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MECANISMOS DE REMOÇÃO DE CROMO(VI) EM SOLUÇÃO POR ZEÓLITA E VERMICULITA PRÉ-TRATADAS COM FERRO(II)

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Dissertação de mestrado apresentada como exigência parcial para obtenção do título de Mestre em Ciências, ao Programa de Pós-Graduação *Strictu-Sensu* do Instituto de Ciências Ambientais, Químicas e Farmacêuticas da Universidade Federal de São Paulo – Campus Diadema.

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RESUMO

As atividades industriais podem causar a contaminação de solos e águas ao despejar efluentes contendo metais, como o cromo hexavalente (Cr(VI)), que é altamente tóxico à saúde humana e animal. Nesse contexto, o presente trabalho avaliou a capacidade da zeólita e vermiculita pré-tratadas com Fe(II) em reduzir o Cr(VI) em solução. Os minerais naturais foram pré-tratados com Fe(II) em diferentes condições de temperatura (ambiente e 40 ^{o}C), tempo (1 e 24 h) e concentração de Fe(II) (0,5 e 1 mol L^{-1}). Os minerais pré-tratados com Fe(II) selecionados de acordo com sua eficiência de remoção de Cr(VI) foram utilizados em testes de remoção de Cr(VI) em batelada para estudar os efeitos do tempo e da concentração. Em seguida, as concentrações de Cr(VI), Fe(II), K$^+$, e Cr(III) foram analisadas nas soluções e nos adsorventes, a fim de avaliar os principais mecanismos envolvidos no processo de remoção de Cr(VI). Os resultados do pré-tratamento revelaram que a vermiculita adsorveu mais Fe(II) (21,8 mg g^{-1}) do que a zeólita (15,1 mg g^{-1}). Em testes de remoção de Cr(VI) ambos adsorventes pré-tratados liberaram Fe(II) que reduziu 100% de Cr(VI) em menos de 1 minuto, de uma solução contendo 20 mg L^{-1} Cr(VI). Considerando que 3 mols de Fe(II) são necessários para reduzir 1 mol de Cr(VI) (3Fe^{+2} + Cr^{+6} → 3Fe^{+3} + Cr^{+3}), o teor de ferro liberado por Z-Fe e V-Fe foi suficiente para reduzir 100% de Cr(VI) em solução com até 50 mg L^{-1} Cr(VI), e cerca de 90% (V-Fe) e 95% (Z-Fe) em solução com 100 mg L^{-1} Cr(VI). Os mecanismos de remoção de Cr(VI) envolveram a troca catiônica entre Fe^{+2} de Z-Fe e K$^+$ da solução de dicromato de potássio, e entre Fe^{+2} de V-Fe e H$^+$ da solução ácida (pH em torno de 5). Em seguida, o Fe^{+2} liberado pela troca iônica reduziu o Cr(VI) a Cr(III), que assim como o ferro oxidado (Fe(III)), foi removido da solução por precipitação. No entanto, quando o pH da solução ficou mais ácido (< 5), o processo de precipitação diminuiu e, consequentemente, parte do Cr(III) permaneceu em solução. A adsorção de Cr(III) por Z-Fe e V-Fe não foi favorecida devido à preferência de seus sítios de troca por outros íons presentes na solução, como K$^+$ e H$^+$, respectivamente. Dessa forma foi possível observar que tanto a zeólita quanto a vermiculita tratadas com Fe(II) são capazes de reduzir Cr(VI) da solução, cuja eficiência pode ser influenciada pelos cátions presentes no meio.

Palavras-chave: Minerais; Ferro(II); Cromo(VI); Troca catiônica; Redox.

ABSTRACT

Industrial activities can cause soil and water contamination by accidentally dumping effluents containing metals, such as hexavalent chromium (Cr(VI)), which is highly toxic to human and animal health. In this context, the present work evaluated the ability of zeolite and vermiculite pretreated with Fe(II) to reduce Cr(VI) in solution. Minerals pretreated with Fe(II) were used in Cr(VI) removal batch tests to study the effects of time and concentration in this process. Then, the concentrations of Cr(VI), Fe(II), K^+, and Cr(III) were analyzed in the solutions and in the adsorbents, in order to evaluate the main mechanisms involved in the Cr(VI) removal process. Pretreatment results revealed that vermiculite adsorbed more Fe(II) (21.8 mg g^{-1}) than zeolite (15.1 mg g^{-1}). In Cr(VI) removal tests both pretreated adsorbents released Fe(II) which reduced 100% of Cr(VI) in less than 1 minute from a solution containing 20 mg L^{-1} Cr(VI). Considering that 3 moles of Fe(II) are needed to reduce 1 mole of Cr(VI) ($3Fe^{+2}$ + $Cr^{+6} \rightarrow 3Fe^{+3} + Cr^{+3}$), the iron content released by Z-Fe and V-Fe was enough to reduce 100% of Cr(VI) in solution with up to 50 mg L^{-1} Cr(VI), and about 90% (V-Fe) and 95% (Z-Fe) in solution with 100 mg L^{-1} Cr(VI). The Cr(VI) removal mechanisms involved the cation exchange between Fe^{+2} from Z-Fe and K^+ from the potassium dichromate solution, and between Fe^{+2} from V-Fe and H^+ from the acidic solution (pH around 5). Then, the Fe^{+2} released by ion exchange reduced the Cr(VI) to Cr(III), which, like the oxidized iron (Fe(III)), was removed from the solution by precipitation. However, when the pH of the solution became more acidic (< 5), the precipitation process decreased and, consequently, part of the Cr(III) remained in solution. Adsorption of Cr(III) by Z-Fe and V-Fe was not favored due to the preference of their exchange sites for other ions present in the solution, such as K^+ and H^+, respectively. To prevent Cr(III) oxidation, it can be removed from the solution by precipitation (correcting pH > 5) or by adsorption using untreated vermiculite. Finally, the ions adsorbed by zeolite and vermiculite can be recovered by cation exchange, enabling the reuse of these adsorbents for subsequent removal of Cr(VI).

LISTA DE ABREVIAÇÕES

aq- aquoso

amb- ambiente

C_0- initial concentration

C_e- equilibrium concentration

CEC- cationic exchange capacity

cm- centímetro

$cmol_c$-centimol de carga

E- removal efficiency

Eh- potencial redox

eq- equação

fig- figura

FTIR- Espectroscopia no infravermelho por transformada de Fourier

g- grama

h- hora

kg- quilograma

L- litro

LOI- loss on ignition

M- molar

meq- miliequivalente

mg- miligrama

min- minuto

mL- mililitro

nm- nanometro

pH- potencial hidrogeniônico

Qe- total de cromo removido por massa de mineral

s- segundo

V- volume/vermiculita

V-Fe- vermiculita tratada com ferro(II)/vermiculite treated with iron(II)

V-Fe/Cr- vermiculita após tratamento do cromo

wt%- porcentagem atômica

XRD- X-ray diffractogram

XRF- X-ray fluorescence

Z- zeólita/zeolite

Z-Fe- zeólita tratada com ferro(II)/zeolite treated with iron(II)

Z-Fe/Cr- zeólita após o tratamento do cromo

μg- micrograma

°C- graus Célcius

SUMÁRIO

1. INTRODUÇÃO
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A presença de contaminantes, como metais tóxicos, em corpos d'água está relacionada, na maioria das vezes, ao descarte indevido de resíduos industriais. Alguns poluentes inorgânicos são encontrados na forma de cátions (chumbo, níquel, cobre) e outros de ânions, como o cromo hexavalente (Cr(VI)), que pode ocorrer na forma de cromato (CrO_4^{2-}) ou dicromato ($Cr_2O_7^{2-}$).

O cromo é um metal que possui estados de oxidação entre -2 e +6 (CHEISS, 2013; BISHOP *et al*., 2014), dentre os quais, os principais são o trivalente (Cr(III)) e o hexavalente (Cr(VI)), que diferem entre si nas características de mobilidade e toxicidade (RAI *et al*., 1989; PALMER & WITTBRODT, 1991; PETTINE *et al*., 1998; EPA, 1998; BRIGATTI *et al*., 2000; CHEISS, 2013; BISHOP *et al*., 2014; SHAHID *et al*., 2017; KWAK *et al*., 2018).

O estado de oxidação do cromo depende do meio em que está inserido. O cromo hexavalente (Cr(VI)) é um metal tóxico para a saúde humana em qualquer concentração, enquanto que, em pequenas quantidades (< 50-200 µg/dia), o Cr(III) é considerado um nutriente para os seres vivos (NRC, 1989; KISER & MANNING, 2010; DULTZ *et al*., 2012).

O cromo é utilizado em diversas indústrias para a produção de cromato, ferrocromo e ligas, revestimento, pigmento, curtimento de couro, proteção de madeiras, cimentos, galvanoplastia, mineração de ouro (PALMER & WITTBRODT, 1991; EPA, 1998; KISER & MANNING, 2010; AHN & DO, 2016), pesticidas (BISHOP *et al.,* 2014), fungicidas (PALMER & WITTBRODT, 1991), processamento de madeira (BARAKAT, 2011), refinamento de petróleo (KISER & MANNING, 2010; BARAKAT, 2011) etc. Devido à toxicidade do Cr(VI), todos os efluentes contendo esse contaminante devem ser tratados antes de serem lançados em corpos d'água, respeitando a legislação vigente.

De acordo com a resolução 357 do CONAMA (2005), a concentração de cromo total não pode ser superior a 0,05 mg L^{-1} nas águas de classe 1, 2 e 3, que podem ser utilizadas pela população. Já a resolução 430, que complementa a 357, determina o limite máximo permitido de Cr(VI) e de cromo total em efluentes de 0,1 mg L^{-1} e 1 mg L^{-1}, respectivamente (CONAMA, 2011).

Dessa forma, vários tratamentos têm sido propostos para remover especificamente o Cr(VI), e a maioria deles se baseia em mecanismos de oxirredução, precipitação e troca iônica. Uma vez que a forma trivalente do cromo é menos tóxica que a hexavalente, reduzir o Cr(VI) se tornou um método comum de tratamento deste contaminante (PALMER & WITTBRODT, 1991). A redução do Cr(VI) para Cr(III) é um processo que ocorre

naturalmente, sendo altamente oxidante e estável apenas em condições de elevado Eh (RAI *et al*., 1989). No entanto, segundo Kwak *et al*. (2018), a taxa de redução pode ocorrer de forma lenta e, por isso, muitos optam por realizar essa reação de forma artificial, utilizando reagentes redutores.

No meio ambiente, a reação de redução do Cr(VI) pode ocorrer pela presença de Fe(II) em solos e minerais (PALMER & WITTBRODT, 1991; PETTINE *et al*., 1998; KWAK *et al*., 2018), matéria orgânica como carbono orgânico, ácidos húmicos e fúlvicos (PALMER & WITTBRODT, 1991; PETTINE *et al*., 1998; EPA, 1998; WHO, 2004; SHAHID *et al*., 2017; MARONEZI *et al*., 2019), H_2S e outros compostos sulforosos (PETTINE *et al*., 1998; PALMER & WITTBRODT, 1991), microorganismos (EPA, 1998), fotorredução (PALMER & WITTBRODT, 1991), entre outros.

A precipitação de espécies de cromo ocorre após reações de oxirredução pelo uso de substâncias redutoras. Assim, o cromo hexavalente muda para a forma trivalente usando, por exemplo, metabissulfito de sódio como agente redutor e, em seguida, soda cáustica para precipitar Cr(III) como hidróxido, formando um lodo que precisa ser devidamente aterrado (MARTINS, 2012).

O processo de precipitação é utilizado em conjunto com a redução e requer o uso de grande quantidade de reagentes químicos, o que muitas vezes torna essa técnica custosa. Outra técnica comum é a combinação de redução de Cr(VI) e subsequente adsorção de Cr(III) da solução. Uma vez que os íons Cr(III) em solução podem retornar ao seu estado oxidado na presença de agentes oxidantes, como íons de manganês, a técnica de adsorção é um mecanismo que pode evitar essa oxidação (EARY *et al*., 1988; PALMER & WITTBRODT, 1991; KWAK *et al*., 2018).

O tratamento por adsorção consiste basicamente em transferir os contaminantes em solução para uma fase sólida (adsorvente) (BARAKAT, 2011). Os materiais mais comuns utilizados são as resinas poliméricas (MARTINS, 2012) e sintéticas orgânicas (BARAKAT, 2011) e, dependendo do adsorvente utilizado, o custo desse processo pode ser elevado (AGUIAR *et al*., 2002; KAN *et al*., 2017). Por outro lado, o uso de adsorventes alternativos pode minimizar os gastos e, até mesmo, melhorar a eficiência de remoção de contaminantes do meio. Nesse sentido, minerais com alta superfície específica e capacidade de troca iônica podem viabilizar o tratamento desses efluentes. Dentre esses minerais destacam-se os do grupo das zeólitas e dos filossilicatos expansíveis 2:1, como a vermiculita.
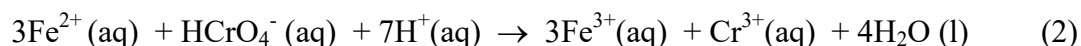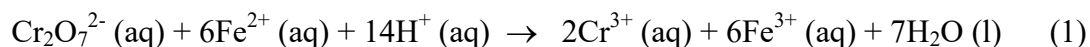
As zeólitas são aluminossilicatos porosos com carga permanente negativa devido à substituição de parte do silício por alumínio na estrutura tetraédrica, o que gera um *déficit* de carga (BARRER, 1982). Este *déficit* de carga é compensado pela presença de cátions trocáveis dentro dos poros conectados por adsorção, que podem ser substituídos por outros cátions (PABALAN & BERTETTI, 2001). Os poros das zeólitas possuem tamanho fixo e, geralmente, são preenchidos por água e íons como K^+, Na^+, Ca^{2+} ou Mg^{2+} por meio de ligações fracas (INGLEZAKIS & ZORPAS, 2012). Existem vários tipos de zeólita, sendo as mais comuns e mais exploradas a clinoptilolita, mordenita, chabazita (INGLEZAKIS & ZORPAS, 2012).

Apesar das zeólitas apresentarem propriedades importantes para o tratamento de efluentes, uma desvantagem é o fato do Brasil não possuir grandes depósitos destes minerais, portanto, a necessidade de importá-las pode tornar o tratamento mais caro (SHINZATO *et al.,* 2020). Por outro lado, o Brasil possui grandes depósitos de vermiculita, que assim como as zeólitas, possui elevada capacidade de troca catiônica. A vermiculita é um mineral filossilicático, e possui estrutura lamelar com duas camadas tetraédricas de silício e alumínio, e uma octaédrica de alumínio ou magnésio (tipo de camada 2:1) (MEUNIER, 2005; BRADL, 2005). Pode ser formada a partir da alteração de outros minerais ou da precipitação direta das soluções (SPARKS, 2003). Esse mineral apresenta carga permanente negativa (devido a substituição isomórfica que ocorre principalmente nas camadas tetraédricas entre o Si^{4+} e o Al^{3+}) e é expansível (JACKSON, 1979).

Assim como a zeólita, a vermiculita também necessita de cátions trocáveis para neutralizar a carga negativa, sendo que os sítios de troca se localizam na região interfoliar desses minerais. No caso dos minerais 2:1, a adsorção também pode ocorrer na superfície externa, porém, em menor intensidade (SPARKS, 2003). Esses cátions geralmente são K^+, Ca^{2+}, Mg^{2+} ou Na^+ (MEUNIER, 2005). Segundo Bradl (2005), os argilominerais em geral possuem como característica, alta superfície específica, carga superficial negativa e capacidade de adsorver cátions.

Assim sendo, esses minerais têm dificuldade em adsorver ânions, como os que contêm cromo hexavalente (CrO_4^{2-} e $Cr_2O_7^{2-}$). Por outro lado, a adsorção direta desse ânion também possui desvantagens, uma vez que o cromo permanece no seu estado tóxico (PALMER & WITTBRODT, 1991; MARONEZI *et al*., 2019). Para resolver essa problemática, vários estudos têm proposto o pré-tratamento desses minerais com um agente redutor, como o Fe(II), a fim de reduzir o Cr(VI) a Cr(III) (KISER & MANNING, 2010; LV *et* al., 2014; AHN &

DO, 2016; KWAK *et al*., 2018). As reações de redução de Cr(VI) na forma de dicromato (BRIGATTI *et al*., 2000; KWAK *et al*., 2018) e hidrogenocromato (KISER & MANNING, 2010) pelo Fe(II) ocorrem em meio ácido e são representadas nas equações 1 e 2.

$$Cr_2O_7^{2-} (aq) + 6Fe^{2+} (aq) + 14H^+ (aq) \rightarrow 2Cr^{3+} (aq) + 6Fe^{3+} (aq) + 7H_2O (l) \quad (1)$$

$$3Fe^{2+} (aq) + HCrO_4^- (aq) + 7H^+(aq) \rightarrow 3Fe^{3+}(aq) + Cr^{3+}(aq) + 4H_2O (l) \quad (2)$$

O uso de minerais pré-tratados com Fe(II) tem a vantagem de não necessitar de ácidos. Como os sítios de troca da zeólita e vermiculita são naturalmente ácidos (sítios ácidos de Brönsted e Lewis) (DEKA, 1998), a redução do Cr(VI) por Fe(II) pode ocorrer sem adição de ácido. Além disso, a quantidade de lodo formado seria menor, quando comparado ao uso direto de sais de Fe(II), devido à precipitação do Fe(III) excedente não utilizado na redução.

Apesar de alguns trabalhos terem testado o uso de zeólitas (KISER & MANNING, 2010; LV *et al*., 2014; AHN & DO, 2016) e vermiculitas (LIU *et al*., 2010; KWAK *et al*., 2018) pré-tratadas com Fe(II) para remover Cr(VI) da solução, e apresentarem resultados promissores, nenhum deles descreveu de forma detalhada os mecanismos envolvidos no processo de remoção de Cr(VI) por esse minerais.

Portanto, o presente trabalho avaliou os principais mecanismos envolvidos na remoção de Cr(VI) em solução por amostras de zeólita e vermiculita pré-tratadas com Fe(II), bem como o seu pré-tratamento. A capacidade de seus sítios de troca em manter e liberar o ferro na forma reduzida também foi avaliada. O uso desses minerais, por sua vez, permite também que haja seu reaproveitamento (por meio de regeneração por troca iônica), possibilitando a recuperação dos íons adsorvidos de interesse econômico e evitando seu descarte em aterros sanitários.

2. OBJETIVOS

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2.1 Geral

Analisar a capacidade das amostras de zeólita e vermiculita pré-tratadas com Fe(II) em reduzir Cr(VI) em solução, e compreender os principais mecanismos envolvidos nesse processo.

2.2. Específicos

- Avaliar os métodos de pré-tratamento com Fe(II) nas amostras de zeólita e vermiculita;

- Verificar a capacidade dos minerais de estudo em manter e liberar íons de ferro na forma reduzida por meio de troca iônica;

- Comparar a eficiência de remoção de Cr(VI) em solução pelos minerais pré-tratados em função do tempo de contato e da concentração inicial de Cr(VI);

- Analisar os mecanismos envolvidos na remoção de Cr(VI), bem como a interação dos íons resultantes do processo de oxirredução com os materiais de estudo.

3. ARTIGO

Maria Isabel Garcia Rosa, Gabriella de Andrade Boga, Suellen Silva Vieira Cruz, Fabio Ramos Dias de Andrade, Sheila Aparecida Correia Furquim, Mirian Chieko Shinzato. Environmental Science and Pollution Research.
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Mechanisms of chromium(VI) removal from solution by zeolite and vermiculite modified with iron(II)

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ABSTRACT

The efficiency of zeolite and vermiculite modified with Fe(II) was evaluated to reduce Cr(VI) from aqueous solutions. Adsorbents were treated with $Fe(SO_4).7H_2O$ to saturate their exchange sites with Fe(II) ions. 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 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) ($3Fe^{+2} + Cr^{+6} \rightarrow 3Fe^{3+} + Cr^{+3}$), the iron contents 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). Analysis of Fe(II), Cr(III), Cr(VI) and K^+ of the final adsorbents and solutions these tests indicated that K^+ ions (from $K_2Cr_2O_7$ solution) was the main cation adsorbed by Z-Fe, while vermiculite does not absorb any of these cations. Therefore, the main mechanisms of Cr(VI) removal involved cation exchange between $Fe^{2+} \leftrightarrow K^+$ (from dichromate solution) in zeolite, and $Fe^{2+} \leftrightarrow H^+$ (from acidic solution) in vermiculite. Reduction of Cr(VI) by Fe(II) followed by the precipitation of Cr(III) and Fe(III). However, when solution pH< 5, the acidity limited the precipitation and, consequently, part of Cr(III) remained in solution. These Cr(III) ions were not adsorbed by zeolite and vermiculite, due to the preference of their exchange sites for K^+ and H^+, respectively. The Fe(II) remained in V-Fe after the Cr(VI) removal tests could also be reused to reduce 100% of Cr(VI) from solution with < 10 mg L^{-1} Cr(VI).

Keywords: Zeolite; Vermiculite; Iron(II); Chrome(VI); Cation exchange; Redox; Precipitation.

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 (< 50-200 μg/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 human health in any concentration (Hawley et al. 2004). Therefore, all effluents containing Cr(VI) must be treated before being discharged into water bodies.
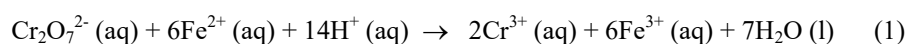
Removal of Cr(VI) from industrial effluents is usually done by precipitation of Cr(III) as hydroxide, after redox reactions by the use of reducing substances, such as sodium metabisulphite. Chemical precipitation also requires the use of large quantities of reagents, such as sodium hydroxide, which often makes this technique expensive (Srivastava and Thakur 2007).
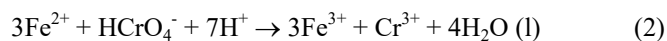
Treatment of Cr(VI)-contaminated effluents is also possible by combining reduction of Cr(VI) and adsorption of Cr(III). Cr(III) ions can return to its oxidized state in the presence of oxidant agents, such as manganese ions, but adsorption prevents reoxidation (Eary et al. 1988; Palmer and Wittbrodt 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 Si^{4+}/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 tetrahedral (Si^{4+}-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 on 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.

$$Cr_2O_7^{2-} \text{ (aq)} + 6Fe^{2+} \text{ (aq)} + 14H^+ \text{ (aq)} \rightarrow 2Cr^{3+} \text{ (aq)} + 6Fe^{3+} \text{ (aq)} + 7H_2O \text{ (l)} \quad (1)$$

$$3Fe^{2+} + HCrO_4^- + 7H^+ \rightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O \ (l) \qquad (2)$$

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 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; Ahn and Do 2016; Kwak et al. 2018), the mechanisms involved in this process are not well detailed. 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), imported from Cuba by Celta Brasil, 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.

Mineralogical composition of zeolite (Z) was analyzed in an X-ray diffractometer (XRD) (D8 Advance/Bruker). The conditions used in this determination were: radiation CuKα, angular range $2\theta°$ 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 Mg^{2+}. Natural and heated minerals samples were analyzed in XRD (D8 Advance/Bruker) with following conditions: angular range from 2° to 36° $2\theta°$, step size of 0.01°/2θ°, angular velocity of 1 s step^{-1}. Samples treated with ethylene glycol were analyzed using angular range of 3-35 2θ°; 0.02º/2θº of step, speed of 5 s step^{-1}.

Chemical composition of zeolite and vermiculite was determined by X-ray fluorescence (XRF) spectroscopy (Axios Advanced PANanalytical). 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 remained in solution was 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 FeSO$_4$.7H$_2$O 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 at 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 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 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 $FeSO_4.7H_2O$ 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} H_2SO_4 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. 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 $K_2Cr_2O_7$. 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, 18 mg L^{-1} Cr(VI) solution was used. A 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, and 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 effect of the initial Cr(VI) concentration on the adsorption efficiency was assessed using 1 h of contact time (determined in the previous test).

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. 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. Concentration of K^+ (from $K_2Cr_2O_7$ 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 (Qe, mg g^{-1}) was determined by equation (4).

$$E = (\frac{(C_o - C_e)}{C_o}) \times 100 \qquad (3)$$

where E is the removal efficiency (%); C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}).

$$Q_e = (\frac{(C_o - C_e)}{m}) \times V \qquad (4)$$

where Qe is equal to the total Cr removed (mg g^{-1}) by the mass (m) of the mineral (g), C_0 and C_e are the initial and equilibrium 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} H_2SO_4 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 restige-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 CuKα, angular range 2θ° 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

Adsorbents used in this study were vermiculite and zeolite. Vermiculite was clearly identified by X-ray diffraction (XRD) due to its strongest reflections at 1.4, 0.98, 0.48, 0.36 and 0.29 nm in the Mg-saturated sample (Fig.1). The reflection related to the (001) plane remained constant at 1.4 nm after saturation with ethylene glycol and collapsed to close to 1 nm after heating the K-saturated sample (Chen 1977).
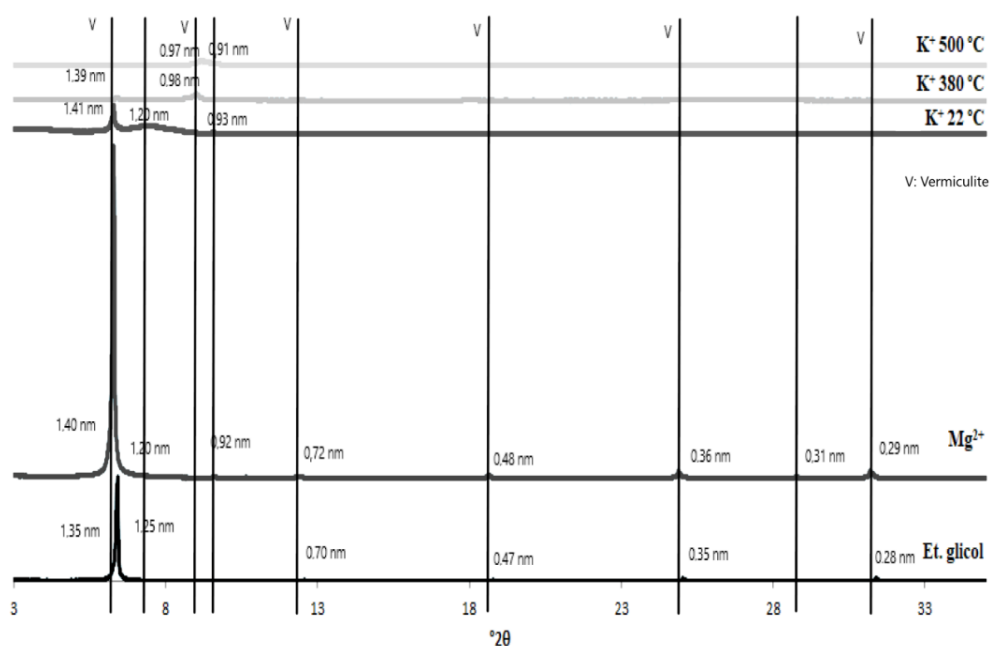
Fig. 1 - XRD data of vermiculite.

Zeolite used in this study is a natural mixture of clinoptilolite and mordenite. Minor reflections related to quartz are also identified in zeolite diffractogram (Fig. 2). Chemical composition of zeolite and vermiculite is presented in Table 1. Significant amounts of Fe_2O_3 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% Cr_2O_3 in the composition.
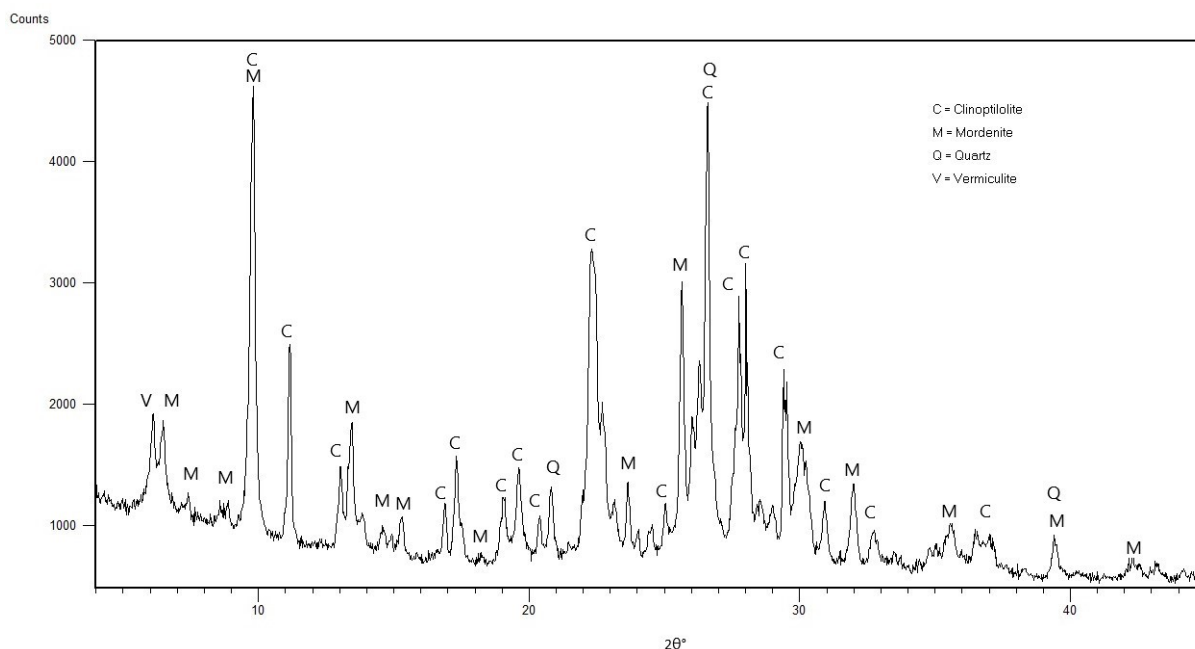

Fig. 2 - XRD data of zeolite (Z).

Table 1 - Chemical composition of the mineral adsorbents. Loss on ignition (LOI) at 1050 ^{o}C.

Adsorbent	SiO₂	Al₂O₃	Fe₂O₃	MnO	MgO	CaO	Na₂O	K₂O	TiO₂	P₂O₅	ZnO	Cr₂O₃	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 $Fe(SO_4).7H_2O$ 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 $1 mol\ L^{-1}$ $Fe(SO_4).7H_2O$.

The 100% efficiency of Cr(VI) removal were observed in one treatment of zeolite (2) and in two treatments of vermiculite (1 and 3) (Fig. 3). The efficiency of ion 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).
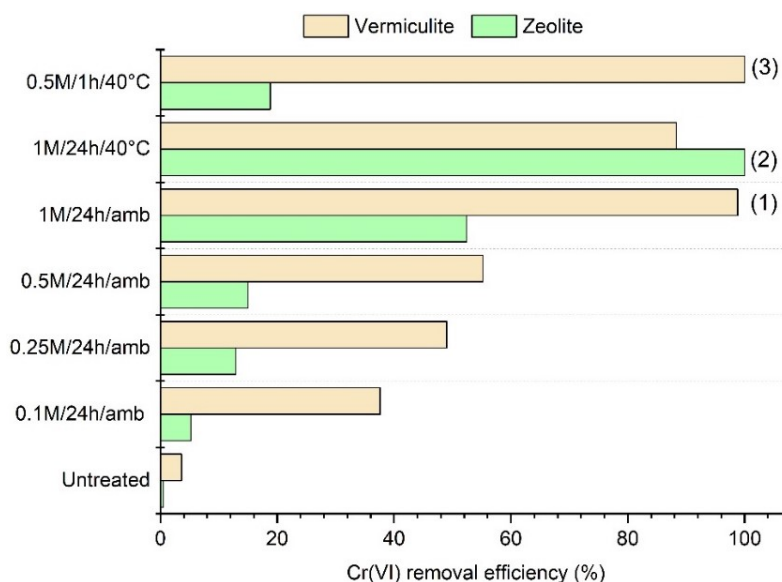

Fig. 3 - Removal of Cr(VI) efficiency (%) by untreated and modified zeolite and vermiculite samples, under different concentrations of $FeSO_4.7H_2O$/time/temperature. Samples with 100% of Cr(VI) removal efficiency: (1), (2) and (3).

The exchangeable cations of the zeolite pores (K^+ and Ca^{2+}) have smaller hydrated radii (respectively, 0.33 nm and 0.41 nm) than Fe^{2+} (0.45 nm), whereas the hydrated radius of Mg^{2+} (0.43 nm) in the interlayer

space of vermiculite is close to the hydrated radius of Fe^{2+} (Strawn et al. 2020). Therefore, the exchange of Fe^{2+} with vermiculite is more efficient than with zeolite. This is probably the reason why zeolite requires higher $FeSO_4.7H_2O$ 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} $FeSO_4.7H_2O$/ 24 h/ 40 ^{o}C and 0.5 mol L^{-1} $FeSO_4.7H_2O$ / 1 h/ 40 ^{o}C.

Sample	Before	After treatment
	Fe(II) content (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, in spite of 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 Mg^{2+} (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, Ca^{2+} (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 solution containing 18 mg L^{-1} Cr(VI). 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.

Since three moles of Fe(II) are required to reduce one mole of Cr(VI) (eq. 1 and 2), and the Cr(VI) removal was 0.90 mg per gram of Z-Fe and V-Fe, at least 2.90 mg of Fe(II) are needed to reduce them. Acidic extraction conducted on 1 g of Z-Fe and V-Fe (before and after the batch tests of Cr(VI) removal) revealed how much Fe(II) was released from these minerals to reduce Cr(VI) (Fig. 4). Concentration of Fe(II) before Cr(VI) removal (on the left side of the plots of figure 4) displays minor variations among experiments, because they were performed between 8 and 14 days after treatment of zeolite and vermiculite with Fe(II), and part of Fe(II)) may have been oxidized.
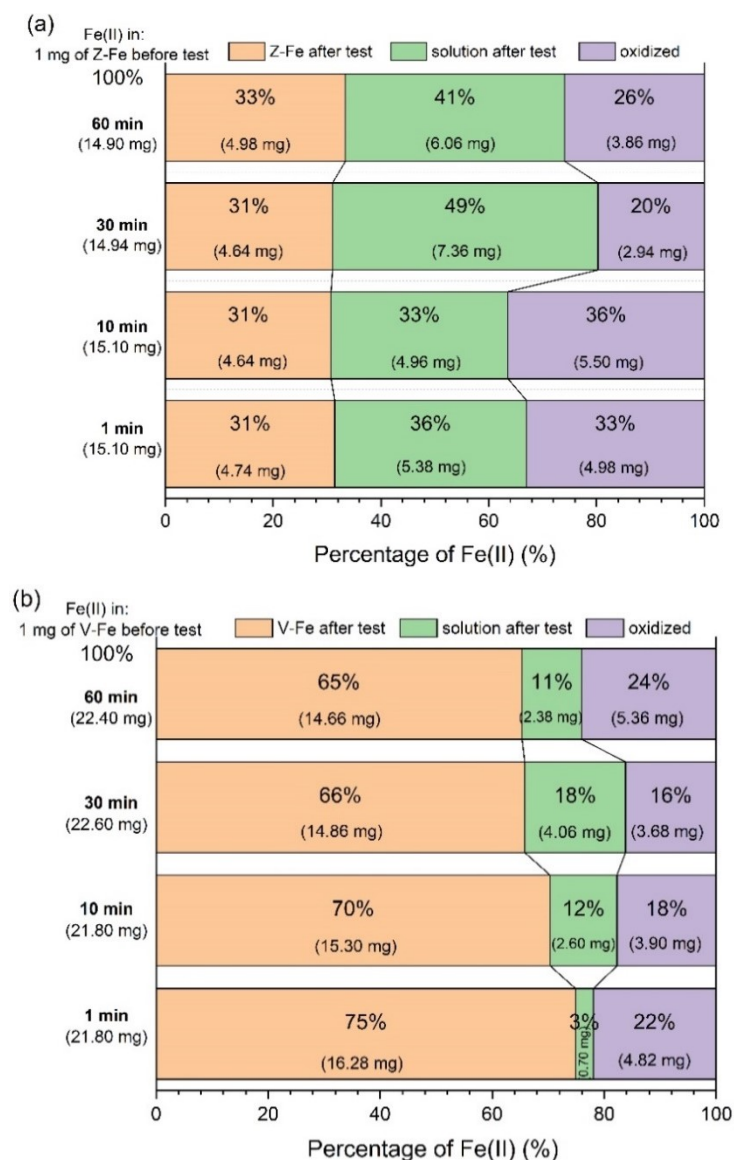
Fig. 4 – Percentage of Fe(II) in Z-Fe and V-Fe before and after Cr(VI) removal test as a function of time (1 to 60 minutes), and the contents of Fe(II) remained in solution and oxidized in redox process. The values in brackets correspond to the content of Fe(II) in 1 g of minerals and 50 mL of solution of 18 mg L^{-1} Cr(VI).

The difference between the Fe(II) level before and after the batch test corresponds to the fraction released from Z-Fe and V-Fe. 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 (Fig. 4). 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).

The amount of Fe(II) released from Z-Fe and V-Fe remained higher than the minimum needed (2.90 mg) to reduce Cr(VI) in all the time intervals (Fig. 4). Z-Fe released more Fe(II) (regardless of time) than V-Fe, whose content of released Fe(II) increased with time (Fig. 4). 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. 5).
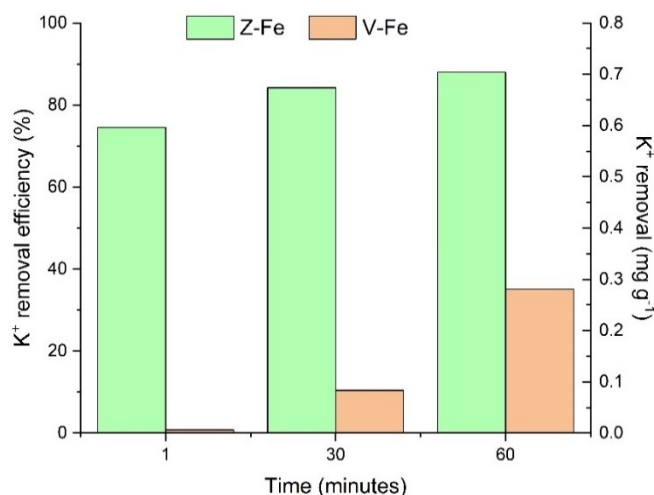
Fig. 5 – Efficiency (%) and removal (mg g^{-1}) of K$^+$ from K$_2$Cr$_2$O$_7$ solutions by Z-Fe and V-Fe during Cr(VI) removal test as a function of time.

The decrease of K$^+$ concentration in solution with time (Fig. 5) as well as the release of Fe(II) to solution (Fig. 4) 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$^+$ ↔ 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). This is probably why V-Fe released less Fe(II) in solution than Z-Fe, under the experimental conditions, however this hypothesis must be confirmed by the analysis of V-Fe basal reflection, through DRX analysis (item 3.4) (Fig. 4).

The results of second set of batch tests of Cr(VI) removal performed with samples underwent 60 minutes batch tests revealed that the remained iron in Z-Fe (4.98 mg) and V-Fe (14.66 mg) were still in reduced form, even after one year. There was partial Cr(VI) removal by both adsorbents, significantly higher in V-Fe (43.3% of removal efficiency; 0.39 mg g^{-1}) compared to Z-Fe (15.8% of removal efficiency; 0.14 mg g^{-1}). Efficiency of V-Fe was higher because remaining Fe(II) in V-Fe was higher than in Z-Fe. In spite of its drop in efficiency, V-Fe can still be reused to remove low levels of Cr(VI) in 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 46.80 mg L^{-1} Cr(VI) to 94% in solution with 95.30 mg L^{-1}. Similarly in V-Fe, which efficiency went from 100% in solutions with 18 and 46.80 mg L^{-1} down to 89% in solution with 95.30 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 95.30 mg L^{-1}, while V-Fe it increased from 0.9 to 4.2 mg g^{-1} in the same range of concentration (Fig. 6).
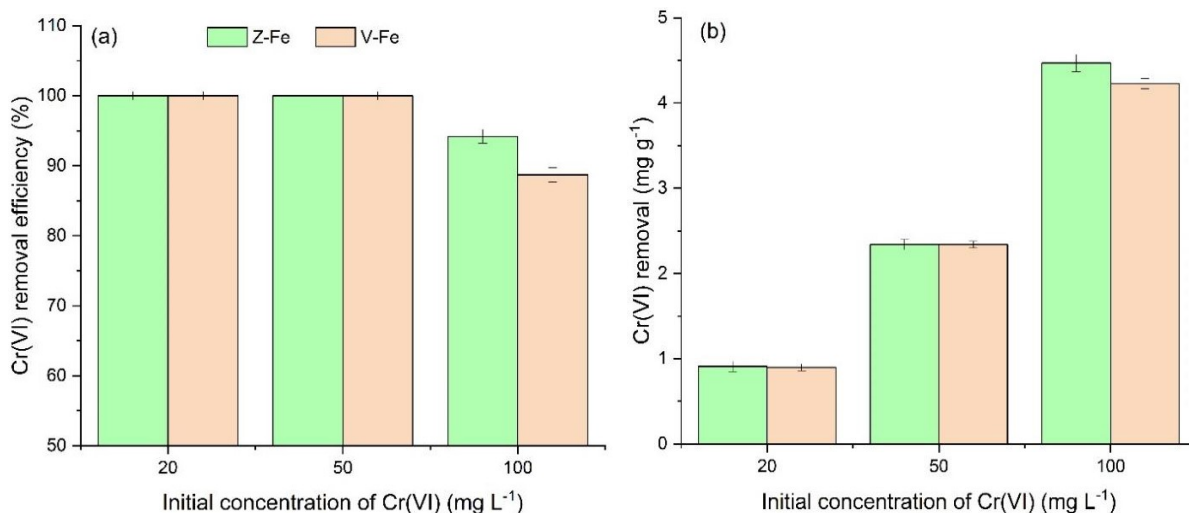
Fig. 6 - Removal (a) efficiency (%) and (b) capacity (mg g^{-1}) of Cr(VI) from solution by Z-Fe and V-Fe as a function of initial Cr(VI) concentration (mg L^{-1}). Error bars indicate two standard deviations.

Considering that to reduce one mole of Cr(VI) it is required 3 moles of Fe(II), the amount of Fe(II) required to reduced Cr(VI) present in 50 mL of solutions with initial concentration of Cr(VI) of 18, 46.80 and 95.30 mg L^{-1} are2.90 mg, 7.54 mg and 15.28 mg, respectively. The observed decrease in the efficiency of Cr(VI) removal from solutions with 95.30 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 solution.

Concentration of Fe(II) was determined in the adsorbents before and after the batch tests, as well as in the final solution (Fig. 7). The amount of Fe(II) released from Z-Fe and V-Fe to solution and to the oxidized fraction (hydroxide precipitates) increased with the increase in Cr(VI) concentration, from 18 to 95.30 mg L^{-1}, due to the increase of K$^+$ concentration (from potassium dichromate) in solution, which is probably the main cation exchanged with Fe(II).
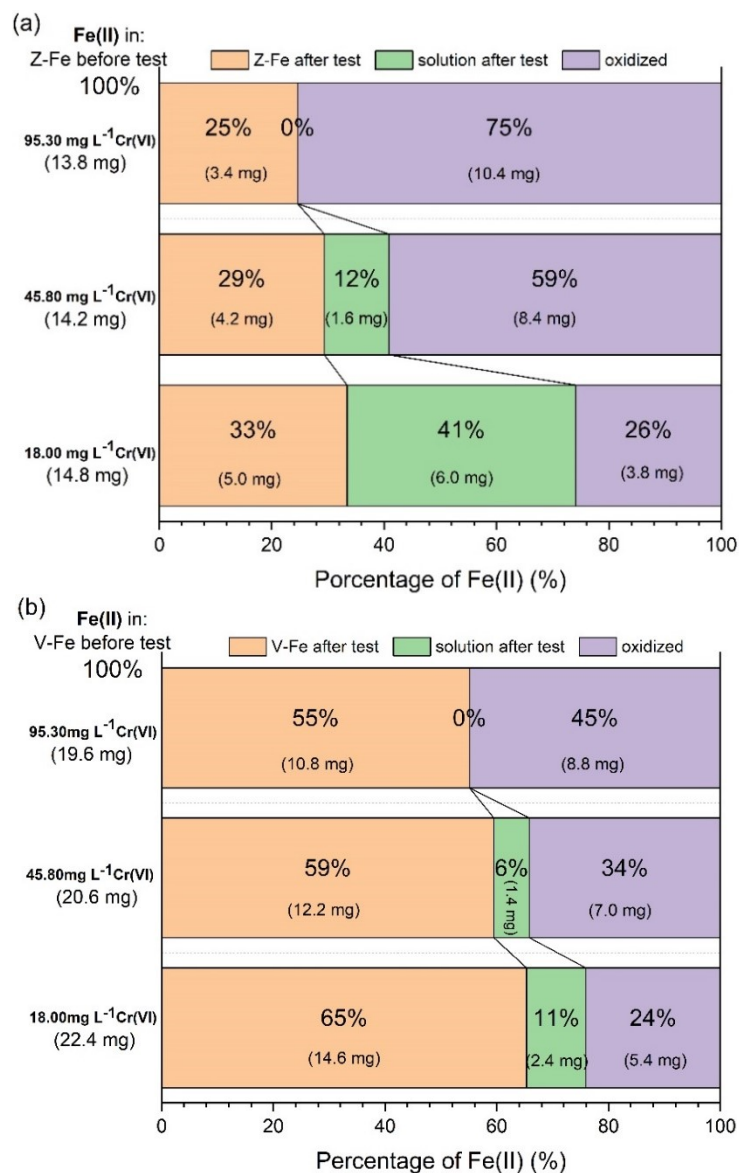
Fig. 7 - Percentage of Fe(II) in Z-Fe and V-Fe before and after Cr(VI) removal test as a function of Cr(VI) concentration (18, 45.8 and 95.3 mg L^{-1}), and the contents of Fe(II) remained in solution and oxidized in redox process. The values in brackets correspond to the content of Fe(II) in 1 g of minerals and in 50 mL of Cr(VI) solutions.

In solution with initial Cr(VI) concentration of 18 mg L^{-1} (containing 13.4 mg L^{-1} K^{+}), 100% of K^{+} was removed by Z-Fe (corresponding to K^{+} removal of 0.67 mg g^{-1}). The K^{+} removal efficiency of V-Fe was 44.7%, related to K^{+} removal of 0.3 mg g^{-1} (Fig. 8). After batch test conducted with 95.30 mg L^{-1} of Cr(VI), the K^{+} removal efficiency decreased (92.2 %) while the K^{+} removal increased to 3.35 mg g^{-1} for Z-Fe (Fig. 8). The efficiency of V-Fe was much smaller (34%), corresponding to K^{+} removal of 1.21 mg g^{-1}. This result revealed the high efficiency of Z-Fe in removing K^{+} from solution likely by ion exchange than V-Fe.
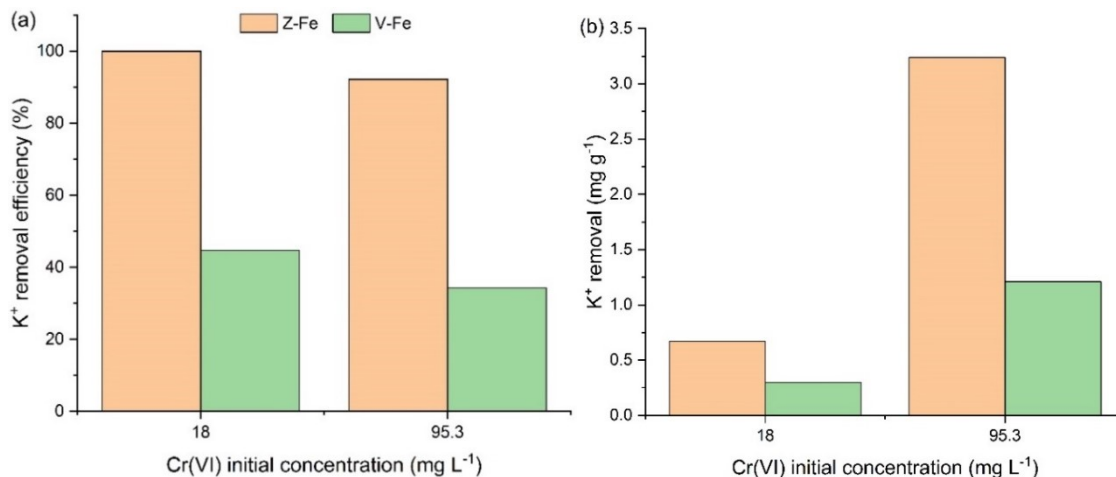
Fig. 8 - Efficiency (%) and (b) removal of K^+ (mg g-1) by Z-Fe and V-Fe as a function of initial concentration of Cr(VI). Concentration of K^+ (mg L^{-1}) in the final solution of tests conducted with initial concentration of 18 and 95.30 mg L^{-1}Cr(VI) with Z-Fe and V-Fe.

In contrast to the tests performed with lower Cr(VI) concentrations, Fe(II) was not detected in solution with 95.30 mg L^{-1} Cr(VI), and the fraction of oxidized iron increased with Cr(VI) concentration (Fig. 7). The required amount of Fe(II) to fully reduce the Cr(VI) in 50 mL of a solution with 95.30 mg L^{-1} is 15.28 mg (Table 3). The actual amount of Fe(II) released in the batch tests was 10.40 mg for Z-Fe and 8.80 mg for V-Fe. However, after batch tests with 95.30 mg L^{-1} Cr(VI), the fraction of Fe(II) remaining in Z-Fe and V-Fe was not released to reduce all Cr(VI) in solution. Probably the release of Fe(II) from Z-Fe and V-Fe depends on the availability of ions in solution to promote cation exchange. This hypothesis will be discussed in item 4.

Iron-rich clay minerals reduce Cr(VI) and eventually the 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. 9). The difference between the Cr(VI) content in the samples before the batch test and the fraction of Cr(III and VI) remained in solution corresponds to the Cr precipitated fraction (Fig. 9).

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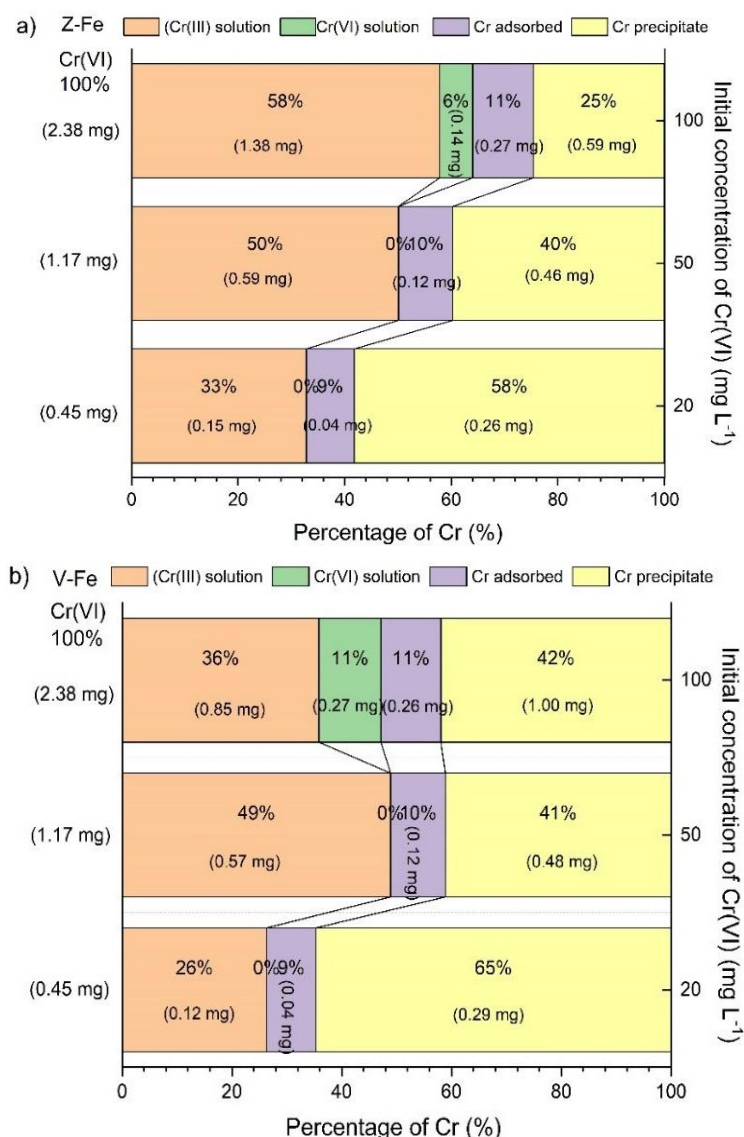
Fig. 9 - Chromium distribution in batch tests with different concentrations of Cr(VI).

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 mg L^{-1} Cr(VI), and then, decreased by 95.3 mg L^{-1} Cr(VI). Nevertheless, considering the chromium mass (in milligram) of each fraction, it also increased with the increase of the Cr(VI) concentration (Fig. 9).

As part of Cr(III) and Fe(II) remained in solution, the precipitated fraction of chromium were probably in form of Cr(III) hydroxides. In both experiments the precipitated Cr(III) is the larger fraction at 18 mgL^{-1} Cr(VI) test, and decreased with the increase of the Cr(VI) concentration. Nevertheless, considering the mass value (mg) of the precipitated Cr(III), it increased with the increase of the Cr(VI) concentration.

The presence of Cr(VI) in solution after batch tests was detected only in experiments with high initial concentration of Cr(VI) (95.3 mg L^{-1}) (Fig. 9). In those experiments, Fe(II) was not detected in solution, indicating the role of dissolved Fe(II) in chromium reduction. Therefore, the absence of Fe(II) (Fig. 7) and the presence of 6% of Cr(VI) in the 95.3 mg L^{-1} Cr(VI) solution (Fig. 9) 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).

The removal of Cr(III) from solution is important to prevent its oxidation to Cr(VI). The test conducted in a previous study using untreated vermiculite to remove Cr(VI) 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 solution. Kiser and Manning (2010) observed that natural zeolite (faujasite) can also adsorb Cr(III) from solution.

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. 10 and 11) before and after batch tests with solution from 100 mg L^{-1} Cr(VI). Both materials present 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).
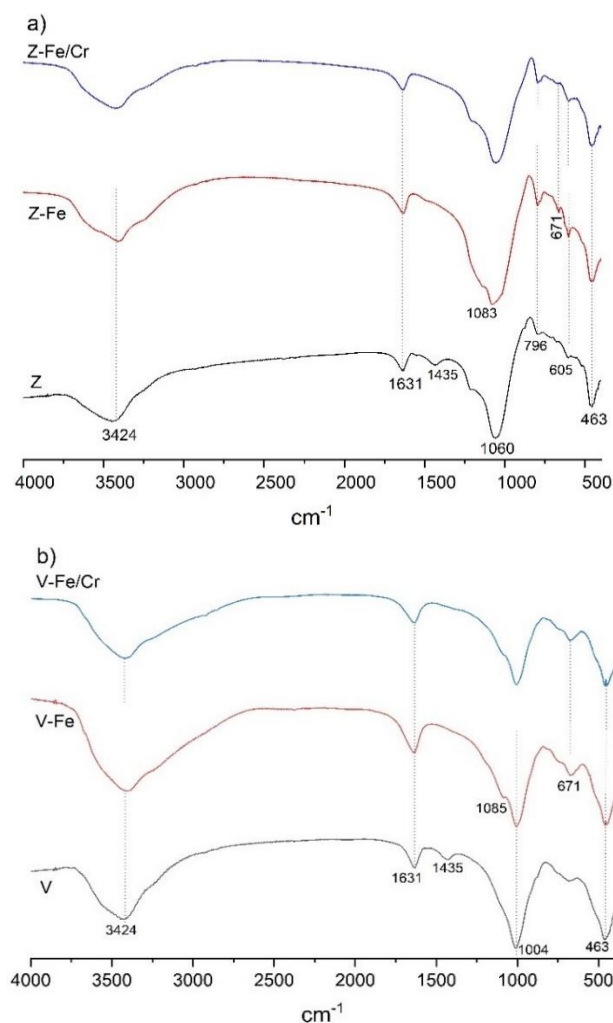

Fig. 10 - FTIR spectra of (a) zeolite (Z-Fe and Z-Fe/Cr) and (b) vermiculite (V-Fe and V-Fe/Cr).

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.11). Only Z-Fe presented reflections related to lausenite, an iron(III) sulfate (Fe$_2$(SO$_4$)$_3$·5H$_2$O) (Fig. 11). This crystallographic phase refers to the precipitation of the oxidized iron from FeSO$_4$.7H$_2$O solution, used to modify the mineral adsorbents.
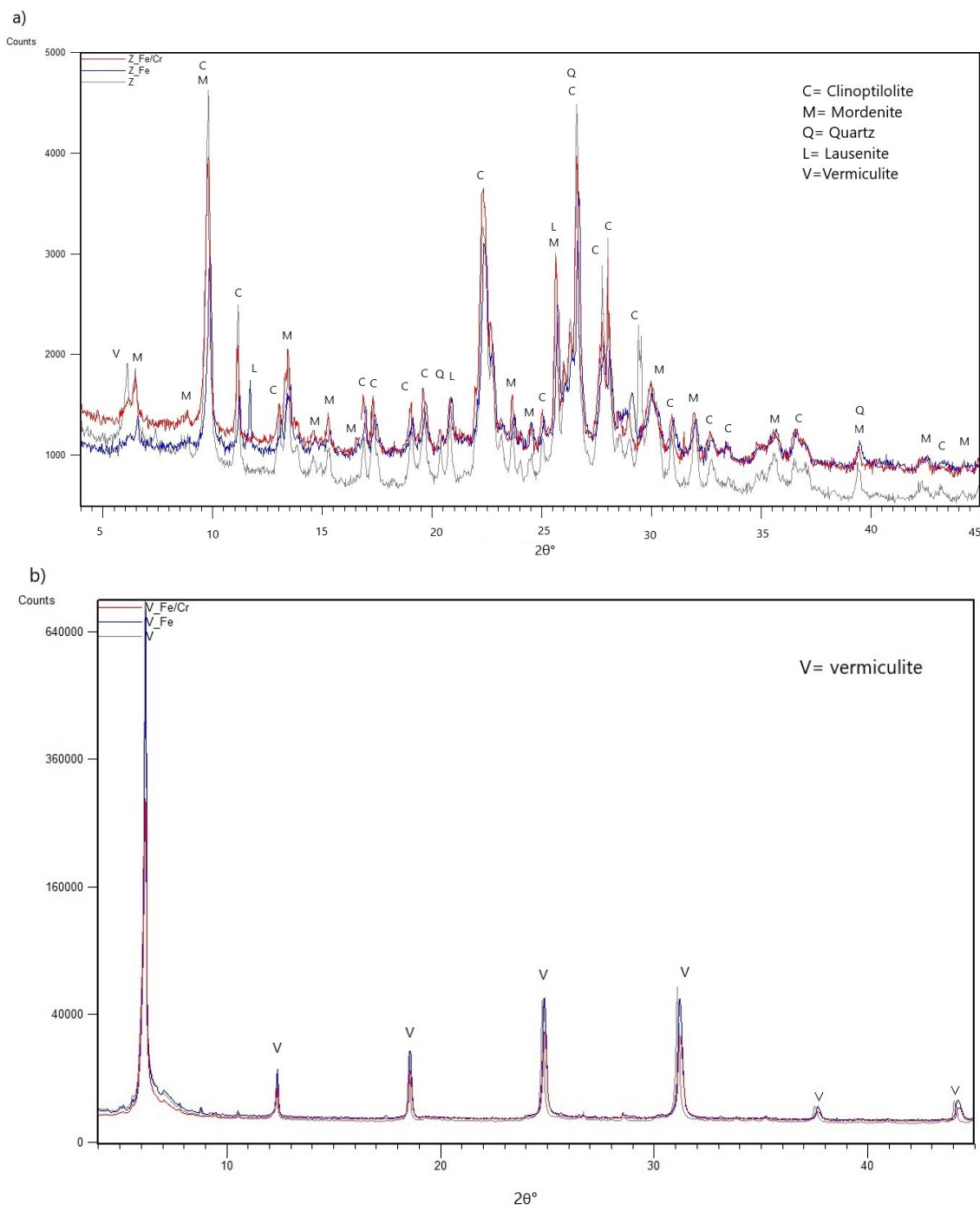
Fig. 11 - X-ray diffractograms of (a) zeolites (Z, Z-Fe and Z-Fe/Cr) and (b) vermiculites(V, V-Fe and V-Fe/Cr).

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. 11). Amorphous or poorly ordered products, such as a mixed phase of $Cr_xFe_{1-x}(OH)_3$ 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 $Cr(OH)_3$. As Cr(III) and Fe(III) precipitates are very stable under most soil conditions, they can be landfilled without further treatment.

4. 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 (meq) of Fe^{2+}, Cr^{3+} and K^+ 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 4).

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

	CEC	Fe^{2+} (initial)	Fe^{2+} (out)	K^+ (in)	Cr^{3+} (in)
		(meq in 0.5 g mineral)			
Z-Fe	1.3	0.25	0.19	0.43	0.015
V-Fe	1.1	0.35	0.16	0.015	0.015

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). Potassium ions from $K_2Cr_2O_7$ solution (0.43 meq) displaced almost all Fe(II) (0.19 meq) and other cations (0.24 meq) from zeolite pores. 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, neither potassium (0.015 meq) nor chromium(III) (0.015 meq) should be the main cation exchanged with Fe(II) (0.16 meq) of the interlayer space of vermiculite. 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.11).

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 to 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 become 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).

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 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 at 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 solution and, consequently, released Fe(II). In aqueous solution, the H^+ ions are in form of hydrated hydronium (H_3O^+. nH_2O), which did not change the interlayer space of vermiculite, maintaining the reflection of 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, increase 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 phase (eq. 5) (Schwertmann et al. 1989). The ion exchange and redox mechanisms which involves, respectively, the removal and consume of H^+, increase the pH of the solution and, consequently, increase the Cr(III) precipitates fraction (Fig. 9).

$$xCr(III)\ (aq) + (1 - x)Fe(III)\ (aq) + 3H_2O\ (l) \rightarrow (Cr_xFe_{1-x})(OH)_3\ (s) + 3H^+\ (aq) \qquad (5)$$
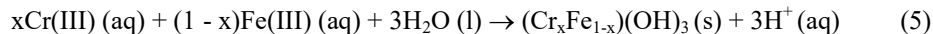
On the other hand, the hydrolysis and precipitation of Fe(III) and Cr(III) lowers pH (eq. 5), suppressing the precipitation of $Cr(OH)_3$ or the mixed Fe(III)/Cr(III) hydroxide (Seaman et al. 1999), and leaving part of the Cr(III) ions in solution (Fig. 8). To verify whether the precipitation of iron and chromium can actually decrease the pH of the solution, 0.07 g of $FeSO_4.7H_2O$ (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 considered 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 the Fe(II) and not Cr(III), as Na^+ has 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 solution has to be removed to prevent its oxidation back to Cr(VI). The Cr(III) removal from solution can be done by precipitation (increasing pH > 5) or by adsorption using untreated vermiculite or zeolite, as discussed earlier. In the last case, the presence of competing ions, such as, H^+ and K^+ must be considered and controlled.

Liu et al. (2010) used Fe(II)-vermiculite to remove Cr(VI) and obtained a maximum removal efficiency of 99.5% at pH 1, and concluded that Cr(VI) reduction depends on the acidity of the solution. 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) have to 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 addition of acids to increase the Cr(VI) removal efficiency.

The contribution of the iron(III) precipitate phase to the adsorption of Cr(VI) 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 solution.

5. CONCLUSIONS

Untreated zeolites and vermiculite exhibit no or little affinity for Cr(VI) adsorption, respectively. However, they have high ability to adsorb Fe(II) ions, which can 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 (K^+, Ca^{2+}) are smaller, requiring a solution with higher concentration of $FeSO_4.7H_2O$ for mineral treatment.

The main mechanisms involved in the Cr(VI) removal were the ion exchange followed by 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 solution than V-Fe, and, consequently, released more Fe(II) ions into 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 low concentration of Cr(VI) (<10 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). Reduction of Cr(VI) lead to precipitation of Fe(III) and Cr(III) hydroxides and decreased the pH of 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 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).

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4. CONCLUSÕES
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O estudo permitiu entender os principais mecanismos envolvidos na remoção de Cr(VI) utilizando zeólita e vermiculita tratadas com Fe(II). As amostras sem tratamento não foram eficientes na remoção de Cr(VI). Já o tratamento com Fe(II) foi muito eficaz em ambas as amostras, no entanto, a quantidade de Fe(II) adsorvida pela vermiculita foi maior que pela zeólita.

Nesse caso, os cátions trocáveis dos minerais (Mg^{2+} na vermiculita e K^+ e Ca^{2+} na zeólita) e das soluções (Fe^{2+}) foram determinantes nesse processo de troca, que favoreceu a entrada daqueles com menor raio iônico hidratado nos sítios de troca dos minerais.

Os íons Fe(II) adsorvidos pela zeólita e vermiculita foram deslocados para solução por troca iônica, porém por cátions distintos. Na zeólita, esse íon foi trocado pelo potássio da solução de dicromato de potássio, enquanto na vermiculita a troca foi realizada com os íons hidrônio (H_3O^+) da solução ácida. Uma vez liberado para a solução, os íons Fe(II) reagiram quase instantaneamente com o Cr(VI) da solução, reduzindo-o à Cr(III).

A quantidade de Fe(II) liberado pelos minerais foi maior que o necessário para reduzir 100% de Cr(VI) presente em soluções com até 50 mg L^{-1} de Cr(VI). Nesses casos, o excesso de Fe(II) permaneceu em solução. Nas soluções com 100 mg L^{-1} de Cr(VI) as eficiências de remoção de Cr(VI) caiu para 90% (vermiculita) e 95% (zeólita), e não houve sobra de Fe(II) na solução.

A fração reduzida do cromo, por sua vez, foi influenciada pelo pH da solução. Em pH>5, o Cr(III) precipitou, provavelmente, associado ao Fe(III). A precipitação causou a diminuição do pH da solução (<5) que, ao mesmo tempo, passou a inibi-lo e manter os íons de Cr(III) em solução. A fração de Cr(III) em solução não foi efetivamente adsorvida pelos minerais, devido à competição com outros cátions de menor raio iônico hidratado (como K^+ e H^+), cuja preferência é maior pelos sítios de troca da zeólita e vermiculita.

Para evitar que o Cr(III) em solução seja oxidado a Cr(VI), esses íons podem ser removidos por adsorção pela vermiculita (natural, ou seja, sem tratamento), ou ainda por precipitação, corrigindo-se o pH (>5) da solução.

O presente estudo revelou, portanto, a importância de conhecer os mecanismos de remoção de Cr(VI) envolvendo a troca catiônica, uma vez que vários parâmetros, como o pH e tipos de íons presentes na solução, podem interferir na sua eficiência.

5. REFERÊNCIAS (DA INTRODUÇÃO)

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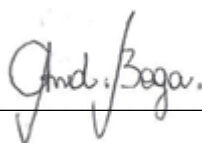
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ANEXOS

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Eu, Gabriella de Andrade Boga, co-autora do artigo "Mechanisms of chromium(VI) removal from solution by zeolite and vermiculite modified with iron(II)" autorizo a aluna de mestrado do PPGAAI, Maria Isabel Garcia Rosa, a utilizar o artigo para o trabalho de dissertação de mestrado intitulado "Mecanismos de remoção de cromo(VI) em solução por zeólita e vermiculita pré-tratadas com ferro(II).

15 de junho de 2021

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Assinatura