Evaluation by Continuous Flow Configuration of Inorganic Adsorbents Qualified for Cr(VI) Removal through Batch Experiments

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Abstract

This article reports on the results of pilot-scale tests for a variety of Cr(VI) inorganic reductants/adsorbents with respect to their potential implementation in drinking water treatment. Among the zero valent metals examined, only iron can completely reduce/remove Cr(VI), while the leached concentrations of most metals were found to overpass the respective drinking water regulation limit (examined metals: Fe^0, Mg^0, Zn^0, Cu^0). Iron sulphides can minimize Cr(VI) at sub-ppb level, however the leached Fe(II) concentration was substantially higher, than the drinking water regulation limit of 0.2 mg/L. Iron oxy-hydroxides (FeOOH) proved effective for Cr(VI) removal at almost sub-ppb levels, preserving simultaneously the water quality; however, the relatively low uptake capacity in this case (0.1 mg Cr(VI)/g) is a significant drawback for the subsequent full-scale implementation. Among the examined adsorbents only magnetite presented sufficient uptake capacity (4 mg Cr(VI)/g), considering the Cr(VI) breakthrough concentration of 10 μg/L without downgrading the important water quality characteristics, and thus, this material is mostly qualified for drinking water treatment.

Keywords

Cr(VI) removal, drinking water, RSSCTs, inorganic adsorbents, evaluation

INTRODUCTION

The pollution of ground waters by the presence of Cr(VI) has long been recognized as a severe environmental issue, following the indications for harmful effects on human health and other life forms (Costa, 2003; Linos et al.,2010). Along with its severe toxicity, the verification of Cr(VI) natural formation (Morrison et al., 2009; Kaprara et al., 2015; Kazakis et al., 2015) has made it a priority pollutant, crucial to be removed from water streams, designated as potable water sources. Up to date, several methods have been developed to remove Cr(VI) from water, such as chemical reduction (Mitrakas et al., 2011), adsorption (Mohan et al., 2006), ion-exchange (Dabrowski et al., 2004), membrane separation (Korus et al., 2009), electrodialysis (Nataraj et al., 2007) and phytoremediation (Cervantes et al., 2001). The respective literature survey indicates that among them, the most effective include a Cr(VI) reduction step to the insoluble and non-toxic Cr(III) form. In this direction, several inorganic reductants/adsorbents have been widely studied through batch experiments, such as zero valent metals (Montesinos et al., 2014), iron oxy-hydroxides/oxides (Simeonidis et al. 2015) and iron sulphides (Houda, 2007).

Among metals evaluated for reactivity towards Cr(VI) reduction through the performance of batch experiments, zero valent iron (ZVI) appears to be the most promising and several researchers have investigated its ability to remove Cr(VI) from aqueous solutions (Melitas et al., 2001; Niu et al., 2005; Chang et al., 2014), reporting high reduction rates and uptake capacity. A variety of other zero-valent metals (Al^0, Cu^0, Mg^0, Ni^0, Si^0 and Zn^0) have also been evaluated for Cr(VI) removal. Despite the increased reduction potentials of some metals in comparison to Fe^0, their uptake capacity in practice is restricted by the surface passivation in aqueous media. Complete reduction of Cr(VI) is achieved only by practicing Zn^0, Cu^0 and Mg^0 (Rivero-Huguet et al., 2009; Lee et al., 2013).

Within the group of iron oxy-hydroxides/oxides, magnetite (Fe_3O_4) presents the most promising solution for Cr(VI) removal, as it combines reductive and adsorption capacity (Simeonidis *et al.*, 2015). Specifically, the presence of Fe(II) ions on the structure of magnetite creates a surface reductive environment, able to reduce Cr(VI) dissolved in aqueous phase to insoluble Cr(III) forms, which remain attached to the surface (Gallios *et al.*, 2008). Granular ferric hydroxide has also been tested for Cr(VI) removal from drinking water sources, presenting maximum adsorption capacity 0.8 mg Cr(VI)/g in batch tests (Asgari et al., 2008).

Iron sulphides efficiency to reduce Cr(VI) has also been documented (Zouboulis et al., 1995; Patterson et al., 1997; Houda et al., 2007) with Mullet et al. (2004) reporting a removal capacity more than 100 mg Cr(VI)/g FeS at pH 7.

Although interesting experimental results indicate that the aforementioned materials can be successfully used for Cr(VI) removal, the application of these technologies in drinking water treatment depends mainly upon the satisfaction of certain pre-requirements, starting with the feasibility of the method to achieve residual Cr(VI) concentrations at very low ppb levels. This requirement should also be accompanied by the low operational time of the process, the feasibility of implementation in continuous flow full-scale operation, the sustainability of major physical and chemical characteristics of water and the acceptable capital and operating costs.

The aim of this study was to assess the ability of several inorganic reductant/adsorbent materials to meet the prerequisites for drinking water treatment by examining their efficiency under a continuous flow, Rapid Small Scale Column Tests (RSSCTs) configuration. Their evaluation towards Cr(VI) removal is focused on their ability to decrease residual Cr(VI) concentration below the recently established by the State of California (California Regulations Related to Drinking Water, 2014) regulation limit of 10 μg Cr(VI)/L in drinking water.

MATERIALS AND METHODS

Reagents

All metals examined were chemically pure, in granulated form. Iron oxy-hydroxides/oxides/sulphides were prepared at kilogram-scale by the aqueous co-precipitation of iron/sulfide salts in a two-stage continuous flow reactor similar to that described by Tresintsi et al. (2012). Important details of synthesis parameters are presented in Table 1. A chemically pure fused FeS and a pyrite ore (provided by Hellas Gold S.A.) were also tested for Cr(VI) removal.

Table 1. Synthesis parameters for the iron oxides/sulfides examined.

Material tested	Synthesis reagents	Reagents ratio	Synthesis pH
Fe_3O_4	$FeSO_4.H_2O$ / $Fe_2(SO_4)_3 \cdot 9H_2O$	Fe^{II}:Fe^{III} 1:2	12
FeOOH	$FeSO_4.H_2O$ / H_2O_2	Fe(III)	4
FeS	$FeSO_4.H_2O$ / Na_2S	Fe:S 1:1	10
Fe_2S_3	$Fe_2(SO_4)_3 \cdot 9H_2O$ / Na_2S	Fe:S 2:3	4

Procedure

In order to simulate the performance of a full-scale column, RSSCTs were designed upon the respective proportional diffusivity relationships, which appear to accurately mimic larger scale performance, working at 2 min Empty Bed Contact Time (EBCT). The adsorption columns (ID= 1.1 cm) were filled with the material granules under examination at a bed height of around 14 cm and fed from the top with 0.4 L/h of 100 μg/L Cr(VI) solution in artificial water, which was prepared according to National Sanitation Foundation (NSF) standard by dissolving 252 mg $NaHCO_3$, 12.14 mg $NaNO_3$, 0.178 mg $NaH_2PO_4 \cdot H_2O$, 2.21 mg NaF, 70.6 mg $NaSiO_3 \cdot 5H_2O$, 147 mg $CaCl_2 \cdot 2H_2O$ and 128.3 mg $MgSO_4 \cdot 7H_2O$ in 1 L of distilled water (Figure 1). Process pH was adjusted to 7.0±0.5 and temperature at 20±1^o C. Samples were periodically collected from the effluent and analyzed for residual Cr(VI) concentration.

Determination of the residual chromate was performed by the diphenylcarbazide spectrophotometric method, using a Perkin Elmer Lambda 2 UV/VIS spectrophotometer, while the other metals concentrations were measured either by flame or by Graphite Furnace Atomic Absorption Spectrophotometry (GF-AAS), using a Perkin Elmer AAnalyst 800 instrument.

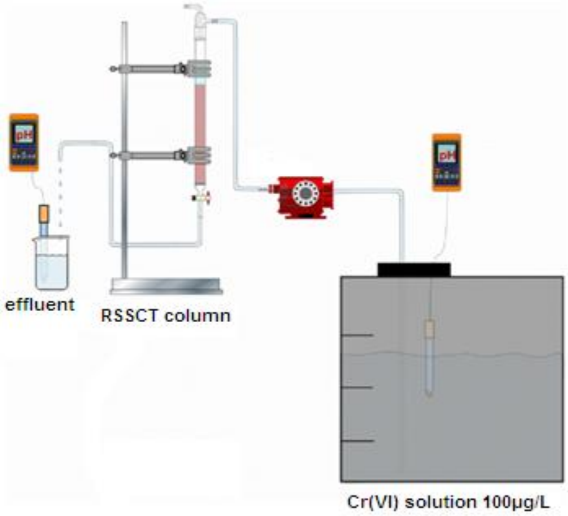

Figure 1. Experimental set-up for continuous flow process.

RESULTS AND DISCUSSION

Zero valent metals

The treatment of Cr(VI) solution through a Fe^0 column resulted in the complete removal of Cr(VI), while the relatively high residual iron concentration in the effluent implied that Fe^0 was oxidised to Fe(II), which in turn contributed to Cr(VI) reduction (Figure 2). Therefore, Fe^0 is not recommended for Cr(VI) removal from potable water, since the leached Fe(II) concentration was measured around 2 orders of magnitude higher, than the legislative regulation limit of 0.2 mg/L.

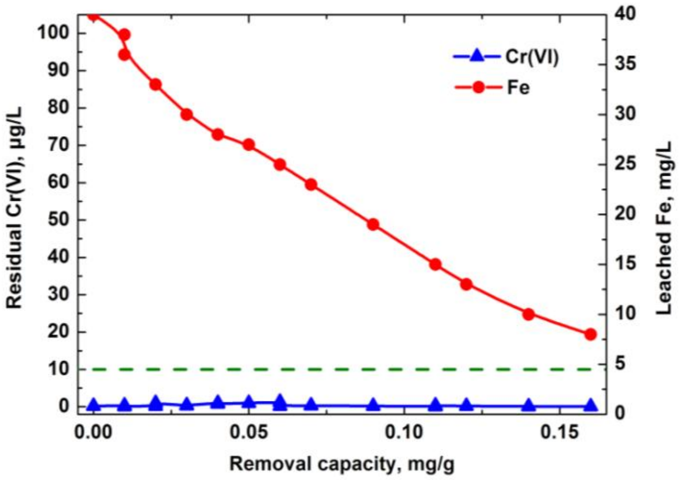

Figure 2. Breakthrough curve of Cr(VI) removal by the application of Fe^0 column (experimental conditions: initial Cr(VI): 100 μg/L, pH: 7.2±0.1, EBCT: 2 min, particle size: 0.25-0.5 mm, T: 20±1°C).

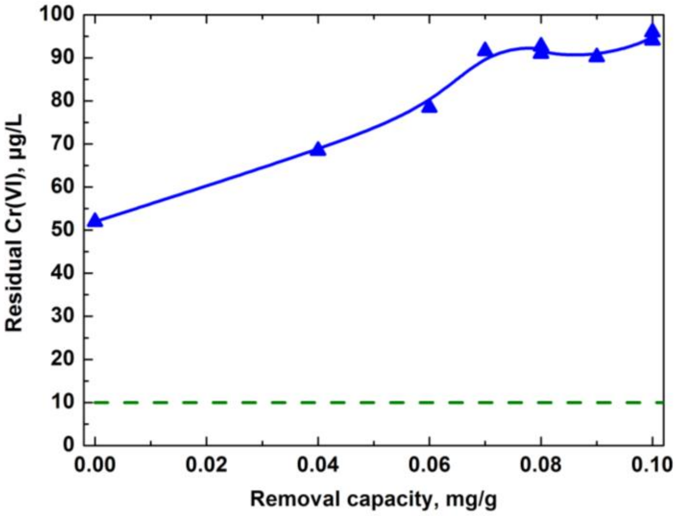

Figure 3. Breakthrough curve of Cr(VI) removal by the application of Mg^0 column (experimental conditions: initial Cr(VI): 100 μg/L, pH: 7.2±0.1, EBCT: 2 min, particle size: 0.1-0.5 mm, T: 20±1^o C).

In the case of Mg^0, the significant increase of pH value (>11), due to hydrolysis to $Mg(OH)_2$, favoured the release of hydrogen (H_2) gas (Lee at al., 2013), which inhibited Cr(VI) reduction, resulting in turn in a residual concentration higher than 50 μg/L – the respective maximum allowable drinking water concentration limit (Figure 3).

Zn^0 in continuous flow configuration failed to remove Cr(VI) to sub-ppb levels, presenting a rather moderate efficiency, with Cr(VI) residual concentration ranging between 10 and 20 μg/L for an inflow pH 7 and between 5 and 10 for an inflow pH 6.5 (Figure 4). The leached concentration of Zn was determined 8±2 and 12±3 mg/L respectively, indicating the need for an additional treatment step regarding the removal of residual Zn, since the respective quality standards for drinking water permit Zn concentration up to 5 mg/L. The latter (supplementary) treatment is expected to increase significantly both capital and operational costs. Similar results were also observed for the case of Cu^0, which achieved rather moderate effluent Cr(VI) concentrations, i.e. between 20-30 μg/L (data not presented).

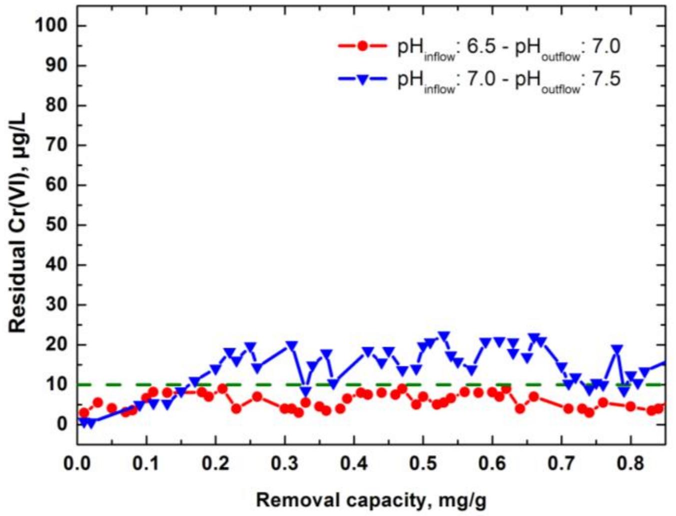

Figure 4. Breakthrough curve of Cr(VI) removal by the application of Zn^0 column (experimental conditions: initial Cr(VI): 100 μg/L, EBCT: 2 min, particle size: 0.1-0.25 mm, T: 20±1^o C).

Table 2. Metals concentration in the outflow of pyrite ore column.

Exp. conditions	As μg/L	Cd μg/L	Cu μg/L	Fe μg/L	Mn μg/L	Pb μg/L	Zn μg/L	Cr(VI) μg/L
Start up	5	ND	ND	ND	ND	50	>1500	85
Equilibrium	5	ND	ND	ND	ND	30	320	90
Detection limit	1	0.1	20	50	20	1	10	1.4
Regulation limit	10	5	$2x10^3$	200	50	10	-	10

ND: Not detectable

Iron sulphides

Although the laboratory synthesized FeS was found capable to remove Cr(VI) down to concentrations below the respective method's concentration detection limit (1.4 μg/L), the observed material's disintegration resulted to Fe leaching/dissolution at concentrations far higher, than the respective regulation limit of 0.2 mg/L (Figure 5). In the case of fused FeS, no disintegration was observed, but the concentration of leached Fe surpassed the 5 mg/L.

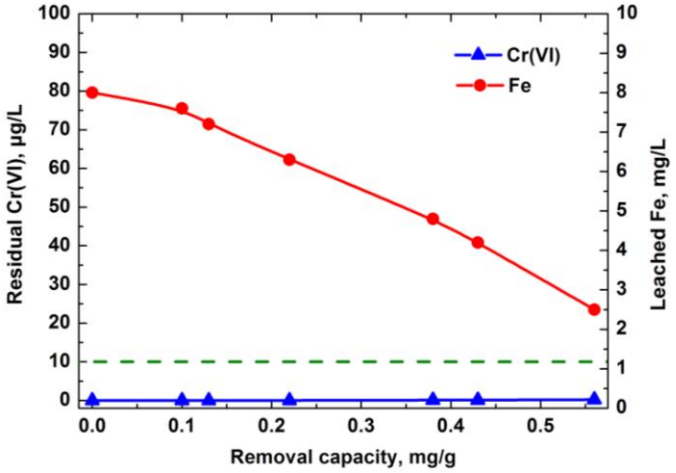

Figure 5. Breakthrough curve of Cr(VI) removal by the application of a FeS column (experimental conditions: initial Cr(VI): 100 μg/L, pH: 7.2±0.1, EBCT: 2 min, particle size: 0.25-0.5 mm, T: 20±1°C).

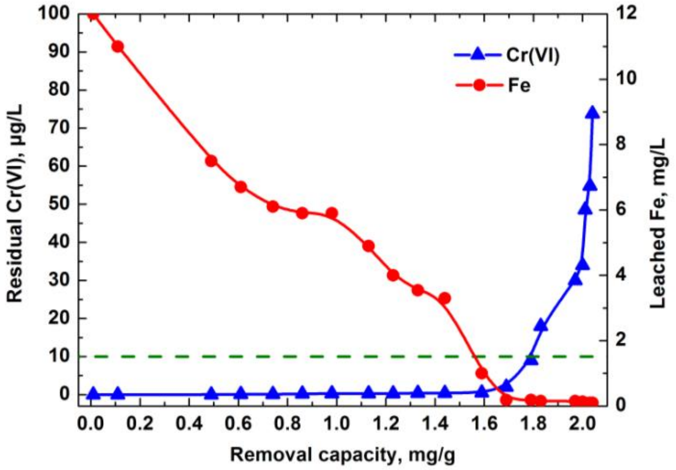

Figure 6. Breakthrough curve of Cr(VI) removal by the application of a Fe_2S_3 column (experimental conditions: initial Cr(VI): 100 μg/L, pH: 7.2±0.1, EBCT: 2 min, particle size: 0.25-0.5 mm, T: 20±1°C).

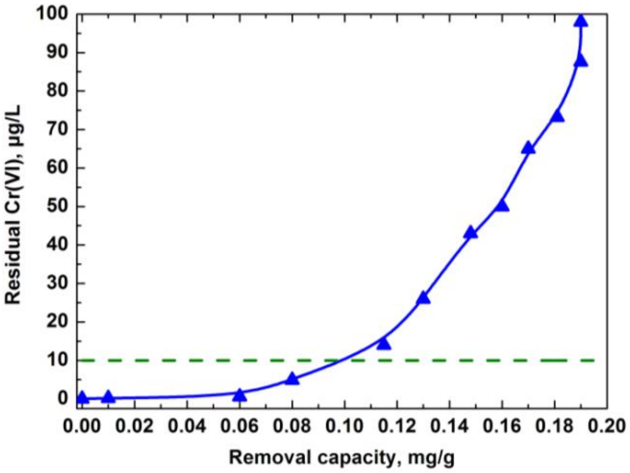

Figure 7. Breakthrough curve of Cr(VI) removal by the application of FeOOH column; (experimental conditions: initial Cr(VI): 100 μg/L, pH: 7.2±0.1, EBCT: 2 min, particle size: 0.25-0.5 mm, T: 20±1°C).

The leached Fe(II) concentration from the Fe_2S_3 column was gradually decreased, reaching the drinking water regulation limit of 0.2 mg/L after the treatment of 10^4 bed volumes of water (adsorption capacity 1.7 mg Cr(VI)/g Fe_2S_3), whereas the outflow Cr(VI) concentration remained below the method's detection limit. However, as soon as the leached Fe(II) concentration was minimized, the respective Cr(VI) concentrations in the treated water over passed the upcoming drinking water regulation limit of 10 μg/L, as well as the current one of 50 μg/L (Figure 6).
A pyrite ore was also tested, but it presented low Cr(VI) removal efficiency and leaching of several other metals, especially Pb (Table 2). Conclusively, iron sulphides were not qualified for drinking water treatment.

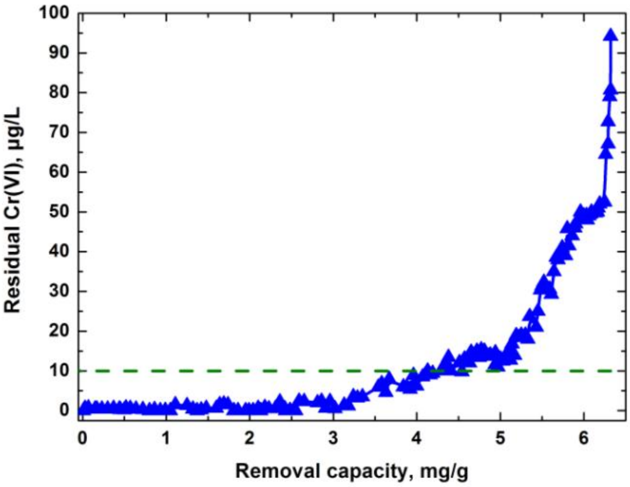

Figure 8. Breakthrough curve of Cr(VI) removal by the application of Fe_3O_4 column; (experimental conditions: initial Cr(VI): 100 μg/L, pH: 7.2±0.1, EBCT: 2 min, particle size: 0.25-0.5 mm, T: 20±1°C).

Iron oxy-hydroxides and oxides

Iron oxy-hydroxides (FeOOH) presented very low uptake capacity regarding Cr(VI) (0.1 mg Cr(VI)/g) at the breakthrough concentration of 10 μg/L, however without modification of major water quality characteristics (Figure 7). Similarly, when using magnetite (Fe_3O_4), it was not found to alter water quality characteristics, whereas it minimized the residual Cr(VI) concentrations down to sub-ppb level. In contrast to FeOOH, Fe_3O_4 achieved a sorption capacity close to 4 mg Cr(VI)/g for the residual concentration of 10 μg/L (Figure 8). This is probably attributed to magnetite's ability to reduce Cr(VI), before adsorbing it as Cr(III). Regarding the leached Fe, concentrations below the legislative maximum permissible concentration limit of 50 μg/L were always detected for the examined iron oxy-hydroxides or oxides.

CONCLUSIONS

The evaluation of several inorganic reductants/adsorbent materials by applying a continuous flow configuration revealed that, opposed to promising results obtained by batch experiments, most of these materials cannot be applied for drinking water treatment applications, due either to low uptake capacity towards Cr(VI) removal (e.g. for the cases of FeOOH, Cu^0), or because of metals' leaching above the respective drinking water regulation limits (e.g. for the cases of Fe^0, Mg^0, Zn^0, FeS, Fe_2S_3). In contrast, magnetite presents an adequate Cr(VI) removal capacity, achieving residual Cr(VI) concentrations at very low ppb levels, whereas meeting all major pre-requirements for drinking water treatment application with respect to the low-cost and environmental restrictions.

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