Degradation Kinetics and Mechanism of Polychloromethanes Reduction at Co-MoS$_2$/Graphite Felt Electrode

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Abstract: In this study, the electrochemical dechlorination of different polychloromethanes (CCl$_4$, CHCl$_3$, and CH$_2$Cl$_2$) on a Co-MoS$_2$ graphite felt cathode was investigated. The Co-MoS$_2$ electrocatalyst was prepared hydrothermally on a graphite felt support. The prepared catalyst’s characterization revealed the formation of hybridized CoSx and MoS$_2$ nanosheets deposited on the pore structures of graphite. The influencing factor for the electro-dechlorination parameters such as applied current density, pH, and sample concentration on the dechlorination rate was optimized. A significant capacitive reduction current density peak of approximately 1 mA/cm$^2$ was noted for CCl$_4$ at a potential of −0.3 V (vs. AgCl). The dechlorination mechanism was attributed to the stepwise hydrogenolysis mechanism that involves the organochlorides bond cleavage by H$_*$ insertion. It was noted that the Co-MoS$_2$ graphite felt electrode exhibited excellent catalytic activity toward the reduction of each of the chlorinated compounds with high selectivity toward the higher-order organochloride. Moreover, the dechlorination rates for each of the compounds were suited to the first-order kinetic model, and the estimated apparent rate constants showed the dechlorination in the following sequence CHCl$_3$ (k$_2$ = 1.5 × 10$^{-3}$ s$^{-1}$) < CCl$_4$ (k$_1$ = 2.8 × 10$^{-3}$ s$^{-1}$). 

Keywords: halogenated organics; electrochemical dechlorination; catalyst electrode; kinetic model

1. Introduction

Polychloromethanes that include carbon tetrachloride and chloroform are among the most ubiquitous classes of volatile halogenated contaminants commonly found in surface water, groundwater, and soil [1]. These compounds have been discharged into the environment because of their extensive use as organic solvents by several industrial processes [2]. Due to their toxicity and persistence in nature, many dehalogenation treatment approaches [3–6] have been offered toward their safe removal or detoxification in contaminated environmental samples.

Over the years, the reductive dehalogenation technique over heterogeneous catalysts has been sought as a viable treatment option for organochloride remediation in the aqueous sample [4]. This treatment approach refers to as hydrodechlorination often employs an active reductive catalyst with a hydrogen source to facilitate the reaction of chlorinated organic with formed nascent hydrogen (atomic) to produce hydrochloric acid (HCl) and a new C-H bond for the organic [7]. The hydrodechlorination reaction is highly sought for its effectiveness toward the cleavage of the C–X bonds (X: Cl, Br, F) of organic halides under mild reaction conditions [8]. Conventional dechlorination approaches suffer catalyst
aggregation and deactivation. They require a reducing agent (hydrogen donor), which can be expensive, and they are unable to offer a complete reduction for some organic halides [4]. The electrocatalytic dehalogenation approach was advanced as a simple, fast, and environmentally friendly approach for organochlorides reduction to circumvent these perceived limitations and provide a robust dechlorination treatment approach. Electrocatalytic hydrodechlorination employs a catalyst electrode and an externally applied electron (applied current) that serve as the reactant to initiate the reduction process through catalytic generation of reductive species (H*- atomic hydrogen) that effectively detoxify the organochloride contaminants [1]. In this approach, the reductive species are continuously generated in situ via water dissociation and does not require the addition of a hydrogen donor. Compared to the hydrodechlorination reaction, the cathodic polarization of the catalyst electrode during electrocatalytic hydrodechlorination processes serves to protect the electrode against deactivation, which in turn, allows for its long-time usage.

The pathway for the electrocatalytic dehalogenation reaction has been demonstrated to involve the following sequence of reactions provided in Equations (1)–(4).

\[
\begin{align*}
2H_2O + 2e^- + M & \rightarrow 2[H^*_{ads}]M + 2OH^- \quad \text{(Volmer Reaction)} \\
2[H^*_{ads}] & \rightarrow H_2 \\
H_2 + M & \rightarrow 2[H^*_{ads}]M \\
(R - Cl)_{ads} + [H^*_{ads}]M + e^- & \rightarrow (R - H)_{ads} + Cl^- + M \quad \text{(Dechlorination Reaction)}
\end{align*}
\]

where \(M\) denotes the catalyst metal, \((R - Cl)_{ads}\) is the adsorbed organochloride on the catalyst surface, and \([H^*_{ads}]\) represents the chemisorbed atom or hydrogen.

According to the provided equations, it is evident that the catalyst electrode plays a pivotal role in the dechlorination reaction as it aids in the H* formation and supplies the needed electrons for water dissociation. Hence, an electrode material with superior catalytic activity to generate sufficient H* is required for the rapid and effective dechlorination reaction [9].

Several studies have demonstrated the excellent catalytic activities of noble metals-based catalyst electrodes that include palladium (Pd) and silver (Ag) toward the complete dechlorination of several types of organic halides [10–16]. Pd possesses a lower hydrogen overpotential as a cathode electrode for the dechlorination reaction [10]. Moreover, it can maintain a significant generation of surface-bound H* for effective dechlorination due to its strong affinity for absorbing hydrogen onto its lattice. To date, the use of these noble metals in real applications is restricted because of their scarcity and prohibitive cost.

The quest for effective, low-cost electrocatalysts for reductive water treatment has seen the emergence of several transition metals and their composites as electrodes with comparable catalytic properties to those of precious metals. Recent studies have demonstrated the excellent catalytic properties [17–20] of Co-doped MoS\(_2\) for H* formation, which can effectively be used to reduce organochloride. It was reported that the hybridized CoS\(_x\) and MoS\(_2\) formed during the Co doping of MoS\(_2\) (Co-MoS\(_2\)) leads to the formation of catalytic active surface edge sites that enable the accelerated surface-bound H* formation [19]. Despite the successful application of Co-MoS\(_2\) for the reductive treatment of organochloride, the true nature and mechanistic detail of the electrode reaction is still lacking in the literature. Moreover, knowledge of the electrode kinetics and reaction mechanism is crucial for electrochemical reactor design and sizing in real-life applications.

Hence, in this study, we report the kinetics and mechanistic investigation of the electro-reductive dechlorination of selected polychloromethanes CCl\(_4\), CHCl\(_3\), and CH\(_2\)Cl\(_2\) Co-MoS\(_2\) catalysts supported on a graphite felt electrode. The Co-MoS\(_2\) catalyst was prepared through the hydrothermal synthesis route and was deposited on the graphite felt in situ. In addition, reports have shown that the rate of dechlorination reaction is highly dependent on the operating conditions [10,21]. For this reason, we investigated the
influence of operating parameters that include solution pH, applied current densities, and reaction time to elicit their effect on the organochloride’s reduction by the electrode.

2. Results and Discussion

2.1. Material Characterization

A detailed material characterization of the prepared Co-MoS$_2$-GF electrode can be found in our previously published work [17]. However, we provide a brief description of the salient features of the electrode in the following paragraphs.

The bare GF used as a support for the Co-MoS$_2$ catalyst deposited has a porous 3-D interlaced fiber structure. The deposited Co-MoS$_2$ on the GF shows agglomerated-particles active edge sites. Moreover, TEM analysis results depict a layered corrugated structure that was due to MoS$_2$ crystalline phases [22,23]. The appearance of orderly spaced lattice fringes with an inter-planar distance of 0.35 nm in the HRTEM result further confirms the crystalline phase of Co-MoS$_2$ [24].

The identification of the chemical composition of Co-MoS$_2$ catalysts through the X-ray photoelectron spectroscopy (XPS) analysis reveals the presence of a hybrid Co-MoS$_2$ composite based on the appearance of molybdenum (Mo), cobalt (Co), and sulfur (S) elements. The deconvolution of the high-resolution spectrum for each of the elements shows that for Mo, its spectrum presents two paired peaks at binding energies of 233 and 228 eV assigned to Mo 3d3/2 and Mo 3d5/2 oxidation states, respectively [25]. In the case of Co, its spectrum shows two peaks at binding energies of 802 and 780 eV that were attributed to the Co$^{2+}$ (Co 2p1 and Co 2p3) oxidation state [26]. On the other hand, the sulfur spectrum reveals a significant peak at 168 eV that suggests the existence of sulfur in the S$^{2-}$-oxidation state (S 2p3/2). The findings from the electrode characterization were able to substantiate the existence of hybridized CoS$_2$-MoS$_2$ composites on the GF surface during synthesis.

2.2. Electrode Cyclic Voltammetric Analysis

CV analysis was employed in verifying the catalytic property of the prepared Co-MoS$_2$-GF electrode toward H* formation for the dechlorination reaction. The CV was recorded in the presence and absence of the substrate (polychloromethanes), as illustrated in Figure 1. In the absence of the substrate (blank-background electrolyte), the voltammogram showed a minimal reduction peak at 0.2 V (vs. Ag/AgCl) attributed to water dissociation. This small capacitive current peak displayed in the substrates’ absence indicates apparent H* formation on the active sites during water reduction. Moreover, the significant peaks observed in each substrates’ presence suggest the potential contribution of formed H* toward reducing the compounds. Among the organochlorides, CCl$_4$ showed the highest reduction peak at approximately $-0.3$ V (vs. Ag/AgCl) with a capacitive current density of $\sim$1 mA/cm$^2$, indicating the higher-order electrode selectivity of the organochloride. Meanwhile, CH$_2$Cl$_2$ and CHCl$_3$ showed moderate peaks at the same $-0.3$ V (vs. Ag/AgCl) potential. In addition, it can be inferred from Figure 1 that the intensity of the reduction peaks is consistent with the number of chlorine atoms present in the compounds.

The reduction route exhibited by the Co-MoS$_2$-GF cathode in the CV represents the hydrogenolysis mechanism that involves the organochlorides bond cleavage by H* insertion [13]. This is based on the significant reduction peak displayed by each of the compounds at the same potential. It is worth noting that this finding corroborates some reports [27–29] that presented a hydrogenolysis mechanism for these organochlorides based on the formation of significant peaks, as revealed from the CV scan.
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Figure 1. Cyclic voltammetry scan for the Co-MoS2-GF cathode in the absence (blank background electrolytes, 0.5 M of Na2SO4) and presence of 5 mM of each of the CCl4, CHCl3, and CH2Cl2. Scan rate, 10 mV/s.

2.3. Influence of Operational Parameters
2.3.1. Effect of Applied Current Density

Current density is a crucial electrolysis parameter that controls the electrode’s electron transferability to the substrates [30]. Therefore, in this study, the influence of current density variation from 2.5 to 15 mA/cm2 on the reduction efficiencies of CCl4, CHCl3, and CH2Cl2 was investigated. As illustrated (Figure 2), all the compounds showed a positive dechlorination trend as the current density was raised from 2.5 to 15 mA/cm2. CCl4 presented a significant reduction of 60% at 2.5 mA/cm2, which increased to around 85% at 10 mA/cm2 at 30 min for electrolysis time in both cases. Moreover, at the same electrolysis time, CHCl3 and CH2Cl2 presented a much lower dechlorination efficiency (35%) at 2.5 mA/cm2, which increased to the 75 to 80% range at higher current densities.

Figure 3 shows the effect of applied current density toward the electrode faradaic current efficiency for each organochloride. As illustrated in Figure 3, the electrode exhibited a decreasing current efficiency trend as the current density was raised from 2.5 to 15 mA. The highest current efficiencies were noted at the lowest current densities with values of 45%, 19%, and 12.5% for CCl4, CHCl3, and CH2Cl2, respectively. The downward trend in the electrode’s current efficiency was attributed to the dominance of the hydrogen evolution reaction (HER) over the dechlorination reaction (as evidenced by increased H2 bubble formation). According to Tafel’s step in the HER-catalyzed reaction, most generated H* recombined toward H2 formation [31].
In general, the electrode showed a high selectivity for CCl$_4$ dechlorination at lower current densities than CHCl$_3$ and CH$_2$Cl$_2$, but presented a relatively close dechlorination rate at higher current densities for all compounds. Moreover, the high organochloride dechlorination observed at high current densities was attributed to the high amount of charge loading to the electrode surface that facilitated the enhanced generation of H* (from water dissociation).

2.3.2. Effect of Solution pH

Solution pH is an important parameter that affects both the anode’s and cathode’s reaction conditions in electrochemical processes. The influence of sample pH at acidic (pH 3), neutral (pH 7), and basic (pH 12) was investigated and is presented in Figure 4. A decreased dechlorination efficiency as the pH was varied from acidic to the basic medium.
was observed. After electrolysis, a slight decrease in final pH was noted for all the samples (data not included), suggesting the formation of chloride ions. After 30 min of electrolysis, significant dechlorination values of 75%, 68%, and 50% were obtained under acidic conditions for CCl₄, CHCl₃, and CH₂Cl₂, respectively, whereas, under the neutral condition, a slight decrease in reduction efficiency was noted for each compound. Moreover, at the basic pH 12, all the compounds presented a meager reduction in the range of 30 to 10%.

Figure 4. pH Variation on the dechlorination efficiency of the organochlorides (experimental conditions: 5 mM concentration of CCl₄, CHCl₃, and CH₂Cl₂, electrolysis time: 30 min, current density: 15 mA/cm²).

Generally, reports have demonstrated that under acidic conditions, the electrocatalytic dechlorination reaction is usually enhanced because of significant protons (H⁺) in the solution, which are easily converted to H* at the electrode surface [32]. The enhanced reduction observed at pH 3 and pH 7 was likely due to H* generation on the electrode active sites, which facilitated the hydrogenolysis of the organochlorides. In addition, the lower reduction observed in the pH 12 could likely be due to high hydroxyl groups in the solution that led to the electrode surface passivation [33].

The above findings have demonstrated that the Co-MoS₂-GF electrode possesses an excellent reductive capability for the organochlorides under both acid and neutral conditions that are pH ranges characteristic of aqueous industrial waste streams.

2.3.3. Kinetic Modeling and Mechanism of Degradation

To further elucidate the mechanism of reducing the organochlorides, a kinetic study of the degradation of each of the individual compounds was conducted. Figure 5 shows the time degradation profile for each compound. As illustrated, all the compounds showed a rapid and progressive increase in degradation efficiency with the passage time in the following order CCl₄ > CHCl₃ > CH₂Cl₂. Various concentrations of organochlorides ranging from 1 to 5 mM were evaluated for their dechlorination rates. The degradation efficiencies for the organochlorides were observed to be highly dependent on their initial concentration. CCl₄ showed final degradation rates of 98%, 92%, and 85% at the respective concentrations of 5, 2, and 1 mM. Similarly, CHCl₃ presented the same trend in degradation rates (90%, 88%, and 80%) for the same concentrations but slightly lower degradation efficiencies. CH₂Cl₂, on the other hand, presented a much lower final degradation rate of <72% for all the initial concentrations investigated.
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Based on these, we proposed a stepwise reduction mechanism of organochlorides, as shown in Figure 5.

The first-order reaction kinetics was fitted to the stepwise electroreduction (as shown in Figure 6) of CCl₄, CHCl₃, and CH₂Cl₂, as well as the sum of the formation of Cl⁻ from each step with the reaction time using Equation (5):

\[
[Cl^-]_t = \sum_{i=0}^{n} [Cl^-]_0 e^{-kt}
\]  

where \([Cl^-]_0\) is the initial concentration and \([Cl^-]_t\) are the sum of the concentrations (M) of chloride anions of each first-order step at time \(t(s)\), \(k\) is the rate constant (s⁻¹), and \(n\) is the number of first-order steps used for each halomethane.

As illustrated in the kinetic profiles and the simulated rate constants, it is clear that the degradation rate for the organochlorides increased in the following sequence, CH₂Cl₂ < CHCl₃ < CCl₄. The trend shows that a higher number of halogens possessed a more considerable electron affinity in the organochlorides, pointing to the increased reactivity with the number of halogen atoms present. Moreover, electron affinities also increased in the following order CH₂Cl₂ < CHCl₃ < CCl₄, which matches the trend of the rate constants. Considering the above findings, it is suggested that a stepwise reduction in the organochlorides took place via the formation of intermediate compounds subsequently formed during the electroreduction processes. Additionally, these findings further suggest the occurrence of an indirect reduction process mediated by cathodic surface-generated atomic H* by the Co-MoS₂ graphite felt electrode. The proposed mechanism is schematically shown in Figure 6.

Figure 5. Concentration variation on measured chloride ions from the dechlorination rate of CCl₄ (red), CHCl₃ (blue), and CH₂Cl₂ (green) for each of the 0.825 mM concentrations of the organochlorides after electrolysis.
Figure 6. Schematic representation of the electrocatalytic reduction of organohalides at Co-MoS₂/graphite felt electrode and rate constants for each dechlorination step.

3. Materials and Methods

3.1. Materials

The following list of chemicals supplied by Sigma Aldrich Co (St. Louis, MO, USA) were employed in the study: cobalt(II)nitrate hexahydrate (Co(NO₃)₂·6H₂O), thiourea (CH₄N₂S), ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄), sodium sulfate (Na₂SO₄), chloroform (CHCl₃), carbon tetrachloride (CCl₄), dichloromethane (CH₂Cl₂), and pentane (C₅H₁₂). PAN-based graphite felt (100 × 100 × 5 mm) sourced from Jiangsu Sutong Carbon Fibre Co. Ltd. (Rugao, Nantong, China) was used to support the catalyst deposition. Deionized water (resistivity 18.2 MΩ) prepared from the Millipore system was used for preparing the supporting electrolyte solution.

3.2. Electrode Preparation and Characterization

Before the catalyst deposition, the graphite felt (GF) (2 × 3 cm dimension) was heated in a furnace (300 °C) for 2 h to remove its hydrophobic groups. Consequently, the Co-MoS₂ catalyst was hydrothermally deposited on it according to the synthesis procedure described in our previous study [17]. In this procedure, a combined solution having 300 mg of ((NH₄)₆Mo₇O₂₄), 300 mg of Co(NO₃)₂·6H₂O, and 900 mg of CH₄N₂S was prepared with 50 mL of deionized water (Milli-Q). The pre-treated GF was added to the solution, and the resulting composition was ultrasonicated for 20 min and then transferred to a stainless-steel-lined autoclave (100 mL vol.). The autoclave was placed in an oven and heated at 200 °C for 24 h. The prepared Co-MoS₂-loaded GF was retrieved from the autoclave after cooling and was thoroughly rinsed with ethanol and water. The amount of Co-MoS₂ loaded was estimated by the gravimetric method (14.2 mg/cm² -2-sided area) after drying at 60 °C for 4 h.

Field-emission scanning electron microscopy analysis (FESEM -TESCAN, Brno-Kohoutovice, Brno, Czech Republic) was employed in examining the surface morphology of the prepared catalyst electrode. The crystalline composition of the catalyst was examined
by transmission electron microscopy (TEM) analysis (JEOL, JEM-F-200, Corporation road, Singapore). Analysis of the catalyst chemical composition was performed through X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific Escalab 250Xi spectrometer (Waltham, MA, USA).

3.3. Electrochemical Characterization

The effectiveness of the prepared Co-MoS$_2$-GF electrode toward the reduction of the selected polychloromethanes (CCl$_4$, CHCl$_3$, and CH$_2$Cl$_2$) and the formation of H$^+$ was verified through cyclic voltammetry (CV) measurements. The CV studies were conducted using an undivided electrolytic cell with a three-electrode system (CoMoS$_2$-GF-working electrode, platinum mesh counter electrode, and Ag/AgCl reference electrode) and a computer-controlled CHI 760E Potentiostat (Austin, TX, USA). Before CV measurements, the supporting electrolyte solutions were bubbled with nitrogen gas for 20 min to remove dissolved oxygen. A solution of 0.5 M of Na$_2$SO$_4$ was used as the supporting electrolyte. The CV was performed in the presence and absence of the target analytes at a scan rate of 10 mV/s with a potential range from −1.0 to 1.0 V.

3.4. Electrolysis Experiments

Dechlorination of the polychloromethanes was conducted using an undivided electrolytic cell (500 mL) with a two-electrode system (the prepared Co-MoS$_2$-GF as the working electrode and platinum mesh as the counter electrode). For the supporting electrolyte, 10 mM of Na$_2$SO$_4$ solution was prepared and de-aerated with nitrogen for 20 min. The synthetic solution of each of the compounds, CCl$_4$, CHCl$_3$, and CH$_2$Cl$_2$ (1–5 mM concentration), was prepared in a de-aerated Na$_2$SO$_4$ solution to obtain the desired concentration. The resulting mixture retained in the sealed volumetric flask was continuously stirred with a magnetic stirrer until the organics dissolved. Electrolysis was performed using a DC power supply (KENWOOD, PD18-10AD, Cole-Parmer, Bunker Court Vernon Hills, IL, USA), and the applied current was monitored with a digital multimeter (Fluke). To avoid concentration polarization, the solution was continuously recycled using a peristaltic pump to ensure adequate mixing.

The influence of the operational parameters that include sample pH (3–11), analyte concentration (1–5 mM), electrolysis time (5–120 min), and applied current density (2.5–15 mA/cm$^2$) was investigated. A 10 mL solution was sampled at a predefined interval, and the sample was extracted with pentane for analysis. The extraction procedure has been described in detail in our previous work [17]. The degradation efficiency of each organochloride and the extracted samples was analyzed with GC-MS. At the same time, the dechlorination efficiency was determined from chloride measurement with ion chromatography (Thermo Scientific).

3.5. Analytical Method

The concentrations of CCl$_4$, CHCl$_3$, and CH$_2$Cl$_2$ from the extracted samples were analyzed with a gas chromatography/mass spectroscopy system (GC-MS) (QP2010 Shimadzu (Kyoto, Japan). The GC-MS analysis method involves an injection port temperature of 180 °C, interface temperature of 220 °C, and ion source temperature of 200 °C.

The formation of chloride (Cl$^-$) ions from the electroreduction of the organochlorides was quantified with Dionex ICS-3000 Ion Chromatography (IC) (Thermo Scientific). The IC system was composed of an eluent generator (KOH), a dual pump (isocratic and gradient), two six-port injection valves fitted with two loops in series (25 and 250 µL), a heated conductivity cell, a column heater, and a post-column reaction system.

The degradation efficiency ($D\%$) of the organochlorides was determined based on the initial concentration before ($C_i$) and final concentration ($C_f$) after electrolysis, as shown in Equation (6).

$$D\% = \left(1 - \frac{C_f}{C_i}\right) \times 100$$  \hspace{1cm} (6)
Meanwhile, the dechlorination efficiency (ratio) was determined according to the following relation:

$$ R \% = \frac{[Cl^{-}_{\text{max}}]}{[Cl^{-}_{0}]} \times 100 $$  \hspace{1cm} (7)

where $[Cl^{-}_{\text{max}}]$ represents the maximum amount of chloride species formed during electrolysis and $[Cl^{-}_{0}]$ denotes the initial concentration of chloride in the solution before electrolysis.

The Coulombic current efficiency (CE) of the dechlorination process was evaluated based on the reduction of each organochloride with Equation (8), as provided:

$$ CE \% = \frac{n_{i}C_{i}}{Q} \times F \times V \times 100 $$  \hspace{1cm} (8)

where $C_{i}$ denotes the amount (mol L$^{-1}$) of each organochloride converted at a particular time; $n_{i}$ represents the number of electron transfers required for a complete chloride cleavage from the compounds ($n_{1} = 8, 6, \text{and} 4$ for CCl$_{4}$, CHCl$_{3}$, and CH$_{2}$Cl$_{2}$, respectively); $F$ is Faraday’s constant (96,486 C mol$^{-1}$); $V$ is the solution volume in the cell (L); and $Q$ represents the charge supplied during electrolysis.

4. Conclusions

In summary, the electrochemical dechlorination of different polychloromethanes (CCl$_{4}$, CHCl$_{3}$, and CH$_{2}$Cl$_{2}$) in the aqueous sample by the Co-MoS$_{2}$ graphite felt cathode was demonstrated. The dechlorination rate of individual polychloromethane was influenced by different operational parameters, including solution pH, applied current density, and initial concentration. For the studied parameters, the increase in current density (2.5 to 15 mA/cm$^{2}$) and initial concentration (1 to 5 mM) both positively impacted the dechlorination process. In contrast, the pH increase (3 to 12) showed a negative impact. The dechlorination rates for the individual organochlorides were suited to the first-order kinetic model with apparent rate constants increasing in the following sequence CH$_{2}$Cl$_{2}$ < CHCl$_{3}$ < CCl$_{4}$. To conclude, experimental findings from the dechlorination rates at different concentrations and the obtained kinetic model parameters showed that the electrode’s mass transfer limitation likely controlled the dechlorination process. This is supported by the rapid and high dechlorination rate achieved for the higher concentration of the compounds than the lower concentration.

**Author Contributions:** Conducted experiment, M.D.; designed the experiment and supervised, M.H.A.-M. and C.B.; analysis, M.N.S. and M.D.; investigated the kinetics and reaction mechanism, A.J. All authors equally participated in writing the manuscript. All authors have read and agreed to the published version of the manuscript.

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