



Mechanisms of chromium(VI) removal from solution by zeolite and vermiculite modified with iron(II)

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Abstract

Mechanisms of Cr(VI) reduction by Fe(II) modified zeolite (clinoptilolite/mordenite) and vermiculite were evaluated. Adsorbents were treated with $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$ to saturate their exchange sites with Fe(II). However, this treatment decreased their CEC and pH_{PZC} , probably due to the dealumination process. Vermiculite (V-Fe) adsorbed more Fe(II) (21.8 mg g^{-1}) than zeolite (Z-Fe) (15.1 mg g^{-1}). Z-Fe and V-Fe were used to remove Cr(VI) from solution in a batch test to evaluate the effect of contact time and the initial concentration of Cr(VI). The Cr(VI) was 100% reduced to Cr(III) by Z-Fe and V-Fe in solution at 18 mg L^{-1} Cr(VI) after 1 min. Considering that 3 mol of Fe(II) are required to reduce 1 mol of Cr(VI) ($3\text{Fe}^{+2} + \text{Cr}^{+6} \rightarrow 3\text{Fe}^{+3} + \text{Cr}^{+3}$), the iron content released from Z-Fe and V-Fe was sufficient to reduce 100% of the Cr(VI) in solutions up to 46.8 mg L^{-1} Cr(VI) and about 90% (V-Fe) and 95% (Z-Fe) at 95.3 mg L^{-1} Cr(VI). The Fe(II), Cr(III), Cr(VI), and K^+ contents of the adsorbents and solutions after the batch tests indicated that the K^+ ions from the $\text{K}_2\text{Cr}_2\text{O}_7$ solution were the main cation adsorbed by Z-Fe, while vermiculite did not absorb any of these cations. The H^+ of the acidic solution (pH around 5) may have been adsorbed by V-Fe. The release of Fe(II) from Z-Fe and V-Fe involved cation exchange between K^+ and H^+ ions from solution, respectively. The reduction of Cr(VI) by Fe(II) resulted in the precipitation of Cr(III) and Fe(III) and a decrease in the pH of the solution to < 5 . As acidity limits the precipitation of Cr(III) ions, they remained in solution and were not adsorbed by either adsorbent (since they prefer to adsorb K^+ and H^+). To avoid oxidation, Cr(III) can be removed by precipitation or the adsorption by untreated minerals.

Keywords Zeolite · Vermiculite · Iron(II) · Chromium(VI) · Cation exchange · Redox

Introduction

Chromium (Cr) is a metal that naturally occurs in the trivalent state (Cr(III)) in minerals, such as chromite and goethite. Cr(III) has low solubility in soil solutions and waters (WHO

2004), and in trace concentrations ($< 50\text{--}200 \text{ }\mu\text{g/day}$), it is an essential nutrient for humans and animals (National Research Council 1989; Kiser and Manning 2010; Dultz et al. 2012). The hexavalent state of chromium (Cr(VI)) is highly soluble and occurs in artificial materials such as CrO_3 and CrO_4^{2-} , which are strong oxidizing compounds and, consequently, highly toxic to the human health in any

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concentration (Hawley et al. 2004). Therefore, all effluents containing Cr(VI) must be treated before being discharged into water bodies.

Removal of Cr(VI) from industrial effluents is usually done by the precipitation of Cr(III) as the hydroxide, after redox reactions by the use of reducing substances, such as sodium metabisulphite. Chemical precipitation also requires the use of large quantities of reagents, such as sodium hydroxide, which often makes this protocol expensive (Srivastava and Thakur 2007). Treatment of Cr(VI)-contaminated effluents is also possible by combining the reduction of Cr(VI) with the adsorption of Cr(III). Cr(III) ions can return to their oxidized state in the presence of oxidizing agents, such as manganese ions, but their adsorption prevents reoxidation (Eary and Rai 1988; Palmer and Wittbrodt 1991; Kwak et al. 2018). Adsorption can also be expensive, depending on the type of adsorbent utilized (Maronezi et al. 2019; Singh 2020).

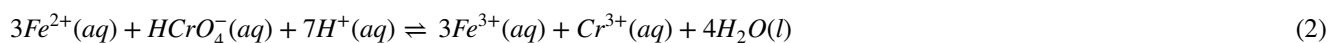
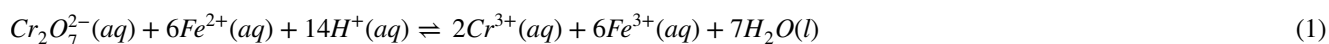
Recent studies have reported the use of different adsorbents suitable for treating toxic substances with several advantages in addition to their manufacturing cost, such as the availability of their precursors (some minerals and solid wastes), adsorption capacity, recycling capacity, biodegradable properties, and chemical stability (Jiao et al. 2021; Salam et al. 2021). Some of such adsorbents are phytogenic magnetic nanoparticles prepared from plant leaf extracts (Ali et al. 2018a, b, 2019a, b), bio-magnetic membrane capsules (Ali et al. 2019c), graphene oxide (Zhang et al. 2019), synthetic hybrid structures and composites (Salam et al. 2020), etc.

Besides synthetic materials, minerals with large specific surface area and high ion exchange capacity, such as zeolites and vermiculite, are also low-cost options with good performance in pollutant removal (Shinzato et al. 2020). Zeolites are aluminosilicates with permanent negative charges derived from the replacement of part of the silicon by aluminum in the tetrahedral framework (Barrer 1982). This negative charge is compensated by cations such as K^+ , Na^+ , and Ca^{2+} held by adsorption inside the pores, which can be replaced by

other cations (Pabalan and Bertetti 2001). Vermiculite is a 2:1 phyllosilicate, which structure is formed by two tetrahedral layers of Si^{4+}/Al^{3+} oxide associated with an octahedral Al^{3+} or Mg^{2+} hydroxide (Meunier 2005). Vermiculite is negatively charged due to unbalanced substitutions, predominantly in the tetrahedral ($Si^{4+}-Al^{3+}$) layer. Its residual negative charge is compensated by the interlayer cations (Jackson 1979).

Negatively charged minerals are usually applied when removing heavy metals from solution (Zamzow et al. 1990; Curkovic et al. 1997; Mier et al. 2001; Wingenfelder et al. 2005; Shinzato 2007; Margeta et al. 2013). Nevertheless, their use for chromate ion (CrO_4^{2-}) removal is not appropriate. Several authors have proposed the use of organic cationic surfactants, such as hexadecyltrimethylammonium bromide (HDTMA-Br), to modify the surface charge of zeolites (Apreutesei et al. 2008; Szala et al. 2015; Huang et al. 2016; Jiménez-Castaneda and Medina 2017). In this method, the resulting mineral is known as an organo-zeolite, which adsorbs (CrO_4^{2-}) onto its surface, while the capacity to adsorb cations in the pores and channels of these organo-zeolites is preserved because HDTMA molecules are too large to enter the structural voids of zeolites.

However, the direct adsorption of Cr(VI) does not change its toxicity, while reduction reactions have the advantage of transforming chromium into a less toxic form. Therefore, in the treatment of water contaminated with Cr(VI), it is more advantageous to use materials that promote a combination of mechanisms such as reduction, adsorption, and co-precipitation (Fang et al. 2021). Reducing agents, such as Fe(II) ions, can also be adsorbed by minerals, such as zeolite and vermiculite, in order to reduce Cr(VI) levels (Kiser and Manning 2010; Lv et al. 2014; Ahn and Do 2016; Kwak et al. 2018). The reduction reactions of Cr(VI) in the form of dichromate (Brigatti et al. 2000; Kwak et al. 2018) and hydrogen chromate (Kiser and Manning 2010) by Fe(II) occur in acidic media and are represented in Eqs. 1 and 2, respectively.



Using minerals as a support for the Fe(II) ions instead of using the dissolved salt is more satisfactory in reducing Cr(VI), as it consumes smaller amounts of Fe(II) salts and does not require the addition of acids to obtain acidic conditions (Brigatti et al. 2000). Although some studies have tested minerals modified with Fe(II) to reduce Cr(VI) (Kiser and Manning 2010; Lv et al. 2014; Lofù et al. 2016; Ahn and Do 2016; Kwak et al. 2018), the mechanisms involved in this process are not well detailed. Therefore, the present study

assessed the main mechanisms involved in the removal of Cr(VI) from solution by redox using zeolite and vermiculite modified with Fe(II). In addition to comparing the Cr(VI) removal efficiency of these two modified minerals, their ability to release Fe(II) by cation exchange and also to maintain these ions in the reduced form within their exchange sites was also evaluated for the first time. This study should also provide useful information for the application of these types of adsorbents in the remediation of water contaminated with Cr(VI).

Materials and methods

Characterization of the adsorbents

The mineral adsorbents used in this study were zeolite concentrate (Z) from Cuba commercialized by Celta Brasil Industry LTDA, and vermiculite (V) from Goiás State, Brazil, provided by Brasil Minérios S.A. Minerals were washed with distilled water, dried at 60 °C for 48 h and ground in a mortar to a grain size < 200 mesh.

The mineralogical composition of zeolite concentrate (Z) was analyzed in an X-ray diffractometer (XRD) (D8 Advance/Bruker) to identify the type of zeolite present in the sample. The conditions used in this determination were radiation CuK α , angular range 2 θ ° from 3 to 65° with a 0.050° step and count time of 0.5 s step⁻¹. X-ray diffraction data were analyzed using a High Score Plus 5.0 (Panalytical) software and the Crystallographic Open Database (Grazulis et al. 2009). Quantitative phase analysis was performed with the Rietveld method and the refinement parameters considered were background, sample displacement, weight fraction, cell parameters, and peak width and shape.

Vermiculite (V) was subjected to XRD analysis using the methods described by Theisen and Harward (1962), Anderson (1963), and Jackson (1979), consisting of heating a sample previously saturated with K⁺ to 350 and 550 °C, and treating with ethylene glycol a sample saturated with Mg²⁺. Natural and heated minerals samples were analyzed with XRD (D8 Advance/Bruker) under the following conditions: angular range from 2 to 36° 2 θ °, step size of 0.01°/2 θ °, angular velocity of 1 s/step. Samples treated with ethylene glycol were analyzed using an angular range of 3–35 2 θ °; 0.02°/2 θ ° of step, speed of 5 s/step.

The chemical composition of the zeolite concentrate and the vermiculite were determined by X-ray fluorescence (XRF) spectroscopy (Axios Advanced PANalytical). The point of zero charge (pH_{PZC}) of the zeolite concentrate and the vermiculite (before and after modification) was also determined. Thirteen samples were prepared by adding (20 mg) of each adsorbent to 20 mL of NaCl (0.1 mol L⁻¹) and the initial pH was adjusted to values within the range 1 to 12 with 0.01 and 0.01 mol L⁻¹ HCl or NaOH. These suspensions were agitated for 24 h at 25 °C, and after being decanted, the final pH was measured using a pH meter (HI2221/Hanna Instruments). The pH_{PZC} was determined by the plot of pH_{initial} vs. pH_{final}, when pH_{initial} = pH_{final} (El-Sayed et al. 2014).

For the determination of cation exchange capacity (CEC) of the zeolite concentrate and the vermiculite (before and after modification), 1 g of each sample was agitated with 50 mL of 1 mol L⁻¹ sodium acetate solution for 2 h. After washing with distilled water and centrifugation, these samples were agitated with 1 mol L⁻¹ ammonium acetate solution for 2 h (Hesse 1971). The sodium ions that remained in the solution were quantified using a flame photometer (DM-62/Digimed). The CEC value corresponds to the Na⁺ concentration in milliequivalents per gram of sample (meq g⁻¹).

In this study, the zeolite concentrate of clinoptilolite-mordenite was named simply as zeolite (Z) and vermiculite as (V).

Preparation of zeolite and vermiculite with Fe(II)

Minerals were saturated with Fe(II) ions at their exchange sites, based on the method proposed by Liu et al. (2010). Zeolite and vermiculite samples (100 g) were mixed with 1 L of FeSO₄·7H₂O solution with different concentrations (0.1, 0.25, 0.5, and 1 mol L⁻¹). In order to achieve the best conditions for modifying the minerals with Fe(II), this test was carried out at room temperature and 40 °C, and with contact times of 1 h and 24 h. After stirring, the mixtures were filtered and washed with distilled water, dried at 80 °C for 48 h, and stored in a desiccator. The zeolite and vermiculite samples treated with Fe(II) were identified as Z-Fe and V-Fe, respectively.

To verify if the untreated and modified samples can remove Cr(VI) from solution, a preliminary test was conducted using 0.5 g of modified minerals and 25 mL of 20 mg L⁻¹ Cr(VI) solution. After being stirred for 120 min and centrifuged (Q222T/Quimis) at 2500 rpm for 15 min, the Cr(VI) concentration was determined in supernatants.

The Fe(II) concentration at the exchange sites of each mineral was quantified before and after treatment with FeSO₄·7H₂O solution, by extracting Fe(II) with an acidic solution, based on the method described by Kwak et al. (2018). In this method, samples (0.5 g) were mixed with 5 mL of 1 mol L⁻¹ H₂SO₄ for 2 h at room temperature; after centrifugation, the extracted Fe(II) concentration was determined in the supernatant. Fe(II) concentration was determined using 4 mL of 1.10-phenanthroline, which forms a complex with Fe(II) giving an orange color, and 4 mL of ammonium acetate buffer solution to intensify this color, a procedure described in SMWW (1999). Fe(II) concentration was quantified in a UV–Vis spectrophotometer (10S/ThermoScientific Genesys) at a wavelength (λ) of 510 nm. The concentration of K⁺ was determined using a flame photometer (DM-62/Digimed).

Cr(VI) removal — batch tests

The Cr(VI) removal was conducted in batch tests, using a 1:50 ratio of modified minerals and solutions prepared with analytical grade K₂Cr₂O₇. These materials were transferred to 50-mL polypropylene tubes and after agitation for a specified time, they were centrifuged and the supernatants analyzed. These tests were performed at room temperature and in triplicate.

The effects of contact time (1 to 60 min) and initial concentration of Cr(VI) (18 to 95.3 mg L⁻¹) were evaluated. To evaluate the influence of time on the efficiency of Cr(VI)

removal of each adsorbent, an 18 mg L⁻¹ Cr(VI) solution was used. The effect of the initial Cr(VI) concentration on the adsorption efficiency was assessed using a 60-min contact time (determined in the previous test).

The second set of batch tests for Cr(VI) removal was performed using Z-Fe and V-Fe that already undergone the 60-min batch tests. This second set of batch tests was performed almost 1 year after the first experiments to verify if the remaining Fe(II) did not oxidize and if this material can be reused in Cr(VI) reduction. During this interval, Z-Fe and V-Fe were kept in a desiccator. A solution with 18 mg L⁻¹ of Cr(VI) was used for the batch tests for 60 min under stirring.

The final samples of all batch tests were centrifuged (Q222T/Quimis) at 2500 rpm for 15 min and the concentrations of Cr(VI), Cr(III), Fe(II), and K⁺ in solution were measured. The concentration of Cr(VI) was determined using the method described by USEPA (1992), by adding 2 mL of 1.5-diphenylcarbazide (dissolved in acetone) and sulfuric acid solution (10%) to give a pH of 2 to 100 mL of the sample solution. The reaction with Cr(VI) forms a pink colored solution, analyzed in a UV–Vis spectrophotometer (10S/ThermoScientific Genesys, 540 nm wavelength). The total Cr content was analyzed by flame atomic absorption spectrometry (FAAS) (SpectrAA 50B/Varian). The Cr(III) concentration was determined by simple difference between the total Cr and Cr(VI) contents. The concentration of K⁺ (from the K₂Cr₂O₇ solution) was determined in the flame photometer (DM-62/Digimed) to verify its influence in the Cr(VI) removal by the minerals, as it can compete with other ions for the mineral exchange sites.

Cr(VI) removal efficiency (*E*%) was determined by Eq. (3), whereas the Cr(VI) removal capacity (*Q_e*, mg g⁻¹) was determined by Eq. (4):

$$E = \left(\frac{C_o - C_f}{C_o} \right) \times 100 \quad (3)$$

where *E* is the removal efficiency (%); *C_o* and *C_f* are the initial and final concentrations (mg L⁻¹), respectively.

$$Q_e = \left(\frac{C_o - C_f}{m} \right) \times V \quad (4)$$

where *Q_e* is the total amount of Cr removed (mg g⁻¹) by the mass (*m*) of the mineral (g), *C_o* and *C_f* are the initial and final concentrations (mg L⁻¹), respectively; *V* is the volume (L) of the solution.

The amount of Fe(II) adsorbed at the mineral exchange sites was evaluated before and after Cr(VI) removal tests, using the previously method described (Kwak et al. 2018) by extracting the Fe(II) with 1 mol L⁻¹ H₂SO₄ for 2 h at room temperature.

Untreated minerals (Z and V), those modified with Fe(II) (Z-Fe and V-Fe) and those used in the batch tests

(Z-Fe/Cr and V-Fe/Cr), were analyzed by the Fourier transform infrared spectroscopy (FTIR) to identify the main functional groups of minerals responsible for removing Cr(VI). This analysis was performed in a Shimadzu spectrometer (model IRP Prestige-21), using the percentage absorption mode, prepared on dry KBr tablets, with a resolution of 4 cm⁻¹ and an accumulation of 50 spectra (scans), with a spectral range of 400 to 4000 cm⁻¹.

Since some precipitates of Cr(III)/Fe(III) hydroxides may have formed during the removal tests, all samples were analyzed by XRD (D8 Advance/Bruker) after the batch tests. The conditions used in this determination were radiation CuKα, angular range 2θ° from 3 to 65° with a 0.050° step and count time of 0.5 s step⁻¹.

Results and discussion

Characterization of the adsorbents

The X-ray diffraction analysis indicated that the zeolite concentrate (Z) is composed by clinoptilolite (55.3%) and mordenite (40.4%), in addition to trace amount of vermiculite (4.2%). Both clinoptilolite and mordenite have a Si/Al ratio > 4 (Chen et al. 2018) and three (3 × 7.6 Å, 3.3 × 4.6 Å, 2.6 × 4.7 Å) and two (6.5 × 7 Å, 2.6 × 5.7 Å) system of channels, respectively (Armbruster and Gunter 2001). Among natural zeolites, clinoptilolite is the most abundant (Ming & Dixon 1987).

Vermiculite was identified by reflections at 1.4, 0.98, 0.48, 0.36, and 0.29 nm in the Mg-saturated sample; reflection at 1.4 nm in sample saturated with ethylene glycol indicated no change in the basal plane; and reflection at 1 nm in the K-saturated sample heated at 350 and 550 °C indicated the collapse of its basal plane (Chen 1977).

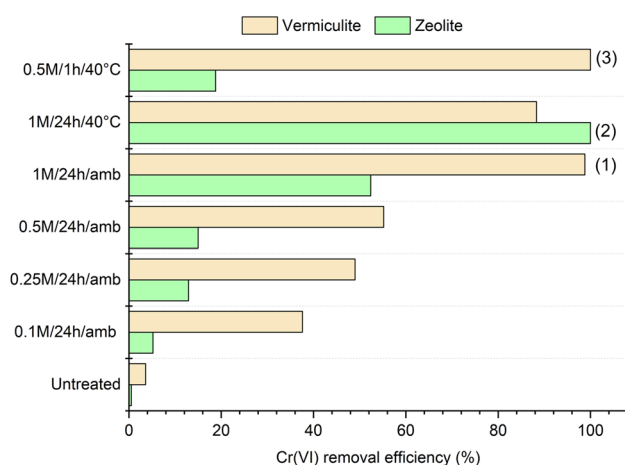
The chemical composition of zeolite and vermiculite is presented in Table 1. Significant amounts of Fe₂O₃ and MgO occur in vermiculite, the former probably occupying octahedral positions and the latter occurring in both the interlayer space and the octahedral sheet. Ca and K occupy exchange sites in both vermiculite and zeolite. Vermiculite sample also presents 0.69% Cr₂O₃ in the octahedral layers.

Treatment of the adsorbents with Fe(II)

Zeolite and vermiculite were treated with a solution of FeSO₄·7H₂O to replace the original cations with Fe(II) by ion exchange. In order to evaluate the best experimental conditions to modify zeolite and vermiculite, the results of Cr(VI) removal efficiency by the untreated and modified samples were analyzed (Fig. 3). Untreated zeolite and vermiculite showed very low efficiency in removing

Table 1 Chemical composition of the mineral adsorbents. Loss on ignition (LOI) at 1050 °C

Adsorbent (wt%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	ZnO	Cr ₂ O ₃	LOI
Zeolite	68.81	11.83	1.92	< 0.10	0.96	2.56	0.92	1.69	0.27	0.02	0.07	< 0.01	10.4
Vermiculite	38.91	11.66	7.69	0.05	25.13	0.61	< 0.01	0.15	1.25	0.01	< 0.01	0.69	13.94

**Fig. 1** Removal of Cr(VI) efficiency (%) by untreated and modified zeolite and vermiculite samples, under different concentrations of FeSO₄·7H₂O/time/temperature. Samples with 100% of Cr(VI) removal efficiency: (1), (2), and (3)

Cr(VI) from solution (respectively, 0 and 3%), while the efficiency of the modified samples improved with increasing Fe(II) concentrations (Fig. 3). The increase in temperature only improved the treatment of zeolite with 1 mol L⁻¹ FeSO₄·7H₂O.

The 100% efficiency of Cr(VI) removal was observed in one treatment of zeolite (2) and two treatments of vermiculite (1 and 3) (Fig. 1). The efficiency of ionic exchange depends on the ionic hydration radius of the exchanged cations, which controls the selectivity for the exchangeable sites (Strawn et al. 2019). Ions with negative hydration enthalpy (larger hydrated radius) tend to stay in the bulk solution, while ions with positive hydration enthalpy (smaller hydrated radius) are more easily attached to the mineral surface (Nightingale 1959).

The exchangeable cations in the zeolite pores, K⁺ and Ca²⁺, have smaller hydrated radii (0.33 nm and 0.41 nm, respectively) than Fe²⁺ (0.45 nm), whereas the hydrated radius of Mg²⁺ (0.43 nm) in the interlayer space of vermiculite is close to the hydrated radius of Fe²⁺ (Strawn et al. 2020). Therefore, the exchange of Fe²⁺ is more efficient with vermiculite than with zeolite. This is probably the reason why zeolite requires a higher FeSO₄·7H₂O concentration, temperature, and stirring time than vermiculite to be modified with Fe(II).

Although vermiculite was treated at room temperature in treatment 1, treatment 3 was chosen because it only consumed half the Fe(II) concentration, and it takes less time (1 h). Therefore, samples of zeolite modified with Fe(II) in treatment 2 and vermiculite from treatment 3 were used in further tests and have their Fe(II) content evaluated (Table 2).

Vermiculite adsorbed more Fe(II) than zeolite. This is due to the similar values of the hydrated radius of Mg²⁺ (0.43 nm), the main exchangeable cation of vermiculite, and the hydrated radius of Fe(II) (0.45 nm); the difference is larger with respect to the hydrated radius of the exchangeable cation of zeolite, Ca²⁺ (0.41 nm) (Strawn et al. 2020).

Furthermore, the pH_{PZC} values of natural zeolite (6.1) and vermiculite (5.8) decreased to the same pH_{PZC} (4.5) after modification with Fe(II). Ahn and Do (2016) also observed a decrease in pH_{PZC} of a natural (unidentified) zeolite from 7.2 to 5.5 after treatment with FeSO₄, while a 6 to 3 decrease in pH_{PZC} of a natural clinoptilolite treated with 0.1 to 0.5 M HCl was also observed by Abdellaoui et al. (2019). These authors suggested that the dealumination of the zeolite structure probably caused a decrease in the pH_{PZC} value, generating very strong Lewis acid sites on the mineral surface.

In our case, the dealumination of zeolite and vermiculite may have occurred during the treatment with 1 mol L⁻¹

Table 2 Point of zero charge (pH_{PZC}), cation exchange capacity (CEC, meq g⁻¹), and content of Fe(II) ions (mg g⁻¹) in the samples of zeolite and vermiculite before and after treatment with

Sample	Before treatment			After treatment		
	Fe(II) (mg g ⁻¹)	pH _{PZC}	CEC (meq g ⁻¹)	Fe(II) (mg g ⁻¹)	pH _{PZC}	CEC (meq g ⁻¹)
Zeolite	1.32 ± 0.06	6.1	2.59	15.1 ± 0.5	4.5	1.48
Vermiculite	0.61 ± 0.03	5.8	2.21	21.8 ± 1.2	4.5	1.51

1 mol L⁻¹ FeSO₄·7H₂O/24 h/40 °C (treatment 2), and 0.5 mol L⁻¹ FeSO₄·7H₂O/1 h/40 °C (treatment 3), respectively

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution, which became acidic (pH around 3) as the iron(III) hydroxides began to precipitate. Dealumination also results in an increase in the Si/Al ratio and, consequently, a decrease in the CEC values of the modified minerals (Table 1).

Cr(VI) removal — batch tests

Effect of contact time

Removal of Cr(VI) by Z-Fe and V-Fe attained 100% during all the periods studied (1 to 60 min) in a solution containing 18 mg L^{-1} Cr(VI), removing 0.90 mg Cr(VI) per gram of Z-Fe and V-Fe. Reduction of Cr(VI) by Fe(II) occurred very fast, corroborating the results of Liu et al. (2010), who also used Fe(II)-modified vermiculite to reduce Cr(VI) in the solution.

After the Cr(VI) removal test, the percentage of Fe(II) that remained in the mineral composition (Z-Fe and V-Fe) and in solution is shown in Fig. 2. The oxidized fraction (%) in Fig. 2 corresponds to the fraction (%) of Fe(II) released by the minerals (69% Z-Fe and 25% V-Fe) minus the fraction found in solution. Although this redox reaction occurs under acidic conditions (Eqs. 1 and 2), pH adjustment of the batch test solutions was not performed, as it remained around 5, and did not affect the efficiency of the Fe(II) released from the modified minerals during Cr(VI) reduction.

Since three moles of Fe(II) are required to reduce one mole of Cr(VI) (Eqs. 1 and 2), at least, 2.9 mg of Fe(II) was needed to reduce 0.9 mg Cr(VI). Acidic extraction performed on 1 g of Z-Fe and V-Fe (before and after the batch tests of Cr(VI) removal) revealed the amount of Fe(II) released from these minerals (Fig. 2). Considering that 1 g of Z-Fe and V-Fe has around 15 mg and 22 mg of Fe(II), respectively, the amount of Fe(II) released from Z-Fe and V-Fe (the removed fraction in Fig. 2) remained higher than the minimum needed (2.9 mg Fe(II), which corresponds to 19.3% for Z-Fe and 13.2% to V-Fe) to reduce Cr(VI) in all periods (Fig. 2). Z-Fe released more Fe(II) (regardless of time) than V-Fe, where the amount of Fe(II) released increased with time.

The release of Fe(II) from Z-Fe probably involved the cation exchange with K^+ from the potassium dichromate solution used as the source of Cr(VI) in the batch test, since the K^+ removal efficiency of this mineral was high and increased with time (Fig. 3).

The removal of K^+ from the solution with time (Fig. 3) as well as the release of Fe(II) into the solution (Fig. 2) was higher in Z-Fe than in V-Fe, which further indicates an exchange between K^+ and Fe(II). Z-Fe adsorbed more K^+ than V-Fe because the exchange $\text{K}^+ \leftrightarrow \text{Fe}^{2+}$ in vermiculite basal space is hampered by the difference in the hydrated radius of the ions. The hydrated radius of K^+ (0.33 nm) is smaller than that of Fe(II) (0.45 nm) (Strawn et al. 2020) and,

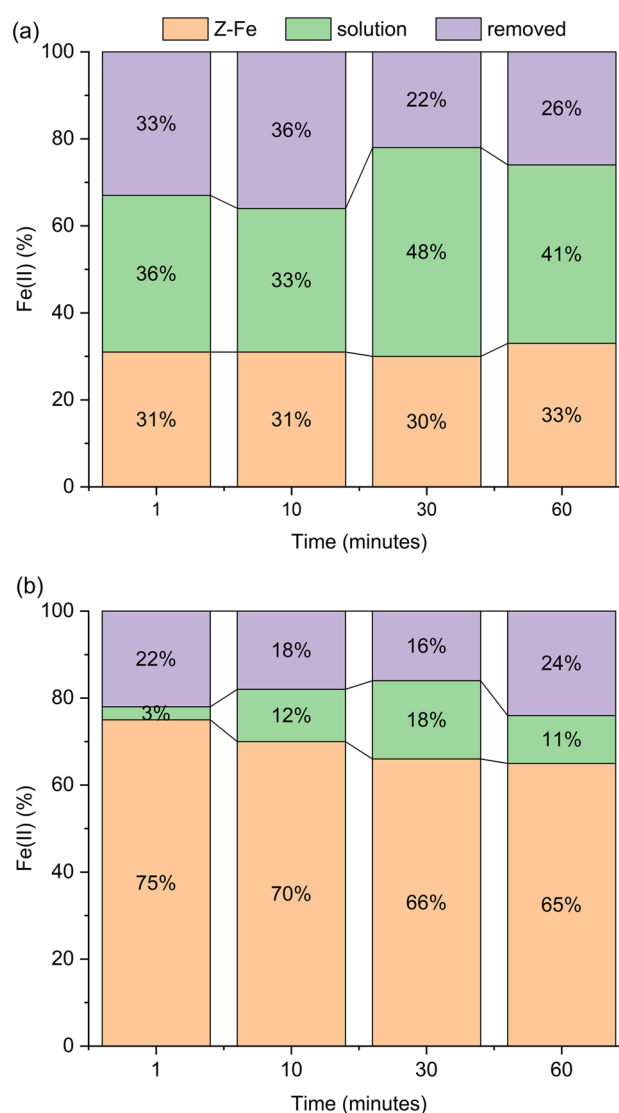


Fig. 2 Percentage of Fe(II) that remained in **a** Z-Fe and **b** V-Fe, and in their respective solutions and removed (oxidized) fractions, after the Cr(VI) removal test, as a function of time (1 to 60 min). The % values correspond to the content of Fe(II) in 1 g of mineral in 50 mL of solution containing 18 mg L^{-1} Cr(VI)

therefore, cation exchange requires a collapse of the internal site, i.e., a decrease in the (001) basal space from 14 to 10 nm, and this change is quite slow (Sparks 2003). However, this hypothesis must be confirmed by the analysis of V-Fe basal reflection, through DRX analysis (discussed in “Characterization of adsorbents before and after batch tests”).

To verify whether the remaining iron fraction of Z-Fe (5 mg) and V-Fe (15 mg) remained in the reduced form, a second set of Cr(VI) removal test was performed with the samples underwent the 60-min batch test. The results revealed that the remaining iron was still in the reduced form, even after 1 year. The Cr(VI) removal by V-Fe was higher (43.3% and 0.39 mg g^{-1} of removal efficiency) than

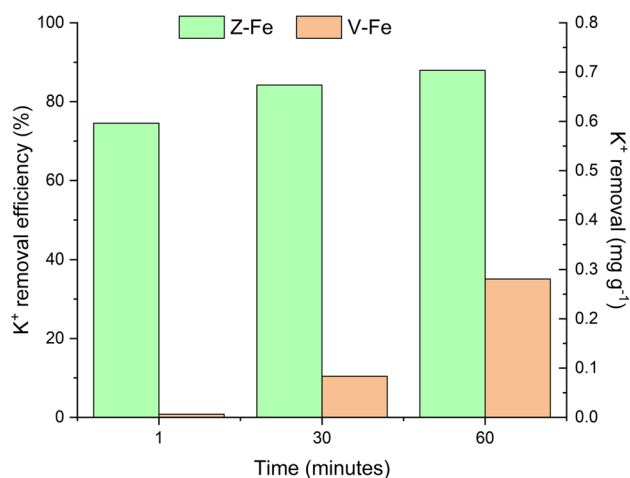


Fig. 3 Efficiency (%) and removal (mg g⁻¹) of K⁺ from K₂Cr₂O₇ solutions by Z-Fe and V-Fe during the Cr(VI) removal test as a function of time

Z-Fe (15.8% and 0.14 mg g⁻¹ of removal efficiency) as a result of possessing more Fe(II) at its exchangeable sites. Therefore, V-Fe can still be reused to remove low levels of Cr(VI) in the solution (< 10 mg L⁻¹). However, to assess how Fe(II) was bound at the zeolite and vermiculite exchange sites to maintain its stability, further investigations are needed, using modern techniques such as X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

Effect of initial Cr(VI) concentration

The increase of Cr(VI) concentration in solution leads to a decrease in the efficiency of its removal by Z-Fe and V-Fe. In tests with Z-Fe, efficiency dropped from 100% in solutions containing 18 and 46.8 mg L⁻¹ Cr(VI) to 94% in solutions containing 95.3 mg L⁻¹. The same effect was seen with V-Fe, where the efficiency went from 100% in solutions containing 18 and 46.8 mg L⁻¹ down to 89% in solution containing 95.3 mg L⁻¹ Cr(VI).

The mass fraction of Cr(VI) that was removed from the solution with respect to the mass of the adsorbents, increased with increasing concentration of the starting solution; for Z-Fe, this proportion increased from 0.9 mg g⁻¹ for tests with 18 mg L⁻¹ to 4.5 mg g⁻¹ with 95.3 mg L⁻¹, while for V-Fe, in the same range of concentrations, it increased from 0.9 to 4.2 mg g⁻¹ (Fig. 4).

Considering again, the need for 3 mol of Fe(II) to reduce one mole of Cr(VI), the amount of Fe(II) required to reduce the Cr(VI) present in 50 mL of the solution with an initial concentration of Cr(VI) of 18 mg L⁻¹ is 2.9 mg (corresponding to 19.3% for Z-Fe and 13.2% for V-Fe), while for solutions containing 46.8 mg L⁻¹ Cr(VI), it is 7.5 mg Fe(II) (50% for Z-Fe and 34% to V-Fe) and for 95.3 mg L⁻¹Cr(VI),

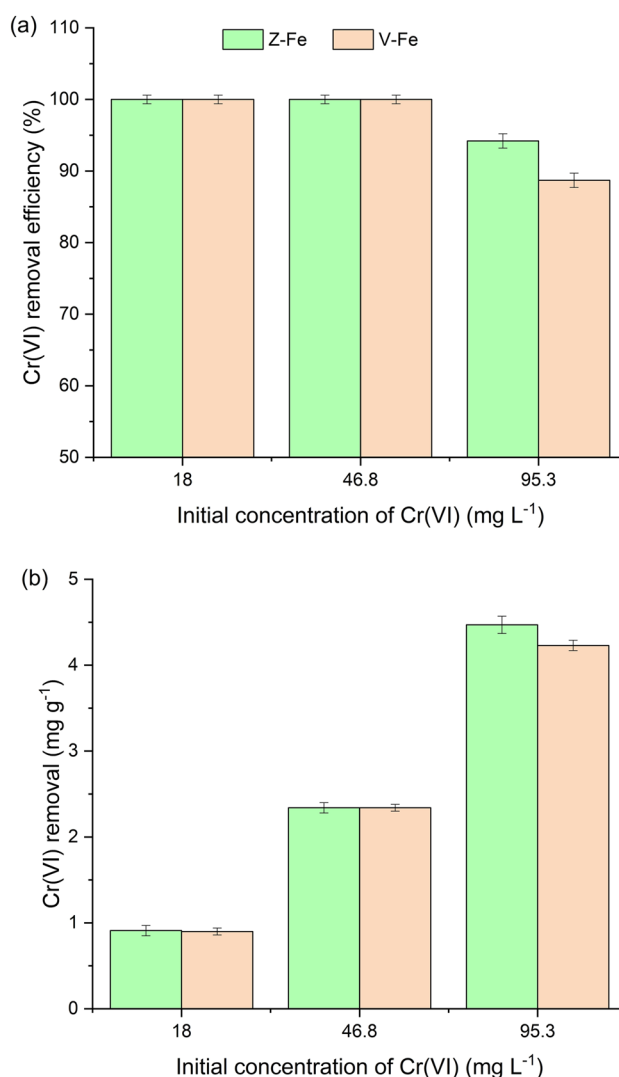


Fig. 4 Cr(VI) **a** efficiency (%) and **b** removal (mg g⁻¹) from solution by Z-Fe and V-Fe, as a function of the initial Cr(VI) concentration (18, 46.8, or 95.3 mg L⁻¹). Error bars indicate two standard deviations

it is 15.3 mg Fe(II) (theoretically 102% for Z-Fe and 69.5% for V-Fe). Therefore, the decrease in the efficiency of Cr(VI) removal from the solution containing 95.3 mg L⁻¹ of Cr(VI) indicates that the amount of Fe(II) released by Z-Fe and V-Fe was not enough to completely reduce the Cr(VI) available in the solution (Fig. 5). The amount of Fe(II) released from Z-Fe and V-Fe into the solution and the removed fraction, which probably oxidized forming hydroxide precipitates, augmented with the increase in Cr(VI) concentration, from 18 to 95.3 mg L⁻¹.

Since the K⁺ content also increased with the increase in Cr(VI) concentration (from potassium dichromate), in the solution containing 18 mg L⁻¹ Cr(VI) and 13.4 mg L⁻¹ K, 100% of K⁺ was removed by Z-Fe (corresponding to 0.7 mg g⁻¹ K⁺ removal). The K⁺ removal efficiency of V-Fe

in this solution ($18 \text{ mg L}^{-1} \text{ Cr(VI)}$) was 44.7%, corresponding to a removal of $0.3 \text{ mg g}^{-1} \text{ K}^+$ (Fig. 6). After the batch test conducted with modified minerals and 95.3 mg L^{-1} of Cr(VI) , the K^+ removal efficiency decreased (92.2%), while the K^+ removal increased to 3.3 mg g^{-1} for Z-Fe (Fig. 6). The efficiency of V-Fe was much smaller (34%), corresponding to a removal of $1.2 \text{ mg g}^{-1} \text{ K}^+$. This result revealed the higher efficiency of Z-Fe in removing K^+ from solution than V-Fe is likely due to ion exchange.

In contrast to the tests performed at lower Cr(VI) concentrations, Fe(II) was not detected in solution with 95.3 mg L^{-1} Cr(VI) , and the removed fraction (oxidized iron) increased

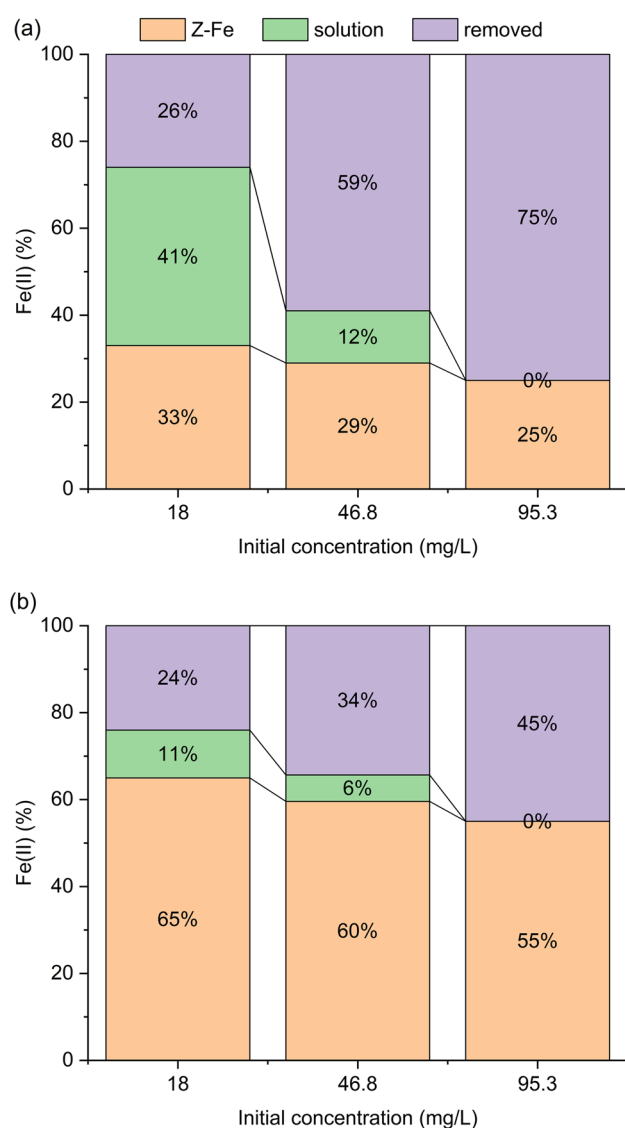


Fig. 5 Percentage of Fe(II) that remained adsorbed to **a** Z-Fe and **b** V-Fe, and in their respective solution and removed fractions after Cr(VI) removal test, as a function of Cr(VI) concentration (18, 46.8, and 95.3 mg L^{-1}). The % values correspond to the content of Fe(II) in 1 g of the mineral and 50 mL of Cr(VI) solution

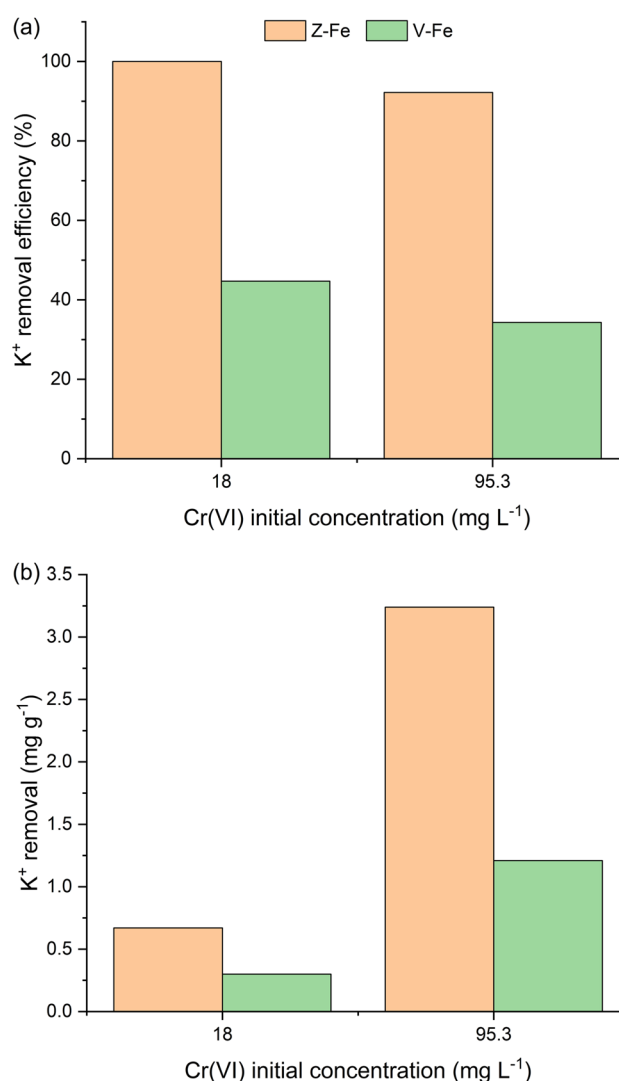


Fig. 6 Potassium **a** efficiency (%) and **b** removal (mg g^{-1}) by Z-Fe and V-Fe, as a function of the initial concentration of Cr(VI) (18 and 95.3 mg L^{-1})

with the increase in Cr(VI) concentration (Fig. 5). The required amount of Fe(II) to fully reduce the Cr(VI) in 50 mL of a solution containing 95.3 mg L^{-1} of Cr(VI) was 15.3 mg (corresponding to 69.5%). The actual amount of Fe(II) released during the batch tests was around 11.2 mg for Z-Fe (75%) and 9.9 mg for V-Fe (45%). However, after batch tests with 95.3 mg L^{-1} of Cr(VI) , the fraction of Fe(II) remaining adsorbed to Z-Fe and V-Fe was not released to reduce more Cr(VI) in the solution. Probably, the release of Fe(II) from Z-Fe and V-Fe was affected by the low availability of exchangeable cations in the final solutions.

Iron-rich clay minerals can reduce Cr(VI) and, eventually, the reduced Cr(III) is bound by electrostatic interactions onto the permanently charged sites, by covalent binding with hydroxyl groups, and by cation exchange (Brigatti

et al. 2000). In order to discover if the reduced chromium was adsorbed by Z-Fe and V-Fe, the Cr(III) content of the adsorbents (after acidic extraction) and solutions was determined (Fig. 7). Therefore, the difference between the Cr(VI) content of the samples before the batch test and the fraction of Cr remaining in the solution was considered as the precipitated chromium fraction (Fig. 7).

An expressive fraction of Cr(III) ions remained in solution (33–58% for Z-Fe and 26–49% for V-Fe), while only 9 to 11% of Cr(III) was fixed to the adsorbents (Fig. 7). The fraction of chromium adsorbed onto Z-Fe and V-Fe is quite low when compared to Cr(III) available in the solution, probably due to its low selectivity for mineral exchange sites under the experimental conditions.

The fraction (%) of Cr(III) that remained in solution increased with the initial concentration of Cr(VI) in Z-Fe, while for V-Fe it increased up to 46.8 mg L⁻¹ Cr(VI), and then, decreased at 95.3 mg L⁻¹ Cr(VI). As part of the Cr(III) and Fe(II) remained in solution, the precipitated fraction of chromium was probably in form of Cr(III) hydroxides. In both experiments, the removed Cr(III) fraction (probably due to its precipitation) is the larger fraction in the 18 mg L⁻¹ Cr(VI) test but decreased with the increase of the Cr(VI) concentration. However, considering its mass value (in milligram), this precipitated fraction increased with the increase in the Cr(VI) concentration (0.5 to 1.2 mg in Z-Fe and 0.6 to 2 mg in V-Fe).

The presence of Cr(VI) in solution after batch tests was detected only in experiments with a high initial concentration of Cr(VI) (95.3 mg L⁻¹) (Fig. 7). In these experiments, Fe(II) was not detected in solution, due to its oxidation during chromium reduction. Therefore, the absence of Fe(II) (Fig. 5) and the presence of 6% Cr(VI) in the solution containing 95.3 mg L⁻¹ Cr(VI) (Fig. 7) indicate that the amount of Fe(II) released by Z-Fe and V-Fe was not sufficient to oxidize all the Cr(VI). Hence, Cr(VI) reduction is highly dependent on the release of Fe(II) (Kwak et al. 2018).

Characterization of adsorbents before and after batch tests

Natural zeolite (Z) and vermiculite (V), as well as their modified samples (Z-Fe and V-Fe) and those resulting from batch tests with a solution containing 95.3 mg L⁻¹ Cr(VI) (Z-Fe/Cr and V-Fe/Cr), were analyzed by FTIR spectroscopy and XRD (Figs. 8 and 9). Analysis of the FTIR spectra revealed that all materials showed bands at 3424 and 1631 cm⁻¹, respectively, referring to the stretching vibrations of the OH groups of water (Zhang et al. 2009; Aloulou et al. 2017) and the bending vibration of the residual water molecules (Aloulou et al. 2017). The band at around 1435 cm⁻¹ is found only in the untreated

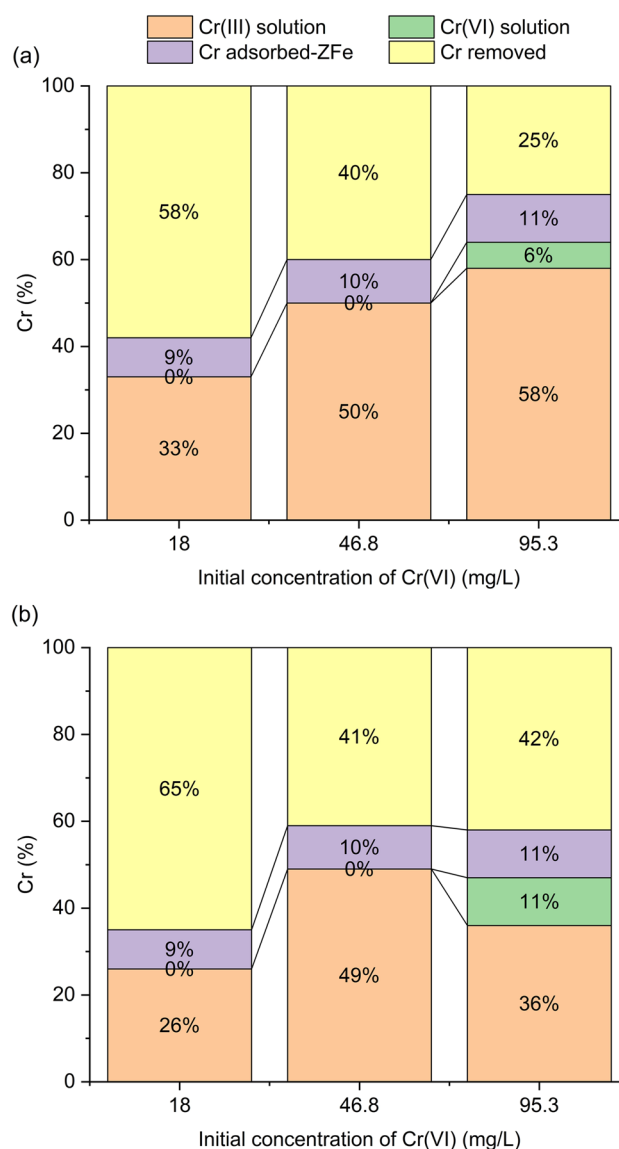


Fig. 7 Percentage of Cr adsorbed onto **a** Z-Fe and **b** V-Fe, and in their respective solutions and removed fractions after Cr(VI) removal test, as a function of Cr(VI) concentration (18, 46.8, and 95.3 mg L⁻¹). The % values correspond to the content of Cr in 1 g of mineral and 50 mL of the Cr(VI) solution

minerals (Z and V) and is attributed to the C–O bond stretching of the adsorbed CO₂ (Polisi et al. 2019).

In zeolite samples (Z and Z-Fe/Cr), bands at 1206 and 1060 cm⁻¹ are attributed to external vibration and internal linkages between SiO₄ and AlO₄ tetrahedra, respectively (Mohamed et al. 2008; Ali et al. 2012). Bands at around 1000 cm⁻¹ (in all vermiculite samples), 670, and 460 cm⁻¹ (in all vermiculite and zeolite samples) are attributed to Si–O–Si stretching and bending vibration (Liu et al. 2010; Ruíz-Baltazar et al. 2015; Huang et al. 2015). In all zeolite

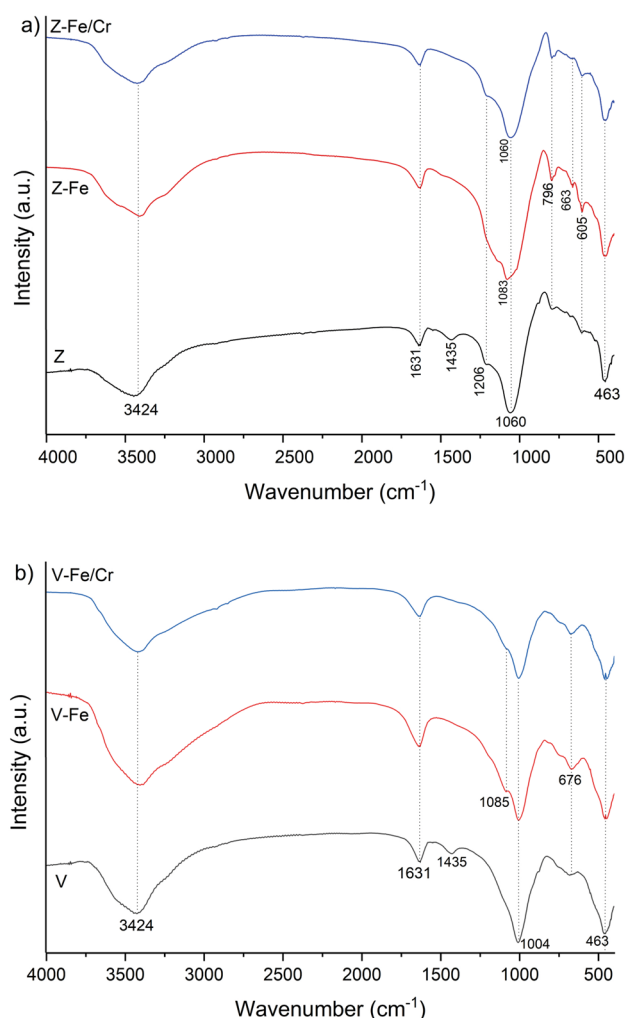


Fig. 8 FTIR spectra of **a** zeolite (Z, Z-Fe and Z-Fe/Cr) and **b** vermiculite (V, V-Fe and V-Fe/Cr)

samples, the band around 790 cm^{-1} is assigned to symmetric stretching of the internal tetrahedra (Charkha et al. 2012).

On the other hand, only the modified minerals (V-Fe and Z-Fe) and V-Fe/Cr presented the band at around 1080 cm^{-1} . According to Zhang et al. (2020), this band can be attributed to tetrahedral asymmetric internal stretching vibrations due to dealumination of zeolites. They also reported that the strong electronegativity of Si relative to that of Al led to a high vibration frequency of this band. Ayad et al. (2020) and Sydorchuk et al. (2020) also observed the presence of 1080 cm^{-1} band, respectively, in zeolite Y and clinoptilolite after the dealumination process.

According to Ma et al. (2021), the occurrence of band shifting at $950\text{--}1090\text{ cm}^{-1}$ is associated to the vibration, length and angle of the Si–O–T bond in zeolites, and it is very sensitive and shifts with a change of Si/Al ratio in zeolites. Therefore, these authors proved that the Si/Al ratio (SAR) of zeolites can be measured by correlating ICP-OES

spectroscopy data with that of position of the IR band at $950\text{--}1090\text{ cm}^{-1}$. They proposed a linear equation to calculate the zeolite SAR: $y = 0.0458x - 43.584$, where y is the SAR and x is the asymmetric stretching frequency of the Si–O–T band in cm^{-1} . Sadrara et al. (2021) also found that drift-FTIR spectroscopy in conjunction with multivariate calibration and classification methods can be used to determine the SAR of zeolite.

Since the equation proposed by Ma et al. (2021) can be used to zeolite with $1 < \text{SAR} < 5$, we calculated the SAR value for our zeolite sample (whose SAR is about 5 according to its chemical composition). We also considered the band at 1060 cm^{-1} for the untreated zeolite (Z) and the band at 1083 cm^{-1} for the modified zeolite (Z-Fe). The resulting SAR value for the untreated zeolite was 5 (which corroborates the value obtained from the chemical composition) and for the modified zeolite (Z-Fe), it was 6. However, the SAR value returned to 5 in Z-Fe/Cr — since in this sample, the band at about 1060 cm^{-1} is present while that at 1080 cm^{-1} is absent (Fig. 8). We believe that during the exchange process with K^+ ions (from the $\text{K}_2\text{Cr}_2\text{O}_7$ solution), part of the iron ions (probably in the form of Fe^{3+}) was displaced from the zeolite cavities to occupy (by isomorphic substitution) the vacant spaces left by Al^{3+} in the tetrahedral sites due to dealumination. Consequently, the value of the Si/Al ratio would not change in this sample. However, to confirm this hypothesis, further studies need to be carried out in the future.

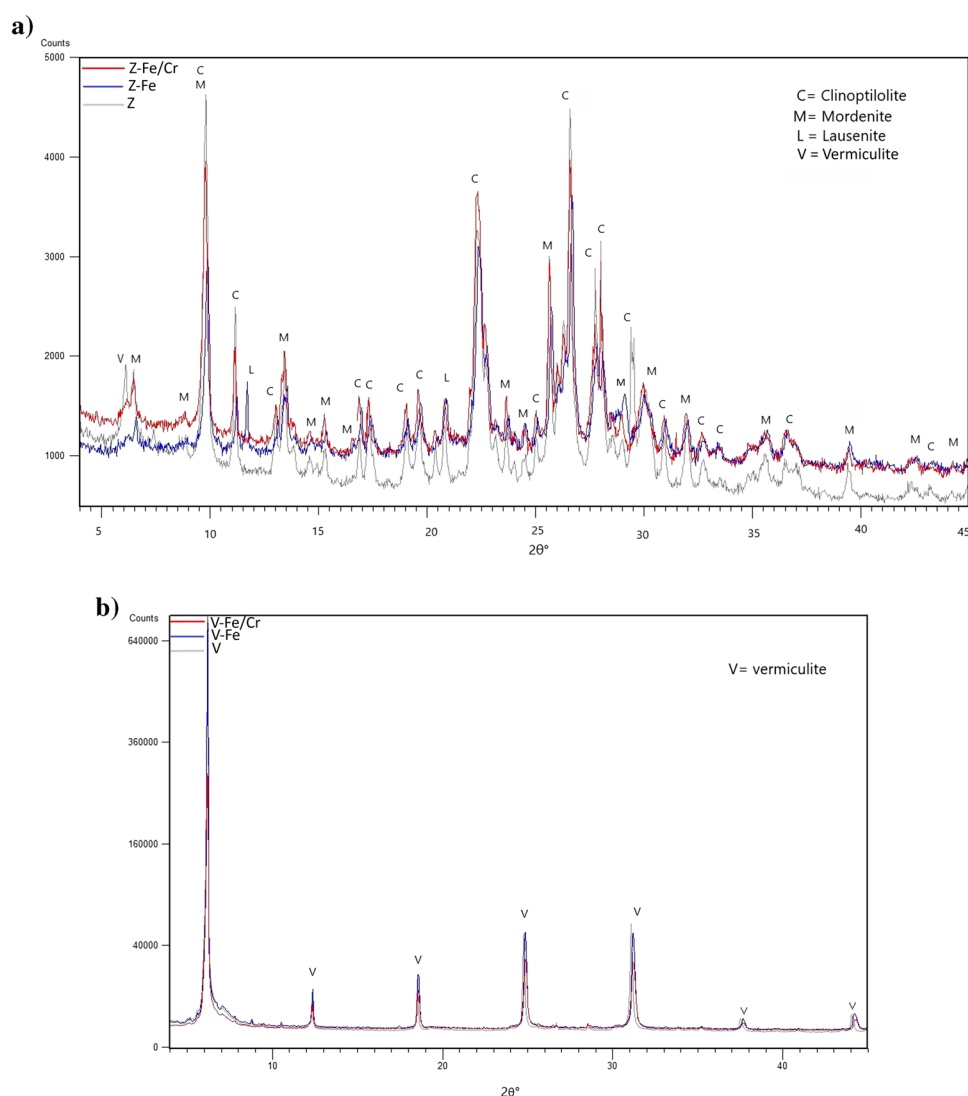
Although the equation proposed by Ma et al. (2021) cannot be used to calculate the SAR of the vermiculite structure (which SAR is 3 according to its chemical composition), the band at around 1080 cm^{-1} also appeared in the modified samples before (V-Fe) and after contact with Cr(VI) (V-Fe/Cr), along with 1060 cm^{-1} .

Therefore, the increase in the Si/Al ratio of Z-Fe and V-Fe corroborates the hypothesis of the occurrence of the dealumination process during the treatment of minerals (as discussed in “Treatment of the adsorbents with Fe(II)” regarding the decrease in pH_{PZC} and CEC values of modified minerals).

X-ray diffractograms of the untreated minerals (Z and V) did not change after Fe(II) treatment (Z-Fe V-Fe) and after the Cr(VI) removal tests (Z-Fe/Cr and V-Fe/Cr) (Fig. 9). Only Z-Fe presented a reflection probably related to lausenite, an iron(III) sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$). This crystallographic phase may have formed by the oxidation of iron from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution, used to modify the mineral adsorbents. However, the presence of this precipitate did not interfere in the removal of Cr(VI) by Fe(II) reduction.

Although reduction of Cr(VI) by Fe(II) leads to the precipitation of Cr(III)/Fe(III), no changes were observed in the crystal structures of zeolite and vermiculite (Fig. 9). Amorphous or poorly ordered products, such as a mixed

Fig. 9 X-ray diffractograms of **a** zeolite — untreated (Z), modified with Fe(II) (Z-Fe) and used in Cr(VI) batch test (Z-Fe/Cr) — and **b** vermiculite — untreated (V), modified with Fe(II) (V-Fe) and used in Cr(VI) batch test (V-Fe/Cr)



phase of $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ must have been formed (Kiser and Manning 2010). Kiser and Manning (2010) observed the formation of a nanoscale precipitate on the mineral surface, which is either a pure Fe(III) or Cr(III) hydroxide, or a mixed Fe(III)-Cr(III) hydroxide. According to Seaman et al. (1999), the solubility of Cr(III) is lower in the mixed hydroxide than in pure $\text{Cr}(\text{OH})_3$. Therefore, the Cr(III) and Fe(III) precipitates are very stable under most soil conditions.

Mechanisms of Cr(VI) removal

Experimental results obtained in this study indicate that zeolite and vermiculite modified with Fe(II) are efficient in removing Cr(VI) from solution by ion exchange followed by redox process. The mechanisms of reduction of Cr(VI)

to Cr(III) by Fe(II) from the modified minerals and the precipitation of the oxidized fractions are discussed below.

Removal of Cr(VI) from solution occurred as Fe(II) was released from Z-Fe and V-Fe (by cation exchange with another cation from solution) and participated in a redox reaction that reduced Cr(VI) to Cr(III). To verify which cations are able to displace Fe^{2+} ions from zeolite and vermiculite, the amount in milliequivalents of Fe^{2+} , Cr^{3+} , and K^+ per gram of the minerals (meq g^{-1}) was evaluated in the final solid samples from the 95.3 mg L^{-1} Cr(VI) removal test and compared with the CEC of modified zeolite and vermiculite (Table 3). The cation exchange capacity (CEC) value of both Z-Fe and V-Fe was higher than their respective Fe(II) content, revealing that their exchange sites were not 100% occupied with Fe(II).

Potassium ions from the $\text{K}_2\text{Cr}_2\text{O}_7$ solution (0.9 meq g^{-1}) displaced 0.4 meq g^{-1} of Fe(II) and 0.5 meq g^{-1} of other

Table 3 Modified zeolite (Z-Fe) and vermiculite (V-Fe) cation exchange capacity (CEC) and concentrations (in meq g⁻¹) of K⁺ and Cr³⁺ in Z-Fe and V-Fe and Fe²⁺ released from both samples (samples from the 95.3 mg L⁻¹ Cr(VI) removal test)

	CEC	Fe ²⁺ (initial)	K ⁺ (in)	Cr ³⁺ (in)	Fe ²⁺ (out)
(meq g ⁻¹)					
Z-Fe	1.5	0.5	0.9	0.03	0.4
V-Fe	1.5	0.7	0.03	0.03	0.3

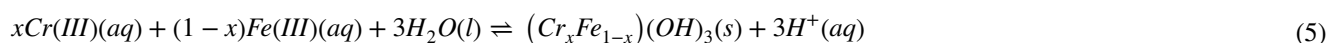
cations from zeolite. Potassium has a smaller hydrated radius (0.33 nm) than iron (0.45 nm) and chromium (0.46 nm) (Nightingale 1959), which leads to its preferential exchange from sites in both zeolite and vermiculite. However, in the case of vermiculite, neither potassium (0.03 meq g⁻¹) nor chromium(III) (0.03 meq g⁻¹) was the main cation exchanged with Fe(II) (0.3 meq g⁻¹) from its interlayer space. These cations may be adsorbed onto the mineral surface. If K⁺ ions were occupying the interlayer space of vermiculite, its basal plane (001) must be collapsed, hindering extensive ion exchange; nevertheless, no change in the XRD of vermiculite was observed after the Cr(VI) removal test (Fig. 9).

During the Cr(VI) removal tests, the pH solution remained acidic (around 5) in both the zeolite and vermiculite samples. The Brønsted acid sites (bridging hydroxyls neighboring the tetrahedrally coordinated Al sites) and Lewis acid sites (assigned to aluminum in defect positions or extra-framework Al species) (Li et al. 2017) of these minerals may contribute to the decrease in pH due to ionic exchange processes. The pH of the solution becomes more acidic when the exchange

process occurs between more hydrated cations (Ca²⁺ in zeolite and Mg²⁺ in vermiculite) than for the less hydrated cations (K⁺ from solution), causing a decrease in water content, and dissociating the residual water (Yariv and Cross 1979).

The acid solution, in turn, can effectively interfere in the cationic exchange process, as H⁺ competes with other cations in solution for the minerals exchange sites, as observed with vermiculite. Shinzato et al. (2020) observed that NH₄⁺ adsorption by vermiculite in acidic solution was more affected than by zeolite. They found that maximum NH₄⁺ adsorption occurred at pH 5 for zeolite and pH 7 for vermiculite. In our tests, the pH of all solutions remained slightly acidic (around 5). Therefore, the H⁺ ions in acidic solutions probably affected the cation exchange of vermiculite competing with K⁺ for the exchangeable sites.

In this context, vermiculite removed H⁺ ions from the solution and, consequently, released Fe(II). In aqueous solutions, the H⁺ ions are in form of hydrated hydronium (H₃O⁺·*n*H₂O), which did not change the interlayer space of vermiculite, maintaining the reflection of the basal plane (001) at 1.44 nm (Bokij and Arkhipenko 1977). Removal of H⁺ ions by vermiculite, in turn, released Fe(II) to reduce Cr(VI), a process which also consumes H⁺ (Eqs. 1 and 2) and, consequently, increases the pH of the solution. After reduction, at *pH* > 5, Cr(III) readily precipitates as Cr(OH)₃ (Seaman et al. 1999), and in the presence of Fe(III), it precipitates as a mixed hydroxide phase (Eq. 5) (Schwertmann et al. 1989). The ion exchange and redox mechanisms which involve, respectively, the removal and consumption of H⁺ increase the pH of the solution and, consequently, increase the precipitated fraction of Cr(III) (Fig. 7).



On the other hand, the hydrolysis and precipitation of Fe(III) and Cr(III) lower the pH (Eq. 5), suppressing the precipitation of Cr(OH)₃ or the mixed Fe(III)/Cr(III) hydroxide (Seaman et al. 1999), and leaving the remaining Cr(III) ions in solution (Fig. 6). To confirm whether the precipitation of iron and chromium can actually lower the pH of the solution, 0.07 g of FeSO₄·7H₂O (corresponding to 14 mg of Fe(II), which is close to the content of Fe(II) released by vermiculite) was added to 50 mL of solution with 95.3 mg L⁻¹ Cr(VI). After 1 h of contact time, the solution pH (initially around 5) decreased to 4–3, forming a layer of Fe(III)/Cr(III) hydroxide precipitates.

In aqueous solutions with *pH* < 4, the chromium ions are in the form of Cr³⁺, whereas the species Cr(OH)²⁺ occur in solutions with a pH between 4 and 6.5 (Palmer and Wittbrodt 1991). Therefore, Cr³⁺ ions should predominate in solution in pH range 4–3. However, these cations were not adsorbed onto the zeolite and vermiculite exchange sites as

they were less competitive than the K⁺ and H⁺ ions in the solution, respectively.

Considering the *pH*_{PZC} of 4.5 of both modified minerals, Cr(VI) ions (as chromate anions) were not adsorbed onto the minerals surface, which were negatively charged in solutions around pH 5. After their reduction by Fe(II) and precipitation as mixed hydroxides of Cr(III) and Fe(III), the solution pH decrease to 4–3, limiting Cr³⁺ precipitation, as discussed before. In this acidic solution, Cr³⁺ ions were also not adsorbed onto the mineral surface, as they become positively charged when *pH* < *pH*_{PZC}.

Kiser and Manning (2010) suggested that the displacement of Fe(II) from Fe(II)-faujasite was caused by the redox products (Cr(III) or Fe(III)). However, they did not consider the competition with Na⁺ ions, present in the Cr(VI) solution prepared from Na₂CrO₄. We suppose that the Fe(II) ions were displaced by Na⁺ and not by the Cr(III) ions, as Na⁺ has a

greater preference for zeolite exchange sites than Cr(III), due to its smaller hydrated radius (0.36 nm) (Strawn et al. 2019).

The remaining Cr(III) in the solution has to be removed to prevent its oxidation back to Cr(VI). Cr(III) removal from the solution can be performed by precipitation (increasing $pH > 5$) or by adsorption using untreated vermiculite or zeolite. The test conducted in a previous study using untreated vermiculite to remove Cr(III) (100 mg L^{-1}) from solution presented a removal efficiency of 100% (corresponding to a removal of 10 mg g^{-1}). Shinzato et al. (2009) also demonstrated that natural zeolite can be used to adsorb Cr(III) from solution. Kiser and Manning (2010) also observed that natural zeolite (faujasite) can also adsorb Cr(III) from solution. In this case, the exchange process of Cr(III) ions in solution with those of the vermiculite (Mg^{2+}) and zeolite (Ca^{2+}) is favorable, as long as no other cation is present to compete.

Many authors concluded that Cr(VI) reduction by Fe(II)-minerals depends on the acidity of the solution. Liu et al. (2010) used Fe(II)-vermiculite to remove Cr(VI) and obtained a maximum removal efficiency of 99.5% at pH 1. Kiser and Manning (2010) observed that the efficiency of the reduction of Cr(VI) by Fe(II) released from clay minerals increased in the range pH 3–4, while Kwak et al. (2018) conducted all the experiments at pH 3 to prevent the precipitation of Fe(II). In our tests, none of the solutions needed to be corrected with the addition of acid to increase the Cr(VI) removal efficiency, due to the reasons discussed previously.

Despite part of the Cr(VI) may have been adsorbed by Fe(III) precipitates (Ajouyed et al. 2010), this mechanism was not assessed in the present study, as it would also be limited by the reduction process (conducted by Fe(II) ions). Therefore, the adsorption properties of the Fe(III) precipitates can be assessed in the absence of Fe(II), in order to evaluate its capacity in removing Cr(VI) from the solution.

Conclusions

Untreated zeolites and vermiculite exhibit no or little affinity for Cr(VI) adsorption, respectively. However, they have a high ability to adsorb Fe(II) ions, which reduce Cr(VI) in solution when released by cation exchange.

Vermiculite retained more Fe(II) than zeolite, probably because its main exchangeable cation (Mg^{2+}) has a hydrated radius close to that of Fe(II). Exchangeable cations in zeolite (Ca^{2+} , K^{+}) are smaller, requiring a solution with a higher concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ for mineral treatment.

The modification of zeolite and vermiculite could result in an increase in the Si/Al ratio and, consequently, in a decrease in the pH_{PCZ} and CEC values, probably due to the dealumination of their structures (caused by the acidic pH during the treatment with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

The main mechanisms involved in the Cr(VI) removal were ion exchange followed by the reduction process. The Fe(II) of the zeolite exchange sites was displaced by K^{+} from the potassium dichromate solution, while in vermiculite this exchange occurred with the H^{+} ions from an acidic solution.

Under experimental conditions, Z-Fe removed more K^{+} ions from the solution than V-Fe, and, consequently, released more Fe(II) ions into the solution. The release of Fe(II) by vermiculite depended on the pH of the solution. Nevertheless, both V-Fe and Z-Fe samples released enough Fe(II) to reduce 100% Cr(VI) in solutions up to 46.8 mg L^{-1} Cr(VI). The remaining Fe(II) in the exchangeable sites of V-Fe can be further used to treat solutions with a low concentration of Cr(VI) ($< 10 \text{ mg L}^{-1}$).

The rate of the redox reaction between Cr(VI) and Fe(II) is high. In 1 min, 100% of Cr(VI) was reduced (solution with 18 mg L^{-1} Cr(VI)) by both modified minerals. Reduction of Cr(VI) leads to the precipitation of Fe(III) and Cr(III) hydroxides and decreased the pH of the final solution ($pH < 5$). At $pH < 5$, the precipitation of Cr(III) ions was inhibited and they remained in solution. The adsorption of Cr(III) was limited by the competition of K^{+} and H^{+} for the adsorption sites in zeolite and vermiculite, respectively. However, the adsorption of Cr(III) from solution by untreated vermiculite and zeolite can avoid its reoxidation to Cr(VI).

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Declarations

Ethics approval and consent to participate Not applicable.

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