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DERLEME

AN OVERVIEW ON USAGE OF NANOSCALE ZERO VALENT IRON FOR PHARMACEUTICALS ELIMINATION

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ABSTRACT

Pharmaceutically active compounds are gaining the recognition of emerging environmental contaminants classified as recalcitrant bio-accumulative compounds hence they are regarded as toxic and hazardous chemicals. In this context, efficient treatment processes are needed. Nanotechnology can adequately address many of the water quality issues by using different types nanomaterials. Nano zero valent iron (nZVI) has been applied to remove various organic compounds from aqueous solutions since the removal mechanism depends on adsorption and degradation. This article summarizes the recent knowledge of nZVI in pharmaceutical degradation considering the key factors such as initial contaminant concentration, dosage of bare and modified nZVI, pH of aqueous matrix and reaction time which are mainly examined in the experiments. Additionally, the degradation mechanism of studied pharmaceutical compounds monitored by observing intermediates and end-products is presented.

Keywords: Nano zero valent iron, Pharmaceutical degradation, Nanotechnology, Bimetallic iron

1. INTRODUCTION

The pressure on freshwater resources is increasing rapidly due to the increasing world's demand of food and energy [1]. On the other hand, the shortage of fresh water has been resulted from the contaminated surface/ground water sources. Aquifers are being polluted with multiple problems such as saltwater intrusion, soil erosion, inadequate sanitation, contamination of ground/surface waters by algal blooms and micropollutant; detergents, fertilizers, pesticides, chemicals and heavy metals [2].

Micropollutants, also termed as emerging contaminants, various compounds as well as natural substances. These emerging contaminants contain persistent organic pollutants, microconstituents, cyanotoxins, pesticides and herbicides, disinfection by-products, endocrine-disrupting chemicals (EDCs), pharmaceuticals and personal care products (PPCPs), and a host of other compounds. Pharmaceutically active compounds (PhACs) present in the different matrix have become an issue of concern due to their persistence and their high biological activity at even very low concentrations [3] which also create challenges for water and wastewater treatment processes [4]. The presence of certain PhACs in rivers, lakes, wastewater, sewage treatment plants (STPs), soil, groundwater, and sediments have been determined in previous studies [5, 6, 7]. The dilution effects and some mechanism such as biodegradation and photodegradation or sorption to sediments make them being found at very low concentrations (µg /L or ng/L) [8]. The major concern about low concentration is their toxicity, development of antibiotic resistance in pathogenic bacteria, genotoxicity and endocrine disruption [9]. On the other hand, the "low concentration'' and diversity of these micropollutants not only complicate their detection and analysis procedures but also create challenges for water and wastewater treatment [10]. Several review articles have reported the ecotoxicological effects of PhACs [9] and their occurrence in various water bodies, including groundwater [12], surface water and wastewater [13], and sewage treatment plants [14, 15].

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The substantial effort should be carried out to evaluate the occurrence of various pharmaceuticals and to develop efficient treatment processes to remove them. For that reason many different processes such as coagulation-flocculation, activated carbon adsorption, ozonation and advanced oxidation processes have been applied to remove and degrade these compounds. Many studies on PhACs toxicity, occurrence in the environment as well as the removal processes from different contaminated environment are available in the literature. Some of them are summarized in Table 1.

Table 1. Review papers on pharmaceutically active compounds

Mentioned Issues	**Literature**
Some of the physicochemical and biological treatment methods used for the removal of antibiotics and hormone.	[3]
The occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment.	[10]
Degradation and removal methods of antibiotics from aqueous matrices—A review.	[16]
The occurrence patterns of PPCPs in water environments and the techniques adopted for their treatment in STP/WTP unit processes operating in various countries.	[17]
Pharmaceuticals and personal care products in waters: occurrence, toxicity, and risk.	[18]
The classes, functions, representatives, analytic methods, removal efficiency of PPCPs by wastewater treatment plants of the frequently detected PPCPs.	[19]
The removal efficiency of pharmaceuticals in conventional activated sludge systems and in MBR.	[20]

Biological treatment systems such as activated sludge and biological trickling and different physicochemical treatments such as coagulation, flocculation, or lime softening proved to be ineffective for removing different EDCs and pharmaceutical compounds in various studies [21-23]. Advanced oxidation processes for water and wastewater include electrochemical oxidation, ozonation, photocatalysis, ultrasonic radiation, Fenton and photo-Fenton processes have been examined to develop effective treatment technologies for their elimination. The major concern of applying these processes is the formation of oxidation by-products or transformation products from these compounds. The other disadvantage is high operation costs due to high energy consumption and requirement of additional chemicals.

On the other hand, the advances in nanotechnology have made it possible to apply different types of nanoparticles and/or nanofibers for effectively treating water/wastewater meeting the ever increasing water quality standards. As particle size decreases, the proportion of atoms located at the surface increases which raises its tendency to adsorb, interact and react with other atoms, molecules and complexes to achieve charge stabilization [24]. One of the most widely studied nanoparticle for water treatment is nano metallic iron since its low price and high reactivity. The use of zero valent iron (ZVI) has been started in subsurface treatment as a remediation agent in early 1990s. For example, granular ZVI was first employed in permeable reactive barrier (PRBs) system [25]. The degradation of various contaminants such as chlorinated organic solvents, organochlorine pesticides, polychlorinated biphenlys (PCBs) and heavy metals have been examined with using zero valent iron since all these compounds have received significant attention for groundwater treatment. However, nZVI has already been coated/impregnated with polyelectrolyte, surfactant and a second metal to enhance the dispersibility and surface area and protect the corrosion. Although several studies of using enhanced nZVI as a reactant have been reported in recent years, the efforts on examination of removal performance of PhACs are still lacking.

The goal of this paper is to review the application of nano zero valent iron (nZVI) particles for the elimination of commonly examined pharmaceuticals compounds in the previous studies. For this purpose, the sorption of antibiotics under different experimental conditions such as pH, initial contaminant concentration, dosage of bare and modified nZVI and reaction time and their removal mechanism are summarized.

2. Pharmaceuticals in the Aquatic Environment

The occurrence of PhACs in aquatic system have received attention due to an increase in production and consumption of these chemicals. This production still increases due to the high demands of PhAC in preventing or curing disease and sustaining the development of economic such as aquaculture and livestock farming.

PhACs include prescription and nonprescription human drugs, illegal drugs, and veterinary drugs, as well as their subsequent metabolites and conjugates, including non-steroidal anti-inflammatory drugs (NSAIDs), lipid regulator, anticonvulsants, antibiotics, β-blockers and stimulants and steroid hormones. Among these compounds, non-steroidal anti-inflammatory drugs, carbamazepine and sulfamethoxazole were the most frequently reported compounds in surface water in many countries [10]. PhAC may enter the environment as components of human or animal waste, after incomplete absorption and excretion from the body, or may result from emissions of medical, industrial, agricultural, or household wastes [26-29]. They can be considered to be persistent because of their incomplete degradation, formation of active by-products during biological degradation, and continued discharge into the environment [30].

3. NANOSCALE ZERO-VALENT IRON

Iron typically exists in the environment as iron(II) and iron(III) oxides whereas zero valent iron (ZVI) is an engineered material. The applications of ZVI have focused primarily on the electron-donating properties of ZVI. The core-shell model of ZVI is shown in Fig 1. The core consists of mainly zero-valent iron and provides the reducing power for reactions with many environmental contaminants. The shell is largely iron oxides/hydroxides formed from the oxidation of zero-valent iron that provides sites for chemical complex formation (e.g., chemisorption).

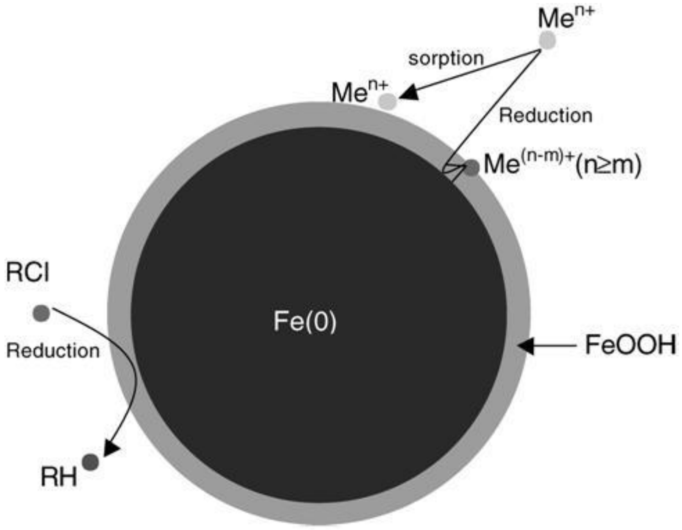


Figure 1. The core-shell model of zero-valent iron nanoparticles [23]

ZVI is fairly reactive in water and can serve as an excellent electron donor, which makes it a remediation material. Reactions at the nanoscale zero-valent iron (nZVI) surface involve many steps, mass transport of molecules to the surface and electron transfer (ET) from the ZVI to the surface adsorbed molecules. The proportion of surface and near surface atoms increases when the particle size decreases. Surface atoms tend to have more unsatisfied or dangling bonds with concomitantly higher surface energy. Thus, the surface atoms have a stronger tendency to interact, adsorb, and react with other atoms or molecules in order to achieve surface stabilization [24].The field scale applications of nZVI for effective reduction of organochlorine compounds including trichloroethylene, perchloroethylene and pesticide, azo dyes besides of inorganic species such as nitrate make it popular in the scientific area on removal of different contaminants in controlled laboratory experiments in recent years [31-34].Although the reduction of these species results in significant reduction of toxicity in most cases, the overall removal of dissolved organic carbon (DOC) is low due to, generated intermediates. Note that the detailed knowledge of remediation for various organic and inorganic contaminants except of PhACs are out of scope of this review.

3.1 Modified Nanoscale Zero Valent Iron

The aqueous corrosion of iron which is the degradation of any material is the main limitation for the application of zero valent iron. The manufacture of all metals from oxide requires an input of energy and as a result the material has a strong thermodynamic driving force to return to its native low-energy state. This process of reversion is most commonly referred to as corrosion [24]. ZVI can be easily oxidized in the presence of oxygen. This hinder its direct application and reduce its reactivity with poor mobility and transport for the continuous in situ environmental remediation [35]. To address this issue, nZVI has been alloyed with a noble metal such as Pd, Pt, Ag, Ni, Cu, etc.

In such electrochemical couples, Fe(0) is considered to behave as an anode, becoming sacrificially oxidized to galvanically protect the noble metal. The chemical reduction of sorbed contaminants at the bimetallic nZVI surface is considered to occur through either direct electron transfer with the noble metal or through reaction with hydrogen produced by oxidation of Fe(0). Hydrogen is likely present as a dissolved gas, some of which is adsorbed to the particle surfaces, with an undetermined fraction possibly present as active metal hydride having undergone diatomic dissociation and reaction with the exposed noble metal [36]. In recent years numerous experimental studies of bimetallic nZVI for contaminant remediation have been carried out with, including Fe/Pd, [37, 38], Fe/Pt [39], Fe/Ag [40] and Fe/Ni [41, 42]. For example, Palladium (Pd) has exhibited extremely high removal efficiency as an additive in Pd/Fe bimetallic catalytic reductants, but the application is limited because of its high cost [43, 44]. Cu and Ni being more economical metals have been examined instead of Pd. The disadvantage of using bimetallic nanoparticles is possible secondary potentially short lifetimes in the subsurface due to surface passivation [45]. Another disadvantage of bimetallic nanoparticles is the added environmental risk related with injecting another metal into the subsurface, especially when using Fe/Ni nanoparticles [45, 46].

nZVI has also been coated/impregnated with polyelectrolyte or surfactant stabilizing the colloidal suspensions in terms of enhancement of its dispersibility and surface area. The support material usually used include clay [47], pumice [48], kaolin [49], resin [50] and carbon materials [51]. The modifications are illustrated in Figure 2 based on the material in synthesis procedure. All these research reported that nZVI composites materials were applied once for contaminant removal with repetitive applications being rare [52]. We summarize the efficiency of modified nZVI onto removal of PhACs Section 5.1.3.

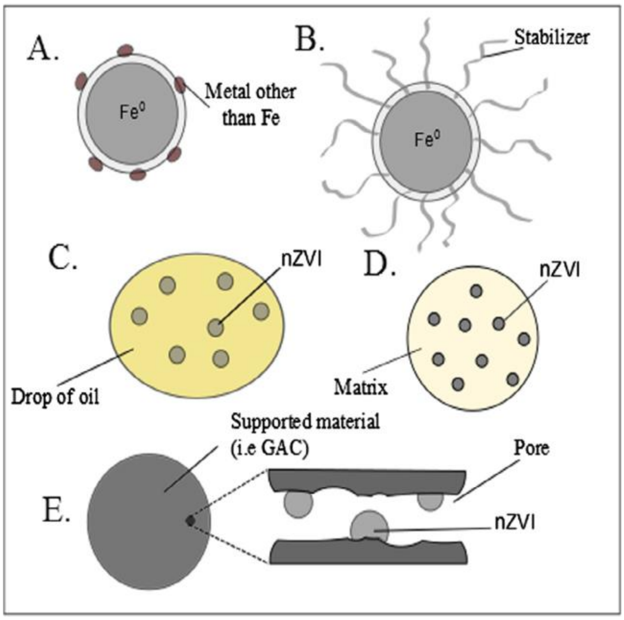


Figure 2. The schematic presentation of nZVI modification methods. (A) Other metal doping, (B) coating the surface of the stabilizing compound, (C) emulsified nZVI (EZVI), (D) encapsulated in matrix, and (E) nZVI deposition on the support [53].

5. Nanoscale zero valent iron on pharmaceuticals elimination

The pharmaceutical degradation has been achieved using bare and supported nZVI particles. Although the number of studies examining the potential of nZVI to eliminate pharmaceutical compounds have increased even to date all the studies are limited to laboratory scale. Since the reductive degradation process largely depends on a set of process variables, such as initial contaminant concentration, reductant dose or surface area, pH of aqueous matrix and contact time, all of them have been examined in many experimental studies as shown in Table 2. Hence we aimed to discuss these factors in detail as following subsections. Additionally, degradation mechanism of studied pharmaceutical compounds monitored by observing intermediates and end-products are also presented to emphasize the reaction between nZVI and pollutant.

Table 2. The conditions of experimental studies with nZVI

Antibiotics	Supported material	nZVI material	Initial Concentration	nZVI dosage	pH	Reaction time	Removal mechanism	Efficiency	Ref.
Chloramphenicol (CAP)	Functionalized biochar	nZVI	3.10 μM/L	-	4-4.5	12-15 h	Adsorption and reduction	Approximately 100%	[52]
Metronidazole (MNZ)	-	nZVI	80 mg/L	0.1 g/L	5.6	5 min	Degradation and adsorption	>99%	[54]
Tetracycline (TC)	Starch	nZVI	500 mg/L	0.2 g/L	6	240 min	Adsorption degradation and flocculation	99%	[55]
Amoxicillin (AMX)	-	nZVI	20 mg/L	0.5 g/L	-	-	Reduction, adsorption and precipitation	-	[56]
	Zeolite					-		-	
	PEG					75 min		100%	
Ampicillin (AMP)	-	nZVI	20 mg/L	0.5 g/L		-		-	
	Zeolite					-		-	
	PEG					-		-	
Metronidazole (MNZ)	-	nZVI	80 mg/L	0.33 g/L	5.6	90 min	Hydrogenation reduction	98.1%	[57]
Chloramphenicol (CAP)	-	nZVI	100 mg/L	1.06 g/L	6.8	5 min	Adsorption, deoxidation and reduction	100%	[58]
Chloramphenicol (CAP)	-	nZVI	0.30 mM	1.8 mM	7	20 min	Reduction	97%	[59]
Tetracycline	-	nZVI	50 mg/L	5 g/L	4	180 min	Adsorption and	91%	[60]

(TC)	Pumice	nZVI	50 mg/L	5 g/l	4		reduction	92%	
Tetracycline (TC) Oxytetracycline (OTC)	- -	nZVI nZVI	60 mg/L 60 mg/L	0.4 g/L 0.4 g/L	6 6	120 min 120 min	Adsorption	97% 80%	[61]
Amoxicillin (AMX)	Bentonite -	Fe/Ni Fe/Ni	60 mg/L 60 mg/L	4 g/L 2 g/L	6 6	60 min 60 min	Adsorption, degradation	>94% -	[62]
Amoxicillin (AMX)	Bentonite	nZVI	20 mg/L	4 g/L	6.7	60 min	Adsorption and reduction	93.5%	[63]
Metronidazole (MNZ)	Carbon spheres	nZVI	60 mg/L	0.8 g/L	5.01	90 min	Adsorption and reduction	96.79%	[64]
Metronidazole (MNZ)	Polyacrylonitrile membrane	nZVI	60 mg/L	18.4 mg/g	7	90 min	Adsorption and reduction	>97%	[65]
Tetracycline (TC)	Polyvinylpyrrolidone	nZVI	100 mg/L	0.1 g/L	6.5	240 min	Adsorption	Approximately 100%	[66]
Tetracycline (TC)	MCM-41-zeolite	nZVI	100 mg/L	1 g/L	5	60 min	Adsorption	98.7%	[67]
Cephalexin (CLX)	Biochar	Fe/Ag	20 mg/L	1.5 g/L	6.15	90 min	Adsorption	>86%	[68]
Metronidazole (MNZ)	Poly(vinylidene fluoride) membrane	nZVI	67.44 g/L		7	120 min			[69]
Amoxicillin (AMX)	Bentonite	Fe/Ni	60 mg/L	4 g/L	6	60 min	Adsorption and catalytic reduction	>94%	[70]
Amoxicillin (AMX) and Cd(II)	Chitosan	Ni/Fe	60 mg/L	0.036 mol/L	5.65	60 min	Adsorption and reduction	93%	[71]
Carbamazepine (CBZ)	-	nZVI	5 mg/L	1 g/L	3 7 11	120 min	Adsorption	0%	[72]
Tetracycline (TC)	-	Fe/Ni nZVI	100 mg/L 100 mg/L	0.1 g/L 0.2 g/L	5 5	300 min	Adsorption and degradation	97.4% 83.7	[73]
Oxytetracycline (OTC)	-	Fe/Cu Fe/Ni nZVI	100 mg/L 100 mg/L 100 mg/L	0.1-0.2 g/L 0.1-0.2 g/L 0.1 g/L	- - -	240 min	Oxidation	71.44% 62.34% 31.05%	[74]
Tetracycline (TC)	Graphene oxide	Cu/Fe	100 mg/L	0.25 g/L	6.5	60 min	Adsorption	Approximately 100%	[75]
Tetracycline (TC) Oxytetracycline (OTC) Chlortetracycline (CTC)	- - -	Fe/Cu	60 mg/L	0.2 g/L 0.6 g/L 0.6 g/L	6	120 min	Adsorption	>90%	[76]
Chloramphenicol	-	Fe/Ag	100 mg/L	1 g/L	6.5	-	Reduction	-	[77]
Tetracycline (TC) Chlortetracycline (CTC)	- -	Fe/Ni Fe/Ni	0.1 g/L 0.4 g/L	60 mg/L 60 mg/L	5 6	30 min 60 min	Adsorption	95%	[78]
Metronidazole (MNZ)	-	nZVI Fe/Pd 1.	- 125 mg/L	0.42 mg/L 0.42 mg/L	3.2	5 min -	-	-	[79]
Enrofloxacin (ENR)	Graphene oxide	nZVI	-	1.25 g/L	6.6	30 min	Oxidation and adsorption	-	[80]
Diclofenac (DF)	-	Fe/Pd	32 µM	-	7.5-8.5	120 min	Adsorption and co-precipitation	Approximately 100%	[81]
Metronidazole (MNZ)	-	nZVI	80 mg/L	0.1 g/L	5.60	90 min	Adsorption and reduction	-	[82]

5.1. Effect of Process Variables

5.1.1. The effect of initial reactants concentrations

It is well known that the dosages of the initial reactants (nZVI and pharmaceutical compound) are important parameters that affect the reaction rate [59]. In a study, initial metronidazole (MNZ) concentration in the ranging from 45 to 100 mg/L was evaluated for MNZ removal. The degradation efficiency of MNZ was 96.15% at an initial MNZ concentration of 45 mg/L in 90 min, while at an initial concentration of 100 mg/L, only 67.14% MNZ was removed. Similar results concerning the effect of initial concentration of target pollutant were also reported by other studies. The removal efficiency of tetracycline (TC) changed slightly with nZVI and reached a maximum value of 98.7% as the initial concentration of TC increased from 19.3 mg/L to 99.0 mg/L, then decreased to 86.9% when the initial concentration further increased to 500 mg/L [67]. The effect of initial cephalexin (CLX) concentration on removal efficiency was examined in the range of 10–40 mg/L. The results showed that the removal efficiency increased prominently as the initial CLX concentration decreased. The reaction rate, k, for CLX removal was 0.0154, 0.0256, 0.0123 and 0.0049 g/mg/min when the solution concentration rose from 10 to 40 mg/L, respectively [68]. The reasonable explanation was that available activities for target pollutant when the concentration was lower, which also meant less probability of contact between pollutant molecules and water chemicals. However, higher concentration resulted in competitive adsorption among the pollutant molecules, due to the adsorption capacity was limited at a fixed adsorbent concentration [70, 83].

On the other hand, at a fixed pollutant concentration nZVI dosage also plays important role in the reaction between the nZVI and pollutant. For instance, the removal efficiency of chloramphenicol was greatly enhanced with the increase of nZVI dosage. This enhancement was due to the catalytic reduction occurring on the surface of nZVI and increasing available surface area for adsorption and reaction sites [84]. The result is in accordance with the studies of modified biochar supported bimetallic Ag/Fe nanoparticles (Ag/Fe/MB) used to remove CLX [68]. The removal efficiency of CLX byAg/Fe/MB was 64.72% at the dosage of 1.0 g/L for 90 min. However, the removal efficiency was nearly 78.87%, 82.92% when the dosage of Ag/Fe/MB was 1.5 g/L and 2.0 g/L, respectively due to that the increase in the mass of Ag/Fe/MB could lead to an enhancement in available active sites for CLX [68]. This behavior was also confirmed by the study of Wu et al. [74] in which oxytetracycline (OTC) removal increased by higher nZVI, Fe/Ni or Fe/Cu bimetallic nanoparticles (BNPs). OTC was almost completely removed within 240 min when the dosage of nanoparticle increased from 0.1 to 0.2 g/L [73]. The degradation profiles of AMX obtained in the reduction tests with different AMX/gnZVI (green zero valent iron nanoparticle) molar ratios (from 1:1.5 to 1:75) were examined. From the results of experiments, it was observed that higher amounts of gnZVI led to the increase in the degradation of AMX: from 50% with the 1:1.5 ratio to 100% with the 1:75 ratio, after a 60 min reaction time[85]. In another study, the removal efficiency of TC increased from 47.9% to 98.7% as the amount of MCM-41-zeolite A(Fe-MCM-41-A) changed from 0.1 g/L to 1.0 g/L after 60 min's reaction. This may be attributed to the increases in both the effective contact area and the number of adsorption sites, as the dosage of adsorbent increased. Then no significant increase of the removal efficiency was found even though the adsorbent dosage increased continuously [67].

5.1.2. The effect of pH

The solution pH is considered as one of the most important factors affecting the removal process of organic and inorganic contaminants with nZVI since nZVI reactivity toward aqueous contaminants change significantly [86, 87]. Generally, nZVI would be corroded too quickly under strongly acidic conditions (pH 3.0), and excessive hydrogen would escape from the solution and lead to the low utilization ratio of Fe(0) [59]. Another view is following that: at lower pH values, the iron corrosion can be accelerated, producing abundant hydrogen for hydrogenation reactions [88]. At neutral and alkaline conditions, a passive film of iron hydroxide forms on the surfaces of nanoparticles, which can inhibit the contact with contaminants thereby further reactions [89]. These arguments have been confirmed with the studies of nZVI usage for the antibiotic degradation. For example; the degradation efficiency of amoxicillin increased as the pH value decreased, and a maximum level of degradation efficiency was observed at pH value of 4. This was explained by the low solution pH value favoring the corrosion of iron in aqueous solution, including the formation of atomic hydrogen and subsequently molecular hydrogen at the Ni surface [70]. Chen et al. [57] examined the effects of initial pH values (pH 3.03, 5.60 and 9.60) on metronidazole (MNZ) removal. The results indicated that the removal efficiency was obviously increased with decreasing pH value. For example, at pH 9.60, 10.9% of the MNZ in the solution was removed within the first 5 min. However, 29.3% and 59.3% of the MNZ was removed from the solutions when the solution pH was decreased to 5.60 and 3.03, respectively, within 5 min. Moreover, the removal efficiency of cephalexin by Fe/Ag/MB was in the range of 88.18% and 42.04% when the initial solution pH value rose from 2 to 9 [68].

On the other hand, the nanoparticles should be much better dispersed in suspension at pH 5 due to the electrostatic repulsion force among particles providing more active sites for adsorption of TC and TC species [73, 74].

The removal efficiency decreased as the increase of the initial pH, which was the same for both Fe/Ni bimetallic nanoparticle (Fe/Ni BNPs) and nZVI. Obviously, Fe/Ni BNPs had higher removal efficiency of TC than that of nZVI. TC removal efficiency reached 97.4%, 79.0%, 43.5% for Fe/Ni BNPs at pH 5, 7, 9, respectively. But it was only 83.7%, 55.6%, 37.9% for nZVI accordingly. The nanoparticles should be much better dispersed in suspension at pH 5 due to the electrostatic repulsion force among particles providing more active sites for adsorption of TC [73]. When the initial pH of the OTC solution was about 5, the removal efficiency of OTC was almost 90% after reacting with Fe/Ni or Fe/Cu BNPs for 4 hr, respectively [73]. Chen et al. [57] also examined the effects of initial pH values (pH 3.03, 5.60 and 9.60) on metronidazole (MNZ) removal. The results indicated that the removal efficiency was obviously increased with decreasing pH value. For example, at pH 9.60, 10.9% of the MNZ in the solution was removed within the first 5 min. However, 29.3% and 59.3% of the MNZ was removed from the solutions when the solution pH was decreased to 5.60 and 3.03, respectively, within 5 min. After 40 min, the removal efficiencies were found to be 94.2%, 2.7% and 52.3% at initial pH of 3.03, 5.60, and 9.60, respectively. In another study, the chloramphenicol (CAP) removal was examined for a series of initial pH values (2.8, 4.8, 6.8, 8.8 and 10.8). The complete removal of CAP was achieved within 8 min at pH:3.0, while complete CAP removal required 15 min, 20 min, and 30 min at pH5.0, 7.0, and 9.5, respectively [58]. The removal efficiency of tetracycline was studied as a function of initial pH (3.0, 6.5, 8.0,10.0) within 4 h since TC exists as a cationic, zwitterionic and anionic species under acidic, moderately acidic to neutral and alkaline conditions. At pH 3.0 and pH 6.5, the removal efficiency of TC was approximately 100%, but at pH 8.0 and pH 10.0it decreased to only 53.5% and 43.1%, respectively [66]. It was consistent with the results reported in a previous study [61] about the adsorption of TC onto nZVI. The highest removal was observed at about pH:5 resulted from the electrostatic attraction between nZVI and TC since nZVI was positively charged at pH<5.38 and negatively charged at pH>5.33 while the pHzpc of ZVI was found to be 5.38 [61].

5.1.3. The effect of modified nZVI

The usage of bare nZVI generally exhibit low performance on removal of pharmaceuticals when compared with modified nZVI. Therefore several researchers have used bimetallic nanoparticle to increase the reactivity of nZVI for pharmaceuticals removal experiments [75,77-79]. Bimetallic nanoscale zero valent iron particles, including Fe/Cu and Fe/Ni BNPs, were examined for oxytetracycline (OTC) removal. Fe/Cu presented remarkable ability for OTC degradation and removed 71.44% of OTC (100 mg/L) in 4 hr, while only 62.34% and 31.05% of OTC was degraded by Fe/Ni and nZVI respectively [74]. To achieve good stability and dispersibility for the Fe/Ni nanoparticles, the chitosan (CS– Fe/Ni) as a stabilizer was used on the removal of amoxicillin (AMX). The removal rate of AMX by CS– Fe/Ni was significantly higher than that of CS–Fe with kobs= 0.07845 and 0.01007, (kobs is the rate constant for the catalytic reaction for steps leading up to product formation) respectively. This was attributed that the formed hydrogen was adsorbed onto the catalytic nickel surface and AMX was then adsorbed onto the surface of Fe/Ni BNPs, leading to the breakdown of AMX by the reductively degraded H radical. Supportive materials such as polyethylene glycol (PEG) and zeolite were used to improve the performance of nZVI as an adsorbent. The results showed 10% more AMX removal and 30% more AMP removal by PEG-nZVI, while nearly 30% more ampicillin removal was found by zeolite-nZVI [56].

5.1.4. The effect of chemistry of aqueous matrix

Besides to reaction conditions, the significance of chemistry of aqueous matrix were considered for removal of PhACs since the various species might effect the reduction and adsorption mechanism. Ahmet et al. [52] reported that synthetic wastewater had slightly positive influence on the overall reduction of chloramphenicol followed by lake and deionized water resulted from high ionic mobility of chloramphenicol towards nZVI particles [52].

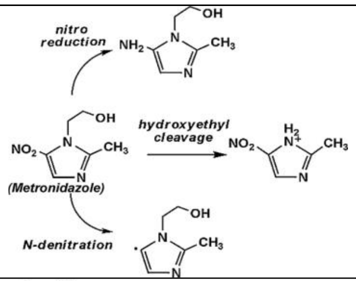
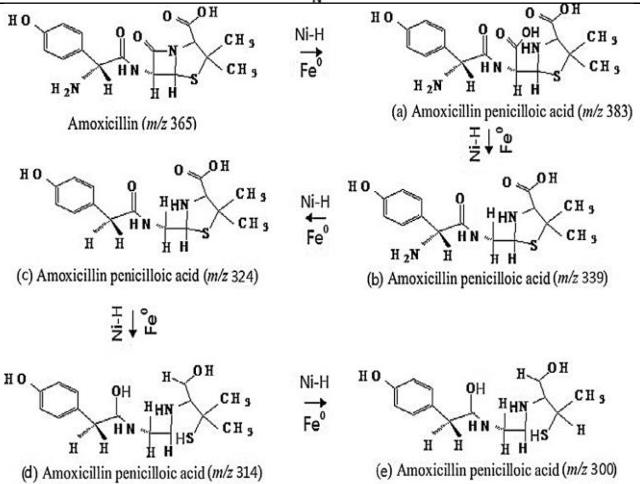
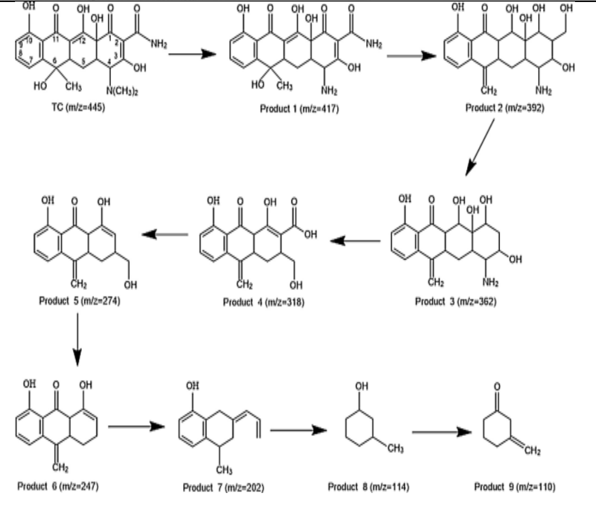
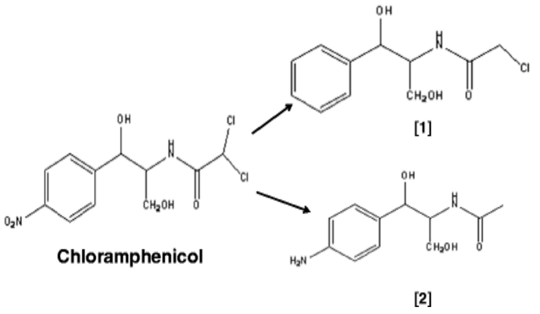
Tetracycline removal with nZVI modified starch was evaluated with NaCI, $CaCI_2$, NaH_2AsO_4. Although they had a little effect on TC removal, the high concentration ion strength improved the sedimentation rate. They concluded that the flocculation (69%) was more important than the degradation and adsorption (30%) on TC removal [55].Yang et al. [69] also examined the influences of calcium and bicarbonate ions on the performance of polyvinylidene fluoride supported nano zero valent iron for metronidazole removal. Those inhibitions were found to be insignificant although they exerted differing degrees of inhibitions of MNZ removal. On the other hand, the competitive anions which might hinder the removal of PhACs have been assessed in a few studies. For instance, Dong et al. [73] determined the great inhibition of NO_3^- among the other anions including $H_2PO_4^-$, SO_4^{-2}, HCO_3^- resulting from redox reaction with NO_3^- when they evaluated the performance of Fe/Ni bimetallic nanoparticle for the degradation of TC. Liu et al. [59] reported that the higher conductivity and salinity led to serious aggregation of nZVI with an average of several micrometers from the experiments of chloramphenicol removal. However, halide additive (as NaCI) accelerated iron corrosion and consequently increased removal of antibiotics [72].

5.2. The Removal Mechanism of Pharmaceutical Compounds

As an electron donor, nZVI is effective in the transformation of a wide array of common environmental contaminants such as chlorinated solvents, organic dyes and pharmaceutical compounds due to its strong reduction characteristics. To speculate the possible degradation or transformation pathway, process can be monitored by observing intermediates and end-products by high performance liquid chromatography–mass spectrometry (HPLC–MS) and liquid chromatography–mass spectrometry (LC-MS). Table 3 shows some degradation products of examined antibiotics.

The removal mechanism of amoxicillin using B-Fe/Ni and CS-Fe/Ni was proposed by Weng et al. [63, 71]. They concluded that the degradation of AMX only by nanoparticles B-Fe/Ni and chitosan supported Fe/Ni via catalytic reduction of AMX by cleaving the β-lactam bond in AMX, as shown in Table 3. LC–MS analysis was carried out on AMX before and after reaction within 60 min. The degradation pathway of amoxicillin by nZVI started with the opening of the β-lactam ring and produced amoxicillin penicilloic acid (m/z 383 $C_{16}H_{21}N_3O_6S$), and then losing COOH (m/z 339 $C_{15}H_{21}N_3O_4S$), NH3 (m/z 324 $C_{15}H_{20}N_2O_4S$), carboxyl-reducing reaction and then opening the five-membered thiazolidine ring (m/z 314 $C_{15}H_{26}N_2O_3S$) [63,71]. Machado et al. [85] concluded the amoxicillin removal as a combination of physical and chemical mechanisms when in contact with nZVI. The fast reduction step was observed followed by adsorption of AMX onto the iron corrosion products and finally capture of AMX by the iron hydroxides.

Table 3. Possible degradation pathways of examined antibiotics

nZVI material	Antibiotic type	Possible pathways	References
nZVI	Metronidazole		[57]
B-nZVI	Amoxicillin		[63]
Fe/Ni bimetallic nanoparticles	Tetracycline		[73]
ZVBMNPs	Chloramphenicol		[77]

Ghauch et al. [56] evaluated ampicillin (AMP) and amoxicillin (AMX) elimination by nZVI. The degradation experiments revealed that AMP was more resistant to ZVI than AMX. AMX was readily transformed to AMX penicilloic acid and probably to undetectable AMX penilloic acid as end product due to decarboxylation reaction occurring with the free carboxyl group by using HPLC/MS. Similarly, AMP was found to be rapidly hydrolyzed to yield AMP penicilloic acid and undetectable AMP penilloic acid.

The removal process of TC after treatment by Fe-MCM-41-A included two key stages, a rapid adsorption rate within the first 30 min followed by a slow removal process at 30–60 min. This behavior was also confirmed with the study of Chen et al. [66] and Hanay and Türk [61].The rapid adsorption rate could be attributed to the large surface area, the appropriate pore size and volume of the adsorbent which can promote the internal mass transfer in adsorption process effectively. Adsorption mechanisms of TC onto Fe-MCM-41-A were also dependent on multiple interactions including hydrophobicity, ion exchange and surface complexes [67]. Dong et al. [73] aimed to evaluated the removal mechanisms of TC by Fe/Ni BNPs considering analysis of total organic carbon (TOC) and liquid chromatography-mass spectrometry (LC-MS). The decrease of TOC in solution and the appearance of intermediate products on the surface of Fe/Ni BNPs indicated that both adsorption and degradation occurred in the reaction process. The possible pathway of tetracycline was also shown in Table 3.

In another study, the removal mechanism of MNZ by nZVI was determined by TOC results. MNZ was not well mineralized and the TOC was hardly reduced by nZVI, which indicated that MNZ adsorption process were not the main mechanism for MNZ removal. The results of UV–vis spectra and FTIR spectra, plausible degradation pathways involving the generation of electrons and hydrogen species were inferred, and a hydrogenation reduction reaction was probably the main removal mechanism of MNZ by nZVI [57]. The results were inconsistent with the results of Fang et al. [82] which the degradation pathways of MNZ were adsorption on the surface of nano zero valent metal (nZVM), followed by nitro reduction, hydroxyethyl cleavage or N-denitration involving the electrons and hydrogen species produced by nZVM with the results of UV–vis spectra and HPLC chromatograms.

Although determining the intermediate products can be necessary to highlight the removal mechanism, the toxicity and biodegradability of these by-products after reaction should be evaluated. As shown in Table 3 chloramphenicol reduction products obtained after nitro-reduction and partial dechlorination of the parent molecule may be considered as relatively safer since para-nitro group of the parent molecule could cause both the hemotoxicity and hypotension in susceptible individuals. Additionally, biodegradability of the reduction products was much higher than that of the nitro-benzene [77]. On the other hand, Halling-Sorenson et al. [90] reported that several tetracycline transformation products were more toxic than their parent on both sludge and tetracycline-sensitive soil bacteria . However, their toxicity will be less significant in the aqueous matrix since sorption of these products on nZVI happened quickly during the reaction [61].

6. REUSABILITY OF nZVI

Reusability is an important factor for evaluating economical applicability of an adsorption material. The modification of nZVI surface results in not only to increase the stability and reactivity of nZVI but also to preserve reusability and separability over repeated cycles. Bentonite supported Fe/Ni nanoparticle exhibited good adsorption efficiency after five rounds of sorption-desorption cycles for amoxicillin removal. The effective reuse of B-Fe/Ni was 2 times [62]. Due to the presence of charged carboxyl groups and hydroxyl groups on the surface of carbon spheres, nZVI with carbon sphere led to longevity over the reaction course for metronidazole removal [64]. On the other hand, oxidation-reduction potential (ORP) can be suggested as a good measurement to determine the reactivity of nZVI. Liu et al. [59] determined that ORP did not come back after 3 rounds with chloramphenicol addition that referred the exhaustion of Fe(0) in the solution.

7. CONCLUSION AND FUTURE PERSPECTIVES

Although adsorption is considered as one of the most promising technique for various contaminants from water and wastewater, it only transfers contaminants from one phase to another and without any degradation and also adsorption capacity can be limited at a fixed concentration of contaminant. Nevertheless, reviewed studies in this paper confirmed that pharmaceuticals removal with nZVI occurred by simultaneous adsorption and reduction process. From the results of degradation experiments, the antibiotic removal process mainly included two stages, a quick adsorption within the first reaction period followed by a slow removal process. It needs to long-term process of these organic contaminants with nZVI due to the possibility of flocculation of Fe-degradation products complex.

Further improvements of nZVI are needed to prevent inactivation at late stage thus allows to prolong the longevity. The selection of a suitable support matrix for nZVI is an important issue for economical applicability. Although there are many efforts for increasing the nZVI reactivity, a few studies are available about maintaining its longevity as well as ability to separate. Accordingly, using bimetallic nanoparticles can be attractive because bimetallic nanoparticles exhibit super magnetic properties, providing easily separated from the liquid phase under an external magnetic field.

On the other hand, the reduction products generated from the incomplete removal of pollutants should be evaluated for toxicity and the degree of biodegradability because the effect of pharmaceutical compounds on human beings is still under debate and the emergency situation is occurred by progressively growing pharmaceuticals industry producing new drugs of unknown environmental hazard. For this purpose, to combine nZVI with other treatment technologies such as Fenton and Fenton-like processes are crucial to the wide application of nZVI particles.

There is still little knowledge regarding possible inhibitions from various constituents such as humic acid, sulfur compounds and other low-molecular-weight inorganic solutes in the aqueous matrix. Moreover, the use of zero valent iron to remove pharmaceuticals from full-scale real wastewater systems should be identified for practical applications.

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