

Article

Sustainable Removal of Cr(VI) from Wastewater Using Green Composites of Zero-Valent Iron and Natural Clays

Slavica Lazarević ^{1,*} , Ivona Janković-Častvan ¹ , Željko Radovanović ² , Zvezdana Baščarević ³ ,
Đorđe Janačković ¹  and Rada Petrović ¹ 

¹ Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia; icastvan@tmf.bg.ac.rs (I.J.-Č.); nht@tmf.bg.ac.rs (Đ.J.); radaab@tmf.bg.ac.rs (R.P.)

² Innovation Center of the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia; zradovanovic@tmf.bg.ac.rs

³ Institute for Multidisciplinary Research, University of Belgrade, Volgina 15, 11000 Belgrade, Serbia; zvezdana@imsi.bg.ac.rs

* Correspondence: slazarevic@tmf.bg.ac.rs

Abstract: Composites for efficient removal of hexavalent chromium Cr(VI) from industrial wastewater were obtained by deposition of nano-zero-valent iron (nZVI), synthesized by environmentally friendly synthesis using oak leaf extract, on inexpensive, natural, readily available and cheap natural raw materials, sepiolite (SEP) or kaolinite/illite (KUb) clay, as support. nZVI particles were deposited from the FeCl₃ solution of different concentrations, with the same volume ratio extract/FeCl₃ solution (3:1), and with different masses of SEP or KUb. Physico-chemical characterization (SEM/EDS, FTIR, BET, determination of point of zero charge) of the composites and nZVI was performed. The results of SEM and BET analyses suggested more homogeneous deposition of nZVI onto SEP than onto KUb, which ensures greater availability of the nZVI surface for Cr(VI) anions. Therefore, the higher Cr(VI) removal at all investigated initial pH values (pH_i) of the solution (3, 4 and 5) was achieved with the SEP composites. The adsorption results indicated that the elimination of Cr(VI) was achieved via the combined effect of reduction and adsorption. The removal of total chromium at pH_i = 3 was approximately the same as that of Cr(VI) removal for the KUb composites, but lower for the SEP composites, indicating lower removal of Cr(III) compared to the reduced Cr(VI). The SEP/nZVI composite with the highest removal efficiency was applied for Cr(VI) removal from real wastewater at pH_i = 3 and pH_i = 5. The results demonstrated the high Cr(VI) removal capacity, validated the assumption that a good dispersion of nZVI particles is beneficial for Cr(VI) removal and showed that the produced green composites can be efficient materials for the removal of Cr(VI) from wastewater.

Keywords: nano-zero-valent iron; green composites; sepiolite; kaolinite/illite clay; Cr(VI) removal; wastewater



Citation: Lazarević, S.; Janković-Častvan, I.; Radovanović, Ž.; Baščarević, Z.; Janačković, Đ.; Petrović, R. Sustainable Removal of Cr(VI) from Wastewater Using Green Composites of Zero-Valent Iron and Natural Clays. *Sustainability* **2024**, *16*, 7904. <https://doi.org/10.3390/su16187904>

Academic Editor: Alessio Siciliano

Received: 16 July 2024

Revised: 14 August 2024

Accepted: 5 September 2024

Published: 10 September 2024



Copyright: © 2024 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 (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Hexavalent chromium (Cr(VI)), originating mainly from industrial activities, such as metal processing, stainless steel welding, chromate production, refractory, tanning and ferrochrome and chrome pigment production [1], poses serious environmental and health risks due to its toxicity and carcinogenicity [2]. Therefore, effective methods for the remediation of Cr(VI)-contaminated water are crucial for both the environment and human health. One of the most important steps in the removal of Cr(VI) from wastewaters is the reduction of Cr(VI) to Cr(III) [3] due to the lower toxicity of Cr(III). Current reduction approaches applied to Cr(VI)-containing wastewaters include photocatalytic, electrochemical, chemical and biological reduction [4].

One promising alternative for Cr(VI) removal is to combine adsorption and chemical reduction technologies. This approach uses environmentally friendly nano-sized zerovalent iron (nZVI) materials due to their strong reduction potential [5]. The reaction mechanism

involves the adsorption of Cr(VI) on the surface of nZVI with Cr(VI) reduction to Cr(III), with the oxidation of nZVI to Fe^{3+} , followed by the precipitation of mixed Cr/Fe hydroxides [6,7]. The advantage of using nZVI is that it is highly reactive; nZVI can rapidly reduce Cr(VI) under a wide range of environmental conditions. However, bare iron nanoparticles tend to agglomerate due to high surface energy and magnetic interactions, which leads to a decrease in the reduction/adsorption capacity [8]. Furthermore, the separation of nZVI from treated aqueous systems is a challenging process [9]. To prevent agglomeration and obtain a high Cr(VI)-removing capacity, nanoparticles of zero-valent iron have been supported on different materials: pillared clay [10], sepiolite [11], montmorillonite [12,13], kaolinite [14,15], bentonite [16], zeolite [17], attapulgite [18], manganese oxides [19], calcium carbonate [20], biochar [21], metal–organic frameworks [22], almond shell [23], graphene [24], etc.

The combination of nZVI with natural minerals offers several advantages for the remediation of Cr(VI), including an increased surface area, enhanced reactivity, improved stability and the adsorption of Cr(III) onto the support material. Natural minerals, such as montmorillonite [25], sepiolite [26,27], bentonite [28] and zeolites [29], possess inherent adsorption capabilities for the removal of Cr(III) ions. By combining the strong reductive power of nZVI (nZVI effectively reduces Cr(VI) to Cr(III)) and high capacity for adsorption of formed Cr(III) ions, a synergetic effect is achieved, resulting in an enhanced removal efficiency and stability.

Sepiolite and kaolinite/illite clay are naturally occurring, non-toxic and widely available minerals with high chemical stability and low reactivity, which help in stabilizing nZVI particles. Furthermore, the utilization of sepiolite and kaolinite/illite clay offers environmentally friendly and cost-effective alternatives to synthetic adsorbents, thereby contributing to the sustainability of the remediation process. The large surface area of sepiolite enhances the dispersion of nZVI particles, improving the reactivity and maximizing their contact with contaminants.

The borohydride reduction of Fe(II) or Fe(III) ions in aqueous solutions is the most commonly used technique for obtaining nZVI particles for the adsorption/degradation of pollutants in water [30–34]. The utilization of plant leaves as biological reducing agents, such as Ginkobiloba [35], green tea extract [36–38], mango peel extract [39], oak, mulberry and cherry leaf extracts [40], Cleistocalyx operculatus leaf extract [41] and extracts from the peel of waste fruits: banana, mango and pomegranate [42], for the reduction of iron (III) is an innovative approach to the environmentally friendly, i.e., green, synthesis of nZVI.

The extracts contain a variety of bioactive compounds, including phytochemicals, enzymes and antioxidants. Plant extracts are non-toxic and more biocompatible than some chemical agents, are readily available and are relatively inexpensive, thereby reducing the production costs of nano-zero-valent iron. Additionally, the components present in plant extracts can act as stabilizers, preventing the agglomeration and oxidation of nZVI particles.

In this paper, the composite materials for Cr(VI) removal from wastewater were synthesized using two local clays, sepiolite and kaolinite/illite, as a support for effectively distributing and stabilizing nZVI. nZVI particles were synthesized by the reduction of Fe^{3+} ions with oak leaf extract. We investigated the mechanisms underlying Cr(VI) reduction and adsorption of Cr(III), as well as the factors influencing the efficiency of the remediation process, such as the type of raw clay for the immobilization, pH_i , time and initial chromium concentration.

2. Materials and Methods

2.1. Materials

Clay “KopoviUb” (Jugo Kaolin, Belgrade, Serbia) (KU_b, in the following text) and sepiolite clay (Intercerd.o.o., Belgrade, Serbia) (SEP, in the following text) were used as a supports for nZVI. Sample characterization was performed and reported previously [27]. The chemicals used in this study ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Lach-ner; $\text{K}_2\text{Cr}_2\text{O}_7$, Hemoss, HNO_3 and KOH, Prolabo) were of analytical grade. All Cr(VI)-solutions were prepared with high-

purity water (18 M Ω /cm). Wastewater from the PPT-TMO company, Trstenik, Serbia, was also used for Cr(VI) removal investigation.

2.2. Oak Leaf Extract Preparation

The extract was prepared with 18.5 g of dry oak leaves and 500 cm³ of distilled water [43]. The suspension was heated on a magnetic stirrer at 80 °C for 15 min. After heating, the extract was separated by filtering. A freshly prepared extract was used in the synthesis to prevent the influence of possible biodegradation of the extract on nZVI synthesis. The total phenolic content of the extract measured by the Folin–Ciocalteu method as described by Skotti et al. [44] was 1543 mg GAE/dm³ of extract.

2.3. Synthesis of nZVI and the Composites

The suspension of 3.0 or 1.5 g SEP, or KUb, and 180 cm³ of extract were treated with an ultrasonic processor (SONICS 750 W, 20 kHz, Sonics & Materials, Inc., Newtown, CT, USA) with a titanium probe (19 mm) for 5 min in order to deagglomerate the SEP or KUb particles. The pH_i of the suspension was adjusted to 5.0 $\pm$ 0.1 by adding 1 mol/dm³ HCl. Synthesis was performed in a stream of nitrogen on a magnetic stirrer by adding 60 cm³ 0.2 mol/dm³ FeCl₃ or 0.1 mol/dm³ FeCl₃ solution (volume ratio extract/FeCl₃ solution was 3:1). Stirring in a stream of nitrogen was continued for 30 min. The suspension was centrifuged after 24 h, and the obtained precipitate was washed with absolute ethanol. The resulting solid phase was dried in a vacuum for 12 h at 60 °C.

The obtained samples are designated as SEP1 and KUb1 (samples synthesized with 3.0 g of SEP or KUb, and 0.2 mol/dm³ FeCl₃ solution) and SEP2 and KUb2 (samples synthesized with 1.5 g of SEP or KUb, and 0.1 mol/dm³ FeCl₃ solution).

The synthesis of nZVI was carried out in a nitrogen stream on a magnetic stirrer using the procedures as previously described (but without SEP or KUb). Instead, 180 cm³ of extract was mixed with 60 cm³ of 0.1 mol/dm³ FeCl₃ solution (the volume ratio of extract to FeCl₃ solution was 3:1).

2.4. Characterization Methods

A Field Emission Gun Scanning Electron Microscope (FESEM) (Tescan MIRA3, Brno, Czech Republic) at 20 kV electron energy in a high vacuum was used to observe the particle morphology of the samples. An Au alloy sputter coating was applied to the samples to ensure conductivity. Energy-dispersive X-ray spectroscopy of the samples was performed on the Oxford instrument INCA x-act (High Wycombe, UK, AZtec 4.3). A Nicolet iS 10 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was used to obtain sample ATR-FTIR spectra. Spectra were recorded in the range of 4000–400 cm^{−1}, with a resolution of 4 cm^{−1} and in 20 scans.

Nitrogen adsorption–desorption isotherms, obtained using a Micromeritics ASAP 2020 instrument (Norcross, GA, USA) were used to determine the specific surface area (S_{BET}) and pore size distribution of the samples. Prior to the adsorption measurements, the samples were degassed at 150 °C for 10 h. The BET method [45] was used to calculate the S_{BET} of the samples from the linear part of the nitrogen adsorption isotherm. The volume of mesopores (V_{meso}) and the pore size distribution were determined according to the Barrett, Joyner and Halenda (BJH) method [46]. The desorption isotherm was used for this purpose. α -plot analysis [47] was used to calculate the volume of micropores (V_{micro}).

The point of zero charge (pH_{pzc}) of the composites was determined by the previously described batch equilibration method [48] in KNO₃ solutions with a concentration of 0.1 mol/dm³, in the pH range of 3 to 10. Equilibration was carried out for 24 h at 25 °C with 0.01 g of the sample in 40 cm³. The pH_{pzc} was obtained from the dependence of pH_f on pH_i as the pH where a plateau appeared on the dependence [48].

2.5. Adsorption Experiments

The adsorption experiments were carried out in a batch mode, at a temperature of 25 ± 1 °C and the initial pH_i of 3.0 ± 0.1 , 4.0 ± 0.1 or 5.0 ± 0.1 . Solutions (40 cm^3) with different initial concentrations were equilibrated with 0.01 g sample for 24 h, in a thermostatic water bath with shaking.

After the separation of the adsorbent, the concentration of Cr(VI) was determined by UV/Vis spectroscopy (Shimadzu UV 1800, Kyoto, Japan) at 542 nm. The corresponding total Cr was determined by an atomic absorption spectrophotometer (AAS) (Perkin Elmer-PinAAcle 900T, Shelton, CT, USA). Equation (1) was used to calculate the removal capacity, q_e (mg/g), the quantity of Cr removed per unit mass of adsorbents:

$$q_e = (c_i - c_e) \cdot V / m \quad (1)$$

where c_i is the initial concentration (mg/dm^3), and c_e represents the equilibrium concentration (mg/dm^3). V (dm^3) and m (g) are the volume of adsorbate solution and the mass of the adsorbent, respectively. The Langmuir [49] and Freundlich isotherm models [50] were used to fit the isotherm data.

The sample with the highest Cr(VI) removal efficiency (SEP2) was used to remove Cr(VI) from wastewater from PPT-TMO company, Trstenik, Serbia, a company for metal coating, at $\text{pH}_i = 3.0 \pm 0.1$ and $\text{pH}_i = 5.0 \pm 0.1$. In the experiments, 40 cm^3 of wastewater and different masses of the SEP2 (from 0.02 to 0.2 g) were equilibrated. The pH_i was adjusted using a H_2SO_4 solution. After 24 h, the suspensions were filtered, the concentration of Cr(VI), total chromium and iron was determined and the pH_f of the solution was measured. The kinetic experiments were performed using 20 cm^3 of wastewater at pH_i of 3.0 ± 0.1 and 5.0 ± 0.1 and 0.02 g of SEP2, for contact times ranging from 1 h to 24 h.

The pseudo-first-order [51], pseudo-second-order [52] and intra-particle diffusion [53] kinetic models were used to fit the kinetic data.

3. Results

In this work, oak leaves were used to obtain the extract as a reducing agent owing to their abundance and high polyphenolic content, which is comparable to the content in green tea [54]. The conditions of extraction (temperature and time) and parameters of nZVI synthesis (concentration of FeCl_3 solution and volume ratio extract/ FeCl_3 solution) were optimized to provide the highest nZVI yield. The conditions for the composite's synthesis were chosen so that no more than 20 wt% of nZVI particles was deposited, to avoid agglomeration due to an excessive amount. The volume ratio of extract/ FeCl_3 solution was the same in all cases as for nZVI synthesis, and the concentration of FeCl_3 solution was the same in the case of SEP2 and KUb2 composites. Having in mind that the extract contains both reducing and capping/stabilizing agents for the nZVI particles [55], during SEP1 and KUb1 synthesis, the concentration of FeCl_3 was increased twice ($0.2 \text{ mol}/\text{dm}^3$), but also the mass of SEP or KUb, to investigate the influence of the mass ratio of FeCl_3 /extract on the quantity of deposited nZVI particles.

3.1. Characterization of the Samples

The results of the EDS analysis are shown in Table 1. It can be noted that there are very high contents of oxygen and carbon in the nZVI sample. Such a large amount of oxygen does not result from oxidizing nZVI, given the relatively low content of iron in the sample (in the case of complete oxidation of Fe, the oxygen content would be $\approx 5.9 \text{ mas. \%}$). The high content of C and O can be explained by the presence of organic matter from the extract of oak leaves, which remained in nZVI as a capping/stabilizing agent. The presence of phosphorus confirms this assumption. Small quantities of Cl in all samples are a consequence of using FeCl_3 in the synthesis. The Fe content in the composites varies significantly depending on the type of clay and the synthesis procedure. In order to determine the nZVI content, it is necessary to subtract the Fe content from the KUb

(1.70 wt%) or SEP (5.95 wt%) [27]. Bearing in mind that the chemical analysis of KUb and SEP was performed without taking carbon into account [27], the chemical compositions of the composites are also given without C in Table 1 (in brackets). The nZVI content in the composites, for both carrier minerals, was lower when the synthesis was performed with a higher concentration of FeCl_3 and a higher mass of KUb or SEP (samples KUb1 and SEP1): the Fe concentration was increased by 0.54 wt% for KUb1 and 1.46 wt% for SEP1, while in the case of a lower FeCl_3 concentration and a lower mass of KUb or SEP, it was increased by 2.42 wt% in the case of KUb2 and 4.55 wt% in the case of SEP2. The content of nZVI was significantly lower than the theoretical value, and the increase in mass ratio of FeCl_3 /extract caused lower nZVI deposition. Obviously, iron salt was an excess reagent, i.e., polyphenols from the extract were limiting reagents. The content of nZVI was higher in the composites with SEP, probably owing to the higher specific surface area and more basic surface functional groups in comparison to KUb—the higher value of pH_{PZC} of SEP [27] indicates a higher basicity of the surface, which provides stronger interactions with acidic groups from extract components on the surface of nZVI.

Table 1. Results of EDS analysis of the nZVI and the composites (in wt%).

Sample	O	C	Mg	Al	Si	P	Cl	K	Ti	Ca	Fe
nZVI	44.45	38.42	-	-	-	1.66	1.49	0.28	-	-	13.70
KUb1	58.75	10.19	0.46	10.24	15.93	0.11	0.11	2.08	0.28	-	1.85
	(61.69)	-	(0.56)	(12.45)	(19.89)	(0.14)	(0.14)	(2.56)	(0.34)	-	(2.24)
KUb2	53.54	19.91	0.43	8.14	12.52	0.29	0.20	1.80	0.36	-	2.82
	(59.55)	-	(0.65)	(12.13)	(19.52)	(0.40)	(0.31)	(2.72)	(0.54)	-	(4.12)
SEP1	50.93	12.72	9.14	1.52	18.08	0.30	0.33	0.98	-	0.09	5.92
	(53.25)	-	(11.59)	(1.98)	(23.56)	(0.40)	(0.43)	(1.26)	-	(0.11)	(7.41)
SEP2	46.15	19.82	6.39	1.25	16.33	0.17	0.36	0.90	-	0.19	8.44
	(57.6)	-	(7.97)	(1.56)	(20.4)	(0.21)	(0.45)	(1.12)	-	(0.24)	(10.5)

The FESEM micrographs of the nZVI and composites are given in Figure 1. FESEM micrographs of the nZVI sample (Figure 1a,b) show the agglomerates of very small particles, about 20 nm.

In Figure 1c,d, plate-like particle aggregates, which are typical of layered clay minerals such as kaolinite and illite [27], can be observed together with the agglomerates of small nZVI particles deposited on the KUb support. In the case of composites SEP1 and SEP2 (Figure 1e,f), the fibrous particles characteristic of the sepiolite structure can be noted, but the presence of nZVI particles is not clearly shown. It is possible that the very small nZVI particles are deposited homogeneously, so they cannot be clearly observed by FESEM analysis, or that nZVI is deposited in the form of a thin film. Although the nZVI particles cannot be seen in FESEM micrographs of SEP1 and SEP2, the change in the cream color of SEP to dark grey during their synthesis provides confirmation of the presence of nZVI.

The FTIR spectra of the nZVI and composites are shown in Figure 2. The bands at 1030 cm^{-1} (C-N stretching vibration for aliphatic amines or/and C-O-C stretching vibration), 1213 cm^{-1} (-C-O-H bonds), 1340 cm^{-1} (C-N stretching vibration of aromatic amines), 1620 cm^{-1} (C=C stretching vibration of the aromatic ring), 1720 cm^{-1} (C=O bonds) [56] and around 3360 cm^{-1} (O-H stretching vibration of polyphenols) [57] in the FTIR of nZVI confirm the presence of organic matter of the extract in the sample. Bands originating from vibrations of Fe-O bonds, stretching bands of Fe-O on the iron oxide occurring at 520 and 760 cm^{-1} , are probably results of the surface oxidation of nZVI particles. Most of these bands are also visible in the FTIR spectra of KUb1, KUb2, SEP1 and SEP2, but at lower intensities because of the lower content, confirming the presence of the organic matter from extracts in the composites. In the FTIR spectrum of SEP1 and SEP2, bands characteristic of the sepiolite structure are present. Also, the bands corresponding to Si-O, Si-O-Si and Si-O-Al bonds, which are characteristic of most clay minerals, can be observed in the FTIR spectrum of samples KUb1 and KUb2. When comparing FTIR spectra

of the composites and starting materials, KUb and SEP [27], a decrease in the intensity of all the characteristic bands was observed, which is probably a consequence of the decrease in vibration intensity due to the presence of organic matter and nZVI.

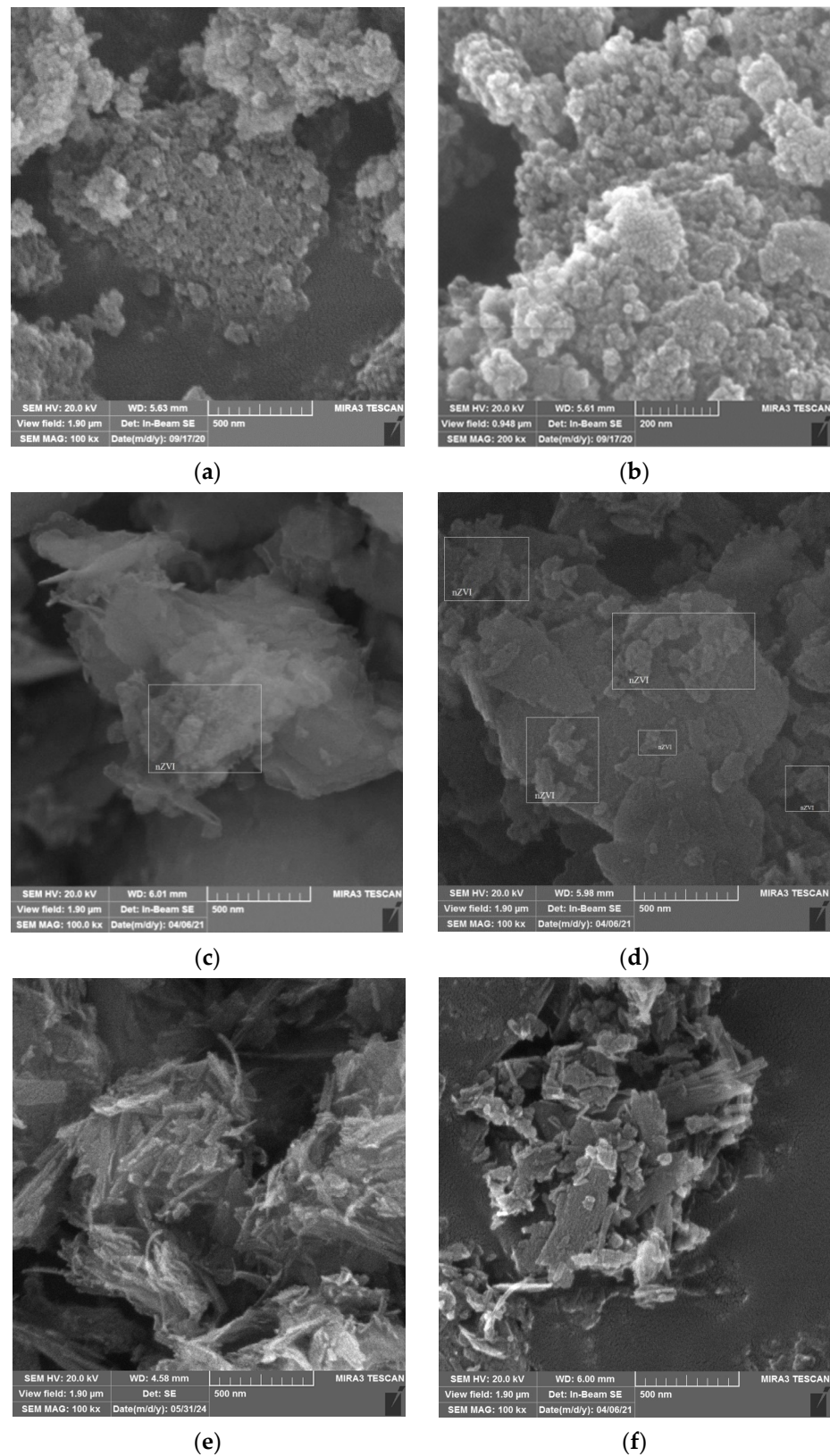


Figure 1. FESEM micrographs of nZVI (a,b); KUb1 (c); KUb2 (d); SEP1 (e); and SEP2 (f).

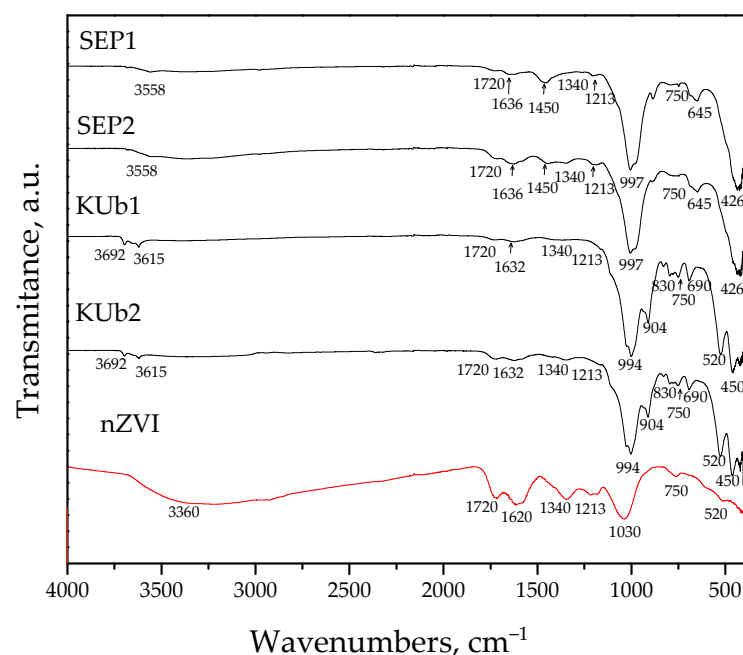


Figure 2. FTIR spectra of samples SEP1, SEP2, KUbl, KUbl2 and nZVI.

Nitrogen adsorption–desorption isotherms at $-196\text{ }^{\circ}\text{C}$ for KUbl, KUbl2, SEP1 and SEP2 and pore size distribution are presented in Figures 3 and 4. The textural properties of the composites are summarized in Table 2. The specific surface area of nZVI was $\approx 0.5\text{ m}^2/\text{g}$. Based on small particles and high agglomeration (Figure 1), it could be assumed that nZVI has a large specific surface area, but clearly the presence of a capping/stabilizing agent caused filling of the pores between nZVI and the low specific surface area.

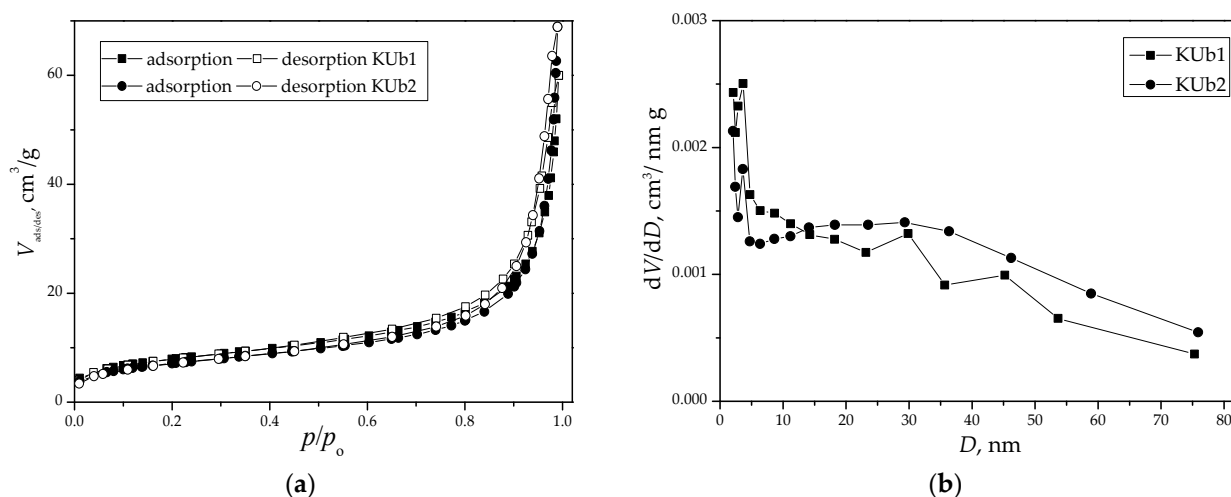


Figure 3. (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of KUbl and KUbl2.

In comparison to pure KUbl [27], the volume of both micropores and mesopores and thus the specific surface area of KUbl and KUbl2 increased. Given the very low S_{BET} of nZVI, it can be assumed that the deposition of nZVI particle agglomerates is not responsible for the increase in surface area, but probably is the reorganization and different packing of plate-like particles of KUbl during the synthesis.

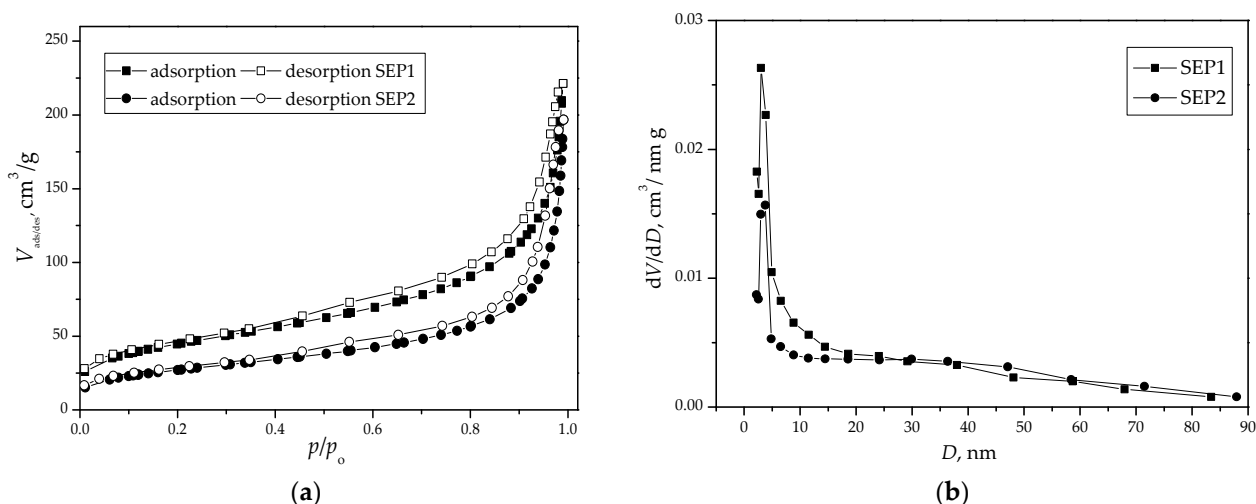


Figure 4. (a) N₂ adsorption–desorption isotherms and (b) pore size distributions of SEP1 and SEP2.

Table 2. Textural properties of the composites.

Sample	S_{BET} , m ² /g	V_{total} , cm ³ /g	V_{meso} , cm ³ /g	V_{micro} , cm ³ /g	$D_{\text{aver.}}$, nm	$D_{\text{max.}}$, nm
KUb1	27.6	0.0850	0.0795	0.0090	14.3	-
KUb2	24.9	0.0983	0.0933	0.0081	17.8	-
SEP1	156.6	0.333	0.306	0.0508	9.66	3.02
SEP2	95.5	0.293	0.278	0.0304	13.1	3.80

Although the S_{BET} decreased with the increase in iron content in the KUb sample, the mesopore volume increased, indicating that additional pores are formed between Fe⁰ particles. The mesopores size distributions of KUb1 and KUb2 are similar, but it can be seen that volume of small pores ($D \approx 4$ nm) decreased and the volume of larger pores (10–60 nm) increased as the quantity of Fe⁰ increased. These results indicate that during the synthesis of KUb1 and KUb2, a new phase was deposited on KUb, which caused an increase in the mesopore volume.

The S_{BET} of SEP1, and especially SEP2, is smaller than the S_{BET} of SEP [27], which is due to a decrease in the volume of micropores, as the volume of mesopores increased compared to pure SEP. This can be a result of the deposition of iron nanoparticles on the sepiolite structural channels, blocking the micropores. This assumption is consistent with the fact that the volume of micropores is lower in SEP2 with a higher Fe content than in SEP1. The higher volumes of mesopores in the composites in comparison to SEP is probably due to the deagglomeration of sepiolite bundles during composite synthesis and their reorganization during the final steps of the synthesis. The decrease in S_{BET} was also demonstrated in the case of the sepiolite/nZVI composite obtained using green tea extract [57].

The results of the determination of the pH_{PZC} of the nZVI and the composites are presented in Figure 5. From the dependences, values of pH_{PZC} were determined as the pH values at which the curve plateau, i.e., the curve inflexion, appears. The pH_{PZC} of nZVI, which is 4.2 ± 0.1 , is much lower than the values of nZVI samples obtained by chemical reduction using NaBH₄ [58,59]. This low value of the pH_{PZC} can be explained by the presence of the compounds of the extract, containing acidic groups.

The values of pH_{PZC} are almost the same for samples KUb1 (5.0 ± 0.1) and KUb2 (4.9 ± 0.1), as well as for samples SEP1 (5.4 ± 0.1) and SEP2 (5.5 ± 0.1). These values are lower than the pH_{PZC} of the corresponding carrier (6.4 ± 0.1 for KUb and 8.4 ± 0.1 for SEP [27]), indicating the deposition of nZVI of lower pH_{PZC} .

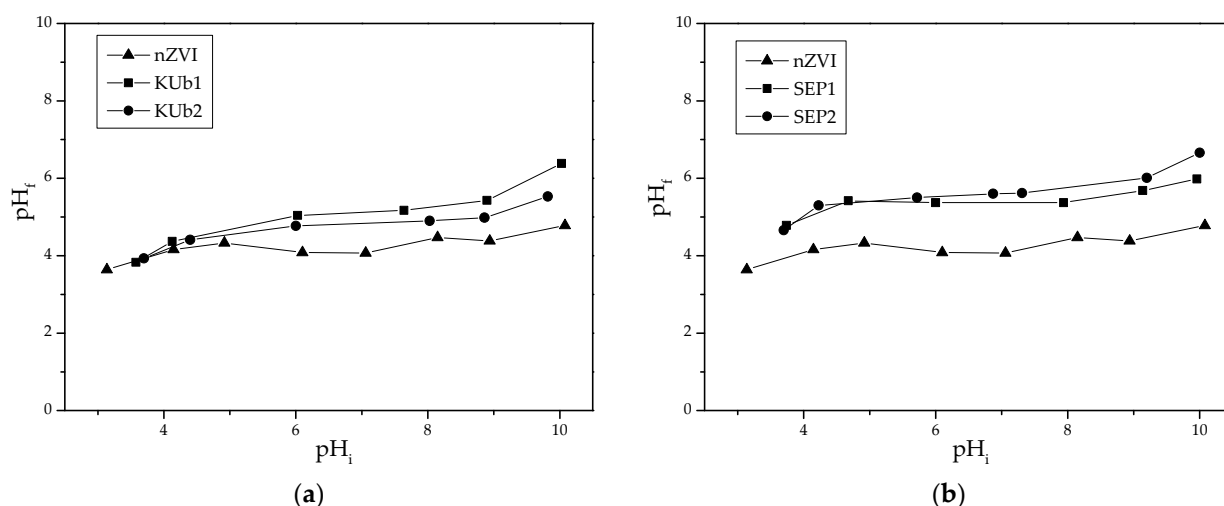


Figure 5. pH_f vs. pH_i during the equilibration of KUb1, KUb2 and nZVI (a), and SEP1, SEP2 and nZVI (b) with KNO_3 solution concentration of 0.1 mol/dm^3 .

3.2. Removal of Cr(VI)

The removal of Cr(VI) using nZVI and composites KUb1, KUb2, SEP1 and SEP2 was investigated at pH_i of 3 ± 0.1 , 4 ± 0.1 and 5 ± 0.1 , and the quantities of Cr(VI) removed are given in Figure 6. Table 3 summarizes the values of the Langmuir constants (q_m (mg/g) represents the maximum adsorption capacity and K_L (dm^3/mg) is the Langmuir constant related to the energy of adsorption) and the Freundlich constant (K_f is the Freundlich constant related to the adsorption capacity ($\text{mg}^{(1-1/n)} \cdot \text{dm}^{3/n}/\text{g}$) and n represents the dimensionless adsorption intensity parameter) [49,50] and R^2 , obtained by nonlinear fitting of the experimental data.

The results show that the removal capacity increased with the pH_i decreasing for all samples, as was expected. It is well known that the stability of Cr(VI) is decreased with the pH_i decreasing, so the efficiency of all processes of Cr(VI) removal is higher at a lower pH_i [60]. On the other hand, it is important to examine the possibility of performing the process at higher pH values in order to reduce the amount of acid required to adjust the pH value. The composites based on SEP have a higher Cr(VI) removal capacity than the KUb-based composites. The samples with a higher nZVI content have a higher capacity, given the negligible Cr(VI) removal capacity of SEP and KUb: the capacity of SEP2 is higher than that of SEP1, and the capacity of KUb2 is higher than that of KUb1 at all pH_i values. The removal capacity was the highest in the case of sample SEP2 at $pH_i = 3$ ($\sim 29 \text{ mg/g}$). Clearly, the content of nZVI is decisive for the removal capacity; thus, SEP composites with a higher content of nZVI have a higher capacity. On the other hand, although the sample KUb2 has a higher content of nZVI than SEP1, the removal capacity of KUb2 is not higher in comparison to SEP1, probably because nZVI particles were deposited more uniformly onto SEP, as was supposed according to FESEM analysis (Figure 1).

It can be seen that the capacities of nZVI for all pH_i values are higher than those of the composites, which is expected, considering the higher content of Fe^0 (Table 1). However, the removal capacity per unit mass of Fe^0 is higher for composites (for example, at $pH_i = 3.0 \pm 0.1$, $\sim 644 \text{ mg/g}$ for SEP2 and 380.3 mg/g for nZVI), which indicates a better availability of nZVI in the composites than in pure nZVI.

It can be seen from Table 3 that the fitting results were more consistent with the Freundlich model in the case of nZVI. The correlation coefficients for the Langmuir and Freundlich models are approximately the same for all composites. Agreement with both models may be the result of a mechanism of removal, a reduction process followed by subsequent adsorption of the formed Cr(III) ions.

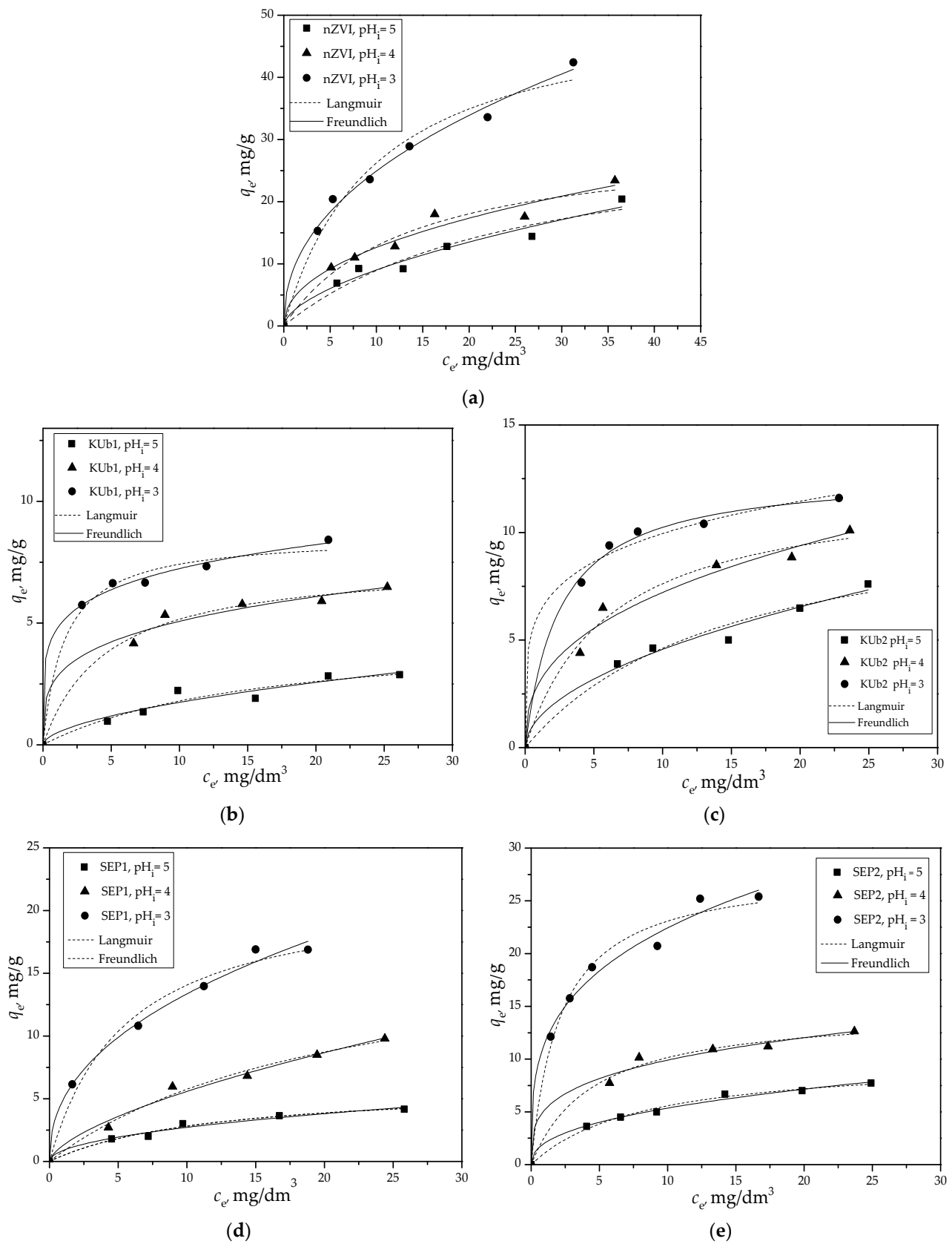


Figure 6. The dependence of the quantity of Cr(VI) removed from the solution on the equilibrium concentration of Cr(VI) in the solution at pH_i of 3.0 ± 0.1, 4.0 ± 0.1 and 5.0 ± 0.1 using nZVI (a), KUb1 (b), KUb2 (c), SEP1 (d) and SEP2 (e).

Table 3. Values of the Langmuir and Freundlich constants and R^2 for the removal of Cr(VI) onto nZVI, KUb1, KUb2, SEP1 and SEP2.

Sample	pH _i	Langmuir Isotherm $q_e = \frac{q_m K_L c_e}{1 + K_L c_e}$			Freundlich Isotherm $q_e = K_f c_e^{\frac{1}{n}}$		
		K_L dm ³ /mg	q_m mg/g	R^2	K_f (mg/g) (dm ³ /mg) ^{1/n}	$1/n$	R^2
nZVI	3.0 ± 0.1	0.101	52.1	0.974	9.00	0.442	0.992
	4.0 ± 0.1	0.075	30.0	0.955	4.40	0.457	0.964
	5.0 ± 0.1	0.038	32.1	0.940	2.36	0.583	0.963
KUb1	3.0 ± 0.1	0.631	8.59	0.986	4.73	0.184	0.994
	4.0 ± 0.1	0.215	7.55	0.987	2.76	0.263	0.982
	5.0 ± 0.1	1.16	4.76	0.964	5.36	0.130	0.982
KUb2	3.0 ± 0.1	0.411	14.66	0.992	6.23	0.203	0.988
	4.0 ± 0.1	0.165	12.26	0.986	3.00	0.379	0.982
	5.0 ± 0.1	0.071	11.42	0.990	1.46	0.505	0.995
SEP1	3.0 ± 0.1	0.180	21.81	0.980	4.93	0.432	0.990
	4.0 ± 0.1	0.046	18.15	0.986	1.28	0.637	0.984
	5.0 ± 0.1	0.084	6.15	0.982	0.885	0.487	0.980
SEP2	3.0 ± 0.1	0.468	28.10	0.982	11.50	0.290	0.988
	4.0 ± 0.1	0.220	14.75	0.986	5.19	0.280	0.982
	5.0 ± 0.1	0.123	10.10	0.992	2.05	0.416	0.992

The mechanism of Cr(VI) removal using nZVI and the nZVI composites involves the transfer of electrons from nZVI to the adsorbed Cr(VI), resulting in its conversion into Cr(III) with the oxidation of Fe⁰ to Fe(III), and adsorption of Cr(III) and Fe(III) cations onto nZVI and/or support (at lower pH values) or precipitation of Cr(OH)₃ or Cr_xFe_{1-x}(OH)₃ (at higher pH values). During equilibration of nZVI and the composites with Cr(VI) solution, pH is increased due to the protonation of the surface functional groups of the materials and the pH final (pH_f) results were, depending on the sample and Cr(VI) concentration: ~3.1–3.3 for pH_i = 3.0 ± 0.1, ~4.5–5.0 for pH_i = 4.0 ± 0.1 and 5.0–5.5 for pH_i = 5.0 ± 0.1. The precipitation of the hydroxides at higher pH values onto nZVI is another reason for the lower efficiency of Cr(VI) removal at higher pH values. So, the idea of using composites instead of nZVI alone is, in addition to avoiding the nZVI agglomeration, that the Cr³⁺ and Fe³⁺ ions are adsorbed on the SEP or KUb, instead of being deposited onto nZVI as hydroxides. It was shown previously [27] that SEP or KUb has a high adsorption capacity for Cr³⁺, where the SEP capacity is higher.

The efficiency of the composites in removing both Cr(VI) and Cr(III) was tested at pH_i = 3.0 ± 0.1, considering the highest removal of Cr(VI) at this pH value. The dependences of q_e total on c_e total were compared with the same dependences for Cr(VI), as shown in Figures 7 and 8. The dependences for KUb1 and KUb2 are almost overlapped, which indicates that the entire quantity of Cr(III) was adsorbed. On the other hand, in the case of SEP1 and SEP2, the removed quantity of total chromium is lower than the removed quantity of Cr(VI), meaning that a portion of Cr(III) stays in the solution without being adsorbed.

The reason for the difference between SEP- and KUb-based composites in the removal of Cr(VI) and total Cr may be the lower capacity of KUb-based composites for Cr(VI) and thus the lower quantity of Cr(III). In the case of SEP-based composites, a higher quantity of Cr(III) was produced, and clearly there was not enough space for their adsorption onto SEP. However, it was shown previously [27] that SEP has a higher adsorption capacity for Cr(III) than KUb, so it can be supposed that incomplete adsorption of Cr(III) in the case of SEP-based composites is a consequence of the good dispersion of nZVI particles onto the SEP surface, as assumed according to FESEM and BET results. In this way, the number of sites for Cr(III) adsorption is decreased. In KUb-based composites, nZVI particles form

agglomerates (Figure 1c,d), and enough space remains on the KUb surface for Cr(III) adsorption. Clearly, good dispersion of nZVI particles onto the support is favorable for Cr(VI) removal but not for Cr(III) adsorption. It should also be mentioned that a low pH (3.0 ± 0.1) is favorable for Cr(VI) reduction but not for Cr(III) adsorption; a lower pH increases the number of protonated surface functional groups, reducing Cr(III) adsorption sites [27].

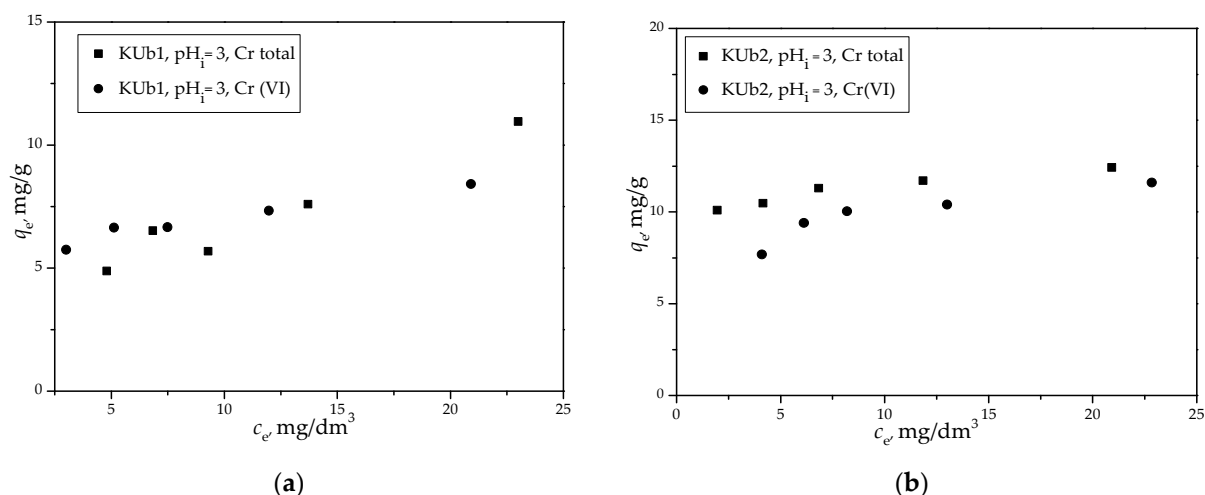


Figure 7. The dependences of the removal capacity of Cr(VI) and Cr total using KUb1 (a) and KUb2 (b) on the equilibrium concentration of Cr(VI) or Cr total in the solution at $pH_i = 3.0 \pm 0.1$.

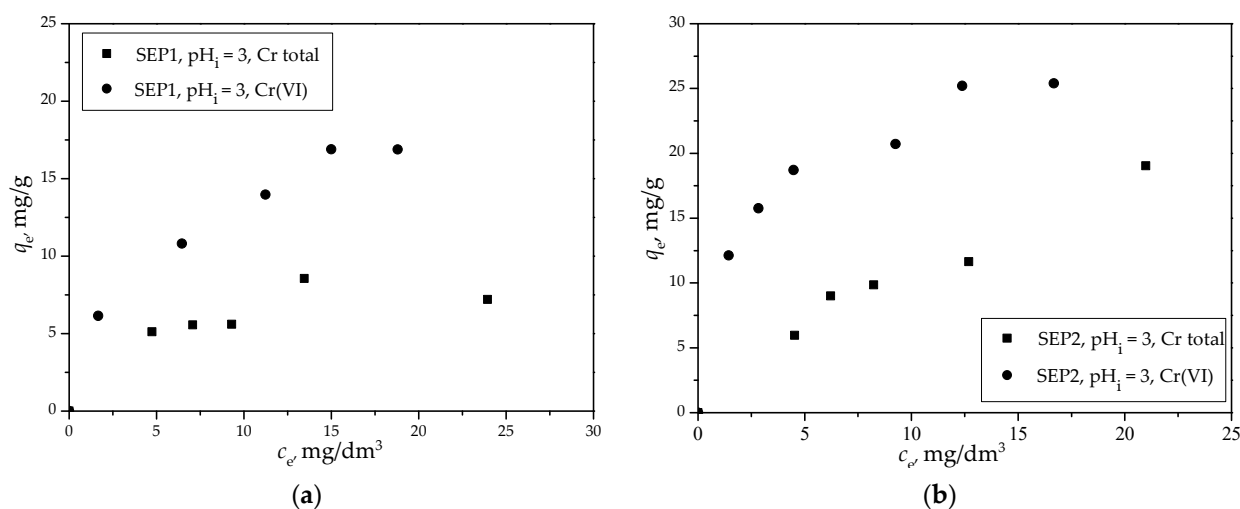


Figure 8. The dependences of the removal capacity of Cr(VI) and Cr total using SEP1 (a) and SEP2 (b) on the equilibrium concentration of Cr(VI) or Cr total in the solution at $pH_i = 3.0 \pm 0.1$.

The removal of Cr(VI) and total chromium from wastewater was investigated using sample SEP2 at $pH_i = 3.0 \pm 0.1$ and $pH_i = 5.0 \pm 0.1$ (Table 4). In addition to the final concentration of Cr(VI) ($c_e(\text{Cr(VI)})$) and total Cr ($c_e(\text{Cr(total)})$) for different masses (m) of SEP2, the removal capacities ($q_e(\text{Cr(VI)})$ and $q_e(\text{Cr(total)})$), final pH values (pH_f), and Fe concentration ($c(\text{Fe})$) were also studied, as given in Table 4.

Table 4. Removal of Cr(VI) and total Cr from wastewater ($c_0(\text{Cr(VI)}) = 55.0 \text{ mg/dm}^3$, $c_0(\text{Cr(total)}) = 54.8 \text{ mg/dm}^3$).

pH_i	$m, \text{ g}$	pH_f	$c_e(\text{Cr(VI)}), \text{ mg/dm}^3$	$q_e(\text{Cr(VI)}), \text{ mg/g}$	$c_e(\text{Cr(total)}), \text{ mg/dm}^3$	$q_e(\text{Cr(total)}), \text{ mg/g}$	$c(\text{Fe}), \text{ mg/dm}^3$
3.0 ± 0.1	0.02	4.55	44.0	22.1	51.2	7.3	0.25
	0.035	4.78	41.8	17.6	49.8	6.7	0.32
	0.05	4.83	37.8	13.8	48.4	5.2	0.43
	0.075	4.91	32.6	11.9	44.6	5.5	0.67
	0.1	5.02	29.5	10.2	42.0	5.2	0.78
	0.2	5.07	19.0	7.2	36.3	3.7	1.7
5.0 ± 0.1	0.02	5.46	50.5	9.0	53.8	2.0	0.02
	0.035	5.50	47.0	9.1	51.5	3.8	0.16
	0.05	5.41	43.6	9.1	49.5	4.2	0.27
	0.075	5.42	39.8	8.1	47.7	3.8	0.37
	0.1	5.42	38.8	6.5	47.6	2.9	0.72
	0.2	5.51	30.3	4.9	42.2	2.5	1.74

The results from Table 4 confirm that the Cr(VI) removal capacity is higher at a lower pH and that the removal of Cr(total) is lower than that of Cr(VI) at $\text{pH}_i = 3.0 \pm 0.1$. Given that cation adsorption increases with an increasing pH value, the removal of Cr(total) is expected to be approximately equal to the removal of Cr(VI) at $\text{pH}_i = 5.0 \pm 0.1$, but this was not the case. The results can offer confirmation of the previous assumption that good dispersion of nZVI particles reduces the number of adsorption sites for Cr^{3+} , but also for Fe^{3+} ions, which are formed by the oxidation of nZVI. It can be seen that $c(\text{Fe})$ increases with an increase in the mass of SEP2, i.e., with an increase in the amount of reduced Cr(VI), but the concentrations are much lower than they would be if all the formed Fe^{3+} ions remained in solution (for example, for $m(\text{SEP2}) = 0.02 \text{ g}$, $11.0 \text{ mg Cr(VI)/dm}^3$ was reduced and $11.8 \text{ mg Fe(III)/dm}^3$ was formed, but the concentration of Fe in the solution is 0.25 mg/dm^3). It should be also mentioned that the pH value of the solution is changed during reduction/adsorption, and the final pH value significantly increased at $\text{pH}_i = 3.0 \pm 0.1$ with an increase in the mass of the composite, while at $\text{pH}_i = 5.0 \pm 0.1$, the pH was slightly increased and close to the value of the point of zero charge (Figure 5b). This significant increase in pH_f for $\text{pH}_i = 3.0 \pm 0.1$ may be the reason for the decrease in the reduction efficiency of Cr(VI) with the increase in the mass of the composite, given that the removal efficiency is not proportional to the mass of SEP2 (Table 4).

3.3. Kinetics of Cr(VI) Removal

A higher Cr(VI) removal capacity of SEP was obtained at $\text{pH}_i = 3.0 \pm 0.1$ than at $\text{pH}_i = 5.0 \pm 0.1$ according to the kinetic studies. The dependences ($q_t \text{ (mg/g)}$)—the removal capacity at time t vs. $t \text{ (min)}$ —time are shown in Figure 9. This is in agreement with the previous results (Figure 6e and Table 4).

Removal occurs in two phases: one where the number and abundance of adsorption/reduction sites is large, and Cr(VI) removal occurs rapidly; and one where adsorption/reduction occurs more slowly because the number of available sites is decreased.

The values of the kinetic parameters used for the fitting of experimental data: the pseudo-first-order kinetic (k_1 —pseudo-first-order rate constant ($1/\text{min}$), and q_e —adsorption capacity at equilibrium (mg/g)), the pseudo-second-order kinetic (k_2 —pseudo-second-order rate constant ($\text{g/mg}\cdot\text{min}$), and q_e —adsorption capacity at equilibrium (mg/g)) and the intraparticle diffusion model (k_i —intraparticle diffusion rate constant ($\text{mg/g}\cdot\text{min}^{1/2}$), C —intercept at the ordinate, related to the boundary layer thickness (mg/g) and R^2) are presented in Table 5.

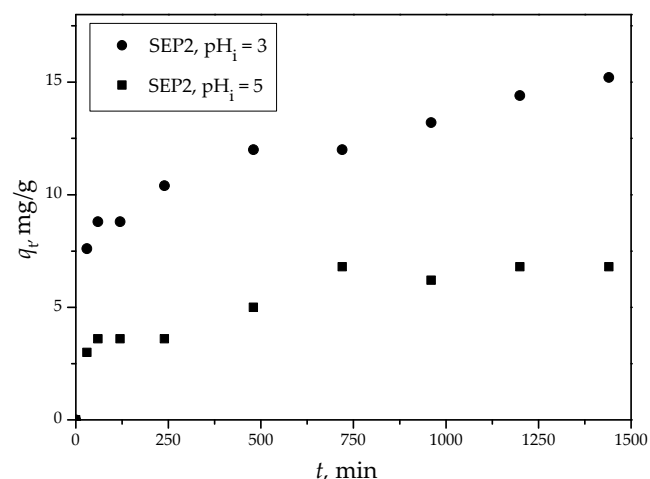


Figure 9. Effect of contact time on the removal of Cr(VI) onto SEP2 at $\text{pH}_i = 3.0 \pm 0.1$ and $\text{pH}_i = 5.0 \pm 0.1$.

Table 5. Pseudo-first-order, pseudo-second-order and intraparticle model fitting kinetic parameters for Cr(VI) removal on SEP2 composite.

pH_i	Model								
	Pseudo-First-Order			Pseudo-Second-Order			Intraparticle		
	$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$			$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$			$q_t = k_i t^{1/2} + C$		
	k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg·min)	q_e (mg/g)	R^2	k_i (mg/g·min ^{1/2})	C (mg/g)	R^2
3.0 ± 0.1	0.0018	8.99	0.880	7.12×10^{-4}	15.27	0.986	0.218	6.71	0.977
5.0 ± 0.1	0.0021	4.70	0.910	1.09×10^{-3}	7.31	0.978	0.210	1.61	0.794

The high value of the correlation coefficient obtained for the pseudo-second-order kinetic model indicates that this model can describe the removal of Cr(VI) from wastewater using composite nZVI/sepiolite.

The dependences q_t vs. $t^{1/2}$ for $\text{pH}_i = 3.0 \pm 0.1$, for the intraparticle diffusion model, consisted of one linear portion, which did not pass through the origin. In the case of $\text{pH}_i = 5.0 \pm 0.1$, the dependences consisted of two linear parts. The first part indicates intraparticle diffusion (also did not pass through the origin) and the second is equilibrium. According to the results, intraparticle diffusion is involved in Cr(VI) removal at both pH_i values but is not the rate-limiting step.

4. Conclusions

Nano-zero-valent iron (nZVI) and its composites with sepiolite (SEP) and kaolinite/illite (KUb) clays, synthesized using oak leaf extract as a reducing agent for Fe^{3+} ions, were applied for the removal of Cr(VI) from water.

It was concluded, according to SEM and BET analysis, that, while keeping the volume ratio of extract to FeCl_3 solution and the mass ratio of SEP or KUb to Fe constant, the nZVI content in the composites depended on the type of clay and the concentration of the FeCl_3 solution. The SEP support provided, owing to higher specific surface area and point of zero charge, a higher content and improved dispersion of nZVI particles, leading to improved Cr(VI) removal across all pH_i (3, 4 and 5) values, with greater Cr(VI) removal at lower pH_i values. The mechanism of chromium removal involves the reduction of Cr(VI) and adsorption of formed Cr(III) on the surface of the support. The adsorption of Cr(III) on the composites was proven by the determination of total chromium removal. The removal of Cr(III) is less effective than that of Cr(VI) for SEP composites, in contrast to KUb composites.

The good dispersion of nZVI particles on the SEP surface was thought to be advantageous for Cr(VI) adsorption/reduction; however, this could also lead to a decrease in the quantity of adsorption sites for Cr(III) and also for Fe(III), which are created when nZVI oxidizes.

The more efficient SEP sample demonstrated almost the same effectiveness in the removal of Cr(VI) from industrial wastewater as from solutions in demineralized water. The adsorption kinetics followed the pseudo-second-order model.

Overall, this study demonstrates that green synthesized composites of nZVI and natural clay supports are promising low-cost materials for effective remediation of Cr(VI)-contaminated waters.

Author Contributions: Conceptualization, R.P.; methodology, R.P., S.L. and I.J.-Č.; formal analysis, S.L., I.J.-Č., Ž.R. and Z.B.; investigation, S.L., I.J.-Č., Ž.R. and Z.B., writing—original draft preparation, S.L.; writing—review and editing, R.P.; supervision, R.P. and Đ.J. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia through the project E!13305 INSOLT-CHR and contract nos. 451-03-65/2024-03/200135 and 451-03-65/2024-03/200287.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available upon request.

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

References

1. Bashir, M.S.; Ramzan, N.; Najam, T.; Abbas, G.; Gu, X.; Arif, M.; Qasim, M.; Bashir, H.; Shah, S.S.A.; Sillanpaa, M. Metallic nanoparticles for catalytic reduction of toxic hexavalent chromium from aqueous medium: A state-of-the-art review. *Sci. Total Environ.* **2022**, *829*, 154475. [\[CrossRef\]](#) [\[PubMed\]](#)
2. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. *Toxicological Profile for Chromium*; Stephen B. Thacker CDC Library: Atlanta, GA, USA, 2012.
3. Ding, J.; Pu, L.; Wang, Y.; Wu, B.; Yu, A.; Zhang, X.; Pan, B.; Zhang, Q.; Gao, G. Adsorption and Reduction of Cr(VI) Together with Cr(III) Sequestration by Polyaniline Confined in Pores of Polystyrene Beads. *Environ. Sci. Technol.* **2018**, *52*, 12602–12611. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Barrera-Díaz, C.E.; Lugo-Lugo, V.; Bilyeu, B. A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction. *J. Hazard. Mater.* **2012**, *223–224*, 1–12. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Gao, Y.; Yang, X.; Lu, X.; Li, M.; Wang, L.; Wang, Y. Kinetics and Mechanisms of Cr(VI) Removal by nZVI: Influencing Parameters and Modification. *Catalysts* **2022**, *12*, 999. [\[CrossRef\]](#)
6. Fu, F.; Dionysiou, D.D.; Liu, H. The use of zero-valent iron for groundwater remediation and wastewater treatment: A review. *J. Hazard. Mater.* **2014**, *267*, 194–205. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Ye, J.; Wang, Y.; Xu, Q.; Wu, H.; Tong, J.; Shi, J. Removal of hexavalent chromium from wastewater by Cu/Fe bimetallic nanoparticles. *Sci. Rep.* **2021**, *11*, 10848. [\[CrossRef\]](#)
8. Liang, W.; Wang, G.; Peng, C.; Tan, J.; Wan, J.; Sun, P.; Li, Q.; Ji, X.; Zhang, Q.; Wu, Y.; et al. Recent advances of carbon-based nano zero valent iron for heavy metals remediation in soil and water: A critical review. *J. Hazard. Mater.* **2022**, *426*, 127993. [\[CrossRef\]](#)
9. Sepehri, S.; Kanani, E.; Abdoli, S.; Rajput, V.D.; Minkina, T.; Lajayer, B.A. Pb(II) Removal from Aqueous Solutions by Adsorption on Stabilized Zero-Valent Iron Nanoparticles—A Green Approach. *Water* **2023**, *15*, 222. [\[CrossRef\]](#)
10. Yuan, P.; Annabi-Bergaya, F.; Tao, Q.; Fan, M.; Liu, Z.; Zhu, J.; He, H.; Chen, T. A combined study by XRD, FTIR, TG and HRTEM on the structure of delaminated Fe-intercalated/pillared clay. *J. Colloid Interface Sci.* **2008**, *324*, 142–149. [\[CrossRef\]](#)
11. Fu, R.; Yang, Y.; Xu, Z.; Zhang, X.; Guo, X.; Bi, D. The removal of chromium (VI) and lead (II) from groundwater using sepiolite-supported nanoscale zero-valent iron (S-NZVI). *Chemosphere* **2015**, *138*, 726–734.
12. Yang, J.; Wang, S.; Xu, N.; Ye, Z.; Yang, H.; Huangfu, X. Synthesis of montmorillonite-supported nano-zero-valent iron via green tea extract: Enhanced transport and application for hexavalent chromium removal from water and soil. *J. Hazard. Mater.* **2021**, *419*, 126461. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Shi, Y.; Wang, X.; Zhong, S.; Chen, W.; Feng, C.; Yang, S. Nano zero-valent iron/montmorillonite composite for the removal of Cr(VI) from aqueous solutions: Characterization, performance, and mechanistic insights. *Appl. Clay Sci.* **2024**, *253*, 107345. [\[CrossRef\]](#)
14. Dai, Y.; Gao, R.; Liu, L.; Zhang, Y.; Hu, P. Structure and properties of nanoscale zero-valent iron supported on multimorphologies kaolinite and its enhanced removal of Cr(VI) from water. *Colloids Surf. A* **2023**, *675*, 132069. [\[CrossRef\]](#)

15. Bhattacharya, M.; Barbhuiya, N.H.; Singh, S.P. Single step synthesis of sulfidated nanoscale iron modified kaolin clay for hexavalent chromium remediation from groundwater. *Groundw. Sustain. Dev.* **2024**, *26*, 101196. [\[CrossRef\]](#)
16. Ye, J.; Luo, Y.; Sun, J.; Shi, J. Nanoscale Zero-Valent Iron Modified by Bentonite with Enhanced Cr(VI) Removal Efficiency, Improved Mobility, and Reduced Toxicity. *Nanomaterials* **2021**, *11*, 2580. [\[CrossRef\]](#)
17. Kim, S.A.; Kamala-Kannan, S.; Oh, S.-G.; Cho, M.; Bae, S.; Oh, B.-T. Simultaneous removal of chromium(VI) and Reactive Black 5 using zeolite supported nano-scale zero-valent iron composite. *Environ. Earth Sci.* **2016**, *75*, 447. [\[CrossRef\]](#)
18. Wei, Y.; Usman, M.; Farooq, M.; Adeel, M.; Haider, F.U.; Pan, Z.; Chen, W.; Liu, H.; Cai, L. Removing Hexavalent Chromium by Nano Zero-Valent Iron Loaded on Attapulgite. *Water Air Soil Pollut.* **2022**, *233*, 48. [\[CrossRef\]](#)
19. Sun, W.; Xu, N.; Jiang, W.; Cheng, G. Mechanistic insights into manganese oxide impacting the oxidation and transport of Cr(III) immobilized by nano-zero valent charged ion particles in water-saturated porous media. *J. Hazard. Mater.* **2024**, *469*, 134050.
20. Cheng, Y.; Dong, H.; Hao, T. CaCO₃ coated nanoscale zero-valent iron (nZVI) for the removal of chromium(VI) in aqueous solution. *Sep. Purif. Technol.* **2021**, *257*, 117967. [\[CrossRef\]](#)
21. Zhou, H.; Ma, M.; Zhao, Y.; Baig, S.A.; Hu, S.; Ye, M.; Wang, J. Integrated green complexing agent and biochar modified nano zero-valent iron for hexavalent chromium removal: A characterisation and performance study. *Sci. Total Environ.* **2022**, *834*, 155080.
22. Zhou, L.; Yi, Y.; Fang, Z. Nanoscale zero-valent iron immobilized by ZIF-8 metal-organic frameworks for enhanced removal of hexavalent chromium. *Chemosphere* **2022**, *306*, 135456. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Shu, Y.; Ji, B.; Cui, B.; Shi, Y.; Wang, J.; Hu, M.; Luo, S.; Guo, D. Almond Shell-Derived, Biochar-Supported, Nano-Zero-Valent Iron Composite for Aqueous Hexavalent Chromium Removal: Performance and Mechanisms. *Nanomaterials* **2020**, *10*, 198. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Wang, H.; Wang, Y.; Liu, Z.; Luo, S.; Romanovski, V.; Huang, X.; Czech, B.; Sun, H.; Li, T. Rational construction of micron-sized zero-valent iron/graphene composite for enhanced Cr(VI) removal from aqueous solution. *J. Environ. Chem. Eng.* **2022**, *10*, 109004. [\[CrossRef\]](#)
25. Essebaai, H.; Lgaz, H.; Alrashdi, A.A.; Habsaoui, A.; Lebki, A.; Marzak, S.; Rifi, E.H. Green and eco-friendly montmorillonite clay for the removal of Cr(III) metal ion from aqueous environment. *Int. J. Environ. Sci. Technol.* **2022**, *19*, 2443–2454. [\[CrossRef\]](#)
26. Kocaoba, S. Adsorption of Cd(II), Cr(III) and Mn(II) on natural sepiolite. *Desalination* **2009**, *244*, 24–30. [\[CrossRef\]](#)
27. Petrović, R.; Lazarević, S.; Janković-Častvan, I.; Matić, T.; Milivojević, M.; Milošević, D.; Veljović, D. Removal of trivalent chromium from aqueous solutions by natural clays: Valorization of saturated adsorbents as raw materials in ceramic manufacturing. *Appl. Clay Sci.* **2023**, *231*, 106747. [\[CrossRef\]](#)
28. Shah, K.H.; Alil, S.; Waseem, M.; Shah, F.; Fahad, M.; Shahida, S.; Khan, A.M.; Khan, A.R. Native and magnetic oxide nanoparticles (Fe₃O₄) impregnated bentonite clays as economic adsorbents for Cr(III) removal. *J. Solut. Chem.* **2019**, *48*, 1640–1656. [\[CrossRef\]](#)
29. Mahjoubi, N.; Araissi, M.; Mhamdi, M.; Elaloui, E. Valorisation, Characterization and Application of Natural Materials (Zeolite and Chert) as Adsorbents for the Removal of Chromium(III) from an Aqueous Solution. *Water Air Soil Pollut.* **2022**, *233*, 246. [\[CrossRef\]](#)
30. Barreto-Rodrigues, M.; Silveira, J.; Zazo, J.A.; Rodriguez, J.J. Synthesis, characterization and application of nanoscale zero-valent iron in the degradation of the azo dye Disperse Red 1. *J. Environ. Chem. Eng.* **2017**, *5*, 628–634. [\[CrossRef\]](#)
31. Huang, X.; Chen, L.; Ma, Z.; Carroll, K.C.; Zhao, X.; Huo, Z. Cadmium removal mechanistic comparison of three Fe-based nanomaterials: Water-chemistry and roles of Fe dissolution. *Front. Environ. Sci. Eng.* **2022**, *16*, 151. [\[CrossRef\]](#)
32. Owija, N.Y.; Kosa, S.A.; Salam, M.A. Removal of cadmium ions from aqueous solution by zero valent iron nanoparticles: Equilibrium and thermodynamic studies. *J. Mol. Liq.* **2021**, *342*, 117462. [\[CrossRef\]](#)
33. Ravikumar, K.V.G.; Dubey, S.; Pulimi, M.; Chandrasekaran, N.; Mukherjee, A. Scale-up synthesis of zero-valent iron nanoparticles and their applications for synergistic degradation of pollutants with sodium borohydride. *J. Mol. Liq.* **2016**, *224*, 589–598. [\[CrossRef\]](#)
34. Eljamal, R.; Eljamal, O.; Khalil, A.M.E.; Saha, B.B.; Matsunaga, N. Improvement of the chemical synthesis efficiency of nano-scale zero-valent iron particles. *J. Environ. Chem. Eng.* **2018**, *6*, 4727–4735. [\[CrossRef\]](#)
35. Li, T.; Zhu, F.; Gao, Y.; Iribagiza, M.R.; Hu, G.; Guan, J. Efficient elimination of Cr(VI) in groundwater using nano zero-valent iron synthesized with Ginkgo biloba extracts: Enhanced mechanism and reduced toxicity. *Environ. Sci. Water Res. Technol.* **2024**, *10*, 339–352.
36. Panić, S.; Petronijević, M.; Vukmirović, J.; Grba, N.; Savić, S. Green Synthesis of Nanoscale Zero-Valent Iron Aggregates for Catalytic Degradation of Textile Dyes. *Catal. Lett.* **2023**, *153*, 3605–3619.
37. Weng, X.; Huang, L.; Chen, Z.; Megharaj, M.; Naidu, R. Synthesis of iron-based nanoparticles by green tea extract and their degradation of malachite. *Ind. Crops Prod.* **2013**, *51*, 342–347.
38. Kadhum, S.T.; Alkindi, G.Y.; Albayati, T.M. Eco friendly adsorbents for removal of phenol from aqueous solution employing nanoparticle zero-valent iron synthesized from modified green tea bio-waste and supported on silty clay. *Chin. J. Chem. Eng.* **2021**, *36*, 19–28.
39. Deewan, R.; Yan, D.Y.-S.; Khamdahsag, P.; Tanboonchuy, V. Remediation of arsenic-contaminated water by green zero-valent iron nanoparticles. *Environ. Sci. Pollut. R.* **2023**, *30*, 90352–90361.

40. Poguberović, S.S.; Krčmar, D.; Maletić, S.P.; Kónya, Z.; Tomašević Pilipovic, D.D.; Kerkez, D.V.; Rončević, S.D. Removal of As (III) and Cr (VI) from aqueous solutions using “green” zero-valent iron nanoparticles produced by oak, mulberry and cherry leaf extracts. *Ecol. Eng.* **2016**, *90*, 42–49. [\[CrossRef\]](#)
41. Le, N.T.; Dang, T.-D.; Binh, K.H.; Nguyen, T.M.; Xuan, T.N.; La, D.D.; Nadda, A.K.; Chang, S.W.; Nguyen, D.D. Green synthesis of highly stable zero-valent iron nanoparticles for organic dye treatment using *Cleistocalyx operculatus* leaf extract. *Sustain. Chem. Pharm.* **2022**, *25*, 100598. [\[CrossRef\]](#)
42. Abida, O.; Van der Graaf, F.; Li, L.Y. Exploratory study of removing nutrients from aqueous environments employing a green synthesised nano zero-valent iron. *Environ. Technol.* **2020**, *43*, 2017–2032. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Machado, S.; Pinto, S.L.; Grosso, J.P.; Nouws, H.P.A.; Albergaria, J.T.; Delerue-Matos, C. Green production of zero-valent iron nanoparticles using tree leaf extracts. *Sci. Total Environ.* **2013**, *445–446*, 1–8. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Skotti, E.; Anastasaki, A.; Kanellou, G.; Polissiou, M. Total phenolic content, antioxidant activity and toxicity of aqueous extracts from selected Greek medicinal and aromatic plants. *Ind. Crops Prod.* **2014**, *53*, 46–54. [\[CrossRef\]](#)
45. Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders and Porous Solids*; Academic Press: Cambridge, MA, USA, 1975.
46. Barrett, E.P.; Joyner, L.G.; Halenda, P.P. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373–380. [\[CrossRef\]](#)
47. Sing, K.S.W. *Surface Area Determination*; Everett, D.M., Ottewill, R.H., Eds.; Butterworths: London, UK, 1970; p. 25.
48. Lazarević, S.; Janković-Častvan, I.; Jovanović, D.; Milonjić, S.; Janačković, Đ.; Petrović, R. Adsorption of Pb²⁺, Cd²⁺ and Sr²⁺ ions onto natural and acid-activated sepiolites. *Appl. Clay Sci.* **2007**, *37*, 47–57. [\[CrossRef\]](#)
49. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403. [\[CrossRef\]](#)
50. Freundlich, H. Concerning adsorption in solutions. *Z. Phys. Chem.* **1906**, *57*, 385–470.
51. Lagergren, S. About the theory of so-called adsorption of soluble substances. *K. Sven. Vetenskapsakad. Handl.* **1989**, *24*, 1–39.
52. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465. [\[CrossRef\]](#)
53. Weber, W.J., Jr.; Morris, J.C. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. ASCE* **1963**, *89*, 31–59. [\[CrossRef\]](#)
54. Lorenzo, J.M.; Muneke, P.E.S. Phenolic compounds of green tea: Health benefits and technological application in food. *Asian Pac. J. Trop. Biomed.* **2016**, *6*, 709–719. [\[CrossRef\]](#)
55. Liu, Y.; Jin, X.; Chen, Z. The formation of iron nanoparticles by Eucalyptus leaf extract and used to remove Cr(VI). *Sci. Total Environ.* **2018**, *627*, 470–479. [\[CrossRef\]](#) [\[PubMed\]](#)
56. Wang, X.; Wang, A.; Ma, J.; Fu, M. Facile green synthesis of functional nanoscale zero-valent iron and studies of its activity toward ultrasound-enhanced decolorization of cationic dyes. *Chemosphere* **2017**, *166*, 80–88. [\[PubMed\]](#)
57. Han, X.; Zhang, H.; Zhang, C.; Zhao, Y.; Zhang, N.; Liang, J. Preparation of Sepiolite Nanofibers Supported Zero Valent Iron Composite Material for Catalytic Removal of Tetracycline in Aqueous Solution. *Front. Chem.* **2021**, *9*, 736285. [\[CrossRef\]](#) [\[PubMed\]](#)
58. Phanthasri, J.; Grisdanurak, N.; Khamdagsag, P.; Wantala, K.; Khunphonoi, R.; Wannapaiboon, S.; Tanboonchuy, V. Role of Zeolite-Supported Nanoscale Zero-Valent Iron in Selenate Removal. *Water Air Soil Pollut.* **2020**, *231*, 199.
59. Habish, A.J.; Lazarević, S.; Janković-Častvan, I.; Jokić, B.; Kovac, J.; Rogan, J.; Janačković, Đ.; Petrović, R. Nano scale zero valent iron (nZVI) supported by natural and acid-activated sepiolites: The effect of the nZVI/support ratio on the composite properties and Cd²⁺ adsorption. *Environ. Sci. Pollut. Res.* **2017**, *24*, 628–643.
60. Ukhurebor, K.E.; Aigbe, U.O.; Onyancha, R.B.; Nwankwo, W.; Osibote, O.A.; Paumo, H.K.; Ama, O.M.; Adetunji, C.O.; Siloko, I.U. Effect of hexavalent chromium on the environment and removal techniques: A review. *J. Environ. Manag.* **2021**, *280*, 111809.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.