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RECOVERY OF LOW CONCENTRATION OF TIN FROM SYNTHETIC WASTEWATER BY USING AN ELECTROGENERATIVE PROCESS

(Pemulihan Timah Berkepekatan Rendah daripada Air Sisa Sintetik dengan Menggunakan Proses Elektrogeneratif)

Muhammad Hakeem Azhan Mohd Azhari[1], Syaza Atikah Nizar[1], Syed Fariq Fathullah Syed Yaacob[1], Ahmad Faiz Abdul Latip[1], Megat Ahmad Kamal Megat Hanafiah[2], and Faiz Bukhari Mohd Suah[1*]

[1]Green Analytical Chemistry Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia.
[2]Faculty of Applied Sciences, Universiti Teknologi MARA, Cawangan Pahang, Lintasan Semarak, 26400 Jengka, Pahang, Malaysia

[*]Corresponding author: fsuah@usm.my

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Abstract

The existence of tin can be toxic and pose significant environmental and health risks if not adequately treated or recovered from water and wastewater before its discharge. One of the electrochemical methods to recover the tin from the aqueous environment is using an electrogenerative process. In this process, a chemical reaction occurred spontaneously in a galvanic cell where the reduction of tin occurred at the cathode and oxidation of zinc occurred at the anode without an external supply of energy. This study employed carbon felt and zinc as electrodes in a batch cell set-up to recover tin (Sn (II)) from its chloride solution. The electrogenerative recovery of tin was optimised with a specific focus on main parameters such as treatment of electrodes, tin initial concentration, deposition time, pH and influence of oxygen. The morphology and composition of the treated electrodes were analysed, too. The finding showed an initial Sn (II) concentration of 50 mg/L was the ideal concentration for recovering more than 96% of tin after 4 hours of operation. The influence of pH was also studied, showing that the optimum deposition process occurred at pH 7. A scanning electron microscopy energy-dispersive X-ray analysis system (SEM-EDX) was also used to observe the morphology of the deposited tin. It is confirmed that Sn (II) has been successfully deposited by the cathodic reduction of Sn (II) ions. Lastly, the electrogenerative process was also used to recover tin from wastewater samples, and satisfactory results of more than 80% recovery were obtained.

Keywords: electrogenerative process, electrodeposition, electrode, tin

Abstrak

Kewujudan timah boleh menjadi toksik dan menimbulkan risiko yang ketara kepada alam sekitar dan kesihatan jika tidak dirawat dengan betul atau diolah dengan baik daripada air dan air sisa sebelum disingkirkan. Salah satu kaedah elektrokimia untuk memulih timah daripada persekitaran akueus adalah dengan menggunakan proses elektrogeneratif. Dalam proses ini, suatu tindak balas kimia berlaku secara spontan di dalam sel galvanik dimana penurunan timah berlaku di katod dan pengoksidaan zink berlaku di anod tanpa bekalan tenaga daripada luar. Dalam kajian ini, karbon serat dan zink digunakan sebagai elektrod dalam penyediaan sel kelompok bagi mendapatkan timah daripada larutan kloridanya. Proses pemulihan secara elektrogeneratif dioptimumkan dengan fokus khusus kepada parameter-parameter utama seperti rawatan elektrod, kepekatan awal timah, masa pengendapan, pH dan pengaruh oksigen. Morfologi dan komposisi elektrod yang dirawat turut dianalisis. Dapatan kajian menunjukkan bahawa kepekatan awal Sn (II) 50 mg/L adalah kepekatan ideal dalam memulih lebih daripada 96% timah selepas 4 jam beroperasi. Kesan pH juga telah dikaji dan menunjukkan bahawa proses peendapan optimum telah berlaku pada pH 7. Sistem analisis sinar-X penyebaran tenaga mikroskop elektron pengimbasan (SEM-EDX) juga digunakan untuk memerhati morfologi timah yang diendapkan. Ini dibuktikan bahawa Sn (II) telah berjaya diendapkan melalui penurunan katodik ion Sn (II) di katod. Akhir sekali, proses elektrogeneratif juga diaplikasikan untuk pemulihan timah daripada sampel air sisa dan keputusan yang memberangsangkan iaitu lebih daripada 80% pemulihan semula telah diperolehi.

Kata kunci: proses elektrogeneratif, pengelektroendapan, elektrod, timah

Introduction

Heavy metals (HMs) in wastewater refer to metallic elements with high atomic weights and densities in wastewater streams. These metals can be toxic and pose significant environmental and health risks if not properly treated or removed from wastewater before discharge or reuse. Industrial processes, such as mining, metal plating, chemical manufacturing, and wastewater from various industries, can contribute to the presence of heavy metals in wastewater. Some common heavy metals of concern in wastewater include lead, zinc, mercury, nickel, cadmium, copper, and tin. The sources and concentrations of heavy metals in wastewater can vary depending on the industrial activities, geographical location, and specific processes involved [1]. These metals can enter wastewater through various pathways, such as industrial discharges, stormwater runoff, or domestic wastewater. HMs in wastewater can harm aquatic ecosystems, human health, and even agricultural productivity if used for irrigation. These persistent metals can accumulate in living organisms, leading to long-term environmental and health concerns [2]. To mitigate these risks, various treatment techniques are employed. Our research highlights the potential of electrochemical methods, such as electrocoagulation or electrochemical precipitation, in removing heavy metals. These techniques induce electrode reactions to facilitate precipitation and separation, offering a practical and effective solution to the problem of heavy metal contamination in wastewater.

Tin is considered a heavy metal and can be found in wastewater because of various industrial activities and domestic sources. While tin is not typically regarded as highly toxic compared to other heavy metals like lead or mercury, its presence in wastewater can still adversely affect the environment and aquatic organisms if not correctly managed. Two significant sources of tin in wastewater include industrial processes and domestic wastewater. Tin is used in industries such as metal plating, electronics manufacturing, and the production of tin-based alloys. Wastewater generated from these processes may contain tin ions or tin compounds. Tin can also enter wastewater through household activities such as cleaning products, cosmetics, and the disposal of tin-containing materials.

The existence of tin in the environment can pose several problems and concerns. Some critical environmental issues are tin-related, such as ecotoxicity, environment persistence and human exposure [3]. While tin is less toxic than other heavy metals, it can still harm living organisms, especially aquatic species. Elevated concentrations of tin in water bodies can harm marine life, including fish, invertebrates, and algae [4]. Chronic exposure to tin can result in reduced growth, reproductive impairments, and alterations in organisms' behaviour and physiological functions [5]. Next, tin, particularly certain forms like organotin, can exhibit persistence in the environment, meaning it can persist for a long time without readily breaking down or degrading [6]. Although the direct health impacts of tin on humans are generally considered low, there is a potential for exposure through the consumption of contaminated food, particularly seafood. Additionally, occupational exposure can occur in industries involving tin and its compounds, potentially leading to workplace hazards.

Analytical procedures known as electrochemical methods use measurements of potential, charge, or current to identify or characterise the chemical reactivity of an analyte. It uses electrical energy to drive chemical reactions at the electrode/electrolyte interface. These methods utilise the principles of electrochemistry to achieve various objectives, such as chemical synthesis, energy storage, corrosion protection, and environmental remediation [7]. One of the applications of electrochemistry is to analyse a solution for trace amounts of metal ions or organic elements. Electrochemical methods involving redox reactions between the anode and cathode have been introduced as electrometallurgy. It can be concluded that the improvement of treatment performance of the current technologies will contribute to a broader application of electrochemical processes in water and wastewater treatment [8]. The electrodeposition method is efficient for pre-treatment wastewater. This method is less suitable for wastewater with low concentrations of analytes and requires higher electrical energy usage [9].

Thus, another alternative technique that can be used to recover tin with low concentration using a much greener approach is introduced to address this issue. An electrochemical technique, the electrogenerative process, operates when the electrochemical reaction happens independently. The benefit of this approach is that the healing process can be generated without external energy sources. In the electrogenerative process, more electronegative metals will be oxidised, and fewer electropositive catholyte ions will decrease and be deposited onto the cathode. An external current flow will be created because of this method's reaction [10]. Additionally, different cell layouts and designs can be used with electrogenerative techniques. This study used an electrogenerated process operating in a batch cell to remove a low concentration of tin from industrial wastewater. The process was also optimised to achieve maximum recovery of tin from the wastewater.

Materials and Methods

All solutions required for the experiment were prepared using analytical-grade chemicals. Tin (II) chloride, sodium chloride, nitric acid, and ethanol employed in this investigation were sourced from Aldrich (Germany). The ion exchange membrane Neosepta ® AM-01 was supplied by Tokuyama Corporation, Japan). Carbon felt (2.0 cm × 5.5 cm × 0.3 cm) and pure zinc foil (2.0 cm × 4.5 cm × 0.05 cm) were used as cathode and anode, respectively. Southern Industrial Gas Sdn. Bhd. They provided the nitrogen gas. A 1000 mg/L tin standard solution (Merck, Malaysia) was diluted to various concentrations for sample and simulated wastewater concentration analysis.

Batch cell design

The static batch cell comprises two electrolyte cell compartments made from Plexiglass, whose materials are durable, sturdy, and lightweight. The dimensions for the cell compartments were 4.7 cm × 5.3 cm × 9.5 cm in size and are detached by an ion exchange membrane. The distance between the anode and cathode was 2.0 cm, while the distance between the electrodes and the membrane was 1.0 cm. The current collectors were attached to a digital multimeter by external conducting wires to complete the circuit. A magnetic stirrer was placed in the middle of the catholyte compartment to stir the catholyte, and the speed was set at 400 rpm throughout the experiment. The experiment was carried out at room temperature, and the arrangement of the experiment is shown in Figure 1

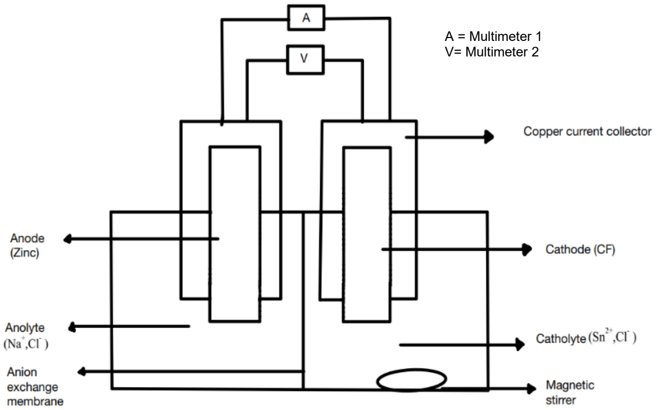

Figure 1. Diagram of a batch cell

Electrodes

In this research, a carbon felt cathode with a greater porosity and conductivity was used. The cathode must first undergo pre-treatment before being used. The dimensions of the electrodes used are displayed in Table 1. The cathode's physical properties are as follows:

specific surface area of 1229 cm^2 g^{-1}, porosity of 94.81%, volume resistivity of 2.22 Ω cm and conductivity of 0.96 S cm^{-1} [11]. As for the anode, the specific surface area is 5.6 cm^2 g^{-1}, density of 7.13 gmL^{-1}, volume resistivity of 5.8×10^{-4} Ω cm and conductivity of 1.6 mS cm^{-1} [11].

Table 1. The dimensions of electrodes used in this study

Type of Electrode	Electrode	Size
Anode	Zinc foil	2.0 cm × 4.5 cm × 0.05 cm
Cathode	Carbon felt	2.0 cm × 4.5 cm × 0.30 cm

Experimental procedure: Pre-treatment of anodes and cathodes

Zinc foil for the anode was cut to the dimensions mentioned in Table 1, and the oxide layer that had formed on the foil's surface was removed with sandpaper. Each time after polishing, the zinc foil was cleaned with distilled water and ethanol to ensure the cleanliness of the surface. Carbon felt must be pre-treated to eliminate impurities and improve the surface moisture characteristics. This experiment's pre-treatment method for the cathode corresponds to the experimental setup recommended by Basri and Suah [12]. Before use, the cathode was activated for eight hours. The cathode was then submerged in a 95:5 (v/v) mixture of ethanol and distilled water for four hours. After four hours, the cathode was rinsed with distilled water and immersed in 0.1 M nitric acid for another four hours. Finally, the cathode was rinsed again with distilled water and stored in distilled water to keep moisture until future use.

Preparation of electrolytes

All the electrolytes were prepared from analytical-grade reagents and distilled water. The anolyte used in the experiment was 0.2 M sodium chloride. It was prepared by diluting the distilled water with the amount of sodium chloride needed in a 1 L volumetric flask. Meanwhile, the catholyte solution was prepared by diluting the distilled water with anhydrous Sn (II) chloride in a 1 L volumetric flask. Subsequently, different concentrations of Sn (II) were prepared in a 250 mL volumetric flask.

Preparation of tin stock solution

The 1000 mg/L tin stock solution was used as a stock solution. To prepare a 100 mg/L of Sn (II) standard solution, 10 mL of the stock solution was diluted in a 100 mL volumetric flask. The solution was diluted to the proper concentration to achieve a final volume of 100 mL. In four separate 100 mL volumetric flasks, 10, 20, 30, and 40 mg/L solutions were prepared from 100 mg/L standard tin solution.

Optimisation of the batch reactor: The effect of initial Sn concentration

Several Sn concentrations have been evaluated to determine the optimum initial concentration of Sn. The initial Sn (II) solution concentrations ranged from 50 to 500 mg/L.

The effect of nitrogen gas purging

Oxygen in the solution could influence the tin recovery. As a result, this study investigated two conditions: with and without the presence of nitrogen gas. Both analyte and catholyte were purged with nitrogen gas.

The effect of pH

The effect of pH on the recovery of 50 mg/L of Sn (II) was investigated by varying the different pH values (pH 4-7) of the analysis using 0.1 M NaOH and 0.1 M HCl.

Electrogenerative process for tin recovery

In the batch cell, the compartments on the right and left sides were marked as cathode and anode, respectively. The anode and cathode compartments acquired 170 mL of the anolyte and catholyte. Subsequently, the anode and cathode were immersed in the compartments at a fixed place. A magnetic stirrer was inserted inside the cathode compartment to stir the catholyte during the electrogenerative process. Next, two multimeters were simultaneously connected to the anode and cathode to measure the voltage (electrical potential) and current (stream of electric flow) throughout the operation. Current and voltage starting values were noted. Any current or voltage variations during the electrogenerative process were noticed and recorded.

Before the experiment, the cathode was cleaned with distilled water and dried. As for the anode, the zinc foil was polished with sandpaper. Subsequently, the nitrogen gas was initially purged into the anolyte and catholyte for 10-15 minutes before the experiment. To track the quantity of Sn (II) present in the solution, 5 mL aliquots of the catholyte were taken every 30 minutes during the experiment. The Sn (II) concentration was evaluated using Atomic Absorption Spectroscopy (AAS; Perkin Elmer AAnalyst 200 Model). The AAS setting is as follows: the use of an air acetylene flame with a 286.3 nm wavelength, a 3.00 L/min acetylene flow rate, a 15.00 L/min oxidant flow rate, and a 0.7 nm slit width.

Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX)

Scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) on a Quanta FEG 650 were used in this investigation to examine the elemental composition of the tin deposition on the carbon felt and to visualise its morphological surface. The tin-coated carbon felt was cleaned with distilled water and kept in the oven overnight. Before analysis, any impurities are to be removed. Analysis of the carbon felt surface before and after deposition was compared.

Recovery of tin from the wastewater

The Sn (II) solution was prepared from Merck analytical-grade stock standards of 1000 mg/L to simulate actual wastewater concentrations. The synthetic wastewater solutions were then prepared by diluting the stock standard. The pH of the synthetic wastewater was adjusted using 1 M HCl and 1 M NaOH. The final Sn (II) concentration in the solutions was diluted to the desired concentrations.

Results and Discussion

This study used a batch cell to find the ideal conditions for recovering a low Sn (II) concentration from its chloride solution using the electrogenerative process. Different catholyte concentrations, the influence of nitrogen gas, and the effect of different pH are some of the parameters assessed in this study. In addition, SEM-EDX was used to analyse the morphological and chemical changes deposited on the cathode.

Electrogenerative studies

In the electrogenerative process, more electropositive ions will be reduced at the cathode while more electronegative metals oxidise. A spontaneous reduction-oxidation reaction represents this chemical reaction. Electrons are lost during an oxidation reaction at the anode, whereas electrons are acquired during a reduction reaction at the cathode. The reactions in the batch cell are represented by the equation below:

Anode: $\mathrm{Zn_{(s)} \leftrightarrows Zn^{2+}{}_{(aq)} + 2e^-}$ E^o= 0.76 (1)

Cathode: $\mathrm{Sn^{2+}{}_{(aq)} + 2e^- \leftrightarrows Sn_{(s)}}$ E^o = -0.14 V (2)

Overall: $\mathrm{Zn_{(s)} + Sn^{2+}{}_{(aq)} \leftrightarrows Zn^{2+}{}_{(aq)} + Sn_{(s)}}$
E_{cell} = 0.62 V (3)

The reaction that occurs in the anode and cathode is represented by equations (1) and (2). The positive value of standard reduction potential indicates that the cell has a positive standard cell potential, which means that the reaction between zinc and tin occurs spontaneously without any external stimulus and can generate an electric potential of 0.62 V. The Gibbs free energy involved in this study may be calculated using the standard reduction potential of the cell, where n is the number of electrons received or released per mole of reactant, Gibb's free energy, F is Faraday's constant and cell potential.

$$\Delta G^\circ = -nFE^\circ{}_{cell} = -nF(E_c - E_a) \qquad (4)$$

Where n is the number of electrons accepted or released in the reaction per mole of reactant, F is the Faraday's constant, $E^\circ{}_{cell}$ is the overall potential of the cell, E_c is the standard reduction potential at cathode and E_a is the standard reduction potential at the anode.

The Gibb's free energy determined in this experiment was -119.64 kJmol^{-1}. Each electrogenerative process has a negative Gibb's free energy, which denotes that the beginning state, or reactants, has more incredible free energy than the final state or products. The reaction is thermodynamically favourable. It means the process releases energy to its surroundings, thus losing free energy. The corresponding ΔG will be negative in this case, indicating an exergonic reaction [12].

Effect of initial Sn (II) concentration

The effect of the initial Sn (II) concentration was examined using a variety of catholyte concentrations of 50, 100, 200, 400 and 500 mg/L. In the context of absorbance measurements, detection for Sn (II) is limited. Thus, it was discovered that the absorbance of

400 mg/L and 500 mg/L exceeded the working range value after sampling was carried out for all concentrations. As a result, the concentration employed for the remainder of this trial was limited to 50, 100, and 200 mg/L.

The maximum tin recovery was recorded at 50 mg/L within 240 minutes of operation (96.01 ± 0.22%) (Figure 2), While for 100 mg/L and 200 mg/L, the tin recovery was (79.18 ± 0.30%) and (48.86 ± 0.17%) within 240 minutes of the operation, respectively. At a high initial concentration, the deposited tin on the cathode surface is denser, which may attribute additional resistance to mass transfer. The abundance of tin ions available in high concentrations causes the rate of electrodeposition to be relatively high. However, as the tin deposit grows, it can become denser, hindering further mass transport of tin ions to the cathode surface. Thus, it is more difficult for tin to reach the electrode surface and participate in the reduction reaction.

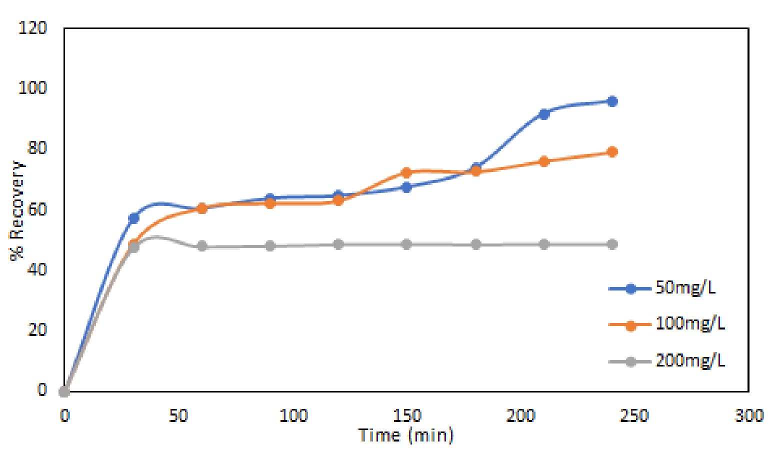

Figure 2. The effect of various catholyte concentrations of $SnCl_2$ for the recovery of tin from its chloride solution

Influence of the absence and presence of nitrogen gas

In the electrochemical deposition process, including the electrogenerative process, the influence of oxygen is significant since the amount of dissolved oxygen in the electrolytes greatly influences the electrodeposition process. Dissolved oxygen lowers the current efficiency for electrodeposition and influences the mass-transfer-controlled electrochemical reduction process, subsequently reducing the recovery or removal capacity [11]. Thus, purging with nitrogen gas into the catholyte and anolyte was necessary before and during the experiment to minimise the presence of dissolved oxygen in the solution. In this study, the impact of the oxygen was further examined under two different circumstances. The first condition involved using nitrogen gas to purge the electrolytes, while the second did not include purging the electrolytes with gas nitrogen. At the initial concentration of 50 mg/L of Sn (II), the percent recovery of tin is only (66.45 ± 0.31 %) in the presence of oxygen as compared to (96.10 ± 0.22 %) without the presence of oxygen, as shown in Figure 3. For initial concentrations of Sn (II) at 100 mg/L and 200 mg/L, the recovery of tin reached a total of (79.18 ± 0.30 %), and (48.86 ± 0.17 %) with the presence of oxygen, respectively. Figure 4 and Figure 5 show the tin recovery for Sn (II) concentrations of 100 mg/L and 250 mg/L without the presence of oxygen produced lower recovery rates of (50.70 ± 0.25%), and (29.82 ± 0.18%), respectively.

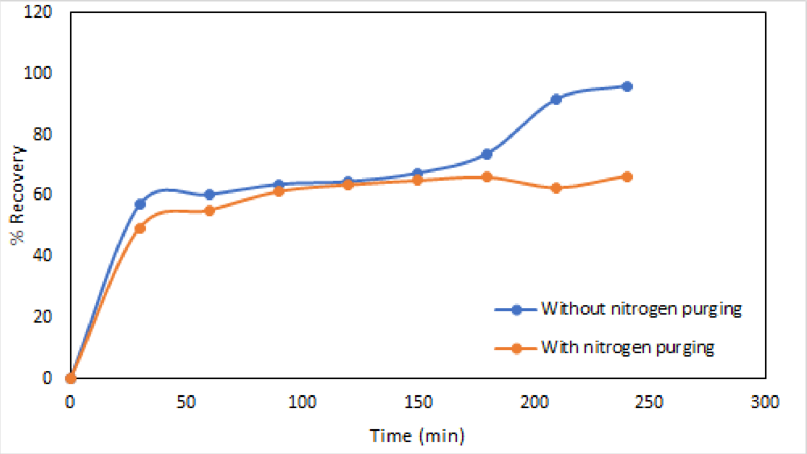

Figure 3. Effect of the presence of oxygen on recovery of tin from its chloride solution at 50 mg/L

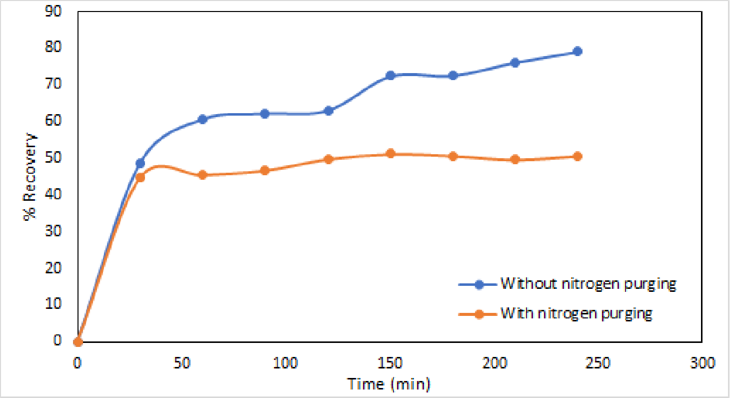

Figure 4. Effect of the presence of oxygen on recovery of tin from its chloride solution at 100 mg/L

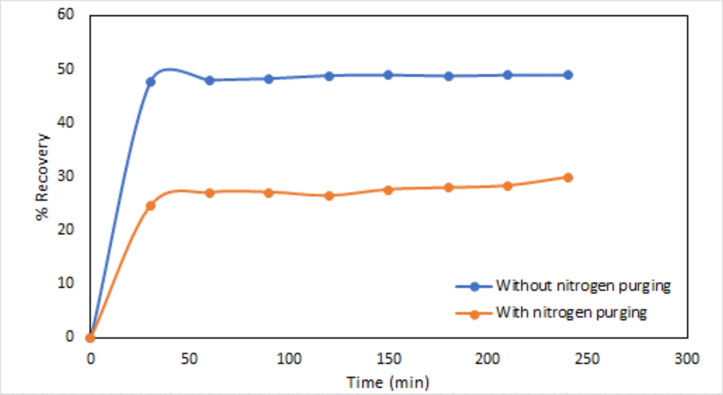

Figure 5. Effect of the presence of oxygen on recovery of tin from its chloride solution at 250 mg/L

Generally, nitrogen gas is often used to displace and remove oxygen from the reaction environment. Oxygen facilitates a metal's reduction process by providing free electrons for cation reduction [13]. However, oxygen did not affect tin recovery in the chloride solution used in this study. This may be due to the higher stability of Sn^0 compared to Sn^{2+}. Furthermore, chloride ions act as electron donors, providing the electrons required to reduce Sn^{2+} to Sn^0.

Effect of pH

The pH plays a crucial role in the efficiency of the electrodeposition process [14]. They reported that pH affects both the kinetics of tin electrodeposition and the stability of tin species in the electrolyte. Therefore, optimising the pH within a suitable range is crucial to maximise the tin recovery. The non-controlled pH condition is the condition where the pH of the electrolytes remains in its initial condition. The pH of the electrolytes is not modified or controlled. The electrodeposition process occurs solely based on the electrolytes' initial pH. It is found that the total recovery of tin (50 mg/L) achieved under the non-controlled pH condition (96.01 ± 0.22%) is slightly lower than the recovery under the pH 7 condition (99.38 ± 0.16%) (Figure 6). A longer time is needed to achieve 90% Sn (II) recovery at pH 4 and 5. The proton reduction occurs due to hydrogen ions competing with cations for the active sites on the electrode surface [15]. The redissolution of deposited metal may occur over time due to the blocking effect of hydrogen evolution.

The electrochemical reaction in tin recovery proceeds at a desirable rate under neutral pH conditions. The current efficiency of recovery also increases as pH increases to pH 7. Tin is reduced at near-neutral and neutral pH values due to the optimum current efficiency developed and the low quantity of hydrogen present at these pH values [16]. Moreover, chloro-complexes can be formed in the presence of chloride ions in acidic solutions due to their ability to coordinate with ligands, eventually facilitating the electrodeposition process in a chloride medium.

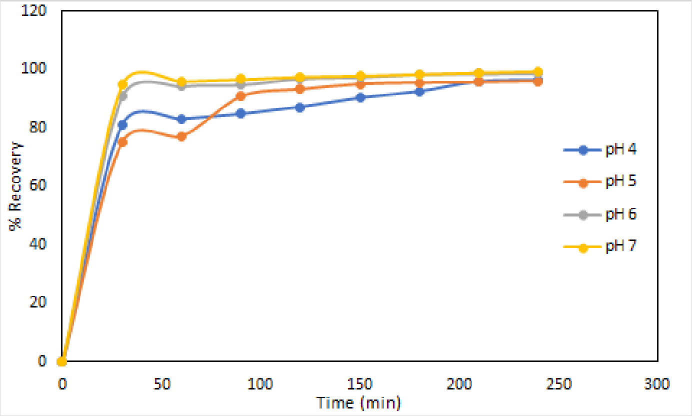

Figure 6. Effect on Sn (II) recovery from its chloride solution at different pH

Kinetic study

The concentration-time relationship for a 3-D electrode operating under mass transport control can be used to illustrate the kinetic of Sn (II) recovery from its chloride solution. It applies to Equation 5, which represents the mass control of carbon felt:

$$\ln\left[\frac{C_t}{C_o}\right] = -\frac{V_o}{V_R} k_m A_e t^{-1} \qquad (5)$$

Where V_o is the catholyte volume, V_R is the total volume of electrolyte in the cell, k_m is the mass transfer coefficient, A_e is the specific surface area of the cathode, and C_t. The metallic ion concentration is a function of operation time. The volumetric mass transport coefficient offers relevant data on the cathode system's performance.

Based on the slope of ln [C_t / C_o] versus time, the values of the volumetric mass transfer coefficients $k_m A_e t$ are derived. It indicates the rate of Sn^{2+} depositing on the cathode at a given rate. Figure 7 shows the result of the concentration-time relationship of the selected concentration of Sn (II). The mass transfer rate consistently decreases with time. Thus, it can be said that the cathode's surface area is diminishing. Also, a decreasing mass transfer rate may indicate that the cathode is becoming less active due to the reduced surface area of the cathode surface.

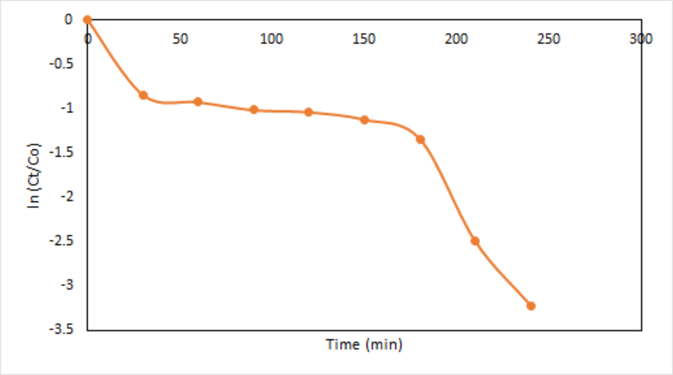

Figure 7. Plots of $\ln\left[\frac{C_t}{C_o}\right]$ *vs* time for 50 mg/L of Sn (II)

Table 2 displays the effectiveness of batch cell performance in recovering tin at various concentrations of Sn (II). It shows the results of tin recovery experiments using different concentrations of tin. Based on Equation 4, since Vo/VR is a constant, the value of the volumetric mass transport coefficient, k_mA_et, is taken from the slopes of ln C_t/C_0 versus time. It represents the rate constant of tin deposition on the cathode. The high value of mass transfer indicates that a significant amount of the target substance has been successfully transferred from one phase to another during the process. As a result, it can be concluded that the high mass transfer influences the recovery of Sn (II) in this electrogenerative process.

Table 2. The recovery of tin from various concentrations of Sn (II)

Sn (II) Concentration (mg/L)	50	100	200
R^2 value	0.8015	0.8576	0.3327
Slope (min^{-1})	-0.0104	-0.0053	-0.0016
k_mA_et (min^{-1})	-0.0827	-0.3775	-0.4031

Surface morphology

Further investigation of the carbon felt's surface morphology confirmed the deposition of tin. SEM and EDX analysis were used to visualise the image and quantify the deposited tin. SEM analysis has proven the electrodeposition of tin on the surfaces of carbon felt. The surface analysis of carbon felt before and after the deposition is presented in Figure 8. Afterwards, the carbon felt turned shiny, indicating tin had been deposited.

Figure 9 shows a layered micrograph image of carbon felt before and after the electrodeposition process. The red and blue colours represent carbon and tin, respectively. The carbon felt structure also consists of large void spaces between the fibres, which shows the large effective surface area.

The elementary analysis of the carbon felt was carried out using EDX analysis. The percentages by weight of elemental tin, oxygen and other elements were obtained from the EDX analysis. Figure 10 shows the spectra of carbon felt before and after the deposition process. In Figure 10(a), the presence of carbon and oxygen elements is due to the composition of high-purity carbon fibres in a carbon felt. Thus, the carbon peak would be the most predominant and intense. Firm peaks with an intensity of 22.8% prove the deposition of tin on the carbon felt, as shown in Figure 10(b). Hence, it is confirmed that tin is deposited on carbon felt.

Recovery of tin from a simulated wastewater sample

The electrogenerative process was applied to recover tin from a simulated wastewater containing tin solution. Table 3 shows satisfactory results in the recovery of tin for both samples (50 and 200 mg/L) after 4 h of the deposition process, with more than 80% of tin recovered. The total recovery of tin can be achieved with additional electrode modifications and experimental design (contact area, time, pH, stirring, and others). These parameters will be tested in the subsequent research. The results obtained in this study are comparable to those of other electrochemical methods in recovering tin from aqueous solutions (Table 4). The percent recovery of tin by the electrogenerative process is higher than other electrochemical methods. It is noted that other methods are only suitable for tin with high concentrations. In contrast, the electrogenerative process is ideal for low concentrations of tin. Due to the high concentrations of tin in the samples, the tin recovery process is combined with other recovery methods, such as pyrometallurgy and hydrometallurgy [17-22].

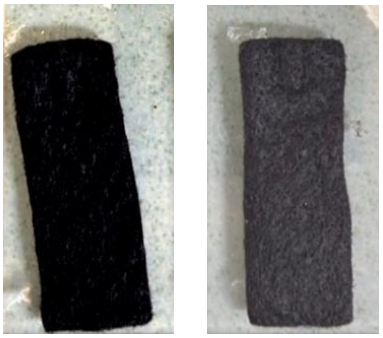

Figure 8. Differences of CF before (left) and after (right) the electrodeposition of tin

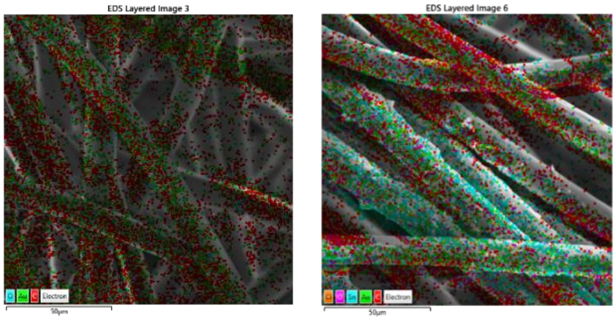

Figure 9. Micrographs (100× magnification) of Sn (II) deposition on the cathode before (left) and after (right) the recovery process

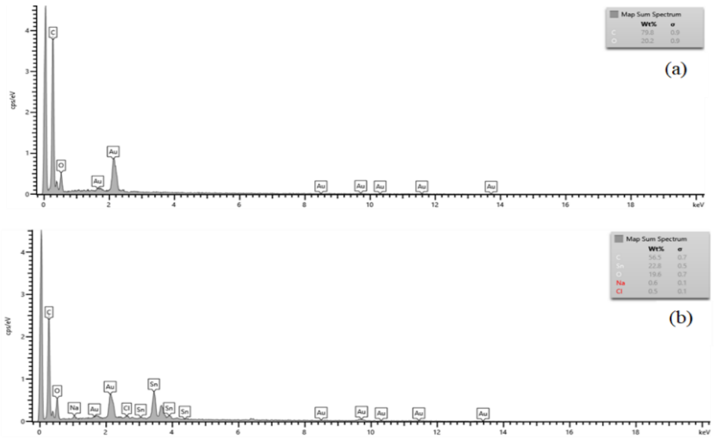

Figure 10. The EDX spectra (a) before and (b) after deposition of Sn (II). Conditions: 50 mg/L of Sn (II) and pH 7

Table 3. The recovery of tin from various Sn (II) concentrations from the simulated wastewater sample

Tin Sample (n=3) (mg/L)	**Recovery (%)**
50	95 ± 0.03
200	80 ± 0.75

Table 4. Comparison of recovery capacities of tin from aqueous solutions by electrochemical methods

Electrochemical Method	**Types of Electrodes**	**Types of Samples**	**Tin Recovery (%)**	**Optimum Recovery Capacity (mgL^{-1})**	**Reference**
Stripping	Cathode: Gold disc Anode: Platinised titanium sheet	Simulated and real waste tin strip solutions	70	1.5×10^5	[17]
Stripping and electrolysis	Cathode: Titanium plate Anode: Tin	Printed circuit boards	85	6.0×10^5	[18]
Cementation and chronoamperometry	Cathode: Graphite Anode: Platinum wire	Tinning sludge	90	3.1×10^4	[19]
Electrodeposition	Cathode: Stainless steel Anode: Platinised titanium plate	Printed circuit boards	Not mentioned	1.0×10^3	[20]
Electrowinning	Cathode: Stainless steel Anode: titanium with ruthenium oxide coating	Printed circuit boards	Not mentioned	Not mentioned	[21]
Electrodeposition	Cathode: Copper Anode: Copper	Printed circuit boards	70-100	1.7×10^3	[22]
Electrogenerative process	Cathode: carbon felt Anode: Zinc foil	Synthetic wastewater	95	50-200	This study

Conclusion

The recovery of Sn using an electrogenerative process is successfully demonstrated in this study. According to the experimental result, it can be concluded that a high percentage recovery of Sn (II) in chloride solutions can be achieved using activated carbon felt. The unique properties of carbon felt surface area and porosity improve mass transfer, increasing the recovery of Sn (II) from chloride solutions. The experimental results indicate that the highest tin recovery was determined (96.01±0.22 %) in 50 mg/L within 240 minutes of operation. This concentration allows for favourable electrochemical conditions, enhancing tin deposition while minimising undesirable side reactions.The presence of oxygen does not affect the performance of tin deposition. The study reveals that the pH adjustment significantly affects the mechanism of tin recovery. By adjusting the pH within the optimal range, the electrodeposition of tin can be enhanced, leading to increased recovery rates and improved efficiency. The analysis identifies that pH 7 is optimal for achieving the highest tin recovery. Finally, SEM-EDX analysis results confirmed tin deposition on the carbon felt surface.

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