

Investigation on the Efficiency of Electro-coagulation Process for Treatment of Different Selenium Species

Mehdi Zolfaghari, Sara Magdouli, Simon Pierre Komtchou and Rayen Tanabene

Abstract— Selenium is an essential non-metal trace element highly required in human life; however, its bio-accumulative characteristics makes this latter a toxic element especially at higher concentration. Until now, adsorption, zero valent iron, biological reduction, ion exchange and membrane separation were widely used to reduce selenium in the effluent. In this study, electrocoagulation process was applied to remove inorganic selenium in a synthetic solution that contained SeO_3^{2-} and SeO_4^{2-} , respectively. Preliminary results of synthetic solution showed that the removal of selenite was 50 to 100% more than selenate. By considering the presence of SeO_3^{2-} free electron pair, it seems that co-precipitation of selenium with aluminium was the main removal pathway of selenite. Fortunately, during electro-coagulation, selenate was reduced to selenite in cathode, which facilitated its removal. Other metalloids such as, chromate and arsenate showed the same behaviour with selenate, and their presence insignificantly interrupt selenate removal efficiency. In optimum conditions with a current density of 0.4 mA cm^{-2} , a time of 52 minutes, aluminum/iron as anode/cathode electrodes, more than 90% of total selenium was precipitated from the solution. The concentration of total selenium in the discharge reached less than $18 \mu\text{g.L}^{-1}$, which respected the maximum allowable discharge of $20 \mu\text{g.L}^{-1}$. The energy consumption and electrode loss were around 66 Wh.m^{-3} and 27 g.m^{-3} , respectively.

Index Terms— Selenate; Selenite; Electrocoagulation; Operation Cost.

I. INTRODUCTION

Selenium (Se) is a complex emerging metalloid with narrow range of toxicity and homeostatic requirement [1-3]. Currently, it is essential for body with a recommended uptake of $55 \mu\text{g.d}^{-1}$; yet, it shows carcinogenic, cytotoxic and genotoxic effects with an uptake more than $4 \mu\text{g.kg}^{-1}.\text{d}^{-1}$ [3-6]. Due to its resemblance with sulfur, it can be substituted during portion synthesis, generating highly toxic organoselenium species [3, 7]. Through bioaccumulation and bio-magnification processes in food chain, they can find their ways easily to human body. Inorganic Se, especially selenite, can also generate high concentration of oxygen free radicals, leading to toxic effects [4, 5, 7]. Mining activity, coal-fired power plants, oil refineries and agriculture are the main anthropogenic sources of selenium in the environment [4-6, 8]. Among them, gold mine processing is

considered the main source of selenium in the nature. Besides, dissolving selenium-rich rock in processing water increases its concentration up to $0.2\text{-}33 \text{ mg.L}^{-1}$ [4, 7]. Selenate, Se (VI), is the fully oxidized form of Se. It is usually predominant in aquatic solution in a wide range of pH as its pKa ($\text{HSeO}_4^-/\text{SeO}_4^{2-}$) is around 1.8. SeO_4^{2-} . Because of the low adsorption and precipitation capacities, it is very difficult to treat [4]. Selenite Se (IV), on the other hand, is the dominant form in moderate redox potential range. Since it has two pKa of 2.70 and 8.54, in neutral pH, it found in the form of biselenite HSeO_3^- [4]. Recently, a major concern is given to establish new regulation limits on its discharge concentration, especially in mine industries. Allowable concentrations of 10 and $20 \mu\text{g.L}^{-1}$ are actually recommended by World Health organization (WHO), and Montreal Metropolitan Community (MWC), respectively [8]. Because of its high solubility, the large volume of generated effluent, and the wide range of its concentration, selenium treatment processes become very expensive and challenging. Based on literature, adsorption [9], zero-valent iron [10], ion exchange [11], lime precipitation [2, 12], coagulation [5], and biological treatment [13] are the main processes reported for selenium removal. Due to the presence of different type and concentration of metalloids in mine effluent, the adsorption processes are quite costly [11]. Moreover, the lack of organic matter in such effluent also challenges the utilization of biological processes [8]. In this context, the potential of electro-coagulation (EC) for selenium removal was tested. EC process is currently based on *in situ* production of coagulants following the application of electrical current. Alum (Al^{3+}) or ferric (Fe^{3+}) cations are generated by oxidation of sacrificial electrode; while, hydroxyl anion (OH^-) are produced by the reduction of water molecule in cathode [14, 15]. Generated aluminum or ferric hydroxide resulted in the precipitation of particulates and metalloids in the solution. Furthermore, the reduction of metalloids occurs in the surface of cathode [16-18]. Negative charge particles generally approach to the anode, in where, they are imprisoned by the metal hydroxide flocs, which can be further separated from the water by electro-floatation owing to the hydrogen production in cathode, decantation, or by filtration [19]. In this study, the removal of two prominent selenium species, selenate and selenite from the aquatic solution was investigated during electrocoagulation process. The type of electrodes, electrolyte, and operating conditions such as, time and current density were optimized. Finally, the effect of pH and other metalloids was examined.

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II. MATERIAL AND METHODS

A. Chemical and effluent sampling

All of the solutions and synthetic effluent used in this study were prepared by de-ionized water and analytical grade chemicals purchased from Sigma-Aldrich, Oakville, Ontario, Canada. The stock solutions of sodium selenite (Na_2SeO_3), sodium selenate (Na_2SeO_4), sodium arsenate ($\text{Na}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$), potassium di chromate (K_2CrO_4) and magnesium sulphate (MgSO_4) with concentration of 2 g L^{-1} were prepared prior to experimentation.

B. Electrocoagulation pilot

In this study, a laboratory scale electrocoagulation reactor equipped with eight electrodes with dimension of $122 \times 102 \text{ cm}$ was used (Figure 1). The direct electrical current for four pair of rectangular anodes and cathodes with 1 cm of interval was provided by a precision DC power supply, TDK Lambda, Fort Worth, Texas, USA. Total volume of three-liter effluent was inserted to two-liter Plexiglas rectangular reaction and retention tanks. The effluent was circulated by means of a peristaltic pump (Masterflex L/S Precision, Cole-Parmer Company, Montreal, QC, CA) with the flow rate of $150 \text{ mL} \cdot \text{min}^{-1}$. NaCl was used to increase the electrical conductivity, as chlorine anions decrease the passivity of electrode [20]. For minimizing the electrical consumption, the mono-polar configuration was selected in this case. In order to evaluate the operation cost, the specific energy consumption and aluminum production was calculated based on Equation 1, and 2, respectively.

$$M = \frac{ItMW_m}{ZF} \quad (1)$$

$$E = \frac{IUt}{V_r} \quad (2)$$

In which M is the mass of produced cation for a volume of treated mine effluent ($\text{g} \cdot \text{m}^{-3}$), I is the current intensity (A), t is the time of reaction (s), MW is the electrode molecular weight ($\text{g} \cdot \text{mol}^{-1}$), Z is the chemical equivalent of metal, F is the Faraday constant ($96500 \text{ C} \cdot \text{mol}^{-1}$), V_r is the volume of the treated effluent (m^3), E is the specific energy consumption ($\text{kWh} \cdot \text{m}^{-3}$), and U is the electrical potential between electrode (V).

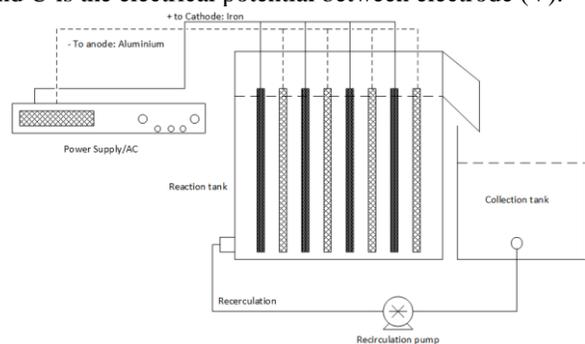


Fig. 1. The schematic view of laboratory-scale electrocoagulation reactor and electrode used for removal of selenium from the mine effluent.

C. Experimental plan

Operating conditions such as, pH, electrical conductivity (b), presence of other metalloids, current density (J), time (t), type of anode, concentration of pollutants significantly influence the energy consumption and the performance of electrocoagulation

process [20, 21]. The first three factors were optimized by conventional multifactor experiments, by fixing all factors and changing only one. While, for the last three, Response Surface Methodology has been used to decrease the number of experiments and assess the possible interaction between factors [20]. The initial pH value of experiment was set at the original pH of synthetic solution (7.2 ± 0.3).

1. Specification of electrical conductivity

In this set of experiment, different concentration of NaCl (0.2, 1, 5, 20, and 100 mM) was added to di-ionized water. The current density was fixed at $0.96 \text{ mA} \cdot \text{cm}^{-2}$. By measuring the electrical potential between electrodes (U), the electrical consumption (E) was calculated by Equation 2. By comparing the operating cost (energy consumption) with material cost (NaCl addition), the optimum salt concentration was derived and used for the rest of experiments. In province of Quebec, the price of electricity for large industries is ($4.91 \text{ \$.kWh}$); while, the worldwide salt cost is around $0.19 \text{ \$.kg}^{-1}$.

2. Specification of anode

Four set of experiments were designed to investigate the efficiency of aluminum (Al) and iron (Fe) for the removal of selenate (Se (VI)) and selenite (Se (IV)). The effluent is prepared by the addition of $10 \text{ mg} \cdot \text{L}^{-1}$ of total selenium, 15 mM of NaCl in 3.5 Liter of deionized water. Around 500 mL of synthetic effluent was set aside for conditioning the EC pilot and three liter was kept for the experiment. For each set of experiment [Al-Se (VI), Al-Se (IV), Fe-Se (VI), Fe-Se (IV)], four different current density ($0.4, 1, 2$ and $4 \text{ mA} \cdot \text{cm}^{-2}$) were investigated for different time interval (10, 20, 60, 40, 80, 120 min). As the value of electrical potential of EC pilot was decreasing during time, the average value (U_{ave}) was taken into the consideration by measuring the performance of experiment in a five-minute time interval (Equation 3).

$$U_{\text{ave}} = \frac{\sum_{i=1}^n U_i}{n} \quad (3)$$

For measuring the selenium removal efficiency, the sample was taken at the beginning and the end of experiment (5 minutes mixing between reaction and retention tank before taking the sample). To measure the sludge production, 500 mL of sample was collected for measuring total dissolved solid (TDS) and total suspended solid (TSS) of effluent.

3. Optimization of time and current density

The effect of current density and time in different concentration of Se (IV) and Se (VI) was investigated with the Response Surface Methodology (RSM). Later on, central composite design (CCD) was used for the optimization of EC process. In this case, three-factorial and two-level of experimental design with three replicas at the center points led to have 11 set of experiments for each selenium species. Total Se removal efficiency (RE), and specific energy consumption (SEC) were set as a response. The range of variables was obtained by primary test. For data evaluation, the response was fitted by a first-order model in the form of polynomial equation (Equation 4).

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j \quad (4)$$

In which Y is the predicted response, X_i are the variable and b_i are the model coefficients. Contribution of time (t), current

density (J) and initial selenium concentration ($[Se_0]$) was calculated by Pareto chart derived from following equation.

$$PI = \left(\frac{b_i}{\sum b_i} \right) \times 100 \quad (5)$$

Inquiring the most influential factors among operating conditions was possible by this mathematical and statistical model; yet, the mechanism of removal could not be deduced from CCD model [20]. The experimental data was analyzed through Design Expert 7.1.3 Software by setting the desired value or range for each variables and responses. Obviously, to minimize the SEC, the current density should be reduced. In the targeted value of initial concentration; total Se removal efficiency had to be maximized. Following this condition, optimizing operating conditions was proposed.

4. Effect of competitive anions and pH

Due to the chemical structure similarities between selenate (SeO_4^{2-}), sulfate (SO_4^{2-}), chromate (CrO_4^{2-}), and arsenate (AsO_4^{2-}), these anions were selected to test the effect of other anions on the performance of EC process. The concentration of other anions was fixed at 10 mg.L^{-1} in the presence of 1 mg of $Se.L^{-1}$; while fixing other operating conditions at their optimum value. Furthermore, the effect of pH was investigated by fixing pH into 2, and 11 by means of concentrated HCl (6 mM) and 5 mM NaOH solution, respectively.

D. Analysis of samples

Samples were taken from the retention tank at the end of each experiment. Due to the lack of organic-selenium complex and the high solubility of selenate and selenite, all samples were filtered by $0.45 \mu\text{m}$ filter paper before analysis. Electrical conductivity, oxidation/reduction potential (ORP) and pH were directly measured by inserting their corresponding probe in retention tank. TDS and TSS were measured based on the water characterization standard method. Alongside with iron and aluminum concentration, total selenium concentration was analyzed by MP-AES (4200, Agilent Technologies, Saint-Laurent, QC, CA).

III. OBSERVATION AND RESULTS

A. Optimization of electrical conductivity

The electrical consumption has the big portion of operating cost. As mentioned before, the electrical conductivity has an important role in determining the resistance of effluent. According to equation 6, increasing the electrical conductivity and surface of electrodes resulted in decreasing the electrical potential and finally the electrical consumption of EC process.

$$U = R \cdot I = \rho \frac{l}{A} \cdot I = \frac{l}{\sigma \cdot A} \cdot I \quad (6)$$

In the mentioned equation, U is the electrical potential (v), R is the resistance of effluent (Ω), I is the current intensity (A), ρ is the resistivity ($\Omega \cdot \text{m}$), l is the distance between electrodes (m), A is the surface of electrode (m^2), and σ is electrical conductivity of solution ($\text{S} \cdot \text{m}^{-1}$). For the first stage of experiment, a synthetic salt solution was used to investigate the relation between ion concentration and electrical conductivity. Firstly, the electrical conductivity of each salt solution with concentration between 0.2 to 100 mM NaCl was measured. Results showed a linear

correlation between concentration of NaCl and electrical conductivity, (equation 7)

$$\sigma (\text{us} \cdot \text{cm}^{-1}) = 100.9 [\text{NaCl}] (\text{mM}) = 1.727 [\text{NaCl}] (\text{mg} \cdot \text{L}^{-1}) \quad (7)$$

Hence, increasing the salt solution, linearly decreased the solution resistivity, leading to lower energy consumption; however, excess salt increased the material cost. The salt concentration was optimized, when the cost of material consumption was equal to the electrical consumption for treatment of each m^3 of effluent.

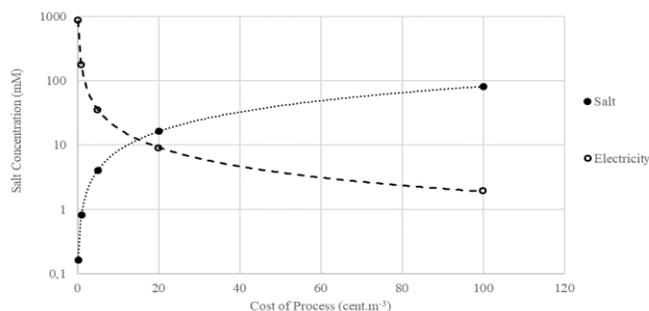


Fig. 2. The cost of process based on the concentration of NaCl salt solution.

As seen in figure 2, the concentration of 14.6 mM of NaCl was selected as the optimum salt concentration for the rest of experiment. Therefore, for each experiment 2.63 g of NaCl was dissolved in 3 Liter of distilled water to reach the electrical conductivity of around $1.5 \text{ ms} \cdot \text{cm}^{-1}$.

B. Optimization of electrode type

Due to their coagulation potential, aluminum, magnesium, and iron are among three main types of sacrificial electrodes widely investigated. Because of their cost and performance, only Al and Fe electrodes were chosen in this study. In literature, Iron-Iron electrode showed the highest removal of metalloids such as, arsenate; yet, the removal efficiency of Fe-Al was also close to 97.8% [19]. Figure 3 presents the performance of energy consumption of two configurations of Al/Fe anode and cathode. Obviously, Iron electrode showed the higher removal efficiency for both selenite and selenate in specific current density; however, the electrical potential between electrodes was higher in Fe electrode, resulting in comparable performance with aluminum anode in the term of energy consumption. Greater weight loss and higher sludge production were other drawbacks of iron anode.

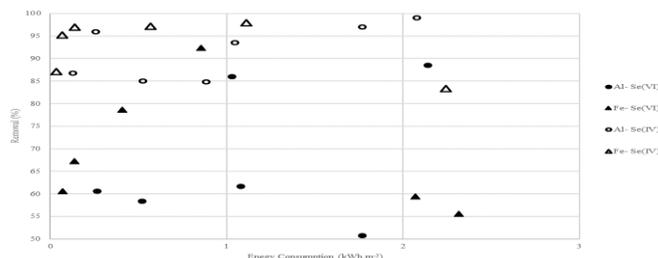


Fig. 3. Selenite and Selenate removal efficiency and specific energy consumption of electrocoagulation process for two configurations of Al/Fe electrodes ($[\text{NaCl}] = 15 \text{ mM}$, $[\text{Se}] = 10 \text{ mg} \cdot \text{L}^{-1}$, $J = 0.45\text{-}4.5 \text{ mA} \cdot \text{cm}^{-2}$ and $t = 10\text{-}120 \text{ min}$).

As shown in Figure 4, due to higher molecular weight of Fe in

comparison with Al (27 to 56 g.mol⁻¹), loss weight and sludge production of iron were significant compared to aluminum.

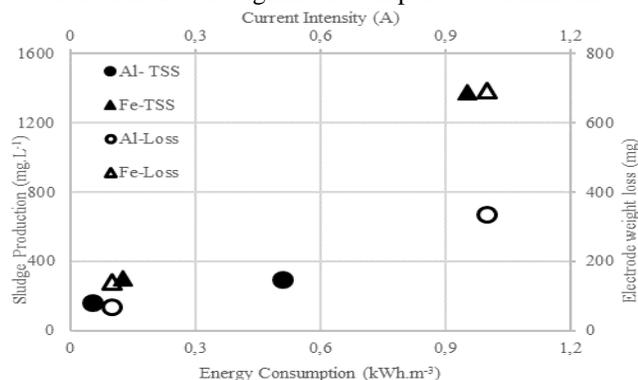


Fig. 3. Comparison of weigh loss of electrode and sludge production of aluminum and iron as the anode ([NaCl] =15 mM, J= 0.1, 1 mA.cm⁻² and t = 60, 120 min).

C. Optimization of current density and reaction time

Since the removal of selenite is significantly higher than selenate, the range of operating conditions for two species was slightly different. The optimized current density and time was predicted based on the following equation derived by CCD model (Table 1).

TABLE I. THE POLYNOMIAL COEFFICIENTS OF CCD MODEL FOR TWO RESPONSES (SELENITE AND SELENATE REMOVAL EFFICIENCY) BASED ON DIFFERENT VARIABLE (X1= T, X2= J, X3= [SE0]).

Coefficients	Se (VI) RE	Se (IV) RE	√E
b ₀	34.65	32.74	0.036
b ₁	1.04	0.87	0.0019
b ₂	1.62	41.1	0.181
b ₃	-16.5	4.4	0
b ₁₂	0	-0.44	0.0061
b ₁₃	0	-0.08	0
b ₂₃	3.09	0	0
R ² (%)	94.8	96.1	96.7

As the predicted correlation coefficient of polynomial equation derived by CCD was more than 0.92 for all cases, this model was effective to predict the experimental value. By looking at Pareto diagram depicted in Figure 5, interestingly, time was a decisive factor for selenate removal; while, the current density showed the highest effect for selenite removal. It seems that the rate of SeO₄²⁻ reduction on the surface of anode is required before any other removal mechanism; therefore the effect of time was more pronounced. On the other hand, adsorption and co-precipitation seemed to be main selenite removal mechanisms. As the production of coagulant increased with higher current density, it showed the highest effect between operating factors. Due to the discharge limit of total selenium (20 µg.L⁻¹), the removal efficiency should be more than 85% for the targeted initial concentration of 0.2 mg Se.L⁻¹, which resembled to the average concentration of total selenium in mine effluent. Consequently, by setting the current density at 0.4 mA.cm⁻², electrolyte concentration of 15 mM NaCl (to reach the electrical conductivity of 1685±28 µs.cm⁻¹), and at room temperature (20 °C), the best selenium removal efficiency should be observed after 52 minutes. In this case, with specific energy consumption of 0.1 kWh.m⁻³, the final concentration of

selenite and selenate reached 18 and 31 µg.L⁻¹, which was close to the predicted value.

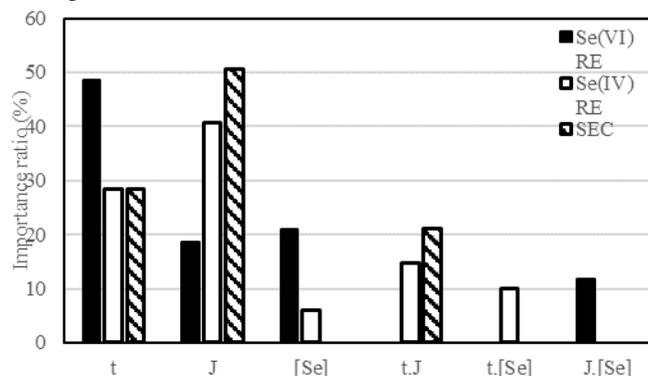


Fig. 5. Importance effect of time (t), current density (J), and initial selenium concentration ([Se₀]) on selenate (Se(VI)), selenite (Se(IV)) and specific energy consumption (SEC) in electro-coagulation process.

D. Effect of metalloids and pH

The different concentration of selenium and the presence of other metalloids could have effect on the performance of EC.

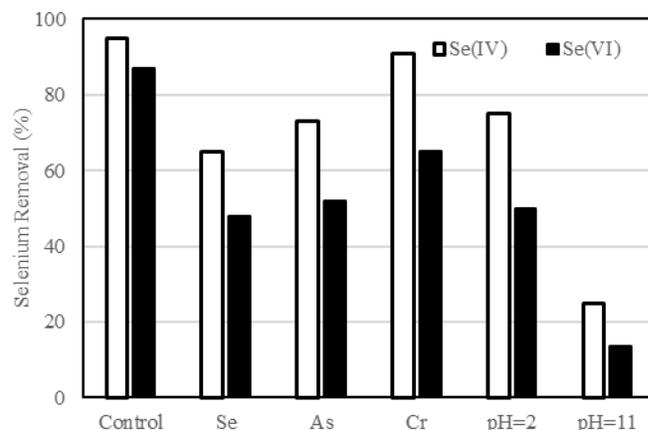


Fig. 6. Effect of pH, excess selenium, arsenic and chrome concentration on the removal efficiency of selenite and selenate (pH = 7.2±0.2, [Se₀] = 1 mg.L⁻¹, [metalloid] = 10 mg.L⁻¹, J= 0.4 mA.cm⁻², t = 52 min, B = 1710±42 µs.cm⁻¹).

As shown in Figure 6, the interference of selenium itself, was higher than other metalloids. Similar structure of arsenate (AsO₄²⁻) and selenate (SeO₄²⁻) led to have more interference with selenate than selenite. Fortunately, the adsorption and precipitation processes seemed to be unaffected in the presence of sulfide ions [6]. pH of effluent has also an effect on the removal of metalloids. As shown in result, same as literature, neutral pH showed the best performance during EC process.

IV. DISCUSSION

The mining industry has long used coagulation to remove suspended solids, colloids, prior to filtration or sedimentation [17]. Thus, EC could be a replacement method for mine effluent treatment [20]. Due to the oxidizing conditions of mining process, selenium is mainly found in the form of selenate, this latter is less reactive and responsive to treatment in comparison to selenite. Hence, its reduction to selenite is favorable for total

selenium removal [17]. Previous studies showed that during EC process, both metal cations (mostly divalent and trivalent) and oxyanions (e.g. arsenic, antimony, vanadium, molybdenum, and selenium) are eliminated by the hydroxylated coagulants [16, 20-22]. Four main mechanism are responsible for Se removal: (1) reduction of inorganic selenium species on the surface of anode; (2) adsorption of selenite and selenate on the surface of aluminum and iron hydroxide flocs [4, 5]; (3) formation of insoluble $M_2(SeO_3)_3$ salt through the reaction of SeO_3^{2-} and Al^{3+} or Fe^{3+} [4]; (4) co-precipitation of selenite by replacing hydroxide anions in the structure of flocs [20]. In both last cases, pre-reduction of selenate to selenite is required [5, 16].

During EC, iron and aluminum are forming ferric and alum cations. By reacting with OH^- produced on cathode, polymeric iron or aluminum oxyhydroxides (e.g. $Al_{13}(OH)_{32}^{7+}$) are formed in the vicinity of anode [19]. Negative charge of selenium anions could be easily adsorbed and precipitated by positively charge hydroxides, polyhydroxides, and polyhydroxyoxide metallic compounds [23]. For example, aluminum and iron oxide showed the highest adsorption capacity up to 18 mg.g^{-1} for selenate [6]. On the other hand, negative charge of selenate or selenite directly reacted with positive charge Al or Fe, resulting in the detection of $Al_2(SeO_4)(OH)_3 \cdot 2(H_2O)$, or $Al(SeO_4)(OH) \cdot 5(H_2O)$ in fine amorphous flocs [14, 19, 21].

In accordance with literature, current results also showed that Fe as the anode reached better Se removal than Al. When the iron was used as the anode, produced ferrous cations (Fe (II)) resulted in the reduction of metalloids. Ferric cations (Fe (III)), on the other hand, reacted with hydroxyl anions to form the insoluble ferric hydroxide ($Fe(OH)_3$) or goethite ($FeOOH$) matrix [20]. As ferric hydroxide flocs had higher number of active site than aluminum hydroxide species, they showed higher adsorption affinity for soluble metalloids [5]. Consequently, relevant studies have continuously used Fe as the anode for metalloids removal [13]. Nevertheless, they have used a very high current density (up to 12 mA cm^{-2}) accompanied with a higher production of sludge [24]. Since the cost of EC sludge disposal is between 80 and $130 \text{ $.ton}^{-1}$ [20], using aluminum will be more favorable.

The presence of competing species such as arsenic, phosphate and silicate reduced the performance of treatment. Even though sulfur is similar to selenium, its presence had no effect on the EC performance. On the other hand, the presence of PO_4^{3-} and AsO_4^{2-} was most pronounced, as these species interacted with outer sphere of ferric and aluminum hydroxide, and dramatically changed their ionic strength. For CO_3^- and SiO_3^- species, accumulation and precipitation phenomena on the surface of hydroxyl caused a significant interference [5]. Weakly acidic solution enhanced the formation of hydroxide flocs with higher zeta potential. This fact facilitated the adsorption of the negative charge of selenium salt [5]. Furthermore, in acidic pH, Fe^{3+} or Al^{3+} tended to react with metalloid to form insoluble selenium salt, instead of the formation of $Fe(OH)_3$ or $Al(OH)_3$ [21, 24].

V. CONCLUSION

In this study, electrocoagulation process was used for the removal of selenite and selenate from synthetic effluent. By the separation of these two species, the removal mechanism was derived, which resulted in following conclusions:

- (1) Rather than iron, aluminum was selected as the optimum choice as it produced half amount of sludge in the same condition. Even though the removal efficiency was around 35-60% lower than Fe electrode, higher potential between iron electrodes significantly increased the electrical consumption.
- (2) Time was the most decisive factor in selenate removal, as Se (VI) should be reduced to Se (IV) for further adsorption on the aluminum hydroxyl flocs. Current density on the other hand had the highest effect on selenite removal efficiency.
- (3) In 52 minutes of reaction time, with a current density of 0.4 mA.cm^{-2} , 15 mM NaCl , and at room temperature ($20 \text{ }^\circ\text{C}$), the specific energy consumption was around 0.1 kWh.m^{-3} . Moreover, the selenite and selenate were reduced to 18 and $31 \text{ }\mu\text{g.L}^{-1}$, respectively, within an initial concentration of $100 \text{ }\mu\text{g.L}^{-1}$ of total selenium,
- (4) Reduction on the surface of anode, adsorption to coagulants flocs, precipitation by reaction with Al^{3+} , and co-precipitation of aluminum hydroxyl were the main removal mechanisms of selenium during electrocoagulation process.

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