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Membrane capacitive deionization for the treatment of sulfate, thiosulfate, and thiocyanate from gold mining process water

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Abstract: This study investigated the removal of sulfate, thiosulfate, and thiocyanate (SO₄²⁻, S₂O₃²⁻ and SCN⁻) by membrane capacitive deionization (MCDI) process. An electrochemical cell was fabricated using an anion exchange membrane and a cation exchange membrane placed on a carbon paper electrode, which operated as the anode and cathode. Batch mode experiments were conducted by recirculating single salt solutions of SO₄²⁻, S₂O₃²⁻, and SCN⁻ to determine the maximum removal efficiency. The anode electrode removed 8600 mg SO₄²⁻, 9850 mg S₂O₃²⁻, and 9350 mg SCN⁻ per m² of the electrode. Batch mode experiments were also performed in mixed salt solution containing 100 mg/L SO₄²⁻, S₂O₃²⁻, and SCN⁻ to observe the effect of co-ions on the removal efficiency. In the adsorption phase, salt removal efficiency percentages were determined to be 57% for SO₄²⁻, 57% for SCN⁻, and 88% for S₂O₃²⁻ at 1.2 V. In the desorption phase, the electrodes were regenerated by reversing the operating voltage to -5.0 V. The single-pass mode MCDI experiment showed that both S₂O₃²⁻, and SCN⁻ were removed with a total salt removal of 539.6 mg/m² and 510 mg/m², respectively, during the adsorption phase. In the desorption phase, the removal rates increased to 719 mg/m² for S₂O₃²⁻ and 643 mg/m² for SCN⁻, indicating the electro-oxidation of these ions.

Keywords: water treatment, gold mining process water, membrane capacitive deionization (MCDI), electro-oxidation, sulfide minerals

1. Introduction

Cyanidation is a widely used process in gold extraction, particularly for ores containing sulfide minerals. During the process, cyanide reacts with elemental sulfur and polysulfides to produce thiocyanate, as shown in reactions (1)- (3) (Adams 1990).

$$S^0 + CN^- \leftrightarrow SCN^-$$
 (1)

$$2S^{2-} + 2CN^{-} + O_2 + 2H_2O \leftrightarrow 2SCN^{-} + 4OH^{-}$$
⁽²⁾

$$S_2O_3^{2-} + CN^- \leftrightarrow SCN^- + SO_3^{2-}$$
 (3)

Thiocyanate is a common contaminant in gold mining effluent. It can undergo oxidation reactions and always oxidized to sulfate, as shown in reaction (4)-(5) (Gauguin 1951; 1949).

$$SCN^- + 4H_2O \leftrightarrow SO_4^{2-} + CN^- + 8H^+ + 6e^-$$
(4)

$$SCN^- + 7H_2O \leftrightarrow SO_4^{2-} + CNO^- + 10H^+ + 8e^-$$
(5)

$$SCN^{-} + 7H_2O \leftrightarrow NH_3^{+} + CO_3^{2-} + SO_4^{2-} + 11H^{+} + 8e^{-}$$
 (6)

Thiocyanate is a strong complexing agent, forming compounds with the first group transition metals via nitrogen and with the second and third group transition metals via sulfur (Gould et al. 2012). Thiocyanate, a hydrophilic species, can form compounds with metal sulfides such as Fe, Cu etc. and suppress their flotation (Wang and Forssberg 1996). While thiocyanate is less toxic than cyanide, it is more stable, making it more difficult to eliminate. At high concentrations, thiocyanate can be harmful to both humans and the environment (Kuyucak and Akcil, 2013). Therefore, it is essential to reduce thiocyanate levels in wastewater to an acceptable limit for environmental safety, which is less than 4 mg/L, before discharge (Raper et al., 2019). In the processing of sulfide minerals, thiosalts are produced

by the oxidation of the sulfide group (e.g., pyrite, FeS₂ and pyrrhotite, FeS) by oxygen. They occur as partially oxidized sulfoxy anions like thiosulfate ($S_2O_3^{2-}$), trithionates ($S_3O_6^{2-}$), and tetrathionates ($S_4O_6^{2}$) as shown in the reactions (7)-(10):

$$2FeS_2 + 1/2O_2 + H_2O \rightarrow 2Fe^{2+} + 2OH^- + 4S^\circ$$
 (7)

$$4S^{\circ} + 6OH^{-} \rightarrow 2S^{2-} + S_{2}O_{3}^{2-} + 3H_{2}O$$
(8)

$$3S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2S_3O_6^{2-} + 2OH^{-}$$
(9)

$$4S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 2S_4O_6^{2-} + 4OH^-$$
(10)

These anions are metastable species and oxidize or disproportionate to more stable sulfate, as described by following reactions (11)- (13), (Rao, 2011):

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$$
 (11)

$$S_3O_6^{2-} + 2O_2 + 2H_2O \rightarrow 3SO_4^{2-} + 4H^+$$
 (12)

$$S_4O_6^{2-} + 7/2O_2 + 3H_2O \rightarrow 4SO_4^{2-} + 6H^+$$
 (13)

The products of these chemical reactions enter the process water, resulting in a decline in water quality and further impacting process efficiency (Rao, 2011). The oxidation of thiosalts has been identified as an indirect cause of the acidification of surface waters, which can negatively affect the downstream environment. While thiosalts are relatively non-toxic and not regulated upon release, the sulfuric acid formed through their oxidation can harm aquatic ecosystems (Dinardo and Salley, 1998).

Thiosulfate ions can interact with metal ions, forming complexes that passivate the surface of minerals (Kirjavainen et al., 2002). Jeffrey et al. (2008) showed that gold dissolution in a thiosulfate solution is hindered by surface passivation, primarily due to the adsorption of polythionates ($S_nO_6^{2-}$ where n≥3) onto the gold surface. Residual thiosulfate and its byproducts in leach circuits may suppress downstream flotation. Thiosulfate alters the characteristics of mineral surfaces, resulting in decreased flotation recovery (Öztürk et al., 2018). Additionally, thiosulfate ions can react with dissolved ions from mineral surfaces, forming more stable complexes than those produced with metal xanthates (Bulatovic, 2007). This competition reduces collector adsorption, ultimately leading to a decrease in mineral recovery.

Typical methods for treating thiosalts involve oxidation using hydrogen peroxide and/or ferric sulfate (Range and Hawboldt, 2019). Sulfate removal can be achieved through various technologies such as electrodialysis, adsorption, reverse osmosis, and chemical precipitation (Environmental, 2003). While chemical precipitation is the least costly, it is slow and generates significant waste. Adsorption effectively reduces sulfate concentrations to low levels (Reynolds and Richards, 1996). Ion exchange resins can also remove sulfate, but they require substantial chemicals and produce waste during regeneration (Ozturk and Ekmekci, 2020). Thiocyanate can be treated using several physicochemical and biological techniques (Gould et al., 2012), with common chemical methods including precipitation, wet oxidation, and ozone oxidation. However, these chemical methods can be expensive and produce by-products (Watts and Moreau, 2016; Wang et al., 2020).

Electrochemical treatment technologies have emerged as effective methods for removing thiocyanate and thiosalts from mining and metallurgical effluents. These technologies offer several advantages, including compact size, chemical selectivity, broad applicability, and reduced generation of secondary waste (Alkhadra et al., 2022). Electrooxidation using a boron doped diamond anode **is a** highly effective and cost-efficient method for treating thiocyanate-contaminated industrial effluents (Turan et al., 2020). Additionally, electrochemical advanced oxidation using carbon electrodes presents a promising, environmentally friendly solution for thiocyanate removal from gold mining effluent, especially at low concentrations (Ozturk, 2024). Furthermore, the integration of electro-oxidation with ion exchange offers a scalable and cost-effective approach for managing thiocyanate and thiosalts in gold mining operations (Baker et al., 2024).

In recent years, Capacitive Deionization (CDI) has emerged as a robust, energy efficient, and cost effective technology for desalinating low to medium salinity water (Anderson et al., 2010). It operates on the principle that ions move towards porous electrodes when low potentials (< 1.5 V) are applied (Oren, 2008). It is a two-phase water treatment process. The first phase involves an ion electro-sorption process that adsorbs ions on pairs of carbon electrodes to desalinate water. The second phase involves

regenerating the electrodes by releasing the adsorbed ions (Porada et al. 2013). The membrane capacitive deionization (MCDI) process is a modification of the CDI process utilizing ion-exchange membranes. Membranes are placed in front of the electrodes. During operation, the membranes prevent co-ions from leaving the electrode region during adsorption, improving the salt adsorption capacity (Biesheuvel and Van der Wal, 2010).

This study investigated the removal of SO₄²⁻, S₂O₃²⁻, and SCN- by membrane capacitive deionization process. An electrochemical cell was assembled using carbon paper as both the anode and cathode electrodes, with ion exchange membranes placed in front of the carbon paper. Batch experiments with single salt solutions were conducted to determine the adsorption capacity of the electrodes for each ion at operating voltages of 0 V and 1.2 V. The process efficiency for mixed salt solution was also studied. In addition, regeneration of the electrodes was carried out by reversing the operational voltage to -5.0 V. A single-pass MCDI experiment was conducted over eight adsorption/desorption cycles. The electro-oxidation process was examined in a mixed salt solution containing all ions. The removal efficiency was evaluated by total salt removal (SR) and salt removal efficiency (SRE%).

2. Materials and methods

2.1. Materials

Carbon paper (Sigracet GDL 39AA) was obtained from SGL Carbon. It has a total thickness of 280 µm. Anion exchange membrane (AEM Type 10, exchange capacity: 1.8 meq/g) was obtained from Fuji Film. Cation exchange membrane (CEM, exchange capacity: 2.0 meq/g) was supplied by Shanghai Shanghua.

Analytical grade chemicals were used to prepare the salt solutions. Ammonium thiocyanate (NH₄SCN) was obtained from Carlo Erba. Sodium thiosulphate (Na₂S₂O₃.5H₂O) was purchased from Sure Chem. Sodium sulfate (Na₂SO₄) was provided by Merck. Deionized water (Heal Force Smart) was used throughout the study.

2.2. Desalination experiments

Schematic representation of bench-scale membrane capacitive deionization test setup is given in Fig. 1. The feed solution was pumped with a peristaltic pump (Cole Parmer, Masterflex) through a flow by type capacitive deionization cell. A potential was applied by using a potentiostat (Gamry PCI-4750) during process.

The MCDI cell consisted of two electrodes: an AEM placed on top of carbon paper as the anode, and a CEM placed on top of carbon paper as the cathode. A titanium sheet was used as a current collector. The sizes of current collectors and electrodes were 10X50 mm. The electrodes were separated from each other by a nylon separator. In all experiments, the flow rate of the solution was maintained at 1.5 mL per minute.

Batch mode experiments were performed to determine the removal efficiency of SO_4^{2-} , $S_2O_3^{2-}$, and SCN- by membrane capacitive deionization method. 25 ml sulfate solution at various concentrations; 30 mg/L, 100 mg/L, and 200 mg/L was recirculated through the MCDI test setup for 3 hours at 0 V.

Single salt solutions containing 200 mg/L of SO_4^{2-} , $S_2O_3^{2-}$, and SCN- with a volume of 25 ml were recycled through the test setup at 0 V and 1.2 V for 3 hours to observe the effect of voltage on desalination performance.

Treatment of 25 mL of a mixed salt solution including 100 mg/L of SO_4^{2-} , $S_2O_3^{2-}$, and SCN^- was carried out at 1.2 V for 3 hours at a flow rate of 1.5 ml/min. Concentration of residual ions was measured using ion chromatography (IC, Dionex ICS 3000) at various time intervals during the process. For the regeneration of the electrodes, treated water produced from mixed salt solution test was recirculated through the system at an operating voltage of -5.0 V at a flow rate of 1.5 ml/min for 1 hour.

An adsorption/desorption cycle test was conducted by continuously pumping a mixed salt solution containing 10 mg/L of SO_4^{2-} , $S_2O_3^{2-}$, and SCN^- . The test was performed at an applied voltage of 1.2 V for adsorption and -5 V for desorption for 30 minutes, with a flow rate of 1.5 mL/min. The effluent water sample was collected at the exit of the MCDI cell for chemical analysis. The electro-oxidation test was conducted to treat a mixed salt solution containing 7.5 mg/L of SO_4^{2-} , $S_2O_3^{2-}$, and SCN^- . The applied

potential was set to 5 V, with a flow rate of 1.5 ml/min. Effluent samples were collected for chemical analysis at various time intervals.

The surface morphology of the anode electrode was characterized by scanning electron microscopy (SEM, TESCAN, GAIA3, Triglav, Brno, Czech Republic).



Fig. 1. Schematic representation of membrane capacitive deionization test setup

Process efficiency, measured in the batch-mode, was determined by of total salt removed (SR_B, mg/m² (eq14)) and salt removal efficiency % (SRE_B %, (eq15)).

$$SR_B = \frac{(C_i - C_f)V}{A_e} \tag{14}$$

$$SRE_B[\%] = \frac{(c_i - c_f)}{c_i} \times 100\%$$
(15)

Removal performance, measured in the single-pass mode, was evaluated by total salt removal (SR₅, mg/m^2 (eq16)) and salt removal efficiency (SRE₅ % (eq17)) (Zuo et al. 2018).

$$SR_S = \frac{Q \int_0^t (C_i - C_f) dt}{A_e} \tag{16}$$

$$SRE_{S}[\%] = \frac{\int (C_{i} - C_{f})d_{t}}{C_{i}t} \times 100\%$$
(17)

where, Q (L/s): the flow rate, C_i (mg/L): the initial concentration and C_f (mg/L): the final concentration; t (s): the time; Ae (m²): the area of the anode: V: volume (L).

3. Results and discussion

3.1. Batch mode MCDI

3.1.1. Single salt solution studies

Batch recirculation tests of sulfate solutions at varying concentrations of 30 - 100 - 200 mg/L with a fixed volume of 25 mL were conducted at a constant flow rate of 1.5 mL/min for 3 hours without applying voltage. The concentration of residual sulfate was continuously measured throughout the process to determine the maximum level of adsorption achieved at 0 V.

Fig. 2 presents the total sulfate removal per unit electrode area as a function of time during the operation. The results indicate a clear relationship between concentration and adsorption, with higher initial sulfate levels leading to increased total removal capacities.

At an initial concentration of 200 mg/L, the highest adsorption performance was achieved, resulting in a total sulfate removal of approximately 5600 mg/m². Most of the removal occurred within the first 60 minutes, indicating a rapid initial uptake, likely due to a steep concentration gradient and high availability of accessible surface sites. After 60 minutes, the adsorption rate started to decrease, and the removal of sulfate reached a plateau between 120 and 150 minutes. This indicates that the available surface sites became increasingly occupied, resulting in a slower diffusion of sulfate ions into micropores or less accessible adsorption sites (Tejada-Tovar et al., 2021).

Lower initial sulfate concentrations of 30 and 100 mg/L resulted in significantly reduced total adsorption, plateauing at approximately 500 mg/m² and 3500 mg/m², respectively. At the 30 mg/L concentration, the flat profile suggests that the electrode's maximum capacity was not utilized. This may be due to the limited number of available ions and an inadequate concentration gradient, which hinders deeper pore penetration.



Fig. 2. Total sulfate removal at varying concentrations in a 25 ml solution at 0 V with a flow rate of 1.5 mL/min

The applied potential is a crucial operating parameter in Membrane Capacitive Deionization (MCDI) because it directly drives the electrosorption of ions. This parameter significantly affects ion removal efficiency, and energy consumption (Jiang et al., 2022). In this phase of the study, the impact of voltage on desalination efficiency was investigated by applying 0 V and 1.2 V to 200 mg/L single salt solutions of SO_4^{2-} , $S_2O_3^{2-}$, and SCN⁻. The solutions were pumped at a rate of 1.5 mL per minute for 3 hours. A comparison was conducted to assess the total salt removal for each ion at both 0 V and 1.2 V voltages.

The results are presented in Fig. 3 for the SO_4^{2-} ion, Fig. 4 for the $S_2O_3^{2-}$ ion, and Fig. 5 for the SCNion. The data indicated a significant increase in sulfate removal from 5600 mg/m² to 8600 mg/m² when the potential is applied, as shown in Fig. 3. In addition, thiosulfate removal was enhanced from 7800 mg/m² to 9850 mg/m² (Fig. 4), and thiocyanate levels increased from 6150 mg/m² to 9350 mg/m² (Fig. 5). These findings clearly indicate that applying an external voltage significantly enhances the removal efficiency for all three anions.

The results also reveal that the removal efficiency for thiosulfate is higher than that for sulfate and thiocyanate ions. This increased removal efficiency for thiosulfate can be attributed to its greater anisotropic polarizability (Reichenbach and Wynne, 2018), which enhances the electrostatic interaction with the positively charged electrode (anode) when a voltage is applied (Islam et al., 2021).



Fig. 3. Total sulfate removal from a 25 ml, 200 mg/L sulfate solution at 0 V and 1.2 V with a flow rate of 1.5 mL/min



Fig. 4. Total thiosulfate removal from a 25 ml, 200 mg/L thiosulfate solution at 0 V and 1.2 V with a flow rate of 1.5 mL/min



Fig. 5. Total thiocyanate removal from a 25 ml, 200 mg/L thiocyanate solution at 0 V and 1.2 V with a flow rate of 1.5 mL/min

3.1.2. Mixed salt solution studies

The batch experiment of a mixed salt solution containing 100 mg/L SO_4^{2-} , 100 mg/L $S_2O_3^{2-}$, and 100 mg/L SCN⁻ was performed to investigate the impact of co-ions on the removal efficiency. For this purpose, a 25 ml solution was pumped with a flow rate of 1.5 ml/min at an operating voltage of 1.2 V for 3 hours.

The total salt removal of each ion is presented in Fig. 6. The results showed that the electro-sorption of sulfate and thiocyanate reached an equilibrium state after 60 minutes of operation. The total salt removal was 2600 mg/m² for sulfate and 3150 mg/m² for thiocyanate. In contrast, thiosulfate demonstrated a higher salt removal of 5350 mg/m². Overall, the electrode removed a total of 11100 mg/m² of salt throughout the process.

Fig. 7 illustrates the salt removal efficiency percentages of the ions. The results indicated that the electrodes removed 57% of sulfate and thiocyanate, as well as 88% of thiosulfate within 3 hours of operation.

3.1.3. Regeneration of the electrodes

When the electrodes reached their maximum adsorption capacity, the potential is reversed to facilitate the desorption of the adsorbed ions, resulting in the regeneration of the electrodes. For this purpose, 25 ml of treated water obtained from the mixed salt solution experiment was recirculated through the MCDI test setup at an operational voltage of -5 V with a flow rate of 1.5 ml/min for 1 hour.



Fig. 6. Total salt removal from a 25 ml mixed salt solution containing 100 mg/L SO₄²⁻, S₂O₃²⁻, SCN- at 1.2 V with a flow rate of 1.5 mL/min



Fig. 7. Salt removal efficiency % of 25 ml mixed salt solution containing 100 mg/L SO₄²⁻, S₂O₃²⁻, SCN- at 1.2 V with a flow rate of 1.5 mL/min

The amount of adsorbed and desorbed ions in the electrosorption and desorption phases are compared in Fig. 8. The results indicate that the electrodes adsorbed 2600 mg/m^2 of sulfate during the electrosorption phase, while 2400 mg/m^2 was desorbed in the desorption phase, leading to a recovery of 92%. In contrast, 750 mg of thiosulfate and 900 mg of thiocyanate were recovered during the desorption phase, resulting in recoveries of 14% and 28%, respectively. This lower recovery for thiosulfate and thiocyanate may be due to their oxidation to sulfate at a voltage of 5 V during the desorption stage. Overall, the electrodes desorbed 36.5% of the total adsorbed ions during the desorption process.

3.1.4. Single-pass mode MCDI

In single-pass mode, feed water continuously flows through the MCDI cell. It operates in stages of charging and discharging, during which ions are adsorbed and desorbed as the feed water moves through the cell (Porada et al., 2013). A single pass allows for higher flow rates and is more suitable for larger scale applications where the feed is not continually recirculated (Elewa et al., 2023).

In this part of the study, a mixed salt solution containing 10 mg/L of SO_4^{2-} , $S_2O_3^{2-}$, SCN^- was continuously pumped through the MCDI cell at a flow rate of 1.5 mL/min. The process was carried out continuously for eight adsorption/desorption cycles, each lasting 30 minutes. The applied voltage was set at 1.2 V during the adsorption phase and -5 V during the desorption phase. Effluent samples were collected for chemical analysis at 5-minute intervals.

The concentration changes of each ion during the final cycle are illustrated in Fig. 9. At the beginning of the adsorption phase, concentrations of thiosulfate, and thiocyanate were approximately 4.5 mg/L, which is lower than the initial concentration of the 10 mg/L. This indicates that the electrode continued to remove these ions during the desorption phase of the previous cycle. The removal efficiency of thio-



Fig. 8. Amount of adsorbed and desorbed ions in the electro-sorption and desorption phases

sulfate was greater than that of the other ions, as determined in Section 3.1.2. By the end of the adsorption phase, the concentration of thiosulfate decreased to 2.79 mg/L, while the concentration of thiocyanate remained around 4 mg/L. After 30 minutes of adsorption, the electrodes removed 539.6 mg/m² of thiosulfate and 510.5 mg/m² of thiocyanate, resulting in salt removal efficiencies of 60 ±0.9 % and 57 ±1.2 %, respectively.

In contrast, at the beginning of the adsorption stage, the concentration of sulfate was 14 mg/L, which is greater than the initial concentration of 10 mg/L. This increase can be attributed to the release of sulfate ions during the desorption phase of the previous cycle. The removal efficiency of sulfate was lower than that of the other ions. At the end of the 30-minute adsorption phase, the sulfate concentration decreased to 8.35 mg/L. A total of 202.5 mg sulfate was removed per m² of the electrode, resulting in a salt removal efficiency of 23 \pm 1.1%.

During the desorption phase, the concentration of thiosulfate decreased from 2.79 mg/L to 0.23 mg/L, and the concentration of thiocyanate decreased from 4.23 mg/L to 2.78 mg/L in the first 5 minutes. By the end of the 30-minute desorption phase, 719 mg/m² of thiosulfate and 643 mg/m² of thiocyanate had been removed, resulting in salt removal efficiencies of 80% for thiosulfate and 71% for thiocyanate. On the other hand, the concentration of sulfate began to increase, reaching 14 mg/L by the end of the desorption phase. This increase can be attributed to the electro-oxidation of thiosulfate and thiocyanate to sulfate (Ozturk, 2024).



Fig. 9. Concentration change of SO₄²⁻, S₂O₃²⁻, and SCN- during the final adsorption/desorption cycle

3.1.5. Electro-oxidation studies

The electro-oxidation process involves oxidizing pollutants within an electrolytic cell through reactions with hydroxyl radicals (•OH) generated at the anode surface (Martinez-Huitle and Brillas, 2009). The results presented in Section 3.1.4 demonstrate the electro-oxidation of thiosulfate and thiocyanate at a voltage of 5 V. To investigate this process, a mixed salt solution containing 7.5 mg/L of thiocyanate, thiosulfate, and sulfate was continuously pumped at a rate of 1.5 mL per minute for 240 minutes, maintaining an operating potential of 5 V. Effluent samples were collected for chemical analysis at various time intervals.

The concentration changes of each ion during the process are presented in Fig. 10. The results clearly indicate that the electrode effectively removed all ions within the first 150 minutes of operation. The concentrations of thiosulfate and thiocyanate decreased from 7.5 mg/L to 3.25 mg/L within the first 5 minutes but then slightly increased to around 4 mg/L for the remainder of the operation. The continuous removal of thiosulfate and thiocyanate can be attributed to the electro-oxidation of these ions at the electrode interface. In contrast, the electrode achieved its maximum sulfate adsorption capacity within the first 150 minutes, resulting in an increase in concentration due to the release of sulfate from electro-oxidation process, which reached 11.67 mg/L by the end of the operation.

Fig. 11 illustrates the salt removal efficiency percentage of ions during the electro-oxidation process. The electrode effectively removed approximately 50% of thiosulfate and thiocyanate within the first 30 minutes. However, the salt removal efficiency (SRE%) declined to 31% by the end of the 4-hour operation. In contrast, the removal efficiency for sulfate was lower than that for the other ions, reaching around 30% initially, but then decreasing to 2.6% after 150 minutes.





Fig. 10. Concentration change of SO₄²⁻, S₂O₃²⁻, and SCN⁻ during electro-oxidation process

Fig. 11. Salt removal efficiency % of SO42-, S2O32-, and SCN- during electro-oxidation process

The surface morphology of the anode electrode was examined using scanning electron microscopy (SEM) both before and after the electro-oxidation test. As shown in Fig. 12a, the images clearly demonstrate that the electrode before treatment displays loosely stacked, flake-like structures with high inter-particle porosity. In contrast, Fig. 12b shows a denser packing and reduced inter-layer spacing, indicating structural changes due to the adsorption of ions that bridge or compress the layers after treatment.



Fig. 12. SEM images of the carbon electrode surface before (a) and after (b) electro-oxidation test

4. Conclusions

The results obtained from this study were summarized below:

- During the electro-sorption process, 8600 mg of SO₄²⁻, 9850 mg of S₂O₃²⁻, and 9350 mg of SCN- were removed per square meter of the electrode. This was achieved by recirculating 25 mL of 200 mg/L single salt solutions of each ion at a flow rate of 1.5 mL per minute and applying a voltage of 1.2 V for 3 hours.
- 2600 mg/m² sulfate, 3150 mg/m² thiocyanate, and 5350 mg/m² thiosulfate were removed from 25 ml of the mixed salt solution containing 100 mg/L of SO₄²⁻, S₂O₃²⁻, and SCN⁻ at 1.2 V for 3 hours. SRE% was determined to be 57% for SO₄²⁻, 57% for SCN⁻, and 88% for S₂O₃²⁻.
- Regeneration studies were performed by recirculating the treated water produced from mixed salt solution at a flow rate of 1.5 ml/min at an operating voltage of -5.0 V for 1 hour. The electrodes were regenerated with a recovery of 92% of SO₄²⁻, 14% of S₂O₃²⁻, and 28% of SCN⁻.
- The single-pass MCDI test showed that the electrode removed 539.6 mg/m² of thiosulfate, 510.5 mg/m² of thiocyanate, and 202.5 mg/m² of sulfate, corresponding to removal efficiencies of 60%, 57%, and 23%, respectively, during the adsorption phase.
- During the desorption phase, the electrode successfully desorbed 252 mg of sulfate per square meter of electrode surface. However, thiosulfate and thiocyanate were still being removed, with removal efficiencies of 80% and 71%, respectively. This suggests that electro-oxidation of these compounds occurs at a high operational potential of 5 V.
- The electro-oxidation studies demonstrated the oxidation of thiocyanate and thiosulfate to sulfate. The electrode reached its maximum adsorption capacity for sulfate within 150 minutes of operation, after which the amount of sulfate in the effluent began to increase gradually. In contrast, thiosulfate and thiocyanate were continuously removed throughout the four hours of operation, with the SRE% decreasing from 50% to 31% by the end of the period.
- The study highlights the potential of MCDI for the treatment of gold mining process water. However, further research is needed to evaluate its efficiency. Operating parameters such as adsorption/desorption cycle times, applied voltage, and flow rate in the single pas mode operation

should be investigated. In addition, the long-term performance and stability of the electrodes should be monitored to assess their overall effectiveness.

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