



Research article

A kinetic approach on hexavalent chromium removal with metallic iron

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ABSTRACT

This paper examines the mechanism of Cr(VI) removal with Fe(0), and the possible effect of various experimental parameters, from a kinetic perspective. The experimental data was analyzed using five different kinetic models: three for chemical reactions and two for adsorption processes. It was found that the process fitted well to the zero-order kinetic model for all investigated systems, excepting experiments conducted at 6 °C and those with nano-Fe(0), when the process followed the Ho's pseudo second-order model. Therefore, even though, under acidic conditions, chemical reduction can be generally considered as the main mechanism of Cr(VI) removal with Fe(0), under some experimental conditions (e.g. when working with nano-Fe(0) or at low temperatures), adsorption seems to be the dominant removal path. The enhanced Cr(VI) removal noticed in co-presence of SO₄²⁻ and Cl⁻ anions reiterates the significance of the secondary reductant Fe(II) within the process of Cr(VI) removal with Fe(0).

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1. Introduction

Nowadays, contamination of water environments has become a significant concern, especially in the industrialized countries, due to increasing anthropogenic inputs after the industrial revolution (Chrysochoou and Dermatas, 2015). Because metallic iron (Fe(0)) is a relatively low cost material, readily available, with low toxicity (Btatkeu et al., 2016), important efforts have been focused on the use of Fe(0) for the removal of a wide range of pollutants, both inorganic (e.g. heavy metals (Hashim et al., 2011), metalloids (Vitkova et al., 2017)) and organic (e.g. dyes (Raman and Kanmani, 2016), phenols (Nakatsuji et al., 2015), estrogens (Jarosova et al., 2015)). Heavy metals are particularly problematic contaminants because they are highly toxic, non-biodegradable, and persistent (Pehlivan and Altun, 2008). Chromium is an important metal with widespread use in various industries; as a result, large quantities of this metal have been discharged into the environment due poor storage practices, improper disposal or leakage of chromium waste. In natural environments, chromium can exist mainly in two oxidation states: (+III) and (+VI). Among these two, Cr(VI) exerts the most toxic effects on living organisms, having also the highest

mobility in the environment (Gheju, 2011, and references therein). Over the last decades, Fe(0) has been demonstrated to represent a highly efficient reagent for the removal of Cr(VI) from contaminated waters; however, there is yet no consensus at this time in what regards the mechanism of Cr(VI) removal with Fe(0). The first mechanism, proposed in the nineties (the "reductive precipitation" mechanism) (Cantrell et al., 1995), and widely accepted until our days (Kong et al., 2016), attributed the efficiency of Fe(0)-systems mainly to the direct electron transfer from Fe(0) surface to Cr(VI), coupled with (co-)precipitation of resulted Cr(III). It was probably suggested in agreement with the direct reductive dechlorination mechanism, previously proposed as the most likely cause of chlorinated organics removal with Fe(0) (Gillham and O'Hannesin, 1994). Subsequent studies have, however, acknowledged the importance of another process, Cr(VI) adsorption, as intermediate step within the mechanism of Cr(VI) removal with Fe(0) (Powell et al., 1995). Moreover, it has been indicated that adsorption on some types of Fe(0) (e.g. nano-sized) can be regarded not only as intermediate step, but also as a dominant Cr(VI) removal mechanism by itself (Ai et al., 2008). Recent studies also suggested that, in Fe(0)-H₂O systems, along with co-precipitation (Noubactep, 2015a) and size-exclusion (Yoon et al., 2011), adsorption is one of the main contaminant removal mechanisms, while reduction, when possible, occurs mainly indirectly via Fe(0) corrosion products

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(Noubactep, 2015b). Even though numerous studies investigated the kinetics of Cr(VI) removal with Fe(0) (Gheju, 2011, and references therein), to authors knowledge, the assessment of the kinetic model was not yet used to evaluate the role of different mechanisms within the process of Cr(VI) removal with Fe(0). Therefore, the goal of the present paper was to investigate the importance of different possible removal paths within the mechanism of Cr(VI) removal with Fe(0), as well as the effect of several important parameters, by means of kinetic analysis of experimental data.

2. Materials and methods

Commercially available Fe(0) from Alfa Aesar ($\geq 99\%$, $\sim 1\text{--}2$ mm) and from Merck ($\geq 99\%$, ~ 10 μm) (hereinafter referred to as milli-Fe(0) and micro-Fe(0), respectively) was used as received. In addition, nano-Fe(0) was synthesized via the liquid-phase reduction method with sodium borohydride, following a procedure described by Xi et al. (2010). Cr(VI) removal experiments were carried out in a 1.5 L Berzelius flask, by introducing a mass of 0.5 g Fe(0) into 1000 mL of Cr(VI) solution. The mixture was stirred (200 rpm) using an overhead Heidolph stirrer and, at preset intervals, samples were withdrawn and filtered. Cr(VI) concentration in the filtrate was analyzed by the 1,5-diphenylcarbazide colorimetric method at 540 nm (APHA, 1995), using a Specord 200 PLUS spectrophotometer. The pH of the solutions was set before the experiments by adding small amounts of concentrated H_2SO_4 and measured using an Inolab 7320 pH-meter. The morphology of the synthesized nano-Fe(0) was characterized by the use of transmission electron microscopy (TEM), using a FEI – Titan G2 80–200 microscope. The kinetics of Cr(VI) removal was evaluated using five kinetic equations: three suitable for chemical reactions and two for adsorption processes, as shown in the [Supplementary material](#); in addition, the intraparticle diffusion model was also applied when adsorption was found to be the dominant Cr(VI) removal path ([Supplementary material](#)).

3. Results and discussion

3.1. Effect of pH

The influence of solution pH was investigated at 20 °C, within the range of 1.1–3.5, using a 2 mg/L Cr(VI) solution and micro-Fe(0). It is shown that Cr(VI) removal significantly decreased with

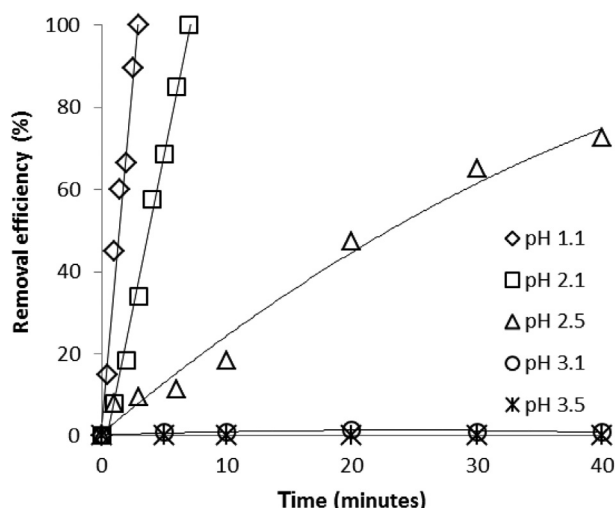
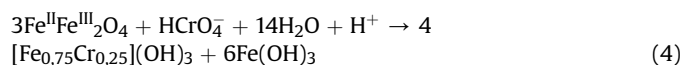
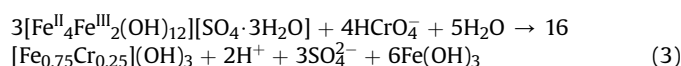
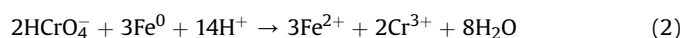


Fig. 1. Effect of pH on Cr(VI) removal with Fe(0).

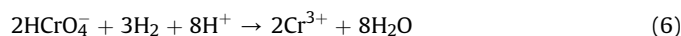
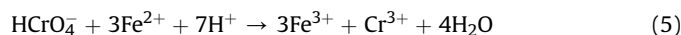
increasing pH, being already almost totally inhibited at pH 3.1 (Fig. 1). This observation can be ascribed to involvement of H^+ ions in processes contributing to Cr(VI) removal in Fe(0)- H_2O system. Cr(VI) removal with Fe(0) is the result of a complex interplay of processes such as adsorption, reduction and (co-)precipitation (Gheju, 2011). However, under the experimental conditions of the present study (acidic pH), the (co-)precipitation process can be excluded. Hence, in our case, only three pathways may be taken under consideration for the removal of Cr(VI) with Fe(0). The first one is adsorption of Cr(VI) on Fe(0), or onto oxide layers existent at Fe(0) surface (Geen et al., 1994):



The second pathway is the heterogeneous Cr(VI) reduction, which involves direct electron transfer from Fe(0) surface, or from corrosion products containing Fe(II) existent at Fe(0) surface (Gheju, 2011):



The third pathway is the homogenous Cr(VI) reduction by products of Fe(0) corrosion (Fe^{2+} and H_2) (Gheju, 2011):



It is obvious that, for most of these reactions, an increase in H^+ concentration will lead to an increase in efficiency of Cr(VI) removal (Le Châtelier's principle). In the same time, pH is an important parameter controlling adsorption of metal ions, due to its influence on adsorbent surface properties and on ions speciation in solution (Jain et al., 2009). Because adsorption of Cr(VI) is the first step of the heterogeneous reduction mechanism, it is clear that, when discussing the effect of pH on Cr(VI) removal with Fe(0), the influence of pH on the adsorption phase should also be considered. Since surface of Fe(0) corrosion products is mostly positively charged, they are good adsorbents for Cr(VI) anions (Noubactep, 2015a). With increasing concentration of H^+ ions in solution, the number of positively charged centers at Fe(0) surface also increases; as a result, the electrostatic forces of attraction which act between Cr(VI) anions and positively charged Fe(0) surface will also increase. In the same time, the competition for positively charged sites between Cr(VI) anions and HO^- ions diminishes with decreasing pH, as a result of decreasing HO^- concentration. The kinetic modeling of experimental data showed that the zero-order kinetic model provided the best match (Table S1 and Figs. S5–S9, [Supplementary material](#)), indicating reduction of Cr(VI) to Cr(III) as the main removal mechanism. This is in agreement with previous studies which have shown that, under acidic conditions, chemical reduction was the main pathway of Cr(VI) removal with Fe(0) (83.3%), and dissolved Fe(II) was the major reductant; nevertheless, adsorption was also responsible for the removal of a small amount of Cr(VI) (16.7%) (Gheju et al., 2016).

3.2. Effect of Cr(VI) concentration

The effect of this parameter was explored at 20 °C, by reacting

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