INHIBITION OF PERCHLORATE ADSORPTION ON TO TAILORED GRANULAR ACTIVATED CARBON BY REDUCED SULFUR SPECIES: THIOSULFATE

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Abstract

The present study was designed to evaluate the effects of reduced sulfur species on the adsorption of perchlorate on tailored granular activated carbon (TGAC); initial experiments focused on thiosulfate. Previous studies using Rapid Small Scale Column tests (RSSCT) showed that perchlorate broke through at 30,000-35,000 bed volumes (BV) when quaternary ammonium surfactants were preloaded onto activated carbon. These tests used groundwater, with 50-60 ppb perchlorate. However, when pilot tests were conducted, breakthrough occurred at 17,000-20,000 BV. It was hypothesized that intermediate-reduced sulfur species, found in the groundwater, were not fully oxidized before entering the treatment system; and they competed with perchlorate for adsorption sites on the TGAC. To test this hypothesis, experiments were conducted using RSSCTs. Deionized distilled water was spiked with 1,000 ppb perchlorate and 1,000 ppb thiosulfate. These experiments showed that thiosulfate caused a competition effect. The control experiment, which had 1,000 ppb of perchlorate but no thiosulfate, showed breakthrough starting at 15,300 BV. With the concentration of thiosulfate being the same as the perchlorate concentration, breakthrough started at 8,000 BV. These experiments reveal that thiosulfate competes with perchlorate for adsorption sites even at a 1:1 mass ratio.

Introduction

Polythionates ($S_nO_6^{2-}$), thiosulfate ($S_2O_3^{2-}$) and polysulfides (S_n^{2-}) are reduced sulfur species that may be found in natural water environments. These species are often referred to as intermediate sulfur species because their oxidation states are between hydrogen sulfide (the most reduced) and sulfate (the most oxidized) (Table 1). With the exclusion of polysulfides, all other intermediate sulfur species are also known as sulfoxyanions (Druschel et al., 2003a). These intermediate sulfur species play an important role in the oxidation of hydrogen sulfide (H_2S) as well as redox transformations of other sulfur containing compounds in the environment (Druschel et.al. 2003b). These sulfoxyanions are not stable forms of sulfur in an oxygenated environment; and they provide key steps between the oxidation and reduction pathways of the sulfur cycle (Druschel et al., 2003b). Intermediate sulfur species are also important in the complexation and stabilization of trace metals in anoxic environments (Veldeman et al., 1990; Webster, 1987). Based on thermodynamic principles, typical concentrations of thiosulfate and polythionates should be less than 0.01% of the total sulfur concentration in an environment (Druschel et al., 2003a). Research that has been conducted indicates that polythionates are abundant in acid crater lakes (Veldeman et al., 1990, Takano et al., 1994 in Druschel et al., 2003b) and in gold ore leaching solutions (O'Reilly et al., 2002). Thiosulfates are found in hydrothermal waters in New Zealand (Webster, 1987), Bulgaria (Veldeman et al., 1990) and the Yellowstone National Park (Xu et al., 2000). Concentration of these species range from 5 to a few hundred micro moles per liter and in some cases up to 12% of the total dissolved sulfur (Druschel et al., 2003c). With this high concentration of intermediate sulfur species found in natural waters, it is speculated that these are formed from the slow and unfinished redox reactions of H_2S to sulfate.
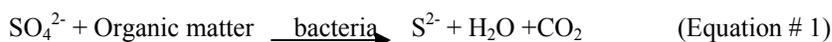
Table 1. Species of Sulfur- Based ions and sulfur valence state

Species	Formula	S Valence
Hydrogen Sulfide	H_2S	-2
Elemental sulfur	S	0
Polythionate (Hexathionate)	$S_6O_6^=$	+1.67
Polythionate	$S_5O_6^=$	+2
Thiosulfate	$S_2O_3^=$	+2
Tetrathionate	$S_4O_6^=$	+2.5
Dithionate	$S_2O_4^=$	+3
Sulfite	$SO_3^=$	+4
Sulfate	$SO_4^=$	+6

The formation and high concentration of these species in the environment are poorly understood. These species are more abundant in their environments than what is expected based on their equilibrium thermodynamic properties. According

to Druschel et al., (2003a) the two major pathways for the production of polythionates and thiosulfate are the oxidation and reduction of H_2S and sulfate respectively. For example, the reduction of sulfate mircobially to form thiosulfate in sediment environment; the reaction of thiosulfate with metal sulfides such as pyrite to form tetrathionate (Xu and Schoonen, 1995); and the formation of thiosulfate from the oxidation of hydrogen sulfide in oxygenated water. The determination of these species kinetics as well as thermodynamic properties is important so that their reactions in the environment are better understood. The lack of or poorly understood properties might be due in part to the difficulty in the analytical process of these intermediate sulfur species in solution due to the ease at which they can be oxidized by oxygen (Veldeman et al., 1990). According to Kamyshny et al., (2004) the competitive ability of the disproportioning rates with the complex formation rates will determine the speciation of these reduced sulfur complexes in the environment.

The compound that is thought to be the key in the formation of these reduced sulfur species in groundwater is H_2S. Hydrogen sulfide is a toxic, harmful compound that is a catalyst to poisoning several body systems, especially the nervous system. Hydrogen sulfide also leads to corrosion in pipes and other equipment (Haimour et al., 2005). The production of H_2S in groundwater is brought about by the microbial process in the sulfur cycle by degrading plants and animals in anaerobic, anoxic and reduced environments. The following equations depict the process that produces H_2S.

$$SO_4^{2-} + \text{Organic matter} \xrightarrow{\text{bacteria}} S^{2-} + H_2O + CO_2 \qquad \text{(Equation \# 1)}$$

$$S^{2-} + 2H^+ \longrightarrow H_2S \qquad \text{(Equation \# 2)}$$

The presence of H_2S in the groundwater is highly dependent on pH (Haimour et al., 2005). The pH impacts the relative concentration of the sulfur species such as bisulfide, sulfide and H_2S in the groundwater system. At pH between 5.0 and 6.0 H_2S is the dominant compound. According to Haimour et al., (2005), H_2S is a volatile compound that can be removed by aeration. Removal of H_2S by aeration at pH greater than 6.5 poses a problem because bisulfide is the dominant specie and it is not very volatile. This allows for the formation of other reduced sulfur species such as polysulfides and polythionates in groundwater that may lead to competitive as well as degradative problems in water treatment systems. With these kinetic and thermodynamic characteristics of H_2S in natural environments, it can be seen that thiosulfate along with sulfite and sulfate are formed from the slow oxidation or the incomplete redox process of hydrogen sulfide to sulfate at pH values above neutral. Thiosulfate can also be produced from the decomposition reactions of many polythionates with hydrogen sulfide as well hydrolysis of these reduced species (Xu et al., 2000). Thiosulfate, polythionates, and polysulfides are also produced during bacterial degradation of pyrite and other metal sulfides (Shippers et al., 1996). Pyrite is the most abundant sulfur –containing mineral. Ueno (1976) studied the removal of sodium sulfide using various oxidants at temperatures ranging between 30 -80 degrees C and at pH values between 10 and 12. Under these conditions thiosulfate and sulfate were produced with a molar concentration ratio of 2:1. Hoffman and Lin (1979) also studied the oxidation of sodium sulfide with air at ambient temperature and pH values between 5.5 and 12.1. Thiosulfate, sulfite, sulfate and colloidal sulfur were observed and molal percent concentration for thiosulfate ranged from 11 to 51 percent. Sulfate was the only other compound that had a molal concentration percent greater than thiosulfate which ranged from 44-64 percent.

The decomposition of thiosulfate in natural aqueous systems is not fully understood. It has been found that thiosulfate formation occurs under low pH and at room temperature between bisulfite and sulfite and tends to accumulate in systems that have cations such as sodium (Na^+) and calcium (Ca^{2+}). The next plausible step after thiosulfate production is the reaction between sulfide and thiosulfate to form elemental sulfur. This step is slow and thus can lead to the accumulation of thiosulfate in the system. This was verified by Kundo et al., (1987), where it was shown that the reaction was dependent on the rate of change of gaseous H_2S to aqueous H_2S. With accumulation of thiosulfate in an aqueous system, polythionates are formed from the degradation of thiosulfate. An example of this is seen where metals such as copper (Cu^{2+}) can oxidize thiosulfate to form tetrathionate in the absence of oxygen. The reaction in the presence of oxygen is more difficult. Further observations have also been shown that thiosulfate and polythionates as it relates to oxidation processes appear at fairly neutral pH rather than at low pH (Elberling et al., 2000). Several researchers that have characterized polythionate reactions suggest that the general pathway for the formation of polythionates is by hydrolysis reaction (Equation # 3) (Meyer and Ospina, 1982).

$$S_xO_6^{2-} + H_2O \longrightarrow S_{x-1}O_3^{2-} + SO_4^{2-} + 2H^+ \qquad \text{(Equation \# 3)}$$
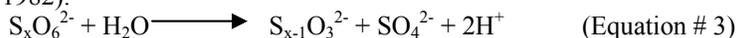
With the possibility of high concentrations of thiosulfate in the natural environments, it can be speculated that thiosulfate along with other intermediate sulfur species can have a significant effect on treatment systems. The formation and accumulation of these polythionate ions in aqueous systems can compete strongly with other anions on exchange sites. For example, tetrathionate will compete with gold thiosulfate on ion-exchange resins therefore affecting the recovery of gold (O'Reilly et al., 2002). The characteristics of the environments where decompositions and oxidations processes occur are not fully understood.

Chun et al. (2000) looked at polythionates interaction with amminehalocobalt (III). It was found that when tetrathionate interacted with this compound, an unexpected cleavage occurs to form an S-S bond, which is followed by a disproportioning process to form pentathionate ion attached to the amminehalocobalt. These observations can lead to the speculation of interactions between polythionates ions with each other through displacement or disproportionate process when they are attached to cationic amine groups. If this mechanism does occur, then treatment systems and other processes that remove ions from their system using the technology of anionic adsorption or have exchange sites will probably have competition between other anionic compounds and these polythionates or sulfur oxyanions. A case in point is the inhibition of perchlorate adsorption to the cationic sites of surfactant tailored granular activated carbon (TGAC). With intermediate sulfur species occupying adsorption sites, this leaves fewer sites available to adsorb the perchlorate anion; and this therefore decreases the effectiveness of perchlorate removal from environmental natural systems by the tailored GAC. Factors such as pH, temperature and ionic strength play a role in the formations of these sulfur oxyanions.

Granular activated carbon has been used as an absorbent for ions in water treatment systems. A technology has been previously developed at Penn State that tailors GAC with cationic surfactants so as to increase the GAC capacity for removing oxyanions such as perchlorate. Parette and Cannon, (2005) looked at the removal of perchlorate using this technology and found that TGAC was able to effectively remove perchlorate from a groundwater from Redlands CA, 30 times longer than GAC that was not tailored. These studies were based on rapid small scale column tests (RSSCTs) conducted at laboratory scale. Such high removal efficiencies were not observed at the demonstration or field scale levels using the same groundwater. Perchlorate broke through at 17,000 bed volume rather than 30,000 -33,000 bed volumes that were observed with RSSCT experiments. Usually, by the time Redlands groundwater was shipped to Penn State, the 55-gallon barrel opened, and the RSSCT experiments conducted, the groundwater had become well oxygenated to the extent that no intermediate sulfur species were detected. However, on one occasion, Redlands groundwater that was shipped to Penn State was immediately employed in RSSCTs; and during this run, intermediate sulfur species were detected; and perchlorate breakthrough occurred at considerably fewer bed volumes, as shown in Figure 1 below. On the basis of this result, we hypothesized that intermediate sulfur species are appearing in the groundwater at the full scale; and these intermediate sulfur species are adversely affecting the removal of perchlorate by the adsorption process onto the TGAC.

This study looks at thiosulfate as an intermediate sulfur species that is very important in most of the oxidation process of intermediate sulfur species. The **objective** of this research has been to determine if thiosulfate significantly affects the adsorption or desorption of perchlorate from tailored granular activated carbon and the amount of thiosulfate and perchlorate laden water that can be processed before breakthrough of perchlorate; All tests were conducted using Rapid Small Scale Column tests (RSSCTs).

Experimental

Materials

The granular activated carbon (GAC) that was used in this experiment is UltraCarb. This is a bituminous coal-based activated carbon that was obtained from Siemens Water Technology (formerly USFilter) of Los Angeles CA. The carbon was ground and sieved to a mesh size of 200x400 which is 38 x 75 μm. The water that was used in this experiment was deionized distilled (DI) water. Anions were measured utilizing a Dionex 120 ion chromatograph.

Dicocoalkyldimethylammonium chloride (Arquad 2C-75) was the surfactant that was used in this experiment. Arquad 2C-75 was chosen because of the two long carbon chains that are present which aids in low leaching of the surfactant from the carbon (Parette and Cannon, 2005, Parette et al. 2005).

The RSSCTs were designed according to Parette and Cannon, (2005). 1.27g of UltraCarb GAC was used and tailored with 33BV of 0.4% Arquad 2C-75 solution. The temperature that RSSCT was conducted at $20\pm2^{o}C$ and flow rates were simulated empty bed contact times (EBCT) of 10 minutes. HPLC pumps (Waters models 501 and 510) were used to provide flow.

Methods

The RSSCT columns were dry packed with UltraCarb and glass wool was packed at both ends. The tailoring process took approximately 3 days, during which the surfactant solution was pumped and recirculated at a rate of 2 ml per minute through the carbon. Deionized distilled water was used to pre-load the surfactant on the GAC.

After preloading the GAC with surfactant solution, DI water that has been spiked with 1mg/L perchlorate and 1mg/L of thiosulfate was passed through the column. A collapsible plastic container was used to store the solution so that additional thiosulfate oxidation would not take place; and thiosulfate make-up and monitoring maintained this 1 mg/L level. The tailored GAC was not washed before the introduction of the spiked DI water. Water samples were collected 2 times per day until saturation, where saturation was defined here as the point where effluent concentration equals to 90 percent of influent concentration.

The Dionex 120 ion chromatograph was equipped with an AS40 auto sampler, a 4mm AS16 column, and a 4mm AG16 guard column was used. The DS4 suppressor was set at 300mA and a temperature of 35°C. A fifty mM sodium hydroxide elluent concentration was used. With a 1mL sample loop, perchlorate was able to be detected at 1μg/L. Calorimetric method was used to determine the concentrations of surfactants (Tsubouchi et al., 1957). This method has a detection limit of 0.1-0.2mg/L.

Results and Discussion

After tailoring, the surfactant solution that was recirculated was analyzed and determined that 0.23g of Arquad 2C-75 was pre-loaded on to the GAC. Compared with other surfactants Arquad 2C-75 has a low loading concentration. Parette and Cannon showed that the Arquad 2C-75 performs comparatively with the other surfactants that had higher loading concentrations. Full-scale data and RSSCT's with both fresh and oxygenated Redlands water are presented in Figure 1.
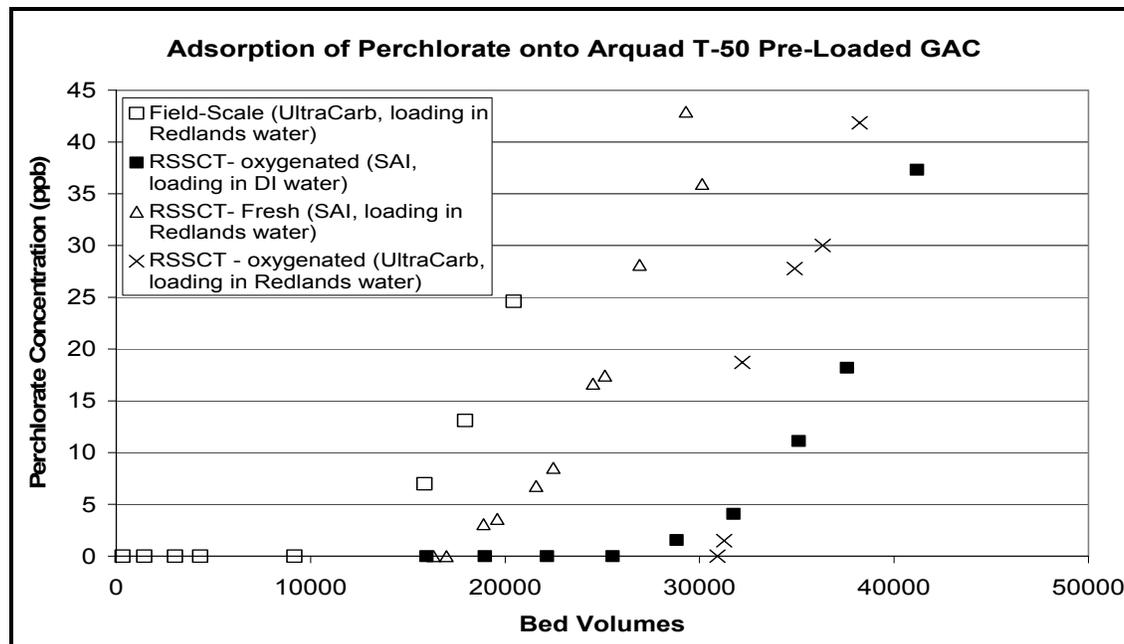

Figure 1: Affect of oxygenation time on perchlorate removal performance: Triangles represents RSSCT's with Redlands groundwater that was freshly sampled and processed; squares is full-scale behavior; exes and squares are for RSSCT's with Redlands groundwater that had become oxygenated in storage.

Two RSSCT were conducted to appraise thiosulfate competition. They were (1) DI water that was spiked with 1 mg/L perchlorate and 1 mg/L thiosulfate; (2) DI water that was spiked with 1mg/L perchlorate (control); Figure 2 depicts the results of the experiment. Figure 2 shows that perchlorate breakthrough when thiosulfate was present occurred at 8,000 bed volumes while breakthrough occurred at 15,000 bed volumes when thiosulfate was not present. This is a 47 percent reduction in the capability of the TGAC to remove perchlorate when the equivalent mass concentration of thiosulfate is present. The DI water is somewhat in reduced form so that the process of transforming thiosulfate to sulfate is slow. Also, the conductivity of DI water (< 1μs/cm) and the non existence of other anions and to some extent metals that might aid the oxidation of thiosulfate are not present, thus leading to this confirmatory results that thiosulfate does compete with perchlorate for adsorption sites.
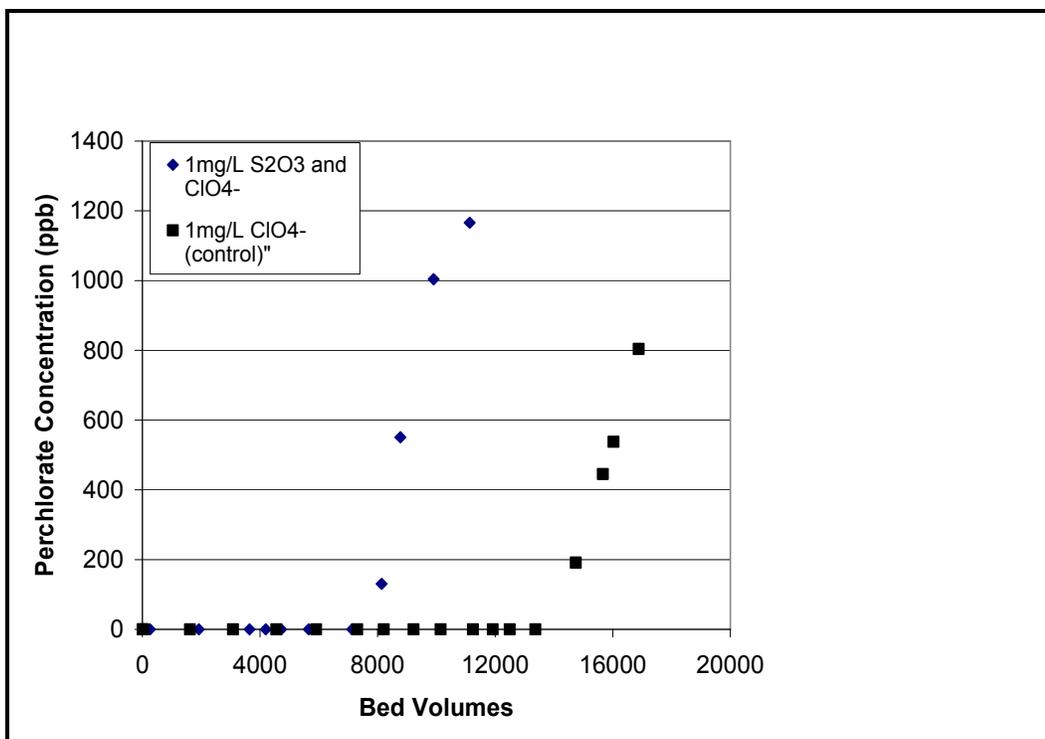
Figure 2 – Comparison of perchlorate breakthrough with and without (control) the addition of 1 mg/L thiosulfate.

Conclusion

It was shown from RSSCT experiments that thiosulfate greatly diminishes the effectiveness of TGAC to remove perchlorate from a DI water source. Also when thiosulfate concentration equals the perchlorate mass concentration, then the results conform to what is observed at the field scale level. The results herein will be supplemented at the Carbon conference with data that indicates that chlorine gas oxidation of thiosulfate will diminish the sulfur species competition with perchlorate for sorption.

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