

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

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Research Article

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Abstract

Mechanisms of Cr(VI) reduction by Fe(II) modified zeolite 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). 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 the solution by batch test to evaluate the effect of contact time and Cr(VI) initial concentration. Cr(VI) was 100% reduced to Cr(III) by Z-Fe and V-Fe from solution with 18 mg L^{-1} Cr(VI) in 1 minute. Considering that 3 moles Fe(II) are required to reduce 1 mole 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 were sufficient to reduce 100% of Cr(VI) in solution by up to 46.8 mg L^{-1} Cr(VI), and about 90% (V-Fe) and 95% (Z-Fe) in solution with 95.3 mg L^{-1} Cr(VI). The assess of the Fe(II), Cr(III), Cr(VI), and K^+ contents of the adsorbents and solutions after batch tests indicated that K^+ ions from $\text{K}^+\text{Cr}^{+6}\text{O}_4^{2-}$ 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. Therefore, the release of Fe(II) from Z-Fe and V-Fe involved cation exchange between, respectively, K^+ and H^+ ions from solution. The reduction of Cr(VI) by Fe(II) caused the precipitation of Cr(III) and Fe(III), and the decrease of pH of the solution to < 5 . As acidity limits the precipitation of Cr(III) ions, they remained in solution and were not adsorbed by both adsorbents (since they prefer to adsorb K^+ and H^+). To avoid oxidation, Cr(III) can be removed by precipitation or adsorption by untreated minerals.

1. 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 (NRC 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 strongly oxidizing compounds and, consequently, highly toxic to the human health in any concentration (Hawley et al. 2004). Therefore, all effluents containing Cr(VI) must be treated before being discharged into water bodies.

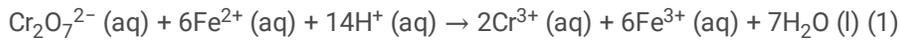
Removal of Cr(VI) from industrial effluents is usually done by precipitation of Cr(III) as hydroxide, after redox reactions by the use of reducing substances, such as sodium metabisulphite. Chemical precipitation also requires the use of large quantities of reagents, such as sodium hydroxide, which often makes this technique expensive (Srivastava and Thakur 2007).

Treatment of Cr(VI)-contaminated effluents is also possible by combining reduction of Cr(VI) and adsorption of Cr(III). Cr(III) ions can return to their oxidized state in the presence of oxidant agents, such as manganese ions, but adsorption prevents reoxidation (Eary et al. 1988; Palmer and Wittbrodt 1991; Kwak et al. 2018). Adsorption can also be expensive, depending on the type of adsorbent (Maronezi et al. 2019; Singh 2020). However, minerals with large specific surface and high ion exchange capacity, such as zeolites and vermiculite, are low-cost options with good performance in pollutant removal (Shinzato et al. 2020).

Zeolites are aluminosilicates with negative permanent charge derived from the replacement of part of silicon by aluminum in the tetrahedral framework (Barrer 1982). This negative charge is compensated by cations such as K^+ , Na^+ , and Ca^{2+} connected by adsorption inside the pores, which can be replaced by other cations (Pabalan & Bertetti 2001). Vermiculite is a 2:1 phyllosilicate, whose structure is formed by two tetrahedral layers of $\text{Si}^{4+}/\text{Al}^{3+}$ oxide connected to an octahedral Al^{3+} or Mg^{2+} hydroxide (Meunier 2005). Vermiculite is negatively charged due to unbalanced substitutions, predominantly, in the tetrahedral ($\text{Si}^{4+}\text{-Al}^{3+}$) layer. Its residual negative charge is compensated by the interlayer cations (Jackson 1979).

Negatively charged minerals are usually applied in removing heavy metals from solution (Zamzow et al. 1990; Curkovic et al. 1997; Mier et al. 2001; Wingenfelder et al. 2005; Shinzato et al. 2007; Margeta et al. 2013). Nevertheless, their use for chromate ions (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 organo-zeolite, which adsorbs (CrO_4^{2-}) on its surface, while the capacity of adsorbing cations in the pores and channels of organo-zeolites is preserved because HDTMA molecules are too large to enter the structural voids of zeolites.

However, the adsorption of Cr(VI) does not change its toxicity, while the reduction reactions have the advantage of transforming chromium into its less toxic form. Reducing agents, such as Fe(II) ions, can be adsorbed by minerals as zeolite and vermiculite in order to reduce Cr(VI) (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 equations 1 and 2, respectively.



Using minerals as support of Fe(II) ions instead of using its dissolved salt is more adequate to reduce Cr(VI), as it consumes smaller amounts of Fe(II) salts and does not require the addition of acids to obtain an acidic condition (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) in solution by samples of zeolite and vermiculite modified with Fe(II) ions. In addition, the ability of their exchange sites to maintain and release iron in reduced form was evaluated. This study can contribute to the understanding of the main mechanisms of removal of Cr(VI) by natural and low-cost adsorbents modified with Fe(II).

2. Materials And Methods

2.1 Materials characterization

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 grain size < 200 mesh.

The mineralogical composition of zeolite (Z) was analyzed in an X-ray diffractometer (XRD) (D8 Advance/Bruker). 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. Vermiculite (V) was treated to XRD analysis with methods described by Theisen and Harward (1962), Anderson (1963), and Jackson (1979), consisting in heating at 350 and 550°C a sample previously saturated with K⁺, and treating with ethylene glycol a sample saturated with Mg²⁺. Natural and heated minerals samples were analyzed in XRD (D8 Advance/Bruker) with 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 zeolite and vermiculite was determined by X-ray fluorescence (XRF) spectroscopy (Axios Advanced PANalytical). For cation exchange capacity (CEC) determination, 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 in a flame photometer (DM-62/Digimed). The CEC value corresponds to the Na⁺ concentration in milliequivalents per gram of sample (meq g⁻¹).

2.2 Preparation of zeolite and vermiculite with Fe(II)

Minerals were saturated with Fe(II) ions in 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 at a contact time 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 zeolite and vermiculite samples can remove Cr(VI) from the 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 minutes and centrifuged, the Cr(VI) concentration was determined in the final solutions.

The Fe(II) concentration of 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 solution. Fe(II) concentration was determined using 4 mL of 1.10-phenanthroline, which forms with Fe(II) a complex of orange color, and 4 mL of ammonium acetate buffer solution to intensify this color, a procedure described at SMWW (1999). Fe(II) concentration was quantified in a UV-Vis spectrophotometer (10S/ThermoScientific Genesys) using a wavelength (λ) of 510 nm. The concentration of K⁺ was determined in a flame photometer (DM-62/Digimed).

2.3 Cr(VI) removal - batch tests

The Cr(VI) removal tests were 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 being agitated for a specified time, they were centrifuged to have their solutions analyzed. These tests were performed at room temperature and in triplicate.

The effects of contact time (1 to 60 minutes) and initial concentration of Cr(VI) (18 to 95.3 mg L⁻¹) were evaluated. To evaluate the influence of time in the Cr(VI) removal efficiency of each mineral, 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 60 minutes of contact time (determined in the previous test).

The second set of batch tests of Cr(VI) removal was performed using Z-Fe and V-Fe that already underwent 60 minutes batch tests. This second set of batch tests was performed almost one year after the first experiments to verify if the remaining Fe(II) did not oxidize and if this material can be reused in the 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 minutes under stirring.

The final samples of all batch tests were centrifuged 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), adding 2 mL of 1.5-diphenylcarbazide (dissolved in acetone) and 4 drops of sulfuric acid (10%) to 100 mL of the sample solution. Reaction with Cr(VI) forms a pink color solution, analyzed on 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). To determine the Cr(III) concentration the total Cr value was subtracted from the Cr(VI) levels. The concentration of K⁺ (from 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 equation (3), whereas the Cr(VI) removal capacity (Q_e, mg g⁻¹) was determined by equation (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_e are the initial and equilibrium concentrations (mg L⁻¹).

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

where Q_e is equal to the total 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); V is the volume (L) of the solution.

The amount of Fe(II) adsorbed on the mineral exchange sites was also evaluated before and after Cr(VI) removal tests, using the method described before (Kwak et al. 2018) to extract 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 used in the batch tests (Z-Fe/Cr and V-Fe/Cr) were analyzed by Fourier transform infrared spectroscopy (FTIR) to identify the main functional groups of minerals responsible for removing Cr(VI). This analysis was performed on the Shimadzu spectrometer (model IRP Prestige-21), using the percentage absorption mode, prepared in dry KBr tablets, with a resolution of 4 cm⁻¹ and 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 form during the removal tests, all samples were analyzed by XRD (D8 Advance/Bruker) after batch tests. 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.

3. Results And Discussion

3.1 Characterization of adsorbents

The X-ray diffraction analysis indicated that zeolite sample is a mixture of clinoptilolite and mordenite, while the vermiculite sample is pure - identified in 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 (indicating no change in the basal plane), and reflection at 1 nm in the K-saturated sample heated at 350 and 550 °C due to the collapse of the 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.

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

Adsorbent	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
	(wt%)												
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

3.2 Treatment of the adsorbents with Fe(II)

Zeolite and vermiculite were treated with a solution of Fe(SO₄)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 Cr(VI) from solution (respectively, 0 and 3%), while the efficiency of the modified samples improved with increasing of the Fe(II) concentration (Fig. 3). The increase in temperature only improved the treatment of zeolite with 1mol L⁻¹ Fe(SO₄)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 mineral surfaces (Nightingale, 1959).

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).

The exchangeable cations of the zeolite pores (K⁺ and Ca²⁺) have smaller hydrated radii (respectively, 0.33 nm and 0.41 nm) 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⁺ with vermiculite is more efficient than with zeolite. This is probably the reason why zeolite requires 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 spent 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).

Table 2
Content of Fe(II) ions (mg g⁻¹) in samples of zeolite and vermiculite before and after treatment with, respectively, 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).

Sample	Before	After treatment
	Fe(II) (mg g ⁻¹)	
Zeolite	1.32 ± 0.06	15.1 ± 0.5
Vermiculite	0.61 ± 0.03	21.8 ± 1.2

Vermiculite adsorbed more Fe(II) than zeolite, despite its slightly lower CEC (2.21 meq g⁻¹) compared to zeolite (2.59 meq g⁻¹). This is due to the closer similarity of the hydrated radius of Mg²⁺ (0.43 nm), the main exchangeable cation of vermiculite, with the hydrated radius of Fe(II) (0.45 nm); the difference is larger in respect to the hydrated radius of the exchangeable cation of zeolite, Ca²⁺ (0.41 nm) (Strawn et al. 2020).

3.3 Cr(VI) removal - batch tests

3.3.1 Effect of contact time

Removal of Cr(VI) by Z-Fe and V-Fe attained 100% in all the time intervals 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) from the solution.

After Cr(VI) removal test, the percentage of Fe(II) remained in minerals composition (Z-Fe and V-Fe) and in solution are indicated in figure 2. In figure 2, the amount of Fe(II) released by minerals minus the Fe(II) found in the solution corresponds to the fraction of iron that was oxidized (removed fractions), while the fraction of Fe(II) released from Z-Fe and V-Fe corresponds to the content of Fe(II) from solution and removed fractions. Although this redox reaction occurs under acidic conditions (eq. 1 and 2), the 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 in reducing Cr(VI).

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

Since three moles of Fe(II) are required to reduce one mole of Cr(VI) (eq. 1 and 2), at least, 2.9 mg of Fe(II) were needed to reduce 0.9 mg Cr(VI). Acidic extraction conducted on 1 g of Z-Fe and V-Fe (before and after the batch tests of Cr(VI) removal) revealed

the contents 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 figure 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 the time intervals (Fig. 2). Z-Fe released more Fe(II) (regardless of time) than V-Fe, whose content of released Fe(II) 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).

Fig. 3 – Efficiency (%) and removal ($mg\ g^{-1}$) of K^+ from $K_2Cr_2O_7$ solutions by Z-Fe and V-Fe during Cr(VI) removal test as a function of time.

The remove of K^+ concentration in the solution with time (Fig. 3) as well as the release of Fe(II) to the solution (Fig. 2) were 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 $K^+ \leftrightarrow Fe^{2+}$ 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, therefore, cation exchange requires a collapse of the internal site, i.e., a decrease in the (001) basal space from 14 nm 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 (item 3.4).

To verify whether the remaining iron fraction of Z-Fe (5 mg) and V-Fe (15 mg) remained in reduced form, a second set of Cr(VI) removal test was performed with samples underwent 60 minutes batch test. The results revealed that the remained iron was still in reduced form, even after one year. The Cr(VI) removal by V-Fe was higher (43.3% and $0.39\ mg\ g^{-1}$ of removal efficiency) than Z-Fe (15.8% and $0.14\ mg\ g^{-1}$ of removal efficiency) for having more Fe(II) content in its exchangeable sites. Therefore, V-Fe can still be reused to remove low levels of Cr(VI) in the solution ($<10\ mg\ L^{-1}$).

3.3.2 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 with 18 and $46.8\ mg\ L^{-1}$ Cr(VI) to 94% in solutions with $95.3\ mg\ L^{-1}$. Similarly in V-Fe, which efficiency went from 100% in solutions with 18 and $46.8\ mg\ L^{-1}$ down to 89% in solution with $95.3\ mg\ L^{-1}$ Cr(VI).

The mass fraction of Cr(VI) removed from solution in 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 solutions of $18\ mg\ L^{-1}$ to $4.5\ mg\ g^{-1}$ for solutions with $95.3\ mg\ L^{-1}$, while for V-Fe, in the same range of concentration, it increased from 0.9 to $4.2\ mg\ g^{-1}$ (Fig. 4).

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

Considering again, the need for 3 moles 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 solutions 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 with $46.8\ mg\ L^{-1}$ Cr(VI) is 7.5 mg Fe(II) (50% for Z-Fe and 34% to V-Fe), and for $95.3\ mg\ L^{-1}$ Cr(VI) is 15.3 mg Fe(II) (102% for Z-Fe and 69.5% to V-Fe). Therefore, the decrease in the efficiency of Cr(VI) removal from solutions with $95.3\ mg\ L^{-1}$ of Cr(VI) indicates that the amount of Fe(II) released by Z-Fe and V-Fe was not enough to reduce Cr(VI) available in the solution (Fig. 5). The amount of Fe(II) released from Z-Fe and V-Fe to the solution and the removed fraction, which probably was oxidized forming hydroxides precipitates, increased with the increase of Cr(VI) concentration, from 18 to $95.3\ mg\ L^{-1}$.

Fig. 5 - Percentage of Fe(II) remained in (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 minerals and 50 mL of Cr(VI) solutions.

Since the K^+ contents also increased with the increase of Cr(VI) concentrations (from potassium dichromate), in solution with $18 \text{ mg L}^{-1}\text{Cr(VI)}$ and $13.4 \text{ mg L}^{-1} \text{ K}$, 100% of K^+ was removed by Z-Fe (corresponding to $0.7 \text{ mg g}^{-1}\text{K}^+$ 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 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 high efficiency of Z-Fe in removing K^+ from solution likely by ion exchange than V-Fe.

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

In contrast to the tests performed with lower Cr(VI) concentrations, Fe(II) was not detected in solution with $95.3 \text{ mg L}^{-1}\text{Cr(VI)}$, and the removed fraction (oxidized iron) increased with Cr(VI) concentration (Fig. 5). The required amount of Fe(II) to fully reduce the Cr(VI) in 50 mL of a solution with 95.3 mg L^{-1} was 15.3 mg (corresponding to 69.5%). The actual amount of Fe(II) released in 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 $95.3 \text{ mg L}^{-1} \text{ Cr(VI)}$, the fraction of Fe(II) remaining in Z-Fe and V-Fe was not released to reduce all 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 on the permanent-charged sites, by covalent binding with hydroxyl groups, and by cation exchange (Brigatti et al. 2000). In order to evaluate if reduced chromium was adsorbed by Z-Fe and V-Fe, the Cr(III) content was determined in adsorbents (after acidic extraction) and solutions (Fig. 7). Therefore, the difference between the Cr(VI) contents in the samples before the batch test and the fraction of Cr remained in the solution was considered the precipitated chromium fraction (Fig. 7).

Fig. 7 - Percentage of Cr adsorbed in (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 minerals and 50 mL of Cr(VI) solutions.

An expressive fraction of Cr(III) ions remained in solution (33% - 58% in Z-Fe and 26% - 49% in V-Fe), while only 9–11% of Cr(III) were fixed in the adsorbents (Fig. 7). The fraction of chromium adsorbed on Z-Fe and V-Fe is quite low 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) remained in solution increased with the initial concentration of Cr(VI) in Z-Fe, while for V-Fe it increased up to $46.8 \text{ mg L}^{-1} \text{ Cr(VI)}$, and then, decreased by $95.3 \text{ mg L}^{-1} \text{ Cr(VI)}$. As part of 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 at the $18 \text{ mg L}^{-1} \text{ Cr(VI)}$ test and, then, decreased with the increase of the Cr(VI) concentration. However considering its mass value (in milligram), this precipitated fraction increased with the increase of 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 those experiments, Fe(II) was not detected in solution, due to its oxidation for chromium reduction. Therefore, the absence of Fe(II) (Fig. 5) and the presence of 6% of Cr(VI) in the $95.3 \text{ mg L}^{-1} \text{ Cr(VI)}$ solution (Fig. 7) indicate that the amount of Fe(II) released by Z-Fe and V-Fe was not sufficient to oxidize all Cr(VI). Hence, the Cr(VI) reduction is highly dependent on the Fe(II) release (Kwak et al. 2018).

3.4 Characterization of adsorbents before and after batch tests

Natural zeolite and vermiculite, as well as Z-Fe and V-Fe, were analyzed by FTIR spectroscopy and XRD (Fig. 8 and 9) before and after batch tests with solution from $100 \text{ mg L}^{-1} \text{ Cr(VI)}$. Both materials presented the main bands around 3424 and 1631 cm^{-1} referred, respectively, to water (Zhang et al. 2009) and deformation of OH bonds (Ruíz-Baltazar et al. 2015); and about 1000 and 460 cm^{-1} related to the vibration of the oxygen bonds with silicon (Si-O-Si) (Liu et al. 2010; Ruíz-Baltazar et al. 2015; Huang et al.

2015). The peak around 1435 cm^{-1} in the untreated minerals (V and Z) is attributed to the elongation of C-O of adsorbed CO_2 (Polisi et al. 2019).

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

Z-Fe and V-Fe presented additional bands near 670 cm^{-1} related to the vibration of Fe-O-H (Camenar et al. 2018) and Fe-O (Liu et al. 2010). The band near 1080 cm^{-1} refers to sulfate ion (Camenar et al. 2018). These bands confirm the adsorption of Fe(II) in minerals after treatment. However, these bands' intensity decreased in both samples with chromium (Z-Fe/Cr and V-Fe/Cr), probably due to the oxidation and precipitation of Fe(III) and Cr(III).

X-ray diffractograms of the untreated minerals (Z and V) did not change with 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 reflections related to lausenite, an iron(III) sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$). This crystallographic phase refers to the precipitation of the oxidized iron from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution, used to modify the mineral adsorbents.

Although reduction of Cr(VI) by Fe(II) lead 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 phase of $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ must be formed (Kiser and Manning 2010). Kiser and Manning (2010) observed the formation of a nanoscale precipitate in the surface of Fe-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 smaller 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.

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

3.5 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 modified minerals and the precipitation of the oxidized fractions were 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 milliequivalent of Fe^{2+} , Cr^{3+} and K^+ per one gram of minerals (meq g^{-1}) was evaluated in the final solid samples from the 95.3 mL g^{-1} Cr(VI) removal test, and compared with the CEC of zeolite and vermiculite (Table 3). The cation exchange capacity (CEC) value of both zeolite and vermiculite was higher than their respective Fe(II) content, revealing that their exchange sites were not occupied 100% with Fe(II).

Table 3
– Zeolite and vermiculite cation exchange capacity (CEC) and concentrations (in meq g^{-1}) of K^+ and Cr^{3+} in Z-Fe and V-Fe and Fe^{2+} released from both samples (samples from 100 mg L^{-1} Cr(VI) removal test).

	CEC	$\text{Fe}^{2+}(\text{initial})$	$\text{K}^+(\text{in})$	$\text{Cr}^{3+}(\text{in})$	$\text{Fe}^{2+}(\text{out})$
	(meq g^{-1})				
Z-Fe	2.6	0.5	0.9	0.03	0.4
V-Fe	2.2	0.7	0.03	0.03	0.3

Potassium ions from $\text{K}_2\text{Cr}_2\text{O}_7$ solution (0.9 meq g^{-1}) displaced 0.4 meq g^{-1} of Fe(II) and 0.5 meq g^{-1} of other 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 preference for the exchange sites of 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}) should be the main cation exchanged with Fe(II) (0.3 meq g^{-1}) of its interlayer space. These cations may be adsorbed on 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 Cr(VI) removal test (Fig. 9).

During the Cr(VI) removal tests, the pH solution remained acidic (around 5) in both 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 of pH due to the ionic exchange process. The solution pH becomes more acidic when the exchange process occurs between more hydrated cations (Ca^{2+} in zeolite and Mg^{2+} in vermiculite) for less hydrated cation (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 in vermiculite. Shinzato et al. (2020) observed that the acidic solutions affected more vermiculite than zeolite in the adsorption of NH_4^+ . They found that maximum NH_4^+ 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 from acidic solutions probably affected the cation exchange of vermiculite competing with K^+ for the exchanging 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 ($\text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}$), which did not change the interlayer space of vermiculite, maintaining the reflection of the basal plane (001) at 1.44 nm (Bokj and Arkhipenko 1977). Removal of H^+ ions by vermiculite, in turn, release Fe(II) to reduce Cr(VI), which process also consumes H^+ (eq. 1 and 2) and, consequently, increases the pH of the solution. After reduction, at $\text{pH} > 5$, Cr(III) readily precipitates as $\text{Cr}(\text{OH})_3$ (Seaman et al. 1999), and in the presence of Fe(III), it precipitates as a mixed phase (eq. 6) (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) lowers pH (eq. 6), suppressing the precipitation of $\text{Cr}(\text{OH})_3$ or the mixed Fe(III)/Cr(III) hydroxide (Seaman et al. 1999), and leaving the remained 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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (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.

At acidic conditions, the remaining fraction of Cr(III) was not adsorbed by zeolite and vermiculite because it is less competitive than K^+ and H^+ , respectively. Kiser and Manning (2010) suggested that the displacement of Fe(II) from Fe(II)-faujasite was caused by redox products (Cr(III) or Fe(III)). However, they did not consider the competition with Na^+ ions, present in the Cr(VI) solution prepared with Na_2CrO_4 . We suppose that the Na^+ ions have been displaced by the Fe(II) 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). The Cr(III) removal from the solution can be performed by precipitation (increasing $\text{pH} > 5$) or by adsorption using untreated vermiculite or zeolite. The test conducted in a previous study using untreated vermiculite to remove Cr(III) from solution with 100 mg L^{-1} revealed 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 the solution. Kiser and Manning (2010) observed that natural zeolite (faujasite) can also adsorb

Cr(III) from the solution. In this case, the exchange process of Cr(III) ions from solution with those of vermiculite (Mg^{2+}) and zeolite (Ca^{2+}) is favorable, as long as no other cation competes with them.

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 pH 3-4, while Kwak et al. (2018) conducted all the experiments under pH 3 to prevent the precipitation of Fe(II). In our tests, none of the solutions have to be corrected with the addition of acid to increase the Cr(VI) removal efficiency, due to the reasons discussed before.

Despite part of Cr(VI) may be 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.

4. 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 main mechanisms involved in the Cr(VI) removal were the 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 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 with up to 46.8 mg L^{-1} Cr(VI). The remaining Fe(II) in exchange 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 minute, 100% of Cr(VI) were reduced in solution with 18 mg L^{-1} Cr(VI) by both modified minerals. Reduction of Cr(VI) leads to precipitation of Fe(III) and Cr(III) hydroxides and decreased the pH of the final solution ($\text{pH} < 5$). At $\text{pH} < 5$ the precipitation of Cr(III) ions was inhibited and they remained in solution. The adsorption of Cr(III) was limited by the competition with K^+ and H^+ for the adsorption sites of zeolite and vermiculite, respectively. However, the adsorption of Cr(III) from solution by untreated vermiculite and zeolite can avoid its reoxidation to Cr(VI).

Declarations

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Consent for publication - Not applicable

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Figures

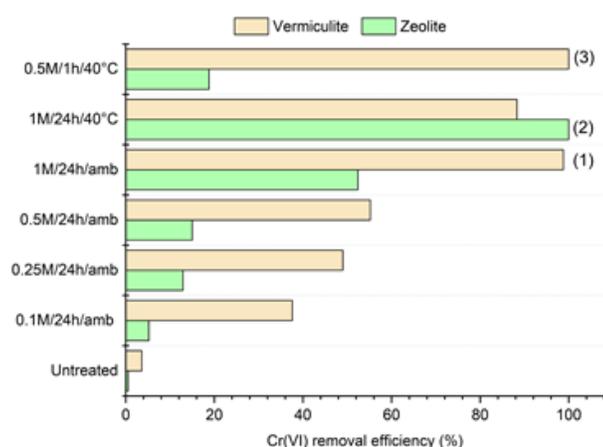


Figure 1

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).

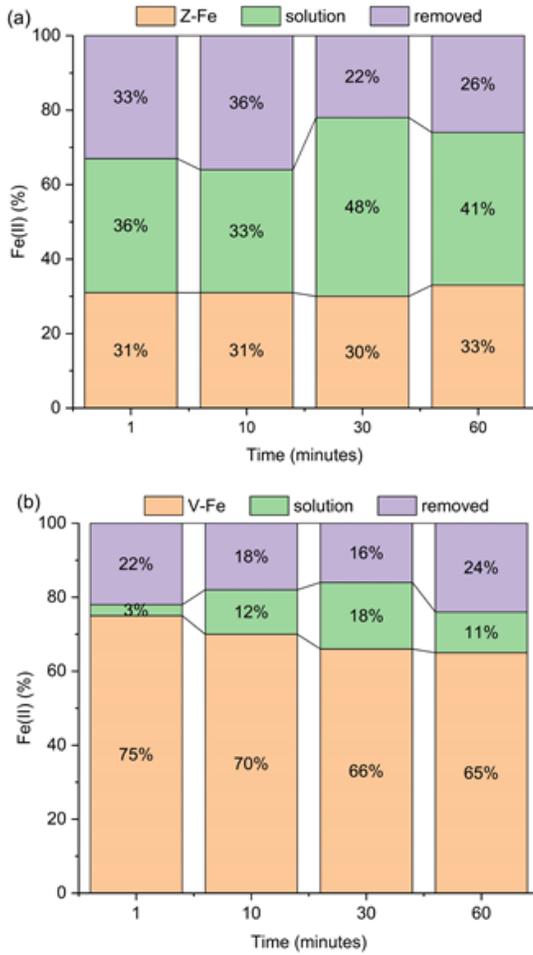


Figure 2

Percentage of Fe(II) remained in (a) Z-Fe and (b) V-Fe, and in their respective solution and removed (oxidized) fractions, after Cr(VI) removal test, as a function of time (1 to 60 minutes). The % values correspond to the content of Fe(II) in 1 g of mineral and 50 mL of solution with 18 mg L⁻¹ Cr(VI).

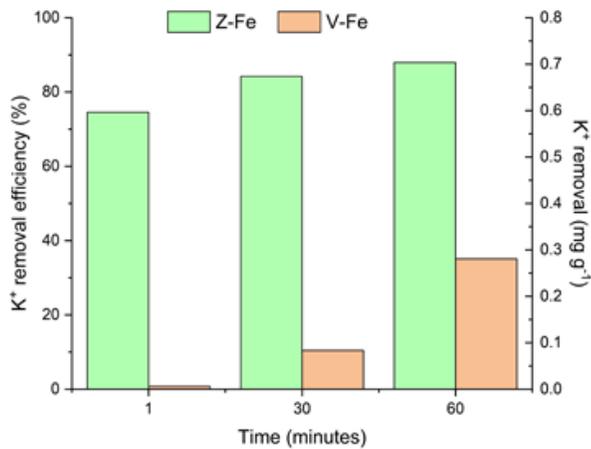


Figure 3

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

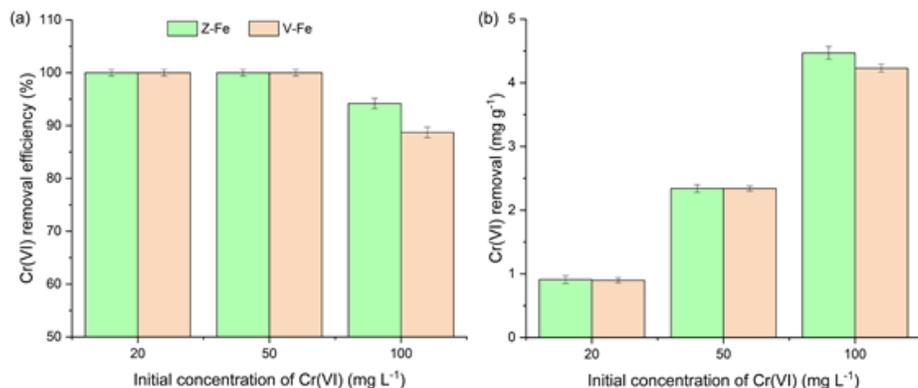


Figure 4

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

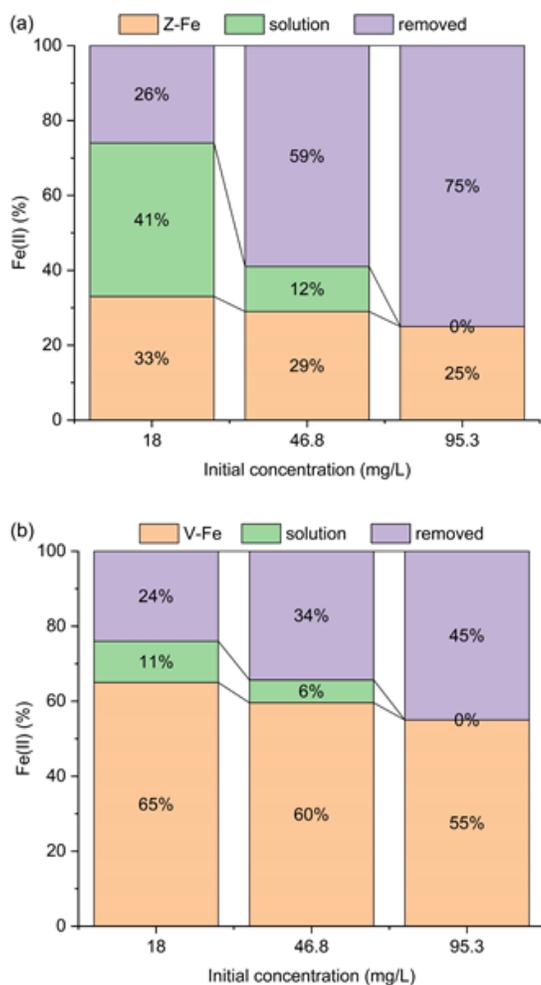


Figure 5

Percentage of Fe(II) remained in (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 minerals and 50 mL of Cr(VI) solutions.

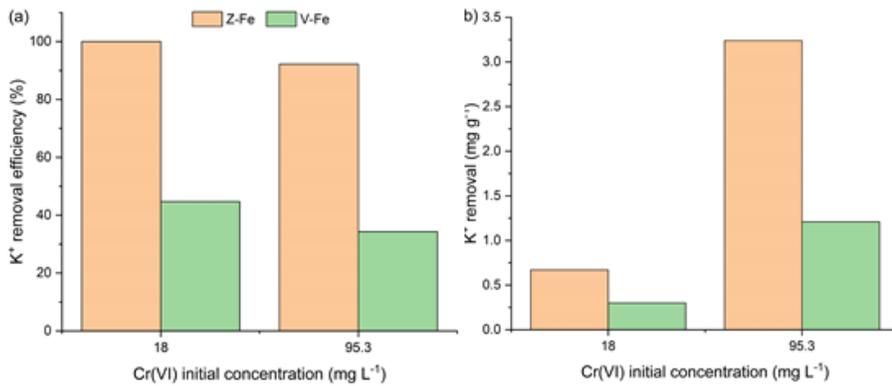


Figure 6

Potassium (a) efficiency (%) and (b) removal (mg g⁻¹) by Z-Fe and V-Fe, as a function of initial concentration of Cr(VI) (18 and 95.3 mg L⁻¹).

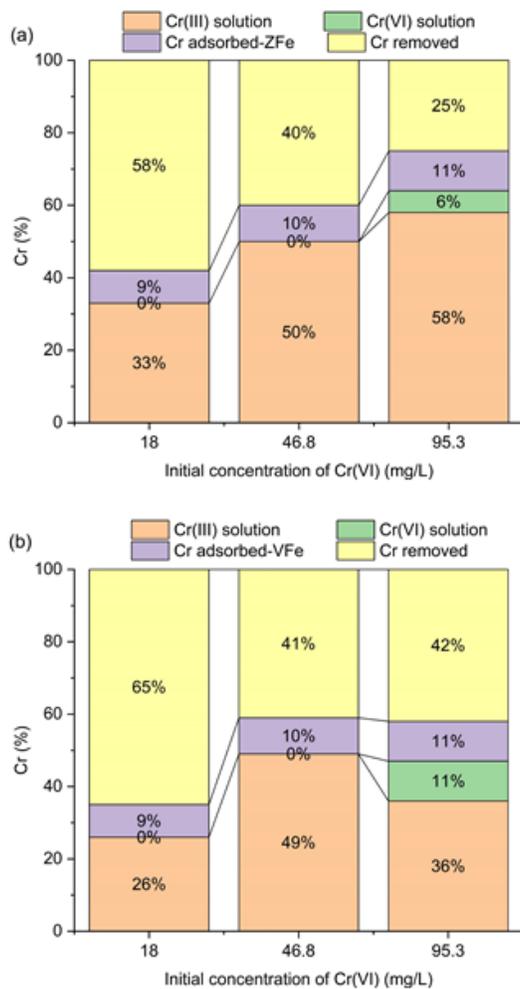


Figure 7

Percentage of Cr adsorbed in (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 minerals and 50 mL of Cr(VI) solutions.

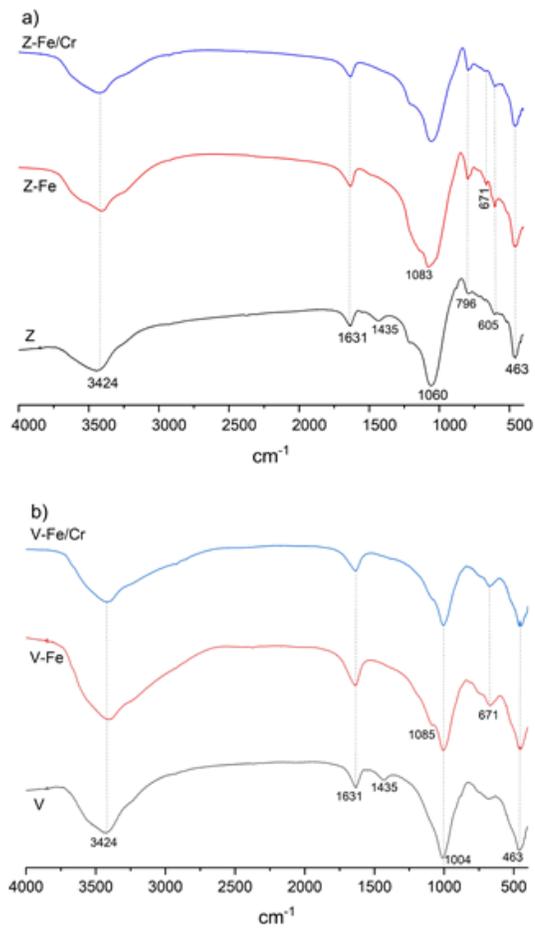


Figure 8

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

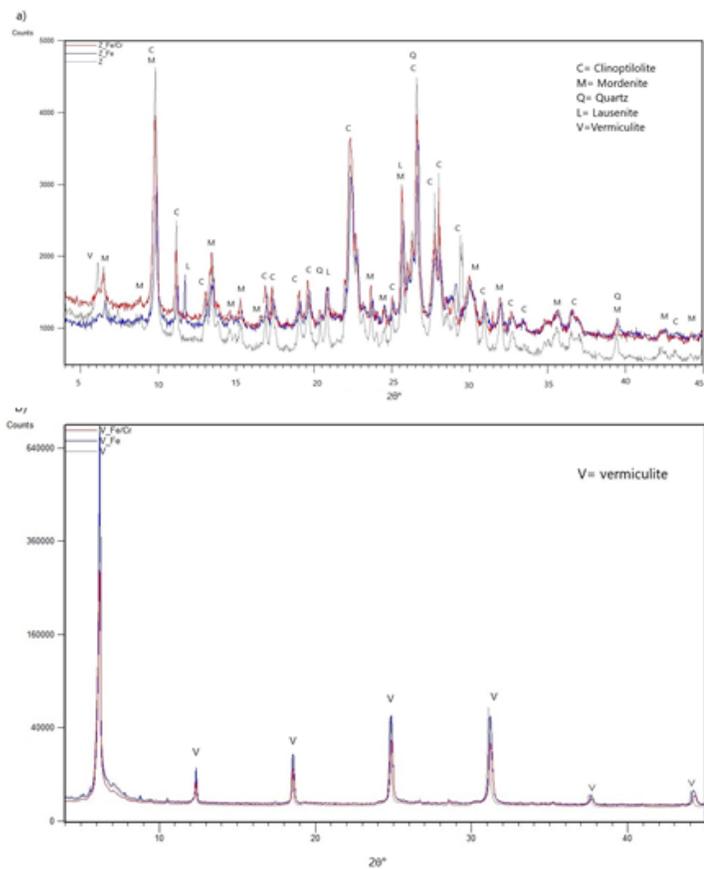


Figure 9

X-ray diffractograms of (a) zeolites – untreated (Z), modified with Fe(II) (Z-Fe) and used in Cr(VI) batch test (Z-Fe/Cr) - and (b) vermiculites - untreated (V), modified with Fe(II) (V-Fe) and used in Cr(VI) batch test (V-Fe/Cr).