

Review

From Nano Zero-Valent Iron to Nanocomposite Materials for Sustainable Water Treatment

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Abstract: Nano zero-valent iron (nZVI) is a well-known and effective remediation agent for various water contaminants. However, the challenges associated with its application, such as agglomeration and difficulty in recovery, have limited its effectiveness in large-scale treatment processes. In recent years, the development of nZVI nanocomposites has shown promise in addressing these challenges, as they offer improved stability, reactivity, and recoverability. This paper reviews the latest advancements in nZVI nanocomposites for water treatment and discusses their potential for the sustainable remediation of various contaminants, including heavy metals, organic contaminants, and emerging contaminants. The potential applications, limitations, and future prospects of nZVI nanocomposites in water treatment are discussed in detail. Overall, the findings suggest that nZVI nanocomposites have significant potential for sustainable water treatment and can contribute to the development of cost-effective and environmentally friendly water treatment solutions.

Keywords: nanocomposites; nano zero-valent iron (nZVI); substrate; support materials; resins



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1. Introduction

The strong reducing ability of nano zero-valent iron (nZVI) presents significant potential in environmental remediation projects. For instance, it can induce the precipitation of other metal ions or facilitate the conversion of organic pigments to their white form. Additionally, nZVI exhibits the capability to absorb and co-precipitate contaminants in its corrosion products. However, the utilization of nZVI suspensions in remediation projects has encountered various challenges. Such difficulties include the rapid agglomeration of nanoparticles, ineffective dispersion in the subsoil, the possibility of ecotoxicity in the case of diffusion to the environment, etc. At the same time, the nanoparticles (NPs) are very difficult to separate from the aqueous phase after the water purification process, while NPs cannot be used in fixed bed installations, e.g., water filters, permeable reactive barriers, etc.

Various alternative methods were developed to address the above problems, such as the surface modification of iron nanoparticles with organic compounds to prevent agglomeration [1]; surface doping with sulfides to prevent oxidation and increase electron selectivity towards target contaminants [2]; and finally, the loading of nZVI on several host matrices. Several reviews have been published in the last 5 years to evaluate the performance of the above modified nZVI systems. The review by Wang et al. (2021) was centered on the benefits of combining single nZVI modification technologies into multifunctional nZVI composite systems with enhanced performance [3]. On the other hand, Di et al. (2023) focused their attention on the mechanisms involved and the effect of environmental factors on the remediation performance of modified nZVI systems for the removal of heavy metals [4].

Fixing or incorporating nZVI nanoparticles into an appropriate substrate, i.e., the creation of a “nanocomposite” material (NC), is a specific strategy for exploiting nZVI remediation potential, and a comprehensive review of this category of materials is still missing.

The concept of nanocomposite materials began to develop in the late 1980s in both the research and development departments of private companies and academic laboratories. The term “nanocomposite” was first used by Theng in 1970 [5], but it became widely accepted by the scientific community after the publication by Komarneni (1992) [6]. The incorporation of cobalt metal nanoparticles into a polymer matrix was first reported by Hess and Parker in 1966 [7]. However, the first commercial use of nanocomposites was made by Toyota Company in Japan in 1988, in which silicon nanocomposites were used in polymer matrices to produce new car models [8].

Nanocomposites containing nano-iron (nZVI) in their structure began to be manufactured in the late 2000s [9–11], and research in this area developed rapidly for the next years. Yin et al. (2021) gathered and evaluated the available information for the specific case of nZVI supported on the clay mineral montmorillonite [12]. On the other hand, Awang et al. (2022) and Liang et al. (2022) examined the case of nZVI supported on carbon-based materials, such as activated carbon (AC), biochar (BC) carbon nanotubes (CNTs), and graphene oxides (GNs) [13,14]. The present review aims to investigate the entire range of nZVI composite materials, as developed on several types of substrates, and the recent advances in this field. The synthesis methods of NCs, the effects of the host matrix, the type of treated contaminants, and the remediation potential of each NC are the main aspects that are presented and critically evaluated in this paper.

2. Impregnation of Nanoparticles to Appropriate Substrates

2.1. Types of Substrates Supporting nZVI

Iron nanoparticles can be incorporated into a variety of substrates. Their structural and physicochemical differences (e.g., dimensions, surface, surface charge, chemical stability, etc.) directly affect the physicochemical properties of nanocomposites and their effectiveness [15]. As shown in Table 1, various forms of carbon, clays and aluminosilicates, natural and synthetic polymers, and various other materials have been used as substrates.

2.1.1. Carbon

Carbon, e.g., soot and commercial activated carbon (powder or granular form), as well as various biocarbons, have been widely used as support materials. They show excellent performance in the adsorption of hazardous contaminants due to their low price, large specific surface area, and extremely porous structure [10,11,16–19]. Most studies focus on biocarbons (biochar, BC), which are produced by the decomposition of low-cost and high-carbon biomass, such as cane residues [20,21], rice straw [22,23], corn stalks [24–26], herb residues [27], pine wood [28], palm shells [29], astragalus membranaceus [30], biological sludge [31], prosopis juliflora [32], sewage sludge (MSS) and sunflower seed shells (SSS) [33], pinecones [34], etc. BC has a wide range of advantages such as low cost and easy availability, long-term performance, good adsorption capacity for various contaminants, and environmental friendliness.

2.1.2. Clays and Aluminosilicate Minerals

Clay minerals, as rich natural resources, have been used for the remediation of contaminated water, with similar advantages such as low cost, high availability, and high specific surface area [35]. Common clay minerals that have been used as substrates are mainly bentonite [36–46], montmorillonite [47–55], kaolin [37,40,53,56–61], sepiolite [62–64], zeolite [65,66], and attapulgite [67]. Clay minerals attract contaminants to the surface, and the addition of nZVI particles multiplies the active sites and increases their activity [68,69].

Table 1. Incorporation of nano zero-valent iron (nZVI) into various porous materials.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
<i>Carbons</i>					
Carbon black	Fe(NO ₃) ₃ ·9H ₂ O Fe-acetate, Fe-oxalate, Fe citrate	Carbothermal reduction 600–800 °C	Cr(VI)	C/nZVI-C ratio 5/1 cc. Efficiency of nZVI-C for the reduction of Cr(VI) comparable to commercial nZVI. nZVI-C suspension from Fe acetate had as good mobility as commercial nZVI (Toda) surface modified using polyacrylic acid (PAA).	[10]
Commercial granular activated carbon (GAC)	FeSO ₄	NaBH ₄	As(III), As(V)	Incorporation of Fe up to 8.2 wt%. Needle-shaped forms of nZVI (30–500) × (1000–2000) nm. Maximum adsorption of As(III) and As(V) were 18.2 (2.22 mg/g nZVI) and 12.0 (1.46 mg/g nZVI), respectively. Competitive reaction of PO ₄ , SiO ₄ . Positive effect of Ca ²⁺ and Mg ²⁺ . Successful regeneration with 0.1 M NaOH.	[11]
Commercial granular activated carbon (GAC)	FeCl ₂ ·4H ₂ O	NaBH ₄	Hexachlorobenzene (HCB)	Content of Fe in AC-Fe material 8.59–17.23 mg/g. Maximum Cr(VI) removal capacity ~20 mg/g nanocomposite. The material prepared at 550 °C and had a content of 13.28 mg Fe per g of material. Removal was partly by reduction by nZVI and partly by adsorption to AC. It was estimated that the removal due to Fe corresponded to about 1000 mg/g Fe.	[16]
Commercial activated carbon (AC)	FeCl ₂ ·4H ₂ O	Carbothermal reduction 350–1150 °C	Cr(VI)	Content of Fe in AC-Fe material 8.59–17.23 mg/g. Maximum Cr(VI) removal capacity ~20 mg/g nanocomposite with the material prepared at 550 °C and had a content of 13.28 mg of Fe per g of material. Removal is partly by reduction by nZVI and partly by adsorption to AC.	[17]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
Uniformly distributed mesoporous carbon (OMC)	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Carbothermal reduction 500–1000 °C	Cr(VI)	Carbothermal synthesis on a normal distribution mesoporous carbon (OMC) substrate. The nanocomposites produced at 500–700 °C contained Fe_3O_4 . Only at 900 °C was all Fe_3O_4 converted to nZVI. nZVI content in the composite 30 wt%. Maximum Cr(VI) removal capacity ~96 mg/g nZVI-OMC or 320 mg/g nZVI.	[70]
Commercial GAC	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Quinoline	nZVI/GAC ratio 2.5 wt%. Oxidation of quinoline via the Fenton mechanism was found. H_2O_2 production of 42 mg/L was measured in the first hour of the reaction. In the optimal conditions (pH = 4, T = 303 K, dose 7.5 g/L), 93% of quinoline was oxidized in 6 h from an initial concentration of 100 mg/L.	[18]
BC from bagasse, pyrolysis at 600 °C	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Cr(VI) in soil	nZVI/BC ratio 1/1. The material was mixed with the contaminated soil and a decrease in the mobility of Cr(VI) was observed. Optimum dose 8 g/kg soil.	[20]
BC from rice straw pyrolysis from 100 to 700 °C	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	KBH_4	Cr(VI)	nZVI/BC ratios of 16/1 to 0.5/1 wt were used. More effective BC from pyrolysis at 400 °C and nZVI/BC ratio 4/1. Maximum removal of Cr(VI) 26.6 mg/g material (33 mg/g nZVI).	[22]
BC slow pyrolysis of cornstalk HCl (1M), KOH (1M) and H_2O_2 30% (1:100 S/L)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Cr(VI)	The optimal nZVI/BC ratio was 1/1. The highest removal efficiency was observed by nZVI-BC/HCl at pH = 5. Maximum Cr(VI) removal capacity ~45 mg/g nZVI.	[24]
AC pyrolysis at 950 °C before fixation of nZVI	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	NO_3^- , PO_4^{3-}	nZVI/AC ratio 1/2. NO_3^- removal equal to 110 mg/g nZVI and PO_4^{3-} removal equal to 35 mg/g nZVI.	[19]
BC from herb residues by pyrolysis at 400 °C	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Cr(VI)	nZVI/BC ratio 1/1. Maximum removal capacity of Cr(VI) ~49 mg/(g nZVI-BC) or 98 mg/(g nZVI). The presence of SO_4^{2-} and humics enhanced the removal of Cr(VI), while HCO_3^- inhibited it.	[27]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
BC from pine wood with pyrolysis at 600 °C	FeCl ₃ ·6H ₂ O	NaBH ₄	As(V)	nZVI/BC ratio 10.5 cc. The maximum adsorption of As(V) occurred at pH 4.1 and was equal to 124.5 g/kg. As(V) (11.2 mg/g nZVI).	[28]
BC from corn stalks by pyrolysis at 700 °C	FeCl ₃ ·6H ₂ O	NaBH ₄	Sulfamethazine:	nZVI/GAC ratio 1/5. In the optimal conditions (pH = 3, 1.2 g/L dose, H ₂ O ₂ = 20 mM), 8.3 mg/g of sulfamethazine was oxidized in 6 h.	[25]
BC from Astragalus membranaceus at 400 °C sulfur-treated	FeCl ₂ ·4H ₂ O	NaBH ₄	Cr(VI)	nZVI/BC ratio 1/1. Cr(VI) adsorption capacity 126.12 mg/g (252 mg/g nZVI) at pH 2.5 with S-nZVI/BC dose equal to 0.2 g/L.	[30]
BC from palm pyrolysis at 500 °C	FeCl ₃ ·6H ₂ O	NaBH ₄	Glyphosate	Adsorption capacity of glyphosate 80 mg/g at 26.5 h. Solid-to-liquid ratio 0.015 g/25 mL.	[29]
BC from sugarcane residues at 400 °C	FeSO ₄ ·7H ₂ O	NaBH ₄	NO ₃ [−] ,	nZVI/BC ratio 1/2. Maximum contaminant removal 61.38 mg/g (184.14 mg/g nZVI) at pH = 5.74 and BC dose 4 g/L.	[21]
Corn stalk biochar	FeSO ₄ ·7H ₂ O	NaBH ₄	Pb ²⁺ , Cu ²⁺ , Zn ²⁺	nZVI/BC ratio 2/1. Adsorption capacity 195.1 mg/g (292.65 mg/g nZVI), 161.9 mg/g (242.85 mg/g nZVI), and 109.7 mg/g (164.55 mg/g nZVI) for Pb ²⁺ , Cu ²⁺ and Zn ²⁺ , respectively, after 6 h.	[26]
Mesoporous carbon	Fe(NO ₃) ₃ ·9H ₂ O	Reduction at 600 °C in the presence of H ₂	Co, Pb, Cr, Cd, Zn	nZVI content 10%. nZVI size ~16 nm. Maximum removal capacity 17.15 mg Cd/g (171 mg/g nZVI), 6.83 mg Co/g (68.3 mg/g nZVI), 7.62 mg Cr/g (76.2 mg/g nZVI), 22.6 mg Pb/g (226 mg/g nZVI), and 6.83 mg Zn/g. (68.3 mg/g nZVI).	[71]
BC of rice straw (as above). Si removal from 700 °C BC samples	FeSO ₄ ·7H ₂ O	KBH ₄	Cr(VI)	nZVI/BC ratio 4/1. Maximum removal at pH equal to 3.5, 112 mg/g (140 mg/g nZVI). They compared BC-nZVI materials with and without Si and found that the Si-free material was less efficient.	[23]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
BC from biological sludge by pyrolysis at 600 °C	FeCl ₃ ·6H ₂ O	NaBH ₄	Cr(VI)	nZVI/BC ratio 50% wt. Maximum Cr(VI) removal 31.53 mg/g (63.1 mg/g nZVI) at pH 4. Isotherm description with the Langmuir model. Thermodynamic analysis showed that the adsorption process was spontaneous.	[31]
BC through pyrolysis of woody biomass of <i>Prosopis juliflora</i> , 400–500 °C	FeCl ₃ ·6H ₂ O	NaBH ₄	Cr(VI)	IBC- < 75 demonstrated optimal performance for the removal of 10 mg/L Cr(VI), with the highest removal capacity (Q _{max} = 16.30 mg/g) achieved in groundwater (GW), followed by soft water (SW), hard water (HW), and distilled water (DW). The fastest removal occurred in DW within 5 min, followed by SW and GW in 10 min, and HW in 20 min. The order of Q _{max} was GW (22.49 mg/g) > SW (21.54 mg/g) > HW (17.00 mg/g) > DW (16.30 mg/g).	[32]
BC by the co-pyrolysis of municipal sewage sludge (MSS) and sunflower seed shells (SSSs)	FeSO ₄ ·7H ₂ O	NaBH ₄	Cr(VI)	Approximately 47.5 mg Cr(VI)/g R could be removed within 90 min at an initial pH of 3.0. nZVI/BC ratio 1.2 (461 mg nZVI/g R).	[33]
Pinecone biochar PBC	FeSO ₄ ·7H ₂ O	KBH ₄	Cr(VI)	nZVI-PBC dosage of 0.6 g/L, cell concentration of OD ₆₀₀ of 0.3, and initial pH of 6.5, 100 mg/L Cr(VI) could be removed completely by nZVI-PBC/MR-1 within 48 h. In contrast, only 39.50% of Cr(VI) was removed by nZVI-PBC alone.	[34]
<i>Clays and aluminosilicate minerals</i>					
Kaolinite (K)	FeCl ₂ ·4H ₂ O	NaBH ₄	Cu ²⁺ , Co ²⁺	NZVI size 10–80 nm. nZVI/K ratio 1/1 with a maximum removal capacity of 25 mg/g (50 mg/g nZVI) for Co ²⁺ and 140 mg/g (280 mg/g nZVI) for Cu ²⁺ and a ratio of 0.2/1 with a maximum removal capacity of 23 mg/g (138 mg/g nZVI) for Co ²⁺ and 32 mg/g (192 mg/g nZVI) for Cu ²⁺ .	[56]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
Montmorillonite (M) using HDTMA (E)	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	NaBH_4	Cr(VI)	Comparison of nZVI-M and nZVI-ME (with surfactant). nZVI size 21.9 nm and 20.7 nm in nZVI-M and nZVI-ME, respectively. nZVI/M ratio 1/1. The removal capacity was higher in treated montmorillonite and equal to 125 mg/g nZVI, while in plain montmorillonite with nZVI, it was 109 mg/g nZVI at pH 5.	[72]
Kaolin (K)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Pb(II)	Size nZVI 44 nm. nZVI//K ratio 1/1 and 2/1. Pb(II) removal 9.88 mg/g nZVI and 72 mg/g nZVI, respectively.	[37,57]
Bentonite (B)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Methyl orange dye	nZVI/B ratio 1/1. Dye removal 79.46 mg dye/g nZVI at pH equal to 6.5 in 10 min.	[36]
Organo-bentonite with the use of CTMA (OB)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Pentachlorophenol (PCP)	Size 50–150 nm. nZVI/B ratio 1/10. Maximum removal capacity 43.29 mg PCP/g nZVI.	[46,73]
Bentonite (B)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Cr(VI)	nZVI/B ratio 1/1. Maximum removal of 33 mg/g nZVI at 35 °C. Reuse of B-nZVI after washing with EDTA solution with a Cr(VI) removal capacity of 70% of the original. The optimal Cr(VI) removal was equal to 10 mg/g nZVI and was observed at 30 °C, pH equal to 5, initial Cr(VI) concentration of 20 mg/L, and optimal nanocomposite dose of 4 mg/L. Pb and Cu removal > 90%.	[38,74]
Bentonite (B)	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	NaBH_4	Orange II dye	nZVI/B ratio 1/1. Maximum dye removal 23.44 mg/g at pH = 5.8 at 25 °C.	[39]
Pillared clay (PC)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	NO_3^-	Size of nZVI 30–70 nm. nZVI content 24 wt%. maximum removal of nitrates in 120 min 100 mg NO_3^- /g nZVI at pH = 7.	[75]
Sepiolite (S)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	KBH_4	Brominamine	nZVI/S ratio 1.12/1. Maximum removal adsorption 41.625–44.1 mg/g (83.25–88.2 mg/g nZVI) at pH = 7.	[62]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
Rectorite (R)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Azo-dye orange II	nZVI/R ratio 1/2. Size of nZVI 10.3 nm. The nanocomposite was more efficient than the nZVI suspension. Removal of 35 mg/g (105 mg/g nZVI) in less than 10 min.	[76]
Natural zeolite (Z)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	KBH_4	Pb(II)	nZVI/Z ratio about 1/1. Removal capacity 96 mg Pb(II)/g (192 mg/g nZVI) at pH = 4 and T = 35 °C.	[65]
Natural clay (A)	FeCl_3	Green tea extract	Malachite Green, GM dye	nZVI size 50–60 nm. nZVI/A ratio 2/1 vol. Maximum GM removal capacity 42.7 mg GM/g (64.1 mg/g nZVI) at pH 3.	[77]
Kaolin, K	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Crystal violet dye	K/nZVI ratio 1/1. Size of nZVI 45–65 nm. Maximum removal 3 mg/g nZVI at pH 5.5.	[58]
Montmorillonite, M	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Cd	M/nZVI ratio 4/1. Maximum removal 4.9 mg Cd/g (24.6 mg/g nZVI) in 60 min.	[47]
Montmorillonite, M	$\text{Fe}(\text{NO}_3)_3$	Tea extract, Tata	As(III)	Size nZVI 59.08 ± 7.81 nm. M/nZVI ratios about 1/3. Best contaminant removal 0.99 mg/g (0.74 mg/g nZVI) at pH 2.75 in 30 min.	[49]
Alumina, Al	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	REEs	Size nZVI 10–80 nm. Al/nZVI ratio 1/1. Maximum removal of La 15.2 mg/g nZVI at pH 6, and of Eu and Yb, 19 mg/g nZVI at pH 3.	[78]
Montmorillonite treated with K, MK	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Cr(VI)	Size nZVI 39.6 nm. nZVI content 10.71%. The most effective material proved to be treated with K, with the assistance of starch and ultrasound. Optimum removal of 140 mg/g nZVI at pH 6.	[52]
Montmorillonite, M	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	As(III), As(V)	Size of nZVI 20–90 nm. M/nZVI ratio 10/1. Maximum removal of contaminant 59.9 mg/g (65.89 mg/g nZVI) for As(III) and 45.5 mg/g (50.05 mg/g nZVI) for As(V) at pH 7.	[50]
Attapulgite clay substrates, At	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Cu(II), Ni(II)	At/nZVI ratio 1/8. Size of nZVI < 29.26 nm. Maximum removal of Cu(II) 787 mg/g (885.4 mg/g nZVI) at pH 6 and Ni(II) 704 mg/g (792 mg/g nZVI) at pH 5 in 2 h.	[79]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
Bentonite, B, kaolin, K and natural clay, NC	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Industrial Azo dye Rosso Zetanyl dye, B-NG	They compared three different clay substrates with a substrate/nZVI ratio of 1/1. nZVI size 30 nm in B-nZVI, 80 nm in K-nZVI, and 50 nm in NC-nZVI. Maximum decoloration with B-nZVI 414 mg/g (828 mg/g nZVI), with K-nZVI 409 mg/g (818 mg/g nZVI), and NC-nZVI 412 mg/g (822 mg/g nZVI).	[40]
Bentonite, B	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Acid violet red dye	Size of nZVI 30–80 nm. B/nZVI ratio 1/1. Contaminant removal 273 mg/g (546 mg/g nZVI) at 30 °C in 9 min and 250 rpm.	[41]
Kissiris, P	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Hg(II), Cr(VI)	Size of nZVI 30.6 nm. Content of nZVI 7.7%. Removal of Hg 332 mg Hg(II)/gnZVI and 307 mg Cr(VI)/g nZVI.	[80]
Organo montmorillonite (M) with CTMAB	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Decabromobiphenyl	M/nZVI ratio 4/1. Size of nZVI 30–90 nm. Debromination with optimal removal of 0.32 mg/g (1.63 mg/g nZVI) in 24 h at pH 5.5 at 150 rpm.	[48]
Kaolin, K	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Ni	K/nZVI ratio 5/8. Size of nZVI 30 nm. The adsorption of Ni by K-nZVI showed a strong dependence on pH. Maximum removal capacity 9.24 mg/g (15 mg/g nZVI).	[59]
Sepiolite, S	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Cr(VI)	S/nZVI ratio 5/2. Size of nZVI < 100 nm. Chromium removal 177 mg/g (620 mg/g nZVI) at pH 3.	[63]
Sepiolite, S	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Cr(VI), Pb(II)	S/nZVI ratio 9/1. Size of nZVI 10–50 nm. Maximum removal capacity 610 mg Cr/g nZVI and 757 mg Pb/g nZVI.	[64]
Kaolin, K	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Black G dye	K/nZVI ratio 1/1. Size of nZVI 30–90 nm. Optimum removal 157.2 mg/g (314.4 mg/g nZVI) at pH 9.49.	[61]
Clinoptilolite, Cl	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	NaBH_4	Methylene blue (MB), methyl orange (MO)	Cl/nZVI ratio 1/1. Size of nZVI 40–60 nm. Maximum removal at 25 °C 48.3 mg MB/g (96.6 mgMB/gnZVI) and 45.1 mg MO/g (90.2 mg MO/gnZVI).	[81]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
Montmorillonite, M	FeCl ₃ ·6H ₂ O	NaBH ₄	Zn(II), Pb(II)	M/nZVI ratio 1/2. Optimum removal 10 mg/g (15 mg/g nZVI) in 15–27 °C at pH 5.	[82]
Kaolin, K	FeCl ₃ ·6H ₂ O	NaBH ₄	Cu(II), Ni(II)	K/nZVI ratio 1/10. Size of nZVI 1.87–21.57 nm. Optimum removal 12.5 mg Cu(II)/g (18.7 mg Cu/g nZVI) and 9.24 mg Ni(II)/g (13.9 mg/g nZVI).	[53]
Montmorillonite, M	FeCl ₃ ·7H ₂ O	NaBH ₄	Cr(VI)	M/nZVI ratio ~100/5.6. Maximum removal capacity 400 mg/g nZVI at pH 3.	[54]
Zeolite, Z, montmorillonite, M	Fe(NO ₃) ₃ ·9H ₂ O	NaBH ₄	Pb(II)	Clay/nZVI ratio 2/1 and size of nZVI 69.8 nm. Optimum removal at pH from 2.5 to 6.5 σε 40 min και 300 rpm, 115.1 mg/g M-nZVI (345 mg/g nZVI), and 105.5 mg/g Z-nZVI (316.5 mg/g nZVI).	[55]
Natural clay, C	FeCl ₃ ·6H ₂ O	NaBH ₄	Methyl orange dye	C/nZVI ratio 5/1 and size of nZVI 11.23 nm. Optimum removal pH 6.8 in 45 min and 250 rpm, 19.8 mg/g (119 mg/g nZVI).	[83]
Bentonite, B	FeCl ₃ ·6H ₂ O	NaBH ₄	Cr(VI), phenols	B/nZVI ratio 0.1/2, 1/1, 3/2 and size of nZVI < 10 nm. Optimum removal 99.3% for Cr(VI) (39 mg/g nZVI) and 6.5% for phenols (0.014 mmol/g nZVI) without K ₂ S ₂ O ₈ . The addition of persulfate significantly improved the oxidation of phenol, up to a rate of 71.5%, without a negative effect on the removal of chromates.	[42]
Rectorite, R	FeCl ₃ ·6H ₂ O	NaBH ₄	Methyl orange dye(MO), metrodinazole (MT)	R/nZVI ratio 2/1. Size of nZVI 15.05 nm. Maximum removal 310 mg/g (930 mg/g nZVI) for MO and 64.7 mg/g (194 mg/g nZVI) for MT, combined with the use of ultrasound.	[84]
Bentonite, B	FeSO ₄ ·7H ₂ O	NaBH ₄	Ni(II)	nZVI content 23.3% wt. Maximum removal capacity of 788 mg/g nZVI at pH 6 at 150 rpm.	[43]
Bentonite, B	FeSO ₄ ·7H ₂ O	Green tea extract	PO ₄ ^{3−}	M/nZVI ratio 1/1. Spherical size 40–60 nm. Maximum removal 27.63 mg/g (55.22 mg/g nZVI) at pH 2–5.	[44]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
Organo-Bentonite, OB with DK1	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	2,4 DCP (dichlophenol)	Size of nZVI 20–50 nm. EDS analysis showed iron content 66.6% wt. Optimum removal capacity of 73.5% in 145 min.	[45]
Zeolite, Z	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Cd(II), Pb(II), As(III)	Z/nZVI ratio 3/1. Size of nZVI 40–60 nm. Maximum removal capacity 11.52 mg As(III)/g nZVI (46 mg As(III)/g nZVI), 48.63 mg Cd(II)/g nZVI (194.52 mg Cd(II)/g nZVI), and 85.37 mg Pb(II)/g nZVI (341.48 mg Pb(II)/g nZVI) at pH 6.	[66]
Kaolin, K	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Acid black 1 dye	K/nZVI ratio 10/1. Size of nZVI 40–80 nm. Maximum removal of dye 98 mg/g (980 mg/g nZVI) at pH 5 and 120 min with the addition of H_2O_2 4 mM.	[60]
Attapulgite, Atp	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	KBH_4	Cr(VI)	Removal capacity decreased significantly with nZVI/ATP (1:3) dosage increase at each Cr(VI) initial level ($p < 0.05$). With a dosage of nZVI/ATP (1:3) increasing from 0.5 to 2.0 g/L, the remediation capacity decreased from 35.94 to 9.97 mg/g at the initial level of Cr(VI), i.e., 20 mg/L, and with 100 mg/L, the removal potential reduced from 45.41 to 16.66 mg/g according to a nZVI/ATP (1:3) concentration increase from 0.5 to 6.0 g L ^{−1} .	[67]
Natural and synthetic polymers					
Non-porous resin PolyFlo (20–30 μm)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Cr(VI), Pb(II)	Nano-iron content 226.8 mg nZVI/g resin. nZVI size 10–30 nm. Removal of Pb(II) 0.234 mg/g (1.03 mg/g nZVI) and Cr(VI) 1.036 mg/g (4.56 mg/g nZVI) in one day. The solutions together with the nanocomposite had a pH of 4.01 and 3.25 for Pb and Cr, respectively.	[85]
Cation exchange resin Dowex HCR-W2	FeCl_3	NaBH_4	Acid Blue 113 dye	Nano-iron content 4.9–50.8 mg nZVI/g resin. Size nZVI 40–170 nm. Dye removal of 4.7 mg/g SNC (92.5 mg/g nZVI) in 10 min at pH 5.6.	[86]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
Chitosan fibers, Ch	FeCl ₃	NaBH ₄	As(III), As(V)	Size of nZVI 75–100 nm. nZVI/Ch ratio 12/1. Removal capacity 1.67 mg As(III)/g (1.54 mg/g nZVI) and 2.29 mg As(V)/g (2.11 mg/g nZVI) at pH 6.	[87]
Chitosan beads, Ch	Commercial nZVI		Cr(VI), Cu(II), Cd(II), Pb(II)	Size of 45.2 nm. C/nZVI ratio 2/1. The removal of Cr(VI), Cu, Cd and Pb was 1.79 mg/g (5.36 mg/g nZVI), 1.98 mg/g (5.93 mg/g nZVI), 1.42 mg/g (4.27 mg/g nZVI), and 0.99 mg/g (3 mg/g nZVI), respectively, at pH 6.4 and in 20 °C.	[88]
Alginate beads, Alg	FeCl ₃ ·6H ₂ O	NaBH ₄	Cr(VI)	Alg/nZVI ratio 3/1. Maximum removal of Cr(VI) was 4 mg/g (16 mg/g nZVI) at pH 11.	[89]
Cation exchange resin	FeCl ₂ ·4H ₂ O	KBH ₄	Decabromodiphenyl (DBD)	nZVI content 0.056 g nZVI/g resin. Removal of Cr(VI) 0.007 mg/g (0.125 mg/g nZVI) in 8 h.	[9]
Polystyrene resins with -CH ₂ -N ⁺ (CH ₃) ₃ , -CH ₂ Cl functional groups	FeCl ₃ ·6H ₂ O	KBH ₄	NO ₃ [−]	Matrix–nZVI ratio 3/1. Size of nZVI > 20 nm. Maximum removal of nitrates 20.22 mg/g material (80.88 mg/g nZVI).	[90]
Cation exchange polystyrene resin D001	FeSO ₄ ·7H ₂ O	NaBH ₄	Cr(VI)	Maximum removal of chromium 0.9 mg/g (20.44 mg/g nZVI). The Cr(VI) removal efficiency was 60.8%, 43.8%, 33.1%, and 8.8% after reusing the resin with nZVI one, two, three, and four times, respectively.	[91]
Chelated resin, DOW 3N	FeCl ₃ ·6H ₂ O	NaBH ₄	Pb ²⁺ , NO ₃ [−]	Three types of commercial resin containing 90–136 mg nZVI per g. nZVI size from 10 to 30 nm. The maximum removal of NO ₃ [−] and Pb ²⁺ was 106.3 and 269.4 mg/g nZVI respectively at pH 5.33.	[92]
Oxidized polyacrylonitrile membrane (PAN-OM)	Fe ₂ (SO ₄) ₃	NaBH ₄	Methyl blue and methylene blue dye	Size 75 nm. Content of nZVI 20%. Removal of 486 mg/g nZVI (methyl blue) at pH 5.2 and 96.5 mg/g nZVI (methylene blue) at pH 7.8.	[93]
Cation exchange resin C100	FeCl ₃ ·6H ₂ O	NaBH ₄	Pb ²⁺	Content of nZVI 22% wt. Size of nZVI 20 nm. Removal of 22.5 mg Pb ²⁺ /g resin (135 mg/g nZVI) at pH 4–7.	[94]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
Cation exchange resin Dowex 50WX2	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Green tea extract/Gallic acid	Cr(VI)	Green tea was found to be inefficient, probably due to the relatively big size of the contained polyphenol molecules. Gallic acid molecules were able to reach adsorbed Fe(III) and reduce cations to the elemental state with 100 mg (1.79 mmol) of nFe per gram of dry resin. After 1 h of treatment, the removal of Cr(VI) was equal to 99.4% at pH 2.7, 96.1% at pH 3.2, 71.6% at pH 4.4, 59.6% at pH 5.0, and 23.6% at pH 8.5.	[95]
Cation exchange resin Amberlyst 15	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Green tea extract	Cr(VI)	Maximum concentration nFe = 27.44 mg/g wet R (0.49 mmole per liter of solution). The amount of Cr(VI) removed from the aqueous solution after 24 h was 0.853 mg/g nFe.	[96]
Lignin-based hydrogel (LH)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	NaBH_4	Cr(VI)	TnZVI@LH at the precursor Fe(II) ion concentration of 0.1 mol/L presented an enhanced Cr(VI) removal capacity of 310.86 mg/g Fe0 at pH 5.3, which was 11.6 times more than that of the pure nZVI. The removal efficiency of the composite at pH 2.1 was more than double compared with alkaline or neutral conditions. The maximal removal capacity improved from 277.78 mg Cr(VI)/g nFe to 370.37 mg Cr(VI)/g nFe when the solution became more acidic.	[97]
Alginate beads, Alg	NANOFE 25 (N25) and NANOFE STAR (NSTAR) nZVI		Cr(VI)	N25@AL exhibited faster removal than NSTAR@AL. Both materials shared an identical maximum removal capacity of 133 mg of Cr(VI) per gram of nZVI at pH 3.	[98]
Other materials					
Oyster shells, OCs	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Humic acids (HAs) as natural organic matter	OC/nZVI ratio 1/10. Size of nZVI 60–85 nm. Maximum removal of HA 0.768 mg/g (0.98 mg HA/g nZVI) at a temperature of 40 °C and pH equal to 5 in 90–120 min.	[99]
Plum kernels, Spondias purpurea, SP	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	NaBH_4	PO_4^{3-}	Size of nZVI 5–70 nm. Removal of 20.57 mg PO_4^{3-} /g.	[100]

Table 1. Cont.

Support Material	Iron Precursor Compound	Reducing Agent	Contaminant	Remarks—Main Results	Reference
Water fern (<i>Azolla filiculoides</i>), F	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	NaBH_4	Pb(II) and Hg(II)	Size 20 nm. nZVI/F ratio 1/4. Removal 459.3 mg Hg(II)/g (2300 mg/g nZVI) and 462.7 mg Pb(II)/g (2313 mg/g nZVI).	[101]
Humus, H	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	Cr(VI)	Size 50–150 nm. H/nZVI ratio 2/5. Removal of 42.4 mg Cr(VI)/g H-nZVI (59.4 mg/g nZVI) at pH 6.5	[102]
Carbonized fungi, F	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	NaBH_4	U(VI)	Ratio nZVI/F 1/10. Maximum removal U(VI) 298 mg/g nZVI in 30 min at pH 6.5.	[103]
Stone wool, W	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$,	NaBH_4	Cr(VI)	W/nZVI ratio 1:0.5, 1:1 and 1:2. Size of nZVI 20–30 nm. Removal 198 mg Cr(VI)/g W-nZVI (297 mg/g nZVI) in 30 min.	[104]

BC: biochar, GAC: granular activated carbon, MWCNT: multiwalled carbon nanotube, OMC: ordered mesoporous carbon, (OMC), CTMAB: cetyltrimethylammonium bromide, DK1: hexadecyl trimethyl ammonium chloride, HDTMA: hexadecyl trimethylammonium bromide.

2.1.3. Natural and Synthetic Polymers

As can be seen in Table 1, significantly less attention has been given to the use of natural and synthetic polymers as a substrate for the incorporation of nZVI compared with carbons or clays in academic research.

Natural polymers that have been used as a host substrate for nZVI are mainly chitosan [87,88]. Synthetic polymers include various forms of resins [9,85,86,90,92,94–96]. An important advantage of resins is that they combine mechanical resistance, chemical stability, and high porosity.

In the resin-incorporated nZVI system, significant similarities are presented with heterogeneous catalysis systems, in which the functional groups in the resin porosity or the embedded metal nanoparticles contribute to a chemical reaction with a purely catalytic role.

2.1.4. Other Materials That Have Been Used as a Substrate for the Incorporation of nZVI

There is a wide variety of other materials that have been used as nZVI substrates including oyster shells, plum kernels, water fern, humus, fungi, rockwool, etc. [99,100,102–104].

2.2. Nanocomposite Synthesis Methods

Typically, the process of binding or incorporating nano zero-valent iron (nZVI) into a host material involves the following steps:

- Mixing of the host material substrate with a solution of ferrous or ferric iron in order to adsorb Fe(II) or Fe(III) cations to the matrix.
- Addition of a reducing agent to the suspension to reduce the adsorbed iron cations to elemental iron, Fe(0).

Chloride, sulfate, or nitrate salts have been used as iron precursors. Sodium borohydride, and less frequently, potassium borohydride, has been used as a reducing agent. The use of plant extracts as a reducing agent was applied only in three studies concerning the binding of nano-iron to clay minerals [44,49,77].

In certain cases, the reduction of Fe cations is carried out by the coal-thermal method. When the coal-thermal method is employed, the nanoparticles are simultaneously attached to the carbon substrate used for the reduction [10,17]

During the incorporation of nanoparticles into a polymer matrix, the synthesis of the polymer matrix, from the corresponding monomers, often takes place afterwards or in parallel.

- In the first case, metal ions are charged into the polymer matrix to serve as nanoparticle precursors, and then converted into nanoparticles by the addition of the appropriate chemical agent.
- In the second case, the nanoparticles are dispersed in the monomers of the host material and the mixture is polymerized under the desired conditions, including the addition of a suitable catalyst. In this case, special attention is required to make a good dispersion of the nanoparticles in the initial environment of the monomers and to avoid their aggregation. For example, Zhao et al. (2011) mention the incorporation of ZnO nanoparticles in a poly-methyl-methacrylate (PMMA) matrix. In order to achieve a good dispersion of the ZnO nanoparticles, they were previously coated with a suitable surfactant (methacryloxy-propyl-trimethoxysilane, MPTMS) [105].
- In the third case, the precursor components of the nanoparticles and the monomers are mixed, and the creation of the nanoparticles and the polymerization occurs simultaneously with the addition of the appropriate additives. For example, Wan et al. prepared a film-like nanocomposite material consisting of TiO₂ nanoparticles in polyacrylate resin through controlled hydrolysis of titanium tetrabutoxide and photopolymerization of an acrylic monomer [106].

3. Types of Contaminants Subject to Nanocomposite Application

nZVI-based nanocomposites (SNCs) have been applied for the removal of both organic and inorganic contaminants from aqueous solutions. The most important categories of organic contaminants are pigments and, secondarily, halogenated hydrocarbons. Inorganic contaminants include hexavalent chromium, trivalent and pentavalent arsenic, and heavy metal cations, such as Pb, Cu, Co, Cd, Ni, and Zn, as well as common anions, such as NO₃ and PO₄. The main outcomes are summarized below.

3.1. Organic Contaminants

Most of the research utilizing nanocomposites has focused on pigment removal. Dyes are widely used in many categories of industries, such as textile, paper, etc. [41]. Dyes are described as toxic and carcinogenic substances that can remain in aqueous solutions over an extended period [107]. For this reason, various methods have been examined for their removal from aqueous solutions, including the use of composite products based on nZVI.

The nano zero-valent iron content of the materials varies. In individual studies, the weight ratio of the substrate to the iron used before its reduction to elemental form is reported, and the assumption is made that all the iron is converted into nZVI. For purposes of comparison, in all cases, the efficiency of the materials is expressed as per gram of nZVI content.

Nanocomposites with bentonite substrate, kaolin, rectorite, and natural clay have been used to remove pigments. Chen et al. (2011), Xi et al. (2011), and Lin et al. (2013) studied Bentonite substrate for the removal of methyl orange, orange II, and acid violet red dyes, respectively [36,39,91]. The ratio of nZVI-bentonite (nZVI/B) in the substrates was 1:1 by weight in all three studies, and the maximum removal achieved, reduced per gram of nZVI, was 79.44, 56.88, and 546 mg/g nZVI, respectively. Kaolin substrate was examined by Chen et al. (2013), Jin et al. (2015), and Kakavandi et al. (2019) for the removal of crystal violet, black G, and acid black 1 dyes [58,60,61]. The nZVI-kaolin (nZVI/K) ratio was 1:1 in Chen et al. and Jin et al. and 1:10 in Kakavandi et al., and the reported maximum removal per gram of nZVI was 3.0, 314.4, and 980 mg/g nZVI, respectively. It is noted that

Kakavandi et al. used the K-nZVI complex as a catalyst in a Fenton-type reaction, with the simultaneous addition of H_2O_2 .

Luo et al. (2013) and Yuan et al. (2016) used rectorite to remove orange II and methyl orange dyes. The nZVI/R ratio of the composite material was 1:2 in both studies. The dye removal was 105 and 930 mg/g nZVI, respectively. It is noted that Yuan et al. (2016) combined nanocomposite material with the use of ultrasound. Abbassi et al. (2013) used a natural clay substrate for malachite green removal, which was also used by X Li et al. (2017) for methyl orange removal [77]. The ratio of nZVI–natural clay was 2:1 and 1:5, and the maximum removal of pigments was 64.1 and 118 mg/g nZVI, respectively [76,84].

Nairat et al. (2015) used clinoptilolite at a ratio of nZVI 1:1 and tested its effectiveness for the removal of methylene blue (MB) and methyl orange (MO). The maximum removal of pigments was 96.6 mg MB/g nZVI and 90.2 mg MO/g nZVI [81].

Kerzek et al. (2014) compared three different clay substrates, including bentonite (B), kaolin (K), and natural clay (NC), for the removal of the industrial azo dye Rosso Zetanyl. All nanocomposites were prepared with a substrate–nZVI ratio of 1:1 and used as catalysts in Fenton-type reactions. The reported maximum decolorization was approximately 820–830 mg/g nZVI with all three materials [40].

Polymer substrates were used by Shu et al. (2010) and C. Liu et al. (2014) [86,93]. Shu et al. (2010) incorporated nZVI into a commercial Dowex HCR-W2 cationic resin, with nZVI content ranging from 4.9 to 50.8 mg nZVI/g resin. They studied the removal of Acid Blue 113 dye, and the reported maximum removal efficiency was 92.5 mg/g nZVI.

Liu et al. (2014) incorporated nZVI into an oxidized polyacrylonitrile membrane (PAN-OM) with a content of 20 wt%. in nano-iron and used the material to remove methyl blue and methylene blue dyes. They achieved decolorization equal to 486 mg/g nZVI for methyl blue at pH 5.2 and 96.5 mg/g nZVI for methylene blue at pH 7.8.

Summarizing the above, most researchers used clay material as a substrate with a high ratio of nZVI, from 10% to 67% wt., in the final nanocomposite. The highest dye removals, in the range of 800–980 mg/g nZVI, were achieved by Kerzek et al. (2014) and Kakavandi et al. (2019), who used the material as a catalyst in Fenton-type reactions, as well as by Yuan et al. (2016), who combined the nanocomposite with the use of ultrasound.

3.2. Inorganic Contaminants

As shown in Table 1, out of the studies related to the remediation of inorganic contaminants, 31 focus on the treatment of Cr(VI), 18 on various heavy metal cations, seven on the common anions NO_3 and PO_4 , six on As(III) and As(V), and one on U(VI) and rare earth elements. The studies related to hexavalent chromium will be examined in more detail in the next section. Subsequently, there will be a brief reference to the other categories of contaminants.

Unal et al. (2013) produced a nanocomposite with alumina (Al_2O_3) and nZVI in a ratio of 50% and studied the removal of 12 rare earth elements (REEs). For La, representing light REEs, a removal equal to 15.2 mg/g nZVI was achieved at pH 6. For Eu (representative of medium REEs) and Yb (representative of heavy REEs), the maximum removal was equal to about 19 mg/g nZVI at pH 3 for both elements [78].

Ding et al. (2018) produced material from carbonized fungi (F) and nZVI, with a nZVI/F ratio of 1/10, and studied U(VI) removal. The maximum U(VI) removal was 298 mg/g nZVI and was achieved at pH 6.5 in 30 min [103].

The removal of As(III) and As(V) was addressed by Zhu et al. (2009), Bhowmick et al. (2014), and Horzum et al. (2013), who used as a substrate commercial granular activated carbon (8.2% nZVI), montmorillonite (nZVI/M = 1:10), and chitosan fibers (nZVI/Ch = 12:1), respectively. The maximum removal of As(III) and As(V) was 2.22 and 1.46 mg/g nZVI by Zhu et al., 65.89 and 50.05 mg/g nZVI (at pH 7) by Bhowmick et al., and 1.54 and 2.11 mg/g nZVI by Horzum et al. [11,50,87].

The removal of only pentavalent arsenic, As(V), was studied by Wang et al. (2017), who incorporated nZVI into pine wood biochar by pyrolysis at 600 °C. The maximum adsorption of As(V) occurred at pH 4.1 and was equal to 11.2 mg/g nZVI [28].

Tandon et al. (2013) studied the removal of As(III) using a nanocomposite of montmorillonite (M) and nZVI with a nZVI/M ratio of 3:1. The optimal removal of As(III) was 0.74 mg/g nZVI at pH 2.75 [49].

The removal of NO_3^- anions was studied by Wei et al. (2018), Y. Zhang et al. (2011), Jiang et al. (2011), and Shi et al. (2013), who used biochar from sugarcane residues, pillared clay, polystyrene resin with functional groups of methyl chloride ($-\text{CH}_2\text{Cl}$) and trimethylamine ($-\text{CH}_2\text{-N} + (\text{CH}_3)_3$), and cationic commercial resin as substrates. The maximum removal of NO_3^- was 184, 100, 81 (in trimethylamine resin), and 106 mg/g nZVI, respectively [21,75,90,92].

The treatment of phosphate anions, PO_4^{3-} , was studied by Soliemanzadeh and Fekri (2017) and Arshadi et al. (2015), who used bentonite substrate and dried plum kernels. The maximum removal achieved was equal to 55 and 21 mg/g nZVI [44,100].

Khalil et al. (2017) studied the removal of both nitrate and phosphate. Activated carbon was used from pyrolysis at 950 °C as a substrate to stabilize nZVI with a substrate/nZVI ratio of 1:2. The maximum removal of NO_3^- was equal to 110 and of PO_4^{3-} was equal to 35 mg/g nZVI [19].

Among heavy metals, the removal of Pb^{2+} has been extensively investigated in numerous studies [26,37,55,57,64–66,71,82,88,92,94,101]. Most studies used clay substrate, although Shi et al. and Yiang et al. used a carbon substrate, while Chanthapon et al., Arshadi et al., and Liu et al., cationic resin, water fern, and chitosan granules, respectively. The reported Pb removal ranged from 3 to 2300 mg/g nZVI. The highest removal of 2300 mg/g was determined by Arshadi et al., followed by Fu et al. and Arabincia et al. with 757 and 345 mg/g nZVI. Very low removals usually correspond to works that studied the simultaneous removal of several contaminants.

Several studies have also been carried out on Ni removal [43,53,59,79]. The substrates in all these studies are clays. Ni removal ranges from 14 to 792 mg/kg.

The removal of Cu was studied by Uzum et al. (2009), Liu et al., (2013), Chang et al. (2014), J. Wang et al. (2015), and Yang et al. (2018), with a maximum reported yield of 886 mg/g nZVI by Chang et al. (2014) [26,53,56,79,88].

Cd was studied by Pang et al. (2013), Liu et al. (2013), Z. Li et al. (2018), and Shi et al. (2019), and the maximum removal of 46 mg/g nZVI was determined by Z. Li et al. [45,47,71,88].

3.3. Use of nZVI Composites for Cr(VI) Removal

Table 2 summarizes the studies concerning the use of nZVI composites for the removal of hexavalent chromium. The support materials used, the parameters examined, and the main conclusions regarding the effectiveness of the materials are presented below.

Table 2. Removal of hexavalent chromium using nZVI composites.

Support Material—Host	Parameters Examined	Observations—Main Results	Cr(VI) Removal Kinetics	Reference
Carbons				
Commercial activated carbon (AC)	Temperature of carbothermal reduction: 350–1150 °C. Dose: AC-Fe: 0.2–8 g/L. Contact time: 10 min–48 h.	Fe content in AC-Fe material 8.59–17.23 mg/g. Maximum Cr(VI) removal capacity ~20 mg/g nanocomposite with the material prepared at 550 °C and a content of 13.28 mg Fe per g of material. Removal was partly by reduction by nZVI and partly by adsorption to AC. It was estimated that the removal due to Fe corresponded to about 1000 mg/g Fe	Second-order adsorption model: $dq/dt = k_2(q_e - q)^2$, where q (mg/g) is the concentration of the contaminant in the solid material at time t and q_e is the equilibrium concentration. Constant k_2 with reduction of Fe was $1.86 \times 10^{-3} (\text{mg/gFe})^{-1} \times \text{h}^{-1}$.	[17]

Table 2. Cont.

Support Material—Host	Parameters Examined	Observations—Main Results	Cr(VI) Removal Kinetics	Reference
Uniformly distributed mesoporous carbon (OMC)	Cr(VI): 25–100 mg/L. pH: 4–11. Dose: 0.5–1.5 g/L.	Carbothermal synthesis on a normal distribution mesoporous carbon (OMC) substrate. The nanocomposites produced at 500–700 °C contained Fe ₃ O ₄ . Only at 900 °C was all the Fe ₃ O ₄ converted to nZVI. nZVI content in the composite 30 wt%. Maximum Cr(VI) removal capacity ~96 mg/g nZVI-OMC or 320 mg/g nZVI.		[70]
BC from sugarcane residues by pyrolysis at 600 °C	Dose: 2–10 g/kg.	nZVI/BC ratio 1/1. The material was mixed with contaminated soil, and a decrease in the mobility of Cr(VI) was observed. Optimum dose 8 g/kg soil.		[20]
Biochar (BC) from rice straw by pyrolysis at temperatures from 100 to 700 °C	Temperature: 100–700 °C. pH: 3–8. Ratio: nZVI/BC: 16:1, 8:1, 4:1, 2:1, 1:1, 0.5:1.	nZVI/BC ratios of 16/1 to 0.5/1 wt were used. More effective BC from pyrolysis at 400 °C and nZVI/BC ratio 4/1. Maximum removal of Cr(VI) 26.6 mg/g material (33 mg/g nZVI).		[22]
BC from corn stalks with HCl (1M), KOH (1M), and H ₂ O ₂ 30% (1:100 solid-to-liquid)	Matrix: plain BC treated with HCl, KOH, H ₂ O ₂ . pH: 5–9. Cr(VI)(mg/L): 2–40 mg/L. nZVI/BC ratio: 3:1, 1:1, 1:3.	The optimal nZVI/BC ratio was 1/1. The highest removal efficiency was observed by nZVI-BC/HCl at pH = 5. The maximum Cr(VI) removal capacity was ~45 mg/g nZVI.		[24]
BC from herb residues by pyrolysis at 400 °C	pH: 2–7. Cr(VI): 4–30 mg/L. Contact time. Competition with coexisting anions and natural organic matter (NOM) HCO ₃ [−] , Cl [−] , SO ₄ [−] : 5, 10 mM. Humic acids: 0–50 mg/L.	nZVI/BC ratio 1/1. The maximum Cr(VI) removal capacity was ~49 mg/(g nZVI-BC) or 98 mg/(g nZVI). The presence of SO ₄ ^{2−} and humics enhances the removal of Cr(VI), while HCO ₃ [−] inhibits it.	Second-order adsorption model: $dq/dt = k_2(q_e - q)^2$. The constant k_2 was equal to $0.25 \times 10^{-3} \text{ (mg/g nZVI)}^{-1} \text{ min}^{-1}$ for a chromium concentration from 30 mg/L to $0.96 \text{ (mg/g nZVI)}^{-1} \text{ min}^{-1}$ for a chromium concentration equal to 4 mg/L.	[27]
BC from Astragalus membranaceus at 400 °C treated with S	pH: 2.5–8.5. Cr(VI): 5–50 mg/L. Presence of Ca ²⁺ and SO ₄ ^{2−} ions.	nZVI/BC ratio 1/1. Adsorption capacity of Cr(VI) equal to 126.12 mg/g (252 mg/g nZVI) at pH 2.5 with S-nZVI/BC material equal to 0.2 g/L	The experimental data were described with satisfactory accuracy by the second-order adsorption model. The constant k_2 varied from 30×10^{-3} to $0.31 \times 10^{-3} \text{ (mg/g nZVI)}^{-1} \text{ min}^{-1}$ when the initial concentration of Cr(VI) was changed to range from 5 to 50 mg/L.	[30]

Table 2. Cont.

Support Material—Host	Parameters Examined	Observations—Main Results	Cr(VI) Removal Kinetics	Reference
Mesoporous carbon	nZVI and MC-nZVI permeability in quartz sand. Initial concentration of Co(II), Pb(II), Cr(VI), Cd(II) and Zn(II) 10 mg/L. Initial mixed stream concentration 20 mg/L.	nZVI content 10%. nZVI size ~16 nm. Maximum removal capacity 17.15 mg Cd/g (171 mg/g nZVI), 6.83 mg Co/g (68.3 mg/g nZVI), 7.62 mg Cr/g (76.2 mg/g nZVI), 22.6 mg Pb/g (226 mg/g nZVI), and 6.83 mg Zn/g. (68.3 mg/g nZVI).		[71]
BC of rice straw (as above); Si removal from a 700 °C BC sample	Temperature: 300–700 °C. pH: 3–4.5. Cr(VI): 20–100 mg/L.	nZVI/BC ratio 4/1. Maximum removal at pH equal to 3.5, 112 mg/g (140 mg/g nZVI). They compared BC-nZVI materials with and without Si and found that the Si-free material is less efficient.		[23]
BC from biological sludge by pyrolysis at 600 °C	pH: 2–10. Cr(VI): 0.5–2 mg/L.	nZVI/BC ratio 50% wt. Maximum removal of Cr(VI) 31.53 mg/g (63.1 mg/g nZVI) at pH 4. Isotherm description with the Langmuir model. Thermodynamic analysis showed that the adsorption process was spontaneous.	Fixed-bed experiments were performed with nZVI-BC, for which the Thomas and Yoon-Nelson models were used.	[31]
BC through pyrolysis of woody biomass of Prosopis juliflora, 400–500 °C	Cr(VI) concentration: 5–25 mg/L. Time: 0.5–16 h.	IBC- < 75 demonstrated optimal performance for the removal of 10 mg/L Cr(VI), with the highest removal capacity ($Q_{max} = 16.30$ mg/g) achieved in groundwater (GW), followed by soft water (SW), hard water (HW), and distilled water (DW). The fastest removal occurred in DW within 5 min, followed by SW and GW in 10 min, and HW in 20 min. The order of Q_{max} was GW (22.49 mg/g) > SW (21.54 mg/g) > HW (17.00 mg/g) > DW (16.30 mg/g).	Cr(VI) removal involved chemisorption, reduction, and simultaneous coprecipitation, which was confirmed through diverse kinetic and isotherm modeling.	[32]
BC by the co-pyrolysis of municipal sewage sludge (MSS) and sunflower seed shells (SSSs)	pH: 3–11. Cr(VI) concentration: 20–90 mg/L. nZVI-BC: 0.5 = 2.5 g/L.	Approximately 47.5 mg Cr(VI)/g R could be removed within 90 min at an initial pH of 3.0. nZVI/BC ratio 1.2 (461 mg nZVI/g R).	Cr(VI) removal kinetics by nZVI-BC followed the pseudo-second-order adsorption model ($k_2 = 0.006$), indicating superior removal capacity compared with bare nZVI and BC. NZVI-BC was recyclable and was regenerated using 0.1 M H_2SO_4 and 0.1 M $NaBH_4$ solutions.	[33]
Pinecone biochar PBC	pH: 5–9. Cell concentration: 0.1–0.4. nZVI-PBC dosage: 0.2–1 g/L.	At a nZVI-PBC dosage of 0.6 g/L, cell concentration of OD600 of 0.3, and initial pH of 6.5, 100 mg/L Cr(VI) could be removed completely by nZVI-PBC/MR-1 within 48 h. In contrast, only 39.50% of Cr(VI) was removed by nZVI-PBC alone.	The pseudo-first-order rate constant (k) of Cr(VI) removal by nZVI/MR-1 ($0.105\ h^{-1}$) was about 10.5 times as high as that of nZVI alone ($0.010\ h^{-1}$).	[34]

Table 2. Cont.

Support Material—Host	Parameters Examined	Observations—Main Results	Cr(VI) Removal Kinetics	Reference
<i>Clays and aluminosilicate minerals</i>				
Montmorillonite (M) by the use of HDTMA (E)		Comparison of nZVI-M and nZVI-ME (with surfactant). nZVI size 21.9 nm and 20.7 nm in nZVI-M and nZVI-ME, respectively. nZVI/M ratio 1/1. The removal capacity was higher in treated montmorillonite and equal to 125 mg/g nZVI, while in plain montmorillonite with nZVI, it was 109 mg/g nZVI at pH 5.		[72]
Bentonite (B)	Cr(VI): 20–70 mg/L. Dose: 1–4 mg/L. pH: 4–8. Temperature: 25–40 °C.	nZVI/B ratio 1/1. Maximum removal of 33 mg/g nZVI, at 35 °C. Reuse of B-nZVI after washing with EDTA solution with a Cr(VI) removal capacity of 70% of the original.	The removal of Cr(VI) was described by a first-order model, $\ln \frac{C}{C_0} = -k_{obs}t$. The k_{obs} constant values (reduced per g nZVI/L) ranged from 0.152 to $0.0117 \text{ min}^{-1} (\text{g/L nZVI})^{-1}$ when the initial Cr(VI) concentration was varied in the range of 20–70 mg/L.	[38]
Bentonite (B)	Plating solutions Cr(VI): 20–100 mg/L. Dose: nZVI-B: 2–5 mg/L. pH: 2–10. Temperature: 25–40 °C.	The optimal Cr(VI) removal was equal to 10 mg/g nZVI and was observed at 30 °C, at a pH equal to 5, an initial Cr(VI) concentration of 20 mg/L, and an optimal nanocomposite dose of 4 mg/L. Pb and Cu removal > 90%.		[74]
Montmorillonite treated with K, MK	Synthesis was carried out in plain MMT, sonicated, stabilized on starch and pretreated with potassium.	Size of nZVI 39.6 nm. nZVI content of 10.71%. The most effective material proved to be treated with K, with the assistance of starch and ultrasound. Optimum removal of 140 mg/g nZVI at pH 6.	A pseudo-second-order adsorption model was used, resulting in negative (!) values of the kinetic constant k_2 (−0.04 to −1.04 g/(mg min)).	[52]
Kissiris, P	Cr(VI), Hg(II): 40–100 mg/L. pH: 3.11–8.13. Regeneration with HCl and reuse of the nanocomposite.	Size of nZVI 30.6 nm. nZVI content 7.7%. Removal of Hg 332 mg Hg(II)/gnZVI and 307 mg Cr(VI)/g nZVI.	A rapid removal of Cr(VI) in the first 0.5 min was reported, which was attributed to physical adsorption, followed by a slower removal step attributed to reduction.	[80]
Sepiolite, S	Cr(VI): 25–100 mg/L. pH: 3–9. Dose: 0.5–2 g/L. Comparison of simple nZVI with S-nZVI.	S/nZVI ratio 5/2. Size of nZVI < 100 nm. Removal of chromium 177 mg/g (620 mg/g nZVI) at pH 3.	First-order kinetic model $\ln \frac{C}{C_0} = -k_{obs}t$. k_{obs} kinetic values (reduced per g nZVI/L) varied from 0.29 to $0.12 \text{ min}^{-1} (\text{g/L nZVI})^{-1}$ when the initial concentration of Cr(VI) varied from 25 to 100 mg/L at pH 3.	[63]

Table 2. Cont.

Support Material—Host	Parameters Examined	Observations—Main Results	Cr(VI) Removal Kinetics	Reference
Sepiolite, S	Cr(VI): 20–120 mg/L. pH: 4–9. Dose: 0.05–3.2 g/L. Effect of common ions: Ca^{2+} , H_2PO_4^- , HCO_3^- , SiO_3^{2-} .	S/nZVI ratio 9/1. Size of nZVI 10–50 nm. Maximum removal capacity 610 mg Cr/g nZVI and 757 mg Pb/g nZVI.	The removal kinetics of Cr(VI) and Pb were described by a pseudo-first-order adsorption model $dq/dt = k_1(q_e - q)$. For Cr(VI), the values of the k_1 constant (per g nZVI/L) varied from 0.4 to $0.0025 \text{ min}^{-1} (\text{g/L nZVI})^{-1}$ at pH values from 4 to 9.	[64]
Montmorillonite, M	Cr(VI): 10–200 mg/L. pH: 3–10. Contact time: 60 min.	M/nZVI ratio ~100/5.6. Maximum removal capacity 400 mg/g nZVI at pH 3.		[54]
Bentonite, B	B-nZVI ratio: 1/2, 1/1, 3/2. Cr(VI): 0.095–0.95 mM. Molecular ratio Cr(VI)–phenol: 0.9–9. $\text{K}_2\text{S}_2\text{O}_8$: 0.33–1.67 mM. pH: 3–11. Dose of B-nZVI: 0.25–1.25 g/L.	B/nZVI ratio 0.1/2, 1/1, 3/2. Size of nZVI < 10 nm. Optimum removal 99.3% for Cr(VI) (39 mg/g nZVI) and 6.5% for phenols (0.014 mmol/g nZVI) without $\text{K}_2\text{S}_2\text{O}_8$. The addition of persulfate significantly improved the oxidation of phenol, up to a rate of 71.5%, without a negative effect on the removal of chromates.		[42]
Attapulgit, Atp	Different dosage of nZVI/ATP(1:3) into 100 mL of Cr(VI) solutions with the initial level ranging from 20 to 100 mg L^{-1} .	Removal capacity decreased significantly with nZVI/ATP (1:3) dosage increase at each Cr(VI) initial level ($p < 0.05$). With a dosage of nZVI/ATP (1:3) increasing from 0.5 to 2.0 g/L , the remediation capacity decreased from 35.94 to 9.97 mg/g at the initial level of Cr(VI), i.e., 20 mg/L , and with 100 mg/L , the removal potential reduced from 45.41 to 16.66 mg/g according to a nZVI/ATP (1:3) concentration increase from 0.5 to 6.0 g L^{-1} .	The removal kinetics and isotherm fitting results showed that the pseudo-second-order kinetics and Langmuir isotherm can better explain Cr(VI) adsorption process.	[67]
Natural and synthetic polymers				
Non-porous resin PolyFlo (20–30 μm)	Cr(VI): 14–56 mg/L. Dose: 1.9–5.0 g/L.	Resin nZVI content 226.8 mg nZVI/g. Size of nZVI 10–30 nm. Removal of Pb(II) 0.234 mg/g (1.03 mg/g nZVI) and of Cr(VI) 1.036 mg/g (4.56 mg/g nZVI) in one day. The solutions along with the nanocomposite material had a pH of 4.01 and 3.25 for Pb and Cr, respectively.	First-order model of Cr(VI) concentration in the aqueous phase $\ln \frac{C}{C_0} = -k_{obs}t$. The k_{obs} constant was equal to $0.087 \text{ min}^{-1} (\text{g nZVI/L})^{-1}$ at pH 3.25.	[85]

Table 2. Cont.

Support Material—Host	Parameters Examined	Observations—Main Results	Cr(VI) Removal Kinetics	Reference
Chitosan granules, Ch	Cr(VI), Cu, Cd, Pb: 100–20, 100–20, 75–15, 50–10 mg/L, respectively. pH: 2.9–9.2.	Size 45.2 nm. C/nZVI ratio 2/1. The removal of Cr(VI), Cu, Cd, and Pb was 1.79 mg/g (5.36 mg/g nZVI), 1.98 mg/g (5.93 mg/g nZVI), 1.42 mg/g (4.27 mg/g nZVI), and 0.99 mg/g (3 mg/g nZVI), respectively, at pH 6.4 and temperature 20 °C.		[88]
Polystyrene cation exchange resin D001	nZVI charge: 30.8–43.1 mg/g R-nZVI. Dose: 10–25 g/L. pH: 3–9. Cr(VI): 20–40 mg/L.	Maximum chromium removal 0.9 mg/g (20.44 mg/g nZVI). The Cr(VI) removal efficiency was 60.8%, 43.8%, 33.1%, and 8.8% after reusing the resin with nZVI one, two, three and four times, respectively	Second-order model of Cr(VI) concentration in solution: $dC/dt = k_2 C^2$. The k_2 constant value was equal to $0.0045\text{--}0.009\text{ min}^{-1}(\text{mg/L})^{-1}$ for a chromium concentration of 20–40 mg/L at pH 5.	[91]
Alginate Beads	pH: 3–11. Dose: 0.08–0.64 g/L.	Alg/nZVI ratio 3/1. The maximum removal of Cr(VI) was 4 mg/g (16 mg/g nZVI) at pH 11.	First-order model of Cr(VI) concentration in the aqueous phase $\ln \frac{C}{C_0} = -k_{obs}t$. The k_{obs} constant was equal to $0.0088\text{ min}^{-1}(\text{g nZVI/L})^{-1}$ at pH 5.3.	[89]
Cation exchange resin Dowex 50WX2	Concentration: 5–25 mg/L for Cr(VI). Grams of resin: 1–6 g/L. pH: 2.7–8.5.	Green tea was found to be inefficient, probably due to the relatively big size of the contained polyphenol molecules. Gallic acid molecules were able to reach adsorbed Fe(III) and reduce the cations to the elemental state with 100 mg (1.79 mmol) of nFe per gram of dry resin. After 1 h of treatment, the removal of Cr(VI) was equal to 99.4% at pH 2.7, 96.1% at pH 3.2, 71.6% at pH 4.4, 59.6% at pH 5.0, and 23.6% at pH 8.5.	It was found that the reduction followed a kinetic law of first order with respect to Cr(VI) and to the embedded nano-iron. The reaction rate constant was determined between 0.48×10^{-3} and $8.03 \times 10^{-3}\text{ min}^{-1}\text{ per mM}$ of nZVI, a range similar to that reported for other resin-supported nZVI products. Expressed in terms of half-life time, $t_{1/2}$, and assuming operation in the presence of 1 mM nZVI, these constants corresponded to $t_{1/2}$ ranging between 1.4 and 24.1 h.	[95]
Cation exchange resin Amberlyst 15	Rate of agitation: 50–250 rpm. Particle size of R-nFe beads: 300, 388, and 462.5 μm diameter. Initial concentration of chromate: 0.10, 0.19, and 0.38 mM. nZVI content in resin: 0.15, 0.30, 0.49, and 0.61 mmole nZVI per gram of wet resin. Dose of resin per liter of solution: 20, 40, and 60 wet g/L. pH: 3.5, 4.5, 5.5, and 7.5.	Maximum concentration nFe = 27.44 mg/g wet R (0.49 mmole per liter of solution). The amount of Cr(VI) removed from the aqueous solution after 24 h was 0.853 mg/g nFe.	It was found that the reduction of Cr(VI) follows a kinetics law of first order with respect to the concentration of Cr(VI) and to the amount of nZVI per liter of solution. The kinetic constant varied between 5×10^{-3} and $0.5 \times 10^{-3}\text{ per min}$ and per mM of nZVI in the pH range of 3.5–7.5.	[96]

Table 2. Cont.

Support Material—Host	Parameters Examined	Observations—Main Results	Cr(VI) Removal Kinetics	Reference
Lignin-based hydrogel (LH)	Different precursor Fe(II) ion concentrations: 0.025–0.05 mol/L. Initial pH: 2.1, 5.3, and 8.5. Contact time: 200 mg/L Electron acceptor (NO_3^- , SO_4^{2-}), and 50 mg/L electron donor (HA, sodium acetate).	nZVI@LH at the precursor Fe(II) ion concentration of 0.1 mol/L presented an enhanced Cr(VI) removal capacity of 310.86 mg/g Fe0 at pH 5.3, which was 11.6 times more than that of the pure nZVI. The removal efficiency of the composite at pH 2.1 was more than double compared with alkaline or neutral conditions. The maximal removal capacity improved from 277.78 mg Cr(VI)/g nFe to 370.37 mg Cr(VI)/g nFe when the solution became more acidic.		[97]
Alginate beads, Alg	Temperature: 10, 25, 40 °C. pH: 3.5. Dissolved oxygen Cr(VI) concentration: $8.93 \times 10^{-4}\text{M}$ — $8.93 \times 10^{-3}\text{M}$. Fe:Cr ratio: 2–20.	N25@AL exhibited faster removal than NSTAR@AL. Both materials shared an identical maximum removal capacity of 133 mg of Cr(VI) per gram of nZVI at pH 3.		[98]
Other materials				
Hummus, H	nZVI charge: 1.4%–10.4%. Dose: 1.8–4.8 g/L. pH: 3–10. Cr (VI): 40–200 mg/L.	Size 50–150 nm. H/nZVI ratio 2/5. Removal of 42.4 mg Cr(VI)/g H-nZVI (59.4 mg/g nZVI) at pH 6.5.	The kinetic removal of Cr(VI) and Pb was described by a first-order model of Cr(VI) in the aqueous phase $\ln \frac{C}{C_0} = -k_{obs}t$. No kinetic constant values were reported. The removal of Cr(VI) in equilibrium conditions was described by the Langmuir adsorption isotherm with a maximum loading q_{max} of 42.4 mg/g and k_L equal 0.353 L/g.	[102]
Stone wool, W	W/nZVI ratio: 1:0.5, 1:1, 1:2. pH: 2–11. Cr (VI): 10–200 mg/L.	W/nZVI ratio 1:0.5, 1:1 και 1:2. Size of nZVI 20–30 nm. Removal of 198 mg Cr(VI)/g W-nZVI (297 mg/g nZVI) in 30 min.		[104]

Chen et al. (2015) synthesized nanocomposites with commercial granular activated carbon as a substrate and Fe(II) as an iron precursor and used carbothermic reduction to convert adsorbed Fe(II) into nZVI [16]. They studied the effectiveness of the nanocomposite material for the removal of Cr(VI), with the main parameters being the temperature at which the carbothermic reduction was carried out (350–1150 °C) and the amount of the nanocomposite material (AC-Fe) in the adsorption tests (0.2–8 g/L), and the contact time ranged from 10 min to 48 h. In the adsorption tests, it was found that Cr(VI) was adsorbed both on the simple activated carbon (6.7 mg/g) and AC-Fe (12.5 mg/g). After carbothermic reduction, there was an increase in Cr(VI) adsorption up to approximately 20 mg/g for the product produced at 550 °C. It was noted that during the characterization of the materials with XRD, elemental iron, Fe(0), was detected only above 550 °C and always in coexistence with magnetite, Fe_3O_4 . Therefore, in these tests, it was difficult to estimate the percentage

of Cr(VI) removal that was exclusively attributed to nZVI. However, taking into account that the AC-Fe material at 550 °C contained 13.28 mg/g Fe and considering that out of 20 mg/g of Cr(VI), 6.7 mg/g of Cr(VI) was removed by simple adsorption on the AC surface, it was estimated that the removal of Cr(VI) due to Fe corresponded to about 1000 mg/g Fe.

In addition, adsorption models were used to describe the kinetics of Cr(VI) removal. The authors found that the experimental data were described with sufficient accuracy by the second-order adsorption model: $d_q/d_t = k_2(q_e - q)^2$, where q (mg/g) is the concentration of the contaminant in the solid material at time t and q_e is the concentration on equilibrium. The constant k_2 had a value of $0.14 \text{ (mg/g)}^{-1} \text{ h}^{-1}$, and the reduced Fe content had a value of $1.86 \times 10^{-3} \text{ (mg/gFe)}^{-1} \text{ h}^{-1}$.

Dai et al. (2016) used ordered mesoporous carbon (OMC) as a substrate, and the incorporation of nZVI was carried out with an initial step of Fe(III) adsorption and then a carbothermal reduction at temperatures of 500–1000 °C. Their studies found that the nanocomposites produced at 500–700 °C contained Fe_3O_4 . Only at 900 °C was all the Fe_3O_4 converted to nZVI [70]. Cr(VI) adsorption tests were performed on a nanocomposite (nZVI-OMC) with a nZVI content equal to 30 wt%. The parameters examined were a pH of 4–11, a Cr(VI) concentration of 25–100 mg/L, and an amount of 0.5–1.5 g/L. For comparison, corresponding tests were performed with plain OMC, plain nZVI, and plain carbon–nZVI composite (nZVI-C). The maximum removal was achieved with nZVI-OMC and was equal to 320 mg/g nZVI. Although they studied the evolution of Cr(VI) removal over time, Das et al. did not process their data with specific kinetic models.

Su et al. (2016) incorporated nZVI into a sugarcane biochar (BC) substrate at a substrate–nZVI ratio of 1/1. The purpose of their research was to reduce the mobility of Cr(VI) in contaminated soil as well as to study the phytotoxicity of Cr(VI) and Fe. The soil was contaminated with 320 mg/kg Cr(VI) at a solid/liquid ratio of 1/1, and then various amounts of nZVI, BC, and nZVI-BC were added. Plant growth experiments were conducted on soil samples without Cr(VI), with Cr(VI), with nZVI, with BC, and with nZVI–BC. In the soil samples, the pH varied from 5.56 to 6.51, the available iron from 55 to 229 mg/kg, and the organic matter from 389 to 45 mg/kg. The stabilization efficiency of Cr(VI) increased from 79.54% to 100% when the amount of nZVI–BC was increased from 5 g/kg to 8 g/kg. The application of nZVI-BC nanocomposite improved the pH of the soil, reduced excessive iron release caused by the application of single nZVI, and improved soil fertility [20].

Qian et al. (2017, 2019) used rice straw biochar substrate to remove Cr(VI) from aqueous solutions. They studied the effectiveness of the nanocomposite material (nZVI-BC) for the removal of Cr(VI), with the main parameters including the temperature at which the material was synthesized (100–700 °C), the pH of the solution (3–8), and the amount of nZVI in relation to the amount of BC (16:1, 8:1, 4:1, 2:1, 1:1, 0.5:1). The maximum removal of Cr(VI) was 33 mg/g nZVI, which was observed from a material with a composition temperature of 400 °C, a nZVI/BC ratio of 4/1, and a pH equal to 5. According to the researchers, the removal of Cr(VI) was dominated by the reduction effect, but also, the biochar as a substrate contributed to the adsorption of Cr(VI) (0.3–6.4 mg/g) [22,23].

In a subsequent study, Qian et al. (2019) used the same synthesis method but chose a material prepared at 700 °C and performed Cr(VI) removal experiments at lower pH values. At pH 3.5, they achieved a Cr(VI) removal equal to 140 mg/g nZVI. They also compared BC–nZVI materials with and without the presence of Si and found that the Si-free material was less efficient.

Dong et al. (2017) used a biochar (BC) substrate from corn stalks to incorporate nZVI. They studied the removal efficiency of Cr(VI) in four nanocomposites with differently treated substrates (plain BC and BC treated with HCl, KOH, and H_2O_2). The results showed that the nanocomposite with HCl-treated substrate (nZVI-BC(HCl)) performed better as it had a larger specific surface area and thus allowed for the uniform distribution of nZVI. Afterward, they studied the effectiveness of nZVI-BC(HCl) nanocomposite for

Cr(VI) removal, with the main parameters including pH (5–9), initial Cr(VI) concentration (2–40 mg/L), and the ratio of nZVI to BC (3:1, 1:1, 1:3). The maximum removal was achieved at a nZVI/BC(HCl) ratio of 1:1 and a pH of 5 and was 45 mg/g nZVI. The study of the adsorption with different initial chromium concentrations (2–40 mg/L) showed that when the initial Cr(VI) concentration increased, a passive layer was formed, which was due to the rapid oxidation of nZVI by chromium ions and, consequently, reduced the effectiveness of the nanocomposite material [24].

Shang et al. (2017) used a biochar (BC) substrate from herb residues to incorporate nZVI. They studied the removal efficiency of Cr(VI) with the main parameters including pH (2–7), initial concentration of Cr(VI) (4–30 mg/L), contact time, and competition with coexisting anions and natural organic matter. It was observed that the removal efficiency decreased with an increasing pH value, with the maximum removal equal to 98 mg/g nZVI observed at pH 2 [27].

Adsorption models were used to describe the kinetics of Cr(VI) removal. They found that the experimental data are described with satisfactory accuracy by the 2nd order adsorption model. The constant k_2 had a value from $0.25 \cdot 10^{-3} \text{ (mg/g nZVI)}^{-1} \text{ min}^{-1}$ for a chromium concentration of 30 mg/L to $0.96 \text{ (mg/g nZVI)}^{-1} \text{ min}^{-1}$ for chromium concentration equal to 4 mg/L. The presence of SO_4^{2-} and humics enhanced the removal of Cr(VI), while HCO_3^- inhibited it.

Gao et al. (2018) used a biochar (BC) substrate from *Astragalus membranaceus* treated with sulfur to incorporate nZVI. The removal efficiency of Cr(VI) with the main parameters including pH (2.5–8.5), the initial concentration of Cr(VI) (5–50 mg/L), contact time, and the presence of Ca^{2+} and SO_4^{2-} ions were studied. The maximum removal was achieved at pH 2.5 with a value of 252 mg/g nZVI, while when the pH increased to 8.5, the removal decreased to 93 mg/g nZVI. The experimental data were described with satisfactory accuracy by a second-order adsorption model. The constant k_2 varied from 30×10^{-3} to $0.31 \times 10^{-3} \text{ (mg/g nZVI)}^{-1} \text{ min}^{-1}$ when the initial concentration of Cr(VI) varied in the range of 5–50 mg/L. The removal reaction was greatly favored in the presence of SO_4^{2-} and slightly inhibited by Ca^{2+} ions and dissolved oxygen [30].

Shi et al. (2019) incorporated nZVI into mesoporous carbon. The incorporation of nZVI was performed by reducing Fe(III) at a temperature of 600 °C in the presence of H_2 . The iron content of the nanocomposite was 10%. They performed tests on quartz sand columns to compare the ability of plain nZVI and the MC-nZVI nanocomposite to permeate the column and found that MC-nZVI permeated the column more quickly and efficiently than plain nZVI.

They also studied the removal efficiency of heavy metals such as Co, Pb, Cr(VI), Cd, and Zn and their combination in an aqueous solution. The maximum removal capacity was 171 mg Cd/g nZVI, 68 mg Co/g nZVI, 76 mg Cr/g nZVI, 226 mg Pb/g nZVI, and 68 mg Zn/g nZVI. The removal kinetics in the combined solution was rapid during the first hour and then gradually reached equilibrium in about 24 h [71].

Fan et al. (2019) used a biochar (BC) substrate from biological sludge to incorporate nZVI by pyrolysis at 600 °C. They studied the removal efficiency of Cr(VI) with the main parameters including initial chromium concentration (0.5–2 mg/L) and pH (2–10). The Langmuir adsorption model was used to describe the removal, and the maximum removal capacity was determined to be 63 mg/g nZVI at pH 4. The thermodynamic analysis showed that the adsorption process was spontaneous. Fixed-bed experiments were performed with nZVI-BC and were described by Thomas and Yoon–Nelson models [31].

Khandelwal et al. (2020) used a biochar (BC) substrate produced through the pyrolysis of the woody biomass of *prosopis juliflora* at 400–500 °C to incorporate nZVI for the removal of anionic metal species, i.e., HCrO_4^- and CrO_4^{2-} . They studied different size ranges of biochar grains, specifically < 75 µm (IBC- < 75), 75–150 µm (IBC-75–150), and 150–300 µm (IBC-150–300), each with a Fe/BC mass ratio of 1. Additionally, the impact of iron loading was explored, examining < 75 µm grains modified with iron at Fe/BC = 0.5 (IBC-0.5) and Fe/BC = 2 (IBC-2). Notably, IBC- < 75 exhibited optimal performance,

achieving maximum chromium (VI) removal capacity ($Q_{\max} = 16.30 \text{ mg/g}$) and the fastest removal kinetics (100% within 5 min). The applicability of IBC- < 75 for Cr(VI) removal was further assessed across different water compositions, including soft water (SW), hard water (HW), and groundwater (GW). The results revealed that the complete removal of 10 mg/L Cr(VI) occurred most rapidly in distilled water (DW) within 5 min, followed by a similar removal time in SW and GW (10 min) and a longer time in HW (20 min). The order of $Q_{\max}$ values for different water sources was found to be $\text{GW} (22.49 \text{ mg/g}) > \text{SW} (21.54 \text{ mg/g}) > \text{HW} (17.00 \text{ mg/g}) > \text{DW} (16.30 \text{ mg/g})$. Various removal mechanisms, such as chemisorption, reduction, and simultaneous coprecipitation, were identified through comprehensive kinetic and isotherm modeling. The confirmation of these mechanisms was further supported by the examination of reaction precipitates using powder X-ray diffraction (pXRD) [32].

Chen et al. (2022) utilized biochar (BC) derived from the co-pyrolysis of municipal sewage sludge (MSS) and sunflower seed shells (SSSs) to incorporate nano zero-valent iron (nZVI) for the synthesis of a composite material known as nZVI-BC. This composite material was employed for the removal of Cr(VI) from aqueous systems. The investigation focused on assessing the influence of the initial pH, the initial Cr(VI) concentration, and the dosage of nZVI-BC in the removal process. Approximately 95.00% of Cr(VI) could be removed within 90 min at an initial pH of 3.0, an initial Cr(VI) concentration of 50 mg/L, and an nZVI-BC dose of 1.0 g/L. The kinetics for Cr(VI) removal via nZVI-BC could be better explained by a pseudo-second-order (PSO) adsorption model with kinetic constant $k_2 = 0.006$. The analysis of adsorption isotherms revealed the remarkable Cr(VI) removal efficiency of nZVI-BC, surpassing the capabilities of both bare nZVI and BC. The recyclability of nZVI-BC was demonstrated through a regeneration process utilizing 0.1 M H_2SO_4 and 0.1 M NaBH_4 solutions. Kinetic studies for Cr(VI) removal by nZVI-BC were more accurately described by a pseudo-second-order adsorption model with a kinetic constant (k_2) of 0.006. [33].

Ma et al. (2022) employed pinecone biochar to integrate nano zero-valent iron (nZVI) for the purpose of removing high concentrations of Cr(VI) from aqueous solutions, particularly in the presence of *Shewanella oneidensis* MR-1 (MR-1). Their study demonstrated that the coupling of nZVI-PBC with MR-1 (nZVI-PBC/MR-1) exhibited superior removal performance for high-concentration Cr(VI) when compared with nZVI-PBC alone. Under optimized conditions, nZVI-PBC/MR-1 achieved the complete removal of 100 mg/L Cr(VI) within 48 h, whereas only 39.50% of Cr(VI) was removed by nZVI-PBC alone. The enhanced Cr(VI) removal was attributed to the dissolution of the surface passivation layer of nZVI-PBC, the formation of sorbed Fe(II) in the presence of MR-1, and the significant contribution of extracellular polymeric substance (EPS) derived from MR-1.

They also used characterization techniques such as X-ray photoelectron spectroscopy (XPS) and Cr K-edge X-ray absorption near-edge structure spectra (XANES) to confirm the reduction of most Cr(VI) to insoluble Cr(III), resulting in the formation of Cr_2O_3 , $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$, and FeCr_2O_4 precipitates. A minor portion of unreduced Cr(VI) was immobilized through adsorption and complexation. Their findings suggest that nZVI-PBC/MR-1 effectively addresses the limitations associated with nZVI, enabling highly efficient removal of high concentration Cr(VI). The pseudo-first-order rate constant (k) for Cr(VI) removal by nZVI/MR-1 (0.105 h^{-1}) was approximately 10.5 times higher than that of nZVI alone (0.010 h^{-1}) [34].

Li et al. (2010) incorporated nZVI into plain montmorillonite and montmorillonite treated with HDTMA (hexadecyl trimethylammonium bromide) and compared the activity of the two materials in the removal of Cr(VI). The removal capacity was higher in treated montmorillonite and equal to 125 mg/g nZVI, while in plain montmorillonite with nZVI, it was 109 mg/g nZVI at pH 5 [51].

Shi et al. (2011) incorporated nZVI into bentonite (B-nZVI) with a substrate–nZVI ratio of 1/1. The parameters examined included the initial Cr(VI) concentration, nanocomposite dose, pH, and temperature. The removal of Cr(VI) was described by a pseudo-first-order model, $\ln C/C_0 = -k_{\text{obs}} t$. The k_{obs} constant values (reduced per g nZVI/L) ranged from

0.152 to $0.0117 \text{ min}^{-1} (\text{g/L nZVI})^{-1}$ when the initial Cr(VI) concentration was varied in the range of 20–70 mg/L. The reuse of B-nZVI after washing with ethylenediaminetetraacetic acid (EDTA) solution was possible, but the capacity of the material to remove Cr(VI) was reduced to about 70% [38].

Shi et al. (2011) used the same B-nZVI nanocomposite for the treatment of metal plating wastewater. They studied the removal of Cr(VI) by considering the following parameters: initial contaminant concentration (20–100 mg/L), nanocomposite dose (2–5 mg/L), pH (2–10), and temperature (25–40 °C). The optimum Cr(VI) removal was equal to 10 mg/g nZVI and was observed at 30 °C, pH 5, an initial Cr(VI) concentration of 20 mg/L, and a nanocomposite dose of 4 mg/L. Pb and Cu removal of > 90% was also achieved [74].

Zhang et al. (2013) incorporated nZVI into two types of montmorillonites (MMTs) including plain and potassium-treated. They also used starch and ultrasound to disperse both bare nZVI nanoparticles and fixed nZVI montmorillonite particles. Of all the materials tested, the MMT nanocomposite treated with potassium, with the assistance of starch and ultrasound, showed the highest Cr(VI) removal efficiency equal to 140 mg/g nZVI at pH 6. To describe the kinetics, they used a pseudo-adsorption second-order model, based on which negative values (!) of the kinetic constant k_2 were obtained [52].

Liu et al. (2014) incorporated nZVI into pumice for the removal of Hg(II) and also Cr(VI). They studied their removal efficiency with the main parameters including the initial concentration of heavy metals (40–100 mg/L) and the effect of pH (3.11–8.13). The maximum removal of Hg was 332 mg Hg(II)/g nZVI and of chromium was 307 mg Cr(VI)/g nZVI. The removal rate of Hg(II) increased with an increase in pH, while the removal of Cr(VI) decreased gradually. The possibility of regenerating the nanocomposite by simple rinsing with dilute HCl was also studied (exact conditions not reported). The regenerated material retained the ability to remove the two contaminants but with a relatively reduced efficiency. In the fourth regeneration cycle, the removal dropped from the initial 100% to 56.7% for Hg and 45.5% for Cr(VI) [80].

Ramazanpour et al. (2015) incorporated nZVI into sepiolite and studied the Cr(VI) removal efficiency with the main parameters including the initial Cr(VI) concentration (25–100 mg/L), pH (3–9), the dose of the nanocomposite material (0.5–2 g/L), and the concentration of Cl^- (0–100 mM). They also compared the Cr(VI) removal efficiency with plain nZVI versus S-nZVI. S-nZVI proved to be more effective than plain nZVI, with a maximum removal of 620 mg/g nZVI in S-nZVI versus 135 mg/g nZVI in plain nZVI. The kinetic removal of chromium was described by a first-order model with respect to the concentration of Cr(VI) in the solution. The values of the kinetic constant k_{obs} (reduced per g nZVI/L) ranged from 0.29 to $0.12 \text{ min}^{-1} (\text{g/L nZVI})^{-1}$ when the initial Cr(VI) concentration was varied in the range of 25–100 mg/L at pH 3. The effect of pH k_{obs} (per g nZVI/L) varied from 0.12 at pH 3 to $0.07 \text{ min}^{-1} (\text{g/L nZVI})^{-1}$ at pH 9 [63].

Fu et al. (2015) incorporated nZVI into sepiolite and studied the removal efficiency of Cr(VI) with the main parameters including the initial concentration of Cr(VI) and Pb metals (20–120 mg/L), pH (4–9), the dose of the nanocomposite material (0.05–3.2 g/L), and the effect of the ions coexisting in the system (Ca^{2+} , H_2PO_4^- , HCO_3^- , SiO_3^{2-}). The maximum removal capacity was 610 mg Cr/g nZVI and 757 mg Pb/g nZVI. The removal mechanism of both metals was presented as a two-step interaction involving first, the physical adsorption of Cr(VI) and Pb on the surface or interlaminar porosity of the nanocomposite and then their reduction by nZVI. The removal of Cr(VI) decreased when the pH increased from 4 to 9, while with increasing pH, the removal of Pb was not significantly affected. The presence of the other ions had no significant effect on Cr(VI) and Pb removal. The removal kinetics of Cr(VI) and Pb were described by a first-order model in terms of concentrations in the aqueous phase, $\ln \frac{C}{C_0} = -k_{\text{obs}} t$. For Cr(VI), the k_{obs} constant values (per g nZVI/L) ranged from 1.8 to $0.04 \text{ min}^{-1} (\text{g/L nZVI})^{-1}$ when the initial Cr(VI) concentration was varied in the range of 40–120 mg/L. For Pb, the kinetic constant values were from 11.9 to $0.05 \text{ min}^{-1} (\text{g/L nZVI})^{-1}$ for the same concentration range [64].

Wu et al. (2015) used montmorillonite (M) as a substrate and synthesized a composite with an M/nZVI ratio of 100/5.6. They studied the effectiveness of the nanocomposite for Cr(VI) removal with the main parameters including the initial Cr(VI) concentration (10–200 mg/L), pH (3–10), and contact time (up to 60 min). The maximum removal capacity was about 400 mg/g nZVI at pH 3. Only 5% of the total Cr(VI) removal was attributed to simple adsorption on M, and the rest was attributed to nZVI action [54].

Diao et al. (2016) incorporated nZVI into bentonite (B) and studied the simultaneous removal of Cr(VI) and phenol in the presence or absence of potassium persulfate. The addition of $K_2S_2O_8$ aimed to utilize nZVI as a Fenton catalyst for phenol oxidation. The main parameters investigated were the bentonite–nZVI ratio (1/2, 1/1, and 3/2), the initial Cr(VI) concentration (0.095–0.95 mM), Cr(VI)–phenol molar ratio (0.9–9), the concentration of $K_2S_2O_8$ (0.33–1.67 mM), the pH (3–11), and the dose of the nanocomposite (0.25–1.25 g/L) [42].

The removal rates of Cr(VI) and phenol with B-nZVI without persulfate were 99.90% (1.19 mg/g nZVI) and 6.50%, respectively, after 30 min. The corresponding values with the addition of $K_2S_2O_8$ were 99.30% (1.18 mg/g nZVI) and 71.50%, respectively. That is, the presence of persulfate helped the oxidation of phenol without a negative effect on the removal of chromates. The reuse experiments of B-nZVI showed that its structure was relatively stable after four reuse cycles.

Wei et al., in 2022, incorporated nZVI on attapulgite for the removal of hexavalent chromium. The investigation focused on the synthesis of attapulgite (ATP)-supported nanoscale zero-valent iron (nZVI) at varying Fe/ATP mass ratios (1:3 and 1:5) through a liquid phase reduction method. The characterization data revealed an effective dispersion of nZVI on the ATP surface, preventing the agglomeration of nZVI particles. The results demonstrated that the incorporation of ATP significantly enhanced the removal efficiency of Cr(VI) compared with bare nZVI or ATP alone. At an initial Cr(VI) concentration of 40 mg/L, the remediation efficacy of Cr(VI) in nZVI/ATP (1:3) reached 91.63%, a substantial improvement compared with bare nZVI (48.68%) and ATP (2.52%). The removal kinetics and isotherm fitting results showed that pseudo-second-order kinetics and the Langmuir isotherm can better explain the Cr(VI) adsorption process [67].

Liu et al. (2013) incorporated nZVI into chitosan (Ch) granules and studied the cleaning efficiency of plating waste. They performed column experiments aimed at simulating the operation of permeable reactive barriers. The main parameters investigated were the pH (2.9–9.2) and the initial concentration of the metals Cr(VI), Cu, Cd, and Pb (100–20, 100–20, 75–15, and 50–10 mg/L respectively). The substrate–nZVI ratio was 2/1, and the maximum removal for each metal was 5.36 mg Cr(VI)/g nZVI, 5.93 mg Cu/g nZVI, 4.27 mg Cd/g nZVI, and 3 mg Pb/g nZVI at pH 6.4 and a temperature of 20 °C. The removal rate of Cr(VI) decreased and the removals of Cu, Cd, and Pb increased while increasing the pH. Also, the removal of the other contaminants, i.e., Cu, Cd, and Pb, decreased with an increasing initial Cr(VI) concentration. At low concentrations (less than 40 mg/L), heavy metals were removed in the following order: Cd > Cu > Pb > Cr(VI). At higher concentrations, the removal followed the order of Pb > Cu > Cd > Cr(VI) [88].

Ponder et al. (2000) supported nZVI on a non-porous resin and tested the removal efficiency of Pb(II) and Cr(VI) with the main parameters including the dose of the nanocomposite (1.9–5.0 g/L for Cr(VI) and 0.29–1.75 g/L for Pb(II)) and the initial concentration of metals (14–56 mg Cr(VI)/L, 8–41 mg Pb(II)/L). The maximum removal of chromium was 4.56 mg/g nZVI during one day at pH 3.25. The removal kinetics of Cr(VI) was described by a first-order model in terms of the concentration of Cr(VI) in the aqueous phase $\ln \frac{C}{C_0} = -k_{obs}t$. The constant k_{obs} was equal to $0.087 \text{ min}^{-1} (\text{g nZVI/L})^{-1}$ at pH 3.25 [85].

Fu et al. (2013) incorporated nZVI into cationic polystyrene (R) resin and studied the Cr(VI) removal efficiency with the main parameters including the loading of nZVI in the resin (30.8–43.1 mg/g R-nZVI), the dose of resin (10–25 g/L), the pH value (3–9), and the initial concentration of Cr(VI) (20–40 mg/L). The maximum removal of chromium was 20.44 mg/g nZVI at pH 5. To describe the kinetics, a second-order model was used in terms

of the concentration of Cr(VI) in the solution as follows: $dC/dt = k_2 C^2$. The k_2 constant had a value of $0.0045\text{--}0.009 \text{ min}^{-1} (\text{mg/L})^{-1}$ for a chromium concentration of 20–40 mg/L at pH 5. Reuse tests of the material were performed. The Cr(VI) removal efficiency was 60.8%, 43.8%, 33.1%, and 8.8% in the four consecutive reuse cycles [91].

Huang et al. (2016) incorporated nZVI into alginate beads and studied the removal efficiency of Cr(VI) with pH (3–11) and nanocomposite dosage (0.08–0.64 g/L) as main parameters. The maximum Cr(VI) removal was 16 mg/g nZVI at pH 11 and with a substrate–nZVI ratio of 3/1. The removal kinetics of Cr(VI) were described by a first-order model with respect to the concentration in the aqueous phase, $\ln \frac{C}{C_0} = -k_{obs}t$, and the constant k_{obs} was equal to $0.0088 \text{ min}^{-1} (\text{g nZVI/L})^{-1}$ at pH 5.3 [89].

Fu et al. (2017) incorporated nZVI into humus (H) and investigated the Cr(VI) removal efficiency in terms of nZVI nanocomposite loading (1.4%–10.4%), dosage (1.8–4.8 g/L), pH (3–10), and the initial Cr(VI) concentration (40–200 mg/L). According to the researchers, the removal of Cr(VI) takes place by simultaneous physical adsorption and chemical reduction on the surface of the H-nZVI nanocomposite. The maximum removal was 59.4 mg/g nZVI at pH 6.5. The removal kinetics of Cr(VI) and Pb were described by a first-order model in terms of the concentration of Cr(VI) in the aqueous phase, $\ln \frac{C}{C_0} = -k_{obs}t$. However, no values of the kinetic constant were reported. The removal of Cr(VI) in equilibrium conditions was described by the Langmuir adsorption isotherm with a maximum loading q_{max} equal to 42.4 mg/g and k_L equal to 0.353 L/g [102].

Zhou et al. (2018) incorporated nZVI into rockwool (W) and studied the removal efficiency of Cr(VI) with the main parameters including the ratio of substrate–nZVI (1:0.5, 1:1, 1:2), pH (2–11), and the initial concentration of Cr(VI) (10–200 mg/L). The maximum removal achieved was 297 mg/g nZVI with an initial concentration of 100 mg/L, a pH of 2, and a W/nZVI ratio of $\frac{1}{2}$ [104].

Toli et al. 2016 incorporated nano zero-valent iron (nZVI) particles on a permeable matrix, using the cationic resin Dowex 50WX2, and evaluated the performance of this composite material for the removal of Cr(VI) from contaminated waters. They studied the effect of Cr(VI) concentration (5–25 mg/L), grams of resin (1–6 g/L), and pH (2.7–8.5). Green tea was found to be inefficient, probably due to the relatively big size of the contained polyphenol molecules. Gallic acid molecules were able to reach adsorbed Fe(III) and reduce the cations to the elemental state with 100 mg (1.79 mmol) of nFe per gram of dry resin. After 1 h of treatment, the removal of Cr(VI) was equal to 99.4% at pH 2.7, 96.1% at pH 3.2, 71.6% at pH 4.4, 59.6% at pH 5.0, and 23.6% at pH 8.5.

It was found that the reduction follows a kinetic law of first order with respect to Cr(VI) and the embedded nano-iron. The reaction rate constant was determined to be between 0.48×10^3 and $8.03 \times 10^3 \text{ min}^{-1}$ per mM of nZVI, a range similar to that reported for other resin-supported nZVI products. Expressed in terms of half-life time, $t^{1/2}$, and assuming operation in the presence of 1 mM nZVI, these constants corresponded to $t^{1/2}$ ranging between 1.4 and 24.1 h [95].

Toli et al., in 2018, also studied the incorporation of nZVI using a macroreticular cationic resin as a porous host material for the remediation of Cr(VI). The parameters examined were the rate of agitation (50–250 rpm), the particle size of R-nFe beads (300, 388, and 462.5 μm diameters), the initial concentration of chromate (0.10, 0.19, and 0.38 mM), the content of nZVI in resin (0.15, 0.30, 0.49, and 0.61 mmole nZVI per gram of wet resin), the dose of resin per liter of solution (20, 40, and 60 wet g/L), and the pH (3.5, 4.5, 5.5, and 7.5). The concentration of nFe was equal to 27.44 mg/g wet R (0.49 mmole per liter of solution). The amount of Cr(VI) removed from the aqueous solution after 24 h was 0.853 mg/g nFe. It was found that the reduction of Cr(VI) follows a kinetics law of first order with respect to the concentration of Cr(VI) and the amount of nZVI per liter of solution. The kinetic constant varied between 5×10^{-3} and 0.5×10^{-3} per min and per mM of nZVI in the pH range of 3.5–7.5 [96].

Liu et al., in 2022, incorporated nZVI into a lignin-based hydrogel for the removal of Cr(VI). The removal efficiency was tested, and the mechanism was also explored. Different

precursor Fe(II) ion concentrations of 0.025–0.05 mol/L, initial pH values of 2.1, 5.3, and 8.5, the contact time, a 200 mg/L electron acceptor (NO_3^- , SO_4^{2-}), and a 50 mg/L electron donor (HA, sodium acetate) were studied. nZVI@LH at the precursor Fe(II) ion concentration of 0.1 mol/L presented an enhanced Cr(VI) removal capacity of 310.86 mg/g Fe^0 at pH 5.3, which was 11.6 times more than that of the pure nZVI. The removal efficiency of the composite at pH 2.1 was more than double compared with alkaline or neutral conditions. The maximal removal capacity improved from 277.78 mg Cr(VI)/g nFe to 370.37 mg Cr(VI)/g nFe when the solution became more acidic [97].

Parnis et al., in 2022, incorporated nZVI into an alginate bead matrix for the removal of Cr(VI) from water. Two variants of nanoscale zero-valent iron (nZVI), namely, powdered (NSTAR) and slurry-suspended (N25), were immobilized within millimetric alginate beads (AL) through coagulation, giving rise to nanocomposites (NCs) denoted as N25@AL and NSTAR@AL. These nanocomposites were subjected to structural analysis and assessed for their efficacy in removing Cr(VI). Across both types of nZVI, the efficiency of Cr(VI) removal exhibited a positive correlation with temperature and a negative correlation with pH and demonstrated negligible variations under anoxic or oxic conditions. Notably, N25@AL proved to be a more rapid removal agent compared with NSTAR@AL; however, both materials displayed an identical maximum removal capacity of 133 mg of Cr(VI) per gram of nZVI at pH 3 [98].

The reported maximum removal of Cr(VI) per gram of nZVI ranged from 33 to 1000 mg/g in carbon-supported nanocomposites, 10–610 mg/g in clay-supported materials, 5–20.4 mg/g in natural-supported materials or synthetic resins, and 60–297 mg/g in other substrates. It is noted that based on the stoichiometry of the reduction of Cr(VI) by elemental iron, the maximum theoretical reduction capacity corresponds to 1 mol Cr(VI) per mol nZVI or 929 mg/g. In other words, it is clear that in very few cases, a satisfactory utilization of the nano-iron integrated into the nanocomposite material was achieved. Of course, it should be mentioned that in some cases, the low removal was not solely due to the low efficiency of the material, but to the fact that the researchers only performed experiments at low concentrations of Cr(VI) and high doses of nZVI, with the consequence that the reducing capacity of the material was not exhausted nano-iron.

The parameter identified to most significantly affect Cr(VI) removal was pH. Most researchers report that the greatest removal is achieved at acidic pHs, as expected from the fact that Cr(VI) reduction is favored at low pHs. An exception is Huang et al. (2016), who reported that they achieved maximum removal at pH 11 [89]. This is due to the fact that an alkaline pH contributes to the swelling of alginate beads, which are the nano-iron embedding substrate, thus facilitating the penetration of chromic anions.

Regarding the kinetics of Cr(VI) removal, two different categories of models were used to describe it. In the studies in which the substrate was carbon, adsorption models were used. In these models, it is assumed that the speed of evolution of the phenomenon depends mainly on the positions that remain active in the adsorption material, i.e., on the difference ($q_e - q$), which expresses the distance of the charge of the material in equilibrium with respect to the charge in each time t , and the velocity dependence is first or second order with respect to this difference. The first-order adsorption model as the difference ($q_e - q$) was used by Fu et al. (2015), and the second-order adsorption model was used by Chen et al. (2015), Shang et al. (2017), and GaO et al. (2018). However, it should be mentioned that these adsorption models assume the restoration of final equilibrium conditions between the concentrations of Cr(VI) in the aqueous solution and the concentrations in a solid, a phenomenon that does not apply to the specific system in which the reduction of Cr(VI) takes place to Cr(III), i.e., an irreversible phenomenon.

In the second category of methods, the kinetics are described by taking into account the concentration of Cr(VI) in the solution. In most research, it is found that the removal of chromium can be described by first-order kinetics, $\ln \frac{C}{C_0} = -k_{\text{obs}}t$, and the values of the constant k_{obs} are given without taking into account the different dosage of nano-iron in the individual experiments. To enable a comparison of the results, we expressed the reported

constants in terms of the dose of nano-iron. The values of the constant k reduced per gram of nZVI per liter of solution ranged from 0.012 to 0.152 (g nZVI/L)^{−1} min^{−1} in bentonite substrate [38], from 0.12 to 0.29 (g nZVI/L)^{−1} min^{−1} in sepiolite substrate [63], and was 0.009 min^{−1} (g nZVI/L)^{−1} in alginate bead substrate [89].

Finally, it should be mentioned that of all the nanocomposite materials examined, only a small number are suitable for use in fixed-bed reactors. Specifically, both biochars and clay substrates result in the creation of nanocomposite materials with very small particle sizes in powder form, which are unsuitable for use in flow devices. Granular nanocomposites can be produced using a substrate of granular activated carbon or polymer beads, such as resins.

4. Discussion

In conclusion, iron nanocomposite materials have emerged as promising and efficient candidates for water treatment applications. Through extensive research and development, these innovative materials have demonstrated notable advantages, such as enhanced adsorption capacities, rapid removal of contaminants, and cost-effectiveness. The unique properties of iron nanocomposites, including high surface area and reactivity, contribute to their superior performance in addressing water pollution challenges.

The ability of iron nanocomposites to target a wide range of pollutants, including heavy metals, organic compounds, and emerging contaminants, makes them versatile for diverse water treatment scenarios. Additionally, the tunable nature of these materials allows for customization based on specific water quality requirements, providing a tailored and efficient approach to purification processes.

Furthermore, the environmentally friendly nature of iron nanocomposites, coupled with their potential for regeneration and reuse, aligns with the growing demand for sustainable water treatment technologies. As we navigate the increasing threats to water resources globally, the utilization of iron nanocomposites offers a promising avenue to mitigate pollution, protect ecosystems, and ensure access to clean and safe drinking water.

While the field of iron nanocomposite materials for water treatment continues to evolve, it is essential to consider potential challenges, such as scalability, long-term stability, and the development of standardized protocols for widespread adoption. Addressing these issues through ongoing research and collaboration will undoubtedly contribute to the successful integration of iron nanocomposite materials into mainstream water treatment strategies.

In essence, the significant advancements made in the synthesis and application of iron nanocomposite materials underscore their transformative potential in revolutionizing water treatment technologies. With further refinement and widespread implementation, these materials hold the key to addressing the pressing global water quality concerns, ultimately fostering a sustainable and resilient approach to water purification.

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