Selenium in wastewater: fast analysis method development and advanced oxidation treatment applications

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ABSTRACT

Selenium, a ubiquitous non-metal in nature, is potentially toxic to natural ecosystems due to its bioaccumulation potential. Due to increased monitoring and enforcement of selenium regulations, the need to be able to measure and treat selenium efficiently has taken on an increased importance. The principal aqueous forms of inorganic selenium are selenite (Se (IV)) and selenate (Se(VI)). Selenate, due to its high mobility and lack of affinity to conventional adsorbents, is typically much more difficult to treat and remove. To address both measurement and removal, an analytical method is reported for quantification of selenium in wastewater (WW) using UV-Vis spectrophotometer followed by removal studies using advanced oxidation processes (AOPs). Malachite green and azure blue were selected for colorimetric analysis using UV-Vis. Malachite green indicator showed the best results for analysis. The reported UV-Vis method was applied to establish the effect of AOPs on selenium removal. It was noted that all of the AOP treated samples showed removal of selenium and it was established that the UV-Vis method has a lower limit of detection at 2 mg/L. Further, through this study, it was found that the chemical cavitation yield and selenium removal efficiency peaked at low frequency ultrasound of 40 kHz.

Key words | advanced oxidation processes, analytical method development, selenium, wastewater

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INTRODUCTION

Selenium is an essential trace element needed for all living organisms. Selenium, a non-metal, shares many similar physiological properties with arsenic and chemical behavior with sulfur. It has both chalcophilic (strong affinity with sulfur) and siderophilic (able to form a metallic bond with iron) properties (Nakamaru et al. 2005; Vesper et al. 2008). Despite its essentiality at low concentrations, selenium is a potential toxic element to natural ecosystems due to its bioaccumulation potential. A recent study by Lemly (2018) on selenium poisoning of fish by coal ash wastewater in Herrington Lake, Kentucky showed a total selenium-induced mortality in excess of 25% per year and further confirmed that coal ash discharges into Herrington Lake are contributing selenium to the lake that impacted aquatic life negatively. Elemental selenium is relatively nontoxic and is considered to be an essential trace element, however, it quickly becomes toxic at higher than recommended levels. Selenium pollution has a wide environmental impact range in aquatic and terrestrial life, ecosystems and even

agricultural processes (Chapman et al. 2010; El-Ramady et al. 2014). Environmental contamination by selenium typically occurs at low concentrations, and the importance in remediating selenium-containing environments has been deemed important. Selenium detected in soil and water which further can enter the food chain through the roots of plants or aquatic organisms, leading to possible long term environmental impacts (Staicu et al. 2015). Metallurgical coal mining is considered to be one of the major sources of selenium in wastewater (WW). Selenium source in WW is due to presence of selenium in mine drainage, oil refineries, residues from fossil fuel thermoelectric power plants, metal ores and agricultural drainage water.

Fast determination of selenium in different matrices is an important task in analytical chemistry. The toxic and deficiency levels of selenium for metabolism are rather narrow. There are research works existing in the literature on the development of new analytical methods for the quantitative extraction of selenium from different matrices

including wastewater (Roehl *et al.* 2002; Vriens *et al.* 2015). A range of analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry, electrospray ionization mass spectrometry, hydride generation atomic fluorescence spectrometry, liquid chromatography with tandem mass spectrometry, high-performance liquid chromatography–inductively coupled plasma mass spectrometry, and sequential injection analysis–chemiluminescence, are used for the detection of trace and ultra-trace amounts of selenium and its species (Sutton *et al.* 1997; Roehl *et al.* 2002; Reemtsma 2003; LeBlanc *et al.* 2018).

Spectrophotometric techniques are generally preferred for the determination of analytes because of their simplicity and low cost. The determination of analytes at trace levels can be achieved using a suitable complexing agent. The main drawback of the spectrophotometric method is its poor selectivity. The complex matrix components generally interfere to a large extent; therefore, in most cases, the masking of the interfering species is unavoidable. In addition, the elimination of matrix effects and the determination of analytes present at trace and ultra-trace levels are generally performed using different separation and extraction methods. The first part of this research focuses on the development of a quantification method based on UV-Vis spectrophotometer for analysis of selenium in WW.

Physical, chemical and biological treatment technologies have shown potential for removal of selenium. However, limited success was reported in the removal of selenium from water to less than 5 μg/L at any scale (Sandy & DiSante 2010). Biological processes for selenium removal that focus on microbial reduction of selenium are new approaches that apply facultative heterotrophic bacteria to reduce selenite and selenate. In this process, selenate is first reduced to selenite, and subsequently selenite is reduced by sulfide and precipitates from the solution as selenium sulfide (He & Yao 2010; Hageman *et al.* 2017). The latter is bio-reduced to elemental selenium or organic forms of selenium and sulfide. However, biological process for the selenium removal from mining wastewater is limited by influent concentration and higher operational cost (Tan *et al.* 2016). Li *et al.* (2018) reviewed the adsorption properties of various highly porous metal–organic framework (MOF)-based materials for the efficient removal of toxic metal ions. They reported that MOF-based materials can be used as an advanced treatment method for the removal of toxic metal ions including selenium from WW due to various attractive characteristics, such as high adsorption capacity, fast adsorption kinetics, superior selectivity and

excellent reusability. Zhao *et al.* (2018) reviewed use of polymer-based nanocomposites for the removal of hazardous metal ions from WW. They reported that polymer-based nanocomposites can be used for the removal of diverse heavy metal ions including selenium from WW as these nanocomposites often present superior physical, chemical and mechanical properties, as well as superior compatibility, as compared with single polymers.

Among the different treatment options for the selenium removal, catalytic oxidation treatment has the advantage of forming elemental selenium nanospheres which exhibit unique optical and spectral properties for various industrial applications, i.e. medical, electrical, and manufacturing processes. Advanced oxidation processes (AOPs) has been widely used for the treatment of WW to enhance chemical reaction rate and facilitate the removal of several pollutants. AOPs such as sonication treatment in liquid media involved the generation, expansion, oscillations, splitting and implosions of numerous tiny gas voids called cavities or bubbles. As a result of implosion of cavitation bubbles, extreme localized temperatures and pressures are generated in the centre of the collapsed bubble. This leads to solute thermolysis as well as the formation of hydroxyl radical and hydrogen peroxide. The formation of hydroxyl radical in medium is responsible for the degradation of polar organic compounds (Kirpalani & McQuinn 2006; Mohapatra *et al.* 2011). Further, among the many AOPs, the Fenton process has been proven to be effective for treating recalcitrant organic compounds by using Fe^{2+} and H_2O_2 to produce hydroxyl (-OH) radicals.

The second part of this study focuses on the development of an optimum advanced oxidation process for the treatment of mining wastewater for removal of selenium. This two pronged study addresses the following specific objectives: (i) fast quantification method development for analysis of selenium in wastewater using UV-Vis spectrophotometry; (ii) to develop an optimum condition of AOPs such as ultrasonication, Fenton's oxidation, ferro-sonication (combination of ultrasonication with Fenton's oxidation) and ozonation processes for selenium removal from wastewater.

MATERIAL AND METHODS

Reagents and chemical solution preparation

All chemicals used were of analytical grade. Malachite green, azure B, Arabic gum, methanol, ferrous sulfate

anhydrite were purchased from Sigma Aldrich (Ontario, Canada). High performance liquid chromatography (HPLC) grade water was prepared in the laboratory using a Milli-Q/Milli-RO Millipore system (Milford, MA, USA). Nitric acid, hydro-chloric acid, and hydrogen peroxide were supplied by Fisher scientific (Ontario, Canada).

Arabic gum solution was prepared by adding 10 g of Arabic gum powdered (Sigma Aldrich, Canada) in 100 mL ultrapure milli-Q water (ISO 3696) followed with continuous stirring due to its limited solubility in water. The mixture was continuously stirred at 60 °C to dissolve the Arabic gum completely. Malachite green solution (indicator) was prepared by dissolving 0.05 g of malachite green (Sigma Aldrich, Canada) in 10 mL of milli-Q water followed by stirring until crystals are dissolved. A (0.1%) solution of azure B in methanol–water mixture was used. Potassium iodide solution was prepared by adding 10 g of potassium iodide in 100 mL volumetric flask.

Standard stock solution of Se was prepared by adding 1.0 g of Se^0 (elemental) (Sigma Aldrich, Canada) into 50 mL $(1 + 1)$ HNO_3 solution followed by heating the solution at 80 °C. After proper mixing, the solution was cooled down to room temperature, followed by the addition of 5 mL of sulfuric acid and heating the solution until transparency appears. Standard stock solution of Se(VI) was prepared by dissolving 0.2393 g Na_2SeO_4 (Sigma Aldrich, Canada) in milli-Q water and top it up to the 100 mL mark in a volumetric flask.

Wastewater sample

Control samples and standards for UV-Vis analysis were prepared by introducing reagent grade sodium selenite into double distilled water (conductivity $<0.2\ \mu S/cm$) with various concentrations. Wastewater samples were collected from a metallurgical coal operations site in British Columbia, Canada. Typical ICP and IC assay for the WW used in this study is presented in Table 1.

Procedure for determination of Se(IV) and Se(VI) with azure B

An aliquot of the solution containing 2.0–10.0 μg/mL of selenium was transferred into a series of 10 mL calibrated flasks. A volume of 1 mL of 2% potassium iodide solution followed by 1 mL of 2 M hydrochloric acid was added to it. The mixture was gently shaken until the appearance of yellow colour, indicating the liberation of iodine. Azure B (0.1%, 0.5 mL) was added to the solution and the reaction

Table 1 │ Characteristics of the wastewater used for experiments

	Units	Concentration
pH		7.1
NO_3-N	mg/L as N	58–65
Calcium	mg/L	450
Magnesium	mg/L	380–440
Chloride	mg/L	20.5
Sulphate	mg/L	1,750–2,800
TDS	mg/L	3,799
TSS	mg/L	6.8
Alkalinity	mg/L as $CaCO_3$	550–600
Phosphorus	mg/L	0.007
Temperature	°C	5

mixture was shaken for 2 min. The contents were diluted to 10 mL in a standard flask with distilled water. The absorbance of the resulting solution was measured at 644 nm against a reagent blank. A blank was prepared by replacing the selenium solution with distilled water. The absorbance corresponding to the bleached colour, which in turn corresponds to the selenium concentration, was obtained by subtracting the absorbance of the blank solution from that of the test solution. The amount of the selenium present in the volume taken was computed from the calibration graph.

Procedure for determination of Se(IV) and Se(VI) with malachite green

An aliquot of the solution containing 2.0–10.0 μg/mL of selenium was transferred into a series of 10 mL calibrated flasks followed by the addition of 1 mL of 6 mol/L of hydrochloric acid (HCl), 3 mL of 0.05% Malachite green, 3 mL of 10% potassium iodide (KI) and 3 mL of 10% Arabic gum solution. Further, the flask was topped with 5 mL of double distilled water up to the 25 mL mark. Analysis was carried out by using UV-vis spectrometry at wavelength of 670 nm in 1 cm quartz cell to observe the absorbency of Se(VI) after 30 min.

Further for Se(IV) quantification, 5 mL of Se (VI) standard solution transfer into a 10 mL tube followed by addition of 5 mL of 9 M hydrochloric acid. The mixture was then heated with boiling water bath for some time followed by cool down to room temperature. Se (VI) has been reduce to Se(IV) and analysis was carried out by following the procedure used for Se(IV) determination.

Advanced oxidation treatment of wastewater

Sonication experiment

Low frequency (20 kHz and 40 kHz) ultrasonic experiments were carried out by using an ultrasonic homogenizer (Autotune 750 W, Cole-Parmer Instruments, Vernon Hills, IL, USA). A mid frequency (574 kHz) sonochemical processing system was assembled using a broadband transducer (Ultraschalltechnik-Meinhardt GMBH, Germany). The transducer was installed at the bottom of a coolant-jacketed glass column reactor with a diameter of 5 cm and 100 cm in height. The ultrasound energy was supplied by a power amplifier (HM8001-2) through a function generator (HM 8030-5 and HM 8032). Sonication experiments were carried out at different frequency conditions using two different broadband transducers with the same effective diameter. The reactor was supplied with different power input starting from 16.67 to 83.33%. The cooling system was operated to maintain a constant temperature. The experiment was carried out with a sample volume of 200 mL held within a jacked glass cooling column with 30 min ultrasonic time. Thereafter, ultrasonic treatment was carried out at 20, 40 and 574 kHz, referred as US1, US2 and US3, respectively.

Fenton oxidation and ferro-sonication treatment

Wastewater sample of 500 mL was acidified to pH 3 by using 10 N H_2SO_4 and placed in a 1 L flask. Fenton's oxidation process was conducted at pH 3 to avoid iron hydroxide precipitation. To initiate Fenton's oxidation reaction, H_2O_2 and $FeSO_4$ solution were added to the WW samples with three different conditions: 0.2 mM, 0.4 mM, and 0.8 mM H_2O_2 and $[H_2O_2]_0/[Fe^{2+}]_0 = 50$. Fenton's oxidation was carried out at ambient temperature for 60 min using a shaker at 150 rpm. Thereafter, Fenton's oxidation treatment was carried out under 0.2 mM, 0.4 mM, and 0.8 mM H_2O_2 concentration referred to as FO1, FO2 and FO3, respectively.

Further, for ferro-sonication treatment, 500 mL of WW sample was acidified to pH 3 by using 10 N H_2SO_4 and placed in a 1 L flask. Ferro-sonication pre-treatment was carried out by addition of 0.4 mM of $FeSO_4$ solution in WW followed by ultrasonic pre-treatment under three frequency conditions such as 20 kHz, 40 kHz and 574 kHz with 60 min ultrasonic time. Ferro-sonication treatment carried out under ultrasonic frequency 20, 40 and 574 kHz referred as FS1, FS2 and FS3, respectively.

Ozonation treatment

Ozone was produced using dry air by a laboratory ozone generator (Wedeco, Xylem Water Solutions, Herford GmbH, Germany) which was set at different flow rates of 10, 20, and 30 L/h. The ozonation treatment was carried out for 1 h in an ozone reactor of 1 L working volume capacity, where a ceramic fine bubble diffuser located at the bottom of the reactor and the wastewater was thoroughly mixed with magnetic stirrer to provide efficient mixing conditions in order to ensure the homogeneous distribution of the ozone in the liquid phase. The concentration in the gas-stream was measured optically using an ozone-in-off-gas analyzer (BMT 964 OG, BMT Messtechnik GmbH, Stahnsdorf, Germany). Thereafter, ozonation treatment was carried out with flow rates of 10, 20, and 30 L/h, referred to as OZ1, OZ2 and OZ3 respectively.

RESULTS AND DISCUSSION

Method development for selenium analysis in wastewater samples

Selenium (IV) reacts with potassium iodide in the presence of dilute hydrochloric acid to liberate iodine quantitatively. The liberated iodine selectively oxidizes malachite green dye. The green colour of the dye was developed in an acetate buffer medium (pH 4.5–5.5) on heating in a water bath for 5 min. The absorbance of the dye was measured after 20 min of dilution. The malachite green dye showed maximum absorption at 650 nm, and the reagent blank had negligible absorbance at this wavelength (Figure 1).

The experiments were also carried out by using azure B as the colour agent. The reaction of selenium with potassium iodide in acidic medium liberates iodine. The liberated iodine bleaches the violet colour of azure B to colourless leucoform and the absorbance is measured at 644 nm (Figure 2). From Figures 1 and 2, it was observed that both malachite green and azure B were highly selective and sensitive for the spectrophotometric determination of selenium in WW samples. The adherence to Beer's law was studied by measuring the absorbance values of solutions, varying selenium concentration. A straight line graph was obtained by plotting absorbance against concentration of selenium. The results showed that at 644 nm, Beer's Law was obeyed up to 2 µg/mL of selenium. The molar absorptivity and Sandell's sensitivity for the coloured system were found to be 0.82×10^5 L/moL/cm and 6.53×10^{-4} µg/cm², respectively.
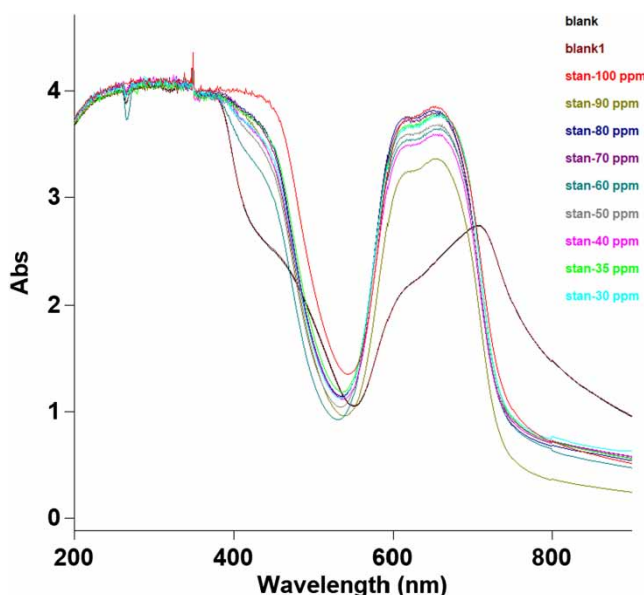
Figure 1 | Absorption spectra of different selenium standard solution with malachite green using UV-Vis spectrophotometry.
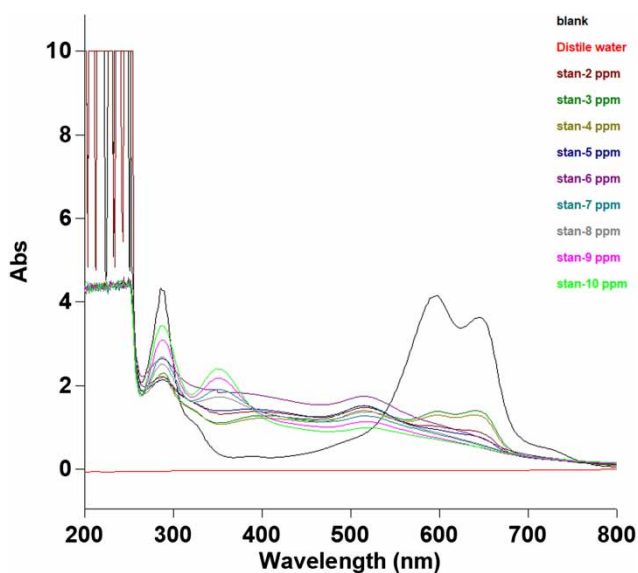

Figure 2 | Absorption spectra of different selenium standard solution with azure B using UV-Vis spectrophotometry.

Krishnaiah *et al.* 2003 studied the use of the spectrophotometric method for determination of selenium in environmental samples. They reported that the statistical analysis of different selenium concentrations showed use of spectrophotometric method produced good precision and accuracy and further obeyed Beer's law for selenium in the concentration range 0.03–3.5 µg/mL (pink colour product) and 0.07–2.5 µg/mL (orange red colour product).

The developed method was applied to the quantitative determination of traces of selenium in mining effluent water. The results obtained by using developed UV-Vis methods were compared with the ICP-MS results. The reagent provides a simple, rapid, sensitive and accurate method for the spectrophotometric determination of selenium. The method needs neither heating for the complete colour development nor extraction into any organic phase. However, it was observed that this developed method worked for selenium determination to a minimum concentration of 2 mg/L. The proposed method has been successfully applied to the determination of traces of selenium in mining effluent water with selenium concentration above 2 mg/L.

Development of an optimum advanced oxidation process for selenium removal from mine wastewater

The selenium concentration was measured by using the developed UV-Vis spectrophotometric method after each treatment. Each analysis was repeated three times. The results were compared with blank solutions of a known concentration of selenium. All the results obtained by UV-Vis were compared with the ICP-MS results for validation of method developed.

The effectiveness of AOPs such as ozonation (O3), ultrasonication (US), Fenton's oxidation (FO) and ferro-sonication (FS) processes was analyzed in terms of reduction of total selenium concentration from WW. Different results obtained during the treatment process is presented in Figure 3.
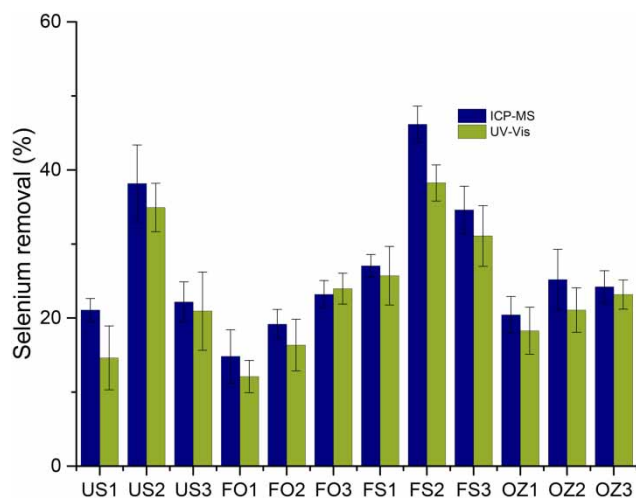

Figure 3 | Selenium removal from wastewater under different AOPs as US1 (20 kHz), US2 (40 kHz), US3 (574 kHz), FO1 (0.2 mM H_2O_2), FO2 (0.4 mM), FO3 (0.8 mM), FS1 (0.4 mM of $FeSO_4$, 20 kHz), FS2 (0.4 mM of $FeSO_4$, 40 kHz), FS3 (0.4 mM of FeSO4, 574 kHz), OZ1 (10 L/h), OZ2 (20 L/h) and OZ3 (30 L/h).

Among all the conditions of the AOPs, ferro-sonication process (combination of ultrasonication and Fenton's oxidation) carried out by adding 0.4 mM $FeSO_4.7H_2O$, ultrasonic frequency 40 kHz, pH 3.0, sample volume 500 mL showed higher removal of selenium (47%) in both UV-Vis spectrophotometry analysis and ICP-MS analysis. Further, ultrasonication treatment carried out with ultrasonic frequency of 40 kHz also showed a comparative selenium removal (38%) from wastewater. However, ozonation and Fenton's oxidation treatment of WW resulted in lower selenium removal as compared to ferro-sonication processes.

The order of efficiency of AOPs for selenium reduction from WW was: FS2 > US2 > FS3 > FS1 > OZ2 > OZ3 > US3 > US1 > FO3 > OZ1 > FO2 > FO, respectively. The reason for higher reduction of selenium concentration during ferro-sonication treatment processes was due to the addition of FeSO4, which enhanced the formation of hydroxyl (OH) radicals from hydrogen peroxide that was produced in the solution during the ultrasonic processes. Ultrasonication induces acoustic cavitation into liquid media, involving the generation, expansion, oscillations, splitting and implosions of numerous tiny gas voids called cavities or commonly referred to as cavitation bubbles. As a result of implosion of cavitation bubbles, extreme temperature and pressure is generated in the centre of the collapsed bubble leading to solute thermolysis, as well as the formation of hydroxyl radical and hydrogen peroxide. The hydroxyl radicals generated during Fenton and ferro-sonication pre-treatment processes have an oxidizing potential of 2.8 V as compared to normal hydrogen electrode and are capable of oxidizing a wide range of metals including selenium from WW. Further, higher selenium reduction from WW in ferro-sonication as compared to Fenton's oxidation processes is believed to be due to the higher efficiency of production of OH radicals.

Further, the reduction in chemical oxygen demand (COD) and ammonia-nitrogen during ozonation (O3), US, FO and FS processes was also observed (Figure 4). Higher reduction of COD (54%) and ammonia-nitrogen (42%) was observed during ozonation treatment with ozone dose 30 L/h, ozonation time 30 min, sample volume 350 mL, pH 7.68. Comparative results for COD and ammonia-nitrogen reduction was also observed during ferro-sonication treatment carried out with the addition of 0.4 mM $FeSO_4.7H_2O$, pH 3 with frequency of 40 kHz, power input 80%, sonication time 1 h, sample volume 500 mL. Further, it was observed that these conditions also favourable for the solubilisation of COD and ammonia-nitrogen removal from mining effluent water. During these pre-treatment
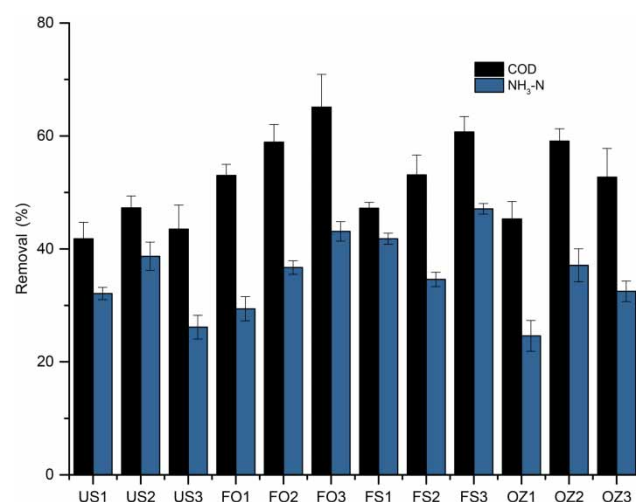

Figure 4 | Reduction in COD and ammonia-nitrogen during different advanced oxidation treatment of wastewater.

processes, organic substances were transferred from solid to the aqueous phase, which resulted in the increase of soluble protein and soluble carbohydrate concentration in the aqueous phase and decrease of COD and SOC in the solid phase. Höfl et al. (1997) compared different AOPs for COD removal from WW. They reported that processes based on hydroxyl radicals were less selective but considerably more effective in COD degradation.

Optimization of ferro-sonication treatment for selenium removal from mining wastewater was carried out in a series of different concentration of $FeSO_4.7H_2O$ (0.2 to 1.0 mM), pH (2.5 to 4), shaking for 1 h at 200 rpm with sample volume of 300 mL and ultrasonic frequency of 40 kHz. All the experiments were carried out in effluent water as well as in standard solution (milli-Q water spiked with a known concentration of selenium). The experimental conditions and percentage of selenium removed is presented in Table 2. Among all the ferro-sonication conditions examined in this study, the $FeSO_4.7H_2O$ concentration of 0.8 mM with pH 2.5 showed the maximum removal efficiency (65% and 53%) of selenium from standard solution and mining wastewater, respectively. However, it was observed that by increasing $FeSO_4.7H_2O$ concentration from 0.2 to 0.8 mM an increase in efficiency of the ferro-sonication treatment with higher selenium removal from standard solution was shown, as well from mining wastewater. Further, optimization of ferro-sonication treatment ultrasonic frequency of 574 kHz for selenium removal from mining wastewater was carried out in a series of different concentrations of $FeSO_4.7H_2O$ (0.2 to 1.0 mM), pH (2.5 to 4), shaking for 1 h at 200 rpm with sample volume of 300 mL. The experimental conditions

Table 2 | Optimization of ferro-sonication treatment under different concentrations of $FeSO_4.7H_2O$ and ultrasonic frequency of 40 kHz for selenium removal (%)

FeSO₄ conc.	0.2 mM		0.4 mM		0.6 mM		0.8 mM		1.0 mM	
	stnd	eff	stnd	eff	stnd	eff	stnd	eff	stnd	eff
pH 4	29	21	38	32	36	31	41	37	48	42
pH 3.5	36	28	46	27	48	41	46	43	43	37
pH 3	38	23	49	41	57	49	55	46	57	49
pH 2.5	42	33	56	45	55	53	65	53	60	57

Stnd, standard solution; eff, effluent water.

Table 3 | Optimization of ferro-sonication treatment under different concentration of $FeSO_4.7H_2O$ and ultrasonic frequency of 574 kHz for selenium removal (%)

FeSO₄ conc.	0.2 mM		0.4 mM		0.6 mM		0.8 mM	
	stnd	eff	stnd	eff	stnd	eff	stnd	eff
pH 4	47	39	54	48	33	27	51	43
pH 3.5	42	40	61	53	59	45	59	46
pH 3	31	26	51	44	37	28	32	28
pH 2.5	27	24	29	23	63	57	39	35

Stnd, standard solution; eff, effluent water.

and percentage of selenium removed is presented in Table 3. Among all the ferro-sonication conditions tried under 574 kHz ultrasonic frequency, $FeSO_4.7H_2O$ concentration of 0.6 mM with pH 2.5 showed the maximum removal efficiency (63% and 57%) of selenium from standard solution and mining wastewater, respectively. Further, decrease in pH from 4 to 2.5 showed that ferro-sonication treatment with higher $FeSO_4.7H_2O$ concentration and lower pH is a favourable condition for higher removal of selenium from mining wastewater. The pH value has a decisive effect on the oxidation potential of -OH radicals because of the reciprocal relation of the oxidation potential to the pH value. Furthermore, the concentration of inorganic carbon and the hydrolytic speciation of Fe(III) species are strongly affected by the pH value (Mohapatra et al. 2013; Pulicharla et al. 2017). Higher removal of selenium from mining wastewater during ferro-sonication process was due to the addition of $FeSO_4$, as well as production of H_2O_2 in the medium during ultrasonic treatment, which enhanced the formation of hydroxyl (OH) radicals in the solution.

CONCLUSIONS

The UV-Vis spectrophotometric method development for analysis of selenium in wastewater samples showed that malachite green indicator was best-suited for selenium analysis. The colour indicator provides a simple, rapid, sensitive and accurate method for spectrophotometric quantification of selenium in wastewater samples. UV-Vis produced comparable results as ICP-MS; however, the UV-Vis approach is limited to concentrations above 2 mg/L. Further, among the AOPs tested (ultrasonication, Fenton's oxidation, ferro-sonication and ozonation) for selenium reduction from wastewater samples, ferro-sonication treatment (a combination of ultrasonication and Fenton's oxidation) showed the best method for selenium removal from wastewater. Ferro-sonication treatment process showed higher selenium removal efficiency due to the utilization of iron to generate more OH radicals. Further, through this study, it was found that the ultrasonic treatment carried out at lower frequency (40 kHz) showed higher removal of selenium from effluent water as compared to mid-frequency ultrasound treatment at 574 kHz. This shows that the removal is influenced by higher cavitation yield as the cavitation yield decreases at higher frequencies due to the formation of capillary instabilities.

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