



Systematic study on the reduction efficiency of ascorbic acid and thiourea on selenate and selenite at high and trace concentrations

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Abstract

Selenate (Se(VI)) and selenite (Se(IV)) are common soluble wastewater pollutants in natural and anthropogenic systems. We evaluated the reduction efficiency and removal of low (0.02 and 2 mg/L) and high (20 and 200 mg/L) Se(IV)_(aq) and Se(VI)_(aq) concentrations to elemental (Se⁰) via the use of ascorbic acid (AA), thiourea (TH), and a 50–50% mixture. The reduction efficiency of AA with Se(IV)_(aq) to nano- and micro-crystalline Se⁰ was ≥ 95%, but ≤ 5% of Se(VI)_(aq) was reduced to Se(IV)_(aq) with no Se⁰. Thiourea was able to reduce ≤ 75% of Se(IV)_(aq) to bulk Se⁰ at lower concentrations but was more effective (≥ 90%) at higher concentrations. Reduction of Se(VI)_(aq) → Se(IV)_(aq) with TH was ≤ 75% at trace concentrations which steadily declined as the concentrations increased, and the products formed were elemental sulfur (S⁰) and S_nSe_{8-n} phases. The reduction efficiency of Se(IV)_(aq) to bulk Se⁰ upon the addition of AA+TH was ≤ 81% at low concentrations and ≥ 90% at higher concentrations. An inverse relation to what was observed with Se(IV)_(aq) was found upon the addition of AA+TH with Se(VI)_(aq). At low Se(VI)_(aq) concentrations, AA+TH was able to reduce more effectively (≤ 61%) Se(VI)_(aq) → Se(IV)_(aq) → Se⁰, while at higher concentrations, it was ineffective (≤ 11%) and Se⁰, S⁰, and S_nSe_{8-n} formed. This work helps to guide the removal, reduction effectiveness, and products formed from AA, TH, and a 50–50% mixture on Se(IV)_(aq) and Se(VI)_(aq) to Se⁰ under acidic conditions and environmentally relevant concentrations possibly found in acidic natural waters, hydrometallurgical chloride processing operations, and acid mine drainage/acid rock drainage tailings.

Keywords Ascorbic acid · Thiourea · Selenium · Chloride · Reduction · Acidic ambient conditions

Introduction

Selenium is an essential trace element of life, whether it is for animals or plants. Adequate amounts of selenium

participate in the antioxidant function of the body regulate the metabolism of thyroid hormones as well as the immune system, and promote the growth of plants (Goldhaber 2003; Lyubenova et al. 2015; Natasha et al. 2018; Ullal et al. 2018). However, excessive amounts of selenium can cause selenium poisoning and ultimately lead to death (Greadl et al. 1998; Rayman 2000; Taylor et al. 2009). In nature and in the environment, selenium occurs in natural geologic ore sources such as phosphate rocks, coal, and black shales. Anthropogenic sources of selenium include coal mining, phosphate mining, smelting of sulfide ores, bitumen mining, coal-fired power plants, agriculture, glass manufacturing, and light batteries (Yadak et al. 2005; Wang et al. 2018; USEPA 2002; Qin et al. 2017a; Favorito et al. 2017; Muscatello et al. 2008; Chappell et al. 2014; Fernández-Martínez and Charlet 2009; Hamilton 2004; Tuzen and Sari 2010; Santos et al. 2015; Wu 2004; Chapman et al. 2010). In natural and mining waste water, typical emission concentrations of selenium

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can range from 3 $\mu\text{g/L}$ to 200 mg/L (Wasewar et al. 2009; Lemly 2004; Khamkhash et al. 2017; USEPA 2002; Twidwell et al. 2000; Kapoor et al. 1995; Sandy and DiSante 2010; Geoffroy et al. 2008; Geoffroy 2011; Benguerel et al. 2010; Monteith et al. 2000; Santos et al. 2015). In drinking water, the WHO and EPA have a set a guideline of selenium content at 40 $\mu\text{g/L}$ (WHO 2011) and 50 $\mu\text{g/L}$ (USEPA 2009), while the European Union's limit is much lower at 10 $\mu\text{g/L}$ (European Commission 1998). The speciation of selenium in water systems is ruled by redox conditions, pH, availability of sorbing surfaces, and biological processes (Dinh et al. 2017; Santos et al. 2015; Estevez et al. 2014). In wastewater treatment, selenite (Se(IV)) and selenate (Se(VI)) are the most common soluble wastewater pollutants, while in natural water systems, selenate is dominant (McCloskey et al. 2008).

It is well known that selenite is easier to reduce than selenate via abiotic or biotic means due to the fact the latter has a lower reduction potential (Koyama et al. 2000; McCloskey et al. 2008). The use of many reducing agents such as zero-valent iron (ZVI) (Yoon et al. 2016; Qin et al. 2017b; Koyama et al. 2000), green rust (Pefait et al. 2000), FeS_2 (Bruggeman et al. 2005), $\text{Fe}(\text{OH})_2$ (Sandy and DiSante 2010), $\text{Fe}(\text{II})_{(\text{aq})}$ (Sandy and DiSante 2010), humic acid (Peng and Xu 1987), bacteria (Staicu et al. 2015; Kora and Rastogi 2016; Steinberg and Oremland 1990; Oremland et al. 2004), Ni and Cu metal (Sandy and DiSante 2010; Hall et al. 1980), Zn powder (Marchant et al. 1978), CuCl (Misra and Tandon 1967), glucose (Jain et al. 2016; De Coninck 1905), TiCl_3 (Tomicek 1927), SnCl_2 (Geoffroy 2011), Na_2S (Geoffroy et al. 2008; Geoffroy 2011), $\text{Na}_2\text{S}_2\text{O}_4$ (Geoffroy et al. 2008; Geoffroy 2011), carbonylhydrazide (Sandy and DiSante 2010), ascorbic acid (Welna et al. 2014, 2017; Matos-Reyes et al. 2010; Pettine 2013; Shaker 1996; Hassan 1991), and thiourea (Welna et al. 2017; Zhang et al. 2011; Alía et al. 1999; Uggerud and Lund 1995; Qiu et al. 2006; Hollander and Yurii 1956) have been documented to treat aqueous selenate and selenite synthetic and industrial wastewater. Unfortunately, some of these reducing agents have setbacks such as high operational or maintenance cost, requirement of higher temperatures, poor efficiencies, and solid-handling problems (e.g., CuCl , TiCl_3 , thiourea (TH), ascorbic acid (AA), glucose, TiO_2 , SnCl_2 , Zn or Cu metal, ZVI, green rust, bacteria, SnCl_2), while in other cases, high toxicity of the by-products or reductants themselves (e.g., $\text{Fe}(\text{OH})_2$, TiO_2 , carbonylhydrazide) has limited their applicability (Sandy and DiSante 2010). Furthermore, some of the reducing agents that have been demonstrated to work in laboratory or industrial case studies such as bacteria (pH 6.5–9), $\text{Fe}(\text{OH})_2$ (pH 8–9), TiO_2 (pH 3.5), carbonylhydrazide (pH 2–4), ZVI (pH 4–9), Na_2S (pH 2–7), $\text{Na}_2\text{S}_2\text{O}_4$ (pH 2–3), and ascorbic acid (pH 2–3.5) have optimal reduction pH ranges above 2, thus limiting their use in highly acidic waste streams (Sandy and DiSante 2010; Geoffroy et al. 2008).

The work of Shaker (1996) on the use of ascorbic acid to reduce selenite to elemental selenium used concentrations that were too high to be applicable to wastewater treatment, and furthermore, the pH used was in the range of 2–3. Similarly, other published works (Oremland et al. 2004; Pettine 2013) on the use of ascorbic acid to reduce selenite to elemental selenium have employed selenite concentrations that were too high (e.g., 167 mM) or too low (e.g., 1 μM) to be applicable to wastewater pollution. Currently, there exists no explicit published literature on the effect of ascorbic acid to reduce selenite to elemental selenium at ambient temperatures. In the case of thiourea, limited work exists in the literature (Qiu et al. 2006; Hollander and Yurii 1956) on its use as a reductant for aqueous selenate or selenite reduction to elemental selenium but often heating above ambient temperatures is required and no insights into the formed phases has ever been given. To the best of the authors' knowledge, there have been no systematic studies on the reduction efficiency of aqueous selenate and selenite in chloride media to elemental selenium (fairly insoluble and environmentally stable) nor detailed characterization of the products formed using ascorbic acid and thiourea under ambient highly acidic conditions (pH < 1) and relevant wastewater concentrations.

Therefore, in our work, we systematically investigated the reduction efficiency and kinetics of different percentages of ascorbic acid, thiourea, as well as a 50–50% combination of both with low (0.02 and 2 mg/L) to high (20 and 200 mg/L) concentrations of aqueous selenite and selenate under highly acidic chloride media at different reactions times. We further characterize solids generated from high selenite and selenate aqueous concentrations via the use of powder X-ray diffraction, ATR-FTIR, and Micro-Raman to verify if the reduction reactions with ascorbic acid, thiourea, and both had gone to completion (i.e., formed elemental selenium) or if some other undesired compounds were produced (e.g., organo-selenite or selenate, elemental sulfur (S^0), and $\text{S}_n\text{Se}_{8-n}$).

Materials and methods

Chemicals

Stock solutions of 1 g/L Se(IV) and 1 g/L Se(VI) were prepared by dissolving sodium selenite (Na_2SeO_3) and sodium selenate (Na_2SeO_4) (98% purity, Shandong West Asia Chemical Industry Co., Ltd.) in distilled water. Thiourea, ascorbic acid (Tianjin Damao Chemical Reagent), and hydrochloric acid (Tianjin Fengchuan Chemical Reagent Technology Co., Ltd.) used in this work were of analytical grade. All glassware was soaked in 5% HNO_3 for at least one night before use and then washed with distilled water three times.

Analytical methods

Reactions of different reducing agents on aqueous Se(IV) and Se(VI)

Batch experiments were used to study the reduction efficiency of 0.02 mg/L, 2 mg/L, 20 mg/L, and 200 mg/L Se(IV)_(aq), or Se(VI)_(aq) with 0.5%, 1%, 2%, and 5% of ascorbic acid, thiourea, as well as a 50–50% mixture of both reducing agents at 2, 6, 10, and 24 h. Our intent in combining both ascorbic acid and thiourea in a 50–50% mixture was to increase the reduction efficiency percentage; removal to the maximum should both behave symbiotically. In our work, a strong acidic environment was employed by using 1.2 M hydrochloric acid solution at room temperature. The reason for using a chloride media environment was that it is often found in coal-fired power plant flue gas desulphurization influent and wastewater, secondary hydrocyclone overflow wastewater from bituminous coal, iron, and steel wastewater, and other selenium containing wastewater environments (Sandy and DiSante 2010; USEPA 2002). These selenium concentrations were chosen because they cover a wide range of waste water concentrations (Khamkhash et al. 2017; USEPA 2002; Twidwell et al. 2000; Sandy and DiSante 2010; Geoffroy 2011; Santos et al. 2015). We chose these percentages of reducing agents because we wanted to use as little as possible to keep their use economical in comparison to others (e.g., SnCl₂·2H₂O, ZVI, CuCl, NH₂NH₂, Na₂S₂O₄). Sampling and analysis of the liquid samples during were taken after 2, 6, 10, and 24 h. Finally, in order to verify the nature of the reduced solids produced, only the reduction reaction using 5% reducing agents and 200 mg/L selenite or selenate for 24 h was used as other conditions produced insufficient amount of solids (< 1 mg) for characterization. The reduction solids were obtained by centrifugation, dried naturally in air, and then grinded for characterization.

Liquid analysis methods and characterization of solids

Liquid analysis was conducted on a HG-AFS model SK-2003A two-channel, non-dispersive atomic fluorescence spectrometer (Beijing, Jinsuokun Technology Developing Co., LTD) equipped with a Se hollow cathode lamp (Beijing Shuguangming Electronic Lighting Instrument Co., LTD). The operating parameters used was a high-voltage PMT operating at 260 V, a lamp current of 60 mA, and an Ar carrier and shield flow rate of 600 mL/min and 800 mL/min, respectively. The atomizer temperature used was 400 °C with an atomizer height of 8 mm. The concentrations of KBH₄ and KOH used were 1.5% (w/v) and 0.5% (w/v), and our carrier liquid was 1.2 M HCl. The instrumental and our method of detection limit were 0.01 µg/L and < 0.1 ng/g (Welna et al. 2017). In our case, the amount of aqueous Se(VI) in solution was determined by

reducing it to Se(IV)_(aq) in a water bath and heating it with 6 M HCl at 95 °C for 30 min. The fluorescence intensity was < 300 counts in comparison to the blank solution when the Se(IV)_(aq) was zero (Tables S1–S3 and Figs. S1–S3). All solution data presented (Figs. 1, 2, and 3 and Tables S1–S3) are averages of ≥ 2 reproducible tests with a standard deviation ≤ 10%.

The powder XRD analysis was performed with a Bruker D8 advanced diffractometer, a copper target (Cu-K_α λ = 1.5406 Å), a monochromator composed of a graphite crystal, and a scintillator detector. The diffractometer used 40 kV and 40 mA. The scans were recorded between 5 and 90° 2θ with a 0.02° step size and an acquisition time of 0.2 s/step.

ATR-FTIR measurements were collected with a Nicolet 6700 Fourier Transform Infrared Spectrometer (FTIR Spectrometer) from Thermo Fisher using a MIRacle single bounce diamond ATR cell from PIKE Technologies. IR spectra was collected over the 4000–400 cm⁻¹ range via the co-addition of 64 scans and with a resolution of 4 cm⁻¹.

Raman Microscopy was conducted on a Thermo Fisher DXR model using the 50× short distance objective and a polarized argon laser operating at 780 nm and 10% of the laser power at the microscope exit. An average of 10 scans was obtained from 3300 to 60 cm⁻¹ to improve the resolution and the statistics of the collection.

Transmission electron microscopy (TEM) imaging and energy dispersive X-ray analysis (EDX) were conducted on selected particles using a Philips CM-200 microscope operating at 200 kV. The samples were prepared by dropping dilute solutions of the particles in ethanol onto 300-mesh carbon-coated copper grids and evaporating the solvent to dryness before inserting them into the sample holder and vacuum chamber.

Results and discussion

In our work, HG-AFS was employed to detect the different amounts of Se(IV)_(aq) and Se(VI)_(aq) as a function of different concentrations of the reducing agents and time (Figs. S1–S3 and Tables S1–S3). Se(IV)_(aq) was able to be detected without the addition of any reducing agents at all times, and the measured concentrations were close to the theoretical values. However, in the case of Se(VI)_(aq), without the addition of reducing agents, the fluorescence intensity and measured concentrations were close to the blank as expected.

The influence of ascorbic acid on the reduction of Se(IV) and Se(VI)

In the case of aqueous Se(IV) at a trace level of 0.02 mg/L (Fig. 1), it can be observed that a rapid decline in fluorescence intensity near that of the blank solution (Table S1 and Fig. S1) was observed at all reaction times investigated

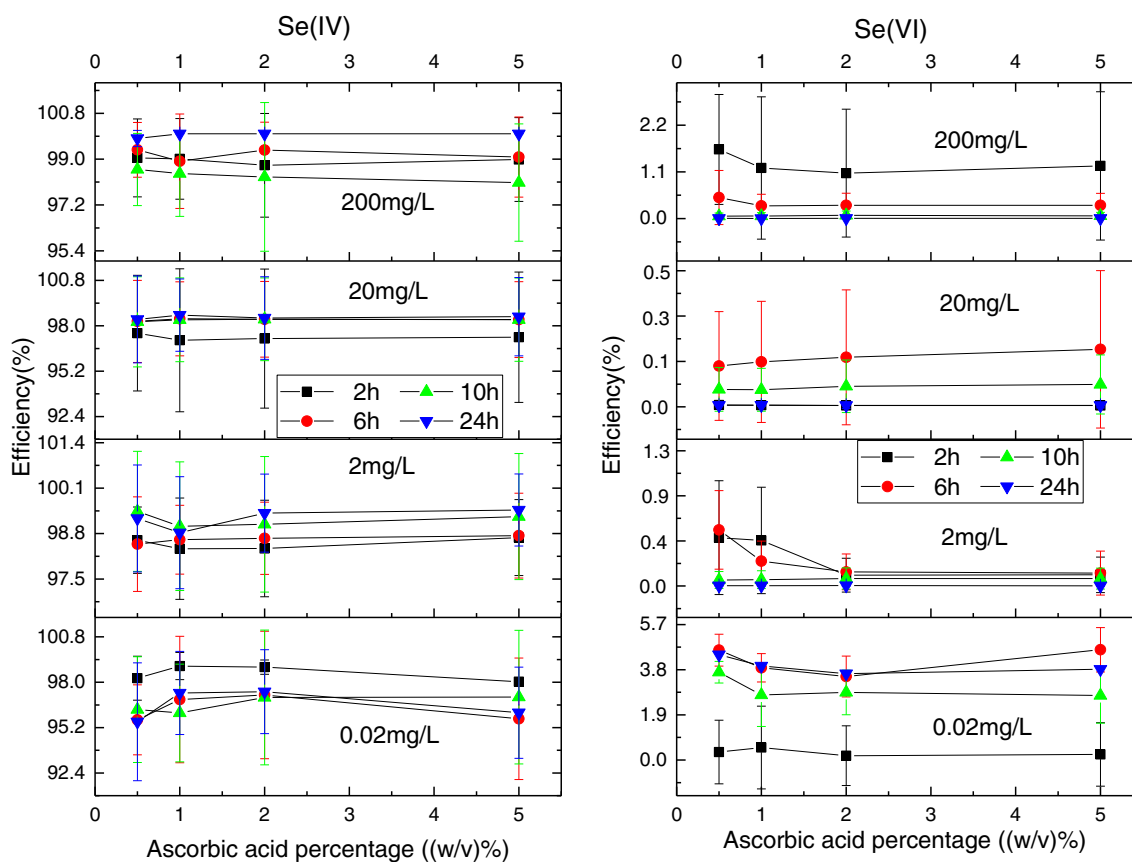


Fig. 1 Reduction efficiency percentage as a function of reaction time and % ascorbic acid added on various concentrations of aqueous Se(IV) and Se(VI)

and all percentages of ascorbic acid added. The amount of reduction from $\text{Se(IV)}_{(\text{aq})}$ to Se^0 was initially observed to be $\sim 98\%$ after 2 h of reaction time which then decreased to $\sim 96\%$ as time increased from 6 to 24 h at all percentages of ascorbic acid added (Fig. 1 and Table S1). At 2 mg/L $\text{Se(IV)}_{(\text{aq})}$ (Fig. 1 and Table S1), the decline in fluorescence intensity was gradual with an increase in reaction time from 2 to 24 h (Fig. S1) and the reduction efficiency observed followed (Fig. 1 and Table S1) at all percentages of ascorbic acid added. That is to say, lower reaction times (2, 6 h) gave reduction efficiencies of $\sim 98\%$ while those at longer times (10, 24 h) increased to $\sim 99\%$ for all percentages of ascorbic acid added. Increasing the $\text{Se(IV)}_{(\text{aq})}$ concentration to 20 mg/L (Fig. 1 and Table S1) showed an even slower gradual decrease in fluorescence intensity (Fig. S1) with an increasing reaction time at all percentages of ascorbic acid added, but in this case, the reduction efficiency (Fig. 1 and Table S1) did not follow it in a similar manner as that observed for the 2 mg/L tests. In this case, after 2 h of reaction time, we observed a reduction efficiency of $\sim 97\%$ which only slightly increased to $\sim 98\%$ after 6 h and then on forward for all percentages of ascorbic acid added. Finally, at the highest concentration used of 200 mg/L $\text{Se(IV)}_{(\text{aq})}$, the fluorescence intensity showed a gradual decrease with reaction time (Fig. S1) for all

percentages of ascorbic acid added which was similar to that observed at 2 mg/L. The reduction efficiency (Fig. 1 and Table S1) in this case did not follow the fluorescence intensity behavior. In general, we observed that after 2–6 h, $\sim 99\%$ of the $\text{Se(IV)}_{(\text{aq})}$ had been reduced which then slightly decreased to $\sim 98\%$ after 10 h and finally increased to 100% after 24 h for all percentages of ascorbic acid added. In this case (similar to that at 2, 20 mg/L), the full reduction took a bit more time in comparison to that at 0.02 mg/L due to the fact that, at higher concentrations, more $\text{Se(IV)}_{(\text{aq})}$ ions were found in solution which needed more time to be effectively reduced from $\text{Se(IV)}_{(\text{aq})}$ to Se^0 . Furthermore, at these high $\text{Se(IV)}_{(\text{aq})}$ concentrations, a clear solution and large amounts of brick red precipitates (Levine 1934) (Fig. S4) were observed at all reaction times and percentages of ascorbic acid added; the nature of which will be discussed in “Solid analysis of reduction precipitates from 200 mg/L aqueous se(IV) and se(VI), 24 h, and 5% reducing agents.”

For aqueous Se(VI), the fluorescence intensities (Fig. S1 and Table S1) for all tested aqueous Se(VI) concentrations at all times with all percentages of added ascorbic acid were close to that of the blank solution except for the 200 mg/L tests. Consequently, it indicates that only a small portion of the aqueous Se(VI) had been reduced to $\text{Se(IV)}_{(\text{aq})}$. At trace levels

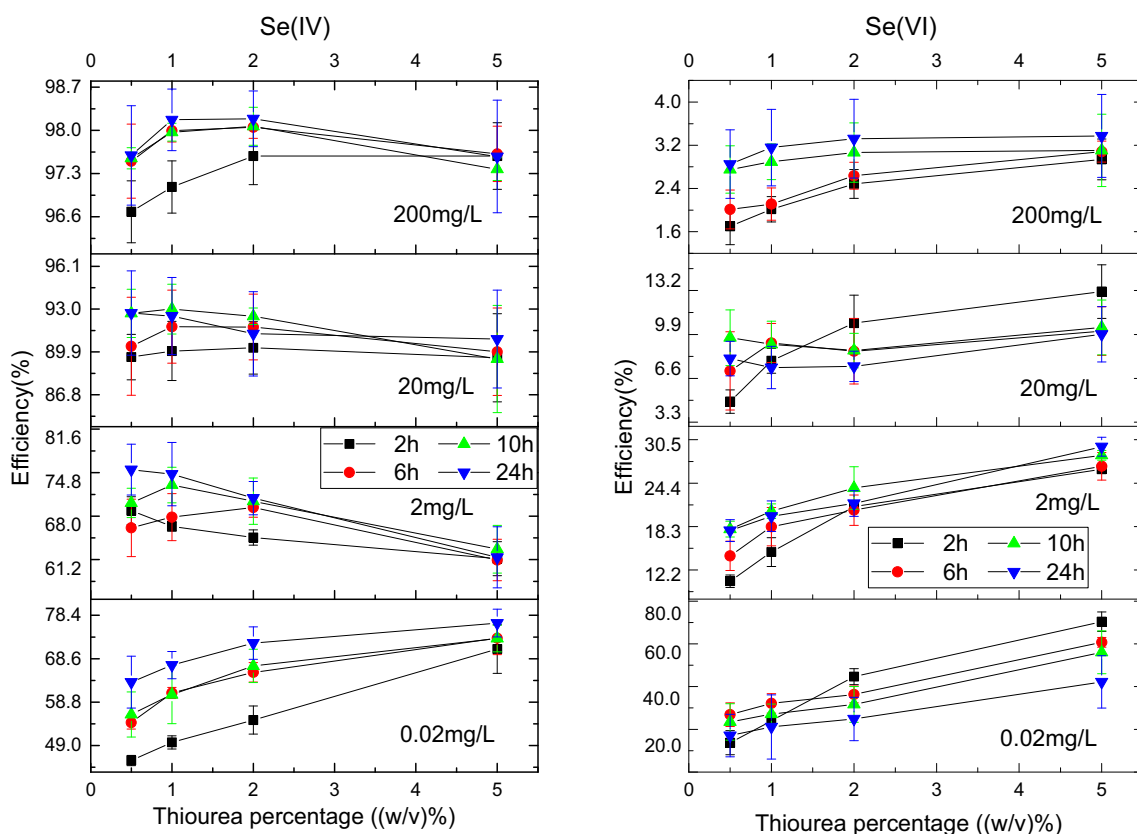


Fig. 2 Reduction efficiency percentage as a function of reaction time and % thiourea added on various concentrations of aqueous Se(IV) and Se(VI)

of aqueous Se(VI) (Fig. 1 and Table S1), namely, 0.02 mg/L, $\leq 0.5\%$ was reduced to Se(IV)_(aq) after 2 h of reaction time and only a maximum of 2.7–4.6% was converted to Se(IV)_(aq) after 6–24 h at all percentages of ascorbic acid added. When 2 mg/L of Se(VI)_(aq) was added to the solution (Fig. 1 and Table S1), $\leq 0.5\%$ of it was converted to Se(IV)_(aq) at all percentages of ascorbic acid added and all reaction times. In this case, a small correlation between percentage of ascorbic acid added and the amount of reduced Se(IV)_(aq) was observed at 2–6 h. We observed that as we increased the percentage of ascorbic acid added to the Se(VI)_(aq), the lower the reduction efficiency in solution and the less the amount of Se(IV)_(aq) that was detected. At 20 mg/L of aqueous Se(VI), the reduction efficiency was observed to be $\leq 0.2\%$ at all percentages of ascorbic acid added and all reaction times. This was similar to what was observed at 2 mg/L thus indicating that the reduction of Se(VI)_(aq)→Se(IV)_(aq) was very small in comparison to what was observed at 0.02 mg/L. However, in this case, the reduction efficiencies remained fairly constant as the percentage of ascorbic acid increased for all reaction times tested. At the highest concentrations used (200 mg/L of Se(VI)_(aq)), the reduction efficiency to Se(IV)_(aq) decreased from 2% after 2 h to 0% after 24 h at all percentages of ascorbic acid added. Accordingly, it indicates that longer reaction times were not favorable for the reduction of Se(VI)_(aq)→Se(IV)_(aq). In this case, the reacting solutions remained largely clear/transparent

for all percentages of ascorbic acid added at all reaction times (Fig. S4) and no solids were precipitated. This is unlike that of the Se(IV)_(aq) case in which a clear solution and red precipitates were observed.

The influence of thiourea on the reduction of aqueous Se(IV) and Se(VI)

The fluorescence intensity of aqueous Se(IV) at trace levels (0.02 mg/L) was observed to decrease as the amount of thiourea added and reaction time was increased (Fig. S2 and Table S2). This is in contrast to what was observed at the same Se(IV)_(aq) concentration with ascorbic acid (Fig. S1 and Table S1) and is indicative that a greater portion of the aqueous Se(IV) remained in solution and was not reduced to Se⁰ with thiourea. In general, it can be observed (Fig. 2 and Table S2) that as the amount of thiourea added and time increased, the percentage of reduction efficiency from aqueous Se(IV) to Se⁰ increased ranging from 46 to 77% after 2–24 h and 0.5–5% thiourea added. For the 2 mg/L case, the fluorescence intensity increased to a lower degree (Fig. S2 and Table S2) (in comparison to that of trace level Se(IV)_(aq)) as the amount of thiourea added increased, but again, it was in contrast to what was observed at the same concentrations with ascorbic acid. Thus again, it indicates that a larger portion of the aqueous Se(IV) remained in solution and was not reduced

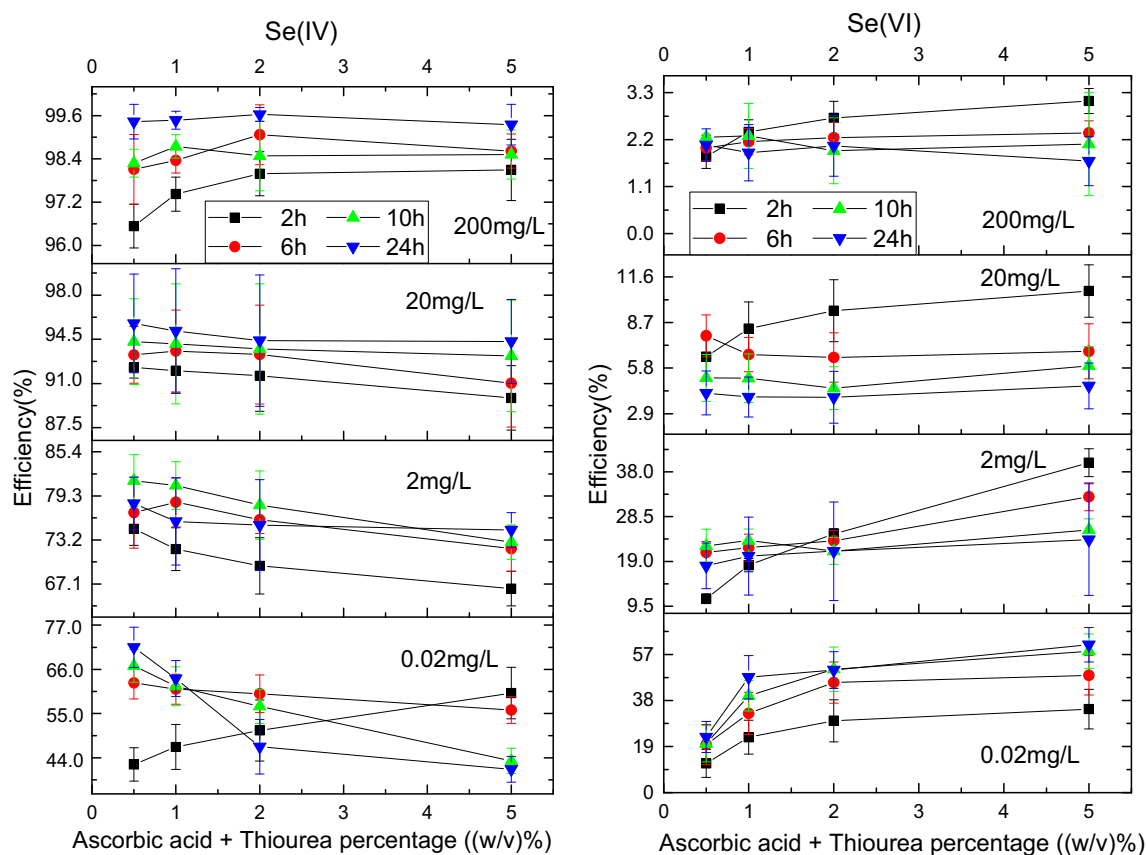


Fig. 3 Reduction efficiency percentage as a function of reaction time and % ascorbic acid + thiourea added on various concentrations of aqueous Se(IV) and Se(VI)

to Se^0 relative to the ascorbic acid experiments. Herein, the majority of the percent reduced $\text{Se(IV)}_{(\text{aq})}$ efficiency occurred between 0.5–1.0% added thiourea ranging from 66 to 75% at 2–24 h after which it decreased to ~62% as the amount of thiourea added increased for all reaction times. At 20 mg/L aqueous Se(IV), the fluorescence intensity (Fig. S2 and Table S2) resembled a parabolic type of behavior that decreased lower in intensity with longer reaction times. In this case, no evident correlation with the amount of reduction percentage efficiency was observed at all reaction times as the amount of percent thiourea added increased as was observed at 0.02 and 2 mg/L. However, as the reaction time increased from 2 to 24 h, the amount of percent reduced aqueous Se(IV) to Se^0 increased from ~89–93% for all percentages of thiourea added. Finally, at the highest concentration of 200 mg/L aqueous Se(IV) tested, we could observe that the fluorescence intensity (Fig. S2 and Table S2) resembled again a parabolic type of behavior observed at 20 mg/L but was in contrast to what was observed for the ascorbic acid case (Fig. S1). Here, we measured an increase in reduction efficiency (Fig. 2 and Table S2) of $\text{Se(IV)}_{(\text{aq})} \rightarrow \text{Se}^0$ from 96 to 98% as the amount of thiourea increased from 0.5–2.0% and 2–24 h. After which, it converged to ~97% at 5% thiourea added and all reaction times. It is worth to note to the reader that, at this high

concentration of aqueous Se(IV), the reacting solutions turned clear with a red precipitate forming (Fig. S5) whose identity will be discussed in “Solid analysis of reduction precipitates from 200 mg/L aqueous se(IV) and se(VI), 24 h, and 5% reducing agents.”

In the case of aqueous Se(VI), the fluorescence intensity (Fig. S2 and Table S2) for all tested Se(VI) concentrations and percentages of thiourea added were not near the blank solution as observed in the ascorbic acid case. Instead, they increased in intensity as the amount of added thiourea increased. Thus, it indicates that in this case, a larger portion of the $\text{Se(VI)}_{(\text{aq})}$ had been reduced to $\text{Se(IV)}_{(\text{aq})}$ in comparison to the ascorbic acid experiments. At the lowest concentrations of $\text{Se(VI)}_{(\text{aq})}$ tested (0.02 mg/L), the fluorescence intensity (Fig. S2 and Table S2), as well as the reduction efficiency (Fig. 2 and Table S2), increased with the added amount of percent thiourea from 14 to 74% between 2 and 24 h. It is worth to note that in this case, a longer reaction times caused a decrease in reduction efficiency where the maximum reduction efficiency occurred after 2 h. At 2 mg/L $\text{Se(VI)}_{(\text{aq})}$, we observed the fluorescence intensity (Fig. S2 and Table S2) as well as the reduction percentage efficiency (Fig. 2 and Table S2) increase with the added amount of percentage thiourea from 11 to 29% between 2 and 24 h. However, in this case, we observed that longer

reaction times had a positive effect on the reduction efficiency as the largest reduction occurred after 24 h. Once 20 mg/L of $\text{Se(VI)}_{(\text{aq})}$ was tested, again, a similar trend was observed as that which was observed at 0.02 mg/L. The fluorescence intensity (Fig. S2 and Table S2) as well as the reduction efficiency percentage (Fig. 2 and Table S2) increased with percentage thiourea added from 5 to 12% after 2–24 h. Again, here, we observed that longer reaction times larger than 2 h had a negative effect on the reduction efficiency as the maximum efficiency occurred after 2 h of reaction time. Finally, at the largest $\text{Se(VI)}_{(\text{aq})}$ tested (i.e., 200 mg/L), we observed a fluorescence intensity and reduction efficiency behavior similar to what was observed at 2 mg/L. Namely, the fluorescence intensity and reduction efficiency increased with the amount of percent thiourea added from 2 to 4% between 2 and 24 h. Again, longer reaction times had a positive effect on the reduction efficiency as the largest efficiencies occurred after 10 h of reaction time. In this case, unlike that of ascorbic acid at the same $\text{Se(VI)}_{(\text{aq})}$ concentrations, the solution turned from clear to a yellow-orange like precipitate (Fig. S5) whose identity will be discussed in more detail in “Solid analysis of reduction precipitates from 200 mg/L aqueous se(IV) and se(VI) , 24 h, and 5% reducing agents.”

The influence of both ascorbic acid and thiourea on the reduction of aqueous Se(IV) and Se(VI)

Our intent in combining both ascorbic acid and thiourea in a 50–50% mixture was to increase the reduction efficiency percentage to the maximum amount possible should both reducing agents behave in concerto. However, our results showed some peculiar solution behavior as discussed below.

For aqueous Se(IV) at 0.02 mg/L, the fluorescence intensity (Fig. S3 and Table S3) behaved like that of thiourea alone and not ascorbic acid nor a combination of both. The reduction efficiency percentage (Fig. 3 and Table S3) behavior was only slightly similar to thiourea. Regardless, a similar portion of the $\text{Se(IV)}_{(\text{aq})}$ remained in solution as was observed in the thiourea case. In general, we observed that as the amount of AA+TH added increased at shorter reaction times (2 and 6 h), the reduction efficiency ranged from 42 to 60%, while at longer reaction times (10 and 24 h), the reduction efficiencies decreased from 72 to 41%. In this case, the combination of AA+TH gave similar reduction efficiency percentages as was observed for the isolated thiourea experiments. At 2 mg/L $\text{Se(IV)}_{(\text{aq})}$, the fluorescence intensity (Fig. S3 and Table S3) and the reduction percentage behavior (Fig. 3) resembled the thiourea tests. In this case, we detected that the more AA+TH that was added, the reduction efficiency percentage decreased from ~81–66% for all reaction times. In here, it was again observed that longer reaction times generally had a positive effect on the reduction efficiency by increasing it. This latter fact is something that was not so clearly observed at the same

$\text{Se(IV)}_{(\text{aq})}$ concentrations with the use of thiourea alone. Interestingly, the combination of AA+TH did increase the overall percentage of $\text{Se(IV)}_{(\text{aq})}$ reduced in comparison to thiourea alone but was lower than that of ascorbic acid (Figs. 1, 2, and 3 and Tables S1–S3). Using 20 mg/L $\text{Se(IV)}_{(\text{aq})}$, we could observe that the fluorescence intensity (Fig. S3) behaved like it was observed for the thiourea case and the reduction efficiency percentage behavior (Fig. 3) was unlike that of the ascorbic acid nor thiourea. In general, we measured that as the amount AA+TH increased from 0.5–5%, the lower the reduction efficiency percentage of $\text{Se(IV)}_{(\text{aq})}$ to Se^0 ranging from 96 to 90% at all reaction times. Furthermore, here, we observed that the longer the reaction time, the higher the reducing efficiency obtained at all percentages of AA+TH added. The combination of AA+TH showed slightly higher efficiencies than the thiourea case alone but was still lower than ascorbic acid. At the highest concentration of $\text{Se(IV)}_{(\text{aq})}$ used (i.e., 200 mg/L), the fluorescence intensity (Fig. S3) behavior was unlike that of thiourea but resembled that of ascorbic acid with the exception that the kinetics were much slower with time. Interestingly, the reduction efficiency behavior (Fig. 3) was only slightly similar to that of thiourea and unlike that of ascorbic acid. This latter fact shows an important behavior that should be considered; although, the fluorescence intensity profile showed one type of behavior, the reduction efficiency does not always follow the same trend. In this case, as the amount of AA+TH added increased at shorter reaction times (2 and 6 h), the higher the reduction efficiency that was measured from $\text{Se(IV)}_{(\text{aq})} \rightarrow \text{Se}^0$, while at longer reaction times, the efficiency remained constant. In general, a range between 97 and 100% reduction of $\text{Se(IV)}_{(\text{aq})}$ to Se^0 was observed for the tested conditions. The combination of AA+TH at such high $\text{Se(IV)}_{(\text{aq})}$ concentrations was similar to both ascorbic acid and thiourea tests alone and did not show any significant increase in reduction efficiency. In this case, upon the reduction of 200 mg/L $\text{Se(IV)}_{(\text{aq})}$, the solutions were transparent with red precipitates at the bottom (Fig. S6) whose identity will be discussed in “Solid analysis of reduction precipitates from 200 mg/L aqueous se(IV) and se(VI) , 24 h, and 5% reducing agents.” It is worth to note that we can hypothesize that the reason why lower reduction efficiencies ($\leq 81\%$) were observed at $\text{Se(IV)}_{(\text{aq})}$ concentrations (0.02 and 2 mg/L) with AA+TH may be a result of the fact that, at these concentrations, the reduction efficiency percentage quantity behaved like TH for which the amount of reduction efficiency percentage was always $\leq 81\%$ (Fig. 2). This lower reduction percentage observed for TH maybe a result of the fact that it has been documented that, upon its reaction with $\text{Se(IV)}_{(\text{aq})}$, it may form $[\text{NH}_2\text{-C(NH)-S-Se-S-(NH)C-NH}_2]$ complexes which may inhibit to some degree its full reduction to Se^0 . Higher reduction efficiencies ($\geq 90\%$) were observed at higher $\text{Se(IV)}_{(\text{aq})}$ concentrations (20 and 200 mg/L) upon the addition of AA+TH likely due to the fact that the system had

contributions from both components (i.e., AA and TH) for which their individual reduction efficiencies were always $\geq 90\%$ (Figs. 1 and 2).

In the case of aqueous Se(VI) at trace concentrations (0.02 mg/L), the fluorescence intensity (Fig. S3) and the reduction percentage efficiency (Fig. 3) were like that of thiourea as we observed an increase in reduction efficiency percentage of Se(VI)_(aq) to Se(IV)_(aq) from 12 to 61% as the amount of AA+TH increased. However, unlike that of thiourea alone (Fig. 2), upon the increase of time, the reduction percent efficiency increased at all percentages of AA+TH added (Fig. 3). Furthermore, the combination of AA+TH resulted in a slight decrease in comparison to thiourea alone but was still much higher in comparison to ascorbic acid (Tables S1–S3 and Figs. S1–S3). A similar trend was observed at 2 mg/L Se(VI)_(aq) where the fluorescence intensity, and the reduction efficiency percentage were like that of the isolated thiourea case (Figs. 2 and 3 and Figs. S2–S3). However, in this case, unlike the thiourea tests, we observed the reduction efficiency percentage decrease from Se(VI)_(aq) to Se(IV)_(aq) with time from 40 to 11% as the amount of AA+TH added increased (Figs. 2 and 3 and Tables S2–S3). Here, an increase in the reduction efficiency percentage of Se(VI)_(aq) to Se(IV)_(aq) was observed upon the addition AA+TH in comparison to thiourea alone. Interestingly, upon the addition of 20 mg/L Se(VI)_(aq), the fluorescence intensity and the reduction efficiency percentage resembled that of thiourea. In general, after the addition of 20 mg/L of Se(VI)_(aq), the reduction efficiency percentage decreased from 11 to 4% with longer reaction times at all percentages of AA+TH added. Little to no correlation with an increase in percent of AA+TH added and reduction efficiency was observed for all reaction times tested. In this case, we observed a slight decrease in the reduction efficiency upon the combination of AA+TH in comparison to thiourea alone, but it was still much higher than the ascorbic acid experiments (Figs. 1, 2, and 3 and Tables S1–S3). Finally, at the highest Se(VI)_(aq) concentration used (i.e., 200 mg/L), a similar behavior was observed as previously described at 20 mg/L Se(VI)_(aq). The fluorescence intensity and reduction efficiency (Fig. 3 and Fig. S3) profiles were similar to that of thiourea with the exception that the highest intensity, as well as the reduction efficiency (2.7%), was observed for the shortest reaction time of 2 h which then decreased with time (1.7%) as the amount of AA+TH increased. This behavior was the inverse of what was observed for thiourea alone, thus indicating that longer reaction times were unfavorable in converting Se(VI)_(aq)→Se(IV)_(aq) as the amount of AA+TH added increased. The addition of AA+TH resulted in slightly lower reduction percentage efficiencies in comparison to that of thiourea alone but were still higher than those observed for ascorbic acid (Figs. 1, 2, and 3 and Tables S1–S3). It is worth to note that upon the reduction of 200 mg/L Se(VI)_(aq), the reacting solutions had a slightly

orange tint with reddish-orange solid precipitates forming (Fig. S6); the characteristics of which will be discussed in “Solid analysis of reduction precipitates from 200 mg/L aqueous se(IV) and se(VI), 24 h, and 5% reducing agents.”

Solid analysis of reduction precipitates from 200 mg/L aqueous Se(IV) and Se(VI), 24 h, and 5% reducing agents

In order to confirm the nature of the solids precipitated in our reactions, we decided to analyze them at the structural and molecular level to observe if indeed the majority of the precipitated reduction products formed were that of elemental selenium (Se⁰) as desired. However, as previously noted, only solids at 200 mg/L Se(VI)_(aq)/Se(IV)_(aq) with 5% added reducing agent(s) and 24 h of reaction time produced enough mass of the solids to conduct characterization analysis. The only exception has been Se(VI)_(aq) with ascorbic acid which produced no solid precipitates due to the low amount of reduction. The XRD, Micro-Raman, and ATR-IR of reference compounds (Se⁰, S⁰, ascorbic acid, and thiourea), our reacted samples and their assignments are shown in Figs. 4, 5, and 6 and Figs. S7–S9 and Tables S4–S6.

In the case of Se(IV)_(aq) with ascorbic acid, the Raman spectra (Fig. 4) showed characteristics of Se–Se stretches but shifted to higher energy ($\sim 247\text{ cm}^{-1}$) and with a broader full width at half max (FWHM) in comparison to the standard elemental Se⁰. The latter characteristic (broad FWHM) can be reasoned as a result of the fact that the generated Se⁰ took a nano-crystalline (Hemalatha et al. 2014) or a semi-crystalline type of form. The shift to higher energy may be attributed to some interactions (e.g., strain/distortion) occurring between the Se–Se bonds and/or lattices domains or due to a nano-crystalline nature or due to the fact that it may have formed the less common Se₆ structures as observed by Oremland et al. (2004) who observed shifts to higher energies (~ 241 and 244 cm^{-1}) for the main scattering peak. Our Raman observations are in agreement with the work of Ezhuthupurakkal et al. (2017) who also observed a similar Raman band at $\sim 250\text{ cm}^{-1}$ which they attributed to be from a nano-crystalline trigonal Se⁰ phase. To further verify the nano-crystalline nature of the Se⁰ nano-particles inferred to be observed from the Raman data, additional TEM analysis was undertaken. From the TEM images (Fig. 5 and Fig. S7), we confirmed that indeed the Se⁰ particles formed were composed of nano-crystalline agglomerates (50–100 nm) that formed micron size spherical particles (1–2 μm) out of which sharp shaped needles (1.5–1.6 μm) grew. Furthermore, in addition to the well-ordered lattice fringes from the (010) at 3.8 Å and (012) at 2.1 Å, we observed a small domain of lattice fringes with spacing's of 4.1 Å (unindexed based on Se⁰ crystallographic data) as well as distorted lattice fringe

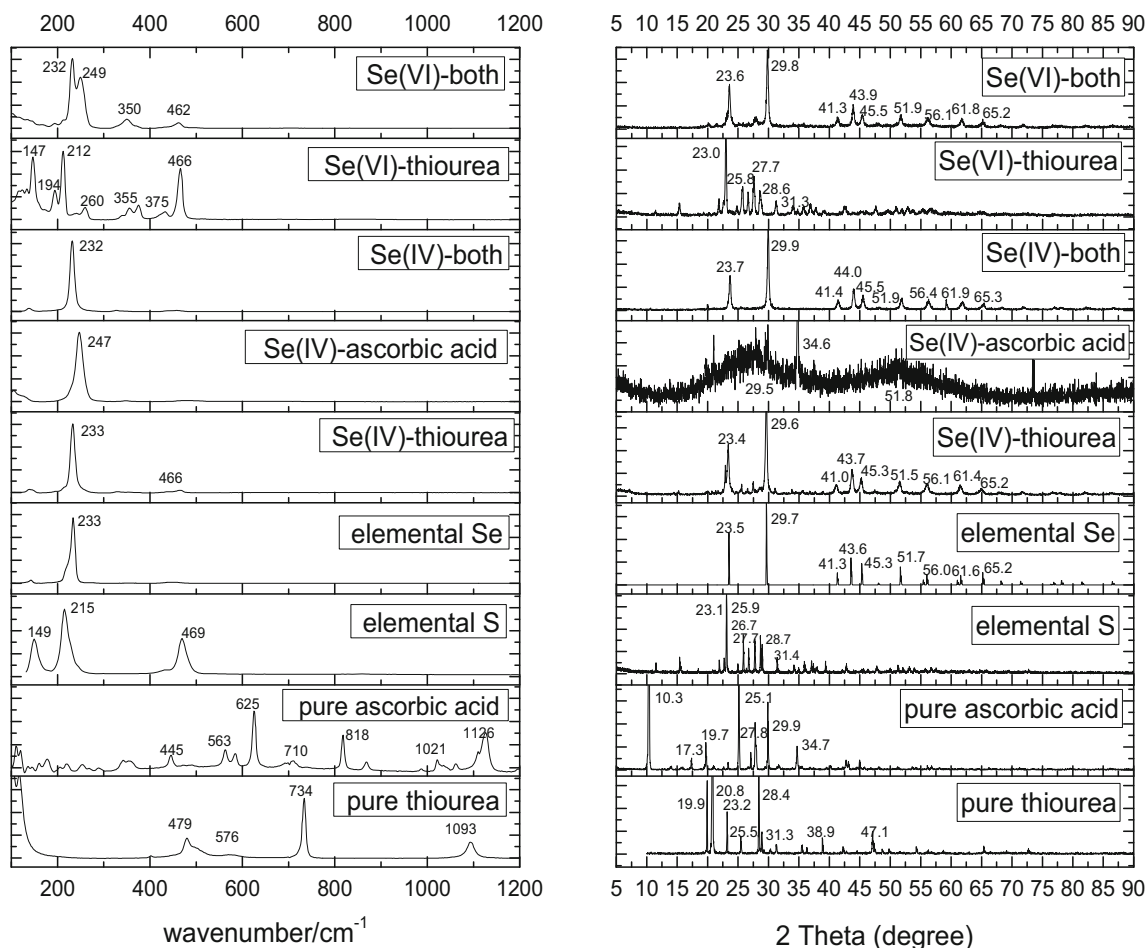


Fig. 4 Micro-Raman and XRD of standard solids as well as reacted solids precipitated at 5% reducing agent, 24 h of reaction time, and 200 mg/L of aqueous Se(IV) and Se(VI)

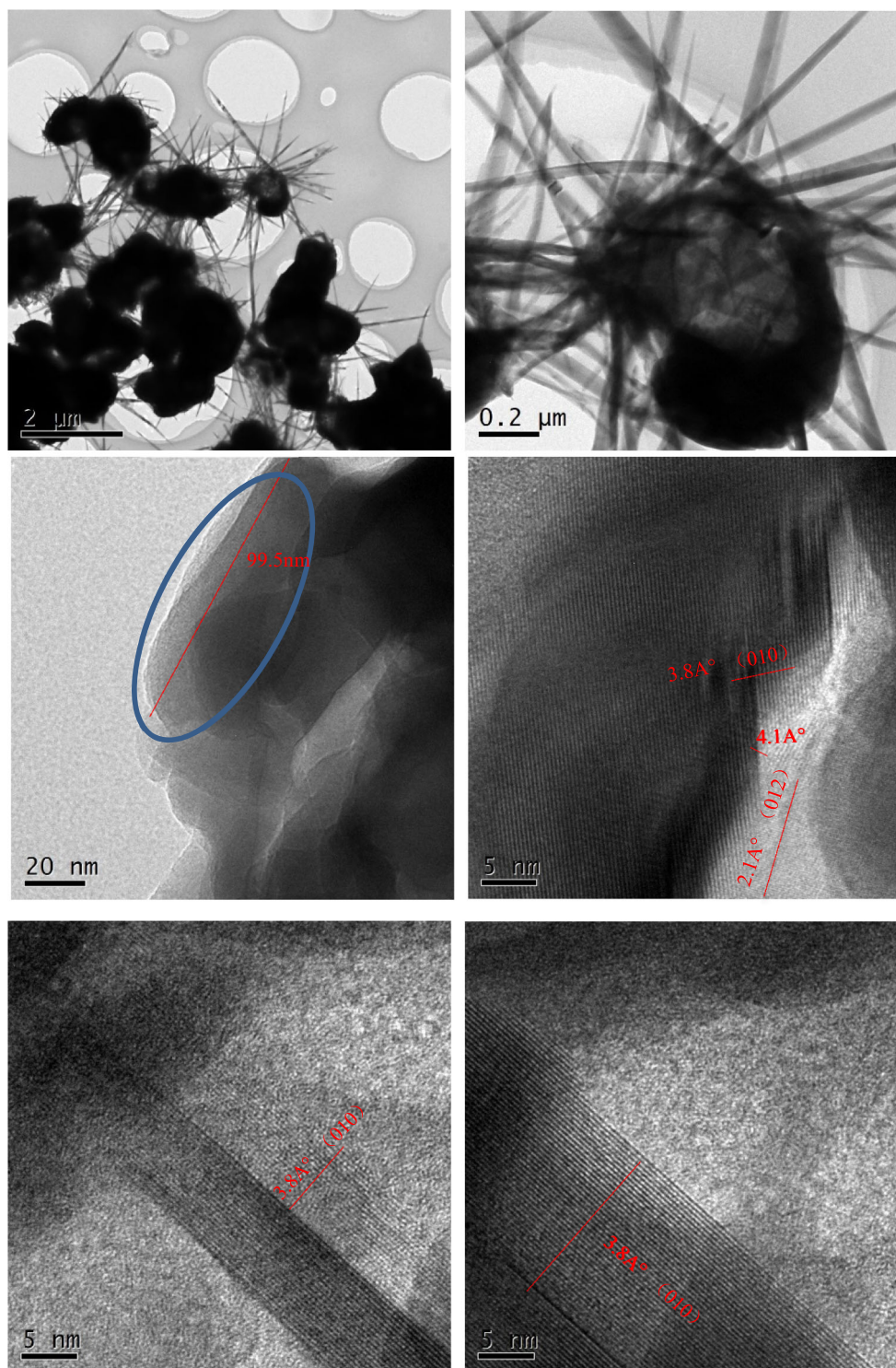
domains which likely contributed the observed shifts to higher energies observed in the Raman spectra (Fig. 4). From the XRD data (Fig. 4), no distinct crystalline peaks were observed from Se⁰ but rather two broad peaks at 29.5° and 51.8° and a crystalline peak at 34.6° were observed. The XRD results are in agreement with the Raman and TEM data indicating that the produced Se⁰ was composed of a nano-crystalline nature as observed in the work of Ezhuthupurakkal et al. (2017) but also some micro-crystalline component. The ATR-IR spectra (Fig. 6) indicated some ascorbic acid had re-precipitated but based on the positions as well as the symmetry of the major bands/functional groups (Table S6) of the pure ascorbic acid, and the re-precipitated ascorbic acid, we can infer that no chemical bonding interactions occurred between the nano- nor micro-crystalline Se⁰ and the re-precipitated ascorbic acid. Therefore, it indicates that the Se⁰ precipitated as an independent phase.

As we hypothesized from the red color of the solid, in the case of Se(IV)_(aq) with thiourea alone, the Raman spectra (Fig. 4) showed only characteristic Se–Se stretches at 233 cm⁻¹

typical of Se⁰ with no characteristic bands from S_nSe_{8-n} compounds nor that of elemental sulfur (S⁰) (Alía et al. 1999; Ward 1968; Laitnen and Steudel 1980). Similarly, the XRD (Fig. 4) showed all major diffraction planes belonged to that of pure hexagonal Se⁰ with no major traces of impurities. Interestingly, the ATR-IR spectra (Fig. 6) again showed that some residual amount of thiourea had re-precipitated from solution but based on the major bands/functional group positions, the interaction between the Se⁰ and thiourea were purely physical (i.e., they both co-precipitated as separate phases). This latter fact has interesting implications in the fact that the re-precipitated thiourea could be separated, recycled, and reused for further Se(IV)_(aq) reduction. However, in our work, the latter implication was not tested as it was out of the scope of the current work.

For tests conducted with AA+TH and Se(IV)_(aq), the Raman spectra (Fig. 4) showed a clear Se–Se vibrational structure at 232 cm⁻¹ typical of Se⁰ with no indications of S_nSe_{8-n} and elemental sulfur (Alía et al. 1999; Ward 1968; Laitnen and Steudel 1980). In agreement, the XRD data (Fig. 4) showed only the presence of pure hexagonal Se⁰ with no major traces

Fig. 5 TEM images of Se^0 produced with 200 mg/L $\text{Se(IV)}_{(\text{aq})}$, 24 h, and 5% AA. The particles are observed to be composed of nano-crystalline-agglomerated particles that form micron-sized sphere-shaped particles out of which sharp needles are formed



of impurities. The ATR-IR data showed that a mixture of AA+TH re-precipitated (Fig. 6), but again, the formation of the latter is independent of the formation of Se^0 .

The reduction of $\text{Se(VI)}_{(\text{aq})}$ with ascorbic acid showed that no solids formed due to the low reduction efficiency percentage observed from $\text{Se(VI)}_{(\text{aq})}$ to $\text{Se(IV)}_{(\text{aq})}$. We reasoned this to be a result of the fact that perhaps, in this case, some insoluble

Se(VI)-AA complexes formed which were not favorable to precipitate under the reacting conditions used or that the reduction reaction is extremely slow under acidic conditions.

In the case of $\text{Se(VI)}_{(\text{aq})}$ with thiourea, the Raman spectra (Fig. 4, Fig. S8) showed no distinct Se^0 stretches between 233 and 245 cm^{-1} but rather the appearance of S–S stretches at 147, 212 and 469 cm^{-1} from elemental sulfur (Ward 1968) as

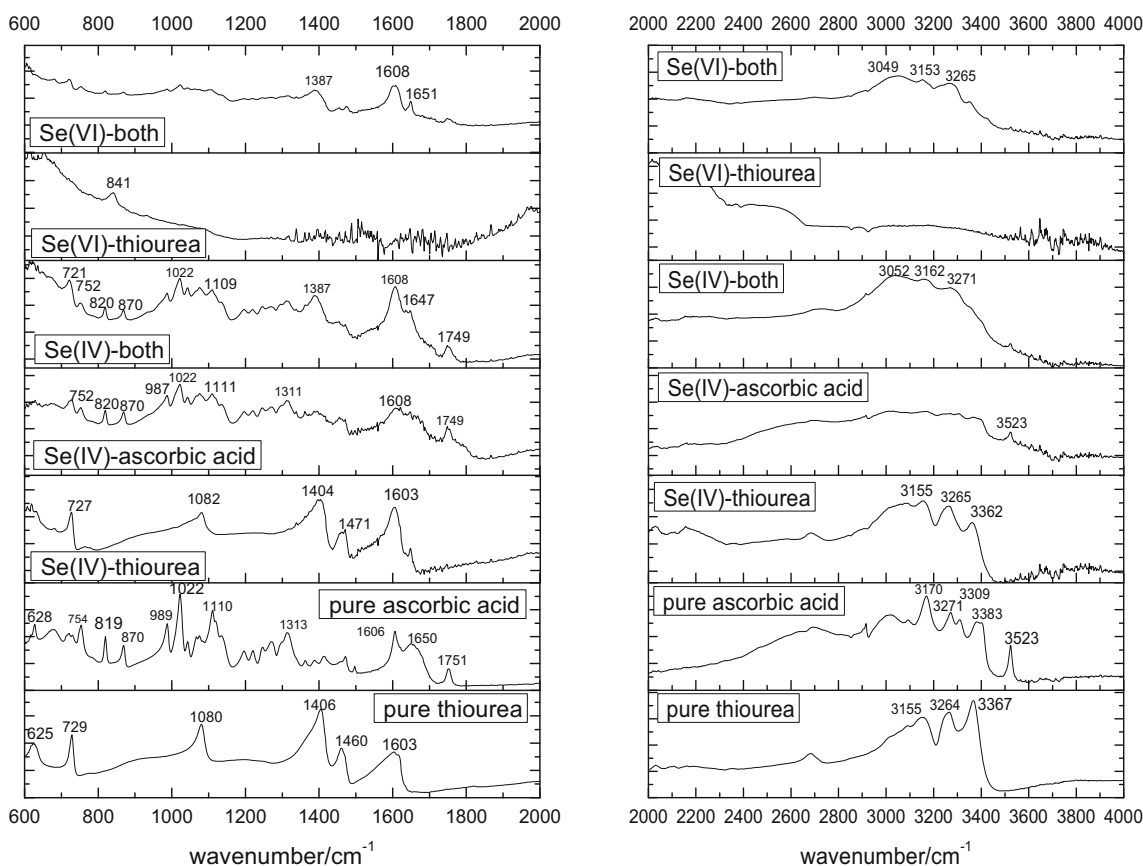


Fig. 6 ATR-IR of standard solids as well as reacted solids precipitated at 5% reducing agent, 24 h of reaction time, and 200 mg/L of aqueous Se(IV) and Se(VI)

well as that of Se–S vibrations from S_nSe_{8-n} compounds between 260 and 433 cm^{-1} (Alía et al. 1999; Ward 1968; Laitnen and Steudel 1980). Our Raman analysis is in agreement with the fact that we observed yellow-orange precipitates upon the addition of thiourea. The XRD analysis (Fig. 4, Fig. S8) again showed no presence of Se^0 and was dominated by S^0 , in agreement with our Raman analysis. In this case, no thiourea was re-precipitated out of solution as observed from the ATR-IR data (Fig. 6).

Finally, reduction of $Se(VI)_{(aq)}$ with AA+TH gave Raman spectra (Fig. 4, Fig. S9) that showed the presence of Se–Se stretches (Se^0) at 232 cm^{-1} as well as that of S–S stretches (S^0) at 462 cm^{-1} and Se–S vibrations from S_nSe_{8-n} type of compounds between 249 and 350 cm^{-1} (Alía et al. 1999; Ward 1968; Laitnen and Steudel 1980). The vibrational analysis was again in agreement with the fact that a reddish-orange type of solids formed upon the addition of AA+TH. The XRD data (Fig. 4, Fig. S9) showed only the presence of Se^0 with no clear indication of a major percentage of S^0 as was observed in the thiourea alone experiment. Hence, it indicates that the amount of S^0 was not significant. The ATR-IR data (Fig. 6) showed that only a small amount of thiourea had re-precipitated from solution with no clear signs of ascorbic acid.

Environmental implications

In natural water such as aquifers, crater lakes and hot springs in active geothermal areas sources from magmatic gases can contribute HCl, HF, and H_2SO_4 which will cause extreme acidic conditions ($pH \leq 1$) (Nordstrom et al. 2000) where natural contaminants in the form of aqueous selenium in various oxidation states maybe present and may have detrimental effects to the surrounding environment and natural wild life.

Similarly, aqueous selenium in various oxidation states is a common unwanted impurity that must be removed in numerous mining industries (e.g., Zn, Ni, Pb, Cu refineries, U, Au, and Ag acid leaching of ores as well as coal mining operations) for which a highly acidic chloride environment ($pH \leq 1$) may be present as a result of the hydrometallurgical chloride (Winand 1991; Adams 2016) technology used (e.g., CESL process (Mayhew et al. 2013), Hydrocopper™ (Hyvarinen et al. 2004), Kell Process (Lidell and Adams 2012), Intec/N-chlo process (Severs 1999; Moyes 1999), Neomet gold process (Harris and White 2011a, b), ZINCEX process (Winand 1991), ELKEN-Falconbridge process (Winand 1991), ORTECH Inc. processes (Winand 1991)), or from chloride-containing mineral sources present in the original ore or concentrate.

Table 1 Selenium removal technologies reported in the literature in comparison to this work

Literature	Treatment Technology	Removal range		Reference
		Se(IV)	Se(VI)	
Literature	Activated alumina adsorption	Removal efficiency of an initial concentration of Se(IV) 100–200 µg/L was > 80% at pH = 3–7.	Selenium (VI) adsorption is poor	Khamkhash et al. 2017; Twidwell et al. 2000.
	Iron(III) co-precipitation	Removal efficiency of an initial concentration of Se(IV) 395 mg/L was 99.9% to 0.3 mg/L at pH = 3.5–7.0.	No removal in a wide range pH	Sandy and DiSante 2010.
	Ferrihydrite adsorption	Removal efficiency of an initial concentration of Se(IV) 1950 µg/L was 95% to 90 µg/L at pH < 8.	The adsorption is not as effective for Se(VI). Selenium (VI) adsorption drops off rapidly with increasing pH and is less than 50% at pH 7.	Khamkhash et al. 2017; Twidwell et al. 2000.
	Ion exchange	Removal efficiency of an initial concentration of Se(IV) and Se(VI) 0.1 mg/L and/or 1 g/L was > 98% at pH < 7.		Golder Associates Inc. 2009; Kapoor et al. 1995.
	Zero-valent iron	Removal efficiency of an initial concentration of Se(IV) 80 mg/L was 20% at pH = 6.0.	Reduction of initial concentration of Se(VI) 50 mg/L drop from 19 to 4.7 µg/L and listed removal was ≥ 99% at pH = 4.0.	CH2M Hill 2013; Qin et al. 2017b; Sandy and Disante 2010
	Ferrous hydroxide reduction	No available information.	Removal efficiency of an initial concentration of Se(VI) 42 mg/L was 95% at pH = 8.8–9.2.	MSE Technology Applications Inc. 2000; Murphy 1988; Sandy and DiSante 2010; Zingaro, R. 1997
This work	Nanofiltration	Removal efficiency of an initial concentration of Se(VI) 24–308 µg/L was > 95% at pH = 6.3–8.5. Similar recoveries were demonstrated for Se(VI) concentrations up to ~1000 µg/L.		Kharaka et al. 1996; Twidwell et al. 2000; Sandy and DiSante 2010
	Ascorbic acid	Removal efficiency ≥ 95% in below 200 mg/L Se(IV), pH < 1	Removal efficiency ≤ 5%	
	Thiourea	Removal efficiency ≤ 75% at low Se(IV) concentrations (0.02 and 2 mg/L), ≥ 90% at higher concentrations (20 and 200 mg/L), pH < 1	Removal efficiency ≤ 75% Se(VI) to Se(IV) at trace concentration (0.02 mg/L), the reduction efficiency steadily dropped to 3%, 12%, and 29% with Se(VI) concentration increased (2, 20, 200 mg/L), pH < 1.	
	Ascorbic acid + thiourea	Removal efficiency ≤ 80% at Se(IV) low concentrations (0.02 and 2 mg/L), ≥ 92% at higher concentrations (20 and 200 mg/L), pH < 1	Removal efficiency ≤ 61% Se(VI) to Se(IV) at low concentration (0.02 and 2 mg/L), < 10% at higher concentrations (20 and 200 mg/L), pH < 1	

Furthermore, acid mine drainage (AMD) and acid rock drainage (ARD) from mine waste rock dump tailings or coal spoils (Egiebor and Oni 2007; Gray 1996; Sandy and DiSante 2010; Banks and Banks 2001; Johnson and Hallberg 2005) may contain highly acidic ($\text{pH} \leq 1$) chloride environments where unwanted aqueous selenium in various oxidation states leaching from the waste tailings may occur and cause harm to the surrounding natural water and its organisms present.

As can be observed from the extensive literature reviews on selenium treatment technologies (Sandy and DiSante 2010; Khamkhash et al. 2017; Santos et al. 2015) for natural and anthropogenic contaminated water systems as well as our own comparison (Table 1), there exists a lack of application method(s) to treat aqueous selenium in various oxidation states in-situ without neutralization for highly acidic ($\text{pH} \leq 1$) water systems that may be dominated in chloride environments. Therefore, our research presented in this work provides an alternative practical inexpensive method to remediated $\text{Se(IV)}_{(\text{aq})}$ and $\text{Se(VI)}_{(\text{aq})}$ in situ without the need for neutralization at ambient conditions under highly acidic ($\text{pH} \leq 1$) chloride environments which may be observed in natural, hydrometallurgical processing operations and AMD/ARD tailings.

A limitation of this study is the fact that the presence of H_2SO_4 which is quite common in natural, hydrometallurgical processing as well as AMD/ARD environments was not included as a result of the fact it was out of the scope of this study. Therefore, future studies to investigate the effectiveness of AA, TH, and AA+TH in reducing $\text{Se(IV)}_{(\text{aq})}$ and $\text{Se(VI)}_{(\text{aq})}$ to Se^0 in the presence of both HCl and H_2SO_4 will be undertaken as limited (TH with $\text{Se(IV)}_{(\text{aq})}$ (Hollander and Yurii 1956)) or no studies exist on this matter.

Conclusion

In this work, we investigated the reduction efficiency of ascorbic acid, thiourea, and a 50–50% mixture of low to high concentrations of $\text{Se(VI)}_{(\text{aq})}$ and $\text{Se(IV)}_{(\text{aq})}$ to form Se^0 as a function of time, percent reductant added, and ambient highly acidic chloride media. Based on our experimental data and results, the following conclusions can be made:

- Ascorbic acid was able to reduce $\geq 95\%$ of $\text{Se(IV)}_{(\text{aq})}$ to nano- and micro-crystalline Se^0 under all reaction conditions tested and thus maybe used to treat highly acidic chloride-containing waste water under ambient conditions in a wide range of $\text{Se(IV)}_{(\text{aq})}$ concentrations quickly and effectively. In contrast, $\leq 5\%$ of $\text{Se(VI)}_{(\text{aq})}$ was reduced to $\text{Se(IV)}_{(\text{aq})}$ with no evidence of Se^0 solids which has been produced under all reaction conditions tested.
- The effectiveness of thiourea to reduce $\text{Se(IV)}_{(\text{aq})}$ to bulk Se^0 was $\leq 75\%$ at low $\text{Se(IV)}_{(\text{aq})}$ concentrations (0.02 and 2 mg/L) and $\geq 90\%$ at higher concentrations (20 and

200 mg/L) at all percentages of thiourea added and all reaction times tested. Thus, its use is only recommended at higher $\text{Se(IV)}_{(\text{aq})}$ concentrations. Thiourea reduced $\leq 75\%$ of $\text{Se(VI)}_{(\text{aq})} \rightarrow \text{Se(IV)}_{(\text{aq})}$ at 0.02 mg/L concentrations which steadily dropped to $\leq 29\%$, 12%, 3% at 2 mg/L, 20 mg/L, and 200 mg/L at all reaction times and percentages of thiourea added. In this case, mixtures of S^0 and $\text{S}_n\text{Se}_{8-n}$ products were formed with no evidence of Se^0 .

- The combination of AA+TH was able to reduce $\leq 80\%$ of $\text{Se(IV)}_{(\text{aq})}$ to bulk Se^0 at low concentrations (0.02 and 2 mg/L) and $\geq 92\%$ at higher concentrations (20 and 200 mg/L) for all reaction times tested and all percentages of AA+TH added. Thus, it makes it suitable for treating $\text{Se(IV)}_{(\text{aq})}$ in highly acidic chloride waste streams under ambient temperatures. In contrast, AA+TH reduced $\leq 61\%$ of $\text{Se(VI)}_{(\text{aq})}$ to $\text{Se(IV)}_{(\text{aq})}$ at low concentrations (0.02 and 2.0 mg/L) and $\leq 10\%$ at higher concentrations (20 and 200 mg/L) under all reaction conditions tested. Furthermore, the combinations of AA+TH-produced solids were mixtures of Se^0 , $\text{S}_n\text{Se}_{8-n}$, and S^0 .

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