



Assessment of Membrane and Electrochemical Technologies for the Treatment of a Selenium-Bearing Mine water: Technology Performance and Effect on Toxicity and Bioaccumulation

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Abstract

Nanofiltration (NF), reverse osmosis (RO), electro dialysis (ED), and electrocoagulation (EC), were all tested at the bench scale for removing selenium (Se) from mine water. All of these technologies reduced the concentration of total Se from 216 µg/L (i.e. 120.1 µg/L of selenate; 59.1 µg/L of selenite, and 0.6 µg/L methyl-selenic acid) in the raw mine water to about 2 µg/L or less in the treated water, equivalent to more than 99% removal. Electro dialysis was found to be the most effective, removing more than 99.5% of the Se. The untreated mine water was toxic to algae. In contrast, RO and NF reduced the toxicity of the mine water, allowing algae to grow between 15,000 to 25,000 cells/mL, while ED and EC did not allow algal growth, likely due to complete removal of essential minerals (ED) or the presence of other contaminants (EC), such as copper. The Se speciation did not change as a result of membrane filtration; however, selenite in the effluent was almost fully transformed to selenate in the brines from the ED and EC treatment processes. The effluent treated by NF and EC generated seleno-cyanate at 0.37 and 1.01 µg/L, respectively. Further testing is recommended at the pilot-scale with the same mine water as well as different mine water.

Keywords Selenium removal · Nanofiltration · Reverse Osmosis · Electro dialysis · Electrocoagulation

Introduction

Selenium (Se) is an essential micronutrient to life and is also known for its narrow window between essentiality and adverse effects (Chapman et al. 2010; Fuziki et al. 2021). Selenium is required for bone metabolism, iodine metabolism, immune function, reproductive success, and many other essential functions (Flueck et al. 2012). Furthermore, selenium deficiency may cause adverse effects in fish, poultry, livestock, and wild mammals (Schubert et al. 1987). On the other hand, once released to the environment, Se accumulates at the base of the food web (e.g. algae, periphyton) and transfers through trophic levels leading to bioaccumulation in fish and birds via dietary exposure (Mendes et al. 2022; Wang 2010). Maternal transfer of the accumulated selenium to developing embryos can lead to teratogenic

effects and limit their survival (Janz 2011). Limited survival of young can then lead to potential population collapse.

Mining operations such as copper (Cu), silver, gold, lead, zinc, uranium, and coal could be important sources of Se. During operations, Se can leach or migrate as soluble species from waste management areas into the water collection systems (Stefaniak et al. 2018). Its concentration in mining wastewaters can range from 3 to 12,000 µg/L (Wasewar et al. 2009). Therefore, Se has a high potential to impact the environment and be a liability to the mining sector, requiring mitigation such as effluent treatment and mine rock segregation, for example.

Where prevention and source reduction strategies cannot be used to control Se concentration in water, treatment technologies can be used to remove Se. Treatment technologies are commonly categorized as either active or passive. Active treatment technologies are capable of handling high Se feed concentrations compared to passive treatment processes. They can be categorized into three major processes: (1) physical, (2) chemical, and (3) biological (Golder Associates Ltd. 2020).

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Examples of physical treatment are membrane separation technologies such as nanofiltration (NF) and reverse osmosis (RO) (Ali and Shrivastava 2021; Zeeshan et al. 2020). It was reported that NF membranes are able to remove between 93.9 and 99.1% of selenium oxyanions (Ali and Shrivastava 2021; He et al. 2016). While NF and RO resulted in almost the same range of removal efficiencies, NF offers several potential advantages including higher permeability and higher monovalent/divalent ion selectivity (lower retention of monovalent), which would therefore limit deionization of the treated water with lower specific energy consumption (Mondal and Wickramasinghe 2008; Shin et al. 2020).

Chemical processes, such as: (1) adsorption and ion exchange, (2) oxidation/reduction, and (3) precipitation, are the most commonly used active treatment technologies for the removal of Se from water. While adsorption is used extensively (Jadhav et al. 2020, 2022; Okonji et al. 2020) for Se removal from synthetic solutions, the process seems to be inefficient for the treatment of actual wastewaters. Furthermore, successful removal of Se using ion exchange appears to require a pre-treatment step, as removal efficiency is highly affected by the presence of competing anions such as sulphate (Ali and Shrivastava 2021). Oxidation/reduction techniques include: (1) electrocoagulation (EC), (2) zero valent iron (ZVI), (3) electrochemical reduction, and (4) photocatalysis.

There is limited research on using EC for Se removal, but all results point to a high removal rate. Depending on the anode material, solids would be generated that are effective chemical reductants of selenate and selenite, which then retain the reduced forms of Se by adsorption, incorporation, or precipitation (Bae et al. 2022). Kazeem et al. (2019) reported that this process could remove up to 98% using iron (Fe) and aluminium (Al) as anodes by increasing the applied current and decreasing the initial concentration. Other results reported a decrease in selenite from 300 µg/L in the raw effluent of a petroleum refinery to 30 µg/L within 6 h, which equates to removal efficiencies of 90% when treated using an EC process with Fe as the anode in a batch airlift reactor (Hansen et al. 2019).

Despite promising results obtained with ZVI technology (Tang et al. 2014), this process is temperature and pH dependent and may potentially need long residence times. In addition, dissolved oxygen and other oxyanions can oxidize the ZVI. Furthermore, this process lacks precision for selenate removal because its reduction capacity is consumed by nitrate and even water (Bae et al. 2022).

Ferrihydrite precipitation with adsorption of Se was the U.S. EPA's best-demonstrated available technology for treating Se in the previous decade (Okonji et al. 2021). However, its removal efficiency is significantly affected by the presence of other oxyanions (Hu et al. 2015). Also, this

precipitation generates large quantities of sludge that could require management to avoid release of Se.

The performance of biological techniques can be adversely affected by variable influent composition, intermittent operations, and cold temperatures, and the approach can generate bioavailable organoselenium species (Gingerich et al. 2018; Golder Associates Ltd. 2020).

Thus, while the development of active treatment for Se removal from mining effluents is on-going, implementation challenges remain, including: (1) the suitability of an active treatment process greatly depends on influent volume, water quality, site constraints, and effluent targets, (2) most of the results reported in the literature have been obtained on a small scale, (3) there is very limited information on the effectiveness of active treatment processes for real effluents, and (4) active treatment technologies with promising results on synthetic solutions have often failed to demonstrate the same performance with real effluents.

The main goal of this study was to investigate and compare performance and technical feasibility of four active treatment processes using the same mine water. This involved pressure-driven membrane-based, and electrically driven active treatment technologies: NF, RO, electrodialysis (ED), and EC. These technologies were chosen for two main reasons:

- (a) There was information in the technical literature about the performance of each technology alone, but not in comparison with other technologies using the same test solutions.
- (b) The authors of this paper had expertise and technical capabilities, including the test systems (membrane separation and electrochemical treatment) and analytical instruments necessary for studying the four technologies.

The second goal of this work was to assess Se bioaccumulation and toxicity of the untreated and treated mine water to ensure that none of the employed technologies transform selenate or selenite into bioavailable forms of Se. The third objective of this study was to investigate how different treatment processes affected Se speciation in treated mine waters and resulted brines. Using removal performance, bioaccumulation, potential toxicity, and speciation results, a fourth objective was to provide recommendations for further development of Se removal processes at a large scale, and thus contribute to the development of best available treatment technologies economically achievable for the mining industry.

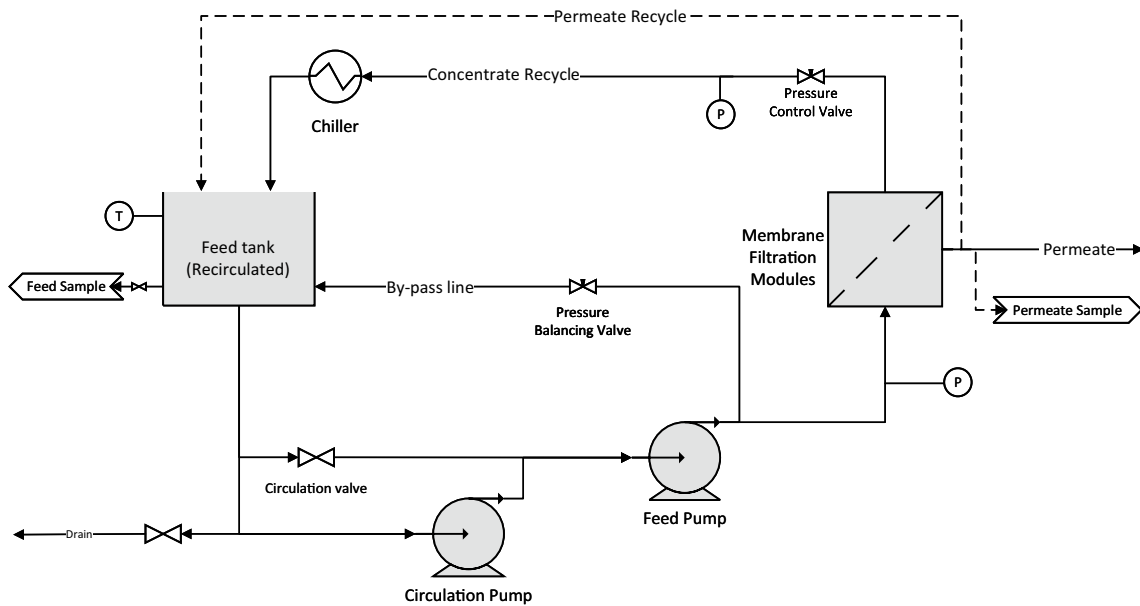


Fig. 1 A schematic of the flat sheet membrane filtration system

Experimental Methods

Materials

Real mine water (MW) was used in all of the treatment experiments. Ultra-trace metal grade 69% v/v nitric acid was used for acidification and dilution. Chemicals for HPLC were chromatography grade and acquired from Millipore Sigma (Canada). The Se standard solution (1000 mg/L) used was ICP grade from SCP Science. Working standard solutions ranged from 1–200 $\mu\text{g/L}$ (5 standard points), which were diluted from 1 mg/L. For Se speciation analysis, sodium selenate, potassium selenocyanate, and methyl seleninic acid were purchased from Millipore Sigma (Canada). Sodium selenite was acquired from Alfa Aesar (Canada).

In microfiltration, NF, and RO trials, Filtanium ceramic membrane, Synder NFX, and TriSept ACM2 membranes of 0.45 μm pore size diameters were used, respectively (Sterlitech, USA). In the ED experiments, Neosepta anion (ASE) and cation (CSE) membranes were used (Ameridia, USA). Hydrochloric and sulfuric acid were used to prepare rinse solutions and were used as received (Fisher Scientific, Canada). In the EC tests, Al, magnesium (Mg), and Fe were used as sacrificial anode (E2metrix, Canada).

Experimental Setup

Nanofiltration/Reverse Osmosis

A flat sheet membrane filtration system was used in this work to reduce the volume of the feed stream and thus

concentrate the Se compounds. The system consisted of three flat sheet membrane modules that can house a variety of flat sheet membranes. Each membrane module had an effective surface area of 60 cm^2 . NF and RO tests were conducted at 400 psi and 25 $^{\circ}\text{C}$. The tests were performed up to 50% recovery and the generated concentrates were used for further treatment using ED and EC processes. A schematic of the NF/RO setup is shown in Fig. 1.

Electrodialysis

A Micro Flow Cell ED system was used in this work (ElectroCell Inc., USA). The system consisted of a micro flow cell unit with four compartments, as shown in Fig. 2. The active electrode (Pt/Ti) area was 10 cm^2 for an individual electrode. Five pairs of ion exchange membranes with a total surface area of 50 cm^2 were used in this work. The cathode and anode rinse solutions were 0.05 M HCl and 0.05 M H_2SO_4 , respectively.

The ED experiments were performed at constant voltage (12 V) without controlling the pH (the initial pH was adjusted to be less than 5) at 25 $^{\circ}\text{C}$. The flowrate of feed, concentrate, and electrolytes were set at 0.2 L/min throughout the experiments, based on previous experience. The ED tests were conducted in three phases:

1. In the first step, the effect of ED duration on selenium removal was investigated.
2. In the second step, the capacity of the system was tested to concentrate the Se in the ED reject. To do this, the

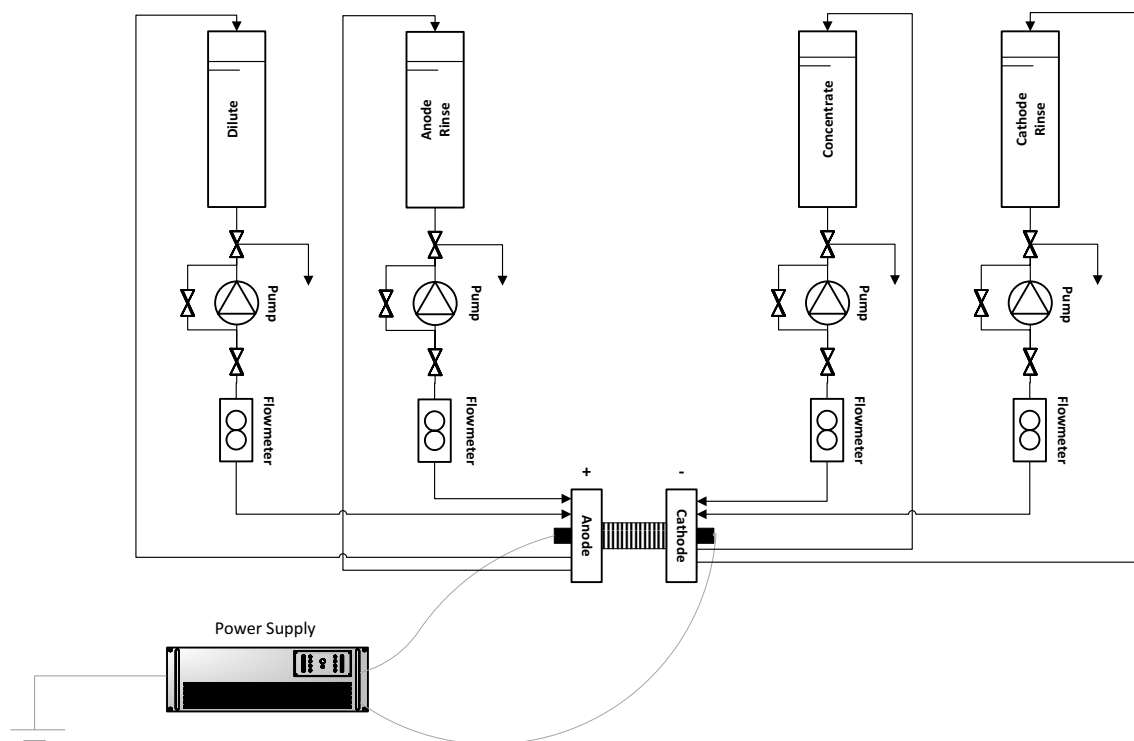


Fig. 2 A schematic of the ED system

concentrate stream was recycled through the ED system while fresh effluent (ME) was fed to the setup.

3. In the third step, the concentrate stream from RO process was fed to the ED system to potentially lower the ED throughput and study the effect of feed concentration on Se removal.

Electrocoagulation

The EC reactor was provided by E2Metrix (Sherbrooke, QC, Canada). The system makes use of E2Metrix's patented ECOTHOR technology (U.S. Patent 9,194,049 B2). The electrodes were arranged in a concentric configuration, with the cathode being a hollow stainless-steel tube with a surface area of 1130 cm². The sacrificial anode was a cylindrical rod with a surface area of 476 cm² placed within the hollow cathode. The anode material was either Al, Mg, or Fe. A schematic of the setup is shown in Fig. 3.

The effects of time, current, initial pH, and sacrificial anode material on the Se removal from the MW were investigated in the EC test. Tests were conducted at 25 °C. The EC tests were also conducted in three phases:

1. In the first step, operating conditions were optimized to find the best conditions for the highest removal efficiency. To this end, the MW was fed to the EC system

and the effect of time, current, initial pH, and sacrificial anode material on Se removal were studied. In this phase, the sludge was removed from the samples using centrifugation.

2. In the second step and at the optimum conditions, the effluent from the EC system was fed to the microfiltration process to remove the sludge formed during electrocoagulation.
3. In the third step, the RO concentrate was fed to the EC process to study the effect of effluent concentration on the performance of the electrocoagulation. Both centrifugation and microfiltration were used to separate the sludge from the treated effluent.

Sludge removal from the treated mine water after EC (smaller volume, i.e. 1.5 L) was performed using a Sorvall ST 40R centrifuge (Thermo Scientific, USA) at 3600 rpm for 10 min.

Microfiltration

A microfiltration system (Sterlitech, USA) was used to separate the sludge from the EC effluent (larger volume, i.e. 15 L). After EC, the treated mine water samples were sent as is, without any separation by sedimentation, to a ceramic membrane filtration process. A process flow diagram of the system is presented in Fig. 4.

Fig. 3 A schematic of the EC system

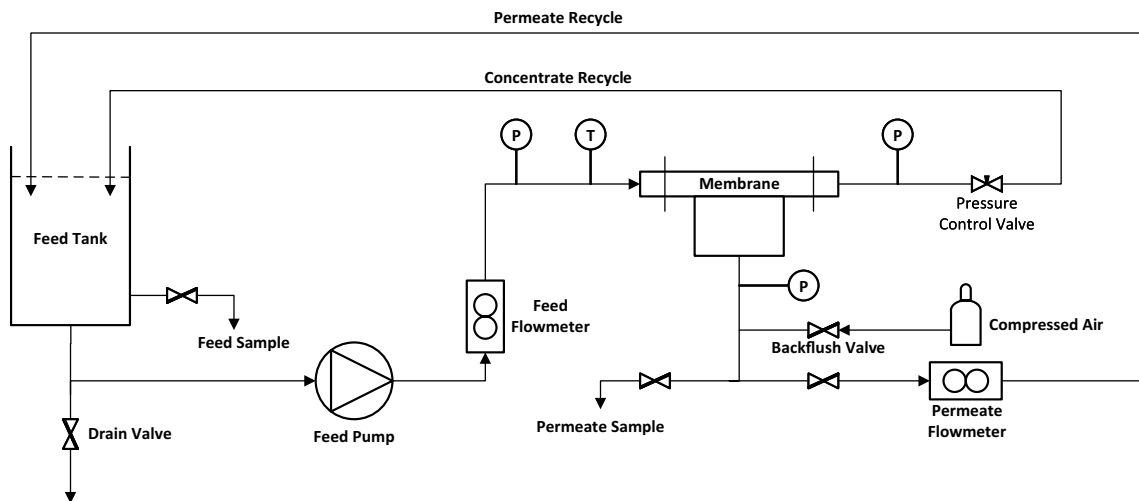
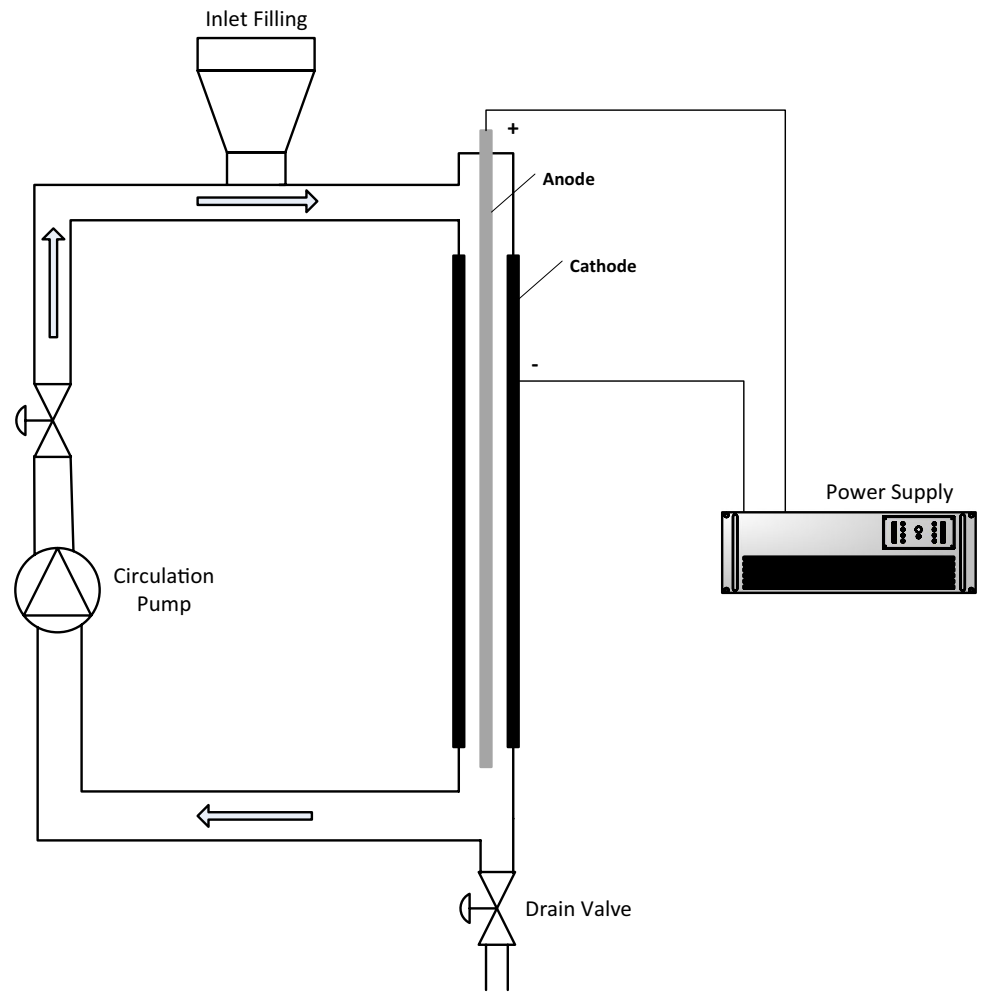


Fig. 4 A schematic of the microfiltration system

Removal rates for all metals and anions studied in this work were obtained using Eq. 1.

$$R_{i,t} = \frac{C_{i,0} - C_{i,t}}{C_{i,0}} \times 100 \quad (1)$$

where R and C indicate removal rate and concentration, respectively, and i and t denote analyte and time, respectively. $C_{i,0}$ shows the concentration of analyte i at time 0 (initial concentration).

Analytical Measurements

Total metal concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Agilent ICP-OES 5110 VDV and inductively coupled plasma mass spectrometry (ICP-MS) analyses (Agilent 8800 QQQ). Selenium speciation was done using a combination of ICP-MS and HPLC. Chloride, nitrate, and sulphate were measured using an ICS 1600, and thiocyanate was measured by an ICS 5000 (Thermo-Dionex). The average of three measurements was reported.

The pH and conductivity were measured using a laboratory benchtop pH/conductivity meter (Hanna HI 5522, USA). Total dissolved solids (TDS) and total suspended solids (TSS) were measured via gravimetric analysis by vacuum filtering samples through 0.45 μm nitrocellulose paper filters and weighing the solids deposited on the filters according to standard methods for the examination of water and wastewater (2540 C&D).

Treatment Tests

Active Se removal tests were conducted using NF, RO, ED, and EC/centrifugation/microfiltration. Each test was repeated at least two times to generate replicates. Methodology and details of each treatment technology are presented in supplementary material (S-1).

Toxicity Test Procedure

Algal growth and bioaccumulation tests were conducted with *Raphidocelis subcapitata* following a modified ECCC (2007) test method (EPS 1/RM/25). A full description of the method can be found in supplementary material (S-2). In brief, each treatment consisted of three replicates (100% v/v; Table S-1), plus two controls consisting of a sterile culture medium. Tests were conducted in 250 mL flasks that contained 100 mL of test solution and $\approx 1,000,000$ algal cells to establish a cell density of 10,000 cells/mL at the start of the experiment. Flasks were capped using autoclaved silicon stoppers with porous membranes to allow airflow and kept on a platform shaker (Innova

2000 platform shaker) at 100 rpm, in a test chamber maintaining 24.5 °C and continuous light (4000 lx) for 96 h.

Algal Growth

Every 24 h, as well as immediately after starting the test (i.e. adding inoculum), 0.5 mL from each flask was removed via 1 mL pipettor and added to 20 mL of Isoton II electrolyte diluent in separate 20 mL cuvettes for use in the Coulter Counter. Each solution, i.e. cuvette, was counted a minimum of five times, removing highest and lowest count and taking the average of remaining three values to establish a daily cell count.

At 0, 48, and 96 h, additional 10 mL water samples were taken from each flask, with a duplicate (10 mL) sample taken from each flask at 96 h. These water samples were taken via 10 mL pipettor and filtered through 0.45 μm syringe filters into 15 mL falcon tubes. Samples were labelled and placed in the freezer prior to Se speciation analysis.

Bioaccumulation

At 96 h, 50 mL samples were taken from each flask via a pipettor, placed into 50 mL centrifuge tubes, and stored in a refrigerator to settle for at least 24 h before centrifuging and acid-digestion. The samples were then centrifuged in an IEC Centra GP8 centrifuge at 2000 rpm for 30 min to separate the algae from the test solution. Then, the supernatant liquid was removed from each sample via a pipettor. The algal pellet was then resuspended in sterile culture media using a vortex mixer and centrifuged again. This process was repeated three times consecutively to allow for adequate rinsing of algal cells.

Following the final centrifuging, the supernatant liquid was removed from each centrifuge tube via a pipettor, with the remaining solution (≈ 5 mL) and pellet resuspended, removed via a pipettor, and placed into 50 mL glass tubes. The samples were dried at 60 °C for at least 48 h before weighing. Following weighing, the samples were acidified, using 1 mL of trace metal grade HNO_3 and covered with parafilm. After 7 days, 0.75 mL of H_2O_2 was added for at least 48 h. 1 mL samples were then taken from each tube and submitted for Se analysis.

Results and Discussions

Chemical Analyses

The MW was first characterized comprehensively to find the concentrations of metals and anions in the sample (Table 1). For those elements not reported, concentrations were below the detection limit.

Table 1 Mean and standard deviation concentrations of water chemistry parameters, nutrients, and trace elements concentrations in untreated mine water. Mean values from three measurements with ± 1 standard error

Water chemistry			
pH			9.2 \pm 0.1
TDS (mg/L)			4730 \pm 250
TSS (mg/L)			Negligible
Conductivity (mS/cm)			5.1 \pm 0.1
Primary anion and cation concentration (mg/L)			
Na	716 \pm 6	Cl ⁻	157 \pm 3
Mg	16 \pm 1	NO ₂ ⁻	6 \pm 1
K	115 \pm 2	NO ₃ ⁻	63 \pm 1
Ca	595 \pm 6	SO ₄ ²⁻	2288 \pm 15
Sr	2 \pm 1	SCN ⁻	460 \pm 7
Metal concentration (μ g/L)			
Li	25 \pm 2	Ga	6 \pm 1
Al	17 \pm 2	As	2 \pm 1
M	15 \pm 2	Se	216 \pm 5
Fe	2 \pm 1	Rb	104 \pm 1
Co	33 \pm 1	Mo	48 \pm 1
Ni	5 \pm 1	Ag	16 \pm 1
Cu	258 \pm 35	Sb	6 \pm 1
Zn	25 \pm 1	Ba	36 \pm 1

Table 2 Concentrations of dissolved selenium, selenite, selenate, seleno-cyanate and methyl-seleninic acid (μ g/L) measured in control, untreated mine water (MW), treated mine water with NF, RO, ED, and EC

Analyte	Control	MW	NF	RO	ED	EC
Dissolved Se	0.8 \pm 0.2	210.4 \pm 5.8	3.6 \pm 0.1	3.4 \pm 0.1	1.7 \pm 0.2	2.4 \pm 0.1
Selenite	BD	59.1 \pm 0.6	0.8 \pm 0.1	0.8 \pm 0.0	0.3 \pm 0.1	0.4 \pm 0.1
Selenate	0.8 \pm 0.1	120.1 \pm 1.0	1.1 \pm 0.1	2.0 \pm 0.1	1.0 \pm 0.1	0.9 \pm 0.0
Seleno-cyanate	BD	BD	0.4 \pm 0.0	BD	BD	1.1 \pm 0.2
Methyl-selenenic acid	BD	0.6 \pm 0.1	BD	BD	BD	BD

Values represent average concentrations over the 5-day exposure period with ± 1 standard error

The results presented in Table 1 suggest high concentration of Se compared to water quality guidelines for the protection of aquatic life in the United States of 1.5 to 3.1 μ g/L (USEPA 2016) and of 2 μ g/L in British Columbia (https://www.google.com/url?sa=i&rct=j&q=&esrc=s&source=web&cd=&cad=rja&uact=8&ved=0CAIQw7AJahcKEwjo7fzsz8OAAxUAAAAAHQAAAAAQAg&url=https%3A%2F%2Fwww2.gov.bc.ca%2Fassets%2Fgov%2Fenvironment%2Fair-land-water%2Fwater%2Fwaterquality%2Fwater-quality-guidelines%2Fapproved-wqgs%2Fbc_moe_se_wqg_companion_document.pdf&psig=AOvVaw1K3HLcqVGH3p_iEyVFIoJ4&ust=1691251844280437&opi=89978449). Copper is also present at concentrations above the metal and diamond mine effluent regulations (MDMER) monthly mean maximum authorized release limit of 100 μ g/L. Finally, cyanide concentrations were below the MDMER monthly mean maximum authorized release limit

of 500 μ g/L. These limits are based on best available treatment technology economically achievable in the case of Cu and cyanide. However, for Se, a BATEA value remains to be confirmed. Levels of nitrate and sulfate are also reported and will be discussed further in this paper as they may affect treatment performance (Nkansah-Boadu et al. 2021) and Se bioaccumulation (DeForest et al. 2017), respectively.

Untreated mine water—Toxicity Testing

Speciation

The concentration of dissolved Se in the untreated mine water was ≈ 200 μ g/L throughout the 96-h exposure (Table 2). Speciation analysis revealed that most of the Se was selenate ($\approx 60\%$), with selenite making up $\approx 30\%$. Seleno-methionine was detected on day 3 at 0.57 μ g/L,

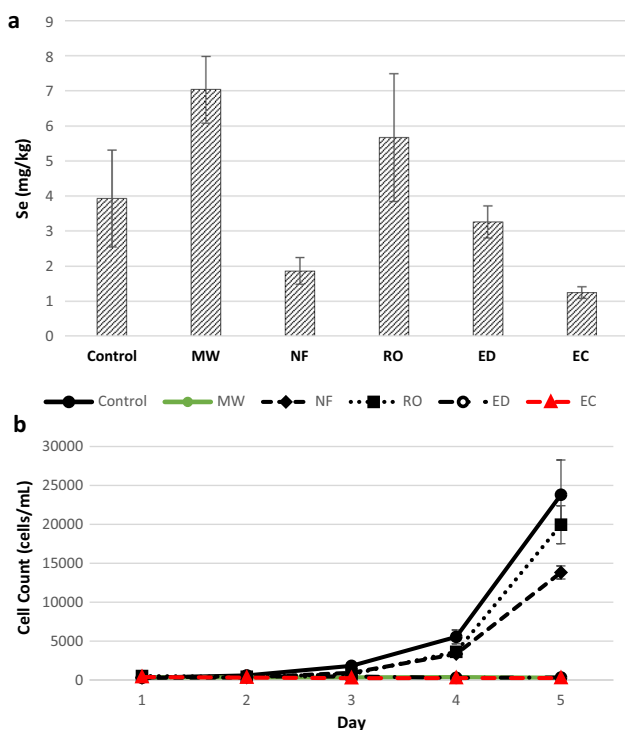


Fig. 5 **a** Bioaccumulation of selenium in algae, and **b** algal growth in control, untreated mine water (MW), and treated mine water with NF, RO, ED, and EC, as a function of days of exposure to selenium

which is $\approx 0.4\%$ of the measured dissolved Se. Selenocyanate and methyl-seleninic acid were consistently measured throughout the 96-h exposure and were relatively stable at concentrations of 0.25 and 0.5 $\mu\text{g/L}$, respectively.

Bioaccumulation

Bioaccumulation of Se was significantly higher in the untreated mine water (7 mg/kg) than in the controls (4 mg/kg; Fig. 5a); however, the values were not as high as expected considering the Se concentrations in the water (Table 2). Previous exposures at 100 $\mu\text{g/L}$ of selenate resulted in algal tissue concentrations of ≈ 90 mg/kg (Jatar 2013). One explanation is that the sulfate levels were quite high in the raw effluent, and sulfate is known to suppress selenate accumulation in plants (DeForest et al. 2017; Jatar 2013; Lo et al. 2015). As the dominant species in the untreated mine water was selenate, it is likely that the high sulfate level of 2 mg/L inhibited uptake into the algae.

Algal Growth

Following 96 h of exposure to the untreated mine water, algal growth was significantly reduced compared to the controls (RM ANOVA, $p=0.002$; Fig. 5b), with only an average cell count of 305 cells per mL compared to 23,805 cells/mL

in controls. The toxicity observed in this treatment completely inhibited algal growth and although previous work has calculated an IC₂₅ (inhibition concentration of 25%) at concentrations of > 116 $\mu\text{g/L}$ Se (Jatar 2013), it is unlikely that selenium was the sole cause of toxicity in this exposure. The analysis of the untreated mine water shows that Cu was at concentrations in the EC₅₀ range (effective concentration at 50%), which would also have contributed to the lack of growth observed (Wang et al. 2018).

Treatment Tests: Nanofiltration and Reverse Osmosis

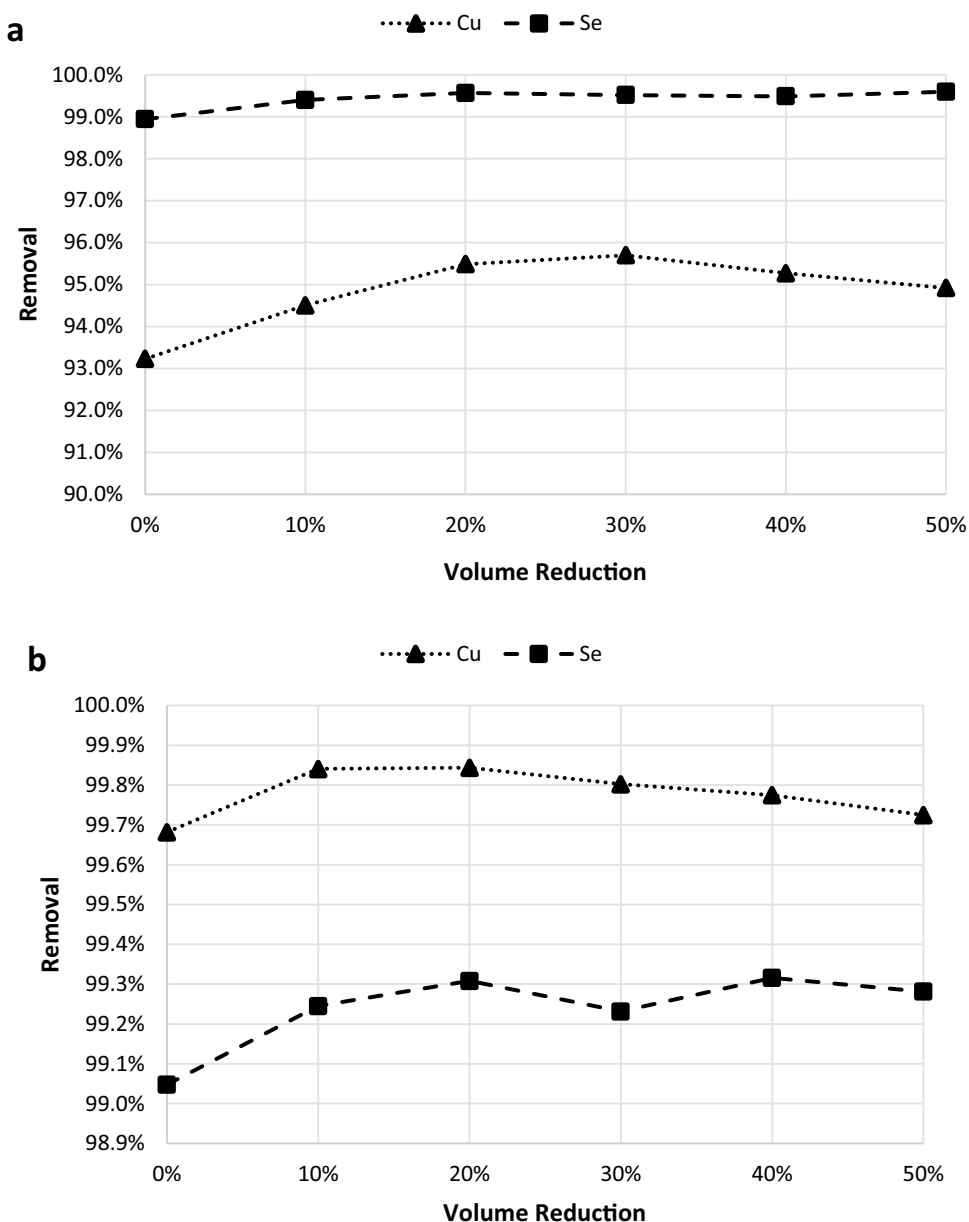
NF and RO were used for two different purposes in this work. First, as a stand-alone treatment process for the removal of selenium and second, as a preliminary step to concentrate the mine water for further investigations using other treatment technologies, i.e. ED and EC.

Rejection performance of the membranes were measured throughout the experiment. Figure 6 shows metals concentration vs. volume reduction for NF (a) and RO (b) at 400 psi and 25 °C. Membrane rejection for each element at different volume reductions are given in Fig. 6a and b.

RO rejection for Cu was higher than that of NF. In the NF permeate, Cu concentrations ranged between 30 and 55 $\mu\text{g/L}$ during the experiment. In terms of Se, both processes performed about the same. Selenium concentrations in the permeate from the NF remained below 3 $\mu\text{g/L}$ throughout the test, while with RO, Se concentrations ranged between 2 and 3.5 $\mu\text{g/L}$.

It has been reported that NF has a lower Se rejection rate than RO, and RO is still the most popular option for the treatment of Se in water. However, working at much lower operating pressures is considered an advantage of NF over RO (Li et al. 2022). Over 99% Se removal by NF in this work is comparable and even greater than what has been reported in the literature, i.e. 74–99.8% (He et al. 2017; Richards et al. 2011) using modified NF membranes such as magnetite nanoparticles/graphene nanosheets incorporated in polyvinyl alcohol and cellulose acetate electro spun nanofibers (Mansour et al. 2020) and polyamide core-shell bio-functionalized matrix NF membranes (Li et al. 2022; Zeeshan et al. 2020). Malhotra et al. used a response surface optimized flat sheet cross flow NF membrane module to reduce the Se content of drinking water. They were able to achieve $> 98\%$ removal at 14 bar. They also reported that Se rejection increased linearly with transmembrane pressure until it reached a plateau at 15 kg/cm^2 . It was also shown that Se rejection increased with an increase in pH from 2 to 12. This could be attributed to the increase in the average negative charge of the Se species with pH (Malhotra et al. 2020). He et al. (2016) also showed 93.9% and 96.5% removal in selenite and selenate, respectively using a

Fig. 6 Membrane rejection **a** NF and **b** RO



thin-film nanocomposite. Chung et al.(2010) reported less retention of selenate with increased recovery due to the increase of concentration polarisation. Generally, Se speciation determines the charge and size; also, NF membrane surface characteristics, especially the surface charge, play key roles in the exclusion of Se by nanofiltration.

Permeate conductivity ranged between 1496 and 1875 $\mu\text{S}/\text{cm}$ during the NF test; however, the variation of permeate conductivity in the case of RO was in the range of 209–336 $\mu\text{S}/\text{cm}$. Anion rejections by NF and RO are compared in Fig. 7. According to the results, NF was not very effective for removing chloride (47%) and

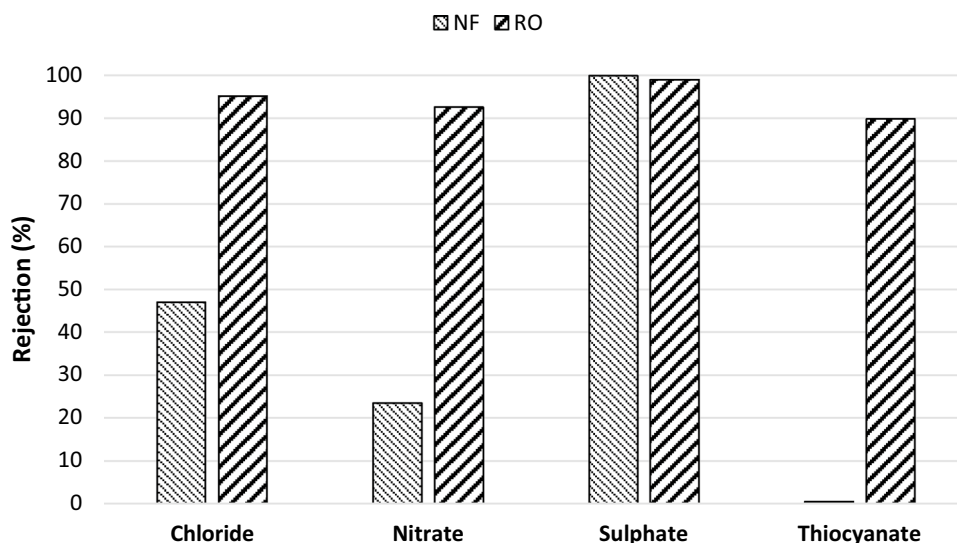
nitrate (23.4%). In contrast, RO was able to achieve 95.1% removal for chloride, 92.6% for nitrate, and 98.9% for sulphate. Thiocyanate removal by RO was about 89.8%; however, NF failed to remove thiocyanate from the untreated mine water.

NF/RO—Toxicity Testing

Speciation

The concentration of dissolved Se in both of these treatments were $\approx 3.5 \mu\text{g}/\text{L}$ throughout the 96 h of exposure

Fig. 7 Removal of anions by membrane filtration



(Table 2). Speciation analysis revealed that most of the Se was selenate, more so in the RO treatment than NF. Seleno-cyanate was consistently measured throughout the 96 h of exposure in the NF treatment only, with relatively stable concentrations of 0.35–0.4 $\mu\text{g/L}$. No other species, except selenate and selenite, were detected in the RO treatment.

According to speciation analysis on the brines produced by NF and RO treatment, selenite and selenate formed almost 24% and 76% of the total dissolved Se, respectively. This is almost the same proportion in the untreated mine water, showing no change in speciation by filtration. This is attributed to the nature of the physical treatment, which involves no chemical transformation in the species.

Bioaccumulation

Bioaccumulation of Se in the RO treatment was similar to the untreated mine water, where an average of 5.6 mg/kg was observed; however, due to the variability within the treatment, no significant differences compared to control were detected (Fig. 5a). When the Se concentrations in the water are compared to the tissue concentrations, the values observed were expected based on previous work (Jatar 2013). No similar bioaccumulation was observed in the NF treatment despite seeing similar dissolved Se concentrations in the water. The only difference between the RO and NF treatments was the appearance of Se-cyanate in the NF treatment along with a lower selenate value compared to RO (1 $\mu\text{g/L}$ in NF and 2 $\mu\text{g/L}$ in NF treatment).

Algal Growth

RO resulted in greater algal growth than NF ($\approx 20,000$ cells/mL compared to 14,000 cells/mL). However, for both the RO and NF treatments, algal growth was similar to the controls, with no significant differences (RM ANOVA, $p > 0.05$; Fig. 5b), indicating that both of these treatments were able to remove the toxicity observed in the raw mine water.

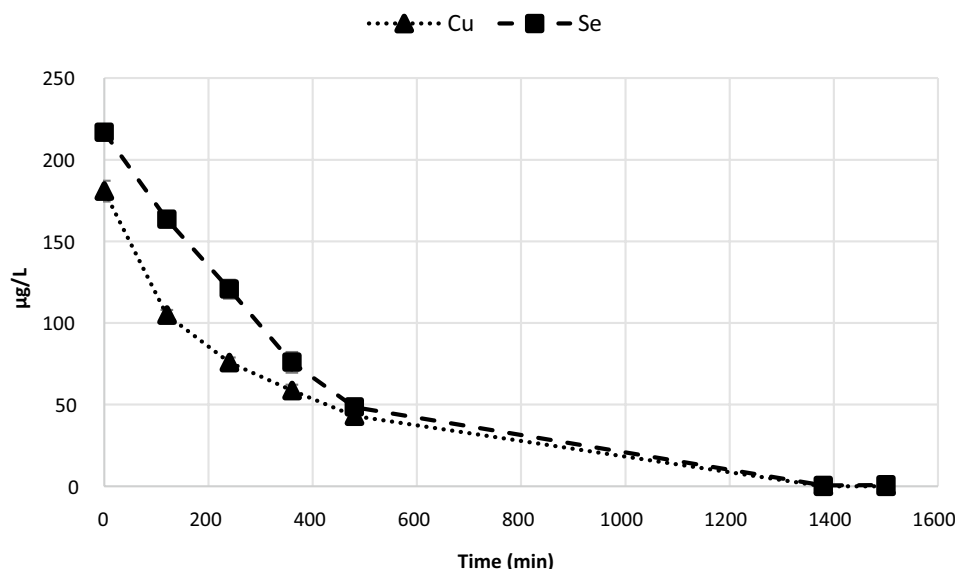
Electrodialysis

In this work, ED tests for the treatment of MW were performed in three steps, as explained earlier. This allowed us to study the effects of time and feed concentration on the performance of ED. To the best of our knowledge, this is the first systematic study that tested the use of ED for Se removal. MW was filtered first using 0.45 μm nitrocellulose paper filters to remove solid particles and avoid damaging the system and specifically the membranes. Filtration did not significantly change the characteristics of the mine water as there was very little suspended solids present. These results are given in the supplemental material (S-2).

Electrodialysis Step 1

In step 1, the MW was used as the feed and the effect of time on removal rates was investigated. More than 99% removal was observed for both Se and Cu after 25 h of ED operation (Fig. 8). The content of Se and Cu in the treated water was less than 1 $\mu\text{g/L}$. Overall, the conductivity of the treated water was less than 20 $\mu\text{S/cm}$, demonstrating almost 99.7% removal efficiency. It is worth mentioning that ED treatment resulted in about 96.7% removal

Fig. 8 MW treatment by electro dialysis, step 1



of chloride, 99.4% removal of nitrate, 99.9% removal of sulphate, and 99.9% removal of thiocyanate. Onorato et al. (2017) used ED for inorganic trace contaminant removal from real brackish groundwater. Selenium was one of the inorganic contaminants present in the effluent with a concentration of almost 20 µg/L. According to their results, only 33%- 48% Se removal was observed, depending on the applied voltage.

Electrodialysis Step 2

In step 2, MW was used as the feed and ED was conducted in three different rounds. In each round, ED was used to treat fresh MW while the concentrate was recycled back into the system. This was done to evaluate how the ED process made the ED effluent more concentrated. From the results obtained in step 1, it was observed that ED duration can be potentially shortened without any compromise in the removal efficiencies (Fig. 8); therefore, ED was operated for a maximum of 21 h in rounds 1 and 2 in this step. However, due to technical difficulties, it was not feasible to continue the operation for more than 19 h in round 3. ED performance in rounds 1, 2, and 3 are shown in Fig. 9a–c, respectively.

After 21 h of ED operation, more than 99% removal was obtained for each element (Fig. 9a). Conductivity dropped to less than 20 µS/cm (overall rejection was almost 99.7%). Anion removals were 98.7% for chloride, 99.7% for nitrate, 99.9% for sulphate, and 99.9% for thiocyanate. Electrodialysis of fresh MW was conducted for another 21 h (Fig. 9b). The concentrate used in this round was from round 1. Again more than 99% rejection was observed for each element. The final concentration of Cu and Se was less than 1 µg/L. The final conductivity of the treated water was almost 22 µS/cm (slightly higher than round 1); however, the overall rejection

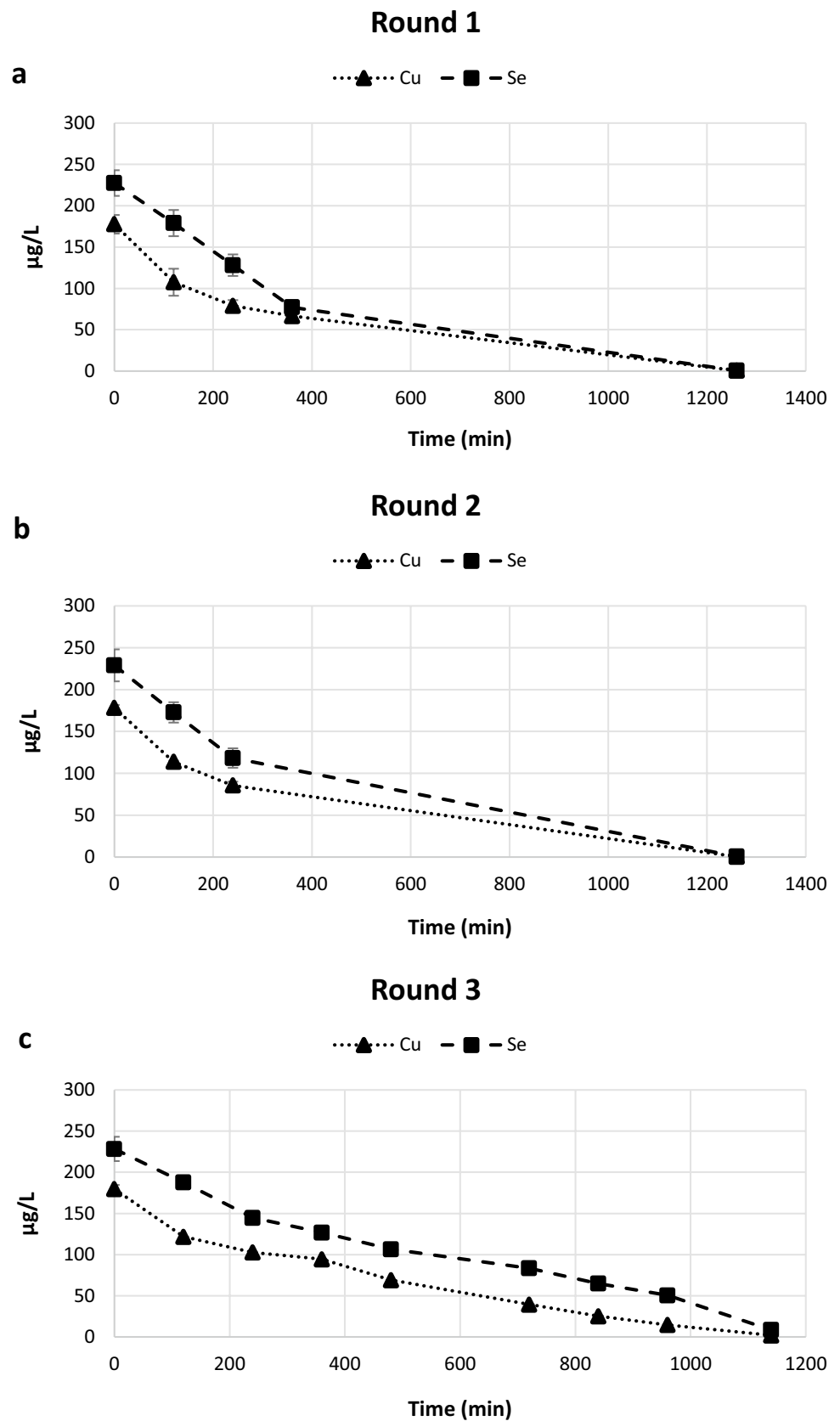
was still >99.6%. Furthermore, the removal rate of chloride was 98.3%, nitrate was 99.7%, sulphate was 99.9%, and thiocyanate was 99.7%. As mentioned earlier, due to technical difficulties with the ED system, the third round did not go beyond 19 h. However, very high removal rates were still achievable. After 19 h of ED operation, Cu and Se concentrations were decreased to almost 2 and 9 µg/L, respectively (Fig. 9c; still more than 96% rejection). The final conductivity was ≈65 µS/cm, representing 99% overall rejection. Anion removal was still at very high levels: 96.7% for chloride, 99.7% for nitrate, 99.7% for sulphate, and 99.5% for thiocyanate. Recycling the concentrate back into the ED system resulted in making the stream more concentrated without much of a drop in ED driving force and removal efficiencies.

Electrodialysis Step 3

In step 3, the concentrate from RO after 50% recovery was fed into the ED system to evaluate the integration of RO with ED and the effect of feed concentration on the ED performance. Removal rates for Cu and Se are given in Fig. 10a and for chloride, nitrate, sulphate, and thiocyanate in Fig. 10b.

As shown in Fig. 10, ED was still effective in removal of different analytes at high feed concentrations (almost two times more concentrated than in the previous steps). After 27 h of ED operation, more than 99% removal was observed for Cu and Se. Comparing the results with steps 1 and 2, removal rates were still >98%, even after 21 h of ED operation. Total rejection was >99.8% based on a final conductivity of almost 65 µS/cm for the treated water. From Fig. 10b, almost complete removal of the anions was achieved using ED (>99.4% rejection for each analyte). Results clearly

Fig. 9 MW treatment by a multi-stage electro dialysis process after **a** round 1, **b** round 2, and **c** round 3, step 2



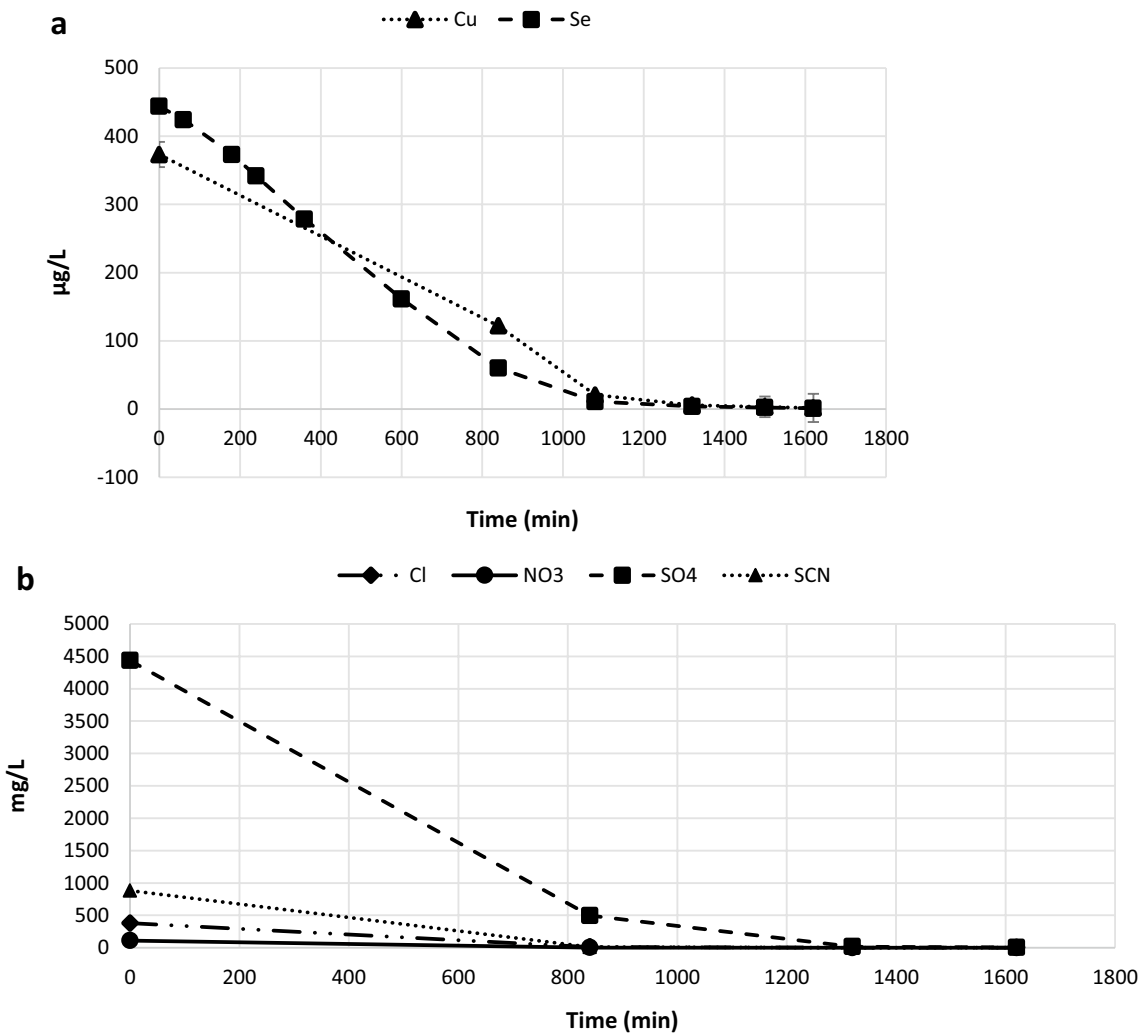


Fig. 10 Treatment of RO concentrate by electro dialysis, step 3, **a** metals and **b** anions concentration

demonstrate the effectiveness of ED for efficient removal of different analytes present in the mine effluent.

Electrodialysis—Toxicity Testing

Speciation

The concentration of dissolved Se in ED Step 1 treatment was $\approx 1.75 \mu\text{g/L}$ throughout the 96-h exposure (Table 2). Similar to the other tests, speciation analysis revealed that most of the Se was selenate, followed by selenite. No other Se species were detected except for one occurrence of seleno-cyanate ($0.16 \mu\text{g/L}$) on day 1, in one replicate.

It is worth mentioning that the ratio of selenate to selenite increased from 3.2 in the untreated mine water to almost 172 in the ED brine, showing the chemical transformation of selenite to selenate through ED. This further emphasizes the importance of speciation studies in brine

management during treatment of Se-contaminated waters by electrochemical processes.

Bioaccumulation

Bioaccumulation of Se was comparable to the control, with an average Se concentration of 3.25 mg/kg, which is as expected given low concentration of Se in the treated water (Fig. 5a). Thus, it is unlikely that the toxicity observed was due to Se. The same can be said for Cu, as concentrations were reduced to $< 1 \mu\text{g/L}$, indicating other factors were contributing to the lack of growth in this treatment.

Algal Growth

Following 96 h of exposure to treated water after electro dialysis (ED Step 1), algal growth was significantly reduced compared to controls (RM ANOVA, $p = 0.002$; Fig. 5b),

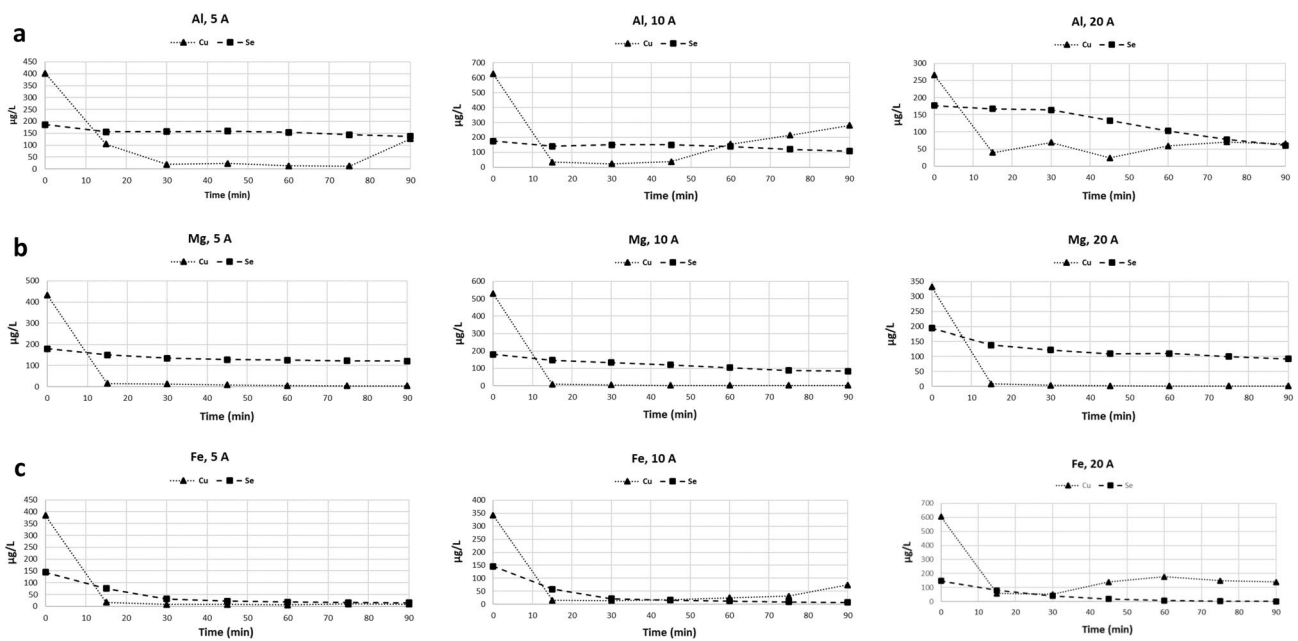


Fig. 11 Removal rates using electrocoagulation at 5, 10, and 20 A using **a** aluminium, **b** magnesium, and **c** iron as anode, step 1

with only an average cell count of 325 cells/mL compared to 23,805 cells/mL in the controls.

Electrocoagulation

EC tests were also performed in three different steps to study the effect of time, current, initial pH, and sacrificial anode material on removal efficiencies.

Electrocoagulation Step 1

In step 1, MW was used as the feed and we attempted to find the optimum operating conditions for the greatest Se removal. To this end, operation time and applied current were varied and metals concentrations were measured with different anode materials: Al, Mg, and Fe. All experiments were carried out at an initial pH of 3. After finding the best anode material and most efficient operation time and current, the effect of initial pH on the removal rates was also investigated. Figure 11 shows the Se and Cu removal rates at different currents using Al (a), Mg (b), and Fe (c) as sacrificial anode material.

Se removal increased with time and current for all three anode materials (Fig. 11). However, separation was not great with Al and Mg. Selenium removal was increased from 26.9% to 38.4% by increasing the current from 5 to 10 A when Al was used as anode. The removal rate further increased to 65.8% at 20 A. The lowest Se concentration observed with Al anodes after 90 min of operation was 61 µg/L.

Magnesium demonstrated a better performance in terms of Se removal only at lower currents compared to Al. The removal rate was 32.2% and 45.1%, at 5 A and 10 A, and slightly increased to 52.6% at 20 A. The Se concentration did not go below 84 µg/L through EC by Mg after 90 min of operation.

The best Se removal was obtained when Fe was used as the anode. Se removal increased from 89.4 to 95.4% and finally 99.1% by increasing the current from 5 to 10 A, and then 20 A, respectively (Fig. 11c). EC by Fe was able to reduce Se concentrations to less than 2 µg/L after 90 min of operation at 20 A.

Regarding Cu removal by electrocoagulation, the Mg electrode demonstrated the best performance, with > 99% Cu removal observed in all trials (Fig. 11b). When Al was used as the electrode, the Cu concentration in the electrocoagulated water decreased first and then increased with time. The increase in Cu concentration happened earlier at higher currents. The same trend was also noticeable in the case of Fe. This might be due to the stability of the flocs generated during electrocoagulation. For Al and Fe, the flocs hypothetically possessed weak, fragile, and porous structures, and could have contained adsorbed and entrapped Cu ions. The flocs lost their structure during the additional collisions that occurred by increasing the current, which resulted in further corrosion of the electrodes and the presence of solid particles in the environment. This eventually caused redissolution of Cu in the electrocoagulated water.

From the results, Fe is the best material for Se removal and a 90 min operation at 20 A will reduce Se concentrations

to < 2 µg/L. Anion removal by EC using Fe was not very good; after 90 min at 20 A and only about 87% nitrate, only 10% of the sulphate, and 33% of the thiocyanate were removed. In comparison with the other reducing materials used in this study, Fe has the benefits of relatively low cost and availability, safety, and better reduction potential in aqueous solutions (Liang et al. 2014).

Our results agreed well with the literature. For example, Bae et al. (2022) reported that Fe anodes could produce almost 100% removal of Se and Staicu et al. (2015) found that the best removal of Se (97%) was obtained at 200 mA using Fe electrodes. Hansen et al. (2019) obtained 90% Se removal after 6 h of operation, using a current density of 153.4 A/m² and a pH of 6.8 and Mavrov et al. (2006) reported 98.7% Se removal at a current density of 4.8 mA/cm², after 20 min of treatment using Fe EC.

Further experiments were conducted to study the effect of initial pH on removal efficiencies of EC by Fe anodes at optimum conditions. According to the results, an increase of initial pH slightly increased the final Se concentration of the electrocoagulated water. After 90 min of

EC, Se concentration dropped to 1.4 µg/L at pH 3; however, the final Se concentration was almost 2.4 µg/L at pH 6 and pH 9.2. Therefore, the rest of EC tests were all performed at an initial pH of 3. It has also been reported that for both Fe- and Al-based coagulants, weakly acidic pH values (normally between 1.5 and 5.5) could increase the formation of hydroxide flocs, producing more active adsorption sites and greater surface potential for the removal of Se from aqueous solutions (Hu et al. 2015; Li et al. 2022).

Electrocoagulation Step 2

In this step, EC was conducted at larger scale (15 L) using the optimum operating conditions from step 1. The resulting sludge was removed by microfiltration instead of centrifugation. This experiment was conducted using Fe as the sacrificial anode at 20 A and 25 °C for a period of 5 h. The trends at the larger scale (15 L) were very similar to those of the smaller scale (1.5 L), with difference in absolute concentration values (Fig. 12). Copper concentrations were reduced to less than 2 µg/L within the first hour of the experiment and

Fig. 12 Electrocoagulation of MW at large scale (15 L feed), step 2, **a** metals (y-axis in logarithmic scale) and **b** anions removal

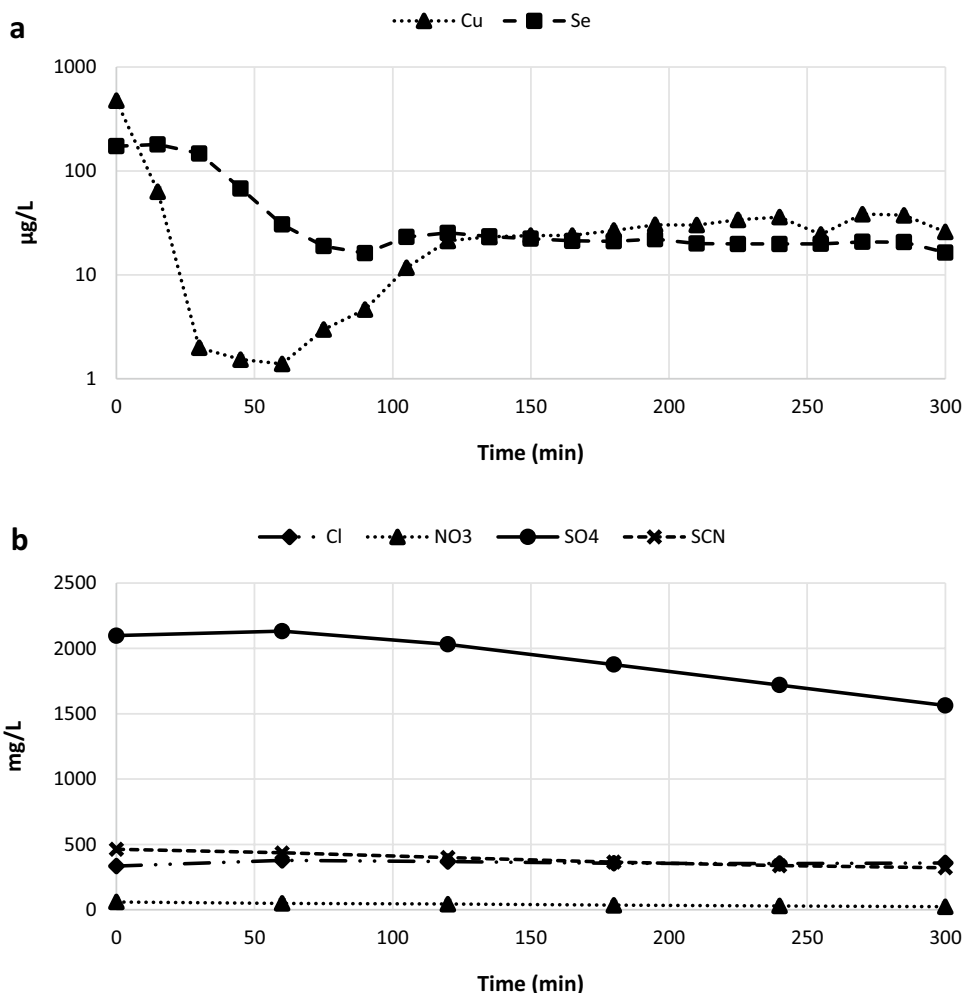
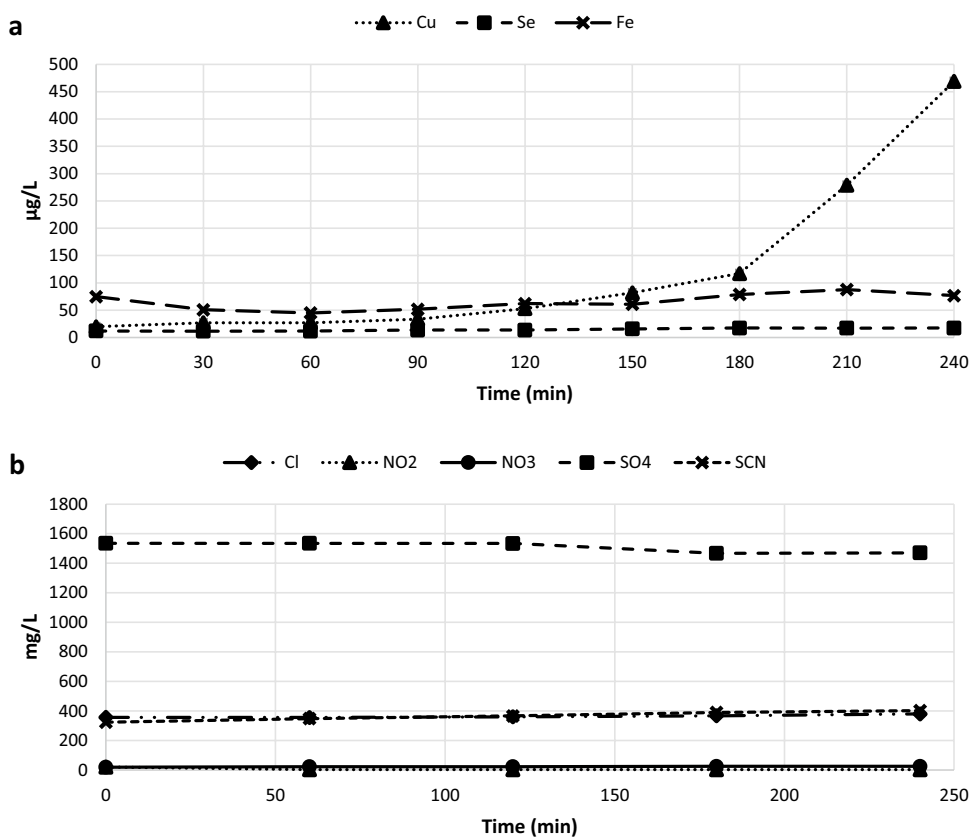


Fig. 13 Microfiltration of the MW treated by EC, step 2, at 40 psi and 25 °C, **a** metals and **b** anions removal



then increased and varied between 20 and 40 µg/L during the test. The intensity of the increment in Cu concentration was smaller in this step. This could be attributed to the larger volume of the solution being electrocoagulated using the same electrode size. In this case, the density of the flocs was smaller and therefore collisions between them were reduced compared with the previous step. As a result, the flocs possessed greater stability.

Selenium concentrations decreased continuously up to 75 min and then reached a plateau at almost 20 µg/L during the rest of the experiment. Unlike the test at smaller scale, the Se content did not drop below 20 µg/L in this trial. This might be due to the size of electrode, which was insufficient for the feed volume used in this step.

No chloride removal was observed. Nitrate, sulphate, and thiocyanate removals were 60.4%, 25.5%, and 30.7%, respectively. The electrocoagulated water was subjected to microfiltration for sludge removal. Figure 13 shows analyte concentrations in the microfiltration test. The average permeate flux in this test was almost 442 LMH.

There was almost no removal in Fe and Se (Fig. 13) as microfiltration is not used to separate dissolved solids. However, Cu concentrations increased with time and the rate of increase significantly increased after almost 2 h of operation. This further proves the instability of the flocs

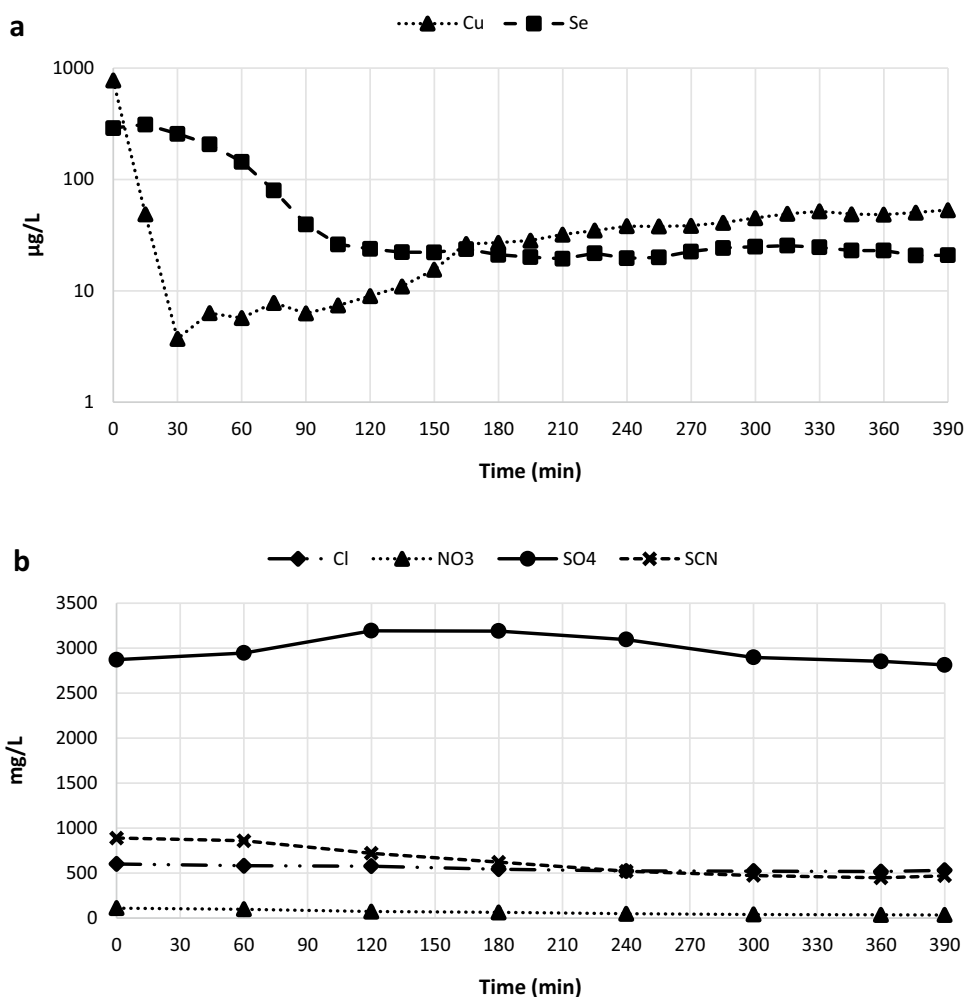
entrapping the Cu. As a result of additional shearing and mixing experienced during filtration, Cu ions redissolved and readily passed through the membrane pores into the permeate. No significant change in the concentrations of chloride, nitrite, nitrate, sulphate, and thiocyanate was noticed in the microfiltration test. The slight increase in the concentration of chloride, nitrate, and thiocyanate over time can also be attributed to floc instability.

Electrocoagulation Step 3

In this step, and to integrate RO with EC and to study the effect of feed concentration on the performance of the electrocoagulation, the RO brine was fed into the EC process. This step was also conducted at large scale (15 L). Figure 14 demonstrates the removal results for both metals and anions after 6.5 h of EC using Fe anodes at 20 A and 25 °C.

Similar to the previous step, Cu concentrations sharply decreased within the first 30 min to less than 4 µg/L and then gradually increased up to almost 50 µg/L after 6.5 h (Fig. 14a). Selenium concentrations also fell quickly, within the first 2 h and reached a plateau at around 20 µg/L. Figure 14b presents anion removal rates: about 11.5% in chloride, 69.4% in nitrate, 2.1% in sulphate, and 47.2% in thiocyanate.

Fig. 14 Electrocoagulation of RO concentrate at large scale (15 L feed), step 3, **a** metals (y-axis in logarithmic scale) and **b** anions removal



Comparing Figs. 12a and 14a shows that a longer EC operation (almost 75 min) was needed to reach the 20 µg/L Se plateau when the feed was more concentrated. However, it took almost 135 min to reach the same concentration when the RO reject was used as the EC feed (with almost two times as much Se).

The EC-treated RO reject was filtered for 4 h using microfiltration to remove the suspended solids (Fig. 15). The average permeate flux in this experiment was almost 508 L/m²/h (LMH).

Selenium concentration in the permeate did not change significantly during microfiltration (Fig. 15a). Iron concentrations decreased by 61.6% throughout the test, while Cu concentrations increased from almost 13 µg/L at the beginning to about 58 µg/L after 4 h due to the unstable structure of the flocs that lost Cu ions into the permeate. Figure 15b also shows no significant reduction in the concentration of the anions analyzed in this study. The small increase in the concentrations of chloride, nitrate, and thiocyanate with time can again be attributed to the instability of the flocs.

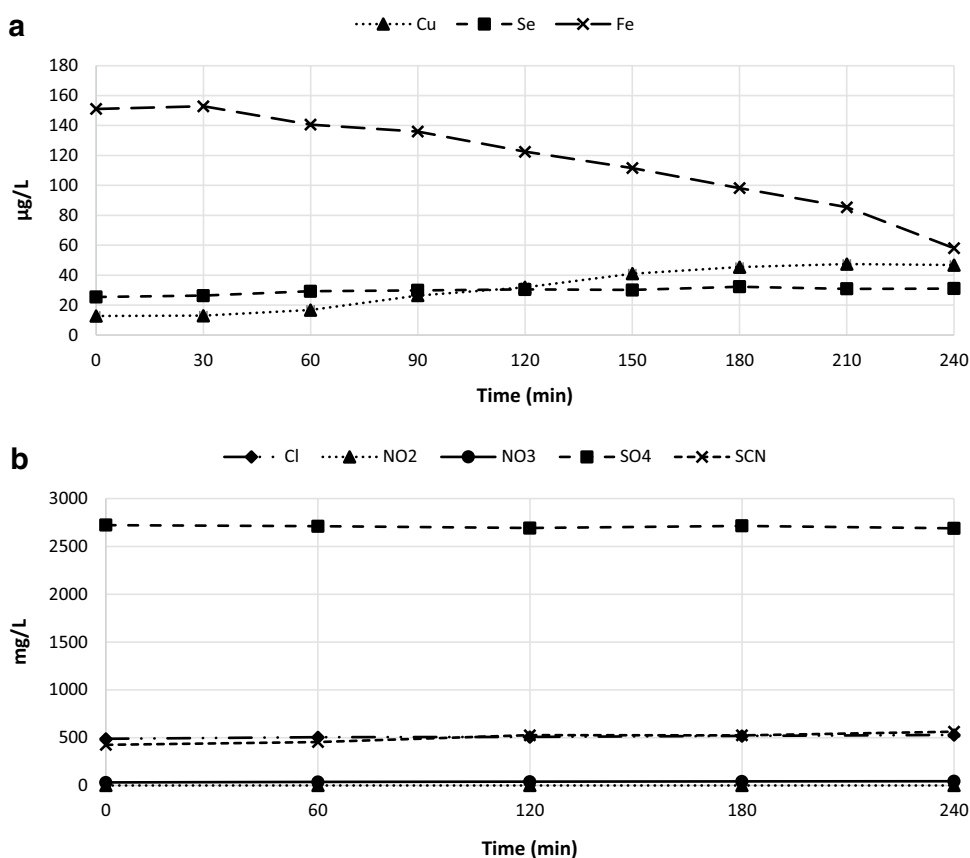
Electrocoagulation – Toxicity Testing

Speciation

The concentration of dissolved Se in the EC treatment was ≈ 2.5 µg/L throughout the 96 h of exposure (Table 2). Seleno-cyanate was the dominant species on days 1 and 3, followed by selenate on day 5. Selenite was low throughout the exposure with an average concentration of 0.3 µg/L.

It should be noted that samples from the EC tests were analyzed again after ≈ 6 months. The Se concentrations in the electrocoagulated water was about 70 µg/L showing that Se trapped in sludge can be redissolved in water if there is no protocol for managing the sludge. It was interesting that almost all of the Se in the electrocoagulated water was selenate, demonstrating complete transformation of selenite to selenate during electrocoagulation.

Fig. 15 Microfiltration of the electrocoagulated RO reject, step 3, at 40 psi and 25 °C, **a** metals and **b** anions removal



Bioaccumulation

Bioaccumulation of Se was the lowest of all treatments with an average Se concentration of 1.25 mg/kg (Fig. 5a), which was due to a complete lack of growth observed. As mentioned previously, the low concentration of Se in the treated water and limited bioaccumulation indicate that it is unlikely that the toxicity observed was due to Se; however, the toxicity of seleno-cyanate is relatively unknown and as it was the dominant species in this treatment, it would be worth investigating further.

Algal Growth

Following 96 h of exposure to treated water after EC using Fe, algal growth was significantly reduced compared to controls (RM ANOVA, $p=0.002$; Fig. 5b), with the lowest average cell count among all treatments (258 cells/mL). EC was able to reduce Se to ≈ 2.5 µg/L; however, it was only able to reduce Cu to 150 µg/L, which is still in the EC50 range for this algal species. Therefore, it is possible that despite the low Se concentrations (2.5 µg/L), the elevated Cu concentrations contributed to the toxicity observed.

Technologies Performance Comparison

A comparison between NF, RO, ED, and EC in terms of metals, anions, and total removal (based on TDS) is made in Fig. 16. Table 3 shows the final concentration of the analytes in the treated MW.

All of the technologies investigated were capable of meeting the major goal of this work, reducing the Se concentration in MW. However, there were considerable differences in terms of overall treatment and TDS reduction. Of the filtration processes, RO was the most efficient in removing metals and anions except for sulphate and thio-cyanate, though the amount of sulphate removal by RO was still satisfactory ($>98.9\%$). Except for Se removal, which was the major goal of this work, EC by iron demonstrated the weakest performance, with almost 21.6% total removal of TDS in the MW. Although more than 99% Se removal was obtained using EC with Fe anodes, handling the sludge created throughout the process and the need for additional stages for further treatment of the electrocoagulated water will significantly add into the complexity of the entire treatment process. ED was the most promising technology. More than 99.7% total removal was obtained using ED while the concentration of analytes in the treated water was negligible, demonstrating the potential of ED treatment to comply

Fig. 16 Removal efficiencies of NF, RO, ED, and EC (using iron electrode) in (a) metal, (b) anion, and (c) total removal

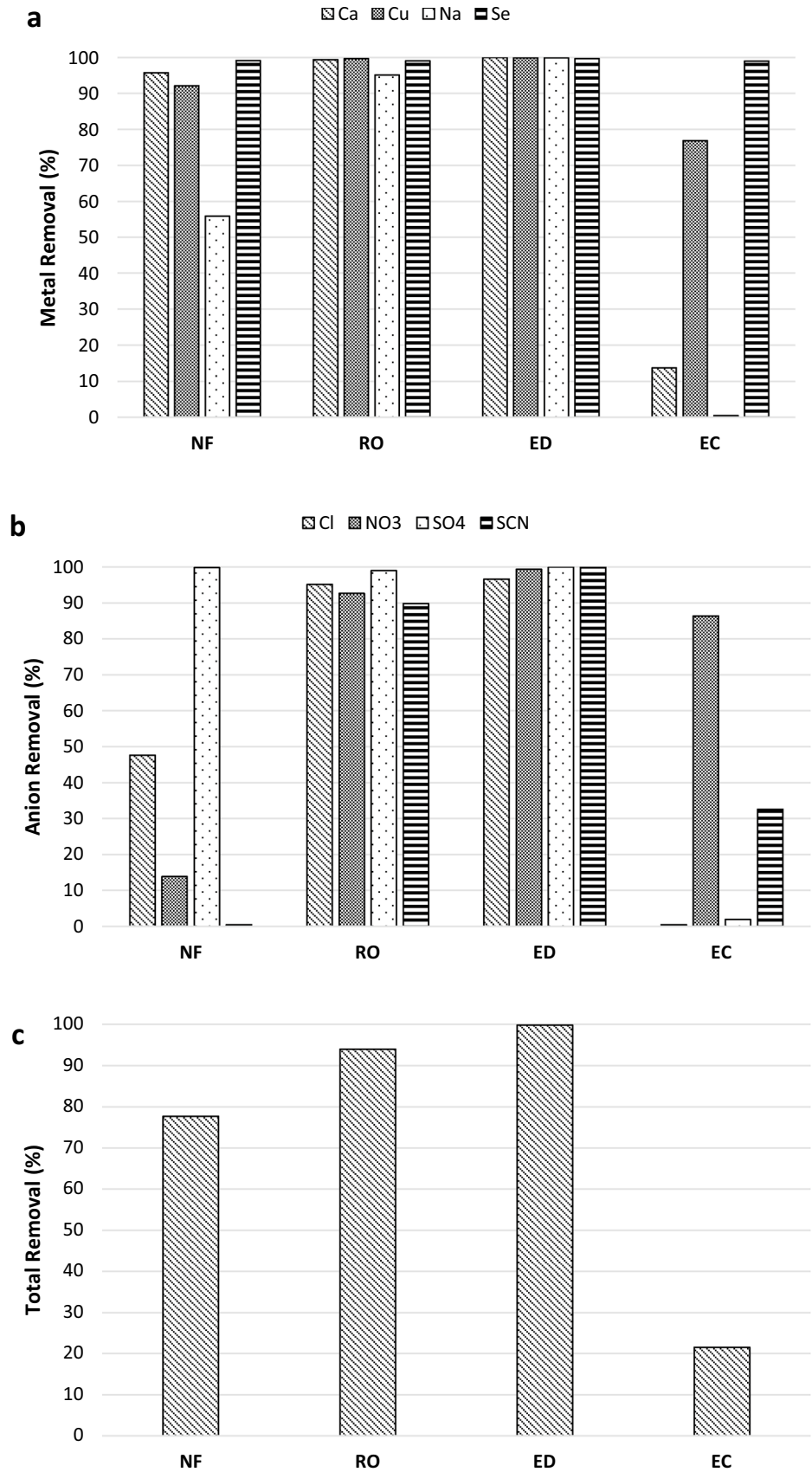


Table 3 Analyte concentration and conductivity of the treated mine water by NF, RO, ED, and EC

Analyte	Inlet	Outlet, NF	Outlet, RO	Outlet, ED	Outlet, EC
Ca (mg/L)	595	30	4	<1	475
Cu ($\mu\text{g/L}$)	258	56	2	<1	140
Na (mg/L)	716	355	35	<1	726
Se ($\mu\text{g/L}$)	216	2	2	<1	<2
Cl^- (mg/L)	157	91	8	6	359
NO_3^- (mg/L)	63	49	5	<1	8
SO_4^{2-} (mg/L)	2288	4	24	<1	2057
SCN^- (mg/L)	460	439	46	<1	312
Conductivity (mS/cm)	5.1	1.6	0.3	0.0	3.0
TDS (mg/L)	4730	1055	285	10	3710

with strict environmental regulations. However, the toxicity observed in this treatment requires further investigation. It is hypothesized that the lack of algal growth is due to a lack of essential minerals in the water (i.e. it is effectively ddH₂O). If this is the case, then remineralization of the treated water would have to be investigated to see if an improvement in algal growth was observed.

From a technical perspective, all of the active treatment processes in this work were technically feasible for Se removal. ED demonstrated high removal rates of metals and anions with simple operation without any applied pressure, is able to generate a high brine concentration, and is less susceptible to scaling; however, it may require high capital costs and suffers from fouling of the expensive ion exchange membranes. The additional potential cost of remineralisation, as discussed below, of the treated water may also need to be considered. NF and RO are mature technologies, easy to scale up and control, and have high metal removal rates, although extra costs related to pretreatment, membrane fouling and durability, scaling, and low water recovery rates could make their feasibility questionable at large scale. Unlike chemical coagulation, EC treats water without the need for hazardous chemicals, which further removes the additional secondary waste concerns; nonetheless, electrode lifetimes, frequent acid cleaning of cathode plates, managing the created sludge, plus post-treatment requirements of the EC process are challenges that need to be considered. None of these processes need thermal energy, but the amount of electrical energy required for their operation is another factor that should be taken into consideration. Furthermore, managing the concentrated brines will be another challenge that should be considered for the purpose of process development.

Effect of Treatment Scenarios on Toxicity/Bioaccumulation

The NF and RO treatments were the only processes able to reduce the toxicity of in the MW. ED and EC both resulted

in inhibition of algal growth. The cause of toxicity in these treatments was unlikely to be due to Se, as both ED and EC reduced Se to < 2 $\mu\text{g/L}$, close to the concentrations observed in the NF and RO treatments. Concentrations of organic forms of Se, known to be bioavailable and accordingly more toxic, were also very low. It is possible that the toxicity observed in the EC treatment was due to elements that were not effectively removed with this treatment (e.g. Cu and SCN^-) as the concentrations were within the EC50 range (Table 3). In contrast, the ED treatment was highly effective at removing all components from the untreated mine water. The lack of algal growth in this treatment was probably due to the lack of essential minerals required for growth (nutrient deficiency; Table 3). This suggests that remineralisation of the treated water would be a critical stage in the treatment process, unless the receiving water has sufficient nutrients to assimilate this low ionic strength water and sustain algal growth. It is often observed that mining effluent discharges lead to eutrophication of receiving environments. ED could limit these negative impacts. Regardless, if ED is selected as a viable Se treatment option, it is essential that additional studies be conducted to investigate whether remineralisation of the effluent water would be needed to limit nutrient deficiency in the receiving environment. The algal growth toxicity tests were a good indicator for treatment efficacy and are recommended for future studies to evaluate the effectiveness of effluent treatments.

Conclusions

In this work, mine water with high concentrations of Se was first characterized and then subjected to active treatment using physical (NF and RO) and electrochemical (ED and EC) processes. The performance of each technology was also further investigated in terms of the removal of some selected metal ions and anions including sodium, calcium, copper, chloride, nitrate, sulphate, and thiocyanate. In addition, untreated and treated mine waters were assessed using

bioaccumulation and toxicity tests and speciation analysis. The following conclusions were drawn based on the test results:

1. All of the processes studied in this work were able to remove more than 99% of the inlet Se, bringing them down to 2 µg/L or less.
2. ED was the most effective technology, not only for removing Se to < 1 µg/L, but also for about 99.8% TDS removal, which would make the treated water suitable for almost any purposes. However, the complete inhibition of algal growth after exposure to the ED effluent might be due to the complete deionization of the effluent. This requires further investigation and more detailed analysis to understand the cause of growth inhibition, whether it is due to deficiency or toxicity.
3. RO ranked second in this work in terms of removal performance. It was also the most effective for decreasing the toxicity of the raw effluent. Although RO was a great process for decreasing the Se concentration to almost 2 µg/L, it was not as efficient as ED for TDS removal (only 94%), especially when it came to thiocyanate rejection (only 89.8%).
4. The treated water from NF had a Se concentration of almost 2 µg/L; however, only 77.7% TDS removal, demonstrating the necessity of additional processes for treating the NF permeate.
5. EC with an Fe anode was placed at the last position in this ranking. It was an effective technology for the removal of Se, dropping the concentration of the electrocoagulated water to less than 2 µg/L after EC. However, with almost 21.6% TDS removal, it is not recommended as a stand-alone treatment process.
6. NF and RO reduced the toxicity of the effluent by allowing algae to grow while ED and EC did not allow algal growth, likely due to complete removal of essential minerals (ED) or the presence of other contaminants such as Cu (EC).
7. Treatment by physical technologies (i.e. NF and RO) did not change the species in the brines much. However, the ED and EC treatments, almost fully transformed the selenite to selenate.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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