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Review Article

Removal of Antibiotics from Aqueous Solutions by Bentonite Supported-Nanoscale Zero-Valent Iron

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Article Info	ABSTRACT
	Nowadays, antibiotics are extensively used in human and animal medicine. The unconscious consumption of antibiotics and their mixing with water sources without adequate treatment have caused environmental problems. Several chemical and physical treatment methods applied for the removal of antibiotics from aqueous media offer alternative solutions by improving the treatment process and using new materials. As in many areas, nanomaterials are also used in treatment methods such as sorption, degradation, and oxidation. Among the nanomaterials, nano zero-valent iron (nZVI) is frequently preferred in treatment processes due to its abundance, cheapness, ease of application, and high removal performance. Besides its many advantages, nZVI agglomerates in the aqueous phase and exhibits unstable behaviors. This limits the surface area required for antibiotic removal and reduces the removal efficiency. In recent years, nZVI has been used in water treatment technologies by being modified with many support materials such as bentonite to minimize particle agglomeration. Bentonite is clay-based support material that provides high removal efficiency and reduces the cost of treatment due to its abundance in nature. In this study, antibiotic pollution and treatment methods in water resources were reviewed and the antibiotic removal performances of bentonite-supported nZVI were investigated. In the studies, it was concluded that the antibiotic removal efficiency increased with the use of support materials.

1. Introduction

In recent years, water quality has been decreasing due to many reasons such as industrialization, anthropogenic activities, urbanization, population growth, and inadequate water management [1]. Pharmaceutical wastes causing this decrease are bioactive compounds that cause water pollution, including seas, oceans, underground, and surface waters [2]. As a source of pharmaceutical waste, antibiotics are among the drug groups with the highest consumption in medicine, agriculture, and aquaculture. The worldwide consumption of antibiotics, which was 63,151 tons in 2010, is expected to increase by 67% by 2030 [3]. Especially developing countries spend 35% of their health budgets on antibiotics. It has been determined that antibiotics are sold without a prescription and used incorrectly and excessively in most countries [4]. Antibiotics are used in the treatment of infections due to inhibition of cell growth and as feed additives due to support animal growth. These chemotherapeutic agents, which inhibit the growth of microorganisms (bacteria, fungi, protozoa, or viruses) are not biodegradable and can bioaccumulate in the environment even at very low concentrations. Antibiotic compounds such as tetracyclines, tylosin, sulfamethazine, amprolium, and nicarbazine are found in wetlands and soils that are close to urban or agricultural areas [5].

The entry of antibiotics into water resources is mainly attributed to two reasons. The first of these is the contamination of surface water, groundwater, and soil by entering the sewerage and wastewater network [6]. Antibiotic contamination by sewage rises from the excretion of approximately 70% of antibiotics through feces and urine without being digested [7]. Apart from this, the fact that wastewater treatment plants are not designed for antibiotic treatment has created antibiotic resistance in wastewater treatment plants [8]. The second main cause of antibiotic pollution is the disposal of expired antibiotics that are consumed in hospital services or domestic [9]. In addition to the fact that hospital wastewater is an environment where antibiotic resistance is intense, it also contains other pollutants that microorganisms can transfer genes [10]. Some different antibiotics such as β-lactam, streptomycin, and aminoglycosides are produced naturally by bacteria in the soil [11]. Antibiotics can affect the bacterial colony found in wastewater networks. In addition, bacterial activities in sewage treatment systems are inhibited in the presence of antibiotics, and it may alter the decomposition of organic matter [12, 13]. Although the concentration of antibiotics in wetlands is very low (e.g., ng or μg), the accumulation of antibiotics in humans, animals, and plants can also cause diseases [14, 15].

Various adsorbents such as nZVI are used for the removal of antibiotics from wastewaters. However, due to the low particle size of these adsorbents, agglomeration limits the surface area and reduces the removal capacity. For this reason, natural mineral clays such as bentonite are used as support materials for nZVI for the removal of antibiotics due to their high chemical and mechanical stability, high cation exchange capacity, and large surface area. Bentonite is one of the effective particle stabilizers in the supported nZVI system which reduces aggregation and improves removal capacity. In this study, the synthesis of nZVI/bentonite supported-nZVI and their removal performances of antibiotics from wastewaters were investigated.

2. Antibiotic Pollution in Water Sources

The rapid increase in antibiotic consumption has led to detectable concentrations in aquatic environments such as groundwaters, surface waters, agricultural ecosystems, and sewage waters. In recent years, new studies have been carried out to detect antibiotics and their derivatives in aquatic environments depending on the developments in water treatment technologies. In a study, active ingredients of antibiotics such as erythromycin, macrolides and clarithromycin, ciprofloxacin, norfloxacin, enrofloxacin, and lomefloxacin were detected in tap water in Madrid (Spain), Macau, and Guangzhou (China) [16]. Similarly, ciprofloxacin (653 ng/g), norfloxacin (5770 ng/g), oxytetracycline (652 ng/g), and ofloxacin (1290 ng/g) were found in water samples collected from the Pearl, Hai, Liao, and Yellow rivers in China [17]. López-Serna et al. (2013) reported that 72 drugs and 23 by-products appeared in the groundwaters of Barcelona (Spain) [18]. In another study, the presence of erythromycin, sulfamethoxazole, and trimethoprim, was detected between 0.10-16.6 ng/L in the water of the Bohai sea and these concentrations have been reported to pose a risk to sensitive aquatic organisms [19]. Unlike other pollutants in water, antibiotics have high biological activity on various organisms. The physicochemical properties of antibiotics may rise presence in the environment and make easier bioaccumulation (Table 1) [20]. Reasons for purification of aqueous solutions containing antimicrobial compounds can be summarized as below:

- Production/consumption of a high amount of antibiotics by humans and animals on a world scale

- Large amounts of antibiotics/metabolites/drugs reach the environment through the sewage system (feces or urine)

- Throwing expired antibiotics/metabolites/drugs into the environment which may pollute the ecosystem

- Accumulation of antibiotics by food chain or drinking water

- The lack of awareness about antibiotic pollution and its health risks to the environment [21].

Table 1. General physicochemical properties of pharmaceutical wastewater [22]

Parameter	Average value
Chemical oxygen demand COD (mg/L)	1000-10000
Biological oxygen demand BOD (mg/L)	500-2500
Total nitrogen (TN)(mg/L)	500-1500
Total phosphorus (TP) (mg/L)	50-250
Suspended solids (SS) (mg/L)	200-500
Chromaticity (times)	500-1000
Temperature (°C)	25-80
pH	1-8

3. Treatment Process of Antibiotics from Wastewater

The wastewaters are the main source for the transport of antibiotics to urban areas and it is critical to treat wastewaters before discharge into the environment [23]. Antibiotic accumulation in the environment occurs with discharges from wastewaters of pharmaceutical industries, hospitals, and medical centers, which contain high drug contamination in their wastewaters [24]. Antibiotic pollution in water resources causes potentially toxic effects on microorganisms, plants, animals, and humans [25]. Many treatment methods such as adsorption [26], membrane filtration [27], oxidation [28], biodegradation [29], reverse osmosis [30], Fenton reactions [31], coagulation-flocculation [32] are used for the treatment of antibiotics from wastewater (Table 2). Conventional water treatment technologies including biological treatment, filtration, coagulation, flocculation, and sedimentation have been found to be ineffective in eliminating antibiotics completely [33]. The disadvantages of these methods are the cost of implementation, catalyst management, and toxicity of by-products [34].

Choi et al. (2007) extensively investigated the ion exchange method for the removal of pharmaceutical compounds, and they reported that the method was ineffective due to backwashing and clogging of resins [35]. The distinctive properties of reverse osmosis (RO) are the lack of phase change and low energy consumption. In RO systems, the average antibiotic removal rate changes around 90.2% and 90.3% for distilled water and river water, respectively. By using two or three sequent RO units, 99%, and 99.9% removal rates can be achieved in the treatment, respectively. The use of RO in water treatment systems is generally economical but may be more suitable for removing antibiotic compounds from drinking water [36]. Nanofiltration (NF) membranes are a promising method for antibiotic removal from wastewaters. Drewes et al. (2002) investigated some treatment technologies (activated sludge, filter, NF, and RO) to remove drugs from treatment plant water. None of the drugs were detected in tertiary treatment after NF and RO [37]. Because most pharmaceutical contaminants have a low molecular weight, ultrafiltration (UF) is seldomly used in the treatment of pharmaceutical waters. Ultrafiltration activated carbon and coagulation were used to remove some pharmaceuticals. The average removal efficiency was found to be 29% for UF, 50% for activated carbon, and 7% for coagulation [38].

In general, membrane filtration (MF) and UF processes are not used single for antibiotic removal due to low performance. So, these processes are applied with other purification methods such as NF or RO [39]. It has been reported that the removal efficiencies of some antibiotics such as diclofenac, fluoxetine, gemfibrozil, omeprazole, sulfamethoxazole, and trimethoprim varied about 24 and 68% with membrane bioreactors and activated sludge processes [40]. Treatment of tetracycline-class antibiotics in synthetic and river wastewaters was investigated by granular activated carbon and coagulation techniques. Both coagulation and activated carbon filtration were found to be efficient in tetracycline removal. However, filtration is more effective in the removal of tetracycline, doxycycline-cyclate and chlortetracycline-HCl which are difficult to remove by coagulation [41]. Li et al. (2008) examined the decomposition of oxytetracycline (OTC) in an aqueous solution by ozonation. OTC was treated with ozone at pH 11 for 60 min. The results showed that ozonation improves the biodegradation of the wastewater and the by-products of OTC were more toxic than the main compound after partial ozonation [42]. Similar studies have shown that ozonation is effective in the removal of antibiotics from wastewaters, but these treatment processes require high cost and energy [43]. Alaton et al. (2004) investigated ozonation of penicillin formulation wastes such as amoxicillin trihydrate and β-lactamase inhibitor potassium clavulanate at pH 2.5 and 12.0 with different initial H_2O_2 concentrations. The overall

effectiveness of chemical oxygen demand removal ranged from 10% to 56% by ozonation and 83% by ozone/H_2O_2 [44]. Oxidizing materials such as chlorine or hypochlorite are often preferred in the purification/disinfection units in water treatment systems due to their low costs. In this method, main antibiotics oxidate inactive small molecules by chlorination. A high concentration of chlorine is required to remove more than 90% of antibiotics. The main limitation of this method is by-products are more harmful than the initial component [45]. Several antibiotics are photosensitive (e.g., quinolones, tetracyclines, sulfonamides). The photolysis of antibiotics in the aquatic media varies for each compound according to the physical and chemical properties of antibiotics. In a study examining the optical degradation of tetracyclines, the removal efficiency was found to be approximately 80%. However, it was concluded that the wastewater treated with the by-products released because of photolysis is more toxic than the inlet wastewater. Compared to other methods, photolysis is slightly efficient for the removal of antibiotics, and it can only be applied in wastewaters containing photosensitive impurities and low COD concentration [46]. Incomplete photoconversion and photodegradation can conduce to the formation of unstable and toxic by-products. The amount of biodegradation for most pharmaceutical compounds studied at the laboratory scale is low. In general, biodegradation processes are not suitable for antibiotic removal [47]. Some antibiotics such as amoxicillin, imipenem, and nystatin are partially biodegradable. Ciprofloxacin, ofloxacin, metronidazole, and lincomycin are not biodegradable. So, the genotoxicity of these compounds is not eliminated [48]. Unlike other treatment methods, adsorption is considered very effective for removing antibiotics from water or wastewater. Adsorption has several merits such as low initial investment cost, easy applicability, and high efficiency [49]. Antibiotic removal from wastewaters by adsorption depends on the physicochemical properties of the adsorbent and the antibiotic. Studies have shown that the adsorption behaviors of antibiotics are very complex. The adsorption efficiency of antibiotics is characterized by several factors. These are adsorbent type, initial concentration of target compounds, pH, temperature, etc. [50]. The main sorption mechanisms of antibiotics include ion exchange, surface complexation, and hydrogen bonding [51].

Table 2. Superior and weak properties of some methods used in the treatment of antibiotic-containing wastewaters [52]

Advantage	Disadvantage
Oxidation, Ozonation, Treatment with OCl$^-$/H$_2$O$_2$	
Integrated/hybrid physical and chemical process	Require some chemical substances and pre-processing
Easy, fast, and effective process	Produce and management of oxidants
Output quality (effective removal of contaminants)	Efficiency depends on the type of oxidant
Increases the biodegradability of the product	The short half-life of ozone
High efficiency and water recycling possibility	Undefined intermediates
No sludge production	Unchanging salinity ratio (ozone)
Disinfection of microorganisms	Formation of volatile compounds, aromatic amines, and sludge
Adsorption/Filtration	
Basic equipment and integration with other treatments	Non-destructive and non-selective processes
Vary range of application	Efficiency depends on the properties of materials
Effective (adsorption) for target pollutants	Regeneration cost of adsorbent/filter
Highly removal efficiency	Elimination of adsorbent (burning or replacement)
High quality of wastewater after treatment	Not suitable for some industries (paper, textile, etc.)
Advanced Oxidation Processes (AOP), Photolysis	
On-site formation of reactive radicals	Suitable for lab-scale wastewater treatment
Require fewer chemicals and no sludge production	Not suitable for large-scale applications
Mineralization and rapid degradation of pollutants	Low yield
Effective removal of antibiotics, drugs, etc.	Formation of intermediates and by-products
Reduction of COD and TOD	

In previous studies, activated carbon [53], bentonite supported nanoscale Fe/Ni bimetallic particles [54], MCM-41 [55], biochar [56] copolymer/Fe_3O_4 magnetic nanocomposite [57], MIL-53(Al) metal–organic framework [58], agricultural waste [59], carbon nanotube [60], graphene oxide [61], SiO_2 nanoparticles [62] have been used as adsorbent for the water treatment of antibiotics.

In recent years, nanomaterials have been found to show better potential in water treatment due to their unique size-dependent properties. Nanomaterials are frequently preferred in adsorption studies with their properties such as large specific surface area, high surface free energy, adequate reactive region, rapid resolution, and super magnetism [63]. Nano-based materials have a wide range of possible applications, including cosmetic, pharmaceutical, and medical uses [64]. The particle size of nanoparticles (dispersion of particles or solid particles) varies range of 10-1000 nm. According to preparation techniques, nanoparticles, nanospheres, and nano capsules are obtained by encapsulation or binding to a nanoparticle matrix. [65].

4. Nano Zero-Valent Iron (nZVI) and Synthesis Methods

Most nanomaterials are inorganic or organic and have incredible potential to eliminate pharmaceutical compounds in aqueous solutions with low cost, ease of use, and high efficiency. In recent years, nanoscale zerovalent iron (nZVI) technology has been successfully used to remove heavy metals [66], phosphorus [67], dyes [68], phenolic compounds [69], pesticides [70], antibiotics [71], chlorinated organic compounds and nitrate [72]. Metallic nanomaterials such as TiO_2 [73], MgO [74], Co/Fe bimetallic [75], iron [76] have been used in antibiotic treatment. In these metallic nanoparticles, as the particle size decreases, the ratio of atoms on the surface increases. These particles have rapid chemical reactivity. Interactions of these particles with other atoms, molecules, and complexes increase surface charge stabilization and provide them to use for environmental remediation [77]. Iron is a metallic nanoparticle and is among the most abundant elements. Iron is very reactive in its elemental state

and easily oxidized under atmospheric conditions. Therefore, it is usually found in the form of magnetite (Fe_3O_4), and hematite (Fe_2O_3) [78].

Nanoscale zerovalent iron (nZVI) is a type of reactive transition metal with a particle size of less than 100 nm (Table 3). Compared with macroscale and nanoscale ZVI, nZVI has several advantages in wastewater treatment. These can be listed as high removal rate, low ZVI dose, controllable toxicity risk, and suitable for removal of many pollutants [79]. Apart from these, nZVI has advantages such as being abundant and cheap, and ease of production and reduction. The interaction/reaction of nZVI with target pollutants changes with the pollutant type. The reaction is a complex process involving adsorption, oxidation, reduction, surface precipitation, and surface complexation [72]. The nZVI consists of a core Fe(0) and an iron oxide shell. The core functions as a reduction, while the outer shell consists of reactive sites for chemical adsorption and electrostatic interactions (Figure 1). The shell of iron oxide has positive charges under acidic conditions and interacts with anionic contaminants. At high pH, the negatively charged surface creates a suitable electrostatic field for cationic pollutants [80]. However, the elimination of contaminants by bare nZVI particles may not be very effective due to their tendency to agglomerate, magnetic properties and the formation of induced precipitates, and their high oxidative properties. In addition, the interaction with other components in the environment and the difficulty of separating the strain from the phase after adsorption also affect the adsorption process [81]. The preparation of nZVI with supporting and dispersing solid material may prevent the agglomeration of nZVI [82]. In recent years, biochar [83], kaolinite [84], wheat straw [85], alkalized MXene [86], activated carbon [87], chitosan [88], carbon [87], clay [89] have been used as supporting material for nZVI in wastewater treatment studies [90, 91].
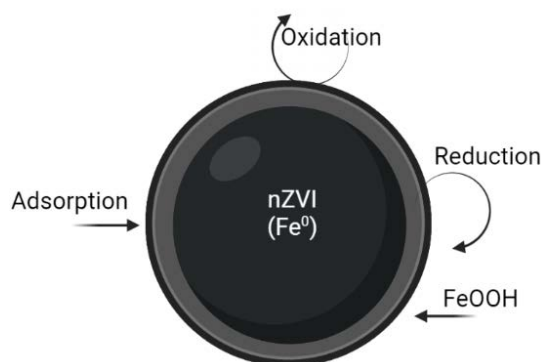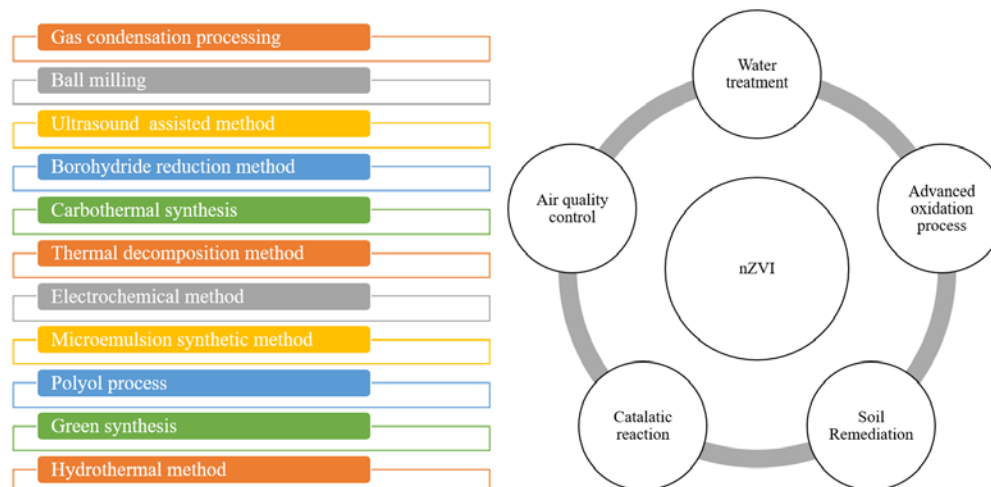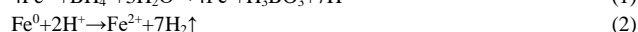

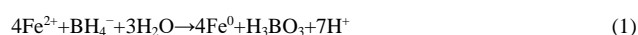**Figure 1.** The structure of nZVI particles [92].

Apart from these, surface modification can be applied to prevent the agglomeration and oxidation of nZVI [93]. By changing the surface properties of the nanoparticle, the dispersion of nZVI in the aqueous medium can be improved. The modification increases the adsorption properties of nanoparticles and reduces their toxic effects [94]. In previous years, nZVI has been modified with coating agents such as sulfite [95], polyvinylpyrrolidone [96], and aluminum hydroxide [97] for antibiotic removal.

Table 3. Physical and chemical properties of nZVI particles [98]

Mean particle size	Less than 30 nm
Specific surface area	Large than 20 m^2/g
Bulk density	0.04 ~ 5 g/cm^3
Chemical compound	O (less than 0.1%), Fe (Surplus), Impurity (less than 0.3)

By this time, many techniques including chemical vapor deposition [99], sputtering gas aggregation [100] thermal decomposition [101], borohydride reduction [102], the electrochemical method [103], etc. have been used to obtain metallic nanoparticles (Figure 2). These production methods are classified as bottom-up or top-down. The bottom-up method is the reduction or restructuring of bulk material to the nanoscale with the help of physical or chemical methods such as etching, grinding, etching and/or grinding [104]. Agglomerated particles with irregular structure and deformed by the effect of physical force are produced with these methods. The second involves physical or chemical methods to break down or reconstruct a bulk material at the nanoscale. The second approach, chemical synthesis, relies on the growth of atom-atom or molecule-molecule nanostructures by positional coupling, and self-assembly [99]. The borohydride reduction method is widely used to produce nZVI particles. Most commonly, nZVI is synthesized by the reduction of iron salts in aqueous media using $NaBH_4$ as the reducing agent. This method provides easy application and chemical homogeneity [102]. In the synthesis by borohydride reduction method, nZVIs are obtained by the reaction of Fe(II) and Fe with $NaBH_4$ or KBH_4 in accordance with Equations (1-2) [103].

$$4Fe^{2+}+BH_4^-+3H_2O \rightarrow 4Fe^0+H_3BO_3+7H^+ \tag{1}$$
$$Fe^0+2H^+ \rightarrow Fe^{2+}+7H_2\uparrow \tag{2}$$

Figure 2. Synthesis methods and environmental applications of nZVI [93,107].

$NaBH_4$ may lead to the formation of boron in the final product that has toxic effects on human and animal health. Also, water in the synthesis reaction induces the formation of Fe-B alcohols and the release of boron to the aquatic media after the process [105]. In general, these methods contain various limitations and problems. Top-down methods are often expensive and required costly equipment. The disadvantages of bottom-up approaches relate to safety issues arising from the toxicity of sodium borohydride which generates flammable hydrogen gas during processing [103,106].

5. Bentonite Supported-nZVI

Natural clay minerals such as clinoptilolite, sepiolite, and bentonite are porous aluminum silicates. Their high cation exchange capacities, low costs, easy applicability, and large surface areas make them attractive as support materials for nZVI. In previous studies, it has been reported that the agglomeration of nZVI decreases with clay support [108]. The particle size of clay minerals is less than 2 μm and they are generally classified into four main groups (kaolinite, illite, smectite, and vermiculite) according to structural formation. The main groups of clay minerals are conventional cationic clay and synthetic anionic clay. Clay minerals consist of two structural units as silica tetrahedral and aluminum/magnesium octahedral. Clays generally have negative surface because of the presence of Al^{3+} or Fe^{3+} in their structures. Tetrahedral layers consist of monolithic tetrahedrons that share every three out of four oxygens. Octahedral layers consist of octahedrons that share oxygen and hydroxyl anion groups with Al^{3+}, Mg^{2+}. These octahedrons are organized in a hexagon array [109, 110]. Bentonite, which is an important raw material among clays, is one of the most suitable natural minerals widely used in removing pollutants from the aqueous environment [111]. It is frequently preferred in environmental and industrial applications due to its ease of application, non-toxicity, low cost, porous structure, large surface area, high thermal and chemical stability [112]. Bentonite is a member of the smectite group and has the molecular formula that consists of mainly aluminum and silicium atoms, $[Al_4Si_8O_{20}(OH)_4].nH_2O$. Due to its environmentally friendly nature, it is also used as a support material for nanoparticles in nanotechnology [113]. Bentonite (montmorillonite) has two tetrahedral layers forming a sandwich-like structure on the octahedral layer. It has a permanent negative charge due to the isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral region and Mg^{2+} for Al^{3+} in the octahedral region [114]. Its three-layer structure (2:1) consists of an Al^{3+} octahedral layer sandwiched between two Si^{4+} tetrahedral layers. The negative surface of bentonite is stabilized by the exchangeable cations (Ca^{2+}, K^+, Na^+ and Mg^{2+}) (Table 4) [115]. Bentonite shows low hydraulic conductivity and good swelling capacity for the removal of antibiotics from wastewater [116]. Bentonite, which is naturally composed of montmorillonite, has an average adsorption capacity. Therefore, chemical modification methods are used to improve antibiotic removal performance in most of the studies [117]. The most important reasons that reduce the adsorption capacity of bentonite in wastewater treatment applications are the formation of stable colloidal suspensions due to its high swelling degree, the blurry image that results from particle aggregation due to low particle size, and the low filtration rate. Therefore, chemical modification methods can also facilitate the post-sorption separation process [118].

Table 4. Physical and chemical properties of bentonite [119, 120]

Color/nature	Light Yellow/ Pozzolanic	**Free swell**	60% by volume
Specific gravity	2.66	**CEC (meq/g)**	0.90
Chemical composition	**Concentration (%)**	**Chemical composition**	**Concentration (%)**
SiO₂	60.85	MgO	3.09
Al₂O₃	14.82	K₂O	0.79
Fe₂O₃	4.38	TiO₂	0.61
CaO	3.67	Other	0.44
Na₂O	3.13		

Clay-supported zerovalent iron is commonly synthesized by liquid-phase reduction (Figure 3). Xi et al (2011) investigated the catalytic degradation of Orange II using Australian bentonite as the support material of nZVI particles. For the preparation of bentonite-supported nZVI, 5 g of bentonite was dispersed in 300 mL of 1 M $NaBH_4$ and the mixture was stirred for 2 h using a magnetic stirrer. Then, a second solution was prepared by dissolving 10 g of $FeCl_2 \cdot 4H_2O$ in ethanol and deionized water and added dropwise into the bentonite solution. The resulting solution was stirred for 1 h, then centrifuged and washed with ethanol [121].
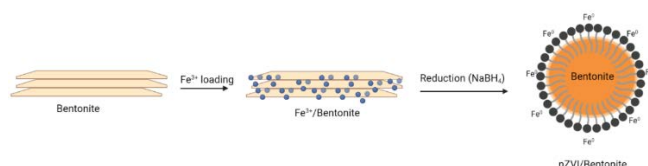

Figure 3. Synthesis of bentonite supported-nZVI [122].

Dehgani et al. (2020) used bentonite-modified nZVI for paraquat removal from aqueous solutions. For bentonite-nZVI synthesis, 100 mL of solution was prepared with 1 g bentonite, 1 g $FeCl_3 \cdot 6H_2O$ and 1 g PEG in 100 mL DI water. The solution was stirred in an ultrasonic bath for 30 min. Then, 50 mL of $NaBH_4$ (0.1 M) was added dropwise while stirring for 2 h. The precipitate was dried in an oven at 70°C for 12 h after separation [122]. Ye et al. (2021) used bentonite-supported nZVI for Cr(VI) removal. Bentonite-supported nZVI was prepared by the chemical reduction method. 1.35 g of $FeCl_3 \cdot 6H_2O$, 0.28 g of bentonite, and 0.5 g of PVP were dissolved in a three-necked flask with 100 mL of ethanol-water solution. The solution was mixed with a mechanical stirrer for 10 min in N_2 environment and 100 mL of 0.2 M KBH_4 was added dropwise with a constant pressure separating funnel [123]. It was found that nZVI particles prepared by the reduction of Fe^{3+} ions with $NaBH_4$ are homogeneously dispersed on the bentonite surface.

6. Bentonite Supported -nZVI on Antibiotic Removal

Removal studies of antibiotics with nZVI synthesized with support materials are limited on a lab scale. The experimental conditions, adsorption mechanisms, and removal efficiencies of some antibiotic samples were presented in Table 5. Antibiotic removal mechanisms with bentonite-supported materials of nZVI may involve multiple mechanisms, including adsorption, oxidation, ion exchange, nitro reduction, N-denitration, and chelation. However, adsorption, reduction, and oxidation are the

main mechanisms for antibiotic-nZVI interactions [90]. For this reason, parameters such as solution pH, temperature, dosage, and initial antibiotic concentration affect the removal efficiency. Guo et al. (2017) studied the removal of tetracycline (TC) by MCM-41-zeolite A loaded nZVI. It was reported that the adsorption of TC between pH 3-9 was completed in 30 min and reached equilibrium in 60 min. It was observed that at pH: 2 and pH: 11, the time for adsorption to reach equilibrium was prolonged and lasted for about 3 h. The amount of adsorbed TC decreased at very low or very high pH levels. For example, with an increase in pH from 2 to 5, the removal efficiency increased from 94.4% to 98.7%. From the experimental results, it was stated that the removal efficiency of TC increased under weak acidic conditions. The decrease in removal efficiency with increasing pH was due to the decrease in electrostatic repulsion and hydrophobic effect [124]. In the antibiotic-adsorbent interaction, if the solution pH is lower than the pH$_{ZPC}$ (point of zero charge) of the adsorbent, the adsorbent surface becomes positive. In this case, the electrostatic attractions between the anionic species of antibiotic and the positively charged adsorbent surface increase, and the removal efficiency increases [125]. It has been reported that solution pH significantly affects the removal efficiency in the degradation of metoprolol with sepiolite-supported nZVI. Removal efficiency increased under acidic conditions and decreased at neutral and alkaline pH [126].

Adsorbent dosage/concentration is another important parameter that affects removal efficiency. Sulaiman et al. (2020) reported that almost all the spironolactone was removed at a dose of 0.25 g/L bentonite-nZVI and the removal efficiency did not change as the adsorbent dosage increased [127]. Similarly, the removal efficiency increased with increasing the bentonite-supported nZVI concentration for the degradation of amoxicillin with bentonite-supported nZVI. As the concentration increased, the total surface area and the number of available active sites for degradation increased. Therefore, more nZVI particles interacted with the antibiotic [128].

Tran et al. (2020) studied oxytetracycline (OTC) degradation with montmorillonite-nZVI. It was stated that a decrease in OTC removal was observed by increasing the OTC concentration from 50 to 200 mg/L with an adsorbent concentration of 0.6 g/L at pH 5.0. The time to reach equilibrium was prolonged at high concentrations such as 150 or 200 mg/L while it decreased at low concentrations. This can be explained by the fact that the active sites on the adsorbent surface interact with oxytetracycline up to a certain concentration, and the removal efficiency decreases as the concentration increases due to the active sites being filled [129]. In some cases, degradation and adsorption mechanisms are seen together. Adsorption can occur at both reactive and non-reactive sites, while the degradation reaction takes place only at reactive sites. In this process, the removal mechanism occurs initially by adsorption and then by the degradation reaction at the active sites. When the initial concentration increases, the accumulation of more pollutants on the adsorbent surface at a fixed adsorbent dosage may prevent the degradation reaction by highlighting the adsorption mechanism [130].

Temperature also significantly affects the antibiotic removal efficiency. As the temperature increases, the kinetic energy of the antibiotic molecules may increase, and it may increase their interaction with the adsorbent surface. For example, Dehgani et al (2020) reported that the adsorption of paraquat with bentonite-nZVI increased with an increase in temperature. The affinity of the paraquat that contact with the adsorbent surface increased as the temperature increased [122]. In antibiotic removal with bentonite-supported nZVI, the increased removal efficiency with increasing temperature may be due to the increase in thermodynamic motion and the average kinetic energy of the molecules, increase in the constant concentration of atomic hydrogen adsorbed for the removal of antibiotics, and the higher energy of the molecules to overcome the activation energy barrier [90].

Table 5. Experimental conditions and removal efficiencies of some antibiotics by bentonite/clay based nZVI materials (C_0: Initial concentration, T: Temperature, t: Time)

Supported material/nZVI	Antibiotic/Drug	Optimum experimental conditions	Removal efficiency/ mechanism
Sepiolite-nZVI [126]	Metoprolol	C_0: 3 mg/L, dose: 0.5 g/L, pH: 3, t: 60 min	67.24% Degradation
MCM-41-ZeoliteA-nZVI [124]	Tetracycline	C_0: 100 mg/L, dose: 1 g/L, pH: 5, t: 60 min	98.7% Adsorption
nZVI [131]	Tetracycline	pH: 2.5–6.5, t: 30 min	90% Adsorption, oxidation, reduction
Bentonite-nZVI [128]	Amoxicillin	C_0: 20 mg/L, dose: 4 g/L, pH: 6.7	93.5% Degradation
Pumice-nZVI [89]	Tetracycline	C_0: 50 mg/L, dose: 5 g/L, pH: 4	92% Adsorption, reduction
Montmorillonite-nZVI [129]	Oxytetracycline	C_0: 100 mg/L, dose: 0.6 g/L, pH: 5, t: 20 min	99% Adsorption, degradation
Montmorillonite-Graphenoxide-nZVI [125]	Tetracycline (TC), Cefazolin (CFZ)	C_0: 5 mg/L, dose: 0.4 g, pH: 7, t: 7 min (TC) and 10 min (CFZ)	TC: 100% CFZ: 86% Adsorption
Sepiolite nanofiber nZVI [132]	Tetracycline	C_0: 20 mg/L, dose: 1 g/L, pH:7	92.67% Degradation
Zeolite PEG-nZVI [133]	Amoxicillin	C_0: 20 mg/L, dose: 0.5 g/L, t: 75 min	100% Degradation
Bentonite-supported Fe/Ni [134]	Amoxicillin	C_0: 60 mg/L, dose: 4 g/L and 2 g/L, t: 60 min	>94% Degradation
Bentonite-supported nZVI [128]	Amoxicillin	C_0: 20 mg/L, dose: 4.0 g/L, pH: 6.7	94.4% Degradation
Bentonite-supported nZVI [127]	Spironolactone	C_0: 100 ± 1.27 mg/L, pH: 7, t: 180 min	99% Adsorption

7. Conclusion

Wastewaters from pharmaceutical industries are among the many factors that reduce water quality and cause environmental pollution. Nanoscale zero-valent iron (nZVI) technologies are one of the new and promising technologies for the treatment of antibiotic-containing wastewaters. In water treatment technologies, bare nZVI can have a minimum effect on the treatment of water contaminated with antibiotics, it can reduce the removal efficiency due to non-stabilized particles. In recent studies, clay-based minerals such as bentonite which has high cation exchange capacity and surface area are used as support materials for nZVI and provide particle stabilization in aquatic environments and prevent agglomeration of nanoparticles.

Bentonite supported- nZVI can increase the removal efficiency of antibiotics and prevent secondary pollution sources in wastewater. However, the use of natural materials as supporting also directly affects the regeneration efficiency of the modified adsorbents.

In this study, treatment methods of wastewaters containing antibiotics, the synthesis methods of nZVI, and the advantages of bentonite supported- nZVI in terms of removal efficiencies of different antibiotics were examined. Considering reviewed literature, it was concluded that bentonite-supported nZVI is an adsorbent with high removal potential for the treatment of antibiotic-containing wastewaters.

Declaration of conflicting interests

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