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Bismuth as a desalination electrode material

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Abstract

Addressing freshwater scarcity and the energy demands of desalination, capacitive deionization (CDI) offers an energy-efficient solution for brackish water treatment by applying low voltages (~ 1.2 V) to capture ions on charged electrodes. Conventional carbon-based CDI, however, is limited to low salt removal capacities (~ 15 mg/g). To enhance performance, hybrid-CDI with Faradaic electrodes, such as bismuth (Bi) nanopowders, is explored for high-capacity, cost-effective chloride capture, and possible desalination of the seawater. This study investigates two morphologically different Bi nanopowder electrodes in 0.1 M NaCl, revealing a sequential electrochemical mechanism - Bi to Bi_2O_3 , BiOCl , and $\text{BiCl}(\text{OH})_2$. Both samples exhibit near-reversible oxide formation, diffusion-controlled oxychloride production, and surface-confined hydroxylated oxychloride formation, though cathodic irreversibility poses challenges for complete film reduction. These findings highlight Bi electrodes' potential for sustainable CDI desalination, with given morphology and purity offering significant advantages

Keywords: Capacitive deionization, desalination, bismuth.

CERCS: P401

Vismut kui magestamise elektrodmaterjal

Lühikokkuvõte

Magevee nappuse ja merevee magestamise energiavajaduse leevendamiseks pakub mahtuvuslik deionisatsioon (CDI) energiatõhusat lahendust riimvee puhastamiseks, kasutades madalaid pingeid ($\sim 1,2$ V) ionide püüdmiseks laetud elektrodidele. Traditsiooniline süsinikupõhine CDI on aga piiratud madala soolaeemaldusvõimega (~ 15 mg/g). Jõudluse parandamiseks uuritakse Faradaic-tüüpi elektrodidega hübriid-CDI süsteeme, näiteks vismuti (Bi) nanopulbreid, mis võimaldavad suurema mahutavuse ja kulutõhususega kloriidide sidumist, ning võivad leia aset merevee desalineerimisel. Käesolev uuring käsitleb kahte elektrokeemiliselt sadestatud ja morfoloogiliselt erinevat Bi nanopulberelektroodi 0,1 M NaCl lahuses, tuvastades järjestikuse elektrokeemilise mehhanismi – Bi muundumine Bi_2O_3 -ks, seejärel BiOCl -ks ja $\text{BiCl}(\text{OH})_2$ -ks. Mõlemad proovid näitavad peaaegu pöörduvat oksiidi moodustumist, difusioonist sõltuvat oksükloriidi tekkimist ning pinnaga seotud hüdroksüülitud oksükloriidi moodustumist. Samas esitab katoodne pöördumatus väljakutseid kile täielikule redutseerumisele. Arvestades valitud morfoloogiat ja puhtust, näitavad tulemused Bi elektrodide olulist potentsiaali säästvaks CDI-tehnoloogiaks ning aitavad paremini mõista Cl^- sidumist Bi elektrodidega magestamisrakendustes.

Võtmesõnad: Mahtuvuslik deioniseerimine, magestamine, vismut.

CERCS: P401

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ABBREVIATIONS

CDI – Capacitive Deionization

CV – Cyclic Voltammetry

DC - Direct current

DHBT – Dynamic Hydrogen Bubble Template

EDS – Energy Dispersive X-ray Spectroscopy

EIS - Electrochemical Impedance Spectroscopy

MCDI – Membrane Capacitive Deionization

RO – Reverse Osmosis

SEM - Scanning Electron Microscopy

INTRODUCTION

Water scarcity is a critical global challenge expected to intensify in the coming years without significant intervention. According to the World Health Organization, as of 2020, two billion people lacked access to safely managed clean water services [1]. Freshwater constitutes only 2.5% of the Earth's water resources, with much of it locked in glaciers or deep groundwater reserves. Seawater and brackish water, which are abundant, contain high salt concentrations approximately 3.5% NaCl in seawater and 1–3% NaCl in brackish water rendering them unsuitable for direct use [2]. Desalination technologies offer a viable solution to reduce salt levels and address freshwater shortages, particularly in water-scarce regions such as Africa, Asia, and the Middle East. Currently, reverse osmosis (RO) and thermal desalination dominate the market, accounting for 60% and 34% of global desalination capacity, respectively. However, these methods are energy-intensive, with RO requiring 3–4 kWh/m³ and thermal desalination consuming 5–60 kWh/m³ [3]. With the United Nations projecting that desalination may be essential for 14% of the global population by 2025, there is an urgent need for sustainable, energy-efficient alternatives [4].

The growing demand for clean water aligns with the United Nations' Sustainable Development Goal 6, which aims to ensure the availability and sustainable management of water and sanitation for all by 2030. Conventional desalination technologies, while effective, pose challenges due to their high energy consumption and environmental impacts, such as brine discharge and greenhouse gas emissions. Electrochemical desalination methods, which leverage electrical energy to separate ions, present a promising pathway toward sustainability. These technologies can potentially integrate with renewable energy sources, reducing reliance on fossil fuels, and their modular design supports decentralized applications, benefiting remote or underserved communities.

Among these emerging technologies, bismuth (Bi) has gained attention as a cost-effective and efficient electrode material for desalination. Unlike expensive alternatives like silver, Bi offers a high theoretical chloride storage capacity of 279.7 mg/g and can reversibly form BiOCl during the desalination process, enabling selective chloride ion capture [5]. This reversible electrochemical conversion between Bi and BiOCl enhances the material's potential for repeated

use, improving both sustainability and cost-effectiveness. The ability to tailor Bi's properties, such as surface area and morphology, further positions it as a candidate for advancing desalination performance.

This thesis explores the practical promise of bismuth electrodes in sustainable desalination applications. The study focuses on synthesizing two distinct bismuth nanopowders via electrochemical deposition and investigating the electrochemical conversion between Bi and BiOCl in a controlled environment. Through systematic electrochemical measurements, we aim to assess the chloride uptake mechanism and its kinetics. By elucidating the performance of bismuth-based electrodes, this work seeks to contribute to the development of efficient, scalable, and environmentally friendly desalination technologies, addressing the pressing global need for accessible clean water.

1 LITERATURE REVIEW

1.1 Bismuth metal

Bismuth is significantly less expensive than silver (approximately \$8.8/kg for Bi versus \$553/kg for Ag as of 2016), making Bi-based chloride-storage electrodes a cost-effective alternative for practical large-scale desalination cells [5]. Moreover, Bi and BiOCl are insoluble under saline aqueous conditions across a wide range of pH and potential, ensuring their sustainable operation in seawater. Other potential benefits under exploration include:

- Nanostructuring and morphology optimization: this involves developing porous bismuth structures and reducing the size of Bi crystals, which can expand the interfacial area and enhance Cl^- diffusion, thereby maximizing the conversion of Bi to BiOCl. For example, electrodeposition can produce nanocrystalline Bi foam electrodes featuring nanoscale, needle-like dendrites that significantly increase surface area [5].
- Composite formation with carbon materials: embedding Bi nanoparticles within porous carbon frameworks can improve charge transfer, ion diffusion, and the availability of electroactive sites, resulting in higher desalination capacities and accelerated reaction rates. For instance, a nitrogen-doped porous carbon matrix (Bi/N-PC) offers high conductivity, superior hydrophilicity, and robust structural stability. This carbon framework also helps suppress phase transformation-induced degradation in bismuth, enhancing overall electrode conductivity [6].
- Limiting the extent of conversion: intentionally restricting the conversion of Bi to BiOCl can improve the electrode's cyclability. The electrode maintains its integrity and performance over repeated cycles by preserving a core region of Bi that serves as the "stem" for the dendritic structure [5].

The electrochemical conversion between Bi and BiOCl involves the following reactions:

Anodic oxidation (desalination):



Cathodic reduction (regeneration):



This reversible process allows for the repeated use of the electrode material, enhancing the sustainability and cost-effectiveness of the desalination system.

1.2 Desalination methods

Distillation, which involves boiling seawater in a still, capturing the steam, and condensing it to produce fresh water, is the most straightforward method for salt removal. However, it is not the most efficient approach due to its high energy consumption. Below is an overview of the primary desalination methods currently in use:

- The reverse osmosis desalination method is the most widely used process and is more energy-efficient compared to other methods. It relies on semipermeable membranes that allow water molecules to pass through while blocking salt. These membranes, typically made of ultra-thin polyamide, are prone to bacterial contamination, so the water must be pre-treated [7].
- Solar Distillation method mimics the natural water cycle by evaporating seawater in large facilities with roof structures where the vapor condenses and is collected as fresh water. While it utilizes solar energy, it requires a significant land area to operate effectively [8].
- Nanofiltration method employs nanotube membranes with higher permeability than those used in reverse osmosis, enabling more water to be processed in a smaller space with reduced energy consumption. These membranes, made from sulfonated compounds, not only remove salt but also filter out traces of pollutants [9].
- The electrodialysis technique involves passing saltwater through electrically charged membranes that capture dissolved salt ions, allowing fresh water to be extracted. There are several variations of electrodialysis, including conventional and reverse methods [10].
- Gas hydrate formation is a method where solid crystals are formed by combining water with a gas, such as propane, under high pressure and low temperatures. During this process, salts and impurities are removed from the water. As the temperature rises, the gas can be recovered, leaving behind fresh water [11].

1.2.1 Advantages and disadvantages of desalination

Desalination is becoming increasingly essential as global freshwater resources decline. According to a UN study published in the journal *Science of the Total Environment*, when combined with responsible water management, desalination could play a crucial role in addressing future water scarcity, despite certain drawbacks that must be acknowledged [11].

However, the desalination process is not without environmental consequences. A significant byproduct is brine, a highly concentrated wastewater containing salt and pollutants. In many cases, this brine is discharged into the ocean, posing risks to marine ecosystems. The study highlighted that approximately 142 million cubic meters of brine are released daily [11]. Additionally, there is a potential risk of brine seepage, which could contaminate coastal aquifers and further impact the environment [7].

1.2.2 Capacitive deionization

Capacitive Deionization (CDI) is an electrochemical desalination technology that removes dissolved ions, such as salts or charged contaminants, from aqueous solutions using porous electrodes [12]. When an electrical potential is applied across two electrodes (typically carbon-based), ions are temporarily adsorbed onto the electrode surfaces through electrosorption, forming electric double layers. The process is energy-efficient compared to conventional methods like reverse osmosis, as it operates at low voltages and enables electrode regeneration by reversing or removing the voltage, releasing the ions back into a waste stream [13]. CDI is particularly promising for brackish water desalination, wastewater treatment, and resource recovery due to its scalability, cost-effectiveness, and reduced environmental footprint [14]. Despite these advantages, CDI and its variant, membrane CDI (MCDI), remain confined mainly to laboratory-scale applications [14]. A significant limitation is the low desalination efficiency, primarily due to the limited salt-removal capacity of capacitive electrodes. State-of-the-art activated carbon electrodes, for instance, typically achieve electrosorption values of only 10–15 mg/g [14]. To enhance CDI performance, electrode materials must exhibit a high specific surface area, optimal pore size, hierarchical porous structure, hydrophilicity, and conductivity [15], [16]. Additionally, conventional CDI systems are constrained to low salt concentrations, typically below 25 mM (~1.5 g/L), due to reduced charge efficiency at higher brine

concentrations [3]. These challenges underscore the need for advanced electrode materials with superior salt-removal capabilities.

Hybrid CDI addresses these limitations by incorporating Faradaic electrodes to boost capacity and energy efficiency. For example, silver/silver-chloride electrodes can achieve high chloride uptake at low voltages, but the high cost of silver and poor conductivity of AgCl hinder practical use [3]. Bismuth (Bi), a more affordable alternative, has emerged as a promising candidate due to its high theoretical Cl^- storage capacity of 279.7 mg/g [5]. Bi can reversibly form BiOCl during desalination, selectively capturing Cl^- ions (Equations 1 and 2). This reversible electrochemical conversion makes Bi a strong candidate for sustainable and cost-effective desalination applications.

1.3 Metal electrodeposition

The dynamic hydrogen bubble template (DHBT) method was utilized by electrochemically depositing metal foams using co-generated hydrogen bubbles as templates [17]. Hydrogen evolution is typically seen as a problem during metal deposition, but DHBT turns this into an advantage by using the formed hydrogen bubbles to create spongy, high surface area metal foams. This method produces open porous structures with extremely high surface areas, allowing for rapid transport of gases and liquids. The resulting metal foams exhibit intrinsically high electrical conductance and contain pores that act as confined reaction spaces, potentially enabling reactions that would not occur at an open electrode interface. Additionally, the size, distribution, and number of pores can be tuned by carefully selecting electrolysis parameters. The fabrication of these metal foams is driven by two main reactions: metal deposition from a solution of its salt and the hydrogen evolution reaction [17].

1.4 Cyclic voltammetry

Cyclic voltammetry is one of the most fundamental and widely used electrochemical techniques for analyzing electrochemical materials and the processes occurring at electrochemical interfaces. Beyond the valuable data it provides, this method highlights two crucial aspects: the structural condition of the electrode surface (including single-crystal characterization) and the detection of impurities within the studied system [18].

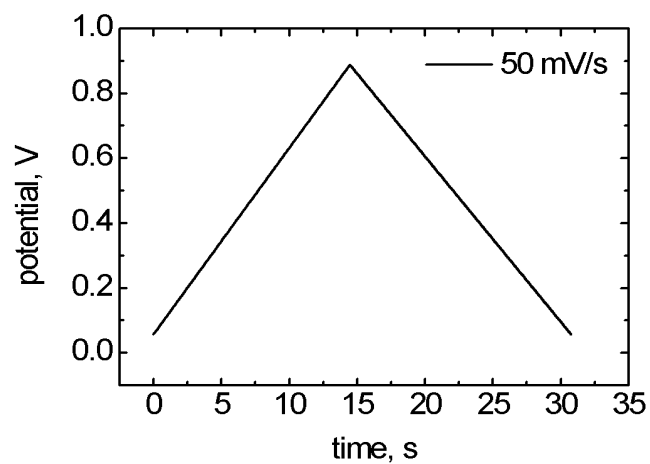


Figure 1. Triangular signal applied in cyclic voltammetry.

This technique consists of recording the current that circulates through the working and counter electrodes when a constant rate potential sweep is applied. The potential sweep is linear in the time scale, which is achieved by introducing a triangular signal, whose slope (in absolute value) represents the scanning rate, ν , (Fig. 1.).

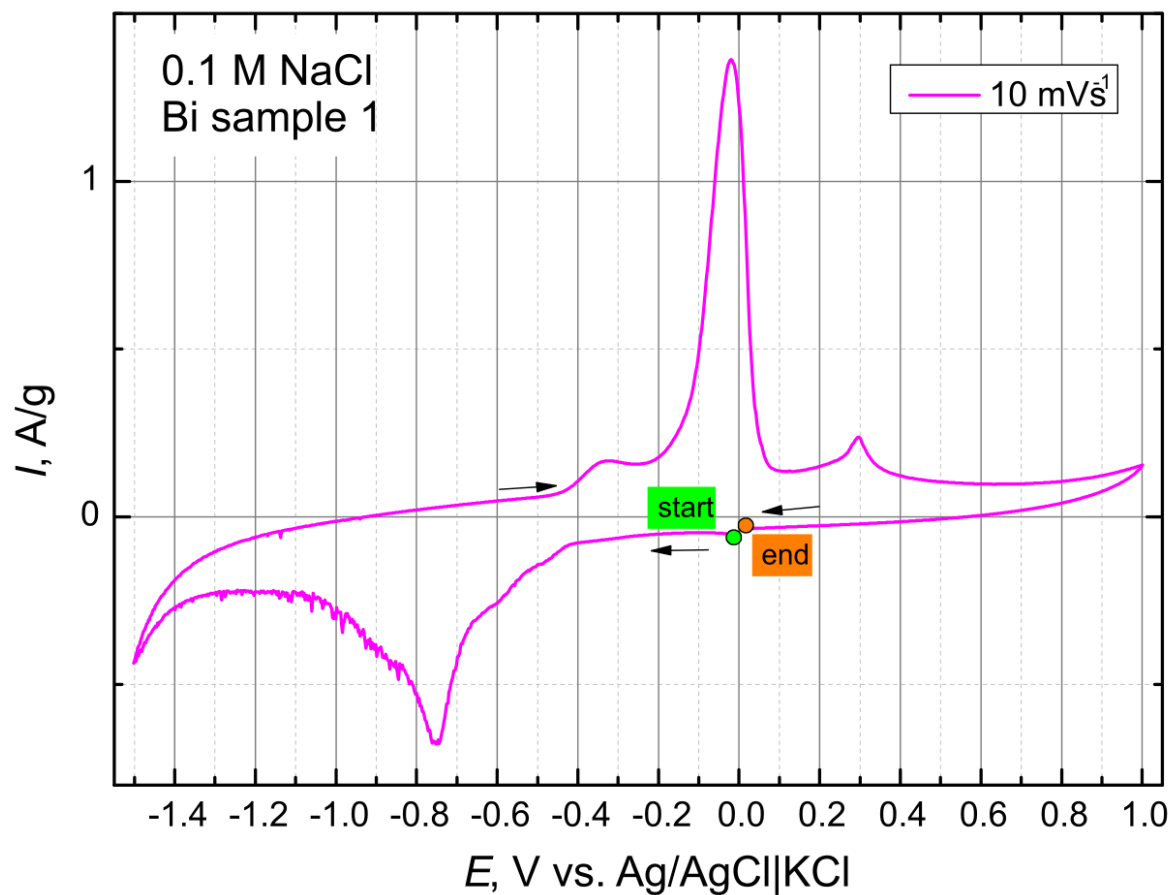


Figure 2. Cyclic voltammogram for Bi powder electrode measured in 0.1 M NaCl aqueous electrolyte at $\nu = 10 \text{ mV} \cdot \text{s}^{-1}$, arrows show a direction of scan.

The representation of current density (I) as a function of potential (E) is known as a voltammogram (Fig. 2.), where the current is normalized by weight - A/g. Various electrochemical processes occurring at the electrode are identified through the presence of oxidation or reduction peaks in the current vs. potential plot. For irreversible reactions with complex mechanisms, these may appear as broad waves. The current peak corresponds to the process occurring at the electrode, while the shape of the voltammetric waveform (or peak) provides insights into the nature and kinetics of the reaction initiated by the applied potential scan [18]. Here, a major cathodic peak corresponds to the reduction of BiOCl to Bi, while an anodic peak indicates the oxidation of metallic Bi to BiOCl .

Electrode processes are generally classified into two major categories: adsorption-controlled and diffusion-controlled processes. In adsorption-controlled processes, the current peak is directly proportional to the applied sweep rate, and the charge transferred during the potential sweeps offers information about the surface coverage of adsorbed species [18], [19].

In contrast, diffusion-controlled processes exhibit a peak current that is proportional to the square root of the potential sweep rate, allowing differentiation from adsorption-controlled mechanisms. Additionally, the waveform shape reflects the kinetics of the redox reaction occurring at the electrode surface [18], [19].

1.5 Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is a versatile imaging technique that employs a focused beam of electrons to analyze the surface of a sample, providing detailed information on surface topography, crystalline structure, chemical composition, and electrical behavior within the top 1 μm or so of the specimen. The electron beam interacts with the sample, generating signals such as secondary electrons, backscattered electrons, and cathodoluminescence, which are used to create high-resolution images. SEM can be equipped with specialized stages, such as hot, cold, or mechanical testing stages, enabling the examination of material behavior under various conditions. For instance, cathodoluminescence (the emission of light) is significantly stronger at temperatures near absolute zero compared to room temperature, resulting in less noisy images when imaging cold specimens. One of the key advantages of SEM over optical microscopy is its large depth of field, which ensures that most of the specimen surface remains in focus regardless of surface roughness. In contrast, optical microscopes operating at high magnification have a very small depth of field, limiting their ability to image uneven surfaces effectively. Additionally, SEM offers superior resolution and magnification, making it an indispensable tool in fields such as materials science, nanotechnology, and biology for studying the micro- and nanoscale features of specimens [20].

1.5.1 Energy dispersive X-ray analysis (EDS)

Energy Dispersive X-ray Spectroscopy (EDS) is a widely used analytical technique for the elemental characterization of materials, commonly integrated with SEM. While SEM provides high-resolution imaging by scanning a finely focused electron beam across a sample surface, EDS enhances this capability by enabling simultaneous elemental analysis through detection of characteristic X-rays emitted from the sample.

EDS is capable of detecting elements ranging from boron (B) to uranium (U), with detection limits typically between 0.1 wt.% and 100 wt.%. One of the key strengths of EDS is its ability to perform both qualitative and quantitative compositional analysis. This includes spatially resolved analysis, allowing users to define specific regions of interest on a sample surface for localized elemental mapping. The integration of EDS into SEM systems allows us to correlate surface morphology with chemical composition in a single analysis workflow [21].

2 THE AIMS OF THE THESIS

In this thesis, we synthesize and characterize bismuth-based electrode materials optimized for desalination applications, emphasizing achieving a high surface area and superior electrochemical performance to enhance the efficiency of hybrid CDI processes. By utilizing electrochemical deposition techniques, we vary bismuth materials' particle size and morphology, which are critical for optimizing chloride ion capture and electrode cyclability. The synthesized materials are characterized using analytical techniques, including Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), and Cyclic Voltammetry (CV), to investigate their structural, compositional, and electrochemical properties. We aim to get more insight on the actual mechanism of desalination, which is usually treated as one step [22], but in reality can be more complicated [5]. These analyses will provide valuable insights into the suitability of bismuth-based electrodes for practical desalination systems and inform future material design strategies. This work contributes to developing sustainable, cost-effective solutions to address the global water scarcity crisis by advancing the understanding of bismuth electrodes in hybrid CDI.

3. EXPERIMENTAL PART

3.1 MATERIALS AND METHODS

3.1.1 Chemicals and instrumentation

Bismuth chloride (BiCl_3 , Merck, reagent grade, $\geq 98\%$), bismuth ammonium citrate ($\text{C}_{12}\text{H}_{22}\text{BiN}_3\text{O}_{14}$, Merck, for microbiology $\geq 99.0\%$), hydrochloric acid (HCl , Fluka, puriss. p.a. $\geq 37\%$), concentrated H_2SO_4 (Fluka, puriss. p.a. $\geq 97\%$), hydrogen peroxide (H_2O_2 , Supelco, 30% wt.), sodium chloride (NaCl , Sigma-Aldrich, ACS reagent, $\geq 99.0\%$), isopropanol (Heneywell, puriss. $\geq 99.5\%$), Nafion perfluorinated resin solution (Sigma-Aldrich, 5 wt. % in lower aliphatic alcohols and water) were used as is. Ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$; Milli-Q purification system by Millipore) was used to prepare all solutions.

An analytical balance, Kern ALJ 200-5DA, was used to weigh all materials for solution preparation and bismuth nanopowder samples after the synthesis.

All electrochemical measurements were performed on Multi Autolab/M204 equipped with the FRA32M module (Metrohm, The Netherlands). Additionally Rigol DHO814 digital oscilloscope was used to monitor the electrode signal. The data was processed using the Python programming language in the Jupyter Lab environment.

3.1.2 Bismuth nanopowder synthesis

The catalyst preparation and testing process consisted of two stages: synthesis of the catalyst powder via electrodeposition from a Bi-containing solution on a glassy carbon substrate, its isolation, ink preparation, and its subsequent electrochemical characterization using CV. Two distinct catalysts were prepared: Bi sample 1, from bismuth ammonium citrate, and Bi sample 2, from a bismuth chloride bath.

Synthesis from bismuth ammonium citrate (30s Deposition) - Bi sample 1.

100 ml solution of 20 mM bismuth ammonium citrate in 1.5 M sulfuric acid for electrodeposition was prepared by dissolving 1.283 g bismuth ammonium citrate in ultrapure water and adding 8.2 mL of 97% H_2SO_4 . The deposition current was fixed at 1 A, and the deposition time was set to 30 seconds. In the electrodeposition process platinum electrode was used as the positive counter

electrode, and a glassy carbon electrode (surface area = 1.23 cm²) was used as the negative electrode - the substrate for the deposition. Controlled immersion was utilized to maintain a consistent deposition area. For the determination of the mass of the deposit, a glassy carbon electrode of initial mass of 0.16870 g was weighted on an analytical balance. In total, there were 13 deposition cycles. After each iteration, the glassy carbon substrate was carefully rinsed with ultrapure water, dried, and the electrochemically deposited Bi nanopowder was removed by sonication (ultrasound bath NE00922, 40kHz, 120W) of the glassy carbon substrate in a vial containing ultrapure water. To determine the faradaic efficiency of the electrodeposition process, the masses for the first three cycles were measured as 0.17118 g, 0.17178 g, and 0.17247 g. The average mass deposited per cycle was calculated as:

$$\text{Average Mass} = \frac{0.17118+0.17178+0.17247}{3} = 0.17181\text{g}. \quad (4)$$

The uncertainty was calculated as the standard deviation of the three masses,

$$\text{Uncertainty } (\pm) = \sqrt{\frac{\sum(\text{mass}-\text{average mass})^2}{n-1}} \text{ yielding } \pm 0.00054 \text{ g} \quad (5)$$

The deposition per cycle was determined as: Deposition per cycle: 0.17181– 0.16870 = 0.00311 g/cycle. The total deposited mass for 13 cycles was: 0.00311 g/cycle × 13 = 0.04043 g. To get the Faradaic efficiency for the deposition of bismuth (Bi), we start by determining the total charge passed during electrolysis of a single iteration. Using the formula

$$Q = I \times t \quad (6)$$

Where our $I = 1$ A and $t = 30$ sec, the total charge Q is calculated to be 30 C. The theoretical mass of bismuth deposited is calculated using Faraday's law of electrolysis:

$$m_{\text{theoretical}} = \frac{Q \times M}{F \times n}. \quad (7)$$

Where, $M = 208.98$ g/mol is the molar mass of bismuth, $n = 3$ is the number of electrons involved in the reduction of Bi³⁺ to Bi and $F = 96485$ C/mol is Faraday's constant. Substituting the values, the theoretical mass is approximately 0.0217 g. Finally, the Faradaic efficiency is calculated as the ratio of the actual mass deposited in a single step (0.00311 g) to the theoretical mass, multiplied by 100. This gives a Faradaic efficiency of approximately 14.33%.

Synthesis from bismuth ammonium citrate (60s Deposition) - Bi sample 2.

100 mL solution of 14 mM bismuth chloride in 1.4 M hydrochloric acid for electrodeposition was prepared by dissolving 0.442 g bismuth chloride in ultrapure water and adding 11.7 mL of 37% HCl. The deposition current was fixed at 1 A, and the deposition time was set to 60 seconds. In the electrodeposition process platinum electrode was used as the positive counter electrode, and a glassy carbon electrode (surface area = 1.23 cm²) was used as the negative electrode - the substrate. Controlled immersion was utilized to maintain a consistent deposition area. To determine the mass of the deposit, a glassy carbon electrode initial mass of 0.14398 g was weighted on an analytical balance. In total, there were 13 deposition cycles. After each iteration, the glassy carbon substrate was carefully rinsed with ultrapure water, dried, and the electrochemically deposited Bi nanopowder was removed by sonication of the glassy carbon substrate in a vial containing ultrapure water. To determine the faradaic efficiency of the electrodeposition process, the masses for the first three cycles were recorded as 0.14513 g, 0.14329 g, and 0.14449 g. The average mass deposited per cycle was calculated as: Average Mass = 0.14513 + 0.14329 + 0.144493 = 0.14430 g (see Eq. 4). The uncertainty was calculated as the standard deviation of the three masses, yielding ± 0.00075 g (see Eq. 5). The deposition per cycle was determined as: Deposition per cycle: 0.14430 – 0.14398 = 0.00032 g/cycle. The total deposited mass for 13 cycles was: 0.00032 g/cycle $\times$ 13 = 0.0102 g. To calculate the faradaic efficiency, the formula of the Equation 6 was used, where current $I = 1$ A and $t = 60$ sec, the total charge Q is calculated to be 60 C. The theoretical mass of bismuth deposited in a single step is calculated using Faraday's law of electrolysis (Eq. 7). Where, $M = 208.98$ g/mol is the molar mass of bismuth, $n = 3$ is the number of electrons involved in the reduction of Bi³⁺ to Bi and $F = 96485$ C/mol is Faraday's constant. Substituting the values, the theoretical mass is approximately 0.0433g. Finally, the Faradaic efficiency is calculated as the ratio of the actual mass deposited (0.00032g) in a single step to the theoretical mass, multiplied by 100. This gives a Faradaic efficiency of approximately 0.739%.

To wrap this up, the process of electrodeposition of bismuth nanopowder from ammonium citrate bath has demonstrated higher faradaic efficiency compared to the bismuth chloride bath.

3.1.3 Material separation by centrifugation and suspension preparation

As mentioned before, the electrodeposited bismuth was removed from the glassy carbon electrode by sonication in an ultrasound bath; this step is done in 45 s, and all of the deposited Bi nanopowder is transferred into water in the form of a suspension. In the next step, this suspension was centrifuged at 3000 rpm, and the water was decanted and replaced with isopropanol. This washing process was repeated three times. A 0.5% Nafion solution was prepared by diluting a 5% stock solution of Nafion in isopropanol by a factor of 10. The purified bismuth nanoparticles were mixed with the diluted Nafion solution in a 1:10 ratio (bismuth nanopowder stock suspension to isopropanol) to prepare the final suspension for analysis. The resulting concentration of Bi in the ink was 0.0101 mg/ul for Bi sample 1 and 0.0102 mg/ul for Bi sample 2.

3.1.3 Physical characterization

The morphological structure of the synthesized materials was investigated using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) mapping. SEM images were measured on FEI Nova NanoSEM 450 using secondary electrons. Acceleration voltage was set to either 3.3 or 5 kV. EDS analysis was performed on Zeiss EVO MA15 system with an Oxford X-MAX 80 energy dispersive detector (EDS), measurements were performed in Variable Pressure mode at 40 Pa chamber pressure using Nitrogen. SEM acceleration voltage in EDS measurements was set to 20 kV.

SEM sample was prepared as follows: 10 μ L of the Bi nanopowder stock suspensions without Nafion were dropcasted on the carbon tape of the SEM sample holder. After the isopropanol dried out, the samples were put into the SEM device for the investigation.

4. RESULTS AND DISCUSSION

This section presents the findings from the physical and electrochemical characterization of two bismuth nanopowders, Bi sample 1 and Bi sample 2, synthesized via electrochemical deposition and evaluated for their potential in electrochemical desalination. The study leverages scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and cyclic voltammetry (CV) to elucidate the morphology, composition, and electrochemical performance of these materials in 0.1 M NaCl. The results are contextualized against prior literature to assess their suitability for chloride capture and release.

4.1 Physical characterization - SEM

SEM was used to investigate the surface morphology of Bi sample 1 and Bi sample 2, revealing distinct structural features that are closely linked to their electrochemical behavior.

- **Bi sample 1** (A and B in Fig. 4.) depict a nanostructured morphology with fine, interconnected particles and uniform distribution, suggesting a porous structure with high surface area ideal for ion diffusion and electrochemical activity. Some nanoparticle agglomeration was observed, yet visible porosity was maintained, enhancing electrolyte accessibility. This aligns with findings by Chen et al. (2019)[15], who demonstrated that nanostructured bismuth electrodes improve desalination performance due to increased active sites [15]. It is worth mentioning that the average particle size is roughly 1 μm in length and 200 nm in width.
- **Bi sample 2** (C and D in Fig. 4.) show even finer but clustered formations, including flake-like and needle-like structures with denser overall packing and higher surface roughness. This morphology may impede ion diffusion in the depth but could enhance mechanical stability during cycling, a particular trade-off noted by Wang et al. [23]. On the other hand, the individual particles are much smaller in this sample and which might result in a higher effective surface area available for the reaction with Cl^- ions.

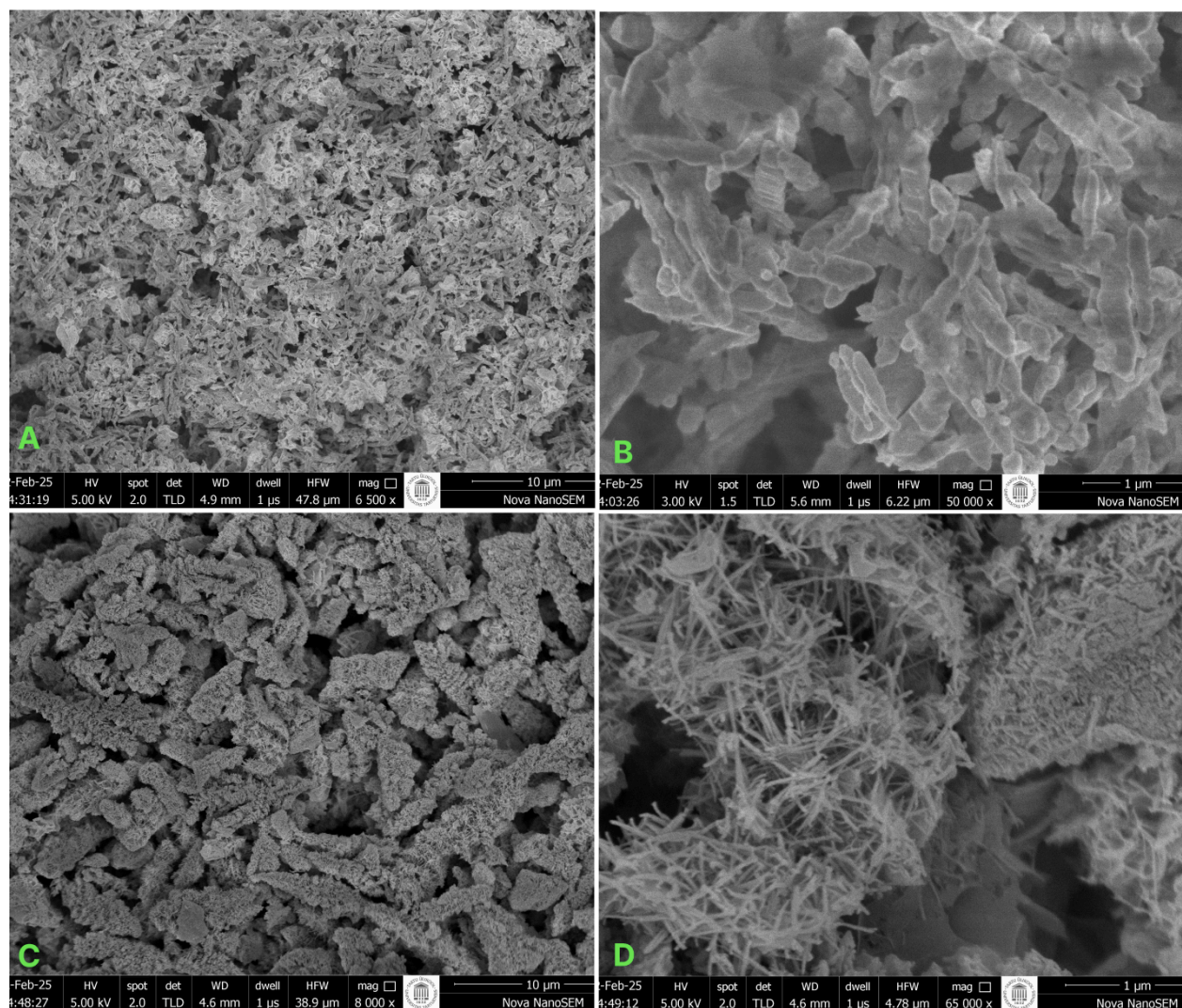


Figure 3. SEM images of Bismuth sample 1 and 2 nanopowder at different magnifications.

4.1.1 Compositional analysis with EDS

EDS analysis of the bismuth nanopowder samples reveals slightly distinct compositional profiles. For Bi sample 1 the EDS graph in Figure 5 displays a sharp, dominant bismuth peak at 2.4 keV, accompanied by multiple secondary bismuth peaks between 8.4 and 14.6 keV. Quantitative analysis confirms a high-purity composition of 86.3% bismuth, with only 1.0% sulfur as a minor contaminant, likely originating from the sulfuric acid used in the electrodeposition bath. Some carbon and oxygen (5.7% and 7.0%) are coming most probably from the sample holder. This high purity together with the observed morphology suggests a clean

active surface area, which is advantageous for desalination processes where bismuth facilitates chloride ion capture through the formation of BiOCl .

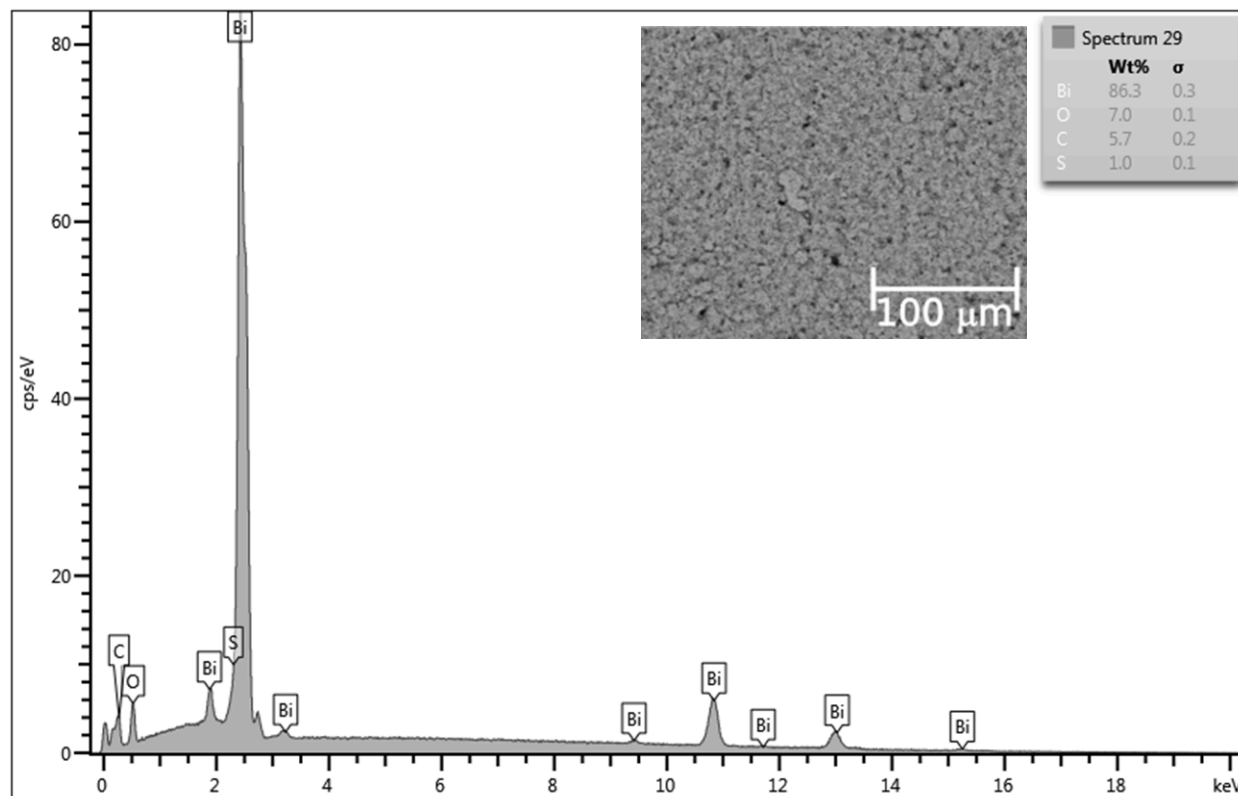


Figure 4. SEM-EDS graph of Bi sample 1 nanopowder.

In the EDS graph for Bi sample 2 in Figure 5 a prominent bismuth peak is observed at 2.4 keV and additional bismuth peaks at 9-11 keV and 13-15 keV. However, its quantitative data indicates bismuth constitutes only 36.7% by weight, with substantial impurities including carbon (50.2%), oxygen (12.4%), and trace copper (0.7%). These impurities are likely coming from the sample holder, especially carbon and oxygen, as during preparation of this sample, a relatively small amount of bismuth nanopowder was used. It is still possible to state that it is pure bismuth. However, the presence of copper is not well understood, and the only possible source can be either bismuth salt or hydrochloric acid used for the solution preparation. Although its homogeneous bismuth distribution supports a uniform morphology, the presence of copper may obstruct active sites, potentially diminishing its efficiency in desalination compared to the Bi sample 1. Thus, while both samples contain bismuth as a primary constituent, the superior purity

of Bi Sample 1 positions it as a more promising candidate for effective chloride ion capture in desalination systems.

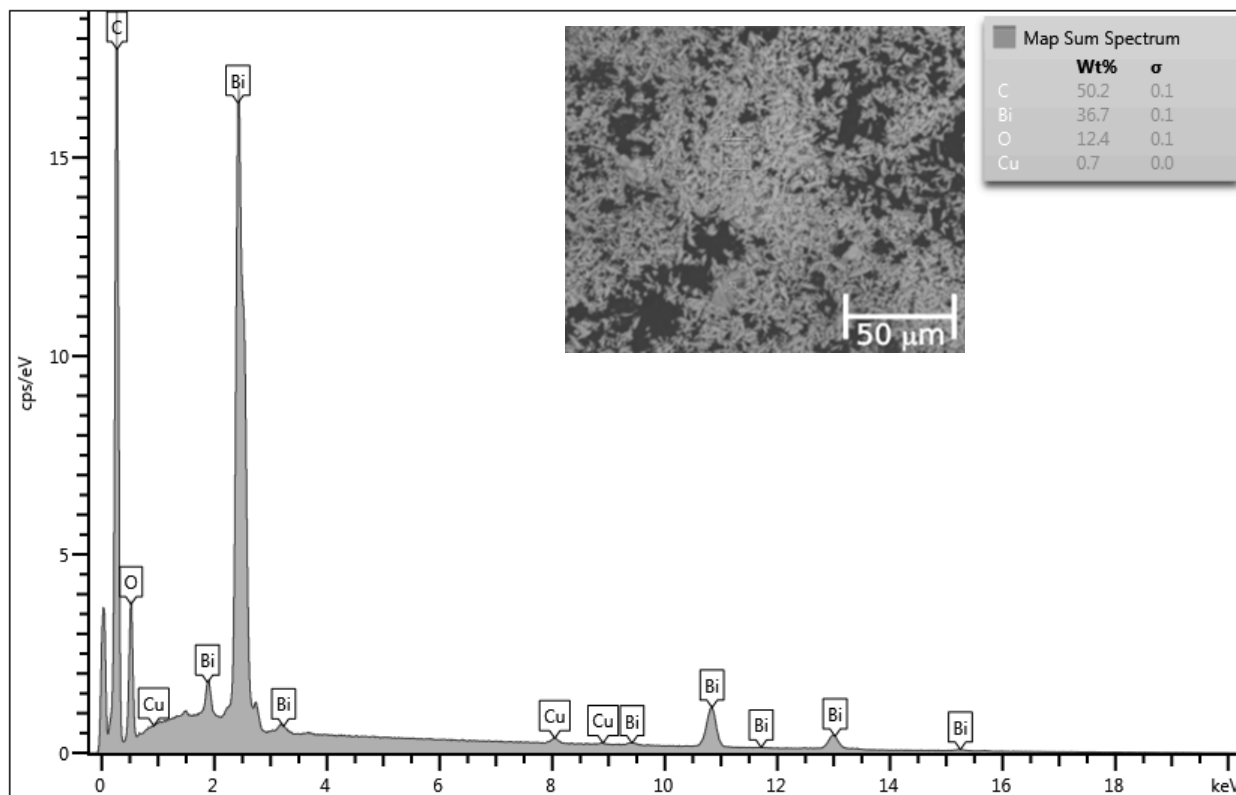


Figure 5. SEM-EDS graph of Bi sample 2 nanopowder.

4.2 Electrochemical characterization - CV results

4.2.1 Randles-Ševčík analysis

The electrochemical characterization of Bi nanopowder electrodes was conducted using cyclic voltammetry (CV) in a 0.1 M NaCl solution, with scan rates of 5, 10, 20, 50, 100, 200, and 500 mV/s to probe the kinetics of the $\text{Bi} \leftrightarrow \text{BiOCl}$ redox couple, critical for chloride capture as established by Nam and Choi [5]. The CV curves revealed complex redox behavior for both Bi samples, exhibiting multiple anodic and cathodic peaks with broad peak separations (see Fig. 6 A and B; Tables A1 and A2 in annex). These peaks are associated with the interconversion between Bi and BiOCl, described by the overall reaction:

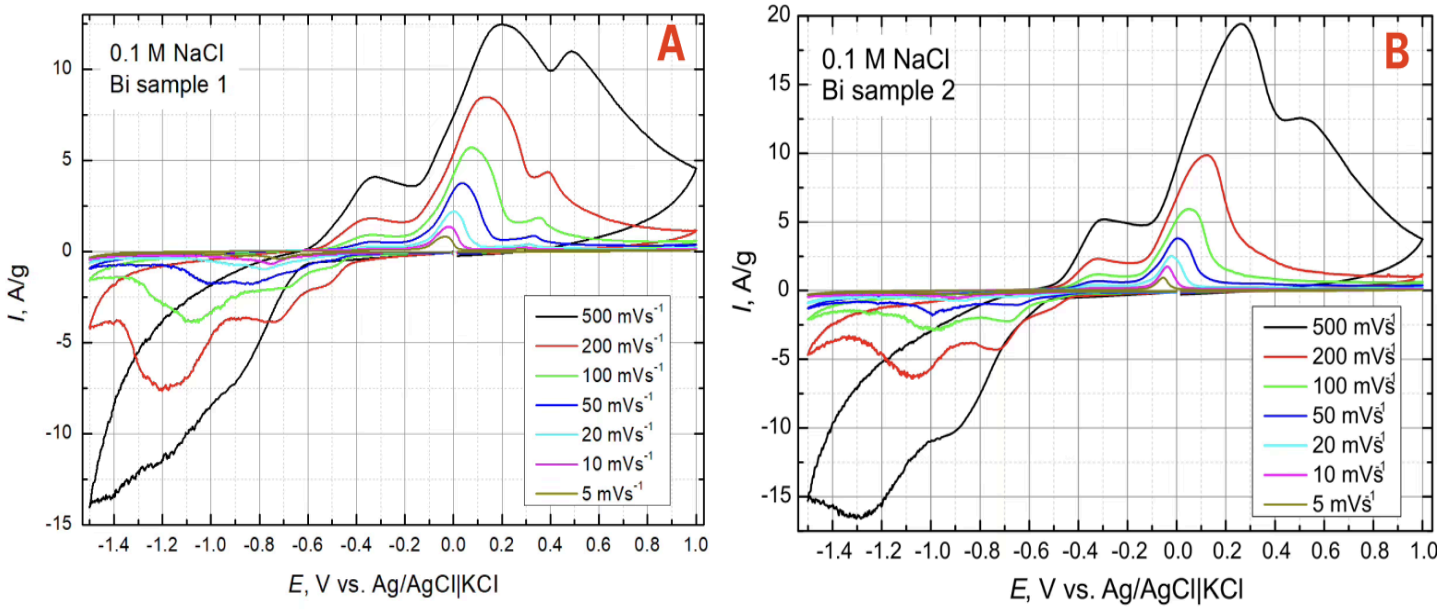
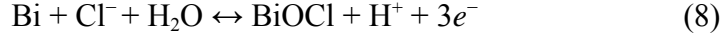


Figure 6. CV data for Bi sample 1 and 2 recorded at different scan rates.

The cathodic and anodic peaks showed clear scan rate dependence, prompting a detailed analysis of peak current i_p behavior. To assess whether these processes were diffusion-controlled, a Randles-Ševčík analysis was performed by plotting i_p against the square root of the scan rate $\nu^{1/2}$, as shown in Figures A1–A18 in the annex. This method is suited for identifying diffusion-limited redox processes, where electroactive species (e.g., Cl^- or H^+) diffuse to the electrode surface, contributing to the redox reaction.

The theoretical basis for this analysis is the Randles-Ševčík equation for a reversible, diffusion-controlled system:

$$i_p = 0.4463 n F A C \left(\frac{n F \nu D}{RT} \right)^{1/2} \quad (9)$$

where i_p is the peak current (A), n is the number of electrons transferred, F is Faraday's constant (96485 C/mol), A is the electrode area (cm^2), C is the bulk concentration of the electroactive species (mol/cm^3), ν is the scan rate (V/s), D is the diffusion coefficient (cm^2/s), R is the gas

constant (8.314 J/mol·K), and T is the temperature (K). This equation predicts a linear relationship between i_p and $v^{1/2}$, reflecting diffusion-limited transport to the electrode surface.

Initial analysis revealed that several anodic and cathodic peaks exhibited linear i_p versus $v^{1/2}$ plots, suggesting diffusion-controlled behavior for species like Cl^- or H^+ involved in the $\text{Bi} \leftrightarrow \text{BiOCl}$ redox process. However, a deeper evaluation using the Randles-Ševčík equation, particularly after applying Cl^- and H^+ concentration values, indicated significant deviations from classical diffusion kinetics for certain peaks. H^+ concentration was calculated from the pH 6.4 of the 0.1 M NaCl solution used in this experiment. The deviations of D , potentially due to surface-confined or mixed kinetic processes, were further explored through log-log analysis (discussed below), which distinguishes diffusion-controlled from surface-controlled behavior.

Table 1. Diffusion coefficients derived from Randles-Ševčík formalism

Bi Sample	Peak	Species	D (cm ² /s)	Interpretation
1	Anodic peak-2	Cl^-	4.55×10^{-9}	Borderline – possibly surface interaction
1	Anodic peak-1	Cl^-	4.94×10^{-10}	Borderline – possibly surface interaction
1	Cathodic peak-1	H^+	9.66×10^{-20}	Unphysically low – not diffusion-controlled
2	Anodic peak-2	Cl^-	1.02×10^{-8}	Borderline – possibly surface interaction
2	Anodic peak-1	Cl^-	7.85×10^{-10}	Quite low – possibly surface interaction
2	Cathodic peak-1	H^+	1.27×10^{-19}	Unphysically low – not diffusion-controlled

2	Cathodic peak-2	H ⁺	3.37×10^{-20}	Unphysically low – not diffusion-controlled
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After converting peak currents from mass-normalized units (A/g) to absolute current (A) using a Python script (see Annex 6.1, Python script was verified by use of generative AI [24]), the derived apparent diffusion coefficients for anodic peaks involving Cl⁻ in Bi Samples 1 and 2 are significantly lower than typical bulk diffusion values for Cl⁻ (10^{-6} to 10^{-5} cm²/s) [25], see Table 1. For example, Sample 2 – Anodic Peak-2 yielded an apparent diffusion coefficient of ($D = 1.02 \times 10^{-8}$ cm²/s), which is 2–3 orders of magnitude smaller than the bulk value (e.g., $\sim 2.03 \times 10^{-5}$ cm²/s) [25]. This reduction likely reflects restricted diffusion due to the high tortuosity of the nanostructured Bi electrode, where the effective diffusion coefficient D_e is related to the bulk diffusion coefficient D_0 by

$$D_e = D_0 / \tau^2 \quad (10)$$

Assuming $D_0 = 2 \times 10^{-5}$ cm²/s, the tortuosity factor is approximately $\tau \approx 44$, indicating a highly tortuous pore structure. Additionally, pseudocapacitive or surface-confined mechanisms, such as Cl⁻ adsorption or BiOCl film formation, may contribute, particularly for peaks with lower coefficients e.g., $D = 4.94 \times 10^{-10}$ cm²/s for Sample 1 – Anodic Peak-1. These findings suggest that some anodic processes are partially influenced by classical diffusion of Cl⁻ from the bulk electrolyte, but significant restrictions or mixed mechanisms dominate.

Tortuosity refers to the convoluted diffusion path through a porous material, like the Bi nanopowders used in this work. In nanoporous electrodes, this can significantly impede ion movement, reducing the effective diffusion coefficient. A relevant analogy is found in lithium-ion battery electrodes, where Nguyen et al. (2020) [26] showed that high tortuosity, especially with dead-end pores, reduces the effective diffusion coefficient due to longer, more tortuous paths, consistent with our observations for Cl⁻ in Bi nanopowders [26].

Other anodic peaks, particularly anodic peak-1 in Bi Sample 1 and Bi sample 2, gave significantly lower diffusion coefficients (down to 10^{-10} cm²/s), suggesting a departure from pure diffusion control. As this value is 4 orders of magnitude lower than the reference values, it likely reflects pseudocapacitive or surface-confined redox activity, where the current is governed by

adsorbed species or redox transformations occurring within a thin interfacial film (e.g., adsorption of Cl^- or BiOCl film formation).

More strikingly, the all cathodic peaks which involve proton-dependent reduction of BiOCl showed diffusion coefficients in the range of 10^{-19} - 10^{-20} cm^2/s , orders of magnitude lower than any physically plausible values for proton transport (typically 10^{-5} to 10^{-7} cm^2/s , as reported in literature) [27]. For instance, Bi Sample 2 cathodic peak-1 yielded $D = 1.27 \times 10^{-19}$ cm^2/s , and Sample 1 – cathodic peak-1 yielded $D = 9.66 \times 10^{-20}$ cm^2/s . These values clearly indicate that the cathodic process is not governed by diffusion of protons from the bulk, but is instead limited by surface phenomena, such as localized proton availability, adsorbed hydroxyl species, or redox-active passivating layers like Bi_2O_3 or BiOCl .

These extremely low diffusion coefficients, combined with the system's characteristics including nanostructured Bi with high surface area, low H^+ concentration at pH 6.4, and broad, asymmetric voltammetric peaks with high separation strongly support the conclusion that the system does not conform to classical semi-infinite diffusion behavior.

At this point, we can conclude that the observed redox mechanism is:

- Surface-confined, where redox-active species are immobilized or weakly mobile on the electrode interface.
- Chemically coupled, involving intermediate film formation or EC (electron transfer–chemical reaction) sequences.
- Kinetically limited, as evidenced by the large anodic–cathodic peak separation (up to 1.6 V) and non-Nernstian behavior.

As such, Randles–Ševčík analysis is not valid for interpreting these cathodic processes, and is only partially valid for select anodic peaks to get an insight on possible reaction properties. More reliable mechanistic insight comes from alternative approaches such as:

- Log-log slope analysis, which distinguishes between diffusion- and surface-controlled regimes based on the current–scan rate exponent,

- Laviron analysis, which evaluates interfacial electron transfer kinetics without assuming diffusion from the bulk.

To further characterize the electrochemical kinetics of Bi nanopowder electrodes in 0.1 M NaCl, a log-log analysis of the peak current i_p as a function of scan rate v was performed (Annex plots in section 3). This method distinguishes between diffusion-controlled and surface-confined redox processes, providing insight into the observed redox reaction mechanisms. In the case of Bi nanopowders, while the material is surface-confined, species such as Cl^- and H^+ , readily available in the electrolyte, participate in the $\text{Bi} \leftrightarrow \text{BiOCl}$ redox reaction (Equation 8), potentially contributing to both diffusion and surface processes.

The peak current for electrochemical processes follows a general power-law relationship:

$$i_p = kv^b \quad (11)$$

where k is a system-dependent constant, and the exponent b indicates the kinetic regime. Taking the logarithm of both sides yields:

$$\log(i_p) = b \cdot \log(v) + \log(k) \quad (12)$$

The slope b serves as a diagnostic criterion:

- $b \approx 0.5$: Diffusion-controlled kinetics, where i_p is proportional to $v^{1/2}$, as described by the Randles-Ševčík equation for a reversible system (Equation 9)
- $b \approx 1.0$: Surface-controlled or pseudocapacitive kinetics, where i_p is proportional to v , as given by the equation for adsorbed species:

$$i_p = \frac{n^2 F^2 A \Gamma v}{4RT} \quad (13)$$

where Γ is the surface coverage of the adsorbed species (mol/cm^2).

- $0.5 < b < 1.0$: Mixed kinetics, reflecting contributions from both diffusion and surface processes.

This approach is well-established in electrochemical literature, with comprehensive treatments provided by Bard and Faulkner (2001) in *Electrochemical Methods: Fundamentals and Applications* [19].

Table 2. Table summarizing the b -values for the log-log analysis of Bi nanopowder samples

Sample	Peak	b -value	R^2 -value	Kinetic interpretation
Bi sample 1	Anodic peak-1	0.8236	0.9967	Mixed
Bi sample 1	Anodic peak-2	0.5977	0.9941	Diffusion
Bi sample 1	Anodic peak-3	0.954	0.9912	Surface
Bi sample 1	Cathodic peak-1	0.7871	0.991	Mixed
Bi sample 2	Anodic peak-1	0.858	0.9928	Mixed
Bi sample 2	Anodic peak-2	0.6244	0.9925	Diffusion
Bi sample 2	Anodic peak-3	0.9617	0.9080	Surface
Bi sample 2	Cathodic peak-1	0.8923	0.9923	Mixed
Bi sample 2	Cathodic peak-2	1.024	0.9994	Surface

Notes:

- b -values near 0.5 indicate diffusion-controlled kinetics, near 1.0 indicate surface-controlled kinetics, and between 0.5 and 1.0 suggest mixed kinetics.
- R^2 -values close to 1.0 confirm reliable log-log fits, with Anodic Peak-3 in Bi sample 2 $R^2 = 0.9088$ being acceptable despite lower linearity.
- Cathodic Peak-2 data is only available for Bi sample 2.

The log-log analysis (Table 2, Annex section 3) revealed predominantly surface-controlled redox processes, particularly for anodic peak-3 in both samples: Bi sample 1 $b = 0.954$, Bi sample 2 $b = 0.9617$, with b -values near 1.0 indicating strong surface confinement, likely tied to pseudocapacitive or adsorption-limited $\text{Bi} \leftrightarrow \text{BiOCl}$ redox reactions.

Anodic peak-1 showed mixed kinetics leaning toward surface control Bi sample 1 $b = 0.8236$, Bi sample 2 $b = 0.858$, while anodic peak-2 was distinctly diffusion-controlled Bi sample 1 $b = 0.5977$, Bi sample 2: $b = 0.6244$, with b -values near 0.5 suggesting Cl^- or H^+ transport.

For cathodic peaks, cathodic peak-1 exhibited mixed kinetics with a surface-controlled tendency Bi sample 1 $b = 0.7871$, Bi sample 2 $b = 0.8923$, and cathodic peak-2 in Bi sample 2 was strongly surface-controlled $b = 1.0214$. High R^2 values (>0.99) confirmed reliable fits for most peaks, except anodic peak-3 in Bi sample 2 ($R^2 = 0.9088$), which remained acceptable. These results underscore a complex electrochemical behavior dominated by surface mechanisms, with diffusion limitations in anodic peak-2, guiding further Laviron analysis of surface-confined processes described by anodic peak-3.

4.2.2 Kinetic Analysis - Laviron's Method:

The Laviron method provides a widely used analytical framework for evaluating electron transfer kinetics in quasi-reversible electrochemical systems. It is particularly applicable to surface-confined or thin-film redox processes where the redox couple undergoes charge transfer at the electrode interface. By analyzing the shift in peak potential position E_p with increasing scan rate in cyclic voltammetry, Laviron's approach allows the estimation of key kinetic parameters namely, the apparent charge transfer coefficient (α) and the standard rate constant (k^0). The method assumes that the electron transfer follows Butler–Volmer kinetics and that mass transport does not limit the reaction. A linear relationship between E_p and the logarithm of the scan rate enables extraction of kinetic parameters without requiring full numerical simulation of the voltammogram, making Laviron's model particularly suitable for comparative kinetic screening of electrode materials under well-controlled conditions.

For a surface-confined, quasi-reversible redox process, Laviron's model relates the anodic peak potential E_p to the scan rate v as follows:

$$E_p = E^0 + \frac{RT}{(1-\alpha)nF} \ln \left(\frac{(1-\alpha)nFv}{RTk^0} \right) \quad (14)$$

This expression can be linearized in terms of $\log(v)$ to yield:

$$E_p = E^0 + \frac{2.303RT}{(1-\alpha)nF} \log(v) + \text{constant} \quad (15)$$

Accordingly, the slope of a plot of E_p vs. $\log(v)$ is given by:

$$\text{Slope} = \frac{2.303RT}{(1-\alpha)nF} \quad (16)$$

At 25 °C ($T = 298$ K), where $\frac{RT}{F} \approx 0.0257$ V, and for a one-electron transfer ($n = 1$), the slope simplifies to:

$$\text{Slope} = \frac{0.0592}{(1-\alpha)} \Rightarrow \alpha = 1 - \frac{0.0592}{\text{slope}} \quad (17)$$

The standard rate constant k^0 can then be calculated by evaluating the equation at a given scan rate and known E^0 , typically taken from the intercept or from an intermediate E_p value. These relationships hold under the assumption of negligible mass transport limitations and quasi-reversible electron transfer conditions met by the peaks identified with high b -values and measurable peak potential shifts.

Laviron's method was employed to evaluate electron transfer kinetics of surface-confined redox processes in Bi nanopowder electrodes, focusing on anodic peaks 1 and 3, selected for their high log-log slope values ($b > 0.85$), (see Table 2), indicating strong surface control. Peaks were required to show a systematic, non-flat trend in E_p versus $\log v$. Table 3 summarizes the kinetic parameters for anodic peaks 1 and 3, with cathodic peaks excluded due failed analysis (see Annex. 4 and 6.2)

Table 3. Laviron Kinetic Analysis Results

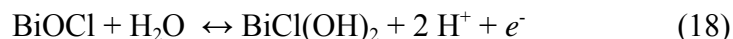
Sample	Peak	Slope (V/(log V/s))	R ²	α	k^0 (s ⁻¹)	Interpretation
Bi Sample 1	Anodic Peak-1	0.00428	0.843	2.00	57.82	Unphysical α ; near-constant E_p , unreliable results
	Anodic Peak-3	0.0914	0.868	0.094	2.94	Surface-confined, quasi-reversible;

Bi Sample 2	Anodic Peak-1	0.00583	0.249	1.47	35.54	Unphysical α ; near-constant E_p , unreliable results
	Anodic Peak-3	0.0766	0.766	0.112	3.28	Surface-confined, quasi-reversible; consistent with Bi sample 1

Notes: Anodic peak-3's low α (approx 0.1) suggests asymmetric energy barriers, possibly due to multi-step redox processes involving BiOCl transformation into species like Bi(OH)Cl₂.

Analysis of anodic peak-3

Anodic Peak-3, appearing at + 0.313 V vs. Ag/AgCl in both samples Bi sample 1 $b = 0.954$, Bi sample 2 $b = 0.9617$, exhibited Laviron-characteristic behavior, with significant E_p shifts and high b -values confirming surface confinement. Using Equations 14–17, the slopes 0.0914 V/log V/s for Bi sample 1, 0.0766 V/log V/s for Bi sample 2 yielded $\alpha = 0.094$ and 0.112 correspondingly, indicating a highly asymmetric energy barrier, consistent with multi-step redox processes, possibly BiOCl transformation into hydrated forms like Bi(OH)Cl₂.



The k^0 values of 2.94 and 3.28 s⁻¹ reflects quasi-reversible kinetics, suggesting moderate electron transfer rates associated with surface film growth. Sample 2's slightly faster k^0 but lower $R^2 = 0.766$ may indicate variability or interference from adjacent redox processes. The peak location supports potential hydroxylation of BiOCl, though spectroscopic evidence is needed to confirm Bi(OH)Cl₂ presence and formation.

Failed Analysis of Anodic Peak-1 and Cathodic Peaks.

Anodic peak-1 Bi sample 1 $b = 0.8236$, Bi sample 2 $b = 0.858$ produced unphysical results (Table 3), with low slopes 0.00428 and 0.00583 V/log V/s yielding $\alpha > 1$, outside the theoretical range ($0 < \alpha < 1$). The near-constant E_p and low $R^2 = 0.249$ for Bi sample 2 suggest near-reversible kinetics or partial diffusion influence, violating Laviron's assumptions.

Cathodic peaks analysis was impossible because all cathodic peaks show negative and unphysical α values (< 0), which leads to invalid results for k^0 . This outcome arises because the peak potentials shift too steeply and nonlinearly, producing negative slopes that break Laviron's theoretical assumptions. It is worth mentioning that cathodic peak-1 ($b = 0.7871$ and 0.8923 for Bi samples 1 and 2) showed diffusion contributions, which was already an indication of possible issues in the analysis. The cathodic peak-2 ($b = 1.0214$ Bi sample 2) lacked sufficient E_p data, and a limited number of points also resulted in unphysical α values. These findings confirm that the cathodic processes are unsuitable for Laviron analysis in the current work.

4.2.3 Calculation of transfer coefficient–electron number product αn for irreversible electrochemical processes.

Additional analysis of cathodic peak-1 and anodic peak-2

Due to the diffusion-controlled nature of anodic peak-2 $b \approx 0.60$ – 0.62 , Laviron analysis was not applicable, as it is suited for surface-confined processes. Instead, the product of the transfer coefficient and electron number αn was calculated from the slope of peak potential E_p versus the logarithm of scan rate ($\log v$), using the relation for irreversible processes.

For irreversible cathodic processes, the peak potential E_p shifts negatively with increasing scan rate (v) due to kinetic limitations, described by:

$$E_p = E^0 - \frac{RT}{\alpha n F} \left[0.780 + \ln \left(\frac{D^{1/2}}{k^0} \right) + \left(\frac{\alpha n F v}{RT} \right)^{1/2} \right] \quad (19)$$

where E^0 is the standard potential, ($R = 8.314 \text{ J/mol} \cdot \text{K}$), ($T = 298 \text{ K}$), ($F = 96485 \text{ mol}$), D is the diffusion coefficient, k^0 is the standard rate constant, α is the transfer coefficient, and n is the number of electrons. The slope of E_p versus $\log_{10}(v)$ is:

$$[\text{Slope} = - \frac{2.303RT}{\alpha n F} = - \frac{0.0592}{\alpha n}, \text{ V/decade (25}^0\text{C)}] \quad (20)$$

Thus:

$$[\alpha n = - \frac{0.0592}{slope}] \quad (21)$$

This relation, derived from Nicholson and Shain's voltammetric theory [28], was applied to the cathodic peaks of Bi Samples 1 and 2, yielding $\alpha n \approx 0.171\text{--}0.276$ and $\alpha \approx 0.057\text{--}0.092$, indicating irreversible reduction in accordance to the overall Equation 8, consistent with diffusion-limited kinetics observed in 0.1 M NaCl.

This approach yields (Python code, Annex 5 and 6.3) for Bi sample 1 anodic peak-2, the slope of 0.11715 V/decade which yields $\alpha n \approx 0.5$, while Bi sample 2's slope of 0.157 V/decade gives $\alpha n \approx 0.38$), reflecting slightly slower kinetics in Bi sample 2, likely due to its denser morphology and impurities.

The αn values 0.38–0.51 suggest slower electron transfer kinetics, consistent with an irreversible or quasi-reversible process, likely BiOCl formation (Equation 8). Assuming $n = 3$ (based on Bi to Bi(III)) $\alpha \approx 0.13\text{--}0.17$, indicating a significant energy barrier, possibly due to Cl^- diffusion limitations and sample high porosity

Together, these findings confirm that the cathodic and anodic processes are more complex than usually reported (Ref. 5-6) and likely involve surface-bound species like BiOCl and some diffusion control. The increasing peak separation and strong scan-rate dependence also suggest kinetic limitations and partial irreversibility [27].

4.2.4 Justification for using 0.1 M NaCl and not the seawater simulated mixture

In our study, we employed a 0.1 M NaCl electrolyte to investigate the $\text{Bi} \leftrightarrow \text{BiOCl}$ redox system, prioritizing mechanistic clarity over direct simulation of seawater conditions. This lower chloride concentration facilitated the resolution of distinct redox features in CV enabling the identification of multiple redox waves. These observations with CV analysis suggest the presence of an intermediate surface-confined transformation of Bi to Bi_2O_3 , preceding the formation of BiOCl and then further step to BiCl(OH)_2 or other oxyhydroxides. Such surface-confined processes are typically independent of bulk ion concentrations, and their detection is often obscured in higher ionic strength environments. Moreover, elevated Cl^- concentrations can introduce additional complexities, such as enhanced chloride adsorption and altered electrode surface interactions, which may mask subtle mechanistic steps. By utilizing a

controlled 0.1 M NaCl medium, we achieved a more selective and specific elucidation of the redox mechanisms, an aspect frequently overlooked in studies focusing solely on desalination performance.

4.2.5 Proposed overall reaction mechanism

The electrochemical behavior of Bi nanopowder electrodes in 0.1 M NaCl involves a multi-step mechanism driven by the interplay of oxide formation, chloride incorporation, and hydroxide interactions at the electrode surface. Initial oxidation forms a passivating Bi_2O_3 layer, followed by chloride-driven BiOCl formation, limited by ion diffusion. At higher potentials, the transformation to hydroxylated species like $\text{BiCl}(\text{OH})_2$, can also promote local pH changes (Equations 8 and 18). While the cathodic processes reversing these steps and both steps involving BiOCl and $\text{BiCl}(\text{OH})_2$ are pH dependent. This sequence, observed in Bi Samples 1 and 2, reflects bismuth's redox cycle and further reactions in chloride media

Cyclic voltammetry (5–500 mV/s) of Bi nanopowder electrodes in 0.1 M NaCl reveals a stepwise electrochemical mechanism for chloride capture and release, consistent with bismuth's behavior in chloride solutions reported by Ekilik et al.[22]. For both Bi Samples 1 and 2, anodic peak-1 exhibits near-reversible Bi_2O_3 formation $\Delta E_p \approx 0.009\text{--}0.015$ V, E_p -0.335 V to -0.3 V, $b \approx 0.82\text{--}0.86$, aligning with primary passivation near the corrosion potential. This rapid, surface-limited oxidation benefits from Sample 1's porous morphology fine particles and Sample 2's even finer structures, initiating oxide layer formation before chloride dominance. Anodic peak-2, with diffusion-controlled BiOCl formation (Equation 8), $\Delta E_p \approx 0.234\text{--}0.314$ V, E_p -0.052 V to 0.262 V, $b \approx 0.60\text{--}0.62$, $a_n \approx 0.38\text{--}0.50$, matches Ekilik et al.'s peak at -0.30 V, where Cl^- transport limits kinetics, particularly in Bi sample 2 due to denser morphology. Anodic Peak-3, showing surface-confined quasi-reversible behavior $\Delta E_p \approx 0.189\text{--}0.205$ V, 0.282 V to 0.487 V, $b \approx 0.954\text{--}0.9617$, $a \approx 0.094\text{--}0.112$, $k^0 \approx 2.94\text{--}3.28$ s⁻¹, suggests $\text{BiCl}(\text{OH})_2$ formation driven further potential increase, consistent with Ekilik et al.'s basic salt formation above at more anodic potentials. Cathodically, irreversible reduction $\Delta E_p \approx -0.429$ to -0.693 V, E_p -0.717 V to -1.41 V, $a_n \approx 0.171\text{--}0.276$ likely reverses BiOCl and other oxidised species to Bi, with Sample 2's finer morphology aiding kinetics.

4.3 Future works

To deepen understanding of the electrochemical mechanism of Bi samples 1 and 2 in 0.1 M NaCl, future experiments should focus on validating the proposed sequential oxidation ($\text{Bi}_2\text{O}_3 \rightarrow \text{BiOCl} \rightarrow \text{BiCl(OH)}_2$) and cathodic reduction processes, addressing the current lack of spectroscopic and thermodynamic data. In-situ X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) of samples isolated at certain potentials in CV can confirm the chemical states and crystal structures of Bi_2O_3 , BiOCl , and BiCl(OH)_2 , prove the process at all anodic peaks, and provide exact pathway for cathodic reduction. Electrochemical impedance spectroscopy (EIS) at these potentials can elucidate charge transfer and diffusion resistances, clarifying the slower kinetics in case of Bi sample due to its denser morphology and some impurities compared to Sample 1's porous structure. Additionally, controlled pH studies using buffered electrolytes can quantify hydroxide effects on BiCl(OH)_2 formation. These feasible experiments, leveraging Bi sample 1's high purity and Bi sample 2's unique morphology, will refine the passivation-depassivation mechanism, enhancing Bi nanopowders' application in desalination.

SUMMARY

The comprehensive analysis of Bi nanopowder electrodes in 0.1 M NaCl, combining SEM, EDS, and voltammetric studies for Bi samples 1 and 2, elucidates a sequential oxidation mechanism underpinning their electrochemical performance for chloride capture. SEM reveals Sample 1's porous, nanostructured morphology and Sample 2's finer, denser flake-like structures. Sample 1's and 2's high surface area and roughness support surface reactions, albeit with diffusion limitations. EDS confirms Sample 1's high bismuth purity against Sample 2's minor impurities (e.g., 0.7% Cu), correlating with Sample 1's better kinetics. Electrochemically, in this system anodic peak-1 exhibits near-reversible Bi_2O_3 formation, leveraging both samples' high surface areas for rapid passivation. Anodic peak-2, with diffusion-controlled BiOCl formation ($\alpha \approx 0.13\text{--}0.17$), benefits from Sample 1's porosity but is hindered in Bi sample 2 by denser morphology and impurities. Anodic peak-3, indicating surface-confined BiCl(OH)_2 formation ($\alpha \approx 0.094\text{--}0.112$, $k^0 \approx 2.94\text{--}3.28 \text{ s}^{-1}$), is faster due to Bi sample 1's purity, though Bi sample 2's roughness aids surface reactions despite lower linearity $R^2 = 0.766$ of the fit. Cathodically, both samples show irreversible reduction ($\alpha \approx 0.057\text{--}0.092$), likely reducing BiOCl to Bi, with Sample 2's finer morphology yielding slightly faster kinetics. It is worth noting that finer morphology will be the first cause to improve the kinetics of this reaction, as active surface area matters.

This sequence of Bi to bismuth oxide to oxychloride to hydroxylated chloride, reversed cathodically, aligns with Ekilik et al.'s stepwise passivation and depassivation in chloride media [22]. Sample 1's morphology and purity make it superior for desalination, though both samples' cathodic irreversibility suggests challenges in complete film reduction.

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Annex

1. Peak analysis

Table A1. Cathodic and anodic peaks Bi sample 1

<i>scan rate</i>	<i>cathodic peak</i>			<i>anodic peak</i>			<i>peak separation</i>
mV/s	# peak	E	I, A/g	E	I, A/g	V	
5	peak-1	-0.717	-0.404	-0.335	0.083		0.755
	peak-1			-0.0383	0.814		
	peak-3			0.282	0.142		
10	peak-1	-0.751	-0.667	-0.335	0.164		0.774
	peak-1			-0.0225	1.349		
	peak-3			0.296	0.238		
20	peak-1	-0.775	-0.968	-0.33	0.287		0.777
	peak-1			0.00249	2.168		
	peak-3			0.309	0.398		
50	peak-1	-0.834	-1.802	-0.33	0.526		0.871
	peak-1			0.0369	3.752		
	peak-3			0.334	0.854		
100	peak-1	-1.08	-3.871	-0.331	0.902		1.154
	peak-1			0.0742	5.693		
	peak-3			0.351	1.851		
200	peak-1	-1.2	-7.634	-0.328	1.822		1.334
	peak-1			0.134	8.446		
	peak-3			0.389	4.376		
500	peak-1	-1.41	-13.861	-0.326	4.071		1.606
	peak-1			0.196	12.475		
	peak-3			0.487	10.990		

It should be mentioned, that even though the cathodic peak-2 was present in Bi sample 1 its sporadic appearance in different scans was a decision factor to omit from the analysis.

Table A2. Cathodic and anodic peaks Bi sample 2

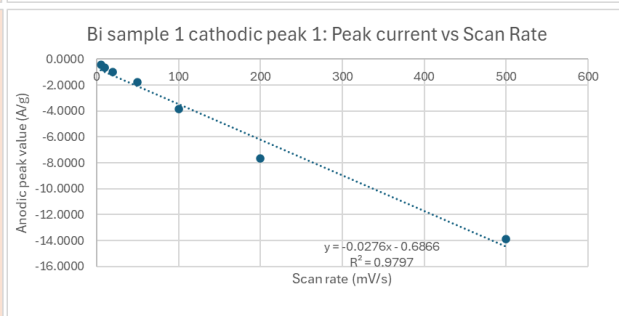
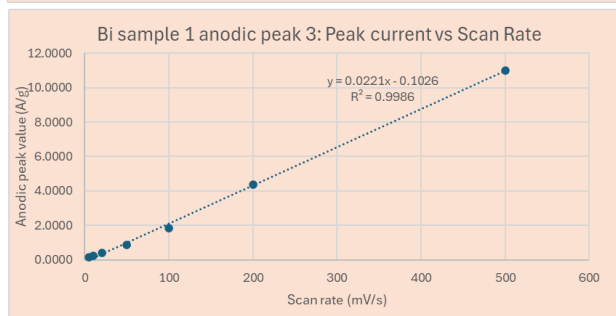
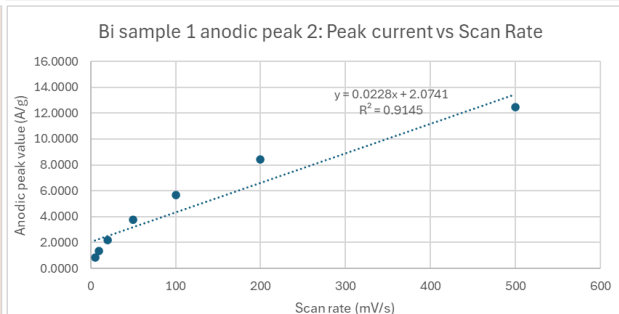
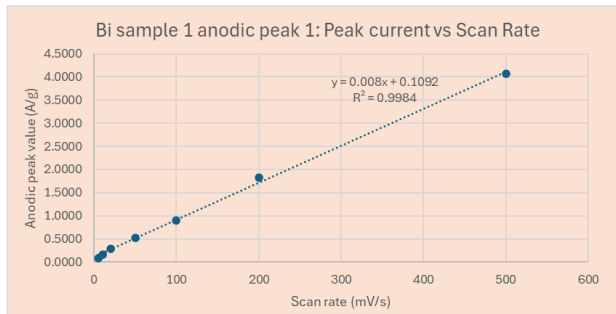
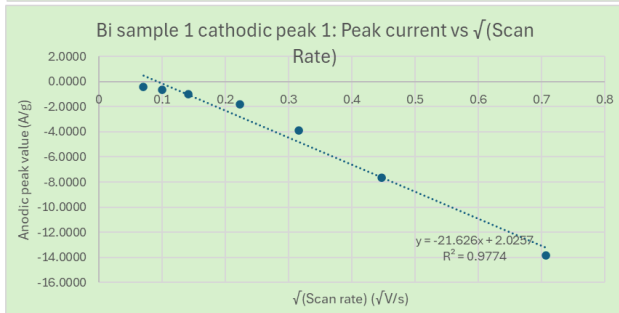
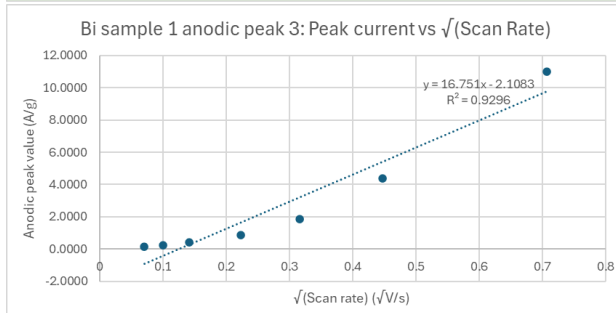
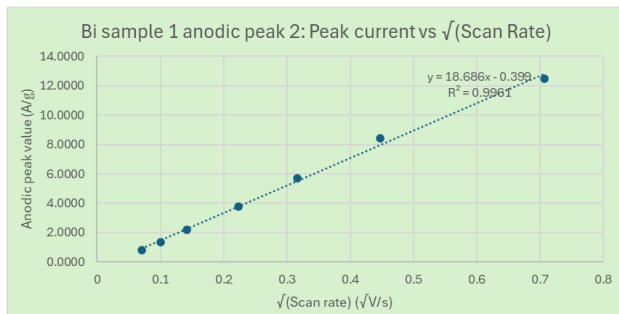
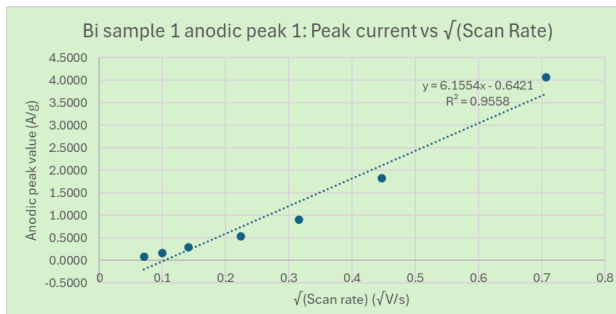
scan rate		cathodic peak		anodic peak		peak separation
mV/s	# peak	E	I, A/g	E	I, A/g	V
5	peak-1	-0.871	-0.252	-0.315	0.085	0.923
	peak-1			-0.052	0.945	
	peak-3			0.298	0.080	
10	peak-1	-0.886	-0.499	-0.318	0.191	0.923
	peak-1			-0.037	1.745	
	peak-3			0.313	0.142	
20	peak-1	-0.914	-0.698	-0.328	0.409	0.934
	peak-1	-0.61	-0.417	-0.02	2.509	
	peak-3			0.325	0.261	
50	peak-1	-0.993	-1.741	-0.317	0.699	0.996
	peak-1	-0.651	-1.043	0.0031	3.801	
	peak-3			0.343	0.512	
100	peak-1	-1	-2.863	-0.318	1.194	1.049
	peak-1	-0.689	-2.235	0.0494	5.947	
	peak-3			0.351	1.833	
200	peak-1	-1.07	-6.362	-0.32	2.331	1.193
	peak-1	-0.734	-4.300	0.123	9.804	
	peak-3			0.368	0.930	
500	peak-1	-1.3	-16.667	-0.3	5.177	1.562
	peak-1			0.262	19.412	
	peak-3			0.487	10.882	

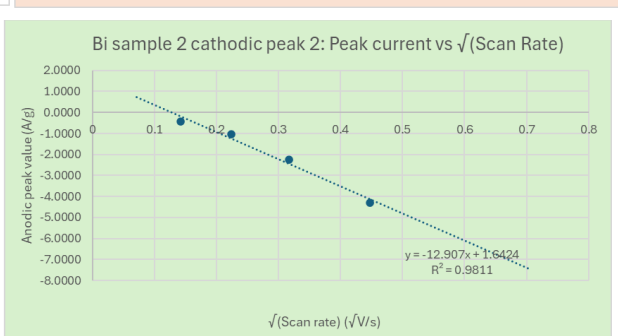
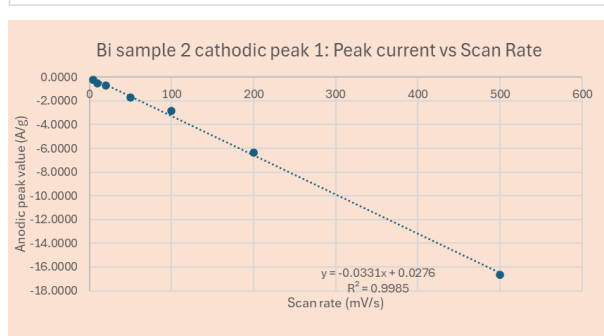
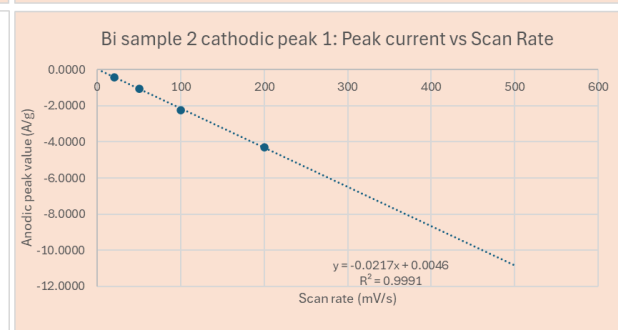
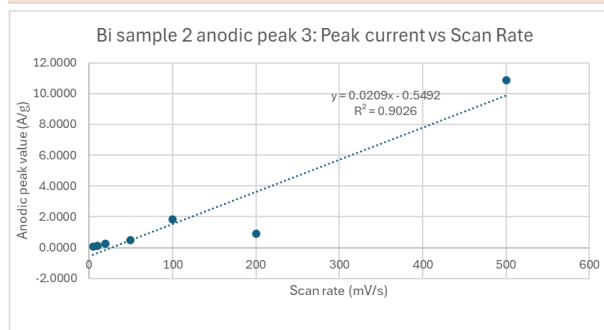
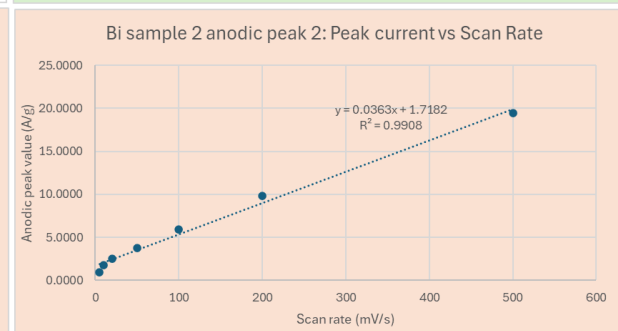
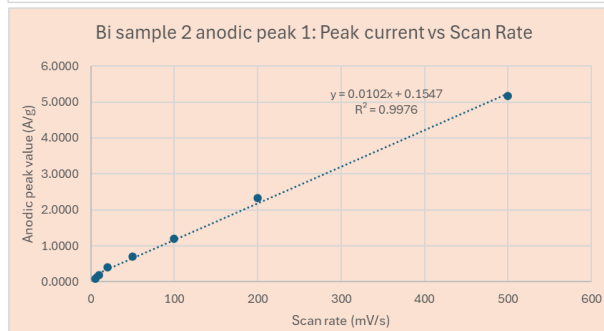
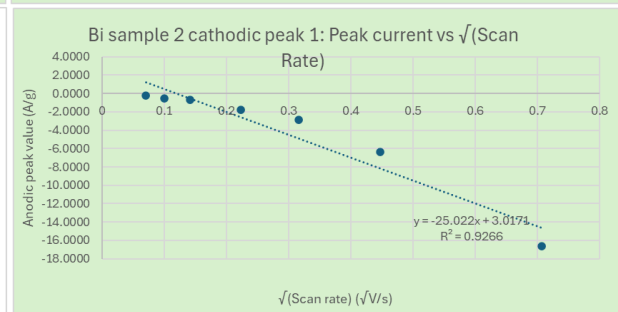
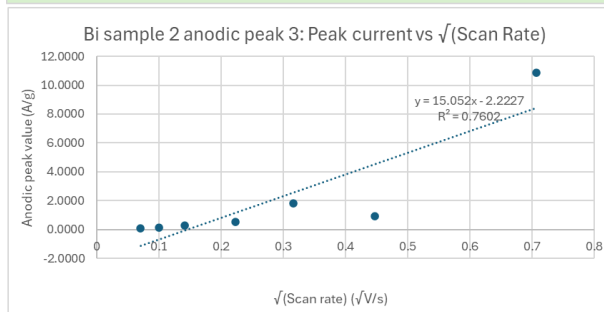
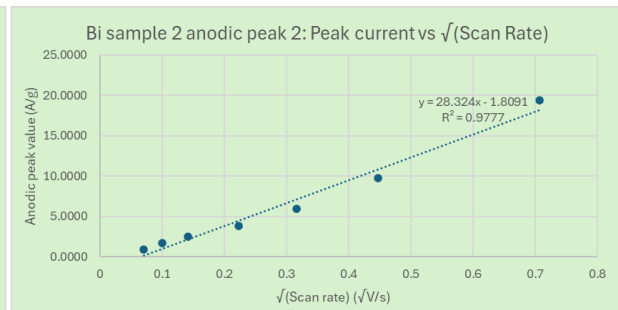
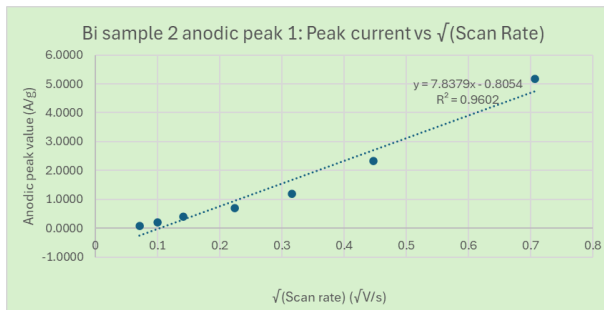
2. Plots for peak vs. scan rate and square root of scan rate dependence analysis (Randles–Ševčík based approach):

The peak currents (both anodic and cathodic) increase significantly with scan rate. This behavior was captured via plots and linear fitting. To examine the diffusion-controlled nature of the redox process, we plotted peak currents against the scan rate and square root of scan rate (in V/s):

- Strong correlation was found for both anodic and cathodic peak currents with scan rate (those plots are marked in orange).
- Strong correlation was found for both anodic and cathodic peak currents with the square of the scan (those plots are marked in green).

NB! Corresponding sample names and peaks are labeled in each plot separately



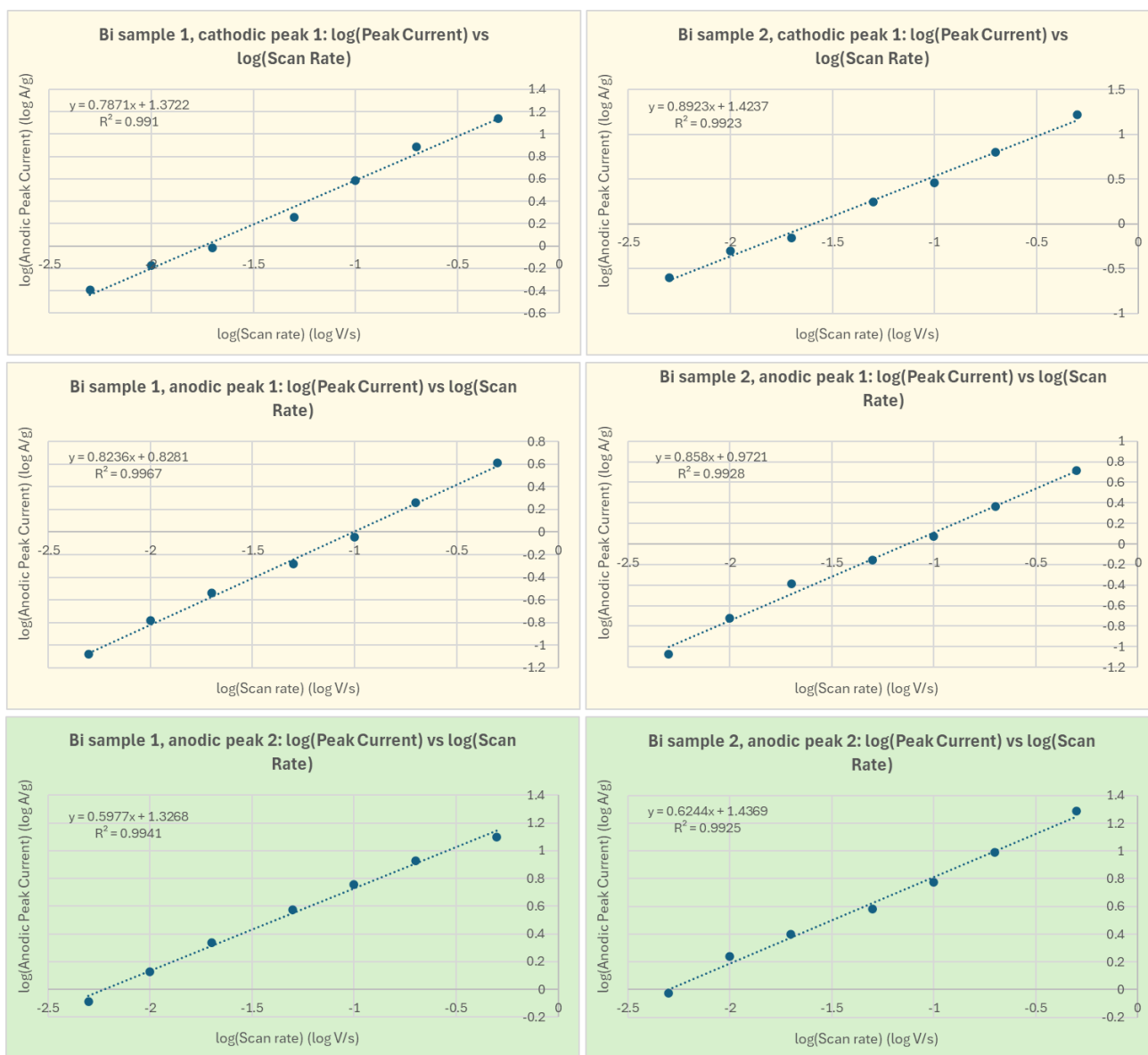


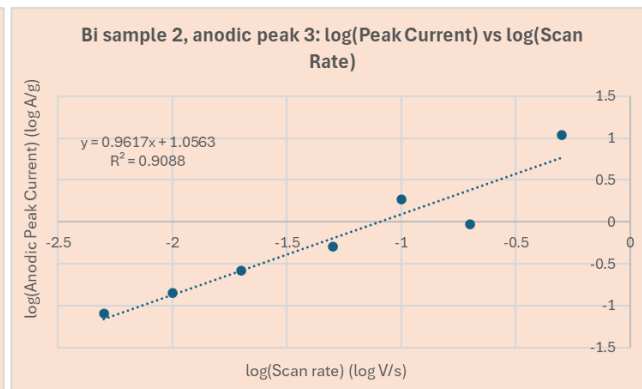
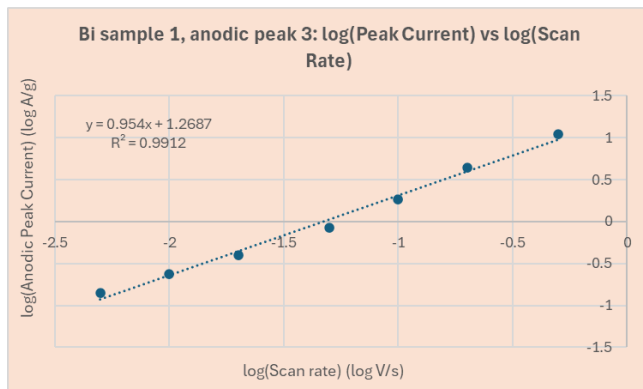
3. Log-log peak analysis:

The log of peak value and scan rate (both anodic and cathodic) show linear dependence. Linear fitting provides b factor and R^2 value.

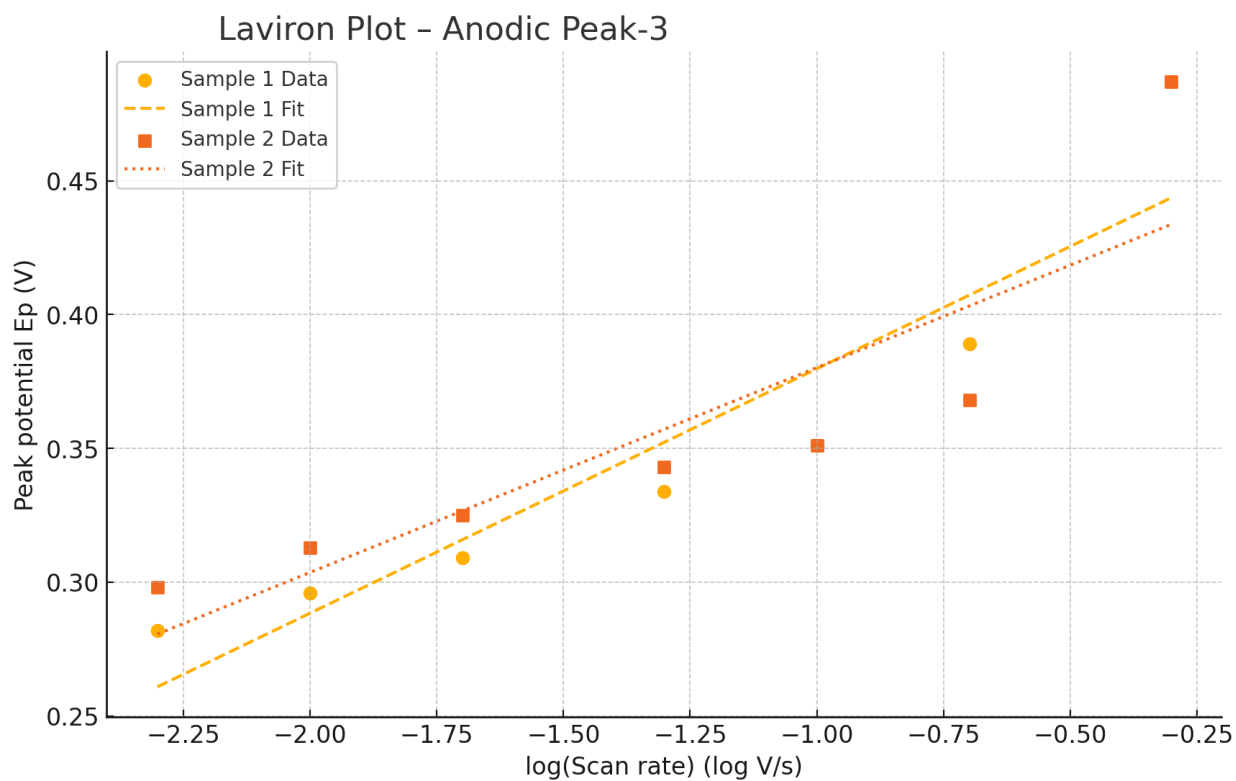
- $b \approx 0.5$: Diffusion-controlled kinetics (marked in green)
- $b \approx 1.0$: Surface-controlled kinetics or pseudocapacitive behaviour (marked in orange)
- $0.5 < b < 1.0$: Mixed kinetics, reflecting contributions from both diffusion and surface processes (marked in yellow).

NB! Corresponding sample names and peaks are labeled in each plot separately

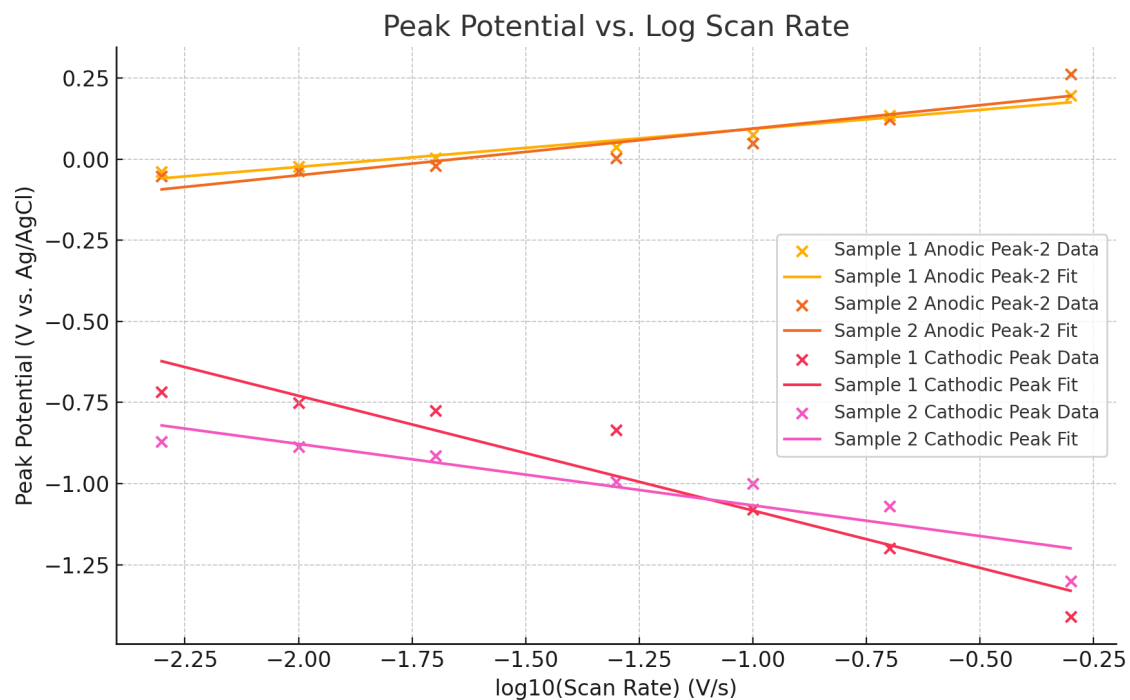




4. Laviron analysis - Plot for anodic peak-3 in Bi sample 1 and 2. (Data for anodic peak-1 which fails the model are not shown).



5. Calculation of Transfer Coefficient αn for Irreversible Electrochemical Processes from Cyclic Voltammetry, plot. Sample 1 is Bi sample 1, Sample 2 is Bi sample 2.



6. Python code

6.1. Code sample for Randles–Ševčík analysis:

What This Code Does:

Handles realistic mass normalization

Corrects for scan rate units

Uses true species concentrations (Cl^- and H^+)

Outputs final diffusion coefficients in cm^2/s , ready for interpretation

Required libraries

import numpy as np

Constants

n = 3 # Number of electrons transferred

A = 0.19625 # Electrode area (cm^2)

T = 298 # Temperature (K)

F = 96485 # Faraday constant (C/mol)

R = 8.314 # Gas constant ($\text{J/mol}\cdot\text{K}$)

Concentrations in mol/cm^3

C_Cl = 0.1 * 1e-3 # Cl^- from 0.1 M NaCl

C_H = 10**(-6.4) * 1e-3 # H^+ from pH 6.4

Mass loading in grams

mass_sample1 = 0.101e-3 # Sample 1: 0.101 mg

mass_sample2 = 0.102e-3 # Sample 2: 0.102 mg

Slopes from peak current vs. $\sqrt{\text{scan rate}}$ ($\text{A/g per (mV/s)}^{0.5}$)

slopes_Ag = {

 "Sample 1 - Anodic Peak-3": 0.0221,

 "Sample 1 - Anodic Peak-1": 0.008,

 "Sample 2 - Anodic Peak-2": 0.0363,

 "Sample 2 - Anodic Peak-1": 0.0102,

 "Sample 2 - Cathodic Peak-1": 0.0331,

 "Sample 2 - Cathodic Peak-2": 0.0217

}

Concentration and mass assignment

peak_conditions = {

 "Sample 1 - Anodic Peak-3": (C_Cl, mass_sample1),

 "Sample 1 - Anodic Peak-1": (C_Cl, mass_sample1),

 "Sample 2 - Anodic Peak-2": (C_Cl, mass_sample2),

 "Sample 2 - Anodic Peak-1": (C_Cl, mass_sample2),

 "Sample 2 - Cathodic Peak-1": (C_H, mass_sample2),

 "Sample 2 - Cathodic Peak-2": (C_H, mass_sample2)

```

}

# Conversion factor: mV/s → V/s (sqrt(1000))
conversion_factor = np.sqrt(1000)

# Randles–Ševčík equation (rearranged for D)
def calculate_diffusion_coefficient(slope_Ag, mass, concentration):
    # Convert from A/g to A, and from (mV/s)^0.5 to (V/s)^0.5
    slope_corrected = (slope_Ag * mass) / conversion_factor
    denominator = 2.69e5 * (n ** 1.5) * A * concentration
    D_half = slope_corrected / denominator
    return D_half ** 2

# Compute final diffusion coefficients
final_D_results = {}
for label, slope_Ag in slopes_Ag.items():
    conc, mass = peak_conditions[label]
    D = calculate_diffusion_coefficient(slope_Ag, mass, conc)
    final_D_results[label] = D

# Output results
for peak, D in final_D_results.items():
    print(f"{peak}: Final D = {D:.2e} cm²/s")

```

6.2. Code sample for Laviron analysis:

What This Code Does:

This code performs Laviron analysis by fitting peak potential vs. log(scan rate) data to extract the electron transfer coefficient (α) and standard rate constant (k^0) for surface-confined redox processes. It also generates a plot showing the experimental data and linear fits for each validated peak to visualize kinetic trends.

```
# Required libraries
import numpy as np
import matplotlib.pyplot as plt
from sklearn.linear_model import LinearRegression

# Constants
R = 8.314    # J/mol·K
T = 298      # K
F = 96485    # C/mol
n = 3        # number of electrons

# Experimental log(scan rate) values [log(V/s)]
log_scan_rates = np.array([-2.30103, -2, -1.69897, -1.30103, -1, -0.69897, -0.30103])

# Peak potentials (V vs Ag/AgCl) for valid peaks
ep_data = {
    "Sample 1 - Anodic Peak-1": np.array([-0.335, -0.335, -0.33, -0.33, -0.331, -0.328, -0.326]),
    "Sample 1 - Anodic Peak-3": np.array([0.282, 0.296, 0.309, 0.334, 0.351, 0.389, 0.487]),
    "Sample 2 - Anodic Peak-1": np.array([-0.315, -0.318, -0.328, -0.317, -0.318, -0.32, -0.3]),
    "Sample 2 - Anodic Peak-3": np.array([0.298, 0.313, 0.325, 0.343, 0.351, 0.368, 0.487])
}

# Color scheme for plot
colors = ["black", "red", "green", "blue"]

# Initialize plot
plt.figure(figsize=(8, 6))

# Perform Laviron analysis
for i, (label, ep_values) in enumerate(ep_data.items()):
    x = log_scan_rates.reshape(-1, 1)
    y = ep_values

    model = LinearRegression().fit(x, y)
    slope = model.coef_[0]
    intercept = model.intercept_
    r2 = model.score(x, y)
```

```

# Calculate Laviron parameters
alpha = (R * T) / (slope * n * F)
Ep_mid = np.interp(-1.0, log_scan_rates, ep_values)
term1 = (alpha * n * F) / (R * T)
ln_k0 = term1 * (Ep_mid - intercept) - np.log(R * T / (alpha * n * F))
k0 = np.exp(ln_k0)

# Print results
print(f"\n{label}")
print(f" Slope = {slope:.5f} V/log(V/s)")
print(f" R2 = {r2:.3f}")
print(f" α = {alpha:.3f}")
print(f" k0 = {k0:.3f} s-1")

# Plot data and fit
plt.scatter(log_scan_rates, ep_values, color=colors[i], label=f"{label} Data")
plt.plot(log_scan_rates, model.predict(x), color=colors[i], linestyle='--', label=f"{label} Fit")

# Finalize plot
plt.xlabel("log(Scan rate) [log(V/s)]")
plt.ylabel("Peak Potential Ep (V vs Ag/AgCl)")
plt.title("Laviron Analysis – Surface-Confined Anodic Peaks")
plt.grid(True)
plt.legend()
plt.tight_layout()
plt.show()

```

6.3. Code sample for Calculation of Transfer Coefficient αn for Irreversible Electrochemical Processes from Cyclic Voltammetry

What This Code Does:

This code calculates αn for Anodic Peak-2 and cathodic peaks of Bi Samples 1 and 2 by fitting peak potentials versus $\log_{10}(\text{scan rate})$ and applying equations for irreversible electrochemical processes.

It outputs αn values and generates a plot of the linear fits.

```
import numpy as np
import matplotlib.pyplot as plt

# Constants
T = 298 # Temperature in Kelvin
R = 8.314 # Gas constant, J/mol·K
F = 96485 # Faraday constant, C/mol
RT_F = R * T / F # RT/F at 25°C = 0.0257 V
factor = 2.303 * RT_F # 2.303 * RT/F = 0.0592 V

# Scan rates (V/s)
scan_rates = np.array([0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5])
log_scan_rates = np.log10(scan_rates)

# Peak potentials (V vs. Ag/AgCl)
# Anodic Peak-2
sample1_anodic2 = np.array([-0.0383, -0.0225, 0.00249, 0.0369, 0.0742, 0.134, 0.196])
sample2_anodic2 = np.array([-0.052, -0.037, -0.02, 0.0031, 0.0494, 0.123, 0.262])
# Cathodic Peaks
sample1_cathodic = np.array([-0.717, -0.751, -0.775, -0.834, -1.08, -1.2, -1.41])
sample2_cathodic = np.array([-0.871, -0.886, -0.914, -0.993, -1, -1.07, -1.3])

# Function to calculate slope and alpha_n
def calculate_alpha_n(peak_potentials, log_scan_rates, peak_type):
    # Linear regression to get slope
    coefficients = np.polyfit(log_scan_rates, peak_potentials, 1)
    slope = coefficients[0] # Slope in V/decade
    # Calculate alpha_n based on peak type
    if peak_type == "anodic":
        alpha_n = 0.0592 / slope
    else: # cathodic
        alpha_n = -0.0592 / slope
    return slope, alpha_n, coefficients

# Calculate for each dataset
results = {}
datasets = [
```

```

("Sample 1 Anodic Peak-2", sample1_anodic2, "anodic"),
("Sample 2 Anodic Peak-2", sample2_anodic2, "anodic"),
("Sample 1 Cathodic Peak", sample1_cathodic, "cathodic"),
("Sample 2 Cathodic Peak", sample2_cathodic, "cathodic")
]

plt.figure(figsize=(10, 6))
for name, potentials, peak_type in datasets:
    slope, alpha_n, coeffs = calculate_alpha_n(potentials, log_scan_rates, peak_type)
    results[name] = {"slope": slope, "alpha_n": alpha_n}
    # Plot data points and regression line
    plt.scatter(log_scan_rates, potentials, label=f"{name} Data")
    plt.plot(log_scan_rates, np.polyval(coeffs, log_scan_rates), label=f"{name} Fit")

# Print results
for name, result in results.items():
    print(f"{name}:")
    print(f" Slope = {result['slope']:.5f} V/decade")
    print(f" alpha_n = {result['alpha_n']:.3f}\n")

# Plot customization
plt.xlabel("log10(Scan Rate) (V/s)")
plt.ylabel("Peak Potential (V vs. Ag/AgCl)")
plt.title("Peak Potential vs. Log Scan Rate")
plt.legend()
plt.grid(True)
plt.savefig("peak_potential_plot.png")
plt.close()

```

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16/05/2025