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Potential application of inorganic sulfur reductants for Cr(VI) removal at sub-ppb level

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ABSTRACT

In this study, the efficiency of inorganic sulfur reductants (ISRs) for the Cr(VI) removal from drinking water at sub-ppb level was evaluated. Particularly, $NaHSO_3$, $Na_2S_2O_3$, $Na_2S_2O_4$, $Na_2S_2O_5$, and Na_2S were examined at doses up to 50 mg S/L, which is equivalent to an increase in sulfate concentration up to 150 mg/L in the treated water. Experimental results showed that the removal efficiency is strongly influenced by solution pH. The optimum pH lies at the range 2–4 for all ISRs tested, whereas their efficiency gradually decreases due to the competition with dissolved oxygen, as reaction pH value increases from 4 to 9. At the typical for natural water pH 7, only $Na_2S_2O_4$ was found capable to reduce an initial Cr(VI) concentration of 100 μg/L down to the sub-ppb level. The reaction kinetics for this reagent showed that 85% of total Cr(VI) removal was achieved within 2 h. It is important to note that at the equilibrium, reached after 8 h, sulfate concentration was safely below the drinking water regulation limit. On the other side, the application of $Na_2S_2O_5$, $Na_2S_2O_3$, and $NaHSO_3$ resulted in residual Cr(VI) concentrations not lower than 60 μg/L, while the addition of Na_2S, which proved more efficient (residual Cr(VI) 18 μg/L), was responsible for an unpleasant odor indicating the sulfide's presence.

Keywords: Cr(VI) removal; Drinking water; Inorganic sulfur reductants

1. Introduction

Chromium is a naturally occurring element found in rock, soil, and groundwater. It is commonly present in the environment in two forms, Cr(III) and Cr(VI). Considering that Cr(III) solubility at common pH range of natural waters (6.5–8.5) is significantly lower than 5 μg/L, it is more than clear that the presence of increased level of naturally occurring chromium should be attributed mainly to Cr(VI) [1]. Cr(VI) can be naturally formed in groundwater, due to the oxidation of Cr(III) present in the soils derived from ultramafic and ophiolitic rocks [2,3]. These soils

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contain chromite grains (0.2–1 mm) that are usually accompanied or covered by manganese oxides (i.e. MnO_2). Manganese oxides, sometimes assisted by microbial reactions, are the main oxidants of chromium in aquatic systems [4,5]. In addition, Cr(VI) can also reach groundwater supplies as an industrial by-product from manufacturing processes for stainless steel, chrome plating, dyes, pigments, leather tanning or wood preservation.

The special interest for chromium arises from the fact that Cr(III) is considered an essential element for human and animal nutrition, while Cr(VI) has been identified as toxic, causing various types of cancer and DNA damage [6]. Although World Health Organization considers Cr(VI) as a priority pollutant, US EPA and European Community limit total chromium to 0.1 and 0.05 mg/L, respectively. However, there is a strong debate worldwide for establishing a maximum contaminant level (MCL) for Cr(VI) at sub-ppb level, increasing the necessity for developing a cost-effective treatment method which will meet this challenge.

The severe toxicity of Cr(VI) has engendered interest in processes for its removal from both industrial effluents and potable water. A significant number of remediation methods have been developed including chemical reduction followed by precipitation [7,8], adsorption [9], ion exchange [10], membrane separation [11], electrodialysis [12], phytoremediation [13], flotation [14], and solvent extraction [15]. Although there is extensive scientific literature, the major part of the afore-mentioned methods refers to the remediation of high Cr(VI) concentrations in acidic environment, while the number of processes related to drinking water treatment is limited. In addition, taking into account that drinking water treatment focuses on Cr(VI) removal at sub-ppb level while maintaining the physicochemical characteristics of water, it becomes even more difficult to establish an effective large-scale process. Among remediation technologies that have been documented to remove chromium from water, the most widely practiced process is the reduction of Cr(VI) and its precipitation as $Cr(OH)_3$. The most promising reductants that have already been practiced are zero-valent iron (ZVI) [7,16], ferrous [Fe(II)] salts [8,17], and various inorganic sulfur reductants (ISRs) [18–26]. Although ZVI removes Cr(VI), its efficiency is strongly influenced by surface passivation while it enriches treated water with dissolved ferrous ions. Ferrous salts effectively remove Cr(VI) at sub-ppb level through the coprecipitation with ferric ions under the following scheme:

$$\mathrm{Cr(VI)_{(aq)}} + 3\mathrm{Fe(II)_{(aq)}} \rightarrow \mathrm{Cr(III)_{(aq)}} + 3\mathrm{Fe(III)_{(aq)}} \tag{1}$$

$$x\mathrm{Cr(III)} + (1-x)\mathrm{Fe(III)} + 3\mathrm{H_20} \rightarrow \mathrm{Cr}_x\mathrm{Fe}_{1-x}\mathrm{(OH)_{3(s)}} + 3\mathrm{H^+} \tag{2}$$

where x can vary between 0 and 1. Ferrous dose is generally 10–25 times higher than that of Cr(VI) concentration [11], which in turn results in a proportional increase in $Cr_xFe_{1-x}(OH)_3$ sludge quantity in comparison to single $Cr(OH)_3$ one.

ISRs have attracted attention from many researchers for Cr(VI) removal. Kim et al. [20] investigated the reaction stoichiometry, kinetics, and mechanism for the reduction of Cr(VI) by hydrogen sulfide (H_2S). They suggested a second-order reaction rate, which increased at low pH resulting in $Cr(OH)_3$ and elemental sulfur formation. Schroeder and Lee [18] examined the reduction of Cr(VI) in natural waters by Na_2S and reported a promising efficiency of sulfides, however, not reaching sub-pbb level. The residual extremely odorous concentration of sulfides is considered as the most significant disadvantage of these technologies. FeS efficiency to reduce Cr(VI) has also been studied by several researchers [21,22,25]. Although interesting results were obtained, which revealed FeS as a promising Cr(VI) reducing agent, they referred to the treatment of high Cr(VI) concentration solutions at acidic pH values not consistent with drinking water treatment. Oxygenated ISRs reduce Cr(VI) to Cr(III), which in turn precipitates as $Cr(OH)_3$, while they are finally oxidized to sulfates. Therefore, their dose is limited by the sulfate's MCL of 250 mg/L. The related studies either concern high Cr(VI) concentrations or low pH values [19,23,24], while a bench-scale study using $NaHSO_3/Na_2SO_3$ showed inefficient Cr(VI) removal [27]. To the best of our knowledge, however, an integrated study on ISRs implementation in view of Cr(VI) removal at sub-ppb level from a natural water matrix was never performed.

The motivation of this study was to investigate the efficiency of the major ISRs for the removal of Cr(VI) from drinking water at sub-ppb level. The reductants examined were $NaHSO_3$, $Na_2S_2O_3$, $Na_2S_2O_4$, $Na_2S_2O_5$, and Na_2S. In this evaluation, the treatment at the pH range between 6 and 8, commonly encountered in natural waters, and a reductants' dose range resulting in total (water plus added) sulfate concentration safely below the regulation limit of 250 mg/L were set as prerequisites. In conformity to the latter, ISRs' doses up to 50 mg S/L were practiced, whereas the influence of solution pH on Cr(VI) removal rate and efficiency were investigated. In addition, the Cr(VI) removal capacity as a function of the ISRs' dose at solution pH 7 was determined. Kinetics experiments were also performed for $Na_2S_2O_4$ and Na_2S observing in parallel the variation of dissolved oxygen concentration.

2. Materials and methods

2.1. Reagents

A 500 mg/L Cr(VI) stock solution was prepared from reagent grade $K_2Cr_2O_7$ (Aldrich). Working standards were freshly prepared by proper dilution of the stock solution in artificial water with composition close to that of natural ones, which was prepared according to National Sanitation Foundation (NSF) standard by 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 $MgSO_4 \cdot 7H_2O$ dissolution in 1 L of distilled water. For each ISR examined, a fresh 2 g S/L stock solution was prepared by diluting the appropriate quantity of reagent grade $NaHSO_3$, $Na_2S_2O_3$, $Na_2S_2O_4$, $Na_2S_2O_5$, and Na_2S in distilled water bubbled with N_2. This procedure was chosen for diminishing ISRs oxidation by dissolved oxygen.

2.2. Procedure

Batch experiments were conducted at 20 ± 1°C temperature by using 200 mL of 100 μg/L (1.92 μM) Cr(VI). The reaction solutions were agitated in an orbital shaker for 24 h to reach equilibrium. The influence of solution pH in the range 2–12 was studied for reductants' dose equal to 10 mg S/L, while pH was adjusted to the targeted value by adding either 0.1 N HNO_3 or 0.1 N NaOH. The removal of Cr(VI) as a function of the reductants' dose at solution pH 7 was investigated by practicing doses of 5–50 mg S/L. In all experiments, the reductants' dose was achieved through the addition of the appropriate volume of stock solution. The pH of water samples, after treatment, was adjusted close to 8 and the suspension of $Cr(OH)_3$ was filtered through a 0.2 μm pore size membrane filter. Fifty milliliters filtrate were acidified with 0.1 mL HNO_3 and 20 mg $NaHSO_3$ was added for residual Cr(VI) reduction. Chromium concentration was calculated through a Cr(III) calibration curve.

The residual reduction capacity of treated water samples, referred hereafter as ISRs residual concentration, was determined as follows: In 100 mL of filtrate, 5 mL of concentrated H_2SO_4 was added and titrated with 0.05 N $KMnO_4$. The end point of the titration was defined by the persisted weak pink color, indicating that the MnO_4^- ions were no longer being reduced.

Kinetic experiments were performed at pH 7 by placing 1,000 mL of 100 μg/L Cr(VI) solution in a beaker and adding 20 mg S/L of either $Na_2S_2O_4$ or Na_2S. At fixed time intervals, samples of the reaction solution were taken, filtered, and dissolved residual Cr(VI) concentration was determined. In addition, dissolved oxygen concentration was monitored using a WTW OXI96 meter.

2.3. Cr(VI) determination

Initial Cr(VI) concentrations were determined by the standard 1,5-diphenylcarbazide method, which is based on the formation of a red–violet colored complex under acidic conditions and quantified spectrophotometrically at 540 nm [28]. A Lambda 2 UV/VIS spectrophotometer Perkin Elmer equipped with 10 cm path-length measurement cells was used. The detection limit of the method, calculated from the seven replicates of 2–5 μg Cr(VI)/L, was estimated to be 1.4 μg/L.

The residual Cr(VI) concentrations were determined by a Perkin Elmer graphite furnace atomic absorption spectrophotometer (GFAAS), model AAnalyst 800. The detection limit of this method, calculated from the seven replicates of 2–5 μg Cr/L, was estimated to be 0.8 μg/L.

3. Results and discussion

3.1. Optimization of chromium determination

During preliminary reaction kinetic experiments, the residual Cr(VI) concentration values determined by the 1,5-diphenylcarbazide method [28] were found to differ significantly from those measured by GFAAS as also observed by Su and Ludwig [29]. For this reason, the understanding and quantification of ISRs influence intensity in each method was required in order to decide for the optimum and more reliable measuring procedure.

In order to estimate the ISRs' influence on Cr(VI) determination by the 1,5-diphenylcarbazide method, three calibration curves were obtained: One, based on the absorbance of four standard solutions with Cr(VI) concentrations of 0, 50, 150, and 250 μg/L and another two corresponding to Cr(VI) solutions with 2 mg S/L and 5 mg S/L $Na_2S_2O_5$ added, respectively (Fig. 1). The results showed a significant influence on absorbance in presence of $Na_2S_2O_5$ and the determination of lower Cr(VI) concentrations as the ISR's concentration increased. This depression of absorption was attributed to the partial Cr(VI) reduction by the $Na_2S_2O_5$, when the acidic reagent was added to yield a final pH of less than 2. Thus, the 1,5-diphenylcarbazide method was considered inaccurate for residual

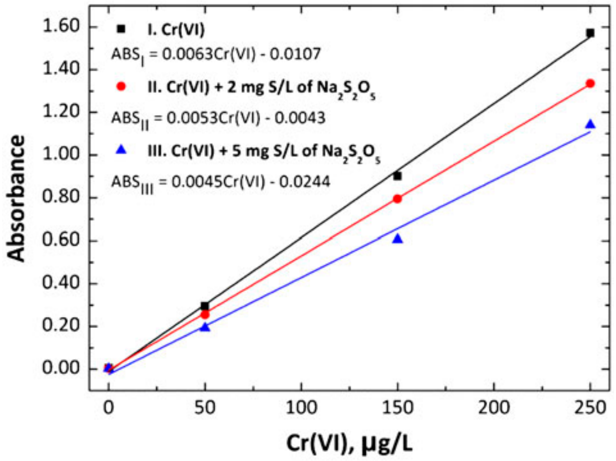

Fig. 1. Absorbance as a function of Cr(VI) concentration using the 1,5-diphenylcarbazide method. **I**: Cr(VI), **II**: Cr (VI) with 2 mg S/L of $Na_2S_2O_5$ added, and **III**: Cr(VI) with 5 mg S/L of $Na_2S_2O_5$ added.

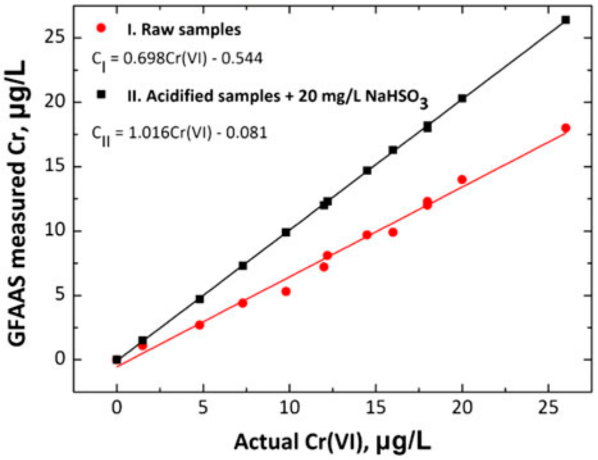

Fig. 3. Cr(VI) in natural water matrix determined by GFAAS against Cr(III) calibration curve. **I**: Raw samples and **II**: Acidified samples with 20 mg/L $NaHSO_3$ added.

Cr(VI) determination, since some reduction capacity was almost always determined in treated water samples, even in equilibrated solutions at batch experiments, due to the presence of residual ISR or any reductive by-products.

For the evaluation of any differences in chromium species' detection by GFAAS, two calibration curves were obtained, one for Cr(III) and one for Cr(VI) (Fig. 2). The divergence in absorption for the two chromium species indicated that chromium must be present solely in one form during determination in order to establish high accuracy. This conclusion is better illustrated in Fig. 3, where the concentration of Cr(VI) in natural water matrix determined against Cr(III) calibration curve is presented. The determined Cr(VI) concentrations by GFAAS were 20–30% lower than the actual ones, while the addition of 20 mg $NaHSO_3$ and 0.1 mL HNO_3 per 50 mL water sample resulted in accurate Cr(VI) determination due to its reduction to Cr(III) form. Conclusively, as long as the Cr(VI) preservation was impractical due to residual ISRs concentration, the residual Cr(VI) concentration of all treated water samples was preserved as Cr(III), by the addition of $NaHSO_3$ and HNO_3, and determined using Cr(III) calibration curve.

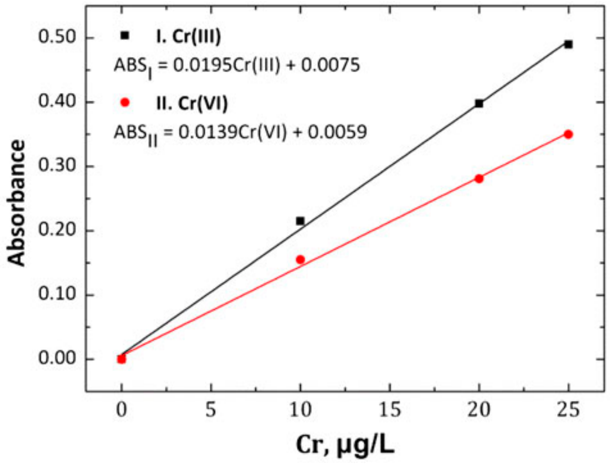

Fig. 2. Calibration curves for **I**: Cr(III) and **II**: Cr(VI) using the GFAAS.

3.2. *Influence of reaction pH*

The influence of solution pH on Cr(VI) removal efficiency was studied with batch experiments at 20 ± 1˚C, pH range between 2 and 12, reaction time 24 h, initial Cr(VI) concentration 100 μg/L, and ISRs' dose 10 mg S/L. Experimental results showed that maximum removal efficiency of all reductants tested was achieved at pH range between 2 and 4, which justify the researchers choice for Cr(VI) reduction at low pH [19,23,24]. However, the reduction of Cr(VI) at such a low pH implies the addition of high dose of acid and a respective base addition for pH correction and $Cr(OH)_3$ precipitation followed by filtration, a procedure that indistinctly degrades the quality of water intended for human consumption. The Cr(VI) removal efficiency of all ISRs studied was gradually decreased as reaction pH value increased from 4 to 9 (Fig. 4), which was attributed to dissolved oxygen competition since it is well known that the reaction rate of oxygen with sulfur reductants is drastically

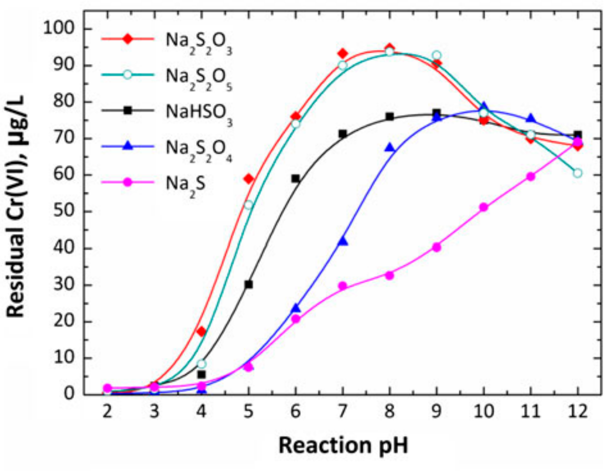

Fig. 4. Influence of reaction pH on Cr(VI) removal (Initial Cr(VI) = 100 μg/L, C_{ISR} = 10 mg S/L, reaction time 24 h, and reaction temperature 20 ± 1˚C).

increased in neutral to alkaline solutions [30]. However, the Cr(VI) removal efficiency of oxygenated ISRs ($NaHSO_3$, $Na_2S_2O_3$, $Na_2S_2O_4$, and $Na_2S_2O_5$) was slightly improved as reaction pH increased from 8 to 12. This apparent disagreement should be probably attributed to the precipitation of $CaCO_3$, since solid phase surface facilitates Cr(VI) reduction efficiency because it promotes the transfer of electrons through bridging ions [31,32].

3.3. *Influence of ISRs dose*

In order to evaluate the efficiency of ISR for Cr(VI) removal at pH commonly encountered in natural waters, batch experiments were conducted practicing ISRs' doses up to 50 mg S/L (Fig. 5), which theoretically resulted in maximum sulfate formation of 150 mg/L safely below MCL of 250 mg/L. The results of Fig. 5 show that $NaHSO_3$, $Na_2S_2O_3$, and $Na_2S_2O_5$ could not achieve residual Cr(VI) concentrations lower than 60 μg/L even at doses up to 50 mg S/L. In contrast, $Na_2S_2O_4$ in a dose of 50 mg S/L resulted in Cr(VI) residual concentration of sub-ppb level. At samples treated with the maximum Na_2S dose of 50 mg S/L, a residual concentration of 18 μg Cr(VI)/L was determined, which was also accompanied by a strong unpleasant odor. This result implies that Cr(VI) removal by Na_2S should be followed by an additional treatment step for remaining sulfide elimination, which in turn significantly increases capital and operational cost.

3.4. *Influence of dissolved oxygen*

The remarkable divergence in Cr(VI) removal capacity as a function of $Na_2S_2O_4$ and Na_2S dose should be attributed to dissolved oxygen competition. The latter is beneficial at low doses while the former seems to be better at higher doses. High Na_2S doses activate the reaction of sulfide with dissolved oxygen diminishing thus, Cr(VI) specific removal value (mg Cr(VI)/g Na_2S). At low dose in contrast, sulfide reacts preferably with Cr(VI) resulting in higher specific removal value. Thus, at sulfide dose up to 10 mg/L the decrease rate of Cr(VI) residual concentration is significantly higher of the corresponding for sulfide dose between 30 and 50 mg/L (Fig. 6(a)). Considering the inverse, almost linear, relation of Cr(VI) residual concentration with $Na_2S_2O_4$ dose, it should be attributed to sulfoxyl radicals, which instantly react with dissolved oxygen and Cr(VI) (Fig. 6(b)). Obviously, the greater the $Na_2S_2O_4$ dose the higher the number of sulfoxyl radicals formed and Cr(VI) removal, resulting in turn in lower residual concentration. It is observed that $Na_2S_2O_4$ eliminated dissolved oxygen within a minute through two successive steps described by the Eqs. (3) and (4) [33].

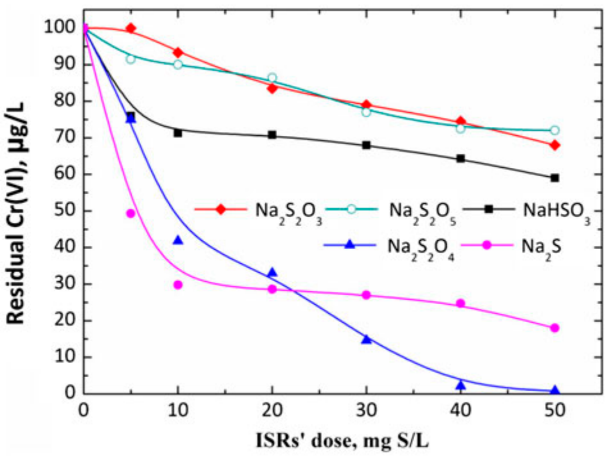

Fig. 5. Influence of ISRs dose on residual Cr(VI) concentration. (Initial Cr(VI) = 100 μg/L, pH 7, reaction time 24 h, and reaction temperature 20 ± 1˚C).

$$S_2O_4{}^{2-} + O_2 + 2OH^- \rightarrow SO_3^{2-} + H_2O \tag{3}$$

$$SO_3^{2-} + 0.5O_2 \rightarrow SO_4^{2-} \tag{4}$$

3.5. *Reaction kinetics*

Since $Na_2S_2O_4$ and Na_2S presented promising efficiency in removing Cr(VI), reaction kinetics were studied for this two ISRs. Fig. 7 clearly shows that Cr(VI) removal rapidly proceeded within the first 2 h, which in turn considerably slowed down reaching

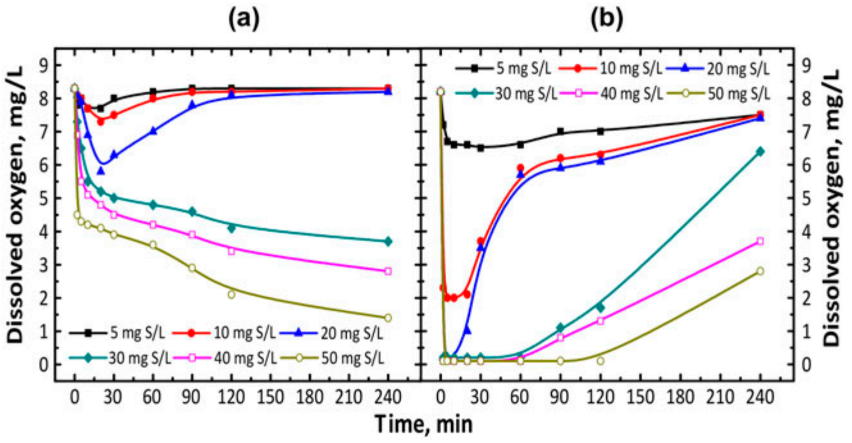

Fig. 6. Dissolved oxygen concentration as a function of reaction time and Na_2S (a) and $Na_2S_2O_4$ (b) dose.(Initial Cr(VI) = 100 μg/L, pH 7).

equilibrium in 8 h. Considering $Na_2S_2O_4$, it is obvious that almost 60% of total Cr(VI) removal was achieved within 20 min, which increased to more than 85% at 2 h, reaching equilibrium residual concentration of 37 ± 2 μg Cr(VI)/L in 8 h. Similarly, Na_2S resulted in 40 and 80% of total removal efficiency within 20 min and 2 h, respectively, reaching also the equilibrium concentration of 31 ± 2 μg Cr(VI)/L in 8 h.

Regarding $Na_2S_2O_4$, it is known that in water it undergoes dissociation and disproportionation reactions to form primarily sulfoxyl radical ($SO_2^{-\bullet}$), sulfites (SO_3^{2-}) or bisulfites (HSO_3^-), and thiosulfates ($S_2O_3^{2-}$), via Eqs. (5) and (6) [34].

$$2S_2O_4^{2-} \leftrightarrow 4SO_2^{-\bullet} \tag{5}$$

$$4SO_2^{-\bullet} + H_2O \leftrightarrow 2SO_3^{2-} + S_2O_3^{2-} + 2H^+ \tag{6}$$

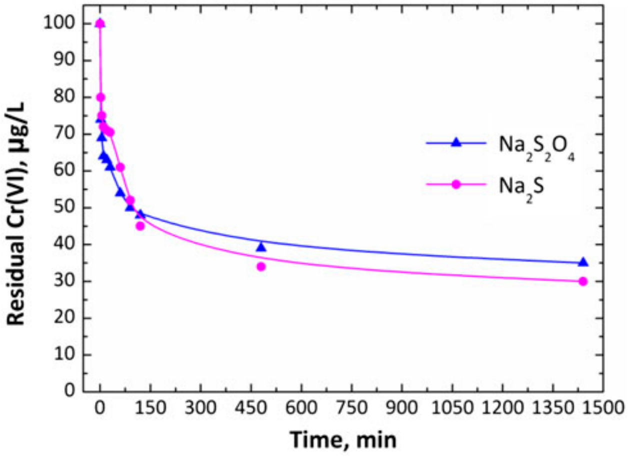

Fig. 7. Reaction kinetics of Cr(VI) (Initial Cr(VI) = 100 μg/L, C_{ISR} = 20 mg S/L, and pH 7).

Finally, sulfites and thiosulfates are oxidized to sulfate and the total reduction capacity of $Na_2S_2O_4$ is described by the simplified Eq. (7):

$$S_2O_4^{2-} \leftrightarrow 2SO_4^{2-} + 6e^- \tag{7}$$

Consequently, the significantly higher Cr(VI) reduction capacity of $Na_2S_2O_4$, along with its fast kinetic within the first 20 min should be attributed to sulfoxyl radicals formation [35]. The dissociation products such as sulfites may significantly contribute to the long-term reduction of Cr(VI) through the reaction (8) [24].

$$2CrO_4^{2-} + 4SO_3^{2-} + 6H^+ \rightarrow 2Cr(OH)_3 + 2SO_4^{2-} + S_2O_6^{2-} \tag{8}$$

Na_2S dissolution in water at pH 7 results in HS^- and H_2S formation almost in equal concentrations, since $pKa_1 = 7.00$ ($H_2S \leftrightarrow HS^- + H^+$), which in turn are oxidized through polysulfide's (S_n^{2-}) formation [36] as follows:

$$S_n{}^{2-} \rightarrow nS_{(s)} + 2nH^+ + 2ne^- \tag{9}$$

Hence, Cr(VI) reduction proceeds though the simplified overall reaction:

$$2Cr^{6+} + 3S^{2-} \rightarrow 2Cr^{3+} + 3S_{(s)} \tag{10}$$

Polysulfide and sulfur solid-phase formation may promote the transfer of electrons, which in turn explains both the fast kinetic of Cr(VI) reduction (Fig. 7), as well as the smooth decrease in Cr(VI) removal efficiency as reaction pH value moves from 4 to 12 (Fig. 4).

Kinetic data of Fig. 7, for both ISRs, were best fitted to equations:

$$Na_2S_2O_4: \quad C_t = 37.9 + 31.7e^{-0.780t} + 30.4e^{-0.010t} \tag{11}$$

$$Na_2S: \quad C_t = 31.8 + 22.0e^{-1.052t} + 46.2e^{-0.009t} \tag{12}$$

which indicates that Cr(VI) removal is a sum of two first-order reactions, while the first part contributes up to 20 min. Therefore, the first part potentially describes the contribution of sulfoxyl radical in Cr(VI) reduction for $Na_2S_2O_4$, as well as the contribution of H_2S/HS^- for Na_2S, with the former to be significantly higher. The second part describes the long-term contribution of dissociation products such as sulfites and thiosulfates, as well as polysulfides.

4. Conclusions

The experimental results of this study indicate that at common pH range 6–8 and matrix encountered in drinking water, $Na_2S_2O_5$, $Na_2S_2O_3$, and $NaHSO_3$ were not found to be promising for Cr(VI) treatment, since their removal efficiency proved significantly low at doses ensuring sulfate addition below regulation limit. Although Na_2S showed sufficient Cr(VI) removal efficiency, the remaining strong unpleasant odor implies additional treatment for sulfide ions elimination, which in turn significantly increases capital and operational cost. Finally, $Na_2S_2O_4$ is the only ISR that achieved residual Cr(VI) concentration at sub-ppb level, while adding to sulfate concentration safely below the regulation limit of 250 mg/L. Complementary, $Na_2S_2O_4$ presents fast kinetics due to its dissociation through sulfoxyl radical formation. Considering $Na_2S_2O_4$ implementation in full-scale treatment plants, at least 2 h reaction time in a plug-flow reactor should be preferable implemented, since a first rate reaction is determined. In addition, a post aeration treatment should be included for oxidation of the residual reductant.

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