron(III)oxide, widespread within the soil and rock matrix, the oldest well-known iron oxides mineral and it is the last product of iron oxides transformation, which made it to be the most stable [28]. It has been a good candidate for different applications, including wastewater treatment. Hematite that was synthesized using pluronic F127-gelatin template, and calcined

at different temperatures, was recently used as an adsorbent and photocatalyst for the elimination of ibuprofen in an aqueous solution [37]. The sample calcined at $500 \text{ }^\circ\text{C}$ removed 55.51 mg g^{-1} (equivalent to 22 %) of ibuprofen at neutral pH by adsorption, whereas during the photocatalytic degradation process, 50 % of the initial concentration was degraded. However, the combination of adsorption and photocatalytic degradation yielded a removal of 80 %.

Maghemite is a ferrimagnetic mineral that is present in soil due to the weathering of magnetite or the heating of other iron oxides [28]. It stands between magnetite and hematite in that it has the same structure as magnetite and the same composition as hematite [38]. Although it is kinetically stable, it slowly turns to hematite and loses its magnetic properties [39]. Like every other iron oxide, its importance in the adsorption and photocatalytic degradation of contaminants has been studied and reported in the literature. One of the advantages of iron oxides is their ability to be reused after removing contaminants. Leone et al., [40], reported that maghemite removed 252 mg g^{-1} of diclofenac at neutral pH [40]. Under the reusability study, it was found that it can remove diclofenac for up to five cycles, and the adsorption was favored at a higher temperature.

The iron-based materials may also be found as oxyhydroxides, which exist in a large variety of structures including goethite ($\alpha\text{-FeOOH}$), akaganeite ($\beta\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), feroxyhite ($\delta\text{-FeOOH}$), and ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), and play an important role in the adsorption of contaminants.

Goethite ($\alpha\text{-FeOOH}$) being the most thermodynamic stable among the iron (oxyhydr)oxides, is a widely spread soil mineral and also a major component of sediments, many ores, and soils [41]. Its structure is made of O^{2-} and OH^- anions which are stacked along [010] directions, while Fe^{3+} , which is surrounded by three O^{2-} and OH^- occupies half of the octahedral interstices (Fig. 2e) [28]. The importance of goethite in the removal of pharmaceutical wastewater cannot be overemphasized. Zhao et al., [42], reported the adsorption of tetracycline, using synthesized goethite. It was observed that over 80 % of tetracycline (50 mg L^{-1} , initial concentration) was adsorbed by goethite at the first 4 h of exposure time of the total 24 h. Aside from strong and rapid adsorption, goethite has been studied to transform tetracycline, leading to the

formation of *N,N*-dedimethylation product [43].

Akaganeite (β -FeOOH, Cl) is often found naturally in an environment such as the marine rich in chloride like rusts, [28]. It has a large tunnel-type structure that is partially filled with chloride anions (Fig. 2f) and has been studied to treat wastewater [44–46]. A study on the removal of oxolinic acid, an antibiotics of the quinolone family using akaganeite was carried out by Marsac et al., [47]. Akaganeite removed approximately 98 % of 10 μ M of oxolinic acid at pH 7.5 marine water. The adsorption was due to the complexation of oxolinic acid in the (010) plane (which is more reactive) of akaganeite. It was also expected that a bridging complex was formed between the Fe at the (100)/(001) plane and oxygens of the carboxylate and keto group of the antibiotic thereby contributing to the adsorption process of the antibiotics on akaganeite.

Ferrihydrite is present naturally everywhere, having a hexagonal crystallographic unit (Fig. 2g), it is highly reactive and used for environmental purposes among others [28,48]. It is commonly present in mine wastes at pH <5, and could also be found in acid mine drainage [49]. Unlike goethite, ferrihydrite is thermodynamically unstable, and it transforms to other stable iron oxyhydroxides (unless stabilized), thereby resulting in a reduction in its high specific surface area and adsorption capacity. Depending on the XRD patterns, it is referred to as 2-line ferrihydrite (2 reflection patterns) or 6-line ferrihydrite (6 reflection patterns) [28]. The application of ferrihydrite for the removal of tetracycline in the rhizosphere environment was recently investigated by He et al. [50]. In that study, ferrihydrite adsorbed 130 mg g⁻¹ of tetracycline in the presence of sodium chloride.

Higher oxidation states of iron exist as +4, +5, +6 and they are known as ferrates [51]. Ferrates(VI), (FeO₄²⁻) (Fig. 2h) are the most stable and easy to synthesize among ferrates [51]. They are a good oxidant and useful in the treatment of wastewater [52,53]. The in situ generation of ferric oxides or hydroxides (due to the reduction of Fe (VI)), made it function effectively as a coagulant, adsorption for the elimination of contaminants, disinfectant of microorganisms, and removal of suspended or colloidal particulates [54,55]. The study carried out by Jiang and Zhou, [56] showed that they can remove >80 % of antibiotics (ciprofloxacin) and 30 % of anti-inflammatory drugs (ibuprofen) at the dose rate of 1 and 2 mg Fe L⁻¹, respectively. The removal of the two pharmaceutical drugs by ferrates is pH-dependent.

Interesting features of some of the iron-based materials are their relatively low toxicity, low cost, large availability, and large reactive surface areas [57]. Modification of iron-based materials has resulted in different morphologies such as core-shell, elongated hexagonal, rock-like, rod-like, and spherical structures among others [58]. However, change in morphology may affect the performance of iron-based materials. Huang et al. [59], noted that the change in the structural morphology of Fe₃O₄@C was the reason behind the reduction of its adsorption capacity for the removal of As (V). Di Iorio et al. [60], also commented that different morphologies of hematite influenced its kinetics and capacity for the adsorption of arsenic.

Iron oxyhydroxides become unstable under acid and reducing conditions, thus requiring Eh and pH control in their applications for water treatment. Studies have shown that leaching of iron from the iron-based materials increases with decrease in the pH of aqueous solution [61], affects its effectiveness for the removal of pharmaceutical drugs, perhaps via adsorption. Another factor that diminishes the performance of iron-based materials is the use of desorbing agents. In an attempt to recover and regenerate pollutant-loaded iron-based materials after adsorption, several desorbing agents such as acids (HCl, HNO₃), among others have been used [62]. These desorbing agents, in one way or the other can reduce the reuse capacity of iron-based materials due to leaching [63]. In the case of photocatalytic degradation, it was reported that iron leaching is an important step that favored the degradation of bisphenol A [64]. The leaching of iron from Fe-BIOCl was responsible for the activation of persulfate, leading to the formation of free radicals and the degradation of levofloxacin [65]. However, as important as iron leaching might be in photocatalytic degradation, its excess was found to be

responsible for the reduction in the degradation of ciprofloxacin by Ag-Fe-TiO₂ [66]. The authors assumed that the excess leaching of iron from Ag-Fe-TiO₂, blocked its active sites making it a dead zone for the photocatalytic process. One should also consider the cost impacts due to the loss of the material by dissolution as well as the consequent accumulation of iron and other elements in the aqueous solution to be treated.

Since the possibility of metal ions being leached in the solution during wastewater treatment may not be ruled out. Iron oxides have been produced as composites with other materials and also in modified forms, as shown in Fig. 2i and j respectively. The incorporation of mesoporous biochar into the matrix of iron oxide nanoparticles has been reported to reduce the leaching of iron from the composites [67]. This will not only slow down the dissolution of metal ions but will also lead to improved stability/efficiency which may not be attained by individual materials. For example, iron oxides/titania nanocomposites that were used as photocatalysts for the degradation of norfloxacin were found to perform better than Fe₃O₄ and titania nanoparticles alone [68]. The addition of 15 % mass ratio of ceria (yCeO₂) to ferrihydrite to form yCeO₂/Fh composites, led to 93.6 % degradation of tetracycline molecules which was found to be higher than 49.2 % that were degraded by ferrihydrite after 60 min [69]. Additionally, modifications prevent the agglomeration of such composites, maintaining their large catalytically active area. A review on the synthesis of different iron oxides can be found in the published paper [24].

2. Possible mechanisms involved during adsorption/ photocatalytic degradation of pharmaceutical drugs on iron-based materials

2.1. Adsorption mechanism

2.1.1. Electrostatic interaction

Electrostatic interactions occur between the charged solid surfaces and the adsorbate in an aqueous solution. It also determines the rate of aggregation and coagulation of particles [72]. This interaction (attraction or repulsion) is a common and well-reported adsorption mechanism between the adsorbent and the adsorbate (Fig. 3a). Considering an oxide surface with terminal hydroxy groups that were protonated or deprotonated at different pH and neutral at the pH termed point zero charges (pHpzc) [73], will likely adsorb cationic and anionic contaminants at pH > pHpzc and pH < pHpzc respectively. The point of zero charge has been defined as the pH at which the net adsorption of potential-determining ions on the oxides is zero [28]. Kosmulski [74] points out that the use in the literature of the two terms (IEP and PZC) are rather confused, the contemporary terminology “restricts the use of the term ‘isoelectric point’ (IEP) to the results obtained by electrokinetic methods, while the term point of zero charge (PZC) is related to the surface charge density σ_0 ”. However, they both provide information about the surface charge of materials. The pHpzc/IEP of some synthesized iron-based materials reported in the literature are; magnetite at pH 6.4–8, maghemite at pH 5.5–7.5, hematite at pH 8.3–9.5, goethite at pH 7.9–8.7, lepidocrocite at pH 7.4–7.7 [74]. Modification/functionalization of iron-based materials has led to an increase/decrease in the pH value of the pHpzc/IEP. Souza et al. [75] observed an increase in IEP of ferrihydrite from pH 7.3 to 8.8 when 20 % Al was incorporated into its structure.

Electrostatic interaction is pH-dependent based on the adsorbent's surface charge and the ionization of the adsorbate. Meanwhile, it is imperative to carry out an analysis that gives information on the surface charge of the adsorbent and know the characteristic behavior of adsorbate at different pH to establish the influence of electrostatic interactions. One of the ways to ascertain this mechanism is through an increase in the ionic strength of the solution [76]. It is expected that whenever an electrostatic attraction exists between the surface of an adsorbent and the contaminant ions, an increase in ionic strength could decrease the adsorption capacity. When there is electrostatic repulsion,

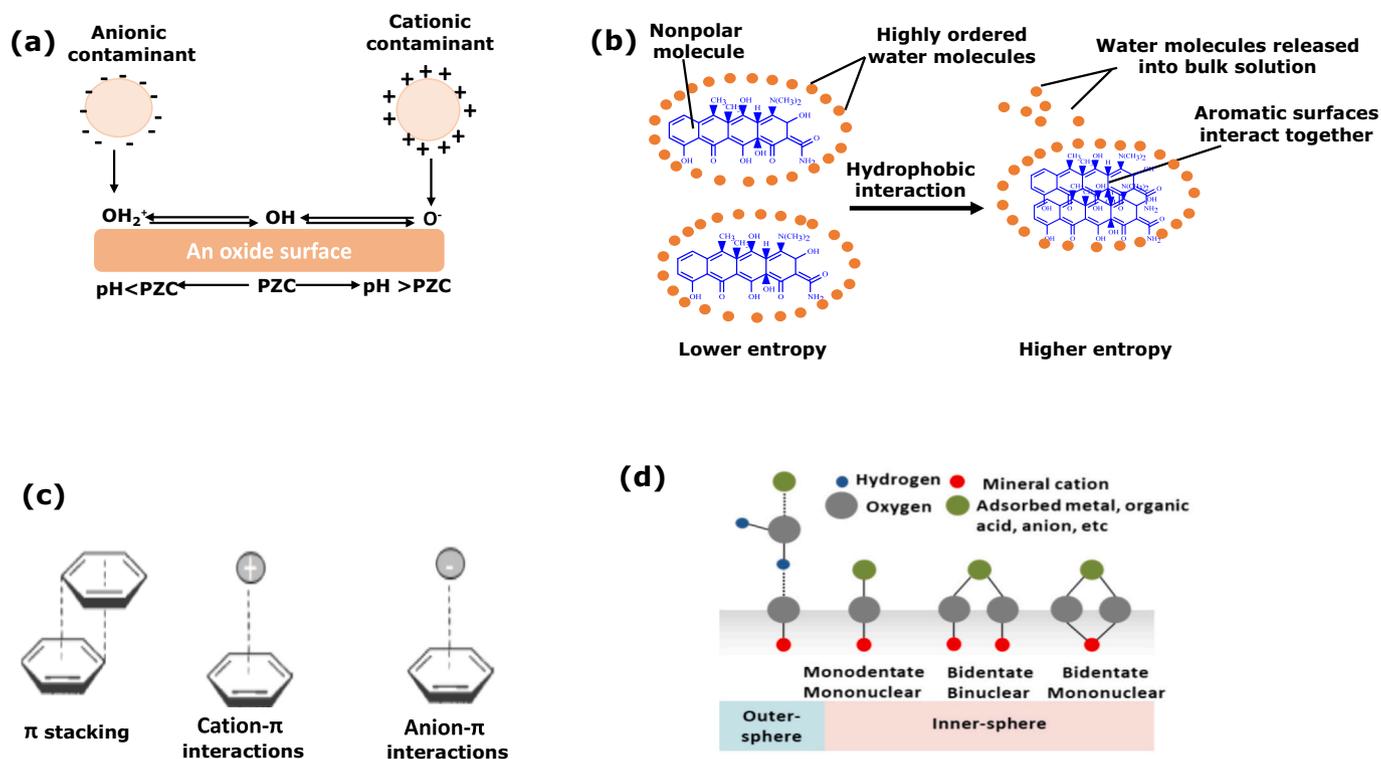


Fig. 3. (a): Schematic electrostatic interaction between ionic adsorbate and charged surface of the adsorbent; (b): hydrophobic interaction; (c): The π -interactions; (d): adsorption complexes on a hypothetical mineral surface.

increasing ionic strength and in turn, the electrical double layer thickness, will decrease repulsion.

The electrostatic attraction was reported for the adsorption of *Acetaminophen*, a pain reliever drug on the surface of magnetite nanoparticles modified with β -Cyclodextrin polymer [77]. The protonation of the amine group of acetaminophen in acidic solutions made it positively charged [78]. Meanwhile, the surface charge of the magnetic polymer was negative between pH 4 and 8; because of this, the existence of electrostatic attraction between the acetaminophen and magnetic polymer led to favorable adsorption of the pharmaceutical. The contribution of electrostatic interaction in the removal of *Sulfamethoxazole* (SMZ), using magnetic biochar was investigated by Reguyal and Sarma, (2018a) [79]. Due to electrostatic attraction between SMZ and the magnetic biochar, the amount adsorbed at acidic pH was greater than that obtained at alkaline pH, while an increase in ionic strength resulted in only a slight increase in the amount adsorbed due to the salting-out effect. In another study, the role of electrostatic interaction in the mechanism of *Cephalexin* (CEP) adsorption on hematite ($\alpha\text{-Fe}_2\text{O}_3$) was investigated by Nassar et al. [80]. The initial pH of the solutions led to an increase in the adsorption capacity for the solutions up to pH 7.5, while a further increase in pH resulted in a significant reduction in the amount removed. This was explained to be due to the negative surface charge of $\alpha\text{-Fe}_2\text{O}_3$ that electrostatically repelled the negatively charged deprotonated COO^- groups of CET molecules. The amount adsorbed also decreased when the ionic strength increased, because of the presence of Cl^- that competed with the COO^- groups of CET. In summary, all these findings showed that ionic strength can be used to ascertain the electrostatic interaction between adsorbents and adsorbates.

2.1.2. Hydrogen bond formation

Hydrogen bond formation between the adsorbate and adsorbent's surface groups is another way through which contaminants could be removed from the aqueous solution. This interaction was first proposed in 1920 by Latimer and Rodebush when they were working on the properties of water [81], and since then it has been widely studied.

According to Chen et al. [82], it is defined as a physical bond that occurs between oxygen (O) and hydrogen (H) atoms that are separated by a distance shorter than 3.5 Å and having an angle smaller than 30° between the donor and acceptor of hydrogen. Much more than this, it is also an interaction between a hydrogen atom (H) with an electronegative atom, such as fluorine (F), oxygen (O), or nitrogen (N) from another molecule (adsorbent or adsorbate), and is weaker than covalent or ionic bonds, but stronger than a van der Waals interaction [83,84]. It is expected that hydrogen bonds could play an important role during the adsorption between the adsorbent and adsorbate bearing functional groups such as amino ($-\text{NH}_2$), carboxyl ($-\text{COOH}$), hydroxyl ($-\text{OH}$), carbonyl ($\text{C}=\text{O}$), and similar groups [85]. This formation of hydrogen bonds can be detected through ATR-FTIR [86], density functional theory (DFT) [87], or other techniques.

FTIR analysis was employed to study the adsorption mechanism of chlortetracycline (CTC) on nano-iron wrapped by graphitic carbon (FGC) via hydrogen bond interaction [88]. Many bands in the spectrum of FGC shifted after the adsorption of CTC, among which are O—H and C—H absorption bands at 3322 and 2922 cm^{-1} , which was due to the interaction between CTC and FGC via hydrogen bond. More so, the adsorption of ofloxacin, a fluoroquinolone antibiotic, on magnetic iron nanoparticles was also confirmed to occur through a hydrogen bond [89]. After analyzing the spectra of magnetic iron before and after adsorption, the authors observed that adsorption bands of O—H at 3424 cm^{-1} and C—O at 1398 cm^{-1} shifted respectively to 3422 and 1383 cm^{-1} due to hydrogen bond interaction between the adsorbent and ofloxacin. Another study reported the use of molecular dynamics simulation to investigate the adsorption mechanism (formation of hydrogen bond, among others) of chlortetracycline on the surface of Fe_3O_4 nanoparticles [90]. The radial distribution function of different functional groups of chlortetracycline toward the Fe_3O_4 nanoparticles was plotted. A radial distribution function (RDF) describes the structure of a molecular system as the variation in particle number density with distance from a reference particle [91]. The plot showed that the molecules of chlortetracycline were adsorbed on Fe_3O_4 nanoparticles via the

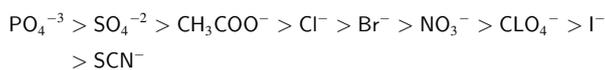
amine and hydroxyl groups due to hydrogen bond formation between the functional groups of chlortetracycline and the oxygen atom of Fe₃O₄ nanoparticle.

2.1.3. Hydrophobic interaction

Another mechanism that explains the interaction between adsorbent and adsorbate is the hydrophobic interaction (Fig. 3b). This interaction occurs due to the tendency of non-polar molecules to unite together in an aqueous solution. Around the middle of the 19th century, the complex problem that is associated with the low affinity of nonpolar molecules for water was discovered, and in this regard, it was postulated as a hydrophobic effect (interaction), that is the aggregation of hydrophobic moieties [92]. Hydrophobic interaction is popularly used in chromatography to describe the tendency toward adhesion between the nonpolar groups of proteins in an aqueous solution and for the separation of protein from impurities [93]. However, the removal of some contaminants was also found to occur through this interaction [94–97].

The association of moiety that is promoted by the effect of hydrophobic interaction is believed to be driven by the desolvation of aromatic surfaces that are interacting together, leading to an increase in the translational entropy of the released water molecules [98]. When hydrophobic molecules are intermixed with water, the total internal energy is lowered in a low entropy state of water [99]. It was added that it is a thermodynamically driven process. Water (a polar solvent), being a poor solvent for proteins (nonpolar molecules), will lead to the aggregation of protein molecules to achieve a state of lowest thermodynamic energy [100]. Before, the aggregation of these non-polar molecules, the molecules of water formed a highly ordered structure around each non-polar molecule. However, the aggregation of the non-polar molecules occurred through the net increase in the entropy of the environment. The aggregation of the molecules leads to a decrease in the surface area of the non-polar molecules' hydrophobic sites, resulting in a less structured condition, in other words, higher entropy, that is the favored thermodynamic state [100], and thus leads to a decrease of Gibbs free energy of the system.

Hydrophobic interaction is more favorable in an aqueous solution of adsorbent and adsorbate that contains a high salt concentration (e.g., NaCl). However, the addition of salts can also weaken the hydrophobic interaction [100]. Salt controls the polarity of a polar solvent and promotes interaction between the hydrophilic and hydrophobic regions of the non-polar molecules and the medium by reducing the solvation of sample molecules and exposing their hydrophobic regions. Listed below are some anions which can promote hydrophobic interaction by decreasing the strength of interaction, from left to right [100].



This mechanism could be ascertained from the information on the partitioning coefficient and solubility of the molecules [101], and also from the effect of ionic strength [102,103] among other ways.

Hydrophobic interaction was proposed as the mechanism of Ciprofloxacin (CIP) on Fe₃O₄/C [104]. According to this study, the adsorption of CIP was maximum at neutral pH. More so, the solubility of the studied antibiotic was very low at pH between 6.0 and 8.7, which implied high hydrophobicity. In another study, Xiang et al. [105] used manganese ferrite-modified biochar (MFB) from vinasse to adsorb pefloxacin mesylate dihydrate (PMD), an example of fluoroquinolone antibiotics. Similar to the earlier report of Shi et al. [104], it was also observed that since the highest amount adsorbed was at pH 5, MFB could offer more hydrophobic sites for the adsorption of PMD that has high water partitioning coefficient. Hence hydrophobicity is related to the water partitioning coefficient and solubility [101], therefore, hydrophobic interaction was proposed as the adsorption mechanism for the removal of PMD.

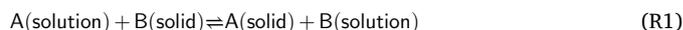
2.1.4. The π -interactions

The π -interactions (Fig. 3c) occur between the electron-rich π system and metal cation (cation- π interactions), anion (anion- π interactions), or another π system (π - π interactions and π donor-acceptor interactions) [106]. In several adsorption processes, cation- π interactions do occur, in this case, metal cations form an interaction with aromatic moieties that are present in organic matter [107]. It was further stated that the strong electrostatic attraction between positively-charged cation and the negatively-charged π electron cloud could lead to cation- π interaction, while the interaction between negatively charged species and electron-deficient aromatic rings results in anion- π interactions [108,109]. The π - π interactions between adsorbent and adsorbate is an adsorption mechanism that is associated with an interaction between a single pair of electrons and a π system in an aromatic ring [110]. This type of interaction in the adsorption process can be investigated using FTIR, theoretical studies, or other techniques.

In the study carried out by Olusegun et al., [17], the authors reported π - π interaction as the mechanism through which tetracycline was adsorbed on the surface of maghemite. This assertion was substantiated by the FTIR analysis of tetracycline and maghemite before adsorption and after the process. According to their report, the C=O band of tetracycline at 1611 cm⁻¹ shifted to 1622 cm⁻¹ after TC adsorption on maghemite. This was proposed as the interaction between the O atom of maghemite and the π electrons of the tetracycline ring. Another study that used nano-akaganeite for the removal of the β -estradiol molecule (though not an antibiotic), reported that the adsorption of the molecule on akaganeite was due to cation- π interactions between the positively charged akaganeite surface and the π -system of the β -estradiol molecule [46].

2.1.5. Ion exchange

Another unique way contaminant is removed by adsorbents is through the exchange of ions. This occurs when adsorbate ions in the solutions are exchanged with similar ions from the surface of solid particles, in this case, an adsorbent [111]. This mechanism of adsorption is a simple reversible process (R1). It is common in the adsorption process in which clay minerals are used as adsorbents [112], but not limited to clay samples [113,114]. The efficiency of adsorbents to remove contaminants through this mechanism depends on their ion exchange capacity. Ion exchange capacity has been defined as the reflection of the ability of an insoluble material to undergo displacement of ions previously attached and loosely incorporated into its structure by oppositely charged ions present in the surrounding solution [115].



The study carried out by Guo et al., [116], investigated the adsorption of tetracycline by nano zero-valent iron (NZVI) modified MCM-41-zeolite A (Fe-MCM-41-A), reported ion exchange as one of the mechanisms that led to the favorable adsorption of the antibiotics. The removal of tetracycline, sulfamethoxazole, and amoxicillin from water using magnetic ion exchange resin (Iron oxide integrated into a macroporous, polyacrylic matrix) was reported to be an anion exchange mechanism that was assumed to be predominated by the exchange of electrons or ions between the active sites of the magnetic resins and the antibiotics [117]. Another study carried out by Pi et al. [118], using extracellular polymeric substances (EPS) modified with magnetic Fe₃O₄ nanoparticles for the adsorption of sulfamerazine, sulfamethazine, and sulfadiazine antibiotics also showed that ion-exchange mechanism influenced the adsorption process.

2.1.6. Complexation

Several electron-rich groups that pharmaceuticals possess have enabled their complexation with different metal ions which then favored their adsorption through the formation of stable metal-ligand complex or intermediate product [119]. Complexation adsorption mechanisms could involve the formation of an inner-sphere or outer-sphere

complexes (Fig. 3d). In the inner sphere complex, there is a direct chemical bond between the adsorbate and the surface of the adsorbent, as in an inner-sphere type solute complex. For the outer-sphere complex, water molecules or hydroxyl groups separate at a critical distance the opposite charged adsorbate and the surface of the adsorbent [120,121]. The effect of ionic strength can be used to determine whether the adsorption mechanism is favored by the inner or outer-sphere surface complex [122]. As outer-sphere complexation relies on electrostatic interactions, the complexes are less stable than those of inner-sphere complexation, which necessarily involves covalent and ionic-type bonding [121].

In the studies that involved the removal of tetracycline from aqueous solutions using iron(III)-loaded cellulose nanofibers and Fe₃O₄ nanoparticles@graphene [123,124], the complexation mechanism was investigated. The authors reported that the adsorption of tetracycline occurred through the inner sphere complexation of tetracycline with Fe ions. Therefore, to verify this, the effect of a co-existing ion was investigated as well. The results showed that ionic strength did not significantly affect the adsorption capacity. Aside from the ionic strength, the existence of a difference in isoelectric point (IEP) or point zero charges (pH_{pzc}) of the adsorbent before and after adsorption is often used to corroborate the contribution of the inner and outer sphere complexation mechanism [125,126].

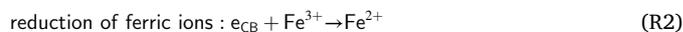
Computational study and X-ray absorption fine structure spectroscopy can be used to investigate the formation of inner-sphere complexation [127]. Models of the solid–solution interface using the basic Stern model that was combined with the charge distribution multisite complexation (CD-MUSIC) model, in which CD-MUSIC calculations were done with the ECOSAT 4.9 program in combination with a recent version of FIT 2.581 had been previously applied to gain insight into the adsorption of tetracycline on the surface of goethite [128]. The study was carried out at both acidic and alkaline aqueous solutions and the results were compared with FTIR analysis of goethite before and after the adsorption of tetracycline. This theoretical study revealed that in an acidic/neutral medium deprotonated tricarbonylamide group interacting with the positively charged surface led to the formation of an inner-sphere monodentate complex ${}^{\ominus}\text{FeTCH}_2^{0.5+}$. Meanwhile, at the alkaline pH, both phenolic diketone and tricarbonylamide groups served as links for the complexation of tetracycline with goethite, leading to the formation of bidentate surface complex Fe₂TC. The latter structure was more stable than the monodentate one, leading to much larger adsorption of tetracycline at alkaline than acidic pH, the authors added.

2.2. Photocatalysis mechanism

Photocatalysis is based on the interaction of semiconductor materials with light and may be described by three important steps (a) light absorption by a semiconductor catalyst to generate electron-hole pairs (excitons); (b) a large portion of excitons can recombine, dissipating their energy by heat or light (or both), however, under controlled conditions, the electron-hole pairs can be separated and transferred to the surface of photocatalysts; for (c) utilization of charges on the surface for redox reactions. The long-lived photogenerated charges on the surface can promote different catalytic reactions, depending on the properties of the surface-adsorbed contaminant species [129]. Photocatalysis is a potential candidate in water treatment due to the green conversion of solar energy into chemical energy leading to the degradation of various organic pollutants [130]. The mechanism of photocatalytic degradation depends on the ability of the catalyst to create electron-hole pairs, which take part in a redox reaction to generate hydroxyl, superoxide and hydrogen peroxide radicals [129,131]. Since electron excitation and transfer in a semiconductor depends on its band structure, and in particular on the value of its bandgap, researchers have been working to provide that the bandgap is not too large to ensure effective electron excitation by the solar energy and subsequent degradation of contaminants.

The mechanism involves the transfer of an excited electron (e⁻) from the valence band to the conduction band of the catalyst due to irradiation energy of photon (that is higher than the energy bandgap of the catalyst), leaving behind a photo-generated hole (h⁺). Generally speaking, the generated holes can react with water to produce hydroxyl radicals (OH[•]). More so, the excited electrons can reduce oxygen to produce H₂O₂, the produced H₂O₂ could subsequently react with excited electrons to further produce hydroxyl radicals (OH[•]) [17].

However, in the case of iron oxide-based materials, it is important to note, that the produced hydrogen peroxide reaction can trigger additional reaction series – the Fenton and photo-Fenton reactions [132–134], and will be discussed below. Additionally, other reactions (R2 and R3) can take place on the surface of iron oxide nanoparticles under illumination:



(At 298 K, the standard potential of the Fe³⁺/Fe²⁺ redox couple is 0.77 V).

The possible mechanisms involved in the photocatalytic degradation of waste pharmaceuticals on iron oxide-based materials can be described based on the band structure of this semiconductor, its bandgap energy (E_g), conduction band energy (E_{CB}), and valence band energy (E_{VB}). The first one (E_g) is typically evaluated based on UV–vis diffuse reflectance spectroscopy using the Tauc approach, whereas the E_{CB} can be assessed through the Mott-Schottky analysis [17,135]. Then, the E_{VB} is the difference between the E_g and E_{CB}.

Literature reports various values of the bandgap energies, depending on the iron oxide studied. The range is between 0.5 eV for magnetite to 2 eV for maghemite [136], while Olusegun et al. (2021) [17] reported the band gap value of 1.83 eV for maghemite. These values were reported for the neutral pH. The band structure of iron oxide can be modified by the environmental pH, but most important – in a controlled way - when the semiconductor is a part of composite materials, changing the photocatalytic properties of the overall system.

Such composites will be presented later in the text for particular photocatalytic degradation processes of different antibiotics. In the case of iron oxide, two mechanisms can be considered at work during the photocatalytic degradation of waste antibiotics: one typical for the semiconducting materials under illumination and the other one related to the photo dissolution of iron oxides. The latter one is characteristic of iron oxides and is called Fenton and photo-Fenton reactions.

Therefore, two mechanisms should be considered for the photocatalytic degradation of antibiotics on iron oxide-based materials and their composites. According to the first mechanism, the illumination of iron oxide generates electrons in the conduction band, e_{CB}, and holes in the valence band, h⁺_{VB}. Then, these highly reactive species can enter a series of surface reactions, involving the electrons in the conduction band (R4, R5) and the holes in the valence band (R6, R7), as follows:



the same time for holes in the valence band

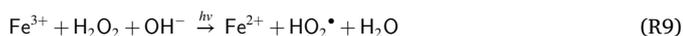


The end-products of the above reactions, the hydroxyl radicals, OH[•], are very reactive and can cause the degradation of the waste antibiotics to carbon dioxide and water as final products.

Suitable modifications of the iron oxide by different dopants can tune its bandgap. The bandgap of hematite increased from 2.22 to 2.45 eV after being doped with ruthenium [137]. Cobalt-doped iron oxides lead

to an increase in bandgap up to 2.5 eV [138]. It was also reported that the bandgap of pure $\text{Fe}_2\text{O}_3 - \text{Fe}_3\text{O}_4$ increased from 2.14 eV to 2.85 eV when it was supported by montmorillonite ($\text{Fe}_2\text{O}_3 - \text{Fe}_3\text{O}_4/\text{montmorillonite}$ composites). However, it reduced to 1.77 eV when the composites were modified with graphene [139]. All these modifications can, also produce other radicals, such as hydroperoxyl radicals HO_2^\bullet , and superoxide $\text{O}_2^{\bullet-}$, radicals, which are further involved in the formation of H_2O_2 and hydroxyl radical OH^\bullet .

The second mechanism of waste pharmaceuticals degradation is related to the formation of hydrogen peroxide, H_2O_2 , by photogenerated electrons in the conduction band and with the well-known photo dissolution of iron oxide leading to free Fe^{2+} and Fe^{3+} ions [140,141] These ions enter the Fenton and photo-Fenton cycle with H_2O_2 , generated in the 2e photoreduction reaction R2 producing more hydroxyl radicals and hydroxyl peroxide radicals (R8 and R9), increasing the effectiveness of photocatalytic degradation of waste antibiotics:



However, reactions R8 and R9 will not be possible in the absence of photoreduction reaction R4 (or H_2O_2 being purposefully added to the solution). It also should be added, that the reaction R7 in the dark is very slow [132,142], but re-generation of Fe(II) can be also accomplished by electrons at the surface of semiconductor under illumination.

The final mineralization of organic pollutants is caused by photocatalytic pathways, involving hydroxyl radicals (OH^\bullet) and hydroxylperoxide radicals HO_2^\bullet (O_2^-) as shown in Fig. 4 (Considering the iron oxides).

The second mechanism of waste pharmaceuticals degradation is related to the formation of hydrogen peroxide, H_2O_2 , by photogenerated electrons in the conduction band and with the well-known photo dissolution of iron oxide leading to free Fe^{2+} and Fe^{3+} ions.

Challenges related to the use of photocatalysts for the treatment of wastewater can be found in a recent review paper [143].

3. Interactions of pharmaceutical drugs with iron-based materials

Pharmaceuticals such as antibiotics and nonsteroidal anti-inflammatory drugs are commonly used and their removal using iron-base materials has been well reported. According to Kümmerer [2], antibiotics are grouped under different categories such as β -lactams (e.g amoxicillin, oxacillin), tetracycline (e.g tetracycline, doxycycline), sulfonamides (e.g sulfamethoxazole), and quinolones (e.g iprofloxacin), among others. The nonsteroidal anti-inflammatory drugs that are used as antipyretic, anti-inflammatory, and analgesic agents include diclofenac, ibuprofen, and acetaminophen among others [144,145]. Therefore, this section centers on the mechanism of their removal from wastewater by iron-based materials.

3.1. Doxycycline

Doxycycline (DOX) is one of the antibiotics that belong to the family of tetracycline which is active against Gram-positive and negative bacteria [36]. Depending on the solution pH, it ionizes to different species. It is in the cationic form at $\text{pH} < 3.5$, while at pH between 3.5 and 7.7 it is zwitterion and at $\text{pH} > 7.7$ it exists as anionic [9]. Its removal from wastewater becomes a necessity just like other antibiotics. Erdite ($\text{NaFeS}_2 \cdot 2\text{H}_2\text{O}$) obtained from goethite, having numerous Fe-S-H and Fe-OH groups, was employed to remove DOX under different conditions, such as solution pH ionic strength and phosphate [146]. This study reported that the DOX removal at acidic pH ($\text{pH} < 5$) is higher than the amount removed at $\text{pH} > 7$, with a maximum adsorption capacity of $1527.17 \text{ mg g}^{-1}$. The adsorption mechanism was attributed to the formation of inner-sphere surface complexation and outer sphere electrostatic attraction between the functional groups of erdite and DOX. It was elucidated that at $\text{pH} < 5$ the amino functional group of DOX is protonated ($-\text{NH}_3^+$), forming stable ligands ($\text{NH}_3^+-\text{S-Fe}$ and/or $-\text{NH}_3^+-\text{O-Fe}$) with the erdite through its available functional groups which facilitated the adsorption process (Fig. 5a). An increase in both ionic strength and phosphate, increased the amount of DOX that was adsorbed, though it was expected that phosphates would hinder the adsorption of DOX due to their affinity for iron ions. However, the adsorption mechanisms of DOX are not only due to its amphoteric nature but also to the surface charge of the adsorbents.

Another study was carried out by Li et al. [147], in which eggshell membrane-derived MgFe_2O_4 was used to effectively remove doxycycline from simulated waste aqueous solutions. This material was reported to adsorb approximately 308 mg g^{-1} of doxycycline at pH 5.4. The results obtained from the effect of solution pH showed that the adsorption mechanism was not related to electrostatic interaction. Therefore, FTIR technique was employed to understand the mechanism that was responsible for the adsorption. It was noted that peaks at 1133 cm^{-1} and 1660 cm^{-1} were due to carbonyl and hydroxyl groups of DOX, respectively, substantially weakened after adsorption, which was ascribed to be due to the formation of a hydrogen bond. The role of π - π stacking interaction which could exist between the aromatic rings of doxycycline (π electron acceptor) and the π electron-rich region of the adsorbent, was not ruled out.

Aside from adsorption, photocatalytic degradation of doxycycline has also been studied. One of the photocatalysts that have been used to degrade DOX (degradation efficiency of 92.18 % within 150 min) in the presence of UV light was $\text{NiFe}_2\text{O}_4/\text{multi-wall carbon nanotubes}$ (MWCNTs) / bismuth oxyiodide (BiOI) with bandgap 1.6 eV [148]. The summary of the degradation mechanism with the effective participation of each constituent in the composites is shown in Fig. 5b. To understand the active species responsible for the photocatalytic degradation, free radical scavengers like 1,4-benzoquinone, isopropyl alcohol, and ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) were added to the solution and the results show that $\bullet\text{OH}$ contribution is minor, implying that $\bullet\text{O}_2^-$ and holes play a major role in the degradation

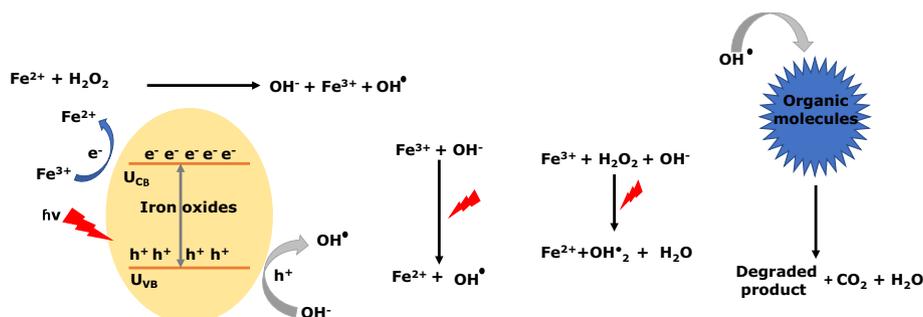


Fig. 4. The schematic illustration of photo-Fenton degradation of organic pollutants by the ferrites upon visible light irradiation modified from [132].

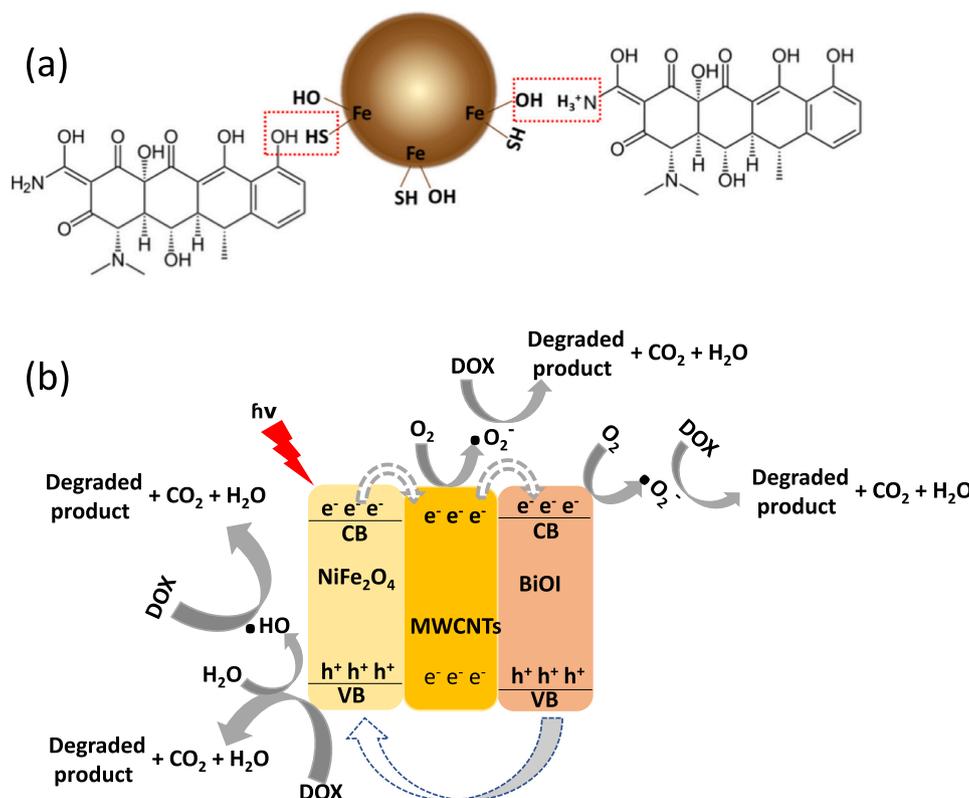


Fig. 5. (a): Interaction between Erdite and doxycycline, (b): Mechanism of DOX photocatalytic degradation by NiFe₂O₄/MWCNTs/BiOI, modified from [148].

process. Upon UV light irradiation, both BiOI and NiFe₂O₄ are excited and generated reactive electrons and holes. In the composite, multi-wall carbon nanotubes (MWCNTs) as shown in Fig. 5b, acted as an electron acceptor from the conduction band (CB) of nickel ferrite and as the transfer channels of an electron to the more positive conduction band (CB) of bismuth oxyiodide (BiOI), thereby prevented the recombination of electrons with holes in the system. Therefore, the electrons (generated by BiOI and those transferred from CB of NiFe₂O₄) at CB of BiOI, were absorbed by O₂ in the solution, leading to the production of reactive oxygen radicals •O₂⁻ which later degraded DOX. At the same time, the same number of holes from the valence band (VB) of BiOI moved to the more negative VB of nickel ferrite, reacted with H₂O, and formed hydroxyl radicals that also participated in the photocatalytic degradation process.

The special tunnel structure of akaganeite, β-FeOOH, has made it an effective photocatalyst for the degradation of some organic contaminants [149,150]. Since the removal process of organic contaminants can be enhanced by adsorption and heterogeneous Fenton degradation, Zhang et al. [151] synthesized sea buckthorn biocarbon@β-FeOOH (SBC@β-FeOOH), for the removal of doxycycline through the adsorption and photocatalytic degradation in a fixed bed column. The idea was for synthesized sea buckthorn biocarbon to provide the adsorption platform for DOX while β-FeOOH acted as the photocatalyst. The mechanism of adsorption as demonstrated in the pH study revealed that electrostatic interaction is involved in the removal of DOX. The adsorbed DOX on the SBC@β-FeOOH was degraded by passing H₂O₂ through the column. The mechanism of the degradation was explained thus: first the generation of •OOH radicals by H₂O₂ through the reduction of Fe³⁺ in SBC@β-FeOOH to Fe²⁺ took place. Subsequently, the SBC@Fe²⁺ further reacted with another H₂O₂ molecule to produce radicals (•OH) and hydroxyl anions. Both •OOH and •OH assisted in the degradation/oxidation of DOX. This showed the great role that iron oxides played in the degradation process. Another heterogeneous Fenton catalytic process carried out by Hong et al., [32] using CoFe₂O₄/H₂O₂ for the degradation of doxycycline

reported the same mechanism as in SBC@β-FeOOH.

3.2. Amoxicillin

Amoxicillin (AMX) is a household name antibiotic that is widely used to treat bacterial infections in humans and animals. It is one of the most commonly used antibiotics, which have been detected in surface water and wastewater treatment plants in countries like India, Italy, and Australia among others [152]. According to documented report, the daily dosage of amoxicillin is higher than other antibiotics. It is one of the essential drugs used in basic health care but unfortunately, it has a low rate of metabolic degradation [152]. The removal of amoxicillin from an aqueous solution by adsorption and photocatalysis processes has been investigated. Kerkez-Kuyumcu et al. [153] prepared magnetic Fe₃O₄/modified graphene nanoplatelets (M-GNPs) for the removal of amoxicillin from aqueous solutions, with a maximum adsorption capacity of 106.38 mg g⁻¹. The pH of the solution was varied from 3 to 11. There was no change in the amount of AMX adsorbed from pH 3 to 5, however, there was a significant reduction in the percentage adsorbed from pH 5 to 11. It is worth noting that AMX has different functional groups: -COOH (pKa₁ 2.69), -NH₂ (pKa₂ 7.49), and -OH (pKa₃ 9.63) that ionize at different pH. A decrease in the amount adsorbed from 5 to 11 was attributed to electrostatic repulsion between negatively charged M-GNPs and AMX. It was observed that there was no significant increase in the adsorption of AMX when ionic strength (KNO₃) was increased from 0.0001 M to 0.001 M. Thus, the electrostatic interaction due to π-π stacking was proposed as the mechanism of adsorption.

A mesoporous adsorbent with FeO_x(OH)_y surface sites, that were produced chemically by restructuring the iron oxides present in red mud obtained from Alcan in Brazil, was used to remove β-lactam antibiotic molecules (e.g., amoxicillin) from aqueous solutions, as reported by Pinto and coworkers [154]. The monolayer adsorption capacity of the adsorbent for the removal of amoxicillin was 39 mg g⁻¹. In a bid to establish the mechanism of adsorption of the targeted antibiotics on the

$\text{FeO}_x(\text{OH})_y$ surface sites, the influence of phosphate and H_2O_2 decomposition was investigated. The results obtained from the presence of competitive adsorbate (phosphate) showed a drastic reduction in the adsorption of amoxicillin. This is because phosphate inhibited the adsorption of amoxicillin (AMX) by the complexation of Fe^{3+} on the surface of the adsorbent. This result suggested that the adsorption occurred on the surface of $\text{FeO}_x(\text{OH})_y$ through Fe^{3+} – AMX complexation. On the other hand, the decomposition of H_2O_2 by Fe^{3+} sites in the presence of AMX was also strongly inhibited due to the complexation of amoxicillin with Fe^{3+} which prevented H_2O_2 from accessing the metal complexation sphere. As shown in Fig. 6a, the adsorption mechanism of amoxicillin on the surface of $\text{FeO}_x(\text{OH})_y$ was through the complexation interaction. Although the complexation interaction was not supported by instrumental analysis such as FTIR, however, it showed that phosphate and H_2O_2 can be used to establish the adsorption mechanism of antibiotics on iron surface sites.

The role of iron oxides in the photo-assisted Fenton degradation of amoxicillin using titanium oxides-graphene (GO)-magnetite was studied by Li et al. [155]. The effect of pH showed that >90 % degradation was obtained at pH 3. Though pH 3 is acidic, for the leaching of Fe, luckily, the leaching of Fe was found to be 0.7 mg L^{-1} which is within the allowable limit of Fe in water [156]. The mechanism (based on the three routes) of the photo Fenton degradation of AMX by TiO_2 -GO- Fe_3O_4 composite under visible light irradiation was explained as shown in Fig. 6b. There was a transfer of excited electrons from TiO_2 to GO. More so, the fast separation of photogenerated electron-hole pairs could probably reduce the recombination of H^+/e^- , which contributed to the degradation of AMX by H^+ leaving the valence band (Fig. 6b, route 1). Magnetite generated an additional OH^\bullet for the degradation of AMX (Fig. 6b, route 2), which was due to the activation of H_2O_2 through the redox potential of Fe(II)/Fe(III) . More so, the excited electron that was transferred to GO could also help to facilitate the reduction process of Fe(III) to Fe(II) and then enhance the Fe(III)/Fe(II) cycle during the Fenton process (Fig. 6b, route 3). It was noted that the cycle of Fe(III)/Fe(II) in the composite led to higher activity and stability for AMX degradation, which confirmed the important role of iron oxides in the whole process.

3.3. Tetracycline

It was in the 1940s that tetracycline was discovered among the class of antibiotics that could prevent the attachment of aminoacyl-tRNA to the ribosomal acceptor (A) site, through the inhibition of protein synthesis [157]. Tetracycline (TC) is a low-cost antibiotic with broad-spectrum activity; making it the second most produced and consumed antibiotic [158]. Its prevalence in the environment is not palatable to humans and the ecosystem, due to this, its removal and photocatalytic degradation mechanism, using iron-based materials have been reported. Ceria (yCeO_2)/ferrihydrite composites synthesized by Huang et al. [69] were found to be excellent photocatalyst for the degradation of

tetracycline. The synergistic effect of the composites resulted in 93.6 % of tetracycline molecules which was higher than the percentage degraded by each component of the composites. The mechanism pathway was proposed as adsorption of TC molecules on yCeO_2 which could occur through both electrostatic interaction or interaction of functional groups and through the interaction of TC molecules with the produced OH^\bullet and O_2^\bullet active radicals. When visible light was irradiated into the system, the adsorption of light energy by yCeO_2 resulted in the production of photo electrons at their conduction band. The produced electron migrated to the surface of the composites yCeO_2 /ferrihydrite which facilitated the transformation of Fe^{3+} to Fe^{2+} , and Ce^{4+} to Ce^{3+} . The addition of H_2O_2 , oxidation of Fe^{2+} and Ce^{3+} to Fe^{4+} and Ce^{4+} respectively, while OH^\bullet were generated simultaneously. On the other hand, the produced photo electrons reacted with O_2 to produce O_2^\bullet . The OH^\bullet and O_2^\bullet active radicals broke down TC molecules. The authors analyzed the composites before and after photocatalytic degradation using XPS. The results showed Fe^{2+} that was absent before the degradation process, now was present after it. Moreover, the peak of Ce^{3+} was enhanced after the process. The mechanism was summarized in Fig. 7a.

Another study was carried out by Wu et al. [159] using ferrihydrite (FED) and goethite (GOE) to remove TC from aqueous solutions. The adsorption capacity of FED and GOE for the adsorption of TC were found ca. 5.65 and 3.25 mg g^{-1} , while their isoelectric point was found to be at pH 6.5 and 7.2, respectively. These two iron minerals were negatively charged at pH higher than IEP. The authors speculated that Fe^{3+} was released from FED in acidic pH values, which complexed with TC and resulted in favorable adsorption at lower pH. The effect of ionic strength showed that the adsorption of the TC was favored by the two minerals when the ionic strength was increased. This was proposed as stable inner-sphere adsorption that occurred through surface complexation. FTIR analysis of TC, after adsorption by the two minerals, showed a shift in the carbonyl group from 1673 cm^{-1} to 1659 cm^{-1} , amino groups at 1526 cm^{-1} shifted slightly, while the ketone group, at 1586 cm^{-1} , could not be detected after adsorption. The authors concluded that carbonyl, amide, and ketone are involved in the complexation mechanism that led to the adsorption of TC on the two minerals (Fig. 7b).

Recently, Olusegun et al. [17] studied the mechanism of photocatalytic degradation of 40 % of tetracycline in solutions within 60 min by maghemite nanoparticles of 1.83 eV bandgap. It was proposed that electrons and holes generated in maghemite by irradiation reacted with oxygen, water, hydroxyl ions, and tetracycline in the solution. The generated holes reacted with OH^- leading to the production of OH^\bullet , the produced hydroxyl radicals then reacted with TC to CO_2 and H_2O as degradation products. Generated electrons were responsible for the oxygen reduction to H_2O_2 . Iron oxides, through photo-dissolution, led to the production of Fe^{2+} and Fe^{3+} . These ions reacted with H_2O_2 to produce the hydroxyl and hydroperoxy radicals, which in turn assisted in the degradation of TC through Fenton and photo-Fenton reactions as summarized in Fig. 7c.

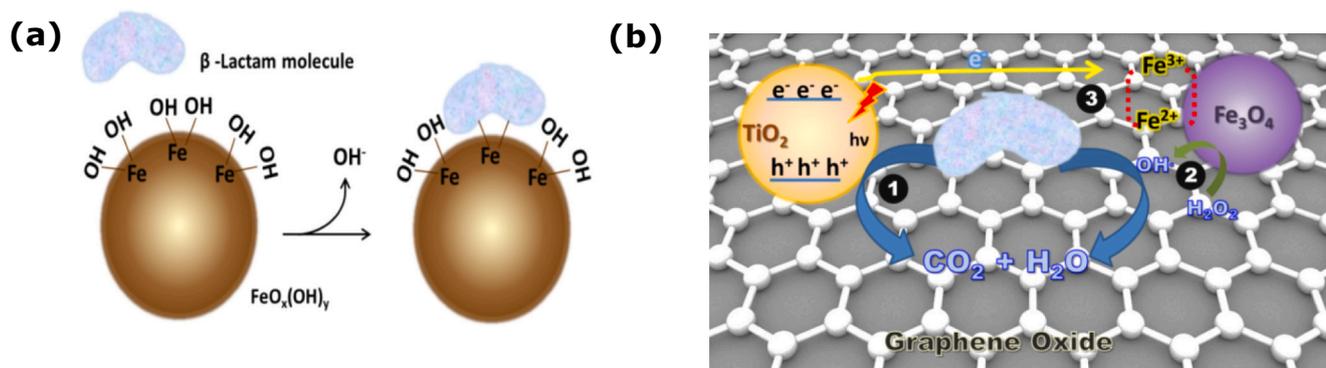


Fig. 6. (a): Complexation/adsorption of AMX on $\text{FeO}_x(\text{OH})_y$ sites; (b): Photo-Fenton degradation of AMX modified from [155].

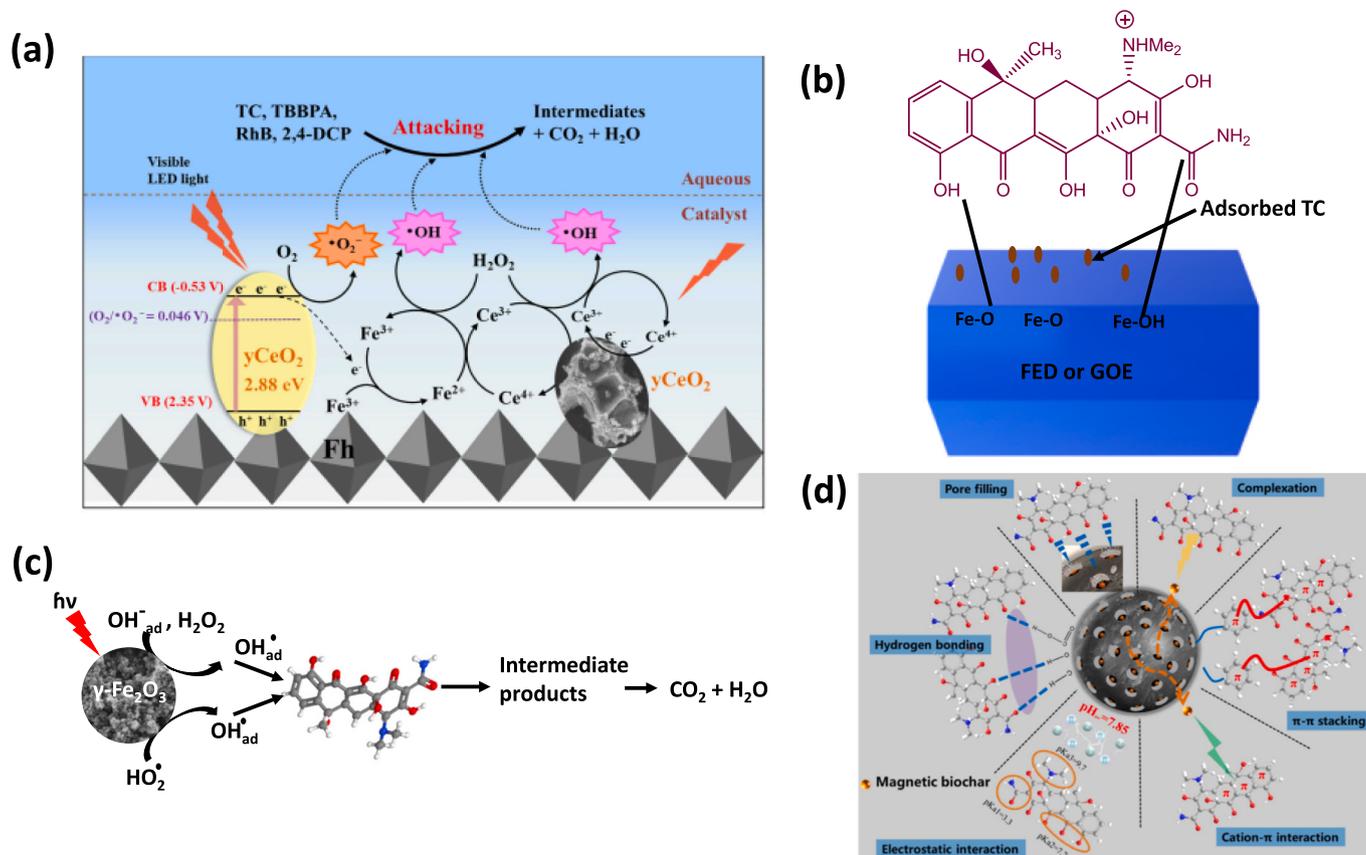


Fig. 7. Mechanism of photocatalytic degradation of tetracycline by (a): $(\gamma\text{-Fe}_2\text{O}_3)$ /ferrihydrate [69]; Reproduced with permission, copyright 2020, Elsevier; (b): ferrihydrate and goethite [159], Reproduced with permission, copyright 2019, Elsevier; (c): maghemite [17], published in MDPI, which is open access and permits copying, adaptation and redistribution under the Creative Common CC BY license; and (d): magnetic biochar [160], published in MDPI, which is open access and permits copying, adaptation and redistribution under the Creative Common CC BY license.

Sun et al., [160] reported the use of magnetic biochar for the adsorption of tetracycline. The study on the effect of solution pH showed that the removal of tetracycline was influenced by pH with the highest adsorption capacity (139.80 mg g^{-1}) recorded at pH 4. It is worth noting that tetracycline exists in different forms in an aqueous solution, depending on pH (just like doxycycline). Based on its pKa, it is present in form of TC^+ (pH < 3), zwitterionic TC^\pm (pH between 3 and 7), and TC^- and TC^{2-} (pH > 7) [161]. Therefore, both surface charge and protonation/deprotonation of TC at different pH influenced its adsorption on the prepared magnetic biochar. The results showed that despite the repulsive force between TC and the magnetic biochar, the adsorption still occurred within the pH values of the investigation. Similarly, Jannat et al. [162] also reported an electrostatic repulsion between TC and Fe-doped zeolite at both acidic and alkaline pH.

To ascertain the adsorption mechanisms, both FTIR and XPS analyses were explored. Some changes were observed in the FTIR peaks of magnetic biochar after adsorption of tetracycline, among which is the peak at 580 cm^{-1} which is related to Fe—O, indicating the interaction between TC and iron cation in the magnetic biochar, since TC generally forms complexes with divalent metal ions [163]. More so, the adsorption peak at 3400 cm^{-1} attributed to the presence of stretching vibration of -OH was noticed to be stronger after the adsorption of TC. This also was suggested to be due to the participation of the hydroxyl group in the adsorption process. It was also observed that the stretching vibrations of C=C and C=O shifted from 1610 cm^{-1} to 1606 cm^{-1} , which also implied their involvement in the adsorption process. In the case of adsorption of TC by Fe-doped zeolite, the peak at 1675 cm^{-1} assigned to the C=O amine group of TC was observed to shift to 1720 cm^{-1} .

Supporting the FTIR results, XPS analysis of magnetic biochar after

the adsorption of TC, showed some differences in the peak areas that were assigned to the presence of carbon (C), oxygen (O), and iron (Fe) in the adsorbent. For carbon (C1s), the peak area at 284.8 eV increased from 1337.01 to 1493.56, while that of oxygen (O1s) at 530.09 eV decreased from 1611.13 to 1511.01, finally for iron (Fe2p) the area of the peak at 710.08 eV decreased from 915.31 to 690.75. Combining the FTIR and XPS results, the participation of Fe—O—Fe, C—O—Fe, C=O/CO, Fe^{2+} , Fe^{3+} , Fe_3O_4 , and FeOOH cannot be overemphasized. Given this, the mechanisms of adsorption of tetracycline using magnetic biochar were proposed to be due to the metal ion complexation, cation - π interactions, hydrogen bonding, and π - π interactions, as shown in Fig. 7d.

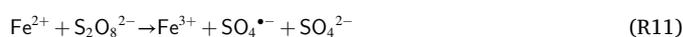
Besides experimental techniques used to determine the adsorption mechanism, theoretical methods became a powerful tool supporting experimental studies. Molecular dynamics (MD) simulation, a computational technique, was used to predict both the adsorption mechanism and isotherm of chlortetracycline on iron oxide nanoparticles [90]. By plotting the radial distribution function of the various functional groups of chlortetracycline toward magnetite atoms, the authors understood the mechanisms involved in the adsorption process. Accordingly, the plot showed that chlortetracycline molecules were adsorbed on the surface of magnetite nanoparticles via both their amine and hydroxyl groups. It was gathered that the peaks of radial distribution function related to amine (NH_2) adsorption were higher and stronger than hydroxyl (OH), which implied that chlortetracycline interacted very well with magnetite through an amine, and resulted in the formation of a hydrogen bond between NH_2 of chlortetracycline and the oxygen atom of magnetite. Aside from the hydrogen bond mechanism, electrostatic interaction was also suggested.

3.4. Ibuprofen

Ibuprofen belongs to the class of propanoic acid derivatives, it is an anti-inflammatory drug that has been widely used among children and adults to relieve pain that occurs in different parts of the body (tooth, head, muscle) and also to lower the rise in body temperature (fever) [164,165]. It has low solubility in water, and its presence in the aquatic has been documented to have harmful effects on microorganisms and fungi, among others [164,166]. It also inhibits the reproduction of waterfleas and fishes [167]. Given this, its removal through adsorption and photocatalytic degradation using iron-based nanoparticles has been reported while the mechanism of interaction has also been elucidated. In the year 2020, Liyanage et al. [168] synthesized Fe₃O₄/Douglas fir biochar (FDB) and applied it to the removal of ibuprofen from aqueous solutions. The point of zero charge (PZC) of FDB is 8.1, and it adsorbed a higher amount of ibuprofen at pH 8, which is above its pK_a 4.91. Ibuprofen being a monocarboxylic acid [169], is dominated by the presence of COO⁻ at pH above its pK_a, therefore, one of the adsorption mechanisms was related to the electrostatic attraction between the positively charged FDB and the COO⁻ group of ibuprofen. It noted that pH above PZC, in which FDB is negatively charged, a significant amount of ibuprofen was adsorbed despite the electrostatic repulsion that was expected to occur between FDB⁻ and COO⁻. The implication of this is that other mechanisms of adsorption occurred in the process. These mechanisms were suggested as hydrogen bond and π-π interaction. Depending on the pH of the solution, the Fe-OH groups of the magnetite could donate or accept nitrogen, while π-π interaction could exist between the aromatic rings of the biochar and ibuprofen as shown in Fig. 8a. Nevertheless, this assumption was not supported by FTIR or other techniques. The adsorption mechanism of ibuprofen on *O*-carboxymethyl-*N*-laurylchitosan/γ-Fe₂O₃ and MnFe₂O₄/GO was as well credited to electrostatic interaction among other mechanisms [170,171].

Another work centered on the reuse of rusted iron particles (RRIP), which has both α-FeOOH and amorphous FeOOH on the shell and zero-

valent iron (Fe⁰) in the core, for the removal of ibuprofen by using both adsorption and persulfate-based advanced oxidation [172]. The study was carried out at pH 7 and the maximum adsorption capacity was 3.47 mg g⁻¹. Although nothing was said about the adsorption mechanism before the degradation process, emphasis was placed on the mechanism that led to the degradation of ibuprofen. The complete degradation of ibuprofen was attributed to RRIP which catalyzed the activation of the oxidant (persulfate), for the generation of radicals. The mechanism of degradation was due to the reduction of Fe³⁺ on the surface of the RRIP to Fe²⁺ by persulfate through the loss of one electron, and resulted in the production of S₂O₈^{•-}. The reduced iron, Fe²⁺ which is less stable, was quickly oxidized to Fe³⁺ by persulfate leading to the generation of SO₄^{•-} + SO₄²⁻. The produced SO₄^{•-}, assisted in the oxidation of hydroxyl ions (OH⁻) to produce hydroxyl radicals (OH[•]), while S₂O₈^{•-} yielded SO₄²⁻ by oxidizing water H₂O, as summarized in reactions R10 to R13. Lee et al., (2020) [173] commented that upon extensive exposure, SO₄^{•-} can rapidly mineralize organic contaminants through the involvement of a more complex oxidation pathway. Therefore, the production of SO₄^{•-} and OH[•] through the activation of persulfate by RRIP, led to the degradation of ibuprofen. The summary of the mechanism is shown in Fig. 8b.



Sulfate radicals can degrade quite a number of pharmaceutical drugs by undergoing a direct electron abstraction and through the transformation of some anions into their corresponding radicals [174]. The role of hydroxyl radical produced along with sulfate radical has been proposed to be significant in the degradation of organic contaminants. However, Ma et al. [175], through the identification of reactive species for the degradation of a pharmaceutical drug using Mg-Fe-

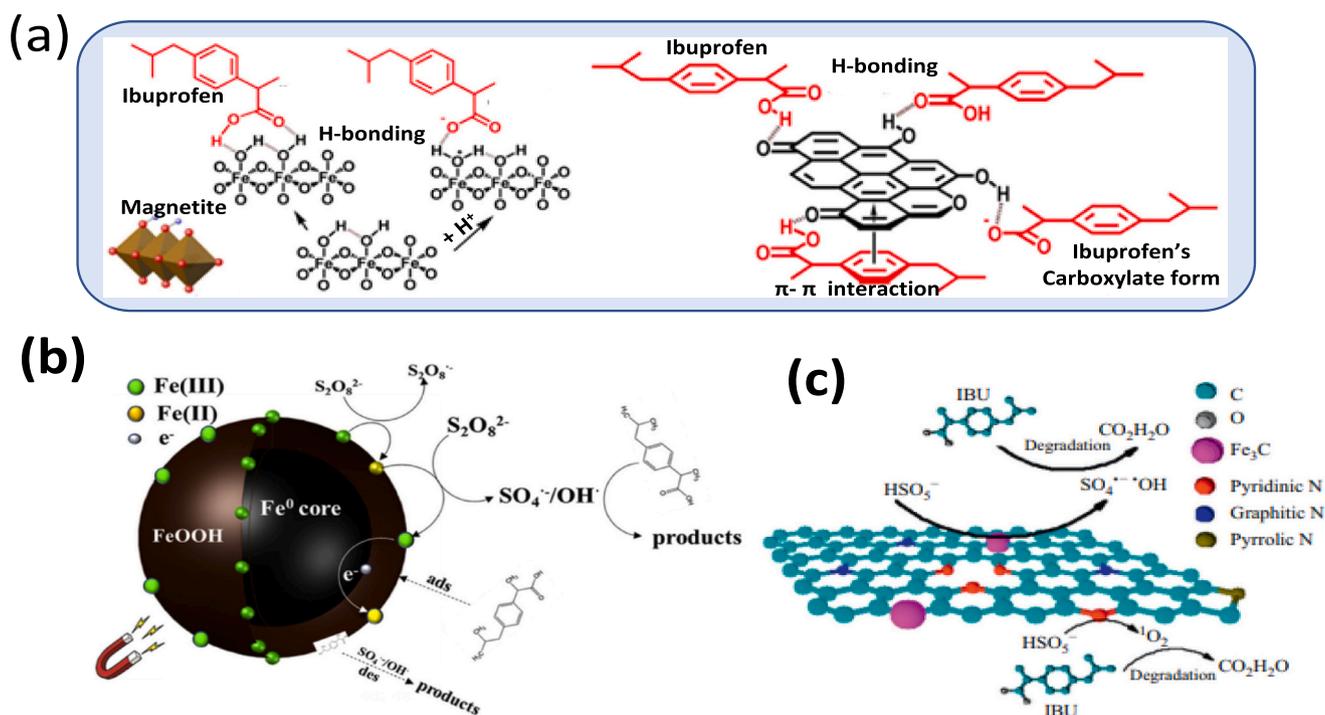


Fig. 8. (a): Adsorption mechanism ibuprofen on Fe₃O₄/Douglas fir biochar [168], Reproduced with permission, copyright 2020, Elsevier (b): Degradation of ibuprofen by reuse of rusted iron particles [172], Reproduced with permission, copyright 2018, Elsevier and (c): Degradation of ibuprofen using Fe₃C nanoparticles embedded in N-doped carbon [176], Reproduced with permission, copyright 2018, Elsevier.

LDH@biochar composite-activated peroxymonosulfate, noted that role of hydroxyl and superoxide radicals was less significant.

Similar to the report of Yin et al., [172] is the study carried out by Zhang et al., [176] in which Fe₃C nanoparticles embedded in N-doped carbon were used to activate peroxymonosulfate for the degradation of ibuprofen. The effect of pH was considered and it was noted that the degradation IBP increased with an increase in pH (till pH 8) then later decreased as the pH got more alkaline, pH > 8. More so, the radical quenching experiments carried out using tert-butanol and ethanol showed that both radicals contributed to the degradation of ibuprofen. The degradation was possible through the reaction with SO₄^{•-} and OH[•] which was produced by the activation of peroxymonosulfate by iron as shown in Fig. 8c. These authors went further to carry out the XPS analysis for estimation of the catalytic mechanism. It was noted that the Fe 2p spectrum before degradation, was deconvoluted into three peaks at 711.3, 725.0, and 719.0 eV, which were assigned to Fe 2p_{3/2}, Fe 2p_{1/2}, and shake-up satellite of Fe³⁺, respectively. After the degradation process, the peaks Fe 2p_{3/2} and Fe 2p_{1/2} were deconvoluted into two peaks which were attributed to Fe²⁺ and Fe³⁺. It was revealed by the high resolution of the XPS spectra that the content of Fe²⁺ increased while that of Fe³⁺ decreased after the degradation process. This confirmed that part of Fe³⁺ was transformed to Fe²⁺ by accepting an electron.

3.5. Acetaminophen

Acetaminophen, also known as Paracetamol (N-(4-hydroxyphenyl)acetamide), is over a counter drug that is one of the most commonly used all over the world to relieve pain and reduce fever [177]. For its broad usage, its worldwide production in 2020 is close to 1 Mt. [178]. It is highly stable, soluble, and hydrophilic; due to this, it is widely exerted with metabolites getting to the soil and water, having an adverse effect on organisms living in aquatic reservoirs. This drug has been even detected in surface and groundwater [179], so its removal is of high importance.

Loc and co-workers [180] have studied the removal of acetaminophen through the adsorption technique. In their study, hematite nanoparticles loaded spherical biochar (H-SB), which was prepared through the direct pyrolysis of glucose-derived spherical hydrochar and FeCl₃, were synthesized and applied for the adsorption of acetaminophen. The result of the effect of pH showed insignificant differences in the amount adsorbed at pH 2, 3, and 4. The amount adsorbed at pH 8 dropped by 14 % when compared to pH 2. Relating the amount adsorbed at pH 8 to 10, there was a drop of 21 %. The surface charge of the synthesized H-SB is negative at pH above 2.5, while acetaminophen was uncharged when the solution pH was <9 (being its pKa value). Therefore, the adsorption at pH <9 was not based on the electrostatic interaction contribution. The adsorption capacity was 49.9 mg g⁻¹ at pH 7.0. As shown in Fig. 9a, the mechanism of adsorption was proposed as firstly, the hydrogen bond between the oxygen atom of H-SB and the hydrogen atom of acetaminophen, secondly π - π interaction between the aromatic ring of the

acetaminophen and the loaded biochar. This was supported by the reduction in the intensity of the C=C bond (1430 cm⁻¹) of H-SB after adsorption of acetaminophen. Thirdly, the ion-dipole interaction, was confirmed by the significant decrease of C-O-Fe vibrations at 554 and 472 cm⁻¹.

Recently, Pattappan et al. [181] produced graphitic carbon nitrate and iron-based metal-organic framework (g-C₃N₄/NH₂-MIL-101(Fe)) through the solvothermal method for the photocatalytic degradation of acetaminophen. The composites degraded 94 % of acetaminophen in an aqueous solution which was more than the amount degraded by the individual entities of the composite. More so to ascertain that the Fenton reaction did not contribute significantly to the degradation process, the experiment that was carried out in the presence of g-C₃N₄/NH₂-MIL-101(Fe) but in the absence of light and H₂O₂, showed that 18 % of acetaminophen was adsorbed. Whereas another experiment in the presence of H₂O₂ and g-C₃N₄/NH₂-MIL-101(Fe) but in the absence of sunlight, it was reported that 12 % of acetaminophen was removed. It was concluded that the photocatalytic degradation was due to the efficient electron-hole separation and the controlled capture of the [•]OH radicals.

During the solar irradiation, electrons were transferred from the valence band (VB) of Fe-MOF (Fe- metal-organic-framework.) and g-C₃N₄ to their respective conduction band (CB), leaving behind holes (h⁺). The effective electron-hole separation (charge separation) was possible due to the transfer of electrons from the CB (having -0.94 eV energy) of g-C₃N₄ to the CB (having -0.53 eV energy) of Fe-MOF as shown in Fig. 9b. The electrons in the CB of Fe-MOF then reacted with O₂ to produce superoxide radical [•]O₂⁻ which promoted the degradation of acetaminophen. The production of the superoxide radical was possible because the CB energy of Fe-MOF is more negative than that of the generation of the superoxide radical (-0.28 eV vs NHE). The hydroxyl radicals were not generated from the system due to their generation potential (2.7 eV vs NHE), which is higher than the VB potentials of both g-C₃N₄ (1.83 eV vs NHE) and NH₂-MIL-101(Fe) (1.11 eV vs NHE). Meanwhile these radicals can be generated after the addition of H₂O₂ to the system.

3.6. Other pharmaceutical drugs

Zheng et al. [182] synthesized a magnetic adsorbent called poly (sodium p-styrenesulfonate hydrate) grafted magnetic carboxymethyl chitosan composites (PMCC) for the removal of ciprofloxacin (CIP). The adsorption capacity of PMCC for CIP was 527.93 mg g⁻¹. The study on the effect of pH showed that changes in the pH of the solution were not consistent with the amount of CIP that was adsorbed. This was due to the functional groups in CIP that exist as cation, zwitterion, and anion at different pH values. The adsorption mechanism was proposed from the FTIR and XPS analysis of PMCC before and after the adsorption. The XPS results showed that the peak at 284.68 eV which is related to C-C/C=C, shifted to 284.54 eV after adsorption. This shift was presumed to be a result of π - π interaction between CIP and the PMCC. This was also

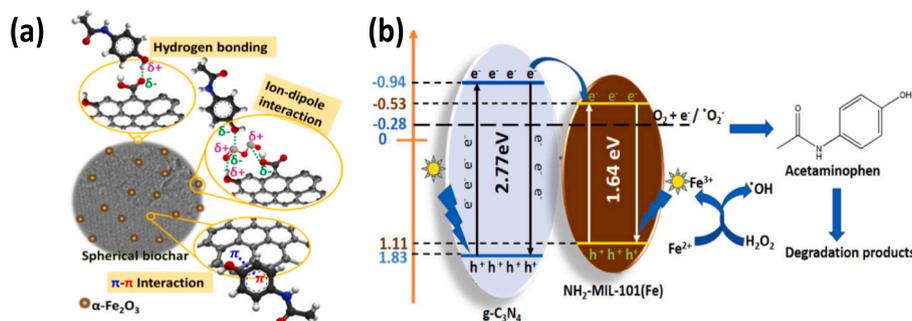


Fig. 9. (a): Mechanisms of acetaminophen adsorption by hematite nanoparticles-loaded spherical biochar (b): Mechanism of photocatalytic degradation of acetaminophen by graphitic carbon nitrate and iron-based metal-organic framework [181], Reproduced with permission, copyright 2022, Elsevier.

confirmed from FTIR spectra in which the C=C peak at 1575 cm^{-1} also shifted to 1625 cm^{-1} after the adsorption. A further possible mechanism was also suggested. This was done by considering the deconvoluted O 1 s XPS of PMCC which comprised Fe—O in Fe_3O_4 , C—O in the alcohol hydroxyl and/or ether groups, and C=O in the carbonyl group. The relative content of these groups before adsorption was 27.05 %, 32.26 %, and 40.68 %, respectively. However, after the adsorption, the content of C—O decreased to 18.82 %, and the proportion of C=O increased to 41.60 %. This was assumed to be due to hydrogen bond interaction. Therefore, combining the pH studies with FTIR and XPS analysis, the authors presumed hydrogen bonding, strong π - π interaction, and electrostatic interaction as the adsorption mechanism for the removal of ciprofloxacin.

Having known the toxicity effects of the presence of levofloxacin (LVX), a micro-pollutant, in the environment, (antibiotic widely used to deal with the Gram-positive and Gram-negative bacterial strains and having higher activity than racemic ofloxacin), Chaturvedi et al. [183] synthesized iron-based metal-organic frameworks (MIL-100(Fe)) for the removal of this compound from the aqueous solutions. The adsorption process was fitted to Langmuir isotherm with a maximum adsorption capacity of 87.34 mg g^{-1} . The study on the effect of pH showed that the adsorption of LVX increases from pH 6 to 9, then declines at pH 10, a negligible amount was adsorbed at pH 11. The surface charge of MIL-100(Fe) was negative for $\text{pH} > 3.2$. Given this, the authors ascribed the adsorption of LVX to the electrostatic attraction between LVX and MIL-100(Fe). They stated that LVX exists in zwitterionic form between pH 5 to 8.5, which facilitated the strong adsorption between pH 6 to 9. However, at higher pH, it became anionic and resulted in the electrostatic repulsion between its molecules and the negatively charged surface of MIL-100(Fe). The possibility of a hydrogen bond mechanism was also suggested in addition to the electrostatic interaction.

Cephalexin (CEX) belongs to the cephalosporin group of antibiotics that is widely used to treat infectious diseases in humans and animals and is also useful in agricultural and aquatic sectors [184]. Since it has low degradability, Rashtbari et al. [185] produced powdered activated carbon that was coated with zero-valent iron nanoparticles (denoted as PPAC-nZVI) for the adsorption of cephalexin (CEX) from aqueous solutions. The maximum adsorption capacity was found to be 87.18 mg g^{-1} . The pH (3–11) of the aqueous solution of CEX was among the parameter that was studied. According to the results, the percentage of CEX that was adsorbed decreased with an increase in pH. This observation was attributed to the electrostatic attraction between the negatively charged CEX molecules and positively charged PPAC-nZVI surface. A minor shift in the FTIR spectra was noticed after adsorption. Therefore, the authors assumed that the shifts that occurred for phenolic O—H peaks, aromatic C=C bonds, and alkoxy C—O bonds, could be due to the interaction between oxygen-containing functional groups of PPAC-nZVI and CEX molecules. In their submission, they established a π - π interaction between sp^2 -hybridized domains of PPAC-nZVI and the aromatic ring of CEX. The possibility of a hydrogen bond was well affirmed as shown in Fig. 10a.

Norfloxacin (NOR) and *Ofloxacin* (OFL) are fluoroquinolones antibiotics, that are commonly used in humans and animals due to their high antibacterial activity against Gram-negative and Gram-positive bacteria [186,187]. To minimize the harmful effects of the class fluoroquinolones antibiotics, Zhao et al., [188] synthesized zero-valent iron that was supported on zeolite and stabilized by polyethylene glycol (PEG-4000) (PZ-NZVI), for the removal of NOR and OFL from aqueous solutions. The surface charge of PZ-NZVI was negative at pH above 3.47 (pHpzc). The maximum adsorption capacity of PZ-NZVI for NOR and OFL is 54.67 and 48.88 mg g^{-1} respectively. The effect of pH showed an increase in the amount of NOR and OFL adsorbed from pH 2 to 4, reached a maximum

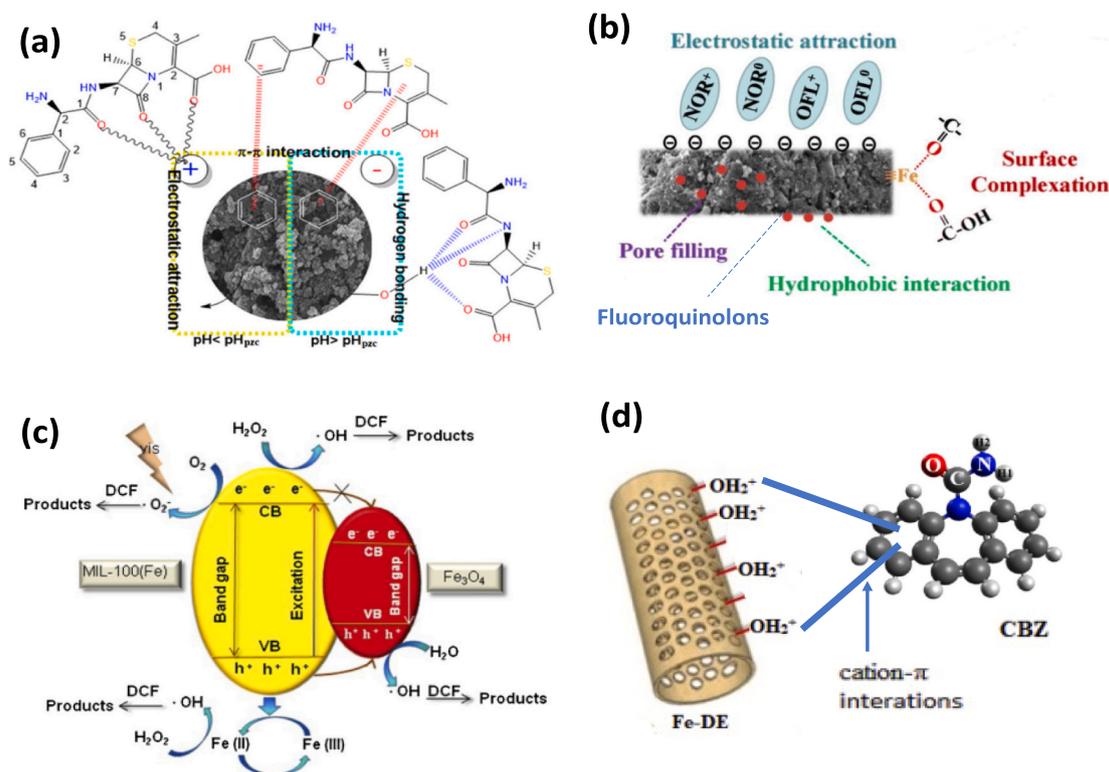
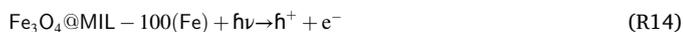


Fig. 10. (a): Electrostatic attraction, hydrogen bonding, and π - π interaction as the adsorption mechanism for the removal of Cephalexin [185]; Reproduced with permission, copyright 2020, Elsevier. (b): adsorption mechanism of NOR and OFL on PZ-NZVI [188]; Reproduced with permission, copyright 2020, Elsevier. (c): the proposed mechanisms of the photocatalytic degradation of diclofenac by Fe_3O_4 @MIL-100(Fe)/vis/ H_2O_2 system [192]; Reproduced with permission, copyright 2019, Elsevier, and (d): cation- π interaction of carbamazepine (CBZ) and iron oxides modified naturally occurring diatomaceous earth (Fe-DE) [198]; Reproduced with permission, copyright 2020, Elsevier.

at 4 to 8, decreased gradually at pH 9 and 10, and declined sharply at pH 11. This behavior was attributed to the cationic, zwitterion, and anionic forms of both antibiotics at different pH. Both electrostatic attraction and repulsion occurred at different pHs, but the adsorption was not limited to electrostatic interaction. Their results on the influence of ionic strength (at pH 6.5) revealed a decrease in the amount of NOF and OFL that was adsorbed by PZ-NZVI, which confirmed that electrostatic attraction was suppressed by the presence of Ca^{2+} . Other mechanisms, such as surface complexation between Fe on the adsorbent and O in the keto and carboxyl groups of the antibiotics, were proposed (Fig. 10b). The possibility of hydrophobic interaction was also assumed to be another possible mechanism in addition to pore filling.

One of the non-steroid anti-inflammatory drugs (NSAIDs) commonly used by humans and animals as an antirheumatic, analgesic, and anti-arthritis agent is *Diclofenac* (2-(2-(2,6-dichlorophenylamino) phenyl) acetic acid) [189,190]. Due to its high usage, it is reported to be present in freshwater and remains absorbed in the soil and on the suspended particles [191]. Like every other pharmaceutical drug, its presence in the environment is not palatable to the well-being of terrestrial ecosystems. Therefore, $\text{Fe}_3\text{O}_4@\text{MIL}-100(\text{Fe})$ was synthesized and used to remove diclofenac sodium through both adsorption and photocatalytic mechanisms [192]. The adsorption study was carried out at pH 6.2, with approximately 400 mg g^{-1} removed. Although the mechanism of adsorption of diclofenac on the synthesized material was not discussed, the photocatalytic degradation mechanism was explained as shown in reactions R14 – R19. Irradiation of visible light on $\text{Fe}_3\text{O}_4@\text{MIL}-100(\text{Fe})$ in the presence of H_2O_2 and diclofenac led to the generation of electron (e^-)-hole (h^+) pair from the Fe–O cluster. The photoinduced electron further reacted with H_2O_2 and O_2 to produce $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals respectively. On the other hand, the generated holes reacted with water to produce $\cdot\text{OH}$ radicals as well. Reactions R18 and R19 introduced the Fenton cycle into the degradation process. In summary, diclofenac was degraded into CO_2 , H_2O , and by-products by the formed active species (h^+ , $\cdot\text{OH}$, and $\cdot\text{O}_2^-$) as shown in Fig. 10c.



Carbamazepine (5H-dibenzazepine-5-carboxamide; CBZ), is classified as class II according to the Biopharmaceutics classification [193]. This was based on its low solubility and permeability, which resulted in its poor bioavailability [194]. This drug is an antiepileptic drug used to alleviate epileptic episodes, and neuropathic pain; and is useful in the treatment of seizures, trigeminal neuralgia, and psychiatric conditions, including depression and bipolar disorder for its stabilization of biological membranes through the binding of the sodium channels [195,196]. It degrades slowly in the environment when released into the water body, thus becoming hazardous to human and aquatic lives [197]. Diatomaceous earth (DE) that was modified with iron-oxide (Fe-DE) was synthesized and applied for the removal of carbamazepine (CBZ) from an aqueous solution by Jemutai-Kimosop et al., (2020) [198]. Considering the effect of solution pH (2–10) on the adsorption of CBZ, it was noticed that increasing the pH of the solution showed an insignificant effect on the adsorption of CBZ. The point of zero charge of Fe-DE was 6 while CBZ existed as neutral species within the studied pH range. Given this, the authors concluded that electrostatic attraction does not play a role in the adsorption mechanism. Therefore, the cation- π interactions between the positively charged surface of Fe-DE and the π aromatic ring

of the CBZ molecule were proposed as the likely mechanism of adsorption as shown in Fig. 10d. This result was similar to what was earlier reported by Rajendran and Sen, (2018) [199] in which hematite was used to adsorb CBZ. It was noted by Rajendran and Sen that solution pH does not present a significant effect on the adsorption of CBZ. However, the proposed adsorption mechanism was hydrogen bonding between amide groups of CBZ and the functional group of hematite.

Nasseh et al., [200] synthesized $\text{FeNi}_3/\text{SiO}_2/\text{CuS}$ (FSC) magnetic nanocomposite for the removal of *Metronidazole* (MNZ) from aqueous solutions. The adsorption capacity of the FSC for removal of MNZ was $135.135 \text{ mg g}^{-1}$. The effect of pH, as a means of proposing an adsorption mechanism, was studied within the range, 3, 5, 7, 9, and 11. The amount adsorbed increased gradually with an increase in pH, peaked at pH 7, and later declined. The pH_{zpc} of FSC was at pH 6.98. At acidic pH, MNZ was said to be protonated ($\text{MNZ}-\text{H}^+$), which resulted in the repulsion between positively charged FSC and $\text{MNZ}-\text{H}^+$, leading to a reduction in the amount of adsorbed MNZ at acidic pH. The maximum amount of MNZ was adsorbed at pH 7 because there was no repulsive force between FSC and MNZ. At $\text{pH} > \text{pH}_{\text{zpc}}$, FSC and $\text{MNZ}-\text{OH}^-$ exhibited the same charge (negative), repelled each other, and resulted in a reduction in the amount adsorbed. The authors presumed that electrostatic attraction may not play a role in the adsorption mechanism. Therefore, complex formation between the FSC surface and MNZ molecules as well as $\pi-\pi$ interaction, was proposed as the major mechanism of adsorption.

Sulfamethoxazole (SMX) is an antibiotic that belongs to the sulfonamides, they are weak acids and highly polar compounds group, used for the treatment of ailments in animals and humans [201,202]. Zhang [203] employed Fe-impregnated graphited biochar to remove SMX from aqueous solutions. The adsorbent was prepared at different impregnating FeCl_3 solutions and pyrolysis temperatures. The synthesized MCB with 300 mM Fe concentration, calcined at 800°C has the adsorption capacity of 187.31 mg g^{-1} for SMX removal. The results from the effect of pH showed that the adsorption of SMX was governed by pH, implying that electrostatic interaction played a role in the adsorption mechanism. The summary of the XPS analysis of MBC after adsorption showed that the signal intensities of oxygen-rich functional groups, like as O–C=O, O–H, and C=O, significantly decreased, indicating that the -OH and -COOH groups of MBC played an important role in the adsorption process through hydrogen bonding or Lewis acid-base interactions, as reported by the authors. FTIR analysis of MBC before and after the adsorption showed that the C=C band at 1645 cm^{-1} shifted to 1589 cm^{-1} , which was assumed to be due to the existence of $\pi-\pi$ electron-donor acceptor interaction. It was added that the Fe species in MBC enhanced its overall adsorption capacity for SMX.

Listed in Table 1 are different iron-based materials and their adsorption and photocatalytic degradation mechanism for pharmaceutical drugs.

4. The influences of environmental factors (natural organic matter, cation, anion) on the removal of pharmaceutical drugs

Different ions (cations and anions) and dissolved organic matters/natural organic matter that are present in environment can influence the removal of pharmaceutical drugs in various ways. Depending on geographical location and anthropogenic activities, the concentration of inorganic anions such as NO_2^- , HCO_3^- , Cl^- , NO_3^- and SO_4^{2-} is within the range of 10^{-5} to 10^{-3} M [227]. Their influences during adsorption and photocatalytic degradation processes differs. To understand the influence of these environmental factors on the treatment and mechanism of pharmaceutical drugs, different authors have reported their findings. Among the authors, Al-Hetlani et al., [228], investigated the effect of cations (sodium, potassium, calcium and magnesium) and anions (chloride, sulfate and hydrogen phosphate) present in tap water on the removal of promazine by activated carbon modified with spinel ferrite nanoparticles. They found out the adsorption capacity reduced from 90.91 to 76.92 mg g^{-1} . It was gathered that the reduction was due to the

Table 1
Adsorption and photocatalytic degradation mechanism of pharmaceutical drugs on iron-based materials.

Iron-based materials	Pharmaceutical drugs	Mechanism		References
		Adsorption	Photocatalytic degradation	
Fe ₃ O ₄ magnetic nanoparticles Mg-Fe-LDH@biochar	Doxycycline	Complexation	Due to •OH, SO ₄ ⁻ and O ₂ ⁻	[36]
	Doxycycline			[175]
Carboxymethyl cellulose and chitosan modified Fe ₃ O ₄ /alkaline Ca-bentonite	Doxycycline	Complexation, electrostatic attraction and deposition		[204]
BiOBr/FeWO ₄ composite	Doxycycline		Due to O ₂ ⁻ and h ⁺	[205]
CoFe ₂ O ₄ /H ₂ O ₂	Doxycycline		Due to •OH	[32]
Magnetic metal-organic framework (MIL-53(Fe)/ Fe ₃ O ₄)	Doxycycline	Electrostatic interaction		[12]
ZnO@/Fe ₃ O ₄	Amoxicillin		Due to •OH _(free) and •OH _(ads)	[206]
Fe ₃ O ₄ /SiO ₂ /CTAB-SiO ₂	Amoxicillin	Electrostatic interactions		[207]
Fe ₃ O ₄ /activated carbon	Amoxicillin	Electrostatic interactions		[208]
ZnFe ₂ O ₄ /PCz	Amoxicillin		Due to •OH and O ₂ ⁻ radicals	[209]
Nanoscale zero-valent iron	Amoxicillin		Due to •OH	[210]
Green synthesized iron oxide nanoparticles	Amoxicillin		Electrostatic interactions	[211]
Iron metal-organic framework (MIL-53(Fe))	Tetracycline hydrochloride	π-π interactions		[212]
Fe-N modified biochar	Tetracycline	Hydrogen bond interaction, surface complexation, π-π stacking		[213]
Nano-iron wrapped by graphitic carbon	Chlortetracycline	Electrostatic interaction, surface complexation, hydrogen bond, and π-π EDA interaction		[88]
Fe ₃ O ₄ /graphene oxide/ZnO	Tetracycline	Electrostatic attraction, π-π interaction, hydrogen bonding, cation exchange, and complexation.	Due to •OH and O ₂ ⁻ radicals	[214]
Hydrous Ferric Oxide	Tetracycline	Electrostatic interactions, hydrogen interactions, and complexation		[215]
Iron(III)-loaded cellulose nanofibres	Tetracycline	Surface complexation, hydrogen bonding, electrostatic interaction and van der Waals force.		[124]
Fe ₃ O ₄ /Bi ₂ WO ₆	Ibuprofen	Complexation	Due to HO ₂ [•] , HO [•]	[216]
Ferromanganese modified biochar (Fe/Mn-BC)	Levofloxacin	Hydrogen bond and π-π stacking		[217]
Zero-valent Iron/activated carbon	Chlortetracycline	Electrostatic attraction and surface complexation		[218]
Magnetite (Fe ₃ O ₄)	Ciprofloxacin	Inner-sphere complexation		[219]
Fe-MCM-41	Norfloxacin	Hydrophobic, electrostatic, π-π interactions, and surface complexation.		[220]
Fe-loaded biochars	Levofloxacin	Hydrogen bonding, electrostatic interactions, and bidentate complexation.		[221]
Fe ₃ O ₄ /GO/citrus	Sparfloxacin	π-π, H-bonding, hydrophobic and electrostatic interactions		[222]
CuZnFe ₂ O ₄ -biochar composite	Sulfamethoxazole	H-bonding, hydrophobic, and π-π interactions		[223]
Fe-pillared montmorillonite	Levofloxacin	Mononuclear bidentate complex		[224]
Fe ₃ O ₄ /sawdust biochar	Sulfamethoxazole	Hydrophobic interactions		[225]
Fe ₃ O ₄ -chitosan	Metronidazole	Electrostatic interactions		[226]

presence of listed cations and anions which competed with the adsorption sites of the magnetic composites via electrostatic interaction thereby hindered the adsorption of promazine. The degradation of carbamazepine by Co-Fe bimetal catalyst was also inhibited in the presence of increased ionic strength (cation and anions) and humic acid [229]. Meanwhile, another report showed that an increase in Na⁺ and Cl⁻ resulted in an increase in the amount of organic pollutant that was removed from an aqueous solution [230]. Therefore, the effect of cations or anions on the adsorption of different organic pollutants is complex because it depends on the structure and properties of the adsorbent and adsorbate [231].

The presence of natural organic matter (NOM) in the environment is due to the decay of.

biological materials, [232] and it has been found to reduce the sorption capacity activated carbon during water treatment. Reguyal and Sarmah [233] investigated the effect of NOM on the adsorption of sulfamethoxazole by magnetic biochar. It was found that the presence of NOM did not inhibit the adsorption of sulfamethoxazole. During photocatalytic degradation, the presence of natural organic matter (NOM), in wastewater containing organic contaminants has been found to absorb light irradiation therefore competing with organic contaminants for the incident light [227]. It was also reported that the reaction of NOM with hydroxyl and sulfate radicals was rapid and inhibited the

degradation of ciprofloxacin due to the competition for hydroxyl and sulfate radicals by NOM that scavenged these radicals [174]. Therefore, NOM interferes with the photocatalytic mechanisms through the inner filter effect and radical scavenging [234].

5. Consideration for future studies

Due to the growing consumption of pharmaceutical drugs to treat various diseases, including veterinary use, their widespread in environment has become a serious and increasing problem affecting public health and ecosystems, thus bringing worldwide concerns for more efficient wastewater treatment. Novel solutions based on the nano-structured iron-oxide particles and their composites offer efficient and relatively simple water remediation. To predict the adsorption mechanism of pharmaceuticals, and to develop robust processes (i.e., resilient to modifications in the wastewater to be treated), there is a need to comprehensively understand the surface properties of iron-based materials [154]. The use of techniques such as FTIR and XPS is encouraging and have been brought relevant results in the understanding of adsorption mechanisms and identification of reaction sites. However, it is quite worrisome that some authors still assumed adsorption mechanisms in their studies without thorough investigation through the use of other techniques. More so, it is high time authors stopped using only

mathematical models (kinetic and isotherms) to predict the mechanism of adsorption. Though these equations are useful fitting tools, they often offer very little in terms of understanding the interaction between adsorbents and adsorbates.

Listed below are some of the concern and consideration for future studies.

- Complementary to the experimental techniques, DFT (density functional theory) calculations can deliver essential information on the mechanism of contaminants removal [235].
- Since iron oxides can be easily modified chemically, doping with transition metals or the formation of its composites can drastically change the physicochemical properties of these materials including the band-gap, enabling the treatment of a broad range of chemicals in the wastewater [236,237].
- One of the main issues with the use of these semiconducting catalysts is the toxicity of the post-products generated within the catalytic or photocatalytic processes. Since these processes lead to the significant degradation of pharmaceutical-based pollutants, still, many of them are toxic. Moreover, natural aquatic reservoirs and wastewater are media full of different compounds and ions that can undergo chemical reactions with the post-products of the degradation leading to the increase of the other compounds that could have adverse effects on the health. Thus, their removal should be maintained along with the degradation or photocatalytic degradation [143].
- Since there are possibilities for iron oxides to easily lose their adsorption capacity due to dissolution and aggregation, therefore, more studies should be carried out on the modification of their surface to improve stability in the operational conditions and improve the sorption capacity, especially the post-catalytic products that should be removed from the solutions [238].
- The possibility of regenerating iron-based thermally stable materials could be investigated rather than focusing solely on chemical solutions for regeneration. Desorbing the adsorbed pharmaceuticals from the thermal stable adsorbents using thermal treatment has proved to be an effective and safer way of ensuring that these contaminants do not find their way back into the environment [239,240].
- There is a deep need to develop post-treatment use of iron-oxides-based materials, especially for their re-use or adsorbed pollutants management.
- Most of the approaches in water remediation are focused on the model compounds rather than the application in real wastewater treatment. Still, too few studies are performed on the real conditions such as drinking water, sewage water, and wastewater. The stability and selectivity of the iron-based materials in different media is an important topic to be included in the investigations.
- There is a need to provide field studies in the area of wastewater and soil remediation. It is important to develop computational models in the complex media far from the laboratory-controlled conditions representing the natural environment.
- There is also a need to determine the impact of the used materials on biota especially when it comes to the field tests, where used materials can easily get to the food chain.

Apart from the high sorption efficiency catalytic properties, and reusability of iron-oxide-based materials, the industrial application of these materials is still limited. For that reason, future studies should emphasize sustainable approaches.

6. Conclusion

The consequences of the accumulation of pharmaceutical-based compounds in the environment lead to several problems like the development of antibiotic-resistant bacterial strains, adverse effects on health through the prolonged exposition on drugs and their metabolites, and impact in the ecosystems. However, extensive efforts have been

made in water remediation technology, still there is a need to develop innovative, low-cost, and efficient strategies to protect the natural environment. Besides many solutions, iron oxide-based materials bring considerable attention to the emerging contaminants treatment in wastewater. They may offer facile separation from the post-treated solutions using external magnets, low costs treatment, high active volume-to-ratio surface and catalytic properties, and high chemical stability making it possible to remove a broad range of chemicals in various pH. Here, a comprehensive review of the pharmaceuticals' adsorption and photo(degradation) mechanisms using iron-based materials has been presented. The tendency of different groups of antibiotics to dissociate to cation, zwitterion, and anion at different pH could not make their mechanism of adsorption a stereotype. Various groups of antibiotics interact differently with each iron oxide surface, but in general, π - π , H-bonding, hydrophobic and electrostatic interactions are most common. Regarding the photocatalytic studies, most of the iron-based materials act by Fenton reaction. It was also shown that the combination of adsorption and photocatalysis is an interesting approach for the removal of contaminants. Besides, this critical review would help in understanding the complexity of the antibiotic treatment with iron-based materials, which is necessary to reach the important goals of contamination elimination such as the re-use of post-treatment materials, the combination with other steps of treatment, the application on the non-laboratory conditions like real wastewater and drinking water, and finally, scaling up of iron-oxide-based materials on the industrial scale.

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

Data will be made available on request.

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