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Abstract

Pharmaceutical contaminants have shown widespread presence in water/wastewater threatening environmental and human health. Existing literature shows that adsorption can efficiently bind pharmaceuticals preventing their transfer into the treated water. However, adsorption only diverts these contaminants from one phase to another requiring the treatment of contaminant-laden adsorbents. Fenton oxidation (H_2O_2-based) has shown good potential for the degradation of pharmaceuticals. But, the practical use of Fenton oxidation is often limited by its higher chemical demands and low contact of oxidizing species with target contaminants. Efforts to overcome these practical obstacles aim to develop efficient heterogeneous catalysts which also benefit from their strong contaminant adsorption capacity. This is the first review that focuses exclusively on dual-functional materials that can effectively adsorb pharmaceutical pollutants (separation-based removal) and promote Fenton oxidation simultaneously (degradation-based removal) in aqueous systems. The dual functionality enables the integration of adsorption and Fenton-based processes (heterogeneous Fenton, photo-Fenton and photocatalysis) to efficiently remove pharmaceuticals. This integration can be achieved using a single material having both functions or by compositing/impregnating different materials. The properties of these materials have important consequences on their treatment efficiency, stability, and regeneration ability. These processes and materials are critically evaluated to illustrate their potential, associated challenges and their key solutions. Some of these challenges originate from the tested materials while others are inherent to the treatment process and the prospects for improvement exist at their intersection. Future research should aim to rationally improve the catalytic and adsorption properties of these materials and explore their practical implementation in wastewater treatment technologies.

Keywords: Wastewater treatment; Hybrid materials; Advanced oxidation processes; Adsorption; Emerging environmental pollutants

1. Introduction

Pharmaceuticals have been identified as an emerging group of environmental contaminants due to their potential hazards to human health and ecosystem [1]. Pharmaceutical contaminants are differentiated from traditional industrial pollutants based on a) their diverse chemical structures, molecular weight, and functionality, b) they are polar molecules having more than one ionizable group whereas the degree of ionization is controlled by the solution pH, c) they are mainly lipophilic in nature though some of them are moderately soluble in water, d) they have the ability to persist in nature, accumulate in life forms, and remain biologically active e) after administration, metabolic reactions can modify their chemical structure [1, 2]. Thus, pharmaceuticals can be excreted without being transformed or metabolized in the form of more polar and lipophilic derivatives. These properties ultimately dictate the fate and removal of pharmaceuticals in the environment differently than the traditional pollutants. Their presence in environment, even in small quantities, can be harmful because they have been specially designed to exert biological effects even at very low concentration [3]. Their contamination in aquatic systems is mainly linked to their misuse in medical and agricultural settings and the release of unregulated effluents (hospital, industrial, domestic, and agricultural) [4]. For example, according to the US Center for Disease Prevention and Control, injudicious antibiotic use may approach 50% [5]. This figure could be worse in developing countries where over-the-counter sales of drugs is highly unregulated [6]. Since traditional water/wastewater treatments are unable to completely eliminate these compounds [7], finding affordable, efficient, and environmentally benign treatments is highly desired to maintain ecological security and a clean water supply.

Many technologies have been tested to remove pharmaceuticals from aqueous systems. Among them, adsorption of pharmaceuticals is known for its simplicity, cost-efficiency, quick pollutant removal, and low sludge production [8, 9]. However, adsorption is a separation-based technique (a phase changing technology) that simply diverts the pollutants from water to another phase, yielding contaminant-laden sorbents which require side-stream disposal or

105 further treatment to avoid the risks of secondary contamination. Unlike adsorption, advanced
106 oxidation processes (AOPs) offer compelling advantage of degrading the organic pollutants.
107 This feature is highly attractive for environmental protection and to enable decentralized
108 treatments wherein the collection and transportation of waste are likely to be troublesome [10].
109 Among AOPs, Fenton-based oxidation processes have received tremendous attention to
110 degrade pharmaceuticals and other organic pollutants [11]. Heterogeneous Fenton oxidation
111 relies on iron oxide catalysts to produce reactive oxygen species (ROS predominantly
112 hydroxyl radicals ($HO^{\bullet}$)) for pollutant degradation. However, Fenton oxidation when applied
113 alone can be environmentally harmful and expensive due to substantial chemical input [1]. To
114 overcome these challenges, dual-functional materials are increasingly studied as
115 heterogenous catalysts and adsorbents [8, 9]. These materials have the potential to
116 simultaneously adsorb pollutants (separation-based removal) and catalyze Fenton oxidation
117 (degradation-based removal). The dual functionality of these materials enables the coupling
118 of adsorption and Fenton oxidation for higher treatment efficiency while reducing the
119 associated costs and limitations of individual techniques (by regeneration of materials and
120 higher elimination of pollutants). Heterogeneous Fenton processes can be further enhanced
121 with additional input of light (photo-Fenton) that has also been explored. These integrated
122 treatments can be used for both ex-situ (after separating the adsorbent) as well as in-situ
123 applications (without separating the adsorbent) by relying on the same materials (Figure 1).
124 This can be achieved either by using a single material having both functions or by
125 compositing/impregnating different materials to develop the dual functionality in a hybrid
126 material. This dual functionality has been the subject of huge amount of research in the recent
127 decade (Table 1 and 2).
128 In integrated processes, adsorption usually accounts for the initial treatment stage to bind
129 pharmaceuticals which are then degraded by the ROS formed during Fenton oxidation.
130 Pollutant adsorption on the surface of dual-functional materials improves the
131 pollutant/catalyst/oxidant contact which enhances the treatment efficiency. Moreover, the
132 degradation of adsorbed pharmaceuticals by subsequent Fenton oxidation allows the

regeneration of the spent material for further treatment cycles. This regeneration and reuse of materials are highly advantageous to reduce the treatment cost and to avoid the generation and disposal of pollutant-laden spent adsorbent. Dual functionality of these materials improves the pharmaceutical degradation while reducing the risks of secondary contamination [12]. The disposal of pollutant-laden spent adsorbent is are addressed by subsequent Fenton oxidation that regenerates the adsorbent by removing the pollution However, in another procedure, Fenton oxidation can be applied as the initial treatment which is followed by adsorption. This procedure allows the elimination of the major organic contaminants by Fenton oxidation and the further removal of their traces and/or byproducts by subsequent adsorption [13, 14]. Thus, integrated treatments combine the benefits of both techniques. These treatments have, therefore, distinct advantages of higher contaminant removal, less oxidant consumption and prevention of secondary pollution.

There exist many reviews that focused on the removal of pharmaceuticals from aqueous environments. However, main focus of these reviews was either various techniques for pharmaceutical removal [1, 2], Fenton oxidation [15, 16], adsorption [9], or with a focus on particular group of adsorbents for example sewage sludge-derived biochar [17], carbon nanotubes [18]. The integration of both processes using dual-functional materials has, however, not been reviewed so far which constitutes the main objective of this article. To our knowledge, this is the first review that focuses on the integration of both treatments by relying on dual-functional materials to eliminate pharmaceutical contaminants from aqueous systems. For this, we compiled the research data from numerous publications (retrieved from Scopus database) evaluating the applications of integrated treatments to eliminate pharmaceuticals in aqueous systems. Dual functionality of iron minerals and their composites with other materials allows the coupling of adsorption with heterogeneous Fenton and photo-Fenton oxidation processes. A brief account of the role of these iron minerals in photo-catalysis is also provided. A critical evaluation of these techniques and materials is provided to demonstrate the promising treatments/materials with a concise explanation of associated limitations and their key solutions. With this review, we intend to offer a useful resource and potential research

directions to explore the practical implications of Fenton-based processes and adsorption for real wastewater treatment plants.

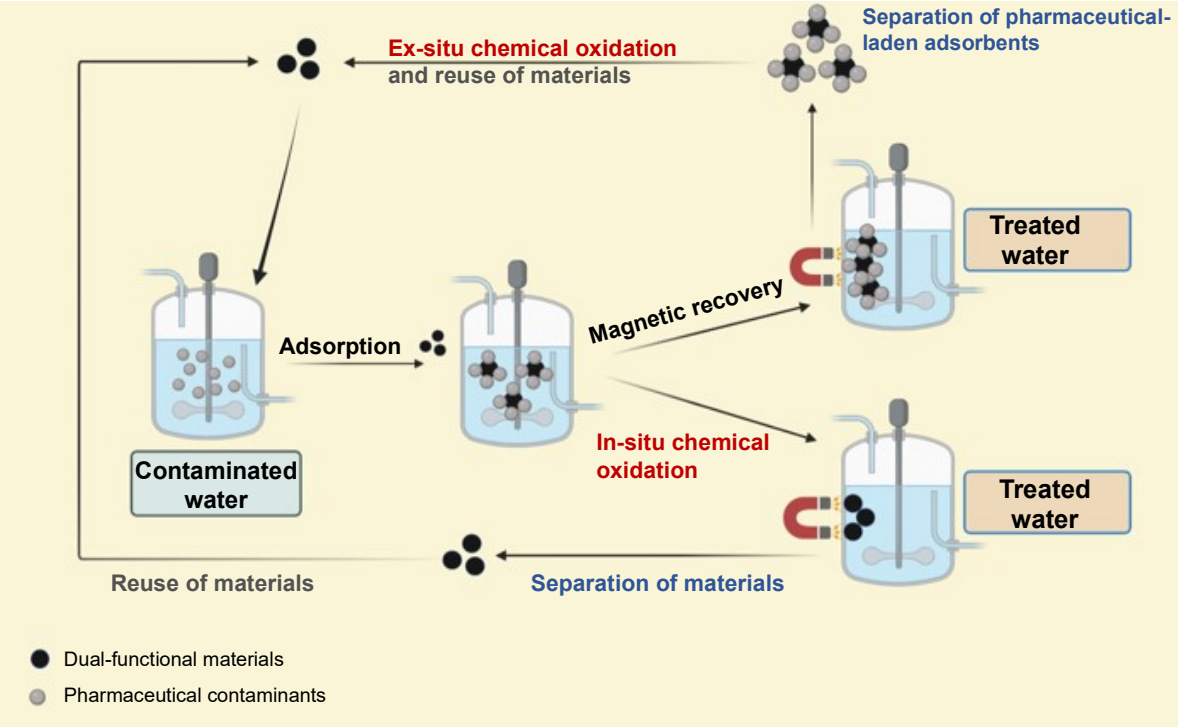

Figure 1: The coupling of adsorption and Fenton oxidation by relying on dual-functional magnetic metal oxide based materials. Adsorption is followed by chemical oxidation to degrade organic contaminants either after separating the contaminant-laden adsorbents (to reduce the contamination volume for ex-situ chemical oxidation) or without separating the adsorbents (in-situ oxidation). In the later system, chemical oxidant is introduced directly in the same reaction medium that generates the clean adsorbents for their reuse. This figure is created using Biorender App.

2. Literature Search Methodology

Scopus database was searched (on November 21, 2021, updated on June 5, 2022) by using these keywords in manuscript titles, abstracts, and keywords TITLE-ABS-KEY: ("Fenton" AND ("adsorption" OR "sorption") AND ("pharmaceutical*" OR "antibiotic*" OR "personal care products")). This search procedure is commonly used in bibliometric studies where the exact phrases are found by using quotation marks ("") which deactivate the synonym feature of search database [11, 19]. Term “or” allows finding various expressions which were coupled by using “and” to ensure the appearance of these words in the TITLE-ABS-KEY of each article. The use of asterisk symbol (*) serves as a wildcard to find the different variations among the

target keywords in the databases. For example, the use of “antibiotic*” allows to find “antibiotic”, “antibiotics”, or other variations of this term. This search returned 238 articles which were read to find if it deals with the use of integrated treatment to remove pharmaceuticals.

3. Coupling of Heterogeneous Fenton oxidation with adsorption

Traditional Fenton oxidation counts on dissolved iron species (Fe(II) mainly) to catalyze hydrogen oxide (H_2O_2) for the generation of $HO^{\bullet}$ radicals that degrade organic pollutants. However, the traditional Fenton process suffers from fundamental drawbacks of maintaining an acidic pH. The $HO^{\bullet}$ radical production is efficient only at an acidic pH (below 4) which is costly and impractical in environmental settings [11]. Moreover, this process leads to the generation of iron sludge after the treatment. To address these drawbacks, heterogeneous Fenton oxidation has been developed that relies on iron-bearing minerals or solids instead of dissolved Fe(II). These iron-bearing minerals and solids can catalyze Fenton oxidation at wide range of pH values [20]. In addition to their catalytic ability, hydrophilic iron oxides also benefit from their capacity to adsorb polar and negatively charged compounds highlighting their dual role in the remediation of pharmaceuticals [8, 9]. A brief description of adsorption coupled with heterogeneous Fenton oxidation using various materials for the removal of pharmaceuticals is provided below (Table 1).

3.1. Pristine nano zero-valent iron (nZVI) and its composites with other materials

Nano zero-valent Fe (nZVI) represents an important material that has been widely used to promote the integrated remediation processes. Here, the removal mechanism involved the adsorption of pharmaceuticals on nZVI surface followed by the production of $HO^{\bullet}$ radicals by its reaction with H_2O_2 (Eqs. 1 and 2) for pollutant oxidation [21, 22].

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe(II) + 2H_2O \quad (1)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^{\bullet} + HO^- \quad (2)$$

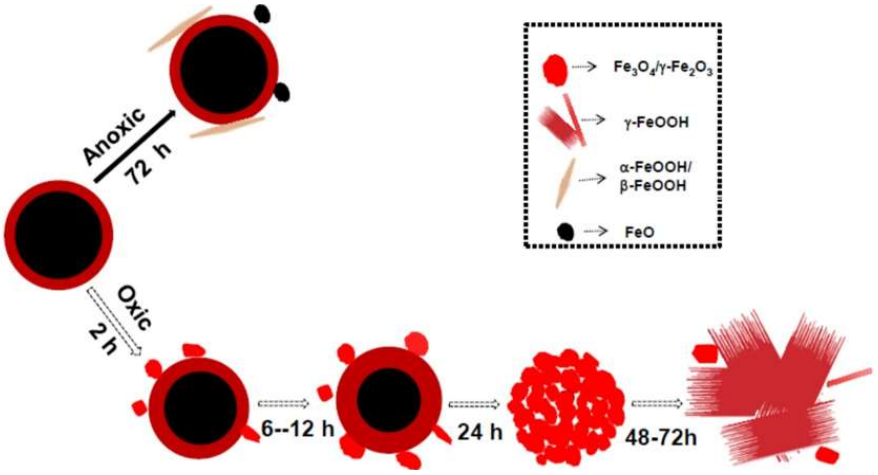

Figure 2: Conceptual model on the passivation evolution of nZVI in water showing the main passivation byproducts. Reproduced with permission from Ref. [23].

Though nZVI particles are highly efficient, they, being highly reactive, are easily oxidized to form oxide layers on its surface which decreases their catalytic ability (Figure 2) [24]. Indeed, the surface passivation of NZVI has been recognized among the major challenges in its successful application to remove pollutants [23, 25]. nZVI corrosion phenomenon is dictated by various factors including the composition of NZVI itself, oxic/anoxic environments, reaction time, and the concentration and type of aqueous species [25]. As such, nZVI can be corroded and transformed into other iron oxides like ferrihydrite, magnetite, etc. which can also contribute in adsorption and/or Fenton oxidation (Figure 2) [26]. Another issue is the magnetic nature of nZVI particles that can cause them to spontaneously agglomerate decreasing their total surface area and efficiency. To address these drawbacks associated with nZVI as dual functional materials, the stability and reactivity of nZVI particles can be improved by three main strategies including (i) the development of bimetallic nanocomposites [24, 27], (ii) by loading nZVI onto a support [22, 28, 29], or (iii) by encapsulating of nZVI particles, for example in three-dimensional graphene network [30]. These strategies improve the stability and reactivity of nZVI while reducing its agglomeration. For example, TEM images of nZVI on various supports indicate its successful attachment preventing its agglomeration (Figure 3). However, pristine nZVI without any support (Figure 3) exhibits particle agglomeration and the presence

of amorphous layers surrounding nZVI particles. These layers have been recognized of iron oxide layers formed by nZVI oxidation [25, 31]. Thus, without support, Fe particles become strongly linked to each other under necklet form. This behavior was, however, not observed in case of bimetallic or composited nZVI (Figure 3 and 4).

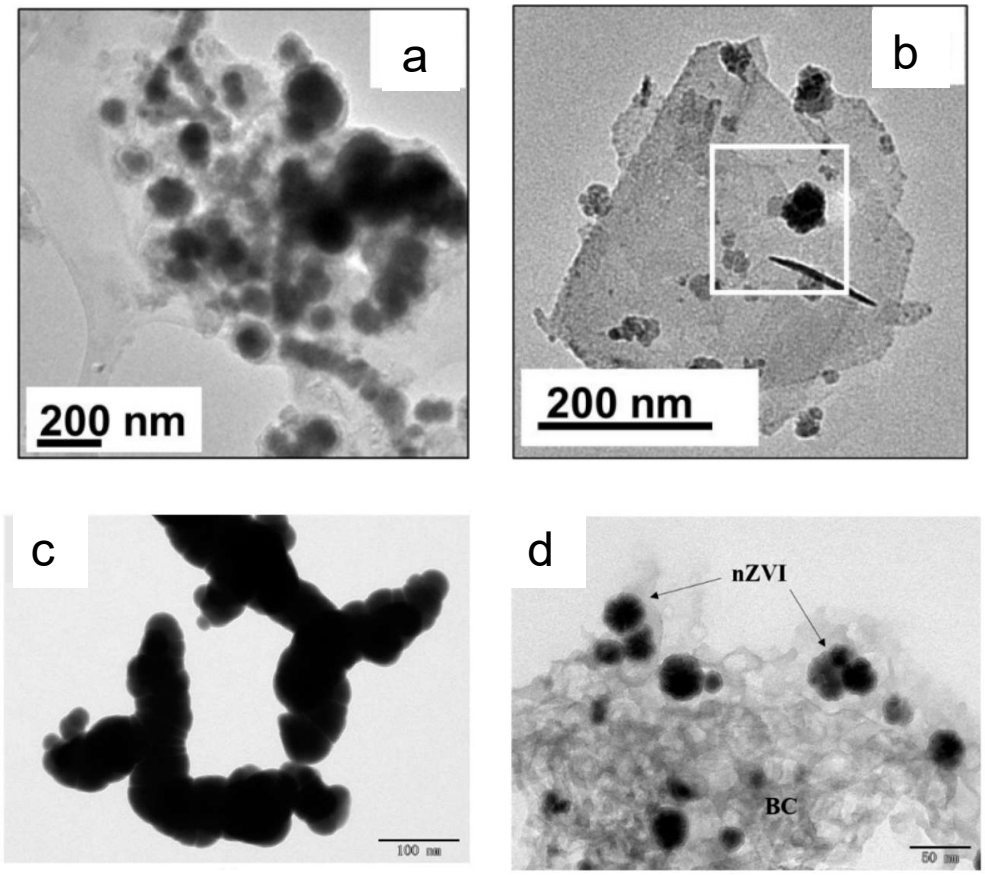

Figure 3: TEM images of pristine nZVI without (a and c) and with its loading onto their respective supports including reduced graphene oxide (b) and biochar (d). Images a and b are reproduced with permission from Ref. [28], while images c and d are reproduced with from Ref. [22], under an open access Creative Commons CC BY 4.0 license.

Bimetallic nanocomposites can be obtained by adding a second metal to nZVI [24, 27]. For this, noble metals (e.g. Pt) [24] and other metals (e.g. Cu) [27] were commonly used due to their significant contribution in enhancing the electron-generation capacity and stability of nZVI as compared to the pristine nZVI. Moreover, this structural modification largely increased the surface area from 25 m^2 g^{-1} (pristine nZVI) to 300 m^2 g^{-1} (Pt0.5/nZVI). This substantial increase in the surface area has been marked as the key reason for an improved adsorption of oxytetracycline by the authors [24]. However, further increase in Pt contents beyond 0.5

wt.% turned nZVI particles into flake agglomeration and thus affected the morphology and reduced the efficiency of nZVI. Similarly, the use of Cu-based bimetallic nZVI removed 56% of ciprofloxacin as compared to pristine nZVI (30% pollutant removal) [27]. In the same study [27], an interesting comparison has been made between the efficiency of Cu/nZVI synthesized by using green tea extract as the reductant (termed as green method) and the one synthesized by traditional chemical method (based on sodium borohydride). Green synthesized Cu/nZVI was found more stable, oxidation resistant and efficient than chemically-synthesized Cu/nZVI as the former removed 81% of ciprofloxacin compared to the 56% removal by the later. This has been linked to the higher dispersion of Cu/nZVI synthesized by green method. Adsorption or Fenton-like oxidation alone were able to remove about 30 and 50%, respectively. However, the integration of both processes removed up to 90% of ciprofloxacin. Authors further reported that adsorption played a major role in pollutant removal in the start of the reaction, but after 5 minutes, desorption started happening with the passage of time due to surface oxidation of nZVI. However, after 20 minutes of reaction, Fenton oxidation began to take over adsorption [27]. The stabilization and efficiency of nZVI/Cu bimetallic particles can be further improved by polyvinylpyrrolidone [32]. Owing to their catalytic potential of Cu species in promoting Fenton oxidation, nano-zerovalent copper (Cu^0) has also been developed as an alternative of nZVI to catalyze iron-free Fenton-like oxidation of ciprofloxacin (Equation 3 and 4) [33]. Also, the substitution of Cu in Fe_3O_4 ($Fe_{3-x}Cu_xO_4$ as the final product) has been found to increase adsorption capacity and HO• radical production during photo-Fenton oxidation of anticancer drugs including 5-fluorouracil and cyclophosphamide [34].

$$2Cu^0 + H_2O_2 + 2H^+ \rightarrow 2Cu^+ + 2H_2O \quad (3)$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + HO\bullet + HO^- \quad (4)$$

Another strategy to improve the stability of nZVI involves the deposition of nZVI particles on a support like biochar [22], reduced graphene oxide [28, 29, 31], cerium oxide [35] etc. which can improve its stability and efficiency (Figure 3). For example, the composites of rGO with bimetallic Pd/nZVI nanoparticles or nZVI particles provided a good solution to address the drawbacks of nZVI based-materials and improved their efficiency [31] (Figure 4). In

275 comparison with 53% removal of oxytetracycline by pristine nZVI, pollutant removal reached
276 83% with bimetallic Pd/nZVI. Pollutant removal improved to 96% with bimetallic
277 nanocomposites of Pd/nZVI/rGO5 (rGO 5% w/w). The removal of oxytetracycline by
278 Pd/nZVI/rGO composite has been linked to adsorption, Fenton-like oxidation, and reduction
279 reactions as demonstrated in Figure 4. In addition to an improved efficiency, the use of
280 Pd/nZVI/rGO5 exhibited better pollutant removal in subsequent treatment cycles.
281 Oxytetracycline removal by pristine nZVI from 53% to 1% in five oxidation cycles whereas the
282 efficiency of Pd/nZVI/rGO5 composite retained 18% of removal efficiency [31]. Compositing
283 nZVI with CeO_2 was also found to improve the efficiency and stability of nZVI [35]. A radical
284 identification experiment linked it to the remarkable production of HO• radical by
285 nZVI/CeO_2 composite as the bare nZVI. The CeO_2 improved the catalyst's adsorption
286 characteristics and electron transfer to improve H_2O_2 decomposition due to the abundance of
287 surface oxygen vacancies [35].
288 The encapsulation of nZVI particles in three-dimensional graphene network has also been
289 proposed as a potential strategy to enhance the stability and efficiency of nZVI [30]. The
290 encapsulation of iron-copper bimetallic NPs within the mesoporous carbon shell (FeCu@C)
291 promoted the catalytic degradation of sulfamethazine [36]. Synergistic catalytic role of Fe and
292 Cu species improved the formation of HO• radicals by promoting ≡Fe(II)/≡Fe(III) redox cycle
293 while the presence of carbon increased the adsorption capacity (63% pollutant removal).
294 Sulfamethazine was completely removed in the integrated process.

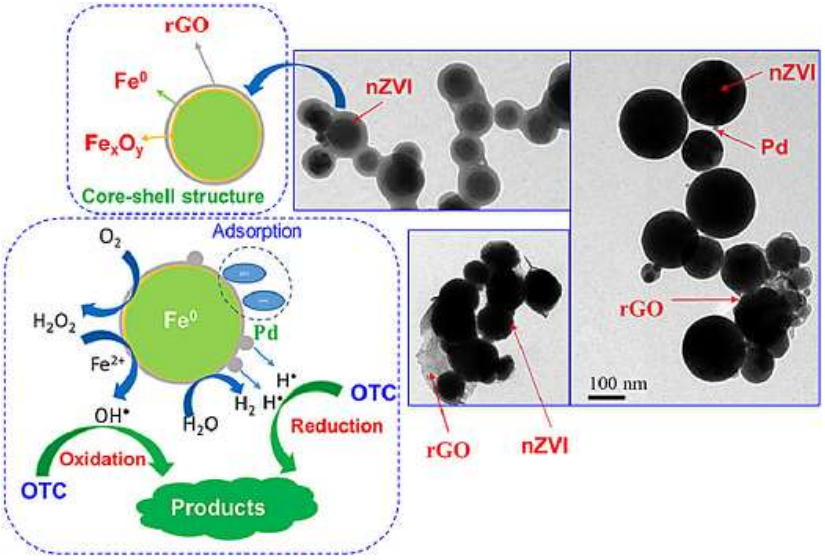

Figure 4: TEM images of nZVI, nZVI/rGO composite, and bimetallic Pd/nZVI/rGO5 nanocomposite. This image is reproduced with permission from Ref. [31]. This image clearly depicts that reduced graphene oxide-supported bimetallic palladium-zero-valent-iron nanocomposites (Pd/nZVI/rGO) prevented the agglomeration nZVI particles and the existence of iron oxide-associated amorphous layers surrounding them.

3.2. Pristine iron minerals having dual functions (adsorption and Fenton catalyst)

Iron minerals have received substantial attention for their demonstrated efficiency in promoting both adsorption and Fenton-based oxidation processes. Owing to the high surface area, iron minerals have been widely used to adsorb variety of pollutants from contaminated water/wastewater. Structural Fe contents of these minerals enable them to catalyze Fenton oxidation at circumneutral pH which is highly advantageous for real scale applications. It should be noted that classical Fenton oxidation (H_2O_2 + soluble Fe(II)) is often limited by the acidic pH range required to avoid the precipitation of soluble Fe(II). However, in case of iron minerals, the entrapment of Fe species within the structure of iron minerals prevents their precipitation leading to an improved catalytic ability over a wide pH range. This quality of iron minerals makes them ideal catalysts for heterogeneous Fenton oxidation. Iron minerals exist in nature as ferric (Fe(III) bearing) or mixed-valent iron minerals (bearing Fe(II) both Fe(III)) [37]. For example, FeOOH-based Fenton-like system showed good capacity (80%) to remove Roxarsone antibiotic and to adsorb arsenic which has been formed as the by-product of Roxarone oxidation. Thus, the dual-functionality of FeOOH allowed the degradation of the

target pharmaceutical while eliminating the risk of secondary contamination [12]. Similarly, Weng et al. [26] found that the use of green synthesized Fe NPs for synergetic adsorption and Fenton-like oxidation removed >90% of ofloxacin and enrofloxacin in a mixed contamination system. After an initial pre-adsorption, these pharmaceuticals were removed by an oxidative degradation in the presence of H_2O_2. These materials also showed good treatment efficiency either if they were reused (>60%) or were applied to remove target pharmaceuticals in the real wastewater (>60%) [26].

Owing to the existence of structural Fe(II), mixed-valent Fe minerals are considered more reactive to catalyze heterogeneous Fenton oxidation [20]. For example, impregnating ferrihydrite on powdered activated carbon demonstrated an excellent adsorption capacity (203 mg g^{-1}) for diclofenac removal. However, subjecting this material to subsequent Fenton oxidation partially removed the adsorbed pollutant along with a decrease in its regeneration ability by 25%. On the other hand, ball-milled magnetite nanoparticles exhibited efficient removal of ciprofloxacin by heterogeneous Fenton oxidation [38]. Indeed, magnetite alone removed up to 43% of ciprofloxacin due to adsorption but ciprofloxacin removal was increased to 89% by subsequent chemical oxidation (H_2O_2 12 mM, Fe_3O_4 1.75 g L^{-1}). It should be noted that magnetite (Fe(II) $Fe(III)_2$ O_4), owing to the presence of structural Fe(II), has emerged as a viable dual-purpose material that has shown higher catalytic ability as compared to the ferric minerals [20]. Moreover, its magnetic nature also facilitates the quick recovery of the spent materials, using an external magnet, from the reaction medium for their reusability or disposal [39]. The reuse of magnetite in four consecutive treatments by Hassani, et al. [38] revealed that the efficiency of magnetite decreased from 89% to 65% in four oxidation cycles. The oxidation efficiency of iron minerals can get decreased by surface oxidation/passivation and Fe leaching and which, if addressed, can recover the treatment efficiency [19]. The efficiency and stability of magnetite can be enhanced by preparing its composites with other reactive materials discussed in following sections.

3.3. Composites of iron minerals and other materials

The development of efficient composites, particularly based on magnetic materials, has received tremendous attention in the recent decade. Compositing magnetic iron minerals with suitable supports can improve the stability and catalytic ability of these iron minerals. Moreover, composites of magnetic iron minerals with other materials are also prepared to introduce the magnetic feature in materials which are otherwise deprived of these characteristics [40-45]. For example, embedding Fe_3O_4 nanoparticles on 3D reduced graphene oxide (rGO) was advantageous to introduce the magnetic feature in the composite adsorbent and improve the catalytic activity of magnetite [40]. This material (Fe_3O_4@rGO) exhibited adsorption capacity (2.78 mmol g^{-1} for ciprofloxacin and 4.76 mmol g^{-1} for tetracycline) much higher than the rGO alone (<1 mmol g^{-1} for both pollutants) and commercial granular activated carbon (<1 mmol g^{-1}). Fe_3O_4 nanoparticles were deposited between the graphene sheets and served as spacers preventing the aggregation of graphene sheets. All the adsorbed amount was completely removed by subsequent Fenton-like oxidation (by introducing H_2O_2) and this material maintained its efficiency for 10 adsorption-oxidation cycles [40]. Total iron loss was only 1% after adsorption-oxidation cycles underscoring the strong stability and high catalytic efficiency of magnetite nanoparticles on rGO. The existence of both Fe(II) and Fe(III) in octahedral layer of magnetite on rGO allowed Fe species to be reversibly oxidized and reduced while retaining the structure [40]. The schematic diagram of this catalytic oxidation along with iron regeneration is presented in Figure 5a. Similarly, using magnetite embedded onto chitosan carbon microbeads adsorbed significant amount (4.18 mg g^{-1}) of doxycycline under flow through conditions at a flow rate of 1.1 mL min^{-1} [46]. Sequential addition of H_2O_2 (5%) to trigger the Fenton oxidation removed up to 95% of the adsorbed pollutant regenerating the magnetite@chitosan carbon microbeads for repeated applications. The regeneration efficiency of this magnetic material increased from 78% to 93% of pollutant removal with an increase in the oxidant dose from 2% to 5% and then decreased to 72% and 55% with further increase in oxidant dose to 8% and 11%. It has been attributed to the scavenging of $HO^{\bullet}$ radicals at higher oxidant doses [47].

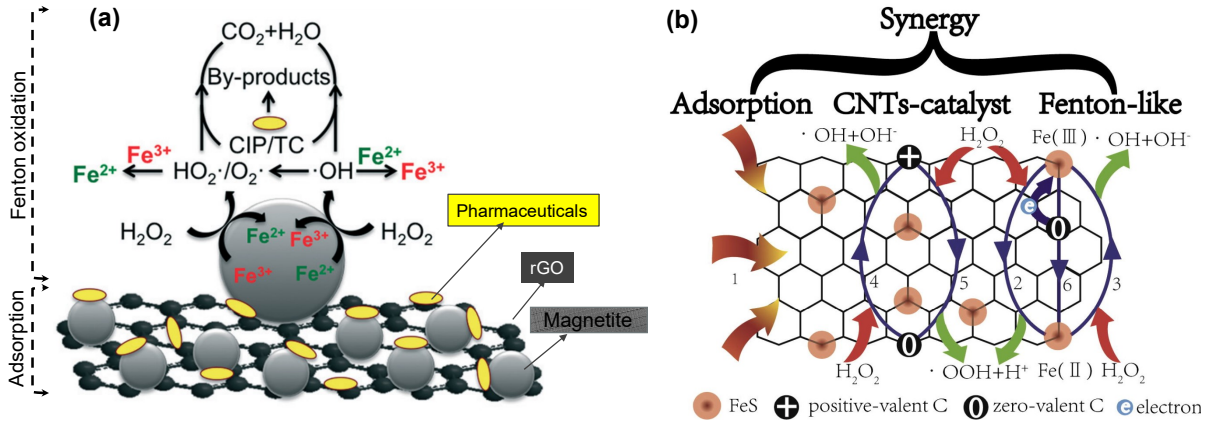

Figure 5: Schematic diagram depicting (a) the removal mechanism of two pharmaceuticals (CIP and TC) on the surface of magnetite decorated on 3D reduced graphene oxide (rGO) (adapted with permission from Ref. [40]) and (b) removal mechanism of ciprofloxacin by Carbon-nanotubes/pyrrhotite catalyst (CNTs/FeS) (reproduced with permission from Ref. [48])

A composite of magnetite with carbon nanotubes (CNTs), synthesized by ball-milling, was used to remove six sulfonamides including sulfanilamide, sulfamerazine, sulfadimethoxine, sulfadiazine, sulfamethazine, and sulfametoxydiazine [49]. The adsorption efficiency of sulfamerazine reached 59%, 70%, and 6% in the presence of magnetite-CNT composite, CNT and Fe_3O_4, respectively. Though, the adsorption capacity of the composite material was lower than CNT, it caused higher pollutant removal by subsequent Fenton oxidation (100%, 71%, and 37%, in the presence of magnetite-CNT composite, CNT and Fe_3O_4, respectively with H_2O_2). Moreover, the presence of magnetite introduces the magnetic character in composite material that facilitated its separation for regeneration. Carbon-nanotubes (CNTs)/pyrrhotite (FeS) also exhibited substantial removal (90%) of ciprofloxacin that has been linked to the synergistic adsorption, Fenton-like oxidation and catalytic degradation by CNTs catalyst [48] (Figure 5b). CNTs possess excellent adsorption capacity owing to its large surface area and porous structure. On the other hand, FeS can produce Fe(II) in solution that would catalyze H_2O_2 to produce $HO^{\bullet}$ radicals for the degradation of ciprofloxacin. Additional trials performed using $HO^{\bullet}$ radical scavengers including potassium iodide (surface-bound radical scavenger) and methanol (scavenger for all the unbounded $HO^{\bullet}$ radicals) revealed that the removal of ciprofloxacin was mainly dependent on unbounded $HO^{\bullet}$ radicals while the contribution of

bounded $HO^{\bullet}$ radicals remains insignificant. Adsorption process alone was able to remove 25% of ciprofloxacin while the removal efficiency reached 90% in integrated process due to the synergistic effect of adsorption and oxidation by free and bounded $HO^{\bullet}$ radicals.

Biochar has also emerged as an important material in the recent decade with many environmental applications. It can be developed from various biomasses. For example, biochar [50] or carbon [51], derived from sewage sludge with sufficient amounts of native Fe, removed pharmaceuticals (90-91%) through synergetic effect of adsorption and Fenton oxidation. Relying on sewage sludge or agricultural wastes to synthesize biochar could reduce the treatment cost while offering an innovative solution for solid waste management [52, 53]. However, depending upon the contents and form of iron in biomass, Fe loading on biochar can be required to improve its catalytic ability. For example, Xie et al. [54] developed composites of Fe_xP/biochar by pyrolysis of phosphorus-containing biomass (yeast) preloaded with FeOOH on its surface. Synergistic adsorption and Fenton-like oxidation removed 99% of sulfamethoxazole. However, the development of composite materials usually involves impregnation method where iron precursor-loaded carbon materials are pyrolyzed or iron oxides are immobilized onto carbon materials. These approaches can be limited by uneven distribution of iron or its oxides on the surface of composite materials. In this regard, direct carbonization of metal organic frameworks (MOFs) to synthesize carbon-based porous materials has been suggested by Gu et al. [55]. They developed a magnetic Fe/porous carbon material via one-step pyrolysis method and found it highly suitable to remove tetracycline. Highest adsorption of 1301 mg g^{-1} onto this material was recorded which was about 6 times higher than activated carbon. The mechanism of adsorption mainly included surface complexation, hydrogen bonding and π–π interactions (Figure 6). Fenton oxidation allowed the regeneration of this material for further treatment cycles where it retained its efficiency (70-79%) [55].

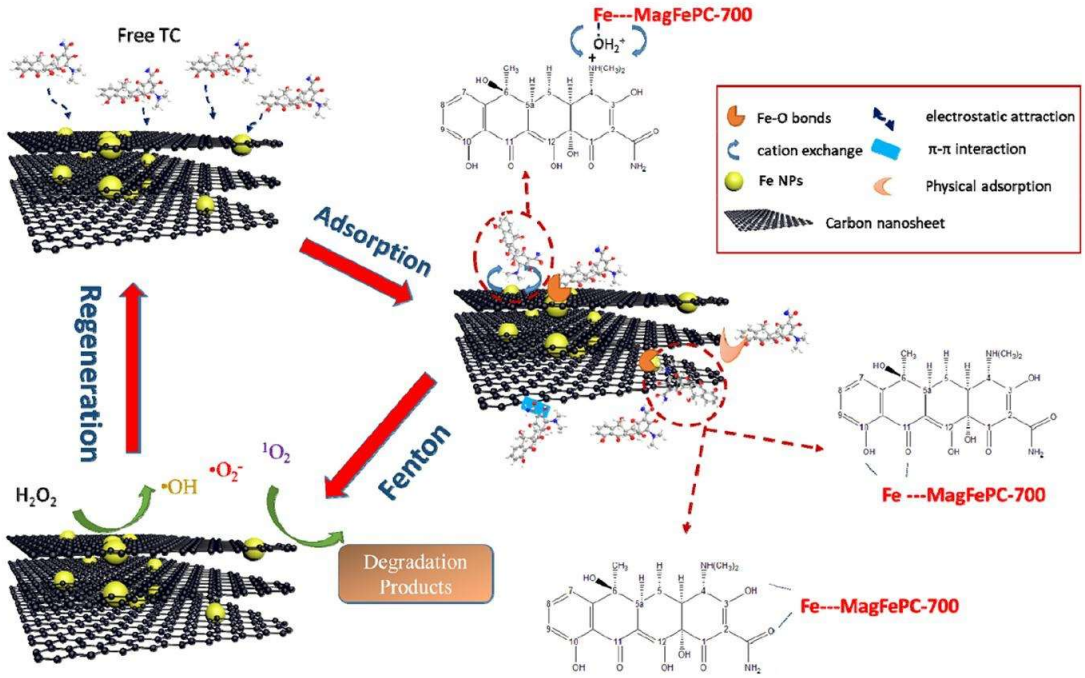

Figure 6: Mechanisms involving the role of magnetic Fe/porous carbon hybrid for the adsorption of tetracycline (TC) followed by Fenton oxidation to regenerate this material. This figure is reproduced with permission from Ref. [55].

Magnetic iron-based carbon materials are also gaining particular interest because of the remarkable adsorption from the mutual role of carbon (C) and Fe, higher catalytic ability associated mainly with Fe species, and easy recovery from aqueous matrix due to their magnetic nature for repeated applications [55-57]. Iron-based MOFs (NH_2-MIL-88B) were found to completely remove pefloxacin from contaminated solution by adsorption followed by Fenton-like oxidation [58]. Adsorption capacity reached 41.4 $mg \cdot g^{-1}$ in 120 min whereas pefloxacin was completely removed by subsequent Fenton-like oxidation. Similarly, Fe_2O_3@covalent organic frameworks (Fe_2O_3@COFs) was synthesized by restricting the growth of Fe_2O_3 in the nanoscale channel of COFs [56]. The use of this material resulted in 45% removal of sulfamethazine (by adsorption) while integration with H_2O_2 completely removed this pollutant.

Recently, magnetic spent bleaching earth carbon was synthesized by the anoxic pyrolysis of spent bleaching earth, a waste product of vegetable oil industry, followed by the in-situ synthesis of magnetite via coprecipitation [59]. The adsorption of tetracycline hydrochloride reached 16% with equilibrium attained in in 60 minutes. Pollutant removal efficiency reached

89% after one minute of oxidant addition in the reaction medium (Figure 7a). An increase in the quantity of this material from 0.5 to 2 g L^{-1} increased the adsorption of tetracycline hydrochloride from 18 to 65% and oxidation 52 to 97% (Figure 7). The development of efficient environmental materials from solid industrial wastes (like that of spent bleaching earth) could be a sustainable solution for resource recovery and solid waste management. However, for all the composite materials, maintaining an optimum level of iron loading is crucial to attain the maximum degradation of pollutants. Increasing iron loading beyond an optimum point makes iron dispersion less homogeneous which reduces the oxidation efficiency [60]. In another study, the loading of Fe_3O_4 on cellulose nanocomposites reduced the iron loss from 19% (from Fe_3O_4) to <1% (in composite sample) while removing about 90% of tetracycline due to the supportive role of adsorption and Fenton-like degradation [61]. It is worth mentioning that adsorption alone was able to remove only 33% of tetracycline. Moreover, the development of bioinspired magnetic cellulose nanocomposites has been suggested as a suitable alternative to the chemically-synthesized supports which are non-degradable, environmentally unsustainable or their synthesis relies on hazardous chemicals [61].

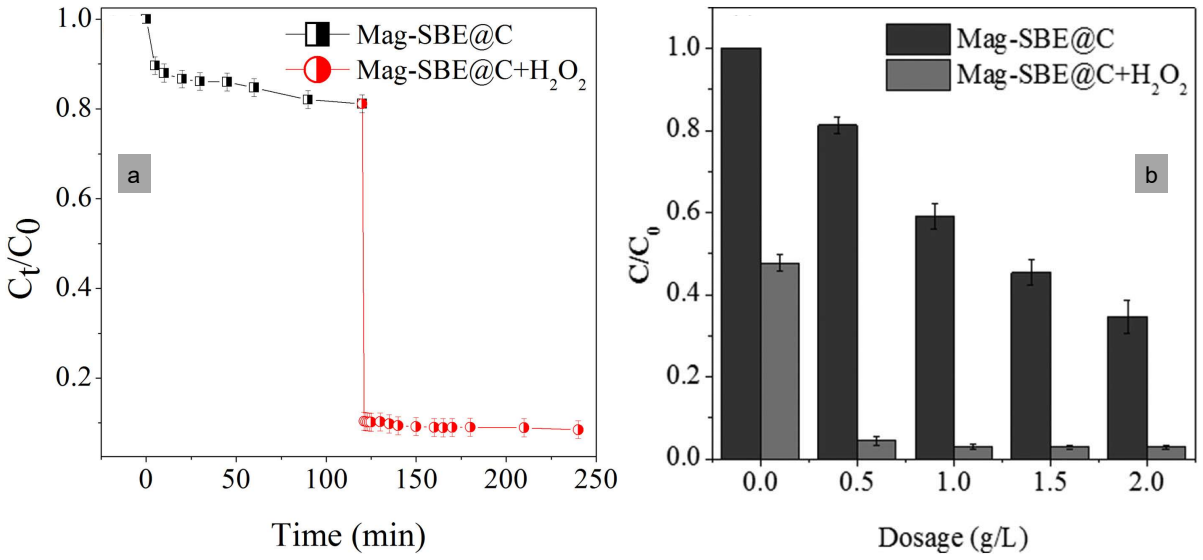

Figure 7: Removal of tetracycline hydrochloride (a) by adsorption on magnetic spent bleaching earth carbon (Mag-SBE@C alone) or in combination with Fenton oxidation (Mag-SBE@C + H_2O_2), (b) with various dosages of Mag-SBE@C. These images are reproduced with the permission from Ref. [59].

462 **Table 1**: Summaries of the studies reporting the integration of adsorption and heterogeneous Fenton oxidation to remove pharmaceuticals in
463 aqueous solutions. Studies are arranged chronologically.

Tested material	Pollutant	Experimental conditions	Removal efficiency	Ref.
CNTs/FeS	Ciprofloxacin (120 mg L^{-1})	Material = 25.5 mg, H_2O_2 =10.3 mmol L^{-1}	25% removal by adsorption alone while 90% removal with synergistic oxidation	[48]
Ce^0–Fe^0-reduced graphene oxide	Sulfamethazine (20 mg L^{-1})	Material = 0.5 g L^{-1}, H_2O_2 = 10 µL, pH = 7, *T* = 25 °C	100%	[29]
Fe_3O_4	Ciprofloxacin (10 mg g L^{-1})	Material = 1.75 g L^{-1}, H_2O_2 = 12 mM, pH = 3	43% removal by adsorption and 88.92% in the presence of oxidant	[38]
FeOOH	Roxarsone (10 mg L^{-1})	Material = 0.1 g L^{-1}, pH = 5, T= 20 ± 2 °C, time = 3 h	80% of roxarsone by Fenton oxidation with simultaneous removal of arsenic, byproduct of oxidation, by adsorption in the same setup	[12]
3D-rGO/Fe_3O_4	Ciprofloxacin (CIP) and tetracycline (TC) (200 µmol L^- each)	Solid = 0.33 g L^{-1} pH 6, time = 72 h, Fe_3O_4 : H_2O_2 = 1:2 molar ratio	Maximum adsorption of 2.78 mmol g^{-1} for CIP and 4.76 mmol g^{-1} for TC followed by the complete oxidation of adsorbed pollutant	[40]
Fe_3O_4@Chitosan carbon microbeads	Doxycycline (25 mg L^{-1})	pH 7, flow rate: 1.1 mL/min, H_2O_2 = 5% wt, Flow-through system	Highest adsorption: 4.18 mg g^{-1} followed by 93% removal by oxidation	[46]
Sewage sludge biochar	Ciprofloxacin (10 mg L^{-1})	Material = 0.2 g L^{-1}, pH 4, H_2O_2 = 10 mM, time = 4 h	About 30% by adsorption but 90% by integrated system	[50]
FeCu@C composite	Sulfamethazine (20 mg L^{-1})	pH = 3.0, material = 0.25 g L^{-1}, [H_2O_2] = 1.5 mM, T = 25 °C.	62% by adsorption alone while 100% removal in integrated process	[36]
Sludge derived carbon	Ofloxacin (30 mg L^{-1})	Material = 1 g L^{-1}, H_2O_2 = 138 mg L^{-1}, time = 540 min	91%	[51]
nZVI/CeO_2	Tetracycline (100 mg L^{-1})	Material = 0.1 g L^{-1}, H_2O_2 = 100 mmol L^{-1}, pH =3, T = 26 °C	93%	[35]
nZVI encapsulated in 3-D graphene network	Sulfadiazine (10 mg L^{-1})	pH 3-4, [H_2O_2] = 3 mM, material = 0.5 g L^{-1}, T = 298 K	81% by adsorption alone and 98% in integrated process	[30]
nZVI/Cu composites	Ciprofloxacin (50 mg L^{-1})	GT-nZVI/Cu (1/0.08) = 0.5 g L^{-1}, pH = 5, T = 293 K H_2O_2 generated in-situ	30 and 50% removal by adsorption or Fenton-like oxidation, respectively. 90% removal by integrated process	[27]
Pt/nZVI nanocomposites	Oxytetracycline (100 mg L^{-1})	Pt0.5/nZVI = 0.3 g L^{-1}, pH = 5, H_2O_2 generated in-situ	99%	[24]
rGO-nZVI nanohybrids	12 pharmaceuticals including antibiotic, anti-inflammatory, anti-seizure, and	t = 10 min, H_2O_2 (15.6 µL, 28-30%), solution vol = 15 mL, Material = 530 mg L^{-1}	95-99%	[28]

	antidepressants (200 µg L^{-1} each)			
nZVI-biochar composites	Ornidazole (100 mg L^{-1})	pH = 3, T = 25 °C, [H_2O_2] = 12 mM, nZVI-Biochar = 0.3 g L^{-1} (mass ratio of 1:2)	80%	[22]
Mussel-inspired magnetic cellulose nanocomposite	Tetracycline (20 mg L^{-1})	Material = 100 mg L^{-1} H_2O_2 = 0.10 M, T = 308.15 K	33% by adsorption and 90% by the integrated system	[61]
nZVI loaded MOF MIL-101(Cr)	Tetracycline	Material = 0.25 g L^{-1}, H_2O_2 = 0.10 M pH = 3 – 7, H_2O_2 = 50 mM, time = 60 min	Adsorption capacity was 625 mg g^{-1}, 93% removal by Fenton oxidation	[62]
Fe_xP/biochar	Sulfamethoxazole (20 mg L^{-1})	Material = 0.4 g L^{-1}, T = 30 °C, H_2O_2 generated in-situ	99%	[54]
Magnetic Cellulose Nanocomposites	Tetracycline (100 mg L^{-1})	Time = 60 min, material = 0.2 g L^{-1},	90% in integrated system while 33% with adsorption alone	[61]
Green synthesized Fe NPs	Ofloxacin & enrofloxacin (50 mg L^{-1} each)	Material = 0.8 g L^{-1}; pH = 7.1; T = 25 °C; H_2O_2 = 40 mM	90-91% for both pollutants	[26]
Fe-modified zeolite	Tartrazine (10 mg L^{-1})	Material = 50 g L^{-1} [H_2O_2] = 2 mM, pH = 3 and T = 20 °C	85% by adsorption while 95% degradation by subsequent oxidation	[63]
Leather waste derived biochar	Sulfamethoxazole (20 mg L^{-1})	Continuous mode, Material = 20 mg L^{-1}, H_2O_2 = 10 mM, pH = 3.0, current velocity = 3.5 mL/min	90% by adsorption and subsequent Fenton oxidation completely regenerated the material	[64]
$FeNi_3$ nanoparticles	Metronidazole (10 mg L^{-1})	Time = 180 min, Material = 0.005 g L^{-1}, and [H_2O_2] = 150 mg L^{-1}	45% by adsorption and 100% by subsequent oxidation	[65]
Fe_2O_3@covalent organic frameworks	Sulfamethazine (10 mg L^{-1})	Material = 1 mg L^{-1}, T = 25 °C, pH = 3, H_2O_2 = 2.6 mM	45% by adsorption and 100% by integration with oxidation	[56]
Poly(aspartic acid) Fe_2O_3-MnO_2 micromotor	Tetracycline (30 mg L^{-1}) with Pb and Cd	Time = 50 mins, H_2O_2 = 3%, material = 80 mg L^{-1}	83% removal of tetracycline and 25% removal of metal mixture by integrated treatment	[66]
Magnetic spent bleaching earth carbon	Tetracycline (0.7 mmol L^{-1})	Material = 1.0 g L^{-1} T = 41 °C, pH = 4.89 and molar ratio of H_2O_2 to pollutant = 277	19% by adsorption and increased to 91% with oxidation	[59]
rGO- supported bimetallic Pd/nZVI nanocomposites	Oxytetracycline (100 mg L^{-1})	Material = 0.1 g L^{-1} (5% rGO), pH = 5.0 and T = 25 °C	53%, 83% and 96% pollutant removal efficiency by pristine nZVI, bimetallic Pd/nZVI, and bimetallic nanocomposites of Pd/nZVI/rGO5, respectively	[31]

Composite of magnetite with carbon nanotubes	Sulfonamides (40 mg L^{-1})	Material = 1 g L^{-1}, H_2O_2 = 24.5 mM, pH = 3	100% removal in the integrated system while 59% by adsorption alone	[49]
Magnetic Fe/porous carbon hybrid	Tetracycline (80 mg L^{-1})	Material = 0.05 g L^{-1}; equilibrium pH = 6; T = 25 °C	Adsorption capacity of 1301 mg g^{-1}, Fenton oxidation regenerated the material while removing the pollution.	[55]
Fe-based MOF, NH_2-MIL-88B	Pefloxacin (20 mg L^{-1})	pH = 6.0, Material = 0.5 g L^{-1}, [H_2O_2] = 8.0 mmol L^{-1} T = 30 °C	Adsorption of 41.37 mg·g^{-1}, with >99% removal by Fenton oxidation	[58]
Mn-CuO	Ciprofloxacin (10 mg L^{-1})	H_2O_2 = 40 mmol L^{-1}; pH = 5.3, material = 1 g L^{-1}, time = 90 minutes	<20% pollutant removal by adsorption while integration with oxidation removed about 80%.	[67]
Fe_3O_4@ZIF-8@ZIF-67 nanocomposite	Tetracycline (160 mg L^{-1})	material = 0.4 g L^{-1}, H_2O_2 = 30 mM, T = 25 °C	89% by adsorption alone while 96% by integrated process	[68]
Pyrite nanosheets	Ciprofloxacin (20 mg L^{-1})	pH = 4, H_2O_2 = 2 mmol L^{-1}, material = 1 g L^{-1}, time = 10 min	20% removal by adsorption and complete removal by subsequent oxidation	[69]

464

4. Coupling of photo-Fenton and photocatalysis with adsorption

Photo-induced processes including photo-Fenton and photocatalysis can be employed in combination with adsorption to remove pharmaceutical compounds. Compared to the traditional Fenton and Fenton-like processes, photo-Fenton involves the photo-reduction of iron(III) to generate ROS under light, especially $HO^{\bullet}$ radicals (Equation 5). Photo-Fenton reaction favors the regeneration of Fe(II) that addresses the rate limiting step of Fenton oxidation (reduction of iron(III) into iron(II)) [70, 71]. The use of Fe(III) is a considerable advantage since it is more stable than Fe(II) at circumneutral pH. In addition, H_2O_2 can be also added to the photo-Fenton process, so classical Fenton reaction occurs. Therefore, a catalytic cycle Fe(III) ↔ Fe(II) is set up.

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + HO^{\bullet} \quad (5)$$

Photo-Fenton oxidation and adsorption are usually integrated using composite materials based on iron oxides composited with different adsorbents (Table 2). Consequently, the composite materials can also trigger photocatalysis in the case the iron-based material is a semiconductor [72-74]. Photocatalysis relies on the formation of electron-hole (e^-/h^+) pairs under light which react further to generate primary ROS (Figure 8). It is worth noting that the isolated use of photo-Fenton/photocatalysis and adsorption processes has been widely studied. However, their simultaneous application is an emerging field with relatively fewer studies. This section illustrates the integration of adsorption with photo-Fenton and photocatalysis for the removal of pharmaceuticals. A brief summary of the salient findings regarding the efficiency of various materials in integrated processes is provided in Table 2. A brief description of these studies is provided in the following sections.

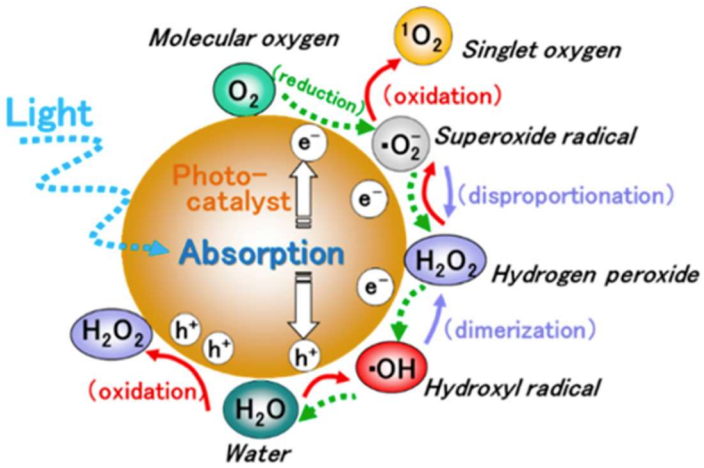

Figure 8: Photocatalytic generation of primary reactive oxygen species (ROS) *via* photocatalytic reduction and oxidation steps of oxygen and water. This figure is reproduced with permission from Ref [75].

4.1. Iron-based materials combined with zeolites and porous alumina

Iron-based spinel structure are widely used photoactive materials, especially for heterogeneous photo-Fenton process. Their combination with zeolite showed promising potential to remove pharmaceutical compounds since zeolites exhibit excellent adsorption properties due to high ion exchange properties, hydrophilic affinities and specific surface area [76, 77]. Indeed, NaX nanozeolite combined with $CoFe_2O_4$ can completely remove paracetamol (20 mg L^{-1}) after 30 min irradiation under UVA light in the presence of H_2O_2, that corresponds to a 50% increase in pollutant removal extent compared to that by adsorption alone [77]. Such a high efficiency is due to the synergy of iron-based catalyst and zeolites, owing to their excellent adsorption capacity and hydrophilic affinities. Higher adsorption improves the contact of paracetamol with the iron-based catalyst enhancing its degradation with photo-Fenton process [76, 77]. Similarly, mesoporous alumina is an excellent adsorbent for the support of photo-Fenton catalyst. Indeed, the combination of meso-Al_2O_3 with Fe(II) can almost completely remove phenol after 60 min in the presence of H_2O_2 under UV light at pH = 3 [78]. Adsorption alone can remove 40% of phenol due to the high chemical and thermal stability of mesoporous alumina along with its high specific surface area. The integration of

adsorption with photo-Fenton process leads to an increase of 60% in degradation extents owing to the oxidative attack of hydroxyl radicals on phenol.

4.2. Iron-based materials combined with biomass-based adsorbents

Biomass-based materials, particularly activated carbon, are considered highly promising due to their natural origin and their sustainable production. Recently, Della-Flora et al. designed an integrated adsorption system with photo-Fenton process to remove a mixture of pharmaceutical compounds (to simulate hospital wastewater) including chloramphenicol, fluconazole, flutamide, flurosemide, gemfibrozil, ibuprofen, losartan, nimesulide and paracetamol [13, 79]. The first step involves the photo-Fenton process which is performed for 15 min under simulated solar light at pH = 4 with a single addition of 100 mg L^{-1} H_2O_2 and multiple additions of Fe(II) (5 mg L^{-1} at 0 min, 5 min and 10 min of treatment time). Subsequently, adsorption process using activated carbon obtained from avocado seeds is performed as post-treatment for 15 min. Such a combination of processes can remove almost completely all the pharmaceutical compounds. Indeed, the photo-Fenton process can degrade from 30% to 80% of the contaminant after 15 min (depending upon pharmaceutical compound), and the remaining contamination including the toxic transformation products can be removed by adsorption. There exist multiple adsorption reactions as illustrated in Figure 9 with the example of flutamide in the presence of activated carbon from avocado seeds [69]. However, the involvement of photo-Fenton process requires the acidification of the water matrix which is not economically viable [70, 71]. In addition, the pH also affects the efficiency of adsorption process through activated carbon [13]. At acidic pH, the chemical structure of the adsorbent is composed of aromatic rings, possesses positively charged surface. Thus most of the target and transformed pharmaceutical compounds, which also contain aromatic rings and are neutral or negatively charged at acidic pH, are easily adsorbed through Coulombic and π-π interactions [13]. It is worth noting that the open-ring transformation products are not efficiently removed by adsorption process due to weak interactions with the adsorbent and strong solubility in water, respectively, but the photo-Fenton process can

efficiently degrade and mineralize this fraction of the contamination [13, 79]. These studies highlight the utility of the adsorption as the secondary process in the integrated system.

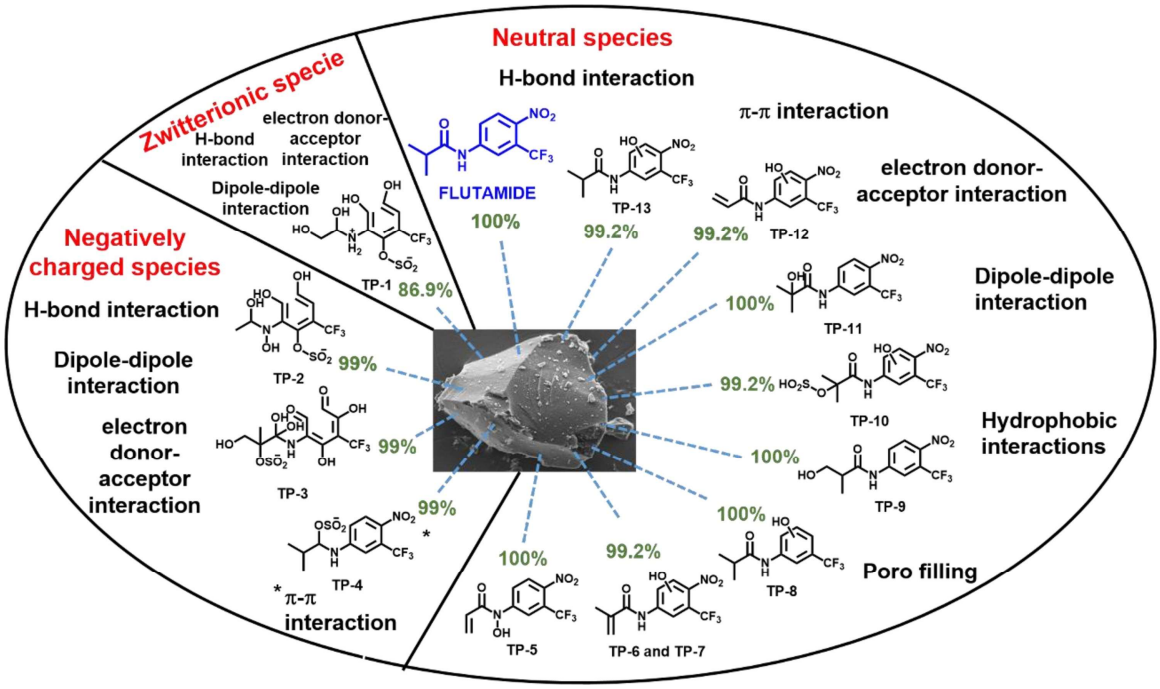

Figure 9: Characterization of activated carbon by scanning electron microscopy and description of proposed adsorption mechanisms and interaction of Flutamide and transformation products after solar photo-Fenton oxidation in hospital wastewater. * represents the percentage of the abundance of each specie at pH 4. This figure is reproduced with permission from Ref. [13].

Another integrated system combining adsorption and photo-Fenton processes has been discussed by Oladipo et al. where tetracycline and phenol have been removed using Fe_3O_4 nanoparticles covered by waste *Cyprus* coffee residue (Fe_3O_4@CC) [72]. Such a composite can adsorb tetracycline with an increase of 50% compared to CC alone and degrade and mineralize efficiently this pharmaceutical compound along with its aromatic intermediates in the presence of H_2O_2 and solar irradiation [72]. As expected, the excellent adsorption capacity of Fe_3O_4@CC was found dependent on the solution pH. Tetracycline exists in cationic form at pH < 3.3, in anionic form at pH > 7.7, and as zwitterion between pH 3.3 and 7.7. Therefore, the optimal adsorption of tetracycline occurred at circumneutral pH and it is due to electrostatic interactions and H-bonding between the waste coffee residue and the iron oxide, respectively, and the pharmaceutical compound [72]. The photo-Fenton process generated ROS (mainly

556 $HO^{\bullet}$ and $O_2^{\bullet-}/HO_2^{\bullet}$), that efficiently degraded tetracycline as well as its degradation byproducts
557 such as phenol, catechol and hydroquinone [72]. Therefore, the use biomass-based adsorbent
558 including activated carbon in integrated adsorption with photo-Fenton system is an interesting
559 strategy for the efficient removal of pharmaceutical compounds. Such adsorbents interact with
560 aromatic contaminants by π-π- and H-bonding, while photo-Fenton process efficiently oxidize
561 the remaining pollution in the solution.
562

563 **4.3. Iron-based materials combined with g-C_3N_4**

564 The integration of adsorption with both photo-Fenton and/or photocatalysis has also been
565 proposed as an innovative system [80, 81]. Indeed, iron-based oxides can also play the role
566 of photocatalyst and adsorbent for the removal of pharmaceuticals. For instance, the
567 composites based on graphitic carbon nitride (g-C_3N_4) and, iron-based oxide (like Fe_2O_3 and
568 $MnFe_2O_4$) belong to such an integrated system [80, 81]. Eventually, an adsorbent can also be
569 included in the composite like graphene [80]. For example, *Zhao et al.* investigated a
570 composite material made of g-C_3N_4 with Fe_2O_3 nanodots [81]. Such a composite can degrade
571 90% of tetracycline in the presence of H_2O_2 after 1 h under visible light. For comparison, the
572 integrated adsorption with photocatalysis (without H_2O_2) and Fenton process (in the dark) can
573 only degrade about 20% and 45% of the target pharmaceutical, respectively [81]. However,
574 the photo-Fenton is not discussed in detail by *Zhao et al.*, although it has probably a significant
575 contribution to the excellent efficiency of the g-C_3N_4/Fe_2O_3 composite. It is also worth noting
576 the g-C_3N_4/Fe_2O_3 composite is highly stable since the efficiency of tetracycline degradation by
577 integrated adsorption with simultaneous photocatalysis and photo-Fenton decreased by about
578 4% after 4 repeated runs. On the other hand, *Wang et al.* [80] prepared g-
579 C_3N_4@$MnFe_2O_4$@graphene composites for the degradation of a wide range of antibiotic
580 compounds including tetracycline, ciprofloxacin, metronidazole and amoxicillin. Such
581 composites integrate a non-photoactive adsorbent, thus combining photocatalysis, photo-
582 Fenton and adsorption (Fig. 10). The photochemical systems also included the use of

persulfate ($S_2O_8^{2-}$) as radical precursor. The pollutant degradation efficiency ranged from 50% to 90% in 10 mM pharmaceutical solutions after 90 min visible light irradiation (depending upon the compound) [80]. In addition, the reusability of such composites is excellent as no significant decrease in removal efficiency was reported after 5 repeated runs. The excellent removal efficiencies of these composite materials were attributed to different reasons. An important one is the type II heterojunction between g-C_3N_4 and iron-based oxide that enhances the charge carrier separation and transport. Another reason is the scavenging of photogenerated electron by the adsorbent, thus increasing the charge carrier lifetime, while the adsorbent is providing active sites for degradation reactions. Also, the presence of Fenton-active elements (like Fe and Mn) in the composite materials can efficiently catalyze Fenton based reactions (including photo-Fenton) for the activation of persulfate and H_2O_2 into inorganic radicals ($HO^{\bullet}$ and $SO_4^{\bullet-}$) which are highly reactive species for the efficient destruction of pharmaceutical compounds [80, 81].

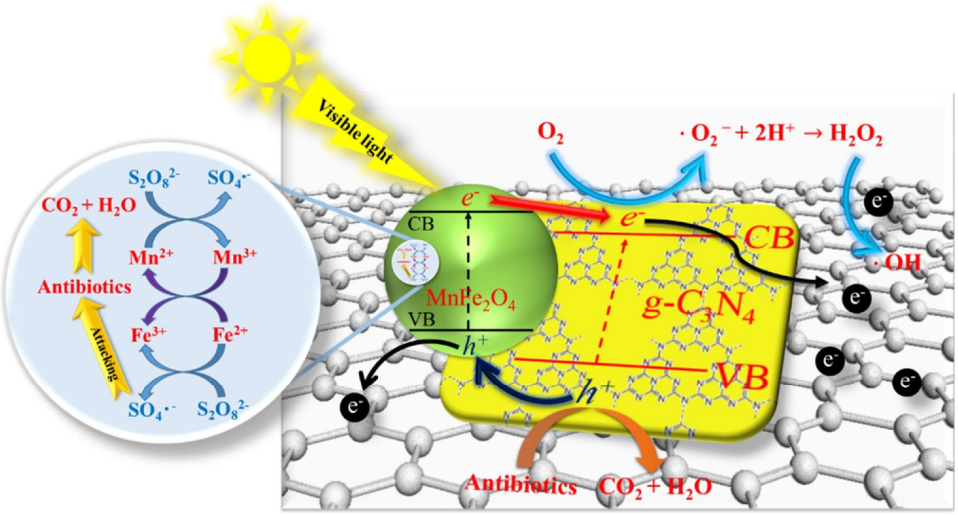

Figure 10: Mechanism for antibiotics degradation in the magnetic g-C_3N_4-$MnFe_2O_4$-graphene/persulfate/vis photo-Fenton system. This figure is reproduced with permission from Ref. [80].

Table 2: Summaries of the studies reporting the integration of adsorption and photo-Fenton oxidation to remove pharmaceuticals in aqueous solutions. Studies are arranged chronologically.

Tested material	Pollutant	Experimental conditions	Removal efficiency	Ref.
Fe(II)/meso-Al_2O_3	Phenol (100 mg L^{-1})	Material = 1 g L^{-1}; pH = 3; t = 60 min; hv = UV; [H_2O_2] = 1 µM	100%	[78]
NaX nanozeolites and $CoFe_2O_4$ nanoparticles	Paracetamol and phenol (20 mg L^{-1} each)	Material = 0.4 g L^{-1}, pH = 3 time = 30min, hv = UVA, [H_2O_2] = 50 mM	99% for both pollutants	[76, 77]
Fe_3O_4/coffee residue	Phenol (100 mg L^{-1})	Material = 1 g L^{-1}, pH = 5, time = 120 min, hv = solar, [H_2O_2] = 1.2 g L^{-1}	100%	[72]
Fe_3O_4@activated carbon	Tetracycline (43 mg L^{-1})	Material = 0.11 g L^{-1}, pH = 3, time = 44 min, hv = UV, [H_2O_2] = 1.9 mM	79%	[82]
Fe_3O_4/graphene oxide nano-composite	Phenol (20 mg L^{-1})	Material = 0.25 g L^{-1}, pH = 5, time = 120 min, hv = UV	98%	[83]
C_3N_4@$MnFe_2O_4$-graphene nanocomposites	Metronidazole (20 mg L^{-1})	Material = 1 g L^{-1}, time = 90 min, hv = visible, [$S_2O_8^{2-}$] = 10 mM	94.5%	[80]
Fe_3O_4@ carbon shell	Tetracycline (60 mg L^{-1})	Material = 0.2 g L^{-1}, time = 10 min, pH = 3, hv = solar, [H_2O_2] = 0.55 M	100%	[84]
Activated carbon and soluble Fe(II)	7 Antibiotics: Ampicillin, clarithromycin, erythromycin, ofloxacin, sulfamethoxazole, tetracycline and trimethoprim (0.1 mg L^{-1} each)	Material = 500 mg L^{-1}, pH = 2.8, time = 180 min, hv = solar, [H_2O_2] = 100 mg L^{-1}, Fe(II) = 5 mg L^{-1}	100% for all	[14]
Fe_3O_4/ reduced graphene oxide composite	Carbamazepine (not reported)	Material = 1g L^{-1}, pH = 6.5, time = 180 min, hv = solar	98%	[85]
$LaFeO_3$ nanoparticl deposited on DiaionTM HP21 resin	Tetracycline (10 mg L^{-1})	Material = 0.2 g L^{-1}, pH = 5.7, time = 180 min, hv = visible, [H_2O_2] = 10 mM	90%	[86]
Graphene oxide-magnetic nanocomposite	Caffeine	pH = 3.0 ± 0.1; H_2O_2 = 5 mmol L^{-1}; catalyst = 0.2 g L^{-1}; caffeine = 1 mg L^{-1}; UV-LED (370 nm)	68% by adsorption while 98% removal by integrated treatment	[87]
Activated carbon and soluble Fe(II)	9 pharmaceuticals Chloramphenicol, fluconazole, flutamide, furosemide, gemfibrozil, ibuprofen, losartan,	Material = 0.7 g L^{-1}, pH = 4, time = 30 min, hv = solar , [H_2O_2] = 50 mg L^{-1}, Fe(II) = 5 mg L^{-1}	80% for fluconazole and 98-99% for the remaining 8 target pollutants	[13, 88]

	nimesulide, paracetamol (0.5 mg L^{-1} each)			
gC_3N_4/Fe_2O_3 hybrids	Tetracycline (20 mg L^{-1})	Material = 0.2 g L^{-1}, time = 60 min, hv = visible, $[H_2O_2]$ = 50 mM	87%	[81]
	Amoxicillin (20 mg L^{-1})		62%	
	Tetracycline (20 mg L^{-1})		91.5%	
	Ciprofloxacin (10 mg L^{-1})		84%	
$MoS_2/FeVO_4$ nanorods composites	Tetracycline (50 mg L^{-1})	Material = 1 g L^{-1}, time = 120 min, hv = visible, $[H_2O_2]$ = 0.1 M	74%	[89]
MoS_2@Schwertmannite	Roxarsone (10 mg L^{-1})	Material = 1 g L^{-1}, pH = 7, time = 40 min, hv = UV, $[H_2O_2]$ = 8.8 mM	85%	[90]
$FeMo_3O_x/g\text{-}C_3N_4$/expended perlite	Tetracycline (25 mg L^{-1})	Material = 1.33 g L^{-1}, time = 120 min pH = 5, hv = visible, $[H_2O_2]$ = 20 $mmol^{-1}$	98%	[91]
	Oxytetracycline (25 mg L^{-1})		93%	
	Chlortetracycline (25 mg L^{-1})		97%	
Electrospun CuS nanoparticles/chitosan nanofiber composites	Tetracycline (10 mg L^{-1})	Material = 0.5 g L^{-1}, time = 30 min, hv = near infrared, Material/H_2O_2 = 0.25 wt%	65%	[92]

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604

4.4. Iron-based materials combined with MoS_2

Other promising materials are those composed of MoS_2 and an iron-based compound. Beside the activation of photocatalysis and photo-Fenton process, MoS_2 has a layered structure that can play a crucial role in organic pollutant adsorption [93]. For instance, Li et al. [93] investigated magnetic $Fe_3O_4/Fe_{1-x}S@MoS_2$ which can efficiently degrade tetracycline in water in the presence of H_2O_2 Under visible light. The advantage of such a composite is its stability, high adsorption capacity and magnetic properties (thus being advantageous for post-treatment separation). However, all the processes including adsorption, photocatalysis and Fenton-based processes are discussed separately, so it is difficult to describe the contribution of each process. Other composites based on MoS_2 have also been investigated for the removal of pharmaceuticals. Liu et al. prepared a $MoS_2/FeVO_4$ composite that can degrade 70% of tetracycline after 1 h reaction under visible light in the presence of H_2O_2 [94]. In addition, after 4 cycles, the degradation efficiency using $MoS_2/FeVO_4$ composite is maintained, thus highlighting its stability. Since the photolysis of H_2O_2 is negligible under visible light, the high degradation extent is due to integrated adsorption with both photo-Fenton and photocatalysis. Indeed, MoS_2 photocatalyst has excellent adsorption properties due to its layered structure. In addition, its combination with $FeVO_4$, another photocatalyst, leads to the formation of a type II heterojunction where the photogenerated e^-/h^+ pairs are efficiently separated, thus producing more reactive oxygen species (including $HO^\bullet$ radicals). Furthermore, $FeVO_4$ contains iron which triggers Fenton-based processes. It is worth reminding that the iron cycle, especially the regeneration of Fe(II), is the limiting step in Fenton process. In $MoS_2/FeVO_4$, the reduction of Fe(III) into Fe(II) is supported by the photogenerated electrons accumulated in $FeVO_4$ and the photo-Fenton reaction (also called iron photolysis).

Wang et al. investigated the efficiency of a composite material of MoS_2 and schwertmannite, an iron based mineral $Fe_8O_8(OH)_{8-2x}(SO_4)_x$ [90]. Schwertmannite has already shown good potential in environmental remediation via adsorption or Fenton-based oxidation processes [95-97]. Therefore, its combination with MoS_2 photocatalyst has been proposed as an efficient strategy for the removal of pharmaceutical compounds. Indeed, MoS_2/schwertmannite can

633 efficiently remove (85% removal) roxarsone by integrated adsorption with photo-
634 Fenton/photocatalysis in the presence of H_2O_2 after 40 min UVA irradiation [90]. This high
635 removal extent has been linked to the efficient iron cycling between Fe(II) /Fe(III). Indeed,
636 similar to $MoS_2/FeVO_4$, the photogenerated electrons in MoS_2 can get transferred in the
637 schwertmannite, thus subsequently reducing Fe(III) into Fe(II), while the iron photolysis under
638 UVA light is also a factor which helps the generation of Fe(II) from Fe(III). In addition, at the
639 composite heterojunction, Fe-O-Mo bond leads also to the reduction of Fe^{3+} by Mo^{4+} [90].
640 *Wang et al.* also highlighted the important role of photogenerated holes along with the attack
641 by hydroxyl radicals in the degradation mechanism of roxarsone [90].
642
643 **4.5. Magnetic composites and other sophisticated iron-based materials**
644 Beside the integrated adsorption with photo-Fenton/photocatalysis, some issues related to
645 post-treatment separation which limits the application of such composite materials. A
646 promising solution is the combination of adsorbent with magnetite (Fe_3O_4) [84]. In addition,
647 Fe_3O_4 is an excellent heterogeneous photo-Fenton catalyst due to the presence of both iron(II)
648 and iron(III), thus being an advantage for the degradation of pharmaceutical compounds in
649 wastewater. Composites based on Fe_3O_4 nanoparticles and carbon-based materials exhibit
650 high specific surface area and can adsorb about 3 time more pollutants than pristine Fe_3O_4
651 [82, 84, 85]. Therefore, in presence of H_2O_2 under solar-like light, a composite based on
652 magnetite modified by thin carbon shell (Fe_3O_4@HCS) can completely degrade tetracycline
653 after 10 min reaction time [84]. Such a composite is stable since a small decrease in
654 degradation efficiency by about 10% is observed after 5 cycles [84]. Fe_3O_4 nanoparticles can
655 be also immobilized on graphene oxide (Fe_3O_4@GO) to trigger integrated adsorption with
656 photo-Fenton process [83]. Such composite can degrade efficiently phenol which is an
657 important precursor for the synthesis of pharmaceutical compounds [83]. Although
658 Fe_3O_4@GO has a lower adsorption capacity than pristine graphene oxide, 80% of phenol can
659 be adsorbed after 2 hours at pH = 5 in the dark while under UV irradiation, the removal extent
660 increases to 98% (from which 80% is fully mineralized) in the presence of H_2O_2. Compared to

661 pristine Fe_3O_4, Fe_3O_4@GO enhances the degradation of phenol by about 30% thank to the
662 integrated adsorption with photo-Fenton process, thus demonstrating the effectiveness of the
663 bifunctional material [83]. It is worth noting Fe_3O_4@GO is also a stable composite with good
664 reproducibility of the results after 3 successive runs while iron leaching do not exceed 0.3 mg
665 L^{-1} [83]. Similarly, reduced graphene oxide (rGO) loaded Fe_3O_4 particles can degrade almost
666 completely carbamazepine (>98%) after 3 h sunlight irradiation. The contribution of adsorption
667 process and the photocatalytic and Fenton-based processes are both about 50%, respectively
668 [85]. Concerning the degradation mechanism, the generation of hydroxyl radicals *via* photo-
669 Fenton process and photocatalysis using Fe_3O_4 can degrade and mineralize the
670 pharmaceutical compounds while the graphene-based adsorbents improve their removal of
671 by π-π interactions [83]. Therefore, the degradation of phenol and carbamazepine using
672 Fe_3O_4@GO and rGO/Fe_3O_4 composite is ascribed to the high adsorption capacity and efficient
673 degradation/mineralization by the hydroxyl radicals [83, 85].
674 More sophisticated magnetic materials can be also designed for the removal of
675 pharmaceuticals [98, 99]. For instance, $FeNi_3$@SiO_2@ZnO can remove completely of
676 penicillin G after 2 h UVA irradiation [99]. In such an integrated system, $FeNi_3$ plays the role
677 of the magnetic component for easy post-separation treatment, while SiO_2 and ZnO are the
678 adsorbent and the photocatalyst, respectively [99]. The photo-Fenton process for such a
679 system has not been yet investigated but it appears promising. It is because a similar
680 composite material, $FeNi_3$/SiO_2, has shown promising ability in coupled adsorption and
681 Fenton-like oxidation for the degradation of metronidazole [98]. About 80% of the
682 metronidazole was removed during this process. Reusability tests showed a slight decrease
683 (of about 8%) in the removal efficiency from the first cycle to the sixth cycle demonstrating the
684 strong stability of this material.
685

4.6. Stability of iron-based materials for integrated adsorption with photochemical process

All the above mentioned composite materials integrate adsorption with photo-Fenton process and/or photocatalysis. However, in such photoactive materials containing iron, it is well known that iron can be leached under light irradiation due to the photolysis of iron. Since most of these composite materials contain an adsorbing component (e.g. carbon-based adsorbents), this potential leaching of iron can be limited, while ternary oxide like $MnFe_2O_4$ is highly stable, so no leaching occurs [83]. In addition, the adsorbents which are initially used for the adsorption of the target contaminants can also adsorb the degradation byproducts, thus (i) removing the remaining pollution which cannot be degrade by photo-Fenton process and (ii) supporting the photochemical reactions at the surface of the composite material [79]. Indeed, the adsorption ability of the composite, not only facilitates the interaction of the contaminant with its surface, but can also increase the transfer of photogenerated radicals leading to higher degradation extents [86]. However, the adsorption process can also affect negatively the photochemical processes where the adsorbed pharmaceuticals (and degradation byproducts) can hinder light utilization by the composite material, thus decreasing the degradation efficiency of the contaminants [86]. Nevertheless, the integrated adsorption with photocatalysis and photo-Fenton process is among the most efficient and innovative methods to efficiently remove pharmaceutical compounds thank to the bifunctionality of such composite materials. Therefore, integrated adsorption with photo-Fenton and photocatalysis is highly relevant for efficient decontamination of wastewaters.

5. Conclusions and outlooks

The use of dual-functional materials to develop integrated treatments based on Fenton oxidation and adsorption could be a highly efficient and cost-effective water treatment. However, it is essential to overcome significant challenges before bench-scale findings can be translated to field applications. Some of these challenges are associated to the treatment

process while others are inherent to the tested materials (heterogeneous catalysts and adsorbents) that pose challenges to treatment system. A brief description of major findings is provided below:

- The development of cost-effective and efficient materials for this purpose is a promising field. It would be highly rewarding to develop materials which are multi-functional, efficient, environment-friendly, stable, and reusable. Innovative materials can broaden the utility of their applications. Magnetic nanomaterials and nanoarchitectures are showing great potential but their practical feasibility, environmental fate, and stability remains questionable. Magnetic materials when exposed to air can develop a passivating layer on its surface that affects the redox reactivity, a phenomenon that turn out to be predominantly significant for nanosized particles with a higher surface-to-volume ratio [20]. Therefore, finding suitable strategies to further improve the stability and efficiency of these materials (e.g. appropriate coating, composites) is needed. In addition to these solid treatments, the addition of other reagents during the reaction may also improve the treatment efficiency. For example, our recent study showed that the application of ascorbic acid, an environment-friendly reducing agent, improved the magnetite-mediated Fenton oxidation for higher removal of pentachlorophenol [100]. The reducing capacity of ascorbic acid enabled the magnetite to maintain its structural Fe(II) contents during the oxidation reaction.
- The development of bioinspired materials has also been suggested as a suitable alternative to the chemically-synthesized supports but better understanding of their stability and efficiency is required in wastewater. Further investigations are certainly needed in order to optimize the operational parameters for high-scale production of bioinspired materials.
- Further integration of these processes with biological treatments should also be sought to make them environmentally attractive. This, however, remains a challenge due to drastic impacts of chemical oxidants on microbial/biota activity which should be

addressed. The chances of improvement exist in preparing the environment-friendly reusable materials, improving the treatment efficiency, and reducing the quantities of chemical oxidants.

- Another critical issue in research focused on hybrid treatments is the laboratory scale investigations. Many studies rely on artificially-contaminated water containing only the target pollutant and often at much higher concentrations. In real systems, however, natural organic matter is found in much higher amounts than target pollutants which would decrease the oxidation efficiency due to non-target consumption of materials and oxidants [10]. Thus, these hybrid treatments could suffer from reduced performance in complex water matrices. For this, more studies are needed on real water/wastewater representative samples to identify the materials with better potential for field scale applications. Moreover, the quality and quantity of contaminated water dictate the choice of appropriate material/treatment. Hence, a thorough site-specific characterization of water is needed prior to their treatment.
- Non-selective nature of adsorption can become a potential drawback in aqueous systems contaminated with a variety of pollutants. To address this, the development of adsorbents with preferential adsorption properties could be advantageous. It will likely concentrate the target pollutants for an ex-situ Fenton oxidation treatment. Moreover, sequential treatment cycles of adsorption and oxidation processes in separate reactors/tanks could also be considered as a means to overcome drawbacks caused by the multi-contamination of real wastewaters. Finally, efforts should be made to upscale the findings to simulated realistic conditions and real field applications.
- Despite success in laboratory, the translation of hybrid treatments for field application remains at an early stage of development. Future research should focus on rationally designing the dual-functional materials for their intended use.

- Finally, an accurate assessment of the value of dual-functional materials with respect to cost and life-cycle impacts is crucial for the successful implementation of these materials.

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Conflict of Interest

The authors declare no conflict of interest.

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