Removal of Ciprofloxacin from Aqueous Solutions by Nanoscale Zerovalent Iron-Based Materials: A Mini Review

Falyouna, Omar
Department of Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Maamoun, Ibrahim
Department of Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Bensaida, Khaoula
Department of Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Sugihara, Yuji
Department of Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

他

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Removal of Ciprofloxacin from Aqueous Solutions by Nanoscale Zerovalent Iron-Based Materials: A Mini Review

Omar Falyouna[1], Ibrahim Maamoun[1], Khaoula Bensaida[1], Yuji Sugihara[1], Osama Eljamal[1]
[1] Environmental Fluid Science, Department of Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Koen Kasuga, Fukuoka 816-8580, Japan.
Corresponding author email: osama-eljamal@kyudai.jp (Osama Eljamal)

ABSTRACT: *Ciprofloxacin is a fluoroquinolone antibiotic developed to fightback several bacterial diseases. The widespread application in human and animal medicine and the low biodegradation resulted in the persistent detection of ciprofloxacin in many water systems. The occurrence of ciprofloxacin threats human and aquatic life by motivating the development of antimicrobial resistant geneses in water. Microscale (ZVI) and nanoscale zerovalent iron (nZVI) were used to efficiently remove ciprofloxacin from aqueous solutions. The aim of this mini review to summarize: (1) the possible routes for ciprofloxacin to enter the environment, (2) the mechanism of oxidizing organic pollutants by nanoscale zerovalent iron (nZVI), (3) the ways to improve the performance of nZVI and overcome its limitations and finally (4) the available treatment systems in the literature which is developed based on NZVI to remove ciprofloxacin from aqueous environments.*

Keywords: Nanoscale zerovalent iron (nZVI)-based materials; Ciprofloxacin; Antimicrobial resistant genes (AMRGs); Oxidation

1. INTRODUCTION

Fluoroquinolones (FQs) are one of the largest classes of antibiotics that extensively used in human and animal medicine to halt the spread of microbial infections [1, 2]. The design of fluoroquinolones (FQs) is evolved over the years to include four generations of these antibiotics [3].

Ciprofloxacin (CIP) is one of the second-generation fluoroquinolones that capable of targeting gram-negative bacteria and some gram-positive bacteria because it includes a fluorine atom in its structure (Table 1) [3, 4]. It is widely and extensively applied to treat many microbial diseases in humans and animals because of its high antimicrobial efficiency and less side effects [5, 6]. As a result of the intensive application and low biodegradation, ciprofloxacin was one of the most frequently detected antibiotics in many aquatic systems in the environment such as rivers, lakes, drinking water and groundwater [7].

The presence of ciprofloxacin in water resources even in low concentrations (ng/L to µg/L) facilitates the development of antimicrobial resistant bacteria (AMRs) [5]. These types of bacteria threat human health and aquatic life because they may cause fatal infections [8].

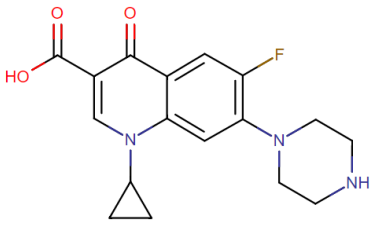
Since the persistent detection of ciprofloxacin and other types of antibiotics in many water environments, the scientists have tried to develop several methods to remove ciprofloxacin from the aquatic systems such as adsorption [9], advanced oxidation processes (AOPs) [10], biodegradation [11], reverse osmosis (RO) [12], nanofiltration and membrane processes [13].

The application of nanomaterials in the field of water and wastewater treatment is getting a significant attention because of their superior performance over the alternative techniques as they can combine several treatment methods in one system such as adsorption and oxidation. Nanoscale zerovalent iron (nZVI) is one of the most important nanomaterials for remediating different types of contaminated waters. It exhibits high adsorption capacity, high surface area and high redox potential which makes it an ideal nanomaterial for removing a wide spectrum of pollutants namely, nitrate [14-17], phosphorus [18-20], radioactive elements [21-24], heavy metals [25-27], pesticides [28], and pharmaceuticals and personal care products (PPCPs) [29].

The aim of this mini review is to summarize the following points:

- The possible pathways for ciprofloxacin to enter the environment.
- The oxidation of organic pollutants by nZVI.
- Methods to improve the efficiency of nZVI in water and wastewater treatment.
- The application of nZVI for the removal of ciprofloxacin from aqueous solutions.

Table 1. Characteristics of Ciprofloxacin

Molecular formula [1,2]	$C_{17}H_{18}FN_3O_3$
Chemical structure [1,2]	
Molar mass [1,2]	331.346 g/mol
log K_{ow} [2]	0.28
pK_a [2]	6.09
Water solubility [1]	30 mg/mL at 20 °C

[1] The reference for this information is [30]
[2] The reference for this information is [31]

2. POSSIBL ROUTES FOR CIPROFLOXACIN TO ENTER THE ENVIRONMENT

There are several routes for ciprofloxacin to enter the environment. When ciprofloxacin is utilized in human medicine, the body will consume a small amount of it and the rest will be discharged with the feces and urine to the sewer system [31]. Eventually, the contaminated domestic wastewater with the residues of ciprofloxacin will reach the conventional wastewater treatment plants (WWTPs). Many previous researchers proved that the WWTPs are not efficient in removing the unmetabolized ciprofloxacin from the effluents of the WWTPs and ciprofloxacin residues are discharged to the surrounding surface water bodies (i.e. rivers and lakes) with the treated wastewater [32]. For example, Marcus Östman et al. studies the occurrence of antibiotics, biocides, and metals in eleven Swedish sewage treatment plants [33]. They found that ciprofloxacin was detected in all samples from the inflow wastewater (116–580 ng/L), in the treated effluents and in the sludge (1600–11000 ng/g) and in the effluents [33].

Also, the application of untreated sludge or the manure of livestock, which contain ciprofloxacin residues, in agriculture facilitates the filtration of ciprofloxacin to the groundwater. M.Boy-Roura et al. reported that ciprofloxacin and sulfamethoxazole were the most frequently detected antibiotics in the alluvial aquifer (Spain) and the surrounding surface water with ng/L concentrations as a result of the application of manures in the agricultural practices in this area [34].

The wastewater of hospital and the antibiotic manufacturing facilities is another important way for ciprofloxacin to enter the environment with elevated concentrations that may reach the level of mg/L [6].

3. THE OXIDATION OF ORGANIC POLLUTANTS BY NZVI

There are several mechanisms for nZVI to remove the contaminants from water, for instance adsorption, coprecipitation, reduction and oxidation [35].

For organic pollutants, nZVI can either adsorb them on the surface or oxidize them through the production of radicals during the reaction with oxygen (i.e. hydroxyl radicals [OH·] or ferryl ions [Fe[IV]) [36].

When nZVI (Fe^0) reacts with oxygen the following reactions will occur depending on the pH of the aqueous medium [36, 37]:

$$Fe^0_{(s)} + O_2 \rightarrow H_2O_2 + Fe^{2+} \quad (1)$$

$$Fe^0_{(s)} + H_2O_2 \rightarrow Fe^{2+} + H_2O \quad (2)$$

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\cdot -} \quad (3)$$

$$Fe^{2+} + O_2^{\cdot -} \rightarrow H_2O_2 + Fe^{3+} \quad (4)$$

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\cdot}\ and/or\ Fe(IV) \quad (5)$$

$$Fe^{3+} \rightarrow Fe^{3+}_{(s)} \quad (6)$$

The solid particles of nZVI (Fe^0) reacts with oxygen to produce hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) [reaction 1]. The highly reactive surface of nZVI may react again with the generated hydrogen peroxide (H_2O_2) to produce water and ferrous ions (Fe^{2+}) [reaction 2]. If reaction 2 occurs in the system, the generated H_2O_2 will be lost and converted to water rather than radicals which will decrease the oxidative capacity of nZVI. On the other hand, if the reaction cycle continues and reaction 3 and 4 occur, more hydrogen peroxide will be produced from the oxidation of ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) by oxygen. Then, the oxidants (Hydroxyl ($OH^{\cdot}$) and/or ferryl ions (Fe(IV)) will be produced through the reaction of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) [reaction 5] [38]. This reaction is known as Fenton reaction [39]. Finally, the resulted oxidants inside the nZVI system will react with the organic pollutants in water to oxidize and degrade them. In reaction 6 the ferric ions will precipitate on the surface of nZVI to form iron oxide layer. This layer will negatively affect the oxidation of organic pollutants by preventing the oxidation of nZVI or by acting as a catalyst for the oxidation of ferrous ions by either oxygen or hydrogen peroxide [36, 37].

The pH of the medium has a strong effect on the nature of the produced radicals in the nZVI system [36, 37]. Under the acid pH, the oxidation of nZVI [reaction 1] is the source of hydrogen peroxide (H_2O_2) where the hydroxyl radicals ($OH^{\cdot}$) will be the dominant oxidants that produced in the system. However, in the neutral pH (pH > 5), nZVI will serve as a source for ferrous ions and the oxidation of ferrous ions [reaction 3 and 4] will be the responsible for generating hydrogen peroxide inside the system. It is believed that, under neutral pH, the more selective and less reactive ferryl ions (Fe(IV)) will be generated.

4. METHODS TO IMPROVE THE EFFICIENCY OF NZVI IN WATER AND WASTEWATER TREATMENT

nZVI particles are highly efficient in removing large groups of organic and inorganic pollutants from water. However, there are some limiting factors hinder or adversely affect the application of nZVI in the environmental remediation of contaminated waters. For example, nZVI particles tend to agglomerate and form a chain-like structure as a result of the high surface energy [40]. Furthermore, the surface of nZVI oxidizes very fast when it is exposed to air and form a passivation layer [41]. These obstacles will reduce the high specific area of nZVI and prevent the interaction between nZVI and the contaminants [41]. In addition, nZVI possess a very low oxidizing capacity towards the organic pollutants where only small fractions of nZVI will be convert to oxidants [36].

There are several approaches which researchers followed in order to tackle these pitfalls and improve the environmental performance of nZVI particles. Some of these methods are as follows:

1. Embracing nZVI particles with different supporting materials, such as zeolite [23], graphene oxide [42], activated carbon [43], biochar [44], and carbon nanotubes [45].
2. Doping the surface of nZVI with noble metals for instance, copper (Cu) [18], nickel (Ni) [46], silver (Ag) [47], gold (Au) [48], and palladium (Pd) [49], to improve the reactivity of nZVI particles.

3. Stabilization of nZVI with different polymers and surfactants, such as polyvinylpyrrolidone (PVP) [50], carboxymethyl cellulose (CMC) [51], starch [52], guar gum [53], and polyacrylamide (PAM) [54].
4. Coating the surface of nZVI particles with thin layer of different materials such as sulfide and magnesium hydroxide [55, 56].
5. Addition of Fenton reagents such as hydrogen peroxide (H_2O_2) [57] and persulfate [58].

The aim of these techniques to prevent the agglomeration of nZVI by reducing the magnetic attraction between the particles, enhance the particle's dispersion, increase the exposure of nZVI surface to react with the pollutants, increase the production of oxidants and finally improve the removal efficiency of nZVI towards many contaminants.

5. THE APPLICATION OF NZVI FOR THE REMOVAL OF CIPROFLOXACIN FROM AQUEOUS SOLUTIONS.

In the literature, there are 13 published articles with the focus on the application of zerovalent iron (ZVI) and nanoscale zero valent iron (nZVI), as a fundamental material, for remediating ciprofloxacin-contaminated waters. Table 2 summarizes these scientific papers with more details about the modifications that applied on ZVI and nZVI, the experimental conditions and the reported maximum removal efficiency of the proposed systems.

There is only two research groups that utilized the microscale zerovalent iron (ZVI) to remove ciprofloxacin from water. João Angelo de Lima Perini et al. applied the zero-valent iron particles (ZVI), without any modifications, to remove ciprofloxacin from aqueous medium. They found that 2.5 g/L of ZVI was capable of removing 85% of 21.58 mg/L ciprofloxacin after 2 hours [59]. However, Nguyen Thanh Hoa et al. recorded 84.5% removal efficiency by only adding 2.25 mM of persulfate (i.e. Fenton reagent) to strengthen the efficiency of 126 mg/L of ZVI to remove 9.96 mg/L ciprofloxacin solution within a shorter time (60 min) [31]. The addition of persulfate in small quantities enhanced the production of radicals in the system which explains the huge reduction in the amount of ZVI from 2500 mg/L to 126 mg/L.

The nano-sized zerovalent iron (nZVI) is more reactive and efficient than the micro-sized zerovalent iron (ZVI). This explains the tendency of researchers to apply nZVI in water treatment rather than ZVI. Eleven projects were conducted to remove ciprofloxacin from water by using nZVI as a core element in their treatment systems.

It can be seen from table 2 that all of the previous researchers reinforced nZVI with one or more of the previously mentioned techniques in section 4 to develop an efficient ciprofloxacin-removal system based on nZVI.

For example, Yingying Shao et al. supported the bare nZVI with wheat straw (WS-nZVI) to overcome the aggregation problem and boost the removal of ciprofloxacin (RE = 97%) [7]. Similarly, Meghdad Pirsaheb et al. [60] and Qiming Mao et al. [61] used carbon dots and biochar, respectively, as supporting materials for nZVI. Qiming Mao et al. further promoted the removal of ciprofloxacin by adding the hydrogen peroxide (H_2O_2) (i.e. Fenton reagent) to significantly enlarge the production of radicals in the system [61]. For the same reason, Sourav Kumar Mondal et al., added the hydrogen peroxide (H_2O_2) with a concentration of 100 mM to 167.54 mg/L of nZVI to accomplish 100% removal efficiency of ciprofloxacin after 50 min [10].

Meghdad Pirsaheb et al. [62] and Rahmani A.R et al. [63] combined nZVI with ultrasonication and the addition of Fenton reagents (i.e. hydrogen peroxide or persulfate) to efficiently uptake ciprofloxacin from aqueous solutions.

Jiwei Liu et al. [30] and Jie Gao et al. [64] synthesized bimetallic Ni/nZVI and sulfide-modified nZVI supported by biochar (S-nZVI/BC), respectively, to effectively activate persulfate in order to produce the strong oxidants ($OH^{\cdot}$ & $SO_4^{\cdot-}$) that responsible for the degradation of ciprofloxacin in water.

Also, Lishuo Chen et al. stabilized the bimetallic nZVI/Cu using the soluble polymer polyvinylpyrrolidone (PVP) where this composite was able to remove 98.4% of ciprofloxacin after 120 min [65]. In another research project, Lishuo Chen et al. used the green tea extracts instead of sodium borohydride to green-synthesize the bimetallic GT-nZVI/Cu nanoparticles [66]. The developed green synthesized bimetallic nanoparticles (GT-nZVI/Cu) (RE = 80%) exhibited a better performance than the traditionally synthesized bimetallic nanoparticles (nZVI/Cu) (RE = 55%) in removing ciprofloxacin from aqueous solutions [66]. It is important to mention that in their both studies, Lishuo Chen et al. applied a weak magnetic field to promote the complete removal of ciprofloxacin from water [65, 66].

6. CONCLUSIONS.

Ciprofloxacin is a second-generation fluoroquinolone antibiotic that is extensively applied worldwide in human and veterinary medicine to treat several bacterial infections. Residues of ciprofloxacin were continuously detected in many water environments (ng/L to µg/L) as a result of its low biodegradability. The effluents of treatment plants which treat domestic, hospital and industrial wastewaters are the main route for ciprofloxacin to enter the environment. The persistent occurrence of ciprofloxacin in water triggers the growth of antimicrobial resistant genes. These genes can put human and aquatic life under serious danger by developing deadly diseases.

Zerovalent iron (ZVI) and nanoscale zerovalent iron (nZVI) were applied to remove and degrade ciprofloxacin in aqueous solutions. The high aggregation and passivation and low oxidative capacity limit the application of nZVI in the treatment of water and wastewater. Several techniques, such as incorporating nZVI with supporting materials, doping noble metals on the surface of nZVI, coating nZVI with polymers or reactive materials and adding Fenton reagents to the nZVI system were employed to fabricate efficient ciprofloxacin-removal systems. This mini review summarizes the developed treatment systems based on NZVI for treating ciprofloxacin-contaminated waters.

Table 2. The utilization of nZVI or ZVI as a base material to remove ciprofloxacin from aqueous solutions.

No.	*Name of the material or system*	*Removal conditions*	*Removal Efficiency (%)*	*Reference*
1	Zero-valent iron **(ZVI)**	Initial CIP concentration = 65μM, initial pH = 6.5, ZVI dosage = 2.5 g/L, contact time = 120 min	85%	[59]
2	Persulfate activated by nano zero-valent iron **(nZVI)**	Initial CIP concentration = 50 mg/L, initial pH = 4.5, PS concentration = 1200 mg/L, nZVI dosage = 120 mg/L, contact time = 60 min	57%	[63]
3	Wheat straw-supported nanoscale zero-valent iron **(WS-NZVI)**	Initial CIP concentration = 50 mg/L, initial pH = 6, WS-NZVI dosage = 1 g/L, contact time = 240 min	97%	[7]
4	Nano zero-valent iron **(nZVI)** encapsulated in carbon dots	N/A	51%	[60]
5	Ultrasonic enhanced zero-valent iron **(nZVI)**-based Fenton reaction	Initial CIP concentration = 100 mg/L, initial pH = 7, nZVI dosage = 117 mg/L, H_2O_2 concentration = 3 mM, aeration = 1.61 L/min, contact time = 60 min	94%	[62]
6	Polyvinylpyrrolidone stabilized **NZVI/Cu** bimetallic particles **(PVP-NZVI/Cu)**	Initial CIP concentration = 100 mg/L, initial pH = 6, nZVI dosage = 0.5 g/L, nZVI/Cu = 1:0.04, weak magnetic field = 2 mT, reaction temperature = 35°C, contact time = 120 min	98.4	[65]
7	Biochar-supported nanoscale zerovalent iron **(BC-nZVI)** activating H_2O_2	Initial CIP concentration = 100 mg/L, initial pH = 3~4, nZVI dosage = 0.4 g/L, doses of H_2O_2= 20 mM, BC:nZVI = 1:1, reaction temperature = 25°C, contact time = 60 min	70%	[61]
8	Zero-valent metal **(ZVI)**-activated persulfate oxidation	Initial CIP concentration = 30 μM, initial pH = 3, ZVI dosage = 126 mg/L, molar dosage of PS = 2.25 mM, contact time = 60 min	84.5%	[31]
9	Persulfate activation by sulfide-modified nanoscale iron supported by biochar **(S-nZVI/BC)**	Initial CIP concentration = 50 mg/L, initial pH = 5, S-nZVI/BC dosage = 0.4 g/L, S/Fe molar ratio = 0.25, doses of PS = 1 mM, contact time = 60 min	89.78%	[64]
10	Green synthesized bimetallic **GT-nZVI/Cu** composites	Initial CIP concentration = 30 μM, initial pH = 6, GT-nZVI/Cu dosage = 0.5 g/L, GT-nZVI/Cu = 1/0.08), weak magnetic field = 5mT, reaction temperature = 35°C, contact time = 90 min	100%	[66]
11	A granular adsorbent-supported **Fe/Ni nanoparticle** activating persulfate system	Initial CIP concentration = 100 mg/L, initial pH = 3.0, PS concentration = 10mM, Ni@PGA dosage = 0.1g, and reaction temperature = 30°C, contact time =12 h.	93.24%	[30]
12	**NZVI**/H_2O_2/Aeration/MF	Initial CIP concentration = 100 mg/L, initial pH = 7.0, nZVI dosage = 600 mg/L, WMF = 40 mT, contact time = 10 min.	97%	[57]
13	Modified Fenton (**nZVI**/H_2O_2)	Initial CIP concentration = 10 mg/L, initial pH = 7.0, nZVI dosage = 167.54 mg/L, H_2O_2 dosage = 100 mM, contact time = 50 min.	100%	[10]

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