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Evaluation of several inorganic reductant/adsorbent materials for Cr(VI) removal by rapid small-scale column tests

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ABSTRACT

This article reports on the results of continuous flow tests for a variety of Cr(VI) inorganic reductants/adsorbents, including zero-valent metals (Fe^0, Mg^0, Zn^0 Cu^0), iron oxides (Fe_3O_4), iron oxy-hydroxides (FeOOH), iron sulphides (FeS/Fe_2S_3) and SnS, with respect to their potential implementation for drinking water treatment. The selection criteria for the examined materials were based on their high efficiency during batch experiments, along with their low toxicity to human health, directly related to the respective regulation limits. Among zero-valent metals tested, only Fe^0 can completely remove Cr(VI), while the leached concentration of Fe and Zn overpasses the corresponding drinking water regulation limits. Iron sulphides can minimize Cr(VI) at sub-ppb level, yet leached Fe(II) concentration is substantially higher than the drinking water regulation limit of 0.2 mg/L. Similarly, SnS can minimize Cr(VI) at sub-ppb level, although leached Sn concentration overpasses the aesthetic limit for drinking water quality. Iron oxy-hydroxide proved effective for Cr(VI) removal at sub-ppb level, preserving simultaneously the water quality. However, its relatively low adsorption capacity (0.1 mg Cr(VI)/g FeOOH) is a significant drawback for full-scale implementation. Among the examined adsorbents only magnetite presented sufficient uptake capacity (4 mg Cr(VI)/g Fe_3O_4) at the breakthrough concentration of the upcoming regulation limit of 10 μg/L, without downgrading water quality, and thus qualified for drinking water treatment.

Keywords: Cr(VI) removal; Drinking water; Reductants; Adsorbents; Evaluation; RSSCTs

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1. Introduction

The pollution of groundwaters by Cr(VI) has long been recognized as an important environmental health issue, following the positive indications for harmful effects of this specie on humans and other life forms [1,2]. Along with its severe toxicity, the verification of Cr(VI) natural (geochemical) formation [3–5] has made it a priority pollutant, crucial to be removed from water bodies (mostly groundwaters), designated as potable water sources. Although US EPA and European Community limit the presence of total chromium in drinking water to 0.1 and 0.05 mg/L, respectively, the adoption of a Cr(VI) maximum contaminant level at 0.01 mg Cr(VI)/L from the state of California (July 1, 2014) is believed to be followed by the establishment of this latter concentration as drinking water regulation limit worldwide in the near future. Therefore, it is considered as necessary to develop efficient technologies that will be able to meet this new requirement.

Up to date, several methods have been developed to remove Cr(VI) from waters, such as chemical reduction [6], adsorption [7], ion exchange [8], membrane separation [9],

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electrodialysis [10] and phytoremediation [11]. The respective literature survey indicates that among them, the most effective treatment techniques include a Cr(VI) reduction step to the insoluble and much less toxic Cr(III) form, which can be easily removed by precipitation as insoluble hydroxide. In this direction, several inorganic reductants/adsorbents have been widely studied, usually by employing batch experiments, such as zero-valent metals [12], iron oxy-hydroxides/oxides [13] and iron sulphides [14].

Among the evaluated metals, regarding reactivity towards the Cr(VI) reduction by performing batch experiments, zero-valent iron appears to be the most promising, and several researchers have investigated its ability to remove Cr(VI) from aqueous solutions [15–17], reporting high reduction rates. A variety of other zero-valent metals (Al^0, Cu^0, Mg^0, Ni^0, Si^0 and Zn^0) have been also evaluated for Cr(VI) removal. Despite the increased reduction potentials of some metals in comparison with Fe^0, their uptake capacity in practice is restricted by their passivation in aqueous media due to surface covering by formed oxides/hydroxides. The complete reduction of Cr(VI) can be achieved only by practicing Zn^0, Cu^0 and Mg^0 [18,19].

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 [13]. Specifically, the presence of Fe(II) ions in the structure of magnetite creates a surface reductive environment, able to reduce dissolved Cr(VI) in the aqueous phase towards insoluble Cr(III) forms, which can remain attached to the surface [20]. The application of granular ferric hydroxide for Cr(VI) removal from drinking water sources in batch experiments is reported to present a maximum adsorption capacity of 0.8 mg Cr(VI)/g [21]. The efficiency of iron sulphides to reduce Cr(VI) has been also documented [14,22,23] with Mullet et al. [24] reporting a removal capacity more than 100 mg Cr(VI)/g FeS at pH 7.

Although the obtained interesting experimental results may 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 applicable method to achieve residual Cr(VI) concentrations at the very low ppb level and considering also the low toxicity of adsorbent materials, evaluated in comparison with the respective drinking water regulation limits. In addition to these requirements, the small overall "reaction" (operational) time of treatment process, the feasibility of implementation in continuous-flow full-scale operation, the sustainability of major physical and chemical characteristics of treated water to be subsequently used as drinking and the acceptable capital and operating costs should be also taken into account.

The aim of this study was to assess the ability of several inorganic reductants/adsorbents materials to meet the prerequisites for drinking water treatment, by examining their efficiency for Cr(VI) removal through continuous flow rapid small-scale column tests (RSSCTs). The evaluation was focused on their ability to decrease the residual/breakthrough Cr(VI) concentration below the expected upcoming regulation limit of 10 μg/L.

2. Materials and methods

2.1. Reagents

All the examined metals (Fe, Mg, Cu, Zn) were of reagent grade and in granulated form. The tested iron oxy-hydroxides/oxides/sulphides were prepared at kilogram-scale quantities by the aqueous co-precipitation of iron, in certain cases with sulphide salts, using a two-stage continuous flow reactor similar to that described by Tresintsi et al. [25]. Similarly, SnS was prepared by the co-precipitation of $SnCl_2·xH_2O$ with Na_2S. The most important details of parameters for their preparation are presented in Table 1. A reagent grade fused FeS (by Merck Chemicals) and an iron pyrite ore (provided by Hellas Gold S.A., Chalkidiki, Greece) were also tested for comparison reasons for Cr(VI) removal.

2.2. Procedure

In order to simulate the performance of a full-scale operating adsorption column, RSSCTs were designed upon the respective proportional diffusivity relationships, which appear to accurately mimic the larger scale performance, working at 2 min empty bed contact time. The adsorption columns (Inner diameter = 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 standard by dissolving 252 mg $NaHCO_3$, 12.14 mg $NaNO_3$, 0.178 mg $NaH_2PO_4·H_2O$, 2.21 mg NaF, 70.6 mg $NaSiO_3·5H_2O$, 147 mg $CaCl_2·2H_2O$ and 128.3 mg $MgSO_4·7H_2O$ in 1 L of distilled water (Fig. 1). Feeding solution pH was adjusted at 7.0 ± 0.1 (and 6.5 ± 0.1 for Zn^0 column) either with 1 N HCl or with 1 N NaOH.

Process temperature was kept constant at 20°C ± 1°C. Samples were periodically collected from the effluent and

Table 1
Composition and surface properties of examined materials

Material tested	Synthesis reagents	Synthesis pH	Surface charge density (mmol [OH^-]/g)	PZC	IEP	Specific surface area (m^2/g)
FeS	$FeSO_4·H_2O/Na_2S$	10	1	11	4.7	5.4
Fe_2S_3	$Fe_2(SO_4)_3/Na_2S$	4	2.6	5.6	6.8	6
FeOOH	$FeSO_4/H_2O_2$	4	2.8	3	7.1	125
Fe_3O_4	$FeSO_4/Fe_2(SO_4)_3$	12	0.9	9.2	6.6	69
SnS	$SnCl_2/Na_2S$	9	2.7	7	2.5	46

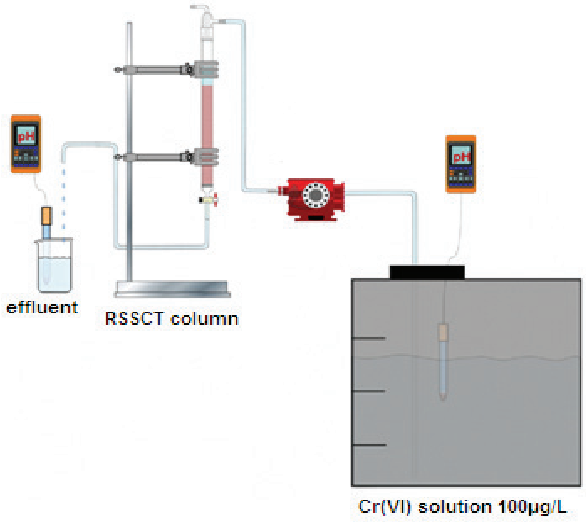

Fig. 1. Experimental setup for continuous flow process (RSSCT tests).

analysed for residual Cr(VI) concentration, as well as for other important leached compounds. The determination of residual chromate was performed by the application of diphenylcarbazide spectrophotometric method, using a Perkin Elmer Lambda 2 UV/VIS spectrophotometer, while the concentrations of other metals were measured either by flame or by graphite furnace atomic absorption spectrophotometry (GF-AAS), using a Perkin Elmer AAnalyst 800 instrument.

3. Results and discussion

3.1. Zero-valent metals

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

The mechanism of chromium removal includes a set of reactions such as:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{1}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{2}$$

$$Cr^{6+} + 3e^- \rightarrow Cr^{3+} \tag{3}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \tag{4}$$

$$xCr^{3+} + (1\text{-}x)Fe^{3+} + 3H_2O \rightarrow (Cr_xFe_{1\text{-}x})(OH)_3\,(s) + 3H^+ \tag{5}$$

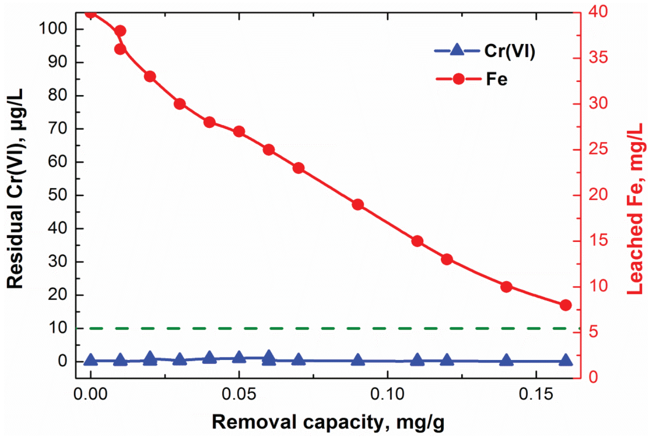

Fig. 2. Breakthrough curve of Cr(VI) using a column filled with Fe^0 (particle size 0.25–0.5 mm).

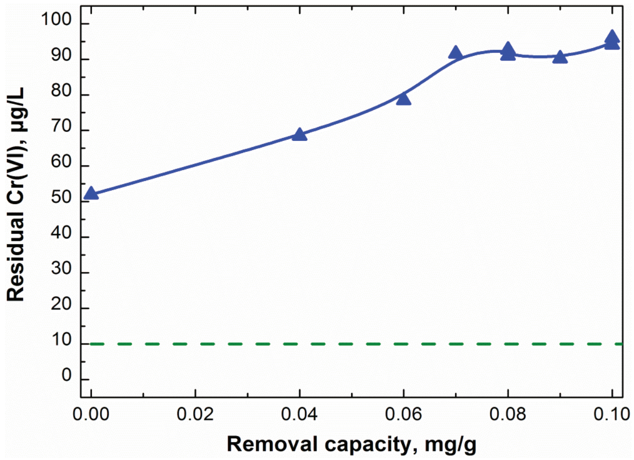

Fig. 3. Breakthrough curve of Cr(VI) using a column filled with Mg^0 (particle size 0.1–0.5 mm).

When Mg^0 was tested, the significant increase of pH value (>11), due to its hydrolysis to $Mg(OH)_2$ (Eq. (6)), favoured the release of hydrogen (H_2) gas [19], which was found to inhibit the reduction of Cr(VI) resulting in turn in a breakthrough concentration even higher than the current regulation limit of 50 µg/L (Fig. 3). Reactions taking place during Mg^0 application in a column are presented in Eqs. (3), (6)–(8).

$$Mg^0 + 2H_2O \rightarrow Mg^{2+} + H_2\uparrow + 2(OH^-) \tag{6}$$

$$Mg^0 \rightarrow Mg^{2+} + 2e^- \tag{7}$$

$$Cr^{6+} + 3e^- \rightarrow Cr^{3+} \tag{3}$$

$$Cr^{3+} + 3H_2O \rightarrow Cr(OH)_3 + 3H^+ \tag{8}$$

Zn^0 in continuous flow configuration failed to remove Cr(VI) to the requested sub-ppb level, presenting a rather moderate efficiency, with the Cr(VI) residual concentration to be ranged between 10 and 20 µg/L for the pH value 7 and between 5 and 10 for the pH value 6.5 (Fig. 4). The leached concentration of Zn was determined as 8 ± 2 and 12 ± 3 mg/L, respectively, suggesting that an additional treatment step should be applied, regarding the removal of residual high Zn concentration, since the (aesthetic) quality standards for drinking water permit a value up to 5 mg Zn/L. It is self-evident that the additional zinc removal will increase significantly both capital and operational cost. Similar results were also observed by examining the Cu^0, which achieved a moderate effluent Cr(VI) concentration, ranging between 20 and 30 μg/L, while the leached Cu concentration was 1.5 ± 0.5 mg/L (Fig. 4).

Cr(VI) removal by zero-valent Cu and Zn can be described by the following equations:

$$M^0 \rightarrow M^{2+} + 2^{e-} \tag{9}$$

$$Cr^{6+} + 3e^- \rightarrow Cr^{3+} \tag{3}$$

$$Cr^{3+} + 3H_2O \rightarrow Cr(OH)_3 + 3H^+ \tag{8}$$

$$M^{2+} + 2H_2O \rightarrow M(OH)_2 + 2H^+ \tag{10}$$

where M is Cu and Zn.

However, the "participation" of Eq. (10) in Cr(VI) process is considered of minor importance due to relatively high solubility of the corresponding hydroxides (K_{sp} $Cu(OH)_2$= 1.6×10^{-19}, K_{sp} $Zn(OH)_2 = 5 \times 10^{-17}$) resulting in turn in leaching of high Cu and Zn concentrations.

3.2. Iron sulphides

Although laboratory-synthesized FeS was found capable to remove Cr(VI) even below the applied analytical method's detection limit of 1.4 μg/L, the observed disintegration of this material resulted to Fe(II) leaching at concentrations far higher than the respective regulation limit of 0.2 mg/L (Fig. 5). In case of using, alternatively, the reagent grade fused FeS, the concentration of leached (dissolved) Fe(II) surpassed 5 mg/L, although no disintegration was observed.

The leached Fe(II) concentration from a column filled with Fe_2S_3 was gradually decreased, reaching the drinking water regulation limit of 0.2 mg/L after the treatment of 10^4 bed volumes of water (resulting to an uptake capacity of 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 overpassed the upcoming drinking water regulation limit of 10 μg/L, as well as the current one of 50 μg/L (Fig. 6).

Cr(VI) reduction by iron sulphides is mainly based on dissolved Fe(II), and it can be described by the overall reaction:

$$Cr^{6+} + 3Fe^{2+} \rightarrow Cr^{3+} + 3Fe^{3+} \tag{11}$$

$$xCr^{3+} + (1-x)Fe^{3+} + 3H_2O \rightarrow (Cr_xFe_{1-x})(OH)_3\ (s) + 3H^+ \tag{5}$$

S^{2-} oxidation also attributes to Cr(VI) reduction; however, final product of this reaction can be complicated due to the complex oxidation states of sulphur. Yellowing of treated water and adsorption bed surface during RSSCTs experiments is indicative of the production of elemental sulphur.

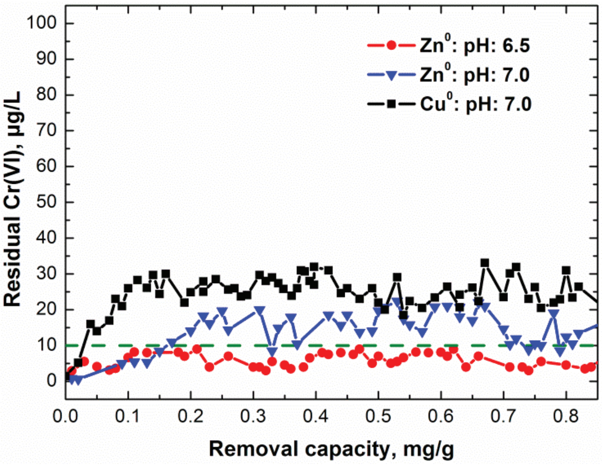

Fig. 4. Breakthrough curve of Cr(VI) using a column filled with Zn^0 (particle size 0.1–0.5 mm) or Cu^0 (particle size 0.25–0.5 mm).

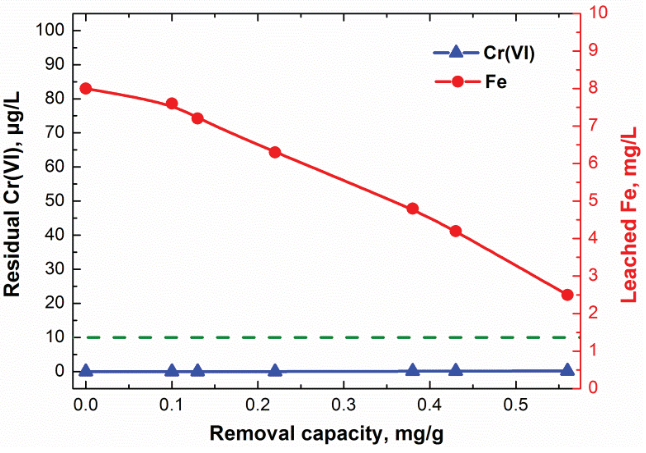

Fig. 5. Breakthrough curve of Cr(VI) using a column filled with FeS (particle size 0.25–0.5 mm).

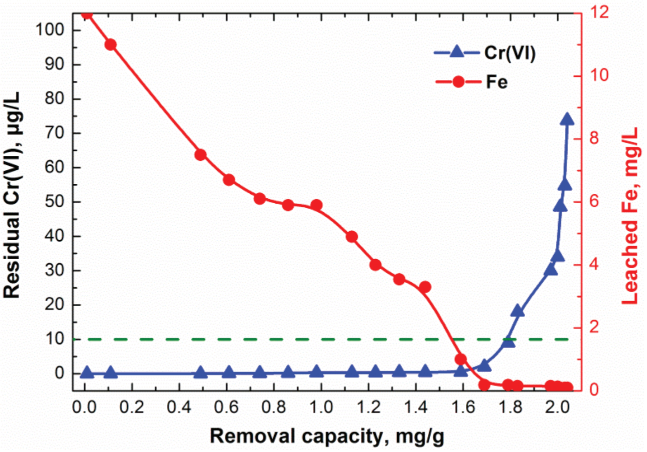

Fig. 6. Breakthrough curve of Cr(VI) using a column filled with Fe_2S_3 (particle size 0.25–0.5 mm).

Eqs. (3), (8) and (12)–(14) describe collateral reactions during Cr(VI) removal under continuous flow application in adsorption bed setup.

$$FeS \rightarrow Fe^{2+} + S^{2-} \tag{12}$$

$$S^{2-} \rightarrow S^{o} + 2e^{-} \tag{13}$$

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \tag{14}$$

$$Cr^{6+} + 3e^{-} \rightarrow Cr^{3+} \tag{3}$$

$$Cr^{3+} + 3H_2O \rightarrow Cr(OH)_3 + 3H^{+} \tag{8}$$

An iron pyrite ore was also tested, which presented low Cr(VI) removal efficiency, as well as leaching of several other metal contaminants, and especially Pb (Table 2). Conclusively, iron sulphides were not qualified in general for drinking water treatment.

3.3. Iron oxy-hydroxide and magnetite

The use of iron oxy-hydroxide (FeOOH) as adsorbent was found to present very low uptake capacity (0.1 mg Cr(VI)/g), regarding Cr(VI) removal at the breakthrough concentration of 10 µg/L, however without provoking any modification of major water quality characteristics (Fig. 7). The low efficiency of FeOOH towards Cr(VI) removal is due to the absence of any reducing ability of this material and is solely attributed to adsorption. Considering its adsorption capacity and the cost of commercially available FeOOH (6–12 €/kg), the treatment cost for the application of FeOOH in full-scale is estimated to range between 0.6 and 1.2 €/m³ for every 10 µg Cr(VI)/L removal.

Similarly to the case of FeOOH, when using magnetite (Fe_3O_4) as reductant/adsorbent, no alteration of water quality characteristics was observed, whereas Fe_3O_4 was found able to minimize the residual Cr(VI) concentration down to sub-ppb level. However, in contrast to FeOOH, Fe_3O_4 was able to achieve a sorption capacity close to 4 mg Cr(VI)/g, regarding the residual concentration of 10 µg/L (Fig. 8). This is probably attributed to magnetite's ability to reduce Cr(VI) (Eqs. (3) and (15)), before adsorbing it as Cr(III) [26]. Regarding the leached (solubilized) Fe(II), the respective concentrations were always found below the detection limit of flame atomic adsorption spectroscopy (50 µg/L) for the examined materials (iron oxy-hydroxide and magnetite).

$$2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + 2H^{+} + 2e^{-} \tag{15}$$

$$Cr^{6+} + 3e^{-} \rightarrow Cr^{3+} \tag{3}$$

3.4. Tin sulphide

Tin sulphide in RSSCTs configuration experiments presented the improved uptake capacity of 10.4 mg Cr(VI)/g,

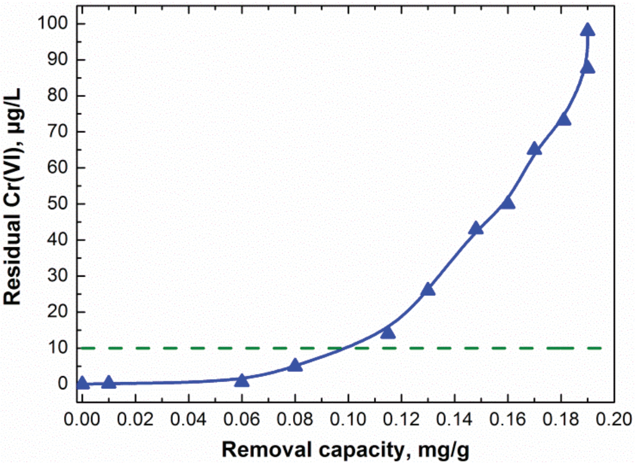

Fig. 7. Breakthrough curve of Cr(VI) using a column filled with FeOOH (particle size 0.25–0.5 mm).

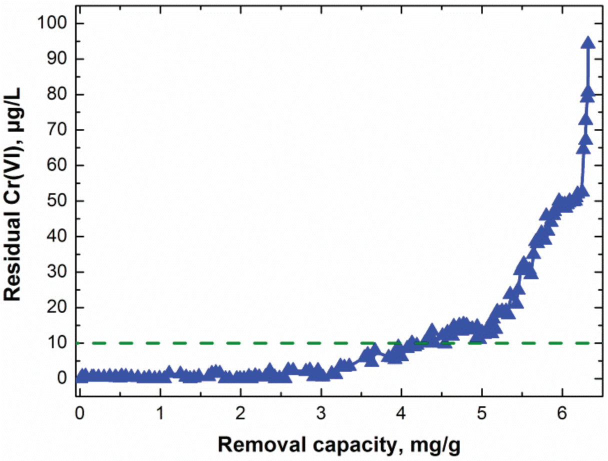

Fig. 8. Breakthrough curve of Cr(VI) using a column filled with Fe_3O_4 (particle size 0.25–0.5 mm).

Table 2
Concentrations of metals in the outflow of a column filled with iron sulphide ore

Experimental 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	>1,500	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	2×10^3	200	50	10	–	10

Note: ND – Not detectable.

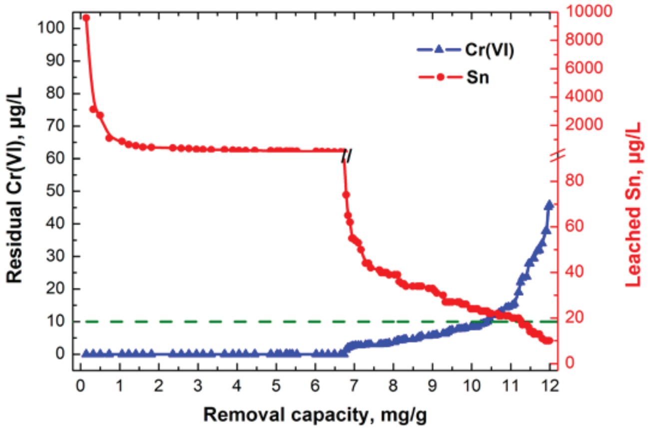

Fig. 9. Breakthrough curve of Cr(VI) by using a column filled with SnS (particle size 0.25–0.5 mm).

regarding the residual Cr(VI) concentration of 10 μg/L. However, the leached Sn concentration in the treated water was up to 10 mg/L at the beginning of the experiment, which gradually decreased to low ppb level at the end. Similarly to Fe_2S_3, as leached Sn concentration was diminished, the breakthrough concentration of Cr(VI) overpassed the upcoming regulation limit of 10 μg/L, as well as the existing regulation limit of 50 μg/L (for total chromium) (Fig. 9).

Mechanism scheme of Cr(VI) removal includes oxidation of Sn^{2+} to Sn^{4+} and oxidation of sulphides to elemental sulphur resulting in reduction of Cr^{6+} to Cr^{3+} as shown by the following reaction equations:

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^{-} \qquad (16)$$

$$S^{2-} \rightarrow S^{o} + 2^{e-} \qquad (13)$$

$$Cr^{6+} + 3e^{-} \rightarrow Cr^{3+} \qquad (3)$$

$$Cr^{3+} + 3H_2O \rightarrow Cr(OH)_3 + 3H^{+} \qquad (8)$$

Although no regulation limit for Sn presence in drinking water is established, a concentration value at ppm level is considered as too high to permit its application in full-scale treatment.

4. Conclusions

The evaluation of several inorganic reductants/adsorbents using a continuous flow configuration, opposed to promising results obtained by the respective batch experiments, revealed that most of these materials cannot be applied at drinking water treatment, due to several limitations, such as: (i) low uptake capacity towards Cr(VI) removal (FeOOH), (ii) inability to meet the upcoming regulation limit of 10 μg Cr(VI)/L (for the cases of Cu^0, Mg^0, Zn^0 metals) and (iii) leaching (solubilisation) of metals to concentrations above the corresponding drinking water regulation limit (for the cases of examined Fe^0, Zn^0, FeS, Fe_2S_3, SnS), indicating the need for an additional treatment step for their removal. In contrast, magnetite presented an adequate Cr(VI) removal capacity, achieving residual Cr(VI) concentrations at very low ppb level, while meeting all major requirements for drinking water treatment, including the low-cost and other environmental restrictions criteria.

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