Article

Nanoscale Zero Valent Iron Supported by Biomass-Activated Carbon for Highly Efficient Total Chromium Removal from Electroplating Wastewater

Bo Zhang, Bo-Hong Zhu *, Xiong Wang and Song-Bai You

School of Metallurgical and Material Engineering, Hunan University of Technology, Taishan Road 88, Zhuzhou 412007, China; 13747@hut.edu.cn (B.Z.); wangxiong@hut.edu.cn (X.W.); yousongbai@hut.edu.cn (S.-B.Y.)

* Correspondence: bohongzhu@hut.edu.cn

Received: 27 October 2019; Accepted: 23 December 2019; Published: 26 December 2019

Abstract: The application potential of nanoscale zero valent iron (nZVI) in wastewater treatment is huge and has attracted a lot of attention. In this study, the composite material BC-nZVI was prepared by emulsion of nZVI and biomass-activated carbon (BC) under the mechanical agitation condition, and was characterized by SEM-EDX, XRD, XPS, and FTIR. The decontamination abilities of BC-nZVI were tested by the removal of total chromium (Cr) from electroplating wastewater. The results showed that the removal efficiencies of Cr in the electroplating wastewater by nZVI particles can be effectively improved when supported with BC, but cannot be improved in its storage capacity. The chemical adsorption process between the Cr and BC-nZVI is the main rate-limiting step in the removal of total Cr from wastewater, and multiple parameters such as dosage, pH, and initial concentration of Cr was found to affect the rate.

Keywords: biomass activated carbon; chromium; electroplating wastewater; nanoscale zero valent iron

1. Introduction

Cr and its compounds are widely used in modern industry, and Cr pollutions of groundwater, surface water, and soil have become a highly regarded environmental issue, as a result of frequent leakage accidents and inefficient pollution control methods [1,2]. As the oxidation states of chromium, Cr(VI) and Cr(III) have different chemical behaviors and biological toxicities [3], Cr(VI) with high oxidation properties is highly toxic to humans and can cause a range of health problems, such as liver damage and pulmonary congestion [4,5]. Cr(VI) is dominated as $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- in aqueous solutions, and is known for its high solubility in both acidic and alkaline solutions [6]. However, as a necessary micronutrient in many organisms, the toxicity of Cr(III) is much lesser than Cr(VI), and is easy to precipitate under weak alkaline conditions in the form of Cr hydroxide $\text{Cr}(\text{OH})_3$. Therefore, reducing Cr(VI) to Cr(III) and then removing Cr(III) by adsorption is considered to be a satisfactory solution [7–9].

Many methods have been applied for removing Cr(VI) from aqueous solutions, such as chemical reduction [10], ion exchange [11], precipitation [12], and adsorption [13]. The most common method is adsorption using alumina, clay, zeolite, and activated carbon as the adsorbing material [14,15]. Unfortunately, these materials do not have the ability to convert Cr(VI) to Cr(III), and results in limited adsorption effects and difficulties in separating and recovering from aqueous media.

In general, to make the discharged water meet the Chinese standard (a total chromium content of less than 1.0 mg/L), three-stage treatment methods, i.e., the initial treatment, intensive treatment, and membrane treatment, are adopted for wastewater treatment. In the initial treatment process,

the concentration of Cr in the treated water can be reduced to 20 mg/L by adding lime for chemical precipitation, and activated carbon for physical adsorption. Subsequently, the organosulfur compound, as the heavy metal catcher, is used for intensive treatment, in conjunction with polyaluminium chloride (PAC) and polyferric sulfate (PFC), and the Cr concentration after this stage can then be reduced to less than 2.0 mg/L. The final stage is used in the membrane treatment to ensure that the residual total Cr concentration in water meets the discharge standard. The treatment of electroplating wastewater by this method is tedious. In the process, pH regulator, reductant, and flocculants need to be added continuously. After treatment, the amount of tailing is large and the treatment cost is high.

Recently, nanoscale zero valent iron (nZVI) particle has been paid much attention for removing heavy metals from groundwater and wastewater, such as Pb, Ni, Zn, Cr, Hg, and As [16–19], as a result of its excellent reduction, adsorption, and magnetism performances. Nevertheless, the reactivity of nZVI particles decreases significantly due to their characteristics of easy agglomeration and oxidation. To solve this problem, several studies have reported loading the nZVI particles onto activated carbon (AC), in view of the fact that AC has a huge specific surface area and a porous structure. Liu [20] found that the removal capacity of AC-nZVI to Pb(II) is 8.2 times higher than that of the activated carbon carrier at 298.15 K and pH = 6.0. Mortazavian [21] synthesized AC-nZVI using a two-step synthesis procedure and the Cr(VI) removal experiments showed that the optimized AC-nZVI is significantly superior than virgin AC applied under the same conditions, and the material maintains a 68% removal efficiency after five cycles. However, the preparation of nZVI particles in the above studies has been prepared using the liquid phase reduction method, as defined in Equation (1):

As the reagent, NaBH_4 has a high toxicity and price. During the reaction process, a large amount of hydrogen is generated, and hence the protection of the argon atmosphere or a vacuum condition is required [22,23]. Significantly, these problems make the nZVI particles difficult to be popularized and applied.

In this study, the emulsion of nZVI and biomass activated carbon (BC) were used as the raw materials to prepare composite material under the mechanical agitation condition. The composite material was characterized by SEM-EDX, XRD, XPS, and FTIR, and its purification capacity were tested by the removal of the total Cr from the electroplating wastewater. In addition, the removal mechanism and kinetics of total Cr from wastewater by BC-nZVI were studied. It was expected that this study can provide a basis for the popularization and application of nZVI composites.

2. Materials and Methods

2.1. Materials and Chemicals

The emulsion of nZVI was obtained using the electrolysis method, and the nZVI nanoparticles were basically smooth spheres, ranging from 40 to 80 nm in size. The total Fe concentration in the emulsion was 30 g/L, and the amount of oxidized Fe was less than 10%. The detailed preparation process of the nZVI emulsion can be found in our previous work [24]. BC was supplied by Xinhong Co. Ltd., Xuzhou, China, which was carbonized from coconut shell at 340 °C with a particle size of 2–4 mm. All other analytical grade reagents (absolute ethanol, hydrochloric acid, sodium dodecyl benzene sulfonate, and sodium hydroxide) were obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. All aqueous solutions used for the experiments were prepared with deionized water.

2.2. Preparation of BC-nZVI Material

The emulsion of nZVI was intermixed with sodium dodecyl benzene sulfonate and absolute ethanol, and was dispersed in a mechanical disperser under nitrogen protection, for 12 h. After dispersal, 100 mL emulsion, 200 g BC, and 200 mL deionized water were sequence added to a 1000 mL conical

flask, and shocked on a horizontal vibrator at 240 rpm. The mixture was cleaned by deionized water after 12 h of shock and dried overnight in a vacuum drying oven, at 45 °C

2.3. Characterization

The surface morphology and element composition of particles was observed with a scanning electron microscope with an energy dispersive spectrometer (SEM-EDX) (SIGMA 300; Carl Zeiss AG, Oberkochen, Hallbergmoos, Germany) operating at 30 kV. The concentration of metal ions in the solution was detected by inductively coupled plasma spectrometer (ICP-OES; P.E., Waltham, MA, USA). The surface characteristics of the nZVI particles were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi; Thermo-VG, Waltham, UK), with monochromatized Al K α X-ray source. The structure and composition of the material were analyzed by Fourier transformed infrared spectra (FTIR) (VERTEX 70; Thermo Scientific, Waltham, UK) varied from 4000–4500 cm⁻¹.

2.4. Removal Mechanism and Performance of Total Cr by BC-nZVI

The untreated wastewater was taken from an electroplating plant in the Yueyang, Hunan Province, China, for the experiments of total Cr removal, as shown in Figure 1. The wastewater sample is slight yellow, and its initial pH value was 4.76. The concentration of total Cr in the wastewater was 292.25 mg/L, and the total amounts of other metal ions (Cu, Zn, As) were less than 0.05 mg/L.

Figure 1. Sampling site and wastewater sample. (a) Sewage treatment tank; (b) the sample of untreated wastewater.

2.4.1. Batch Experiments

The decontamination abilities of materials were tested by batch experiments. The kinetic experiments were carried out by investigating the effects of different materials (BC, nZVI and BC-nZVI) on total Cr removal efficiency with an initial total Cr concentration of 100 mg/L, 400 mg/L of BC-nZVI dosages, temperature of 25 °C, and pH of 4.76. The initial concentration of wastewater was prepared by diluting the original wastewater (292.25 mg/L) with deionized water, the pH value was regulated by hydrochloric acid (0.01 mol/L) and sodium hydroxide (0.01 mol/L), and the temperature was controlled by a thermostatic waterbath.

The BC-nZVI material was placed in the air condition for one day, one week, and one month, respectively, to study its storage capacity.

In addition, the effect of the different BC-nZVI (dry weight of total Fe) dosages (200 mg/L, 400 mg/L, 600 mg/L, and 800 mg/L) on the removal efficiencies of Cr was studied with an initial total Cr concentration of 100 mg/L, temperature of 25 °C, and pH value of 4.76. The different initial concentrations of wastewater (19.98 mg/L, 50.17 mg/L, 100.39 mg/L, and 292.25 mg/L) were prepared by diluting the original wastewater with deionized water. The effect of the different pH values (3.0, 7.0,

and 10.0) on the removal efficiencies of Cr was studied with an initial total Cr concentration of 100 mg/L, 400 mg/L of BC-nZVI dosages, and a temperature of 25 °C. The reaction temperature were set at 20 °C, 40 °C, and 60 °C, and its effect on the removal efficiencies of Cr was investigated with an initial total Cr concentration of 100 mg/L, 400 mg/L of BC-nZVI dosages, and a pH value of 4.76.

The weight of BC-nZVI was weighed with an electronic balance and added to a 250 mL conical flask with 150 mL diluted wastewater. The conical flask was shocked on a horizontal vibrator at 240 rpm for mixing. A total of 4 mL of the solution samples were taken at 5, 10, 20, 30, 40, 50, 60, 90, 120, and 180 min, respectively. The concentration of the metal ions was determined by ICP-OES, and all experiments were conducted in three replicates. The removal efficiency of total Cr was calculated by Equation (2):

$$R(\%) = \frac{(C_0 - C_t) \times 100}{C_0} \quad (2)$$

The equilibrium removal capacity of total Cr [q_e (mg/g)] was calculated by Equation (3):

$$q_e = \frac{(C_0 - C_e) \times V}{w} \quad (3)$$

where C_0 (mg/L) is the initial concentration of total Cr; C_t (mg/L) is the concentration of total Cr at t time; C_e (mg/L) is the equilibrium concentrations of total Cr; V (L) is the experimental solution volume; and w (g) is the dry weight of nZVI in BC-nZVI.

2.4.2. Kinetic Analysis of Total Cr Removal

The pseudo-first-order (PFO, Equation (4)) and pseudo-second-order (PSO, Equation (5)) equations were used to test the removal kinetics of total Cr from wastewater, and the removal mechanism was analyzed using the following equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_e and q_t (mg/g) are the amount of total Cr adsorbed at equilibrium and at time t , respectively; k_1 (min^{-1}) and k_2 ($\text{g}/(\text{mg} \cdot \text{min})$) are the PFO and PSO rate constants, respectively.

3. Results and Discussions

3.1. Synthesis and Characterization of Materials

Figure 2 shows the macrographs and SEM micrographs of BC, nZVI particles, and BC-nZVI material. Clearly, the nZVI particles were spherical with a mean diameter of 40–80 nm. After the stabilization treatment, the agglomeration phenomenon between the particles could be substantially reduced. The BC carbonized from the coconut shell had an abundant pore structure. Using the mechanical agitation method, the nZVI particles showed slight agglomeration, and were mainly distributed in the pores of BC. The nZVI particles distributed on the BC surface were few, after the cleaning treatment by deionized water.

XPS spectra were analyzed (Figure 3). As seen in Figure 3a, the main elements existing on the surface of BC were O and C, and their peaks were located at 532.15 eV and 284.75 eV, respectively. However, it can be seen from the XPS spectra of BC-nZVI that the peaks of Fe 2p appeared at the range of 706.17 eV to 734.94 eV, as shown in Figure 3b. The high resolution XPS spectra for Fe 2p orbit is displayed in Figure 3c. There were two peaks located at 711.6 eV and 725.3 eV corresponding to Fe(III), and two peaks located at 710.0 eV and 722.7 eV, corresponding to Fe(II), respectively [25]. However, the peaks of Fe^0 at 706 eV and 707 eV was not apparently detected in the XPS spectra, which was due

to the rapid formation of iron oxide on the surface of nZVI particles and the XPS technology is only limited to surface detection [20].

Figure 2. Macrographs and SEM micrographs of biomass-activated carbon (BC), nanoscale zero valent iron (nZVI) particles, and BC-nZVI.

Figure 3. Cont.

Figure 3. (a) Wide-scan XPS survey of BC, (b) wide-scan XPS survey of BC-nZVI, and (c) a high-resolution Fe 2p XPS survey of BC-nZVI.

In addition, the sample of BC-nZVI was dissolved by HNO_3 (10 mol/L) and digestion occurred for 3 h. The total Fe ions in acid solution were analyzed by ICP-OES, and the total Fe content in the BC-nZVI was calculated to be 3.52%.

3.2. Degradation Mechanism for Reduction–Adsorption of Cr on BC-nZVI

As seen in Figure 4a, the removal efficiency of nZVI was higher than that of BC but was significantly lower than that of BC-nZVI. At 180 min, the removal efficiency of BC was only 17.13%, which indicated that the physical adsorption by BC was not significant as the solubility of Cr(VI) in acidic water was relatively high. The removal efficiency of nZVI was 52.45% at 180 min, and it showed that the reduction removal by nZVI was superior to the adsorption removal by BC. Xia et al. [26] reported that the nZVI particles were prone to agglomeration and oxidation, which diminished its reactivity. However, after the nZVI particles were loaded onto the BC, their aggregation and oxidation could be reduced, and hence the removal efficiency of BC-nZVI was as high as 94.88%.

Figure 4. Cont.

Figure 4. Comparative removal efficiencies of total Cr using different materials. (a) BC, nZVI, and BC-nZVI; (b) Change of iron content in solution; (c) BC-nZVI with different storage time.

Meanwhile, Figure 4b shows that the adsorption capacity of nZVI particles was extremely low, as compared to that of BC-nZVI. For BC-nZVI, the Fe content in wastewater increased from 0.1 mg/L to 17 mg/L during the reaction time of 0–60 min, as a large number of nZVI particles reacted and appeared in wastewater as an ionic state. As the formation of FeO(OH) occurs with the extension of reaction time, the adsorption capacity of the materials was increased, and the content of Fe in the wastewater decreased slowly. All of above results proved that the process of loading the nZVI onto BC had a positive effect on improving the removal efficiency of nZVI particles.

Figure 4c shows the removal efficiencies of BC-nZVI with different storage times in air. The removal efficiencies decreased from 94.88% to 72.45% and 33.42% at 180 min, when the storage time extended from one day to one week and one month, respectively. This result showed that nZVI particles could not improve the storage capacity although they were loaded onto BC.

The BC-nZVI was dried and crushed after reaction, and the results of the EDX line scanning analysis are shown in Figure 5a. As the mechanical agitation method was applied, the nZVI particles were mainly distributed on the outer layer of BC. In addition, the distribution of element Cr was very similar to that of element Fe, suggesting that the removal of total Cr was not a single adsorption process but was related to nZVI.

The interaction between wastewater and BC-nZVI was observed via FTIR spectra, as shown in Figure 5b. After reaction with wastewater, the corresponding peaks of C-OH in BC-nZVI shifted to 1093 cm^{-1} from 1103 cm^{-1} , and the corresponding peaks of CO-OH shifted to 1556 and 1442 cm^{-1} from 1548 and 1435 cm^{-1} [9]. Meanwhile, the intensity of the wave crest had the obvious change. Moreover, the antisymmetric stretching bands of the COO^- frequency was weakened as a result of the

carboxylic acids and their salts formed complexes with metals, which was consistent with the existing research results.

Based on the above results, the proposed mechanism for the reduction–adsorption of Cr by BC-nZVI can be depicted in Figure 6. There were obvious differences on the surface of nZVI particles, before and after the reaction. A large number of floccules appeared on the surface of particles after treatment, as shown in Figure 6e. The element Cr in wastewater might have existed as HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ and was gradually reduced to Cr^{3+} under the action of Fe^0 and H^+ , as shown in Equations (6) and (7). Meanwhile, Fe^0 was gradually oxidized to Fe^{2+} and Fe^{3+} . Fe^{2+} also had the ability to reduce HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, as shown in Equations (8) and (9). Fe^{3+} was flocculated on the surface of nZVI particles in the form of $\text{FeO}(\text{OH})$, which greatly increased the specific surface area and adsorption capacity of the material. The Cr^{3+} and Fe^{3+} precipitated together, as shown in Equations (10) and (11) and were adsorbed on flocs and BC [25].

Figure 5. (a) SEM and EDX line scanning analysis of BC-nZVI after reaction and (b) FTIR spectra of BC-nZVI, before and after reaction.

Figure 6. Mechanism for the reduction–adsorption of Cr by BC-nZVI. (a,b) SEM micrographs of BC-nZVI before reaction, (c,f) mechanism for the reduction–adsorption of Cr by nZVI, and (d,e) SEM micrographs of BC-nZVI after reaction.

3.3. Kinetic of Total Cr Removal by BC-nZVI

By these two kinetic equations, the removal effect of different materials was calculated, and the fitting of the kinetic data is shown in Figure 7 and Table 1.

Figure 7. Kinetic analysis of reduction–adsorption of total Cr using pseudo-first-order (PFO) (a) and pseudo-second-order (PSO) (b).

Table 1. Kinetic parameters for total Cr removal.

C_0 (mg/L)	q_e (mg/g)	PFO			PSO		
		q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 ($\text{g}/(\text{mg}\cdot\text{min})$)	R^2
nZVI	76.64	78.47	0.0096	0.7955	77.78	0.0016	0.9477
BC-nZVI (One Day)	138.76	143.53	0.0201	0.8326	136.47	0.0009	0.9995
BC-nZVI (One Week)	105.96	96.76	0.0071	0.8271	101.16	0.0011	0.9704
BC-nZVI (One Month)	48.88	42.47	0.0012	0.8174	49.94	0.0026	0.9979

Significantly, the PSO equation matched more with the data than the PFO equation, indicating that the chemical adsorption in this process was the main rate-limiting step of total Cr removal by BC-nZVI [24]. Therefore, it could be concluded from kinetic parameters that adsorption, co-precipitation, and reduction occurred during the Cr(VI) removal process by BC-nZVI. Similarly, previous reports also tested the PFO and PSO models on different nZVI composites materials and found favorable matches [9,25–27]. The equilibrium removal capacity for total Cr were 77.78 mg/g by nZVI, 136.47 mg/g by BC-nZVI (One day), 101.16 mg/g by BC-nZVI (One week), and 49.94 mg/g by BC-nZVI (One month), respectively. This result shows that the equilibrium removal capacity of total Cr by nZVI particles can be effectively improved by supporting it with BC, but this cannot improve its storage capacity, as discussed in the previous section.

In addition, the BC-nZVI exhibited an outstanding removal capacity for total Cr in wastewater, as compared to other nZVI-based materials, as shown in Table 2. The differences were related to the preparation method of the materials. For the other nZVI-based materials [27–29], the nZVI particles were loaded onto the different supporters using the liquid phase method, and hence, the nZVI particles could be evenly distributed in the supporter [21,28]. However, most nZVI particles were mainly

distributed on the outer layer of BC in this study. Here, it should be noticed that the Cr in the wastewater could be easily contacted with the nZVI particles that were distributed on the surface of BC.

Table 2. Comparison of total Cr removal with different materials reported in the literature.

Material	Removal Capacity	Source
PSA- nZVI (poly sodium acrylate)	138.80 mg/g	Jia et al., 2018 [19]
GN-nZVI (graphene nanosheets)	21.72 mg/g	Li et al. [30]
S-nZVI (Starch-stabilized)	20.16 mg/g	Alidokht et al. [31]
nZVI	47.2 mg/g	Montesinos et al. [32]
nZVI	77.78 mg/g	This study
BC-nZVI	136.47 mg/g	This study

3.4. Effect of the Operated Factors on Total Cr Removal

As illustrated in Figure 8a,b, the BC-nZVI dosage and initial concentration had significant effects on the removal kinetics of total Cr. The removal rate in the initial stage increased gradually with the increase of BC-nZVI dosage or the decrease of the initial concentration, as enough nZVI activity sites were provided to react with Cr.

Figure 8. Results of batch experiments as per (a) dosage, (b) initial concentration, (c) pH value, and (d) temperature.

As shown in Figure 8c, the removal efficiencies of total Cr declined from 99.12% to 73.56% with the increase of pH values from 3.0 to 10.0. This suggested that the lower pH value was beneficial to Cr reduction by BC-nZVI. More H^+ was released at lower pH values, which could accelerate the reduction of Cr^{6+} to Cr^{3+} and eliminate ferrous hydroxide on the surface of nZVI particles to generate fresh active sites.

Additionally, the increase in temperature could accelerate the mobility of Cr and theoretically increase the chemical reaction rate [9,23], but there was no obvious effect on the actual process, as shown

in Figure 8d. The reason could be that temperature was not a significant factor when enough nZVI activity sites were provided.

According to the batch experiments results, when the solution was acidic the initial total Cr concentration was not more than 50 mg/L. After more than 400 mg/L BC-nZVI was added, the chromium content in the solution could be lower than 0.5 mg/L after 180 min, which met the Chinese standards for discharged water.

4. Conclusions

The composite material BC-nZVI was successfully prepared by emulsion of nZVI and biomass activated carbon (BC), under the mechanical agitation condition, and was characterized by SEM-EDX, XRD, XPS, and FTIR. Batch experiments confirmed the decontamination abilities of this composite material. The results showed that the removal efficiencies of the total Cr in electroplating wastewater by nZVI particles could be effectively improved when supported with BC, but could not be improve its storage capacity. The composite material in this study had a remarkable removal effect on total Cr from wastewater than the other nZVI-based materials that were prepared by the liquid-phase reduction method. In addition, the composite material synthesized was simpler than the liquid-phase reduction method, and the 99.12% removal efficiency shows a good potential in the remediation of electroplating wastewater.

Author Contributions: Conceptualization, B.Z. and B.-H.Z.; methodology, B.Z.; formal analysis, X.W. and S.-B.Y.; data curation, B.-H.Z.; writing—original draft preparation, B.Z.; and writing—review and editing, B.-H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the Specialized Research Fund for the National Natural Science Foundation of China (No. 51504090), the Natural Science Foundation of Hunan Province, China (No. 2019JJ60062), and the National University Student Innovation Program of China (201811535020).

Acknowledgments: We acknowledge the help received from Guoliang Li, Xichang Wang, and Lang Liu from the Hunan University of Technology, for their assistance in the use of the instruments.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mandiwana, K.L.; Resane, T.; Panichev, N.; Ngobeni, P. The application of tree bark as bio-indicator for the assessment of Cr(VI) in air pollution. *J. Hazard. Mater.* **2006**, *137*, 1241–1245. [[CrossRef](#)] [[PubMed](#)]
2. Javed, M.; Usmani, N. Assessment of heavy metal (Cu, Ni, Fe, Co, Mn, Cr, Zn) pollution in effluent dominated rivulet water and their effect on glycogen metabolism and histology of mastacembelus armatus. *SpringerPlus* **2013**, *2*, 390. [[CrossRef](#)] [[PubMed](#)]
3. Dingtian, Y.; Guoxin, S.; Dongjie, S.; Weimin, C. The resistant reaction of braseniaschreberi winter-bud to Cr⁶⁺ pollution. *J. Lake Sci.* **2001**, *13*, 169–174. [[CrossRef](#)]
4. Lin, W.J. Characteristics and control of Cr pollution in electroplating wastewater. *Environ. Sci. Technol.* **2010**, *33*, 156–158. [[CrossRef](#)]
5. Di Palma, L.; Verdone, N.; Vilardi, G. Kinetic Modeling of Cr(VI) Reduction by nZVI in Soil: The Influence of Organic Matter and Manganese Oxide. *Bull. Environ. Contam. Toxicol.* **2018**, *101*, 692–697. [[CrossRef](#)]
6. Cui, J.; Wang, E.; Hou, Z.; Zhou, R.; Jiao, X. Removal of Chromium(VI) from Groundwater Using Oil Shale Ash Supported Nanoscaled Zero-valent Iron. *Chem. Res. Chin. Univ.* **2018**, *34*, 546–551. [[CrossRef](#)]
7. Zhu, Y.; Jin, Y.; Chang, K.; Chen, Z.; Li, X.; Wu, X.; Jin, C.; Ye, F.; Shen, R.; Dong, W.; et al. Use of molybdenum disulfide nanosheets embellished nanoiron for effective capture of chromium (VI) ions from aqueous solution. *J. Mol. Liq.* **2018**, *259*, 376–383. [[CrossRef](#)]
8. Zhu, F.; Li, L.; Ren, W.; Deng, X.; Liu, T. Effect of pH, temperature, humic acid and coexisting anions on reduction of Cr(VI) in the soil leachate by nZVI/Ni bimetal material. *Environ. Pollut.* **2017**, *227*, 444–450. [[CrossRef](#)]
9. Wu, B.; Peng, D.; Hou, S.; Tang, B.; Wang, C.; Xu, H. Dynamic study of Cr(VI) removal performance and mechanism from water using multilayer material coated nanoscale zerovalent iron. *Environ. Pollut.* **2018**, *240*, 717–724. [[CrossRef](#)]

10. Zhu, S.; Huang, X.; Wang, D.; Wang, L.; Ma, F. Enhanced hexavalent chromium removal performance and stabilization by magnetic iron nanoparticles assisted biochar in aqueous solution: Mechanisms and application potential. *Chemosphere* **2018**, *207*, 50–59. [\[CrossRef\]](#)
11. Xing, Y.; Chen, X.; Wang, D. Electrically regenerated ion exchange for removal and recovery of Cr(VI) from wastewater. *Environ. Sci. Technol.* **2007**, *41*, 1439–1443. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Ren, T.; He, P.; Niu, W.; Wu, Y.; Ai, L.; Gou, X. Synthesis of α -Fe₂O₃ nanofibers for applications in removal and recovery of Cr(VI) from wastewater. *Environ. Sci. Pollut. Res. Int.* **2013**, *20*, 155–162. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Priyantha, N.; Bandaranayaka, A. Interaction of Cr(VI) species with thermally treated brick clay. *Environ. Sci. Pollut. Res.* **2011**, *18*, 75–81. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Huang, T.; Liu, L.; Zhou, L.; Zhang, S. Electrokinetic removal of chromium from chromite ore-processing residue using graphite particle-supported nanoscale zero-valent iron as the three-dimensional electrode. *Chem. Eng. J.* **2018**, *350*, 1022–1034. [\[CrossRef\]](#)
15. Sulaymon, A.H.; Ebrahim, S.E.; Mohammed-Ridha, M.J. Equilibrium, kinetic, and thermodynamic biosorption of Pb(II), Cr(III), and Cd(II) ions by dead anaerobic biomass from synthetic wastewater. *Environ. Sci. Pollut. Res. Int.* **2013**, *20*, 175–187. [\[CrossRef\]](#)
16. Feng, H.; Tang, L.; Tang, J.; Zeng, G.; Dong, H.; Deng, Y.; Zhou, Y. Cu-Doped Fe@Fe₂O₃ core-shell nanoparticle shifted oxygen reduction pathway for high-efficiency arsenic removal in smelting wastewater. *Environ. Sci. Nano* **2018**, *5*, 1595–1607. [\[CrossRef\]](#)
17. Ghosh, S.; Remita, H.; Basu, R.N. Visible-light-induced reduction of Cr(VI) by PDPB-ZnO nanohybrids and its photo-electrochemical response. *Appl. Catal. B Environ.* **2018**, *239*, 362–372. [\[CrossRef\]](#)
18. Guo, X.; Yang, Z.; Dong, H.; Guan, X.; Ren, Q.; Lv, X.; Jin, X. Simple combination of oxidants with zero-valent-iron (ZVI) achieved very rapid and highly efficient removal of heavy metals from water. *Water Res.* **2016**, *88*, 671–680. [\[CrossRef\]](#)
19. Jia, Z.; Shu, Y.; Huang, R.; Liu, J.; Liu, L. Enhanced reactivity of nZVI embedded into super macroporous cryogels for highly efficient Cr(VI) and total Cr removal from aqueous solution. *Chemosphere* **2018**, *199*, 232–242. [\[CrossRef\]](#)
20. Liu, X.; Lai, D.; Wang, Y. Performance of Pb(II) removal by an activated carbon supported nanoscale zero-valent iron composite at ultralow iron content. *J. Hazard. Mater.* **2019**, *361*, 37–48. [\[CrossRef\]](#)
21. Soroosh, M.; Hyeunhwan, A.; Dongwon, C.; Jaeyun, M. Activated carbon impregnated by zero-valent iron nanoparticles (AC/nZVI) optimized for simultaneous adsorption and reduction of aqueous hexavalent chromium: Material characterizations and kinetic studies. *Chem. Eng. J.* **2018**. [\[CrossRef\]](#)
22. Sheng, G.; Shao, X.; Li, Y.; Li, J.; Dong, H.; Cheng, W.; Huang, Y. Enhanced removal of uranium (VI) by nanoscale zerovalent iron supported on Na-bentonite and an investigation of mechanism. *J. Phys. Chem. A* **2014**, *118*, 2952–2958. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Vilardi, G.; Mpouras, T.; Dermatas, D.; Verdone, N.; Polydera, A.; Di Palma, L. Nanomaterials application for heavy metals recovery from polluted water: The combination of nano zero-valent iron and carbon nanotubes. Competitive adsorption non-linear modeling. *Chemosphere* **2018**, *201*, 716–729. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Zhang, B.; Wang, D.P. Preparation of Biomass Activated Carbon Supported Nanoscale Zero-Valent Iron (nZVI) and Its Application in Decolorization of Methyl Orange from Aqueous Solution. *Water* **2019**, *11*, 1671. [\[CrossRef\]](#)
25. Chen, Z.; Wei, D.; Li, Q.; Wang, X.; Yu, S.; Liu, L. Macroscopic and microscopic investigation of Cr(VI) immobilization by nanoscaled zero-valent iron supported zeolite MCM-41 via batch, visual, xps and exafs techniques. *J. Clean. Prod.* **2018**, *181*, 745–752. [\[CrossRef\]](#)
26. Lv, X.; Xu, J.; Jiang, G.; Tang, J.; Xu, X. Highly active nanoscale zero-valent iron (nZVI)-Fe₃O₄ nanocomposites for the removal of chromium(VI) from aqueous solutions. *J. Colloid Interface Sci.* **2012**, *369*, 460–469. [\[CrossRef\]](#)
27. Xia, X.; Ling, L.; Zhang, W.X. Genesis of pure Se (0) nano- and micro-structures in wastewater with nanoscale zero-valent iron (nZVI). *Environ. Sci. Nano* **2017**, *4*, 52–59. [\[CrossRef\]](#)
28. Watts, M.P.; Coker, V.S.; Parry, S.A.; Pattrick, R.A.D.; Thomas, R.A.P.; Kalin, R.; Lloyd, J.R. Biogenic nano-magnetite and nano-zero valent iron treatment of alkaline Cr(VI) leachate and chromite ore processing residue. *Appl. Geochem.* **2015**, *54*, 27–42. [\[CrossRef\]](#)
29. Li, S.; Wang, W.; Yan, W.; Zhang, W.X. Nanoscale zero-valent iron (nZVI) for the treatment of concentrated Cu (II) wastewater: A field demonstration. *Environ. Sci. Process. Impacts* **2014**, *16*, 524–533. [\[CrossRef\]](#)

30. Li, X.; Ai, L.; Jiang, J. Nanoscale zerovalent iron decorated on graphene nanosheets for Cr(VI) removal from aqueous solution: Surface corrosion retard induced the enhanced performance. *Chem. Eng. J.* **2016**, *288*, 789–797. [[CrossRef](#)]
31. Alidokht, L.; Khataee, A.R.; Reyhanitabar, A.; Oustan, S. Reductive removal of Cr(VI) by starch-stabilized Fe⁰ nanoparticles in aqueous solution. *Desalination* **2011**, *270*, 105–110. [[CrossRef](#)]
32. Montesinos, V.N.; Quici, N.; Litter, M.I. Visible light enhanced Cr(VI) removal from aqueous solution by nanoparticulated zerovalent iron. *Catal. Commun.* **2014**, *46*, 57–60. [[CrossRef](#)]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).