

**ADVANCED ELECTROCHEMICAL DEGRADATION OF
DISINFECTION BY-PRODUCTS USING CATALYSTS
MODIFIED ELECTRODES**

BY

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DOCTOR OF PHILOSOPHY

In

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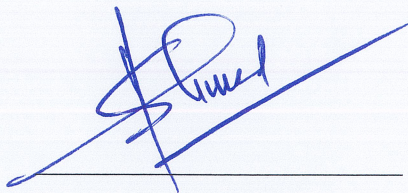
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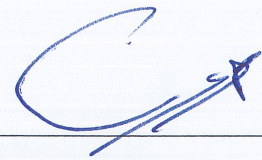


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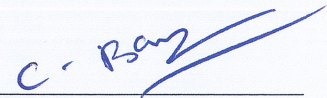


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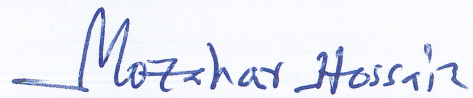
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|This PhD Thesis work is dedicated to my family |

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All praises are due to Almighty Allah for His endless blessing and guidance. It is through His mercy and guidance that I was able to complete this research work. May His peace, blessing and salutations be upon our noble prophet Muhammad (S.A.W), his household, and his companions.

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TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES	X
LIST OF FIGURES	XI
LIST OF ABBREVIATIONS.....	XVI
ABSTRACT	XVII
ملخص الرسالة.....	XIX
1. CHAPTER 1 INTRODUCTION	
.....	1
1.1 Background Information	1
CHAPTER 2 LITERATURE REVIEW.....	6
2.1 Electrochemical Treatment (EC)	6
2.2 Mechanism of Electrochemical Reduction	7
2.3 Electrodes Materials	9
2.4 Previous Studies on Electroreduction of DBPs/Halogenated Organic.....	11
2.5 Research Objectives.....	13
CHAPTER 3	15
EFFICIENT CO-MOS ₂ ELECTROCATALYST FOR CATHODIC DEGRADATION OF HALOGENATED DISINFECTION BY-PRODUCTS IN WATER SAMPLE	15
Abstract	15
3.1 Introduction.....	16

3.2	Materials and Methods.....	19
3.2.1	Materials	19
3.2.2	Preparation of Co-MoS ₂ graphite felt electrode	19
3.2.3	Characterization of CoMoS ₂ -GF	20
3.2.4	Electrochemical characterization	21
3.2.5	Electrochemical Reduction Experiments	21
3.2.6	Analytical Method	23
3.3	Results and Discussion	25
3.3.1	Material Characterization	25
3.3.2	Electrochemical performance of the CoMoS ₂ -GF cathode	31
3.3.3	Electrode Stability and reusability.....	39
3.3.4	Proposed Mechanism of Degradation.....	42
3.4	Summary.....	46

CHAPTER 4..... 47

DEGRADATION KINETICS AND MECHANISM OF POLYCHLOROMETHANES REDUCTION AT CO-MOS₂/GRAPHITE FELT ELECTRODE..... 47

Abstract **47**

4.1 Introduction **48**

4.2 Materials and Methods..... **51**

4.2.1	Materials	51
4.2.2	Electrode preparation and characterization	51
4.2.3	Electrochemical characterization	52
4.2.4	Electrolysis Experiments.....	53
4.2.5	Analytical Method	54

4.3 Results and Discussion **55**

4.3.1	Material Characterization	55
4.3.2	Electrode Cyclic Voltammetric Analysis	57
4.3.4	Influence of operational parameters	59
4.3.5	Kinetic Modelling and Mechanism of Degradation	64

4.4 Summary..... **67**

CHAPTER 5..... 68

BIMETALLIC BISMUTH-COPPER/GF ELECTRODE FOR ENHANCED DEGRADATION OF HALOGENATED AROMATIC ORGANIC COMPOUNDS 68

Abstract	68
5.1 Introduction.....	69
5.2 Experimental Section	71
5.2.1 Materials and Chemicals	71
5.2.2 Electrode Preparation	72
5.2.3 Electrode Characterization	73
5.2.4 Electrochemical Performance of the Electrode.....	74
5.2.5 Analytical Method	76
5.3 Results and Discussion	77
5.3.1 Synthesis of Bi-Cu-GF electrode and characterization	77
5.3.2 RSM Modelling using CCD	83
5.3.3 Kinetic Study.....	99
5.3.4 Degradation Mechanism	102
5.3.5 Electrode Stability.....	107
5.4 Summary	109
 CHAPTER 6	 110
 BIMETALLIC CO-AG-MOF CATALYZED ELECTROREDUCTION OF HALOBENZENE IN THE AQUEOUS PHASE AND THE FORMATION OF BIARYLS VIA SUZUKI COUPLING	 110
Abstract	110
6.1 Introduction.....	111
6.2 Experimental	114
6.2.1 Materials.....	114
6.2.2 Synthesis of Bimetallic Co-Ag-MOF and Co-MOF	114
6.2.3 Prepared Electrocatalyst Characterization	115
6.2.4 General Procedure for Electrochemical Suzuki Coupling Reaction	116
6.3 Results and Discussion	120
6.3.1 Electrocatalyst Synthesis and Characterization.....	120
6.3.2 Cyclic Voltammetry Studies	128
6.3.3 Electrochemical Suzuki Coupling with Co-Ag-MOF Electrode	130
6.3.4 Effect of applied current density	132
6.3.5 Effect of reaction time.....	134
6.3.6 Kinetic study	137
6.3.7 Effect of different boronic acids	141
6.3.8 Electrode Stability.....	141
6.3.9 Mechanism of Electrochemical Reductive Suzuki Coupling	144

6.4 Summary.....	147
CHAPTER 7.....	148
CONCLUSIONS AND RECOMMENDATION	148
7.1 Conclusions	148
7.2 Recommendations	150
REFERENCES.....	152
PUBLICATIONS	166
VITAE	167

LIST OF TABLES

Table 3.1: Comparison of different electrodes applied for degradation of halogenated DBPs reported in literature	38
Table 5.1: Chemical Structure of the selected halogenated aromatic organics	72
Table 5.2: Central Composite Design for the degradation experiment	76
Table 5.3: Factors combination and responses	87
Table 5.4: ANOVA analysis result	88
Table 5.5 : Important features of the models	89
Table 5.6: Kinetics Parameters	101
Table 6.1: Kinetic parameters for the first order model fit for the reactant and product	140
Table 6.2: Cathodic cross-coupling of the aryl halide with different phenylboronic acids	142
Table 6.3: A comparison of biaryls synthesis with MOFs Catalysis and Electroreductive synthesis approach	146

LIST OF FIGURES

Figure 1.1: Chemical structures of some THMs and HAAs compounds	3
Figure 3.1: Schematic diagram of the electrode preparation process and electrolytic reactor setup (1: DC power supply, 2: peristaltic pump, 3: multimeter, 4: platinum mesh as the counter electrode, 5: prepared CoMoS ₂ -GF electrode, 6: Sealed cylindrical reactor)	22
Figure 3.3 : SEM micrograph of the bare graphite felt (a) and after the deposition of CoMoS ₂ catalyst (b) & (c) and TEM & HRTEM image of the synthesized Co-MoS ₂ (d, e, f) deposited on the graphite felt	28
Figure 3.3: XRD patterns (a), TGA result (b), and Raman spectra (c) of bare graphite felt and CoMoS ₂ loaded graphite felt	29
Figure 3.34: XPS spectra of Co-MoS ₂ deposited on the graphite felt showing survey spectra (a) and high-resolution spectra of (b) Mo3d (c) Co3p and (d) S2p	30
Figure 3.3 : Cyclic Voltammogram recorded for (a) bare GF and CoMoS ₂ -GF electrodes in 0.5 M Na ₂ SO ₄ solution in the presence (black & blue lines) and absence (red line) of 0.1 M CCl ₄ , and (b) CoMoS ₂ -GF electrodes in 0.5 M Na ₂ SO ₄ solution with 0.1 M CCl ₄ at different scan rate (10-200mV/s)	34
Figure 3.36: Comparison of the (a) degradation efficiency of the DBPs and (b) current efficiency of CoMoS ₂ -GF and bare GF electrodes	35
Figure 3.37: GC/MS Chromatogram of the extracted halogenated DBPs before and after treatment. (1- Chloroform (CHCl ₃), 2- Carbon tetrachloride (CCl ₄), 3- Dibromochloromethane CHBr ₂ Cl) 4- Bromoform (CHBr ₃), 5- 1,2-Dibromo-3-Chloropropane (C ₃ H ₅ Br ₂ Cl), DBPs conc: 500µg/L, applied current: 30mA, time: 30min)	36
Figure 3.3: The effect of (a) applied current (b) degradation time and (c) anions generation from CoMoS ₂ -GF application for the DBPs reduction.	37

Figure 3.9: Organic halide degradation with the electrode at different cycle number	40
Figure 3.3: Raman Spectra of the CoMoS ₂ -GF before and after 10 cycles of use	41
Figure 3.11 : Linear sweep voltammogram (black line) CCl ₄ in N ₂ - Purged 0.1M TBAC (Tetrabutylammonium chloride) in DMF (Dimethylformamide). The Linear sweep voltammogram of CCl ₄ in N ₂ - Purged 0.1M TBAC in DMF with 0.1wt.% (red line) and 0.5 wt.% (blue line) acetic acid.	43
Figure 3.12:Effect of atomic *H radical scavenger towards the halogenated organic degradation.....	45
Figure 4.1: Cyclic Voltammetry scan for the Co-MoS ₂ -GF cathode in the absence (blank- -background electrolytes- 0.5 M Na ₂ SO ₄) and presence of 5mM of each of the CCl ₄ , CHCl ₃ and CH ₂ Cl ₂ . Scan rate 10mV/s	58
Figure 4.2:Current Density variation on the reduction efficiency of the organochlorides (electrolysis conditions: time- 30 min, solution pH- 6.4, 5mM concentrations of CCl ₄ , CHCl ₃ and CH ₂ Cl ₂).	60
Figure 4.3: Effect of current density variation on the electrode current efficiency for the organochlorides dechlorination	61
Figure 4.4 : pH variation on the dechlorination efficiency of the organochlorides (Experimental conditions: 5mM concentration of CCl ₄ , CHCl ₃ and CH ₂ Cl ₂ , electrolysis time: 30 min, current density: 15mA/cm ²)	63
Figure 4.5 : Concentration variation on dechlorination rate of CCl ₄ (red) CHCl ₃ (green) CH ₂ Cl ₂ (black) and measured chloride ion (blue) for each of the 0.825 mM concentrations of the organochlorides after electrolysis	65
Figure 4.6:Schematic representation of the electrocatalytic reduction of organohalides at Co-MoS ₂ /Graphite Felt Electrode and rate constants for each dechlorination step.	66
Figure 5.1: SEM image (a, b) and EDS result (c) of the prepared Bi-Cu-GF electrode.....	78

Figure 5.2 : XRD spectra of the prepared electrode	79
Figure 5.3 : XPS spectra of the Bi-Cu-GF electrode showing (a) Survey scan (b) Bi4f (c) Cu2p and (d) O1s.....	81
Figure 5.4 : CV studies for (a) Bi-GF and Bi-Cu-GF electrodes in reference electrolyte (0.5 M Na ₂ SO ₄), (b) Bi-Cu-GF electrode for each of the organic halides (100 mg/L solution, 0.5 M Na ₂ SO ₄ as electrolyte, and scan rate 50 mV) (b) Bi-Cu-GF electrode for each of the organic halides at different scan rate (same condition as (b)).....	82
Figure 5.5 : Normal plot of residual for 2,4-D degradation.....	90
Figure 5.6 : Normal plot of residual for CMP degradation.....	91
Figure 5.7: Normal plot of residual for BP degradation	92
Figure 5.8:Externally studentized residual versus predict plot for 2,4-D degradation.....	93
Figure 5.9:Externally studentized residual versus predict plot for CMP degradation.....	94
Figure 5.10: Externally studentized residual versus predict plot for BP degradation .	95
Figure 5.11: Effect of (a) applied current vs Concentration (b) Time vs Current on 2,4-D degradation.....	96
Figure 5.12 : Effect of (a) applied current vs Concentration (b) Time vs Current on CMP degradation.....	97
Figure 5.13 : Effect of (a) applied current vs Concentration (b) Time vs Current on BP degradation	98
Figure 5.14 : Degradation kinetics of the organic halides (Experimental condition: 200 mg/L concentration of the organic halides, applied current- 500 mA, pH- as prepared solution)	100
Figure 5.15: (a) Mass Spectra of 2,4-D after degradation and (b) the proposed degradation scheme	104
Figure 5.16: (a) Mass Spectra of CMP after degradation and (b) the proposed degradation scheme	105

Figure 5.17: (a) Mass Spectra of BP after degradation and (b) the proposed degradation scheme	106
Figure 5.18: Chronoamperometry study of the Bi-Cu-GF electrode.....	108
Figure 6.1 : Schematic diagram of the reaction setup.	118
Figure 6.2 : FESEM images of (a) copper foam and (b, c, d) Co-Ag-MOF coated copper foam and (e, f, g, h) EDS surface elemental mapping.	121
Figure 6.3 : XPS spectra of the Co-Ag-MOF(a) survey scan (b) Ag3d (c) Co2p (d) C1s and (e) O1s	123
Figure 6.4 : (a) Raman spectra and (b) XRD spectra of prepared MOFs.	126
Figure 6.5 : N ₂ adsorption-Desorption Isotherm Plot	127
Figure 6.6: Cyclic Voltammetry measurement recorded for (a) Copper foam and Co-Ag-MOF copper foam and (b) Co-Ag-MOF at a different scan rate.	129
Scheme 1: Electrochemical Suzuki coupling of aryl halides and aryl boronic acid in aqueous medium	130
Figure 6.7 : Chlorobenzene conversion with the MOFs coated copper foam and pristine copper foam electrodes (applied current 180mA, reaction time 30 min, 10mM concentration of Chlorobenzene).....	131
Figure 6.8 : Effect of applied current density on the yield of detected products during electrochemical reductive coupling of chlorobenzene and phenylboronic acid (reaction time- 30 min, 50mM Na ₂ SO ₄ electrolyte, 10mM concentration of chlorobenzene, 10mM phenylboronic acid).	133
Figure 6.9 : Effect of reaction time on aryl's halides conversion and yield of the products (a) 50 mM Na ₂ SO ₄ electrolyte (b) 0.5 M NaOH as electrolyte (10 mM concentration of aryl halides, 10 mM phenylboronic acid, applied current density-30 mA/cm ²).	135
Figure 6.10 : First order kinetic curve fitting with respect to the aryl halides conversion and Biphenyl	139

Figure 6.11: Cyclic experiment for the Co-Ag-MOF electrode (Experimental Conditions: 0.5 M NaOH electrolyte, current density-30mA/cm ² , reaction time-120 min, equimolar concentration of the substrates (chlorobenzene, phenylboronic acid)-10mM).....	143
Scheme 2: Proposed mechanism of electrochemical reductive cross-coupling of the aryl halides with the aryl boronic acid	145

LIST OF ABBREVIATIONS

DBPs	:	Disinfection By-Products
HER	:	Hydrogen Evolution Reaction
CV	:	Cyclic Voltammetry
GF	:	Graphite Felt
Cu-F	:	Copper Foam
CCD	:	Central Composite Design
MOF	:	Metal Organic Frameworks

|

ABSTRACT

Full Name : Mohammed Dauda
Thesis Title : Advanced Electrochemical Degradation of Disinfection By-Products/ Halogenated Organics Using Catalysts Modified Electrodes
Major Field : Civil Engineering
Date of Degree : December 2021

Electrochemical treatment of DBPs and halogenated organics in contaminated water has been a subject of growing research interest due to the numerous benefits it provides over other conventional treatment methods. However, this treatment approach often requires expensive noble-metal catalytic electrode to achieve an efficient treatment process, which has been a major impediment to its wide adoption. In this research work, three different inexpensive transition metals supported catalytic electrodes (Co-MoS₂, Co-Ag/MOF and Bi-Cu) were developed and applied towards the degradation of different aliphatic and aromatic halogenated organic compounds. The electrocatalysts were synthesized by hydrothermal or electrodeposition method and were deposited directly on conductive supports (graphite felt and copper foam) without the need for a binder. The findings from this research work proved that all the prepared electrodes exhibited excellent electrocatalytic performance towards the degradation of the selected organic halides in an aqueous medium.

In the first part of this thesis work, Co-MoS₂ nanosheet electrocatalyst deposited on GF support was prepared by hydrothermal synthesis approach. The prepared electrocatalyst was found to display an excellent catalytic activity comparable to other reported electrodes in literature for the reductive dechlorination of five aliphatic halogenated DBPs that include CHBr₂Cl, C₃H₅Br₂Cl, CHBr₃, CHCl₃, and CCl₄. Its improved degradation performance was ascribed to the synergistic role of its CoS /MoS₂ nanoparticles the accelerated the Volmer step of hydrogen evolution reaction (HER), which aided the production of highly active atomic hydrogen *H reductant. A degradation efficiency of more than 90 % was achieved for each of the five DBPs after

60 min of electrolysis. The mechanism of the organic halides dechlorination was attributed to a stepwise hydrogenolysis mechanism involving the cleavage of the organochloride's bonds by H^* insertion.

In the second part of the study, a bimetallic Bi-Cu electrocatalyst was synthesized by co-electrodeposition of the ionic components of the metals in an aqueous phase onto a GF support. The prepared Bi-Cu electrocatalyst was then applied towards the electrooxidation of selected halogenated aromatic organic compounds (2,4-dichlorophenoxyacetic acid, 4-chloro-3-methyl phenol, 4-bromophenol) as it presented poor performance towards the reduction of the selected compounds. It was discovered that the electrode's bimetallic composition confers a favourable synergistic property. Anodic oxidation of the three selected halogenated aromatic organics was found to proceed efficiently attaining a degradation efficiency of more than 90 % for each organic compound at the optimum condition. The mechanism of organic halide degradation was proposed to involve a sequence of dehalogenation reaction, hydroxylation reaction, and the decomposition of the aromatic rings' C=C bonds mediated by *OH radical attack

In the last part of the study, a novel Co-Ag-MOF electrocatalyst was synthesized by a solvothermal synthesis approach. The prepared electrocatalyst demonstrated excellent performance towards the reduction of three halogenated aromatic organics (chlorobenzene, bromobenzene, and iodobenzene). Based on the electrode's superior performance in reducing the organic halides, the scope of the study was expanded to investigate the formation of biaryls compounds via electrochemical reductive Suzuki coupling of the organic halides with phenyl boronic acid. The findings from the study revealed that the coupling approach was highly influenced by a basic condition, and conversion efficiency of more than 70% was achieved for each of the organic halides, with a corresponding biaryls yield of more than 60%.

This dissertation work makes a significant contribution to the treatment of DBPs and halogenated organic water contaminants by employing inexpensive and readily available transition metals as electrocatalysts, and it may pave the way towards the commercial applications of these electrodes. |

ملخص الرسالة

الاسم الكامل: محمد داودة

عنوان الرسالة : التدهور الكهروكيميائي المتقدم لمنتجات التطهير الثانوية / المواد العضوية المهلجنة باستخدام المحفزات الأقطاب الكهربية المعدلة
التخصص: الهندسة المدنية

تاريخ الدرجة العلمية: تشرين الثاني/نوفمبر 2021

كانت المعالجة الكهروكيميائية لـ DBPs والمواد العضوية المهلجنة في المياه الملوثة موضوع اهتمام بحثي متزايد بسبب الفوائد العديدة التي توفرها على طرق المعالجة التقليدية الأخرى. ومع ذلك ، غالبًا ما يتطلب نهج العلاج هذا قطبًا محفزًا من معدن نبيل باهظ التكلفة لتحقيق عملية معالجة فعالة ، والتي كانت عائقًا رئيسيًا أمام اعتمادها على نطاق واسع. في هذا العمل البحثي ، تم تطوير ثلاثة معادن انتقالية مختلفة غير مكلفة تدعم أقطاب تحفيزية (Co-MoS₂ و Co-Ag / MOF و Bi-Cu) وتم تطبيقها من أجل تحليل المركبات العضوية المهلجنة الأليفاتية والعطرية المختلفة. تم تصنيع المحفزات الكهربية بطريقة الحرارة المائية أو طريقة الترسيب الكهربائي وترسبت مباشرة على الدعامات الموصلة (لباد الجرافيت والرغوة النحاسية) دون الحاجة إلى مادة رابطة. أظهرت النتائج المختلفة من هذا العمل البحثي أن جميع الأقطاب الكهربية المحضرة أظهرت أداء تحفيزيًا كهربائيًا ممتازًا تجاه تحليل الهاليدات العضوية المختارة في وسط مائي.

في الجزء الأول من هذه الأطروحة ، تم تحضير المحفز الكهربائي للصفائح النانوية Co-MoS₂ المودعة على دعامة GF من خلال نهج التوليف الحراري المائي. تم العثور على المحفز الكهربائي المحضر لعرض نشاط تحفيزي ممتاز يمكن مقارنته بأقطاب كهربائية أخرى تم الإبلاغ عنها في الأدبيات لإزالة الكلور المختزل لخمس DBPs أليفاتية مهلجنة والتي تشمل CHBr₂Cl و C₃H₅Br₂Cl و CHCl₃ و CCl₄. يُعزى أداء التحلل المحسن إلى الدور التآزري للجسيمات النانوية / CoS₂ MoS₂ ، حيث تسارعت خطوة فولمر لتفاعل تطور الهيدروجين (HER) ، والتي ساعدت في إنتاج الهيدروجين الذري عالي الفعالية * اختزال H^{*} تم تحقيق كفاءة تحليل تزيد عن 90 ٪ لكل من خمسة DBPs بعد 60 دقيقة من التحليل الكهربائي. تُعزى آلية إزالة الكلور من الهاليدات العضوية إلى آلية التحلل الهيدروجيني التدريجي التي تتطوي على انقسام روابط الكلوريد العضوي عن طريق إدخال H^{*}.

في الجزء الثاني من الدراسة ، تم تصنيع محفز كهربائي ثنائي المعدن ثنائي النحاس عن طريق الترسيب الكهربائي المشترك للمكونات الأيونية للمعادن في الطور المائي على دعامة GF. تم بعد ذلك استخدام المحفز الكهربائي Bi-Cu المحضر نحو الأكسدة الكهربية لمركبات عضوية عطرية مهلجنة مختارة (2،4-ثنائي كلورو فينوكسي أسيتيك حمض ، 4-كلورو-3-ميثيل فينول ، 4-بروموفينول) حيث قدم أداء ضعيفًا تجاه تقليل المادة المختارة مجمعات سكنية. تم اكتشاف أن التركيب المعدني للإلكترود يمنح خاصية تآزرية مواتية. تم العثور على أكسدة أنوديك للمواد العضوية العطرية المهلجنة الثلاثة المختارة لتحقيق كفاءة تحليل تزيد عن 90 ٪ لكل مركب عضوي في الحالة المثلى.

تم اقتراح آلية تحليل الهاليد العضوي لتشمل سلسلة من تفاعل إزالة الهالوجين ، تفاعل الهيدروكسيل ، وتحلل روابط C = C للحلقات الأروماتية بوساطة هجوم جذري . OH* في الجزء الأخير من الدراسة ، تم تصنيع محفز كهربائي جديد Co-Ag-MOF من خلال نهج التوليف الحراري المذيب. أظهر المحفز الكهربائي المحضر أداءً ممتازًا تجاه تقليل ثلاثة مواد عضوية مهلجنة (كلوروبنزين ، بروموبنزين ، أيودوبنزين). بناءً على الأداء المتفوق للإلكترود في تقليل الهاليدات العضوية ، تم توسيع نطاق الدراسة لتحقيق في تكوين مركبات biaryls عن طريق اقتران Suzuki المختزل الكهروكيميائي للهاليدات العضوية مع حمض البورونيك فينيل. كشفت نتائج الدراسة أن نهج الاقتران تأثر بشدة بحالة أساسية ، وأن كفاءة التحويل أكثر من 70 ٪ تم تحقيقها لكل من الهاليدات العضوية ، مع عائد أحيائي مقابل أكثر من 60 ٪. يساهم عمل الأطروحة هذا بشكل كبير في معالجة ملوثات DBPs وملوثات المياه العضوية المهلجنة من خلال استخدام معادن انتقالية غير مكلفة ومتاحة بسهولة كمحفزات كهربائية ، وقد يمهّد الطريق نحو التطبيقات التجارية لهذه

CHAPTER 1

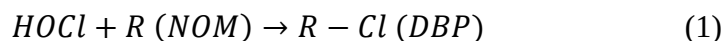
INTRODUCTION

1.1 Background Information

The widespread use of chlorine for water disinfection has played a significant role in the reduction of water-borne diseases in recent years [1]. Chlorination of freshwater from sources like rivers, groundwater, lakes, and desalinated seawater is frequently carried out as a vital component of the treatment train processes for delivering safe drinking water for human consumption. This disinfection approach offers numerous benefits over other methods, such that it is cost-effective, and can offer residual disinfection protection within the water supply distribution system. However, its major challenge has been the unintended chlorinated disinfection by-product (DBPs) formation that arises in the presence of dissolved organic matter (DOC), natural organic matter (NOM) and inorganic substances such as bromide and iodide. These compounds are reported as the major precursors of DBPs formation in drinking water chlorination processes [2]. NOMs constitute the varieties of organic molecules produced during the degradation of plant and human matters. A typical example of NOMs are the humic substances that include humic acid and fluvic acid. DOC in water is the combination of NOMs and other non-humic substances such, carbohydrates, lipids, amino acids, and carboxylic acid [2].

Chlorinated compounds that include chlorine, hypochlorite, or monochloramine when used for water disinfection can interact with these organic compounds either through substitution reaction or direct oxidation to form chlorinated organic DBPs [3]. For example, free chlorine can interact

with humic substances to form different DBPs compounds such as haloacetic acids (HAAs), trihalomethanes (THMs), haloacetonitriles (HANs), haloketones, haloethers and chloral hydrate according to the expression provided below.



Previous reports have shown that humic and fluvic acids (humic substances) exhibit high reactivity with chlorine and they represent a significant portion of dissolved natural organic compounds in fresh water sources like groundwater, lakes and rivers [4]. Surface water sources are generally expected to produce a high concentration of chlorinated DBPs in comparison to ground water sources due to their high concentration of dissolved organic and inorganic components [2]. In the case of desalinated water, DBPs formation during post-disinfection is often expected to be on the lower side due to the occurrence of low organic matters which are mostly removed during desalination operation especially with the reverse osmosis process [5]. However, the practice of blending desalinated water with other water sources could raise the potential of DBPs formation if the organic content of the water source is relatively significant [5]. Furthermore, the formation of brominated DBPs during the pre-disinfection of seawater before desalination or during the blending of desalinated water is an issue of concern. Bromide ions (Br-) are reported to be significant in seawater with a concentration range of about 65 to 155 mg/l [5], Hence, the potential of producing brominated organic compounds is quite likely during both pre-disinfection and blending of desalinated seawater. The commonly produced DBPs in chlorinated product water are THMs and HAAs compounds as illustrated in Figure 1.1. A high concentration of NOMs and bromide ions in raw water has been correlated with a high concentration of THMs formation in the product water [2].

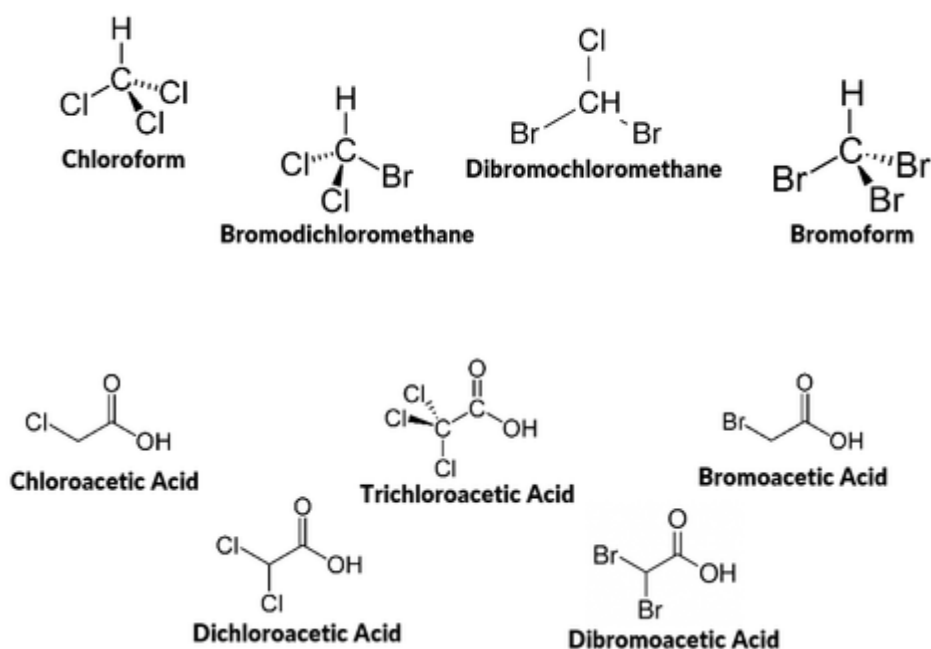


Figure 1. 1: Chemical structures of some THMs and HAAs compounds

Asides from NOMs, the effect of other water constituents (inorganic compounds) on DBPs formation during the water disinfection process have also attracted significant interest. Inorganic ions such as Ca^{2+} and Mg^{2+} ions responsible for water hardness were shown to limit DBPs formation during disinfection [6]. These cations interact with the carboxylic group of some NOMs and limit their interaction with free chlorine. Cu^{2+} ion, on the other hand, has been reported to form complexes with NOMs in solution, which improves the interaction of the created complexes with chlorine towards THMs in disinfected water.[6]. More so, the presence of bromide ions during chlorination have been associated with chloro-brominated THMs formation. THM and HAA compounds in product water are often found in a significant amount at the consumption site of the distribution system as reactions between chlorine and DBPs precursor is not always spontaneous and can take several days till either of the species is consumed [5]. Human exposure routes to these DBPs occurs not only through ingestion, as it has been identified that exposure can also take place through volatilization during cooking and showering event.

Furthermore, THM and HAA compounds have been reported to cause an adverse toxic response to both humans and aquatic lives as they are genotoxic mutagens [2]. Moreover, they are currently regulated in several countries, and water utilities in these countries are required to comply with their maximum contaminant levels (for example US EPA: THM: 80µg/l and HAA: 60 µg/l). Due to the adverse health impact DBPs posed to humans and aquatic lives, it is therefore imperative that an appropriate treatment technology for preventing and removing them from product water or wastewater should be of high priority to water utilities.

Mohd. et al. [2] have shown in their review study several treatment techniques applied for the removal of halogenated DBPs or their precursors in water samples. These treatment techniques include adsorption, biodegradation, reverse osmosis, coagulation/electrocoagulation, advanced oxidation/reduction process and electrochemical oxidation/reduction. Furthermore, the strength and limitations of these treatment techniques have also been highlighted in this study. Reverse osmosis treatment although reported to be quite effective is often faced with the challenge of a toxic waste generation that often requires further treatment. Biodegradation processes are often associated with being slow and do require large capital for setup. Chemical treatment methods such as coagulation and advanced oxidation/reduction require the addition of expensive chemicals which ultimately affect the overall cost of the treatment process. Among these techniques, the electrochemical method offers the most robust treatment approach due to its capacity in converting the DBPs compounds to non-toxic intermediate or complete mineralization without the need for any chemicals [7]. The electrochemical treatment approach is based on oxidation/reduction reactions induced through the application of electric current passing across the interface between the electrodes and the electrolyte medium. The applied current to the electrode can lead to direct electron transfer through the interface to the target substrates to be

degraded or it could lead to electron release from the compound to the interface, which is often termed direct electrochemical treatment [7]. Alternatively, the applied current could induce the formation of highly reactive oxidants or reductants in the aqueous phase that will interact with the target compounds [7]. In this case, the treatment process is called indirect electrochemical treatment. In water treatment applications most especially for halogenated DBPs (THMs and HAAs) removal, the indirect electrochemical oxidation/reduction is commonly preferred as it allows the quick oxidation or reduction of the target compounds. The approach is often enhanced with the aid of catalyst electrodes (electrocatalytic treatment) that can initiate the rapid formation of the reductants or oxidants in the aqueous medium.

Hence, the present study main objective is to explore the application of electrochemical treatment techniques for the removal of some selected halogenated DBPs in a water sample. Furthermore, the study will focus on the development of novel catalytic electrodes that will provide an efficient pathway for the degradation of some selected DBPs compounds.

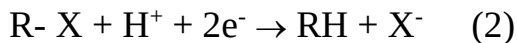
CHAPTER 2

LITERATURE REVIEW

2.1 Electrochemical Treatment (EC)

Electrochemical treatment techniques have undergone several advancements in recent decades in their use in environmental contaminant remediation [8]. Recent research studies have demonstrated the feasibility of electrochemical oxidation/reduction approaches for the abatement of several toxic organics and organic halides such as disinfection by-products in both wastewater and treated water. Generally, the fundamental of direct EC treatment for pollutants removal is based on electron transfer reactions induced by applied electrical current to the electrodes, which can alter the chemical nature of the pollutants to be degraded either through direct electro-reduction or electro-oxidation processes. This approach often implies less/no chemical usage, and the adoption of mild physical reaction conditions [9]. In addition, it offers other benefits that include, high pollutant degradation efficiency, cost-effectiveness, and environmental friendliness [9]. However, the major drawback of EC treatment has been the formation of undesirable intermediates or by-products mostly evident during electro-oxidation processes, which could pose higher toxic properties than the primary pollutant or it could inhibit electrode reactions. These scenarios are mostly encountered during EC treatment of halogenated-organic compounds or organic compounds in the presence of halide radicals. Electro-reduction processes can overcome this drawback by effectively tuning the reaction conditions such that the halogenated-organic compound is transformed to its corresponding primary hydrocarbon [9]. In principle, the

basic pathway of electro-reduction of halogenated organic occurs according to the expression provided as follows,

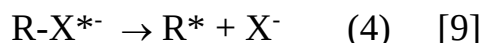
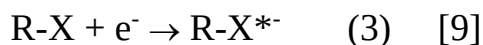
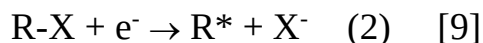


Where, X: Cl, F, Br, and I

Considering the present research work is on DBPs degradation, which is also halogenated organic compounds, our focus will be directed towards the electro-reduction processes. Hence, a brief insight into the reaction mechanisms and electrode materials commonly used for these approaches will be discussed in the following section.

2.2 Mechanism of Electrochemical Reduction

The pathway of direct electrochemical reduction of halogenated organics (R-X) that leads to the reductive cleavage of the R-X bond is well established and is proposed to occur through a stepwise mechanism or a concerted mechanism. The stepwise reduction mechanism involves a sequence of electron insertion steps that is followed by the organic-halogen bond breakage step, whereas the concerted mechanism involves the combination of these two steps occurring simultaneously [10]. In the stepwise mechanism, a single electron transfer to the organic halide takes place which leads to the formation of an activated anion radical (R*) as depicted in both equations 2 and 3 and is followed by the second step reaction that involves the bond cleavage as shown in equation 4.



The organic anion radical produced in Equations 2 and 4 can undergo further reduction to form the corresponding organic anion as shown in equation 5.



The stepwise reductive mechanism has been identified to require a smaller energy barrier (i.e. smaller driving force) compared to the concerted mechanism, due to its lower bond dissociation energy and peak potential [11]. Under the condition where there are no competing reactions on the electrode surface as in the case of an inert electrode, the two mechanisms can be identified by confirming the influence of driving force on the energy barrier, which can change with the available electronic energy levels on the electron-accepting molecule [9]. The stepwise reductive mechanism is generally noted in aromatic molecules due to their ability to accept electrons easily in their available π orbitals. On the contrary, aliphatic molecules often undergo the concerted mechanism because the formed radical anion produced by electron insertion in their σ orbitals is usually not energetically promoted [9]. As earlier mentioned, the validity of these mechanisms is based only on inert electrodes where there is no interaction of the reactants, intermediates, and products with the electrode surface. Practically, this form of electrode is hard to find; however, glassy carbon is widely accepted to possess similar properties to an inert electrode. In the case where a non-inert or active electrode is used, the reduction reaction mechanism is usually more complicated as it must account for particle adsorption to the electrode surface, and the formation of active reductants such as atomic hydrogen, in addition to the stepwise and concerted mechanisms highlighted above.

The use of catalytic cathode electrodes for dehalogenation processes in the aqueous medium has led to the evolution of an entirely different reductive mechanism known as electrocatalytic

hydrogenolysis or hydrodehalogenation. In an aqueous medium, the direct electrochemical reduction of organic halides often presents a challenge because of the high overpotential needed in overcoming the competing hydrogen evolution reaction (HER) at the cathode. To overcome this limitation, a catalytic electrode with lower overpotential is employed to suppress the HER while supplying the atomic hydrogen (H^*) or hydrogen anions generated by water decomposition at the cathode. The formed H^* with strong reducing capability can attack the organic halide leading to the rupture of its R-X bond by hydrogenation reaction [12]. This degradation mechanism has been found to occur both as a direct and indirect approach. The direct approach implies the formed reductant (H^*) is chemisorbed on the electrode surface and its interaction with pollutants takes place at the electrode interface. Whereas in the indirect approach the reductant is generated in-situ in the aqueous phase and the interaction takes place in the solution.

2.3 Electrodes Materials

As discussed, electrode material plays a crucial role in the electroreduction mechanism of halogenated organic compounds. Hence, to achieve an efficient dehalogenation reaction, electrode materials that can accelerate electron transfer to the target compound or enhance the formation of atomic hydrogen (H^*) are highly required. In the published literature, different electrode materials such as noble metals: Palladium (Pd), Platinum (Pt), Ruthenium (Ru), Ruthenium (Rh), Silver (Ag), other transition metals: Iron (Fe) Nickel (Ni), Copper (Cu), carbon materials and their hybrids have all been studied for promoting the reduction of halogenated organic compounds. For direct reduction of organic halides through the activation of the R-X bond by electron transfer commonly encountered in aprotic medium (absence of O-H and N-H bond), Ag electrode has shown superior electrocatalytic activity for such reaction because of its high reactivity with halides anions. While in the case of hydrogenolysis rupture of the R-X bond

through H^* , noble metals are the electrode material of choice because of their inherent advantages toward suppressing or deactivating the competing HER. Among the noble metal, Pd has demonstrated the highest electrocatalytic activity because of its ability at intercalating hydrogen within its lattice structure, which deactivates HER and ensures an ample amount of H^* is available for dehalogenation.

Meanwhile, the quest for an efficient electrocatalyst for organic halides reduction has led to the development of supported composite bimetallic electrodes with superior activity compared to their monometallic counterpart. For example, the formation of a Pd-Ag composite electrode has been found to increase the stability and catalytic activity of the Pd toward the dechlorination of organic halide. He et al.[13] showed that the coating of Ag onto Pd was able to prevent hydrogen embrittlement in the Pd crystal lattice as a result of the diffusion of hydrogen.

In addition, the formation of nano-size supported metal catalyst electrodes has received considerable attention based on their excellent properties at improving electrochemical performance. The reduction of a metal to its nanosized form provides the benefit of an increased surface area to volume ratio, in addition to changes in local properties such as the crystal structure and the introduction of surface functional groups. Peng et al. [14] in their study develop a Pd-Fe composites nanoparticle loaded on nickel foam support via the facile electrodeposition approach. The resulting bimetallic nano-catalyst electrode displayed excellent performance towards the reduction of tetrabromobisphenol A. Moreover, Liu et al. [15] prepared silver nanodendrites that possess fascinating hierarchical structures using the electrodeposition method. The prepared dendritic structured materials exhibited numerous active sites with sharp-edged surfaces and high surface area that was favourable toward the dechlorination of chloroacetic acid in an aqueous medium.

The use of noble metals (Ag and Pd) as electrodes for the electrochemical treatment process has been found to offer an unsustainable approach for future water treatment considering the scarcity and expensive nature of these metals. On this basis, recent studies have been directed toward exploring other inexpensive transition metals (non-noble metal) or carbon-based materials for electroreduction processes.

2.4 Previous Studies on Electroreduction of DBPs/Halogenated Organic

Electroreduction of the halogenated DBPs to stable intermediates or complete reduction of its halides (Cl^-) with the aid of appropriate electrodes generating atomic hydrogen reductant (H^*) have been reported in several studies [16–20]. The use of catalytic electrodes with low overpotential for hydrogen evolution such as Pd, Ag, Co, and many others, have been shown to enhance the reduction process while at the same time minimizing energy consumption. A review of some of these studies highlighting the various electrode employed for the degradation process is provided as follows.

Esclapez M.D et al [21], investigated the effect of different cathode electrode materials that include titanium, stainless steel, and carbon for electrochemical degradation of one of the trichloroacetic acid (TCAA) in the aqueous phase. The mechanism of cleavage of the C-Cl bond of the TCAA was attributed to both direct and indirect reduction approaches. The direct reduction was ascribed to both electron tunnelling and the formation of chemisorbed complexes of the TCAA on the cathode material which aided the degradation process. As for the indirect reduction, the reduction of TCAA was due to its interaction with the atomic hydrogen (H^*) produced on the cathode surface. TCAA was converted to dichloroacetic acid (DCAA) and chloride that were detected after the treatment process. Out of the three electrodes, titanium offers better reduction achieving a fractional conversion efficiency (% reduction) > 80% with an applied current

efficiency > 30%. In a similar study by Liu et al. [16], the use of a bimetallic catalyst electrode made of palladium-Iridium/aluminium oxide (Pd-Ir/Al₂O₃) was investigated. The prepared bimetallic electrode (Pd-Ir) deposited on Al₂O₃ was able to enhance the production of atomic hydrogen (H*) which mediated the reductive conversion of TCAA to its less toxic intermediate -monochloroacetic acid (MCAA). The result from the study shows a 94 % reduction of 500 µg/L initial concentration of TCAA achieved at a current density of 0.9mA/cm for a treatment time of 90 minutes.

To further enhance the degradation of DBPs in an aqueous phase, some studies have explored the use of materials that can serve as both adsorbent and electrode material. These electrode materials usually possess high surface area and functional groups that can capture and concentrate the DBPs for degradation. In a study by Li. Y et al.[22], granular activated carbon (GAC) was deposited on a graphite sheet which served as the cathode in an electrolysis cell and was used for the degradation of several groups of halogenated DBPs. They observed that the GAC was able to offer partial dehalogenation of the DBPs even without electrolysis taking place. This was attributed to the redox-active functional groups of the carbon atoms that include phenols and quinones which acted as capacitors such that they can store and release electrons reversibly. The electroreduction of groups of 17 halogenated DBPs using resin impregnated graphite electrode was reported by Radjenovic J. et al. [23]. The prepared cathode was characterized by its high surface area, low cost, stability and high overpotential for hydrogen evolution [23]. Adsorption of the DBPs onto the resin impregnated cathode was observed to play a significant role in the dehalogenation process. A near-complete cleavage of carbon-iodine bonds was noted at the three applied potentials studied (-700, -800, and 900 mV vs SHE) for a treatment time of 24 hr. While in the case of debromination and dichlorination, an average degradation efficiency of around 73%

and 72% were observed, respectively. Reductive debromination of groups of trihalogenated HAAs was recently reported by Cetó X. et al [24], in their work on sensor development for identifying DBPs. Voltammetry study conducted shows that Br^- reduction tends to occur in the potential range of 0 to -0.5V , while Cl^- reduction was more prominent at a potential of -0.5 to -1.5 . It has been observed that chlorinated DBPs do shows lower electrochemical reductive dehalogenation compared to brominated DBPs [7]. For example, brominated HAAs (TBAA) was reported to undergo complete reduction to acetate, while its chlorinated counterpart tends to stop at MCAA [8].

2.5 Research Objectives

Previous research studies on the electrochemical treatment of DBPs/halogenated organics in water were focused on noble transition metal catalyst electrodes such as silver (Ag), platinum (Pt), palladium (Pd) due to their high catalytic activity. The expensive nature of these metals has been a major challenge affecting the wide adoption of these electrode materials. The current research trend is toward the dispersion or loading of these noble metals or other active transition metals on a highly conductive porous support, such as graphite felt, copper foam, or nickel foam. These porous supports can provide a high surface area for the transition metals deposition while also serving as the current collector for the loaded catalysts. This strategy has been shown to provide an overall efficient treatment process, as it utilizes less amount of the metal catalyst in addition to facilitating the electrode interaction with the target substrate due to the increased surface area provided by supports.

In the current study, the use of conductive porous supports (graphite felt, copper foam) with some selected inexpensive transition metals were explored as catalytic electrodes for the degradation of some selected DBPs/halogenated organic compounds in a water sample. It is anticipated that

the application of these novel non-noble metal catalyst supported electrodes would provide an efficient and sustainable treatment approach for the removal of DBPs/halogenated organic compounds from contaminated water samples. In this dissertation, five inexpensive transition metals (Molybdenum, Cobalt, Silver and Bismuth and Copper) were selected and were used for the preparation of the supported electrodes through the hydrothermal synthesis approach or electrodeposition approach. The prepared electrodes were characterized using the various physico-chemical characterizations tests and electrochemical characterization techniques. The test analyses performed include Field Emission Scanning Electron Microscopy (FE-SEM), Raman Spectroscopy, X-ray Diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), Transmission Electron microscopy (TEM), Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV). The application of the electrodes for the degradation of some selected aliphatic and aromatic halogenated DBPs compounds in spiked water samples was carried out in a batch flow undivided cell and flow through divided cell configurations. The detailed objectives of the work achieved in this dissertation are reported under each chapter as listed.

Chapter 3: Efficient Co-MoS₂-GF electrocatalyst for cathodic degradation of halogenated disinfection by-products in a water sample

Chapter 4: Degradation Kinetics and Mechanism of Polychloromethane reduction at Co-MoS₂-GF electrode

Chapter 5: Bimetallic Bismuth-Copper/GF electrode for enhanced degradation of aromatic halogenated organic compounds

Chapter 6: Bimetallic Co-Ag-MOF Catalyzed Electroreduction of halobenzene's in the aqueous phase and the formation of biaryls via Suzuki coupling

CHAPTER 3

Efficient Co-MoS₂ electrocatalyst for cathodic degradation of halogenated disinfection by-products in water sample

Abstract

The development of non-noble metal electrocatalysts that are efficient and low-cost are being sought as alternatives to noble metals for electrochemical degradation of organic halides. In this study, Co-MoS₂, a non-noble metal electrocatalyst, was synthesized and deposited on graphite felt (GF) via the hydrothermal approach. The functionalized graphite felt was used as a cathode electrode for reductive degradation of halogenated disinfection products from water samples. Five halogenated disinfection byproducts (DBPs), CHBr₂Cl, C₃H₅Br₂Cl, CHBr₃, CHCl₃, and CCl₄ were selected as model compounds, and electro-reductive degradation by the electrode was evaluated. The batch experiments performed with an undivided electrolytic cell revealed that the Co-MoS₂-GF electrode exhibited superior electrocatalytic degradation towards the DBPs compounds compared to other reported electrodes in the literature. Co-MoS₂-GF electrode displayed a current efficiency of ~13 % and degradation efficiency of more than 90 % for each of the DBPs after 60 min of electrolysis. The enhanced catalytic activity of the Co-MoS₂ was ascribed to the synergistic role of CoS /MoS₂ towards the accelerated Volmer step of hydrogen evolution reaction (HER), which aided the production of surface-bound atomic hydrogen *H. Cyclic voltammetry and scavenging experiments clarify the formation of *H during Co-MoS₂-GF catalyzed water reduction and show its contribution to DBPs degradation.

3.1 Introduction

The prevalence of halogenated organics (organic halides) contamination in the environment has aroused significant global concerns due to their hazardous nature [24]. These organic compounds are widely used in several industrial processes and consumer products. As a result, they get discharged into water sources either accidentally or intentionally, creating severe environmental and public health problems[25,26]. Moreover, some halogenated organics are produced during water and wastewater disinfection processes commonly referred to as disinfection byproducts (DBPs). DBPs are byproducts of the water disinfection process that results from chemical disinfectants (chlorine (Cl_2 , HOCl), chlorine dioxide (ClO_2) interaction with the natural organic compounds (NOMs) or/and some halides (Br^- and I^-) present in a water source [4].

These halogenated organics are known to be recalcitrant, toxic, and some are established carcinogenic compounds [27,28]. Due to the toxicity threat posed by human exposure to halogenated DBPs in water, an appropriate treatment technique that will offer an efficient and cost-effective means for their removal in polluted water is currently in high demand. Since the toxicity of halogenated organic results from the halogen atom present in its carbon-halogen bond structure, several treatment approaches have been proposed for the halogen atom's cleavage. Different techniques such as biodegradation [29,30], advanced oxidation/reduction [20], photocatalysis [31], and electrochemical reduction (dehalogenation)[22,32–36] have all been explored. Among these processes, the electrochemical reduction approach stands out as the most efficient and cost-effective technique. It has a high potential of degrading the organic halides to non-toxic intermediate at mild reaction condition without requiring the addition of any chemicals and with no waste production.

Over the past years, the electrochemical dehalogenation technique has gained substantial interest in its organic halide's treatment applications. Several studies have demonstrated the suitability of electroreduction for the abatement of several types of organic halides that include pesticides/herbicides [37], chlorinated solvent [26–28,38,39] and other DBPs [15,23]. The process takes place either as (i) direct reduction at negative potentials, where cathodic electrons are transferred to an organic halide leading to its bond breakage or (ii) through indirect reduction initiated by the catalytic mediated surface adsorbed atomic hydrogen (*H) generated from water electrolysis at a negative potential.

The indirect reduction approach is highly sought after in electroreduction processes due to the high reductive strength of the generated *H that can reduce an organic halide to its primary organic molecule. Moreover, the direct reduction approach is not highly favoured. It is often associated with the formation of partially reduced intermediates that could pose a more perilous threat than the parent organic halide [40].

To promote the indirect electroreduction process, the use of noble metals and some transition metal catalysts electrodes have been explored to facilitate electron transfers to the organic halides and expedite the *H reductant formation. Noble metals such as Palladium (Pd) [41], Silver [15], and other metals that include Iron [42], Nickel [38], and Copper [43], have all been utilized for the reduction of organic halides. Among the explored catalyst, Pd stands out as the most effective for electroreduction of organic halides. This is due primarily to its ability to intercalate hydrogen within its lattice (known as activated H-Pd) to produce the highly effective *H reductant required for efficient dehalogenation reactions [24]. However, Pd's prohibitive cost as a noble metal has served as a limitation towards its extensive use.

Recently, there has been growing interest in utilizing noble metal-free catalysts electrodes [44,45], which have shown promising activity for hydrogen evolution reaction (HER) for organic halide reduction. One of such catalysts identified to possess a promising electrocatalytic activity comparable to Pd is Molybdenum disulfide (MoS₂) [40]. MoS₂ exhibits an excellent ability to generate *H on its surface and H₂ production when employed as a cathode for HER. However, its uses for electroreduction applications do present a challenge due to the competing reactions in water splitting that involve H₂ production and *H generation. These reactions are known as the Volmer step ($\text{H}^+ + \text{e}^- \rightarrow \text{H}^*_{\text{-Cathode}}$) and Tafel step ($\text{H}^*_{\text{-Cathode}} \rightarrow \uparrow \text{H}_2$) in catalyzed HER [46]. To achieve continuous *H generation for effective dehalogenation, the Volmer step needs to be promoted, and the Tafel step suppressed, which can only come to fruition by doping the MoS₂ with a transition metal such as cobalt or nickel [40,47]. Transition metal doping of MoS₂ acts by reducing the kinetic energy barrier of both the Volmer and Tafel steps during catalyzed HER.

On the other hand, the use of porous 3-D carbon materials as an electrode has attracted significant attention due to their numerous advantages over 2-D electrode materials. The extensive porous structure, high surface area, coupled with the excellent conductivity and long-term stability, have positioned 3-D carbon material as a material of choice for several electrochemical applications [48–52]. 3-D carbon materials that include graphite felt (GF) [53], carbon fiber [54], and reticulated vitreous carbon [55] have all been explored either as an electrode or support base for electrocatalyst deposition.

In the current study, cobalt doped MoS₂ deposited on graphite felt electrode was fabricated using the hydrothermal synthesis approach described in the literature [56]. The prepared electrode was employed as a cathode for the dehalogenation of selected DPBs compounds. A study by Huang

et al.[56] reported the same electrode application towards dechlorinating chloroacetic acids to acetic acid. Aside from this, no reported literature is available on the application of cobalt doped MoS₂ towards reducing different types of organic halides in a water sample. Hence, for the first time, we are reporting the electrocatalytic properties of cobalt doped MoS₂ electrocatalyst for the dehalogenation of diverse types of organic halides, including chloroform, trihalomethanes, and halogenated propane.

3.2 Materials and Methods

3.2.1 Materials

Porous graphite felt with dimensions 100 *100 *10 mm was purchased from Jiangsu Sutong Carbon Fibre Co. Ltd (China). Cobalt chloride hydrate (CoCl₂.H₂O), thiourea (CH₄N₂S), ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄), sodium sulfate (Na₂SO₄), chloroform (CHCl₃), carbon tetrachloride (CCl₄), acetone (C₃H₆O), pentane (C₅H₁₂) and TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) all high-grade purity (> 99%) were purchased from Sigma Aldrich (USA). The analytical DBP standard containing five mixtures includes chloroform, carbon tetrachloride, dibromochloromethane, tribromomethane, and 1,2-dibromo-3-chloropropane with a concentration of 200 µg/mL each in acetone was purchased from Restek (USA). A stock solution was prepared by diluting the mixed standard with acetone to the desired concentration.

3.2.2 Preparation of Co-MoS₂ graphite felt electrode

A facile hydrothermal synthesis procedure outlined by [56,57] with some minor modifications was adopted for the catalyst electrode preparation. At first, graphite felt cut to a dimension of 2 * 3 cm was thermally pre-treated in a muffle furnace at a temperature of 300 °C for 2 hours to

enhance its hydrophilicity. Co-MoS₂ was deposited directly on the GF surface by the hydrothermal synthesis approach described as follows. Briefly, a mixture solution containing 300 mg of ((NH₄)₆Mo₇O₂₄), 300mg CoCl₂.H₂O, and 900 mg of C₂H₅NS was prepared with 50 mL of deionized water (Milli-Q). The resulting solution was ultrasonicated for 20 min to give a clear coloured solution. Afterwards, the pre-treated GF was immersed in the solution and was further ultrasonicated for 10 min. After that, the solution containing the GF was transferred into a stainless-steel lined autoclave (100 mL vol.) and was heated in an oven at 200°C for 24 hours. After cooling, the Co-MoS₂ loaded GF was washed continuously with deionized water to remove the unattached residue. Finally, the Co-MoS₂ loaded GF catalyst electrode, referred to as CoMoS₂-GF, was dried in an oven at 60°C for 12 hours and stored in a closed container until further use.

3.2.3 Characterization of CoMoS₂-GF

The catalyst electrode's surface morphological feature was examined using field emission scanning electron microscopy FESEM analysis (TESCAN, Czech Republic). The electrode's thermal stability was explored with thermogravimetric analysis (TGA) in a nitrogen atmosphere using Elmer Perkin TGA 4000. The electrode's crystalline composition was examined through the Transmission Electron Microscopy (JEOL, JEM-F-200) images and the X-ray diffraction pattern acquired using Rigaku X-ray Diffractometer. The X-ray photoelectron spectroscopy analysis and Raman microscopy analysis were employed to characterize the loaded catalyst's chemical composition and structure. The X-ray photoelectron spectra were collected using a Thermo scientific Escalab 250Xi spectrometer at a high vacuum with a monochromatic Al K α (1486.6 eV) X-ray source. At the same time, the Raman spectra were acquired with a LabRAM

HR Evolution Raman spectrometer furnished with a HeNe laser (< 20 mW) laser at an excitation wavelength of 633 nm.

3.2.4 Electrochemical characterization

Cyclic voltammetry (CV) studies were performed to understand the electrochemical performance of the prepared electrode. The studies were conducted in a 50 mL volume undivided electrolytic cell with a three-electrode system consisting of CoMoS₂-GF working electrode, platinum mesh counter electrode, and Ag/AgCl reference electrode all connected to a CHI 760E Potentiostat. The CV scans were performed using 30mL volume of 0.2 M Na₂SO₄ (electrolytes) solution with or without 0.5 M CCl₄ addition, and at the potential range of -1.0 - 0.8 V. The solution pH was maintained at a neutral value (6-7), and several scan rates ranging from 0.01-0.2 V/s were investigated.

3.2.5 Electrochemical Reduction Experiments

To prevent anodic oxidation of the reduced cathodic product, electrochemical reduction experiments are usually performed with a divided electrolytic reactor (separated by proton exchange membrane). However, in this study, an undivided reactor (0.5 L) consisting of a two-electrode system and a recirculatory flow system (provided by a peristaltic pump) shown in Figure 3.1 was employed. In water treatment applications, a divided reactor design will require higher capital expenses and high operating and maintenance costs. Based on this, it is pertinent that the development of an electrochemical reduction system that utilizes an undivided reactor and a low-cost catalyst electrode for degrading the DBPs in water will be of great interest to the relevant stakeholders.

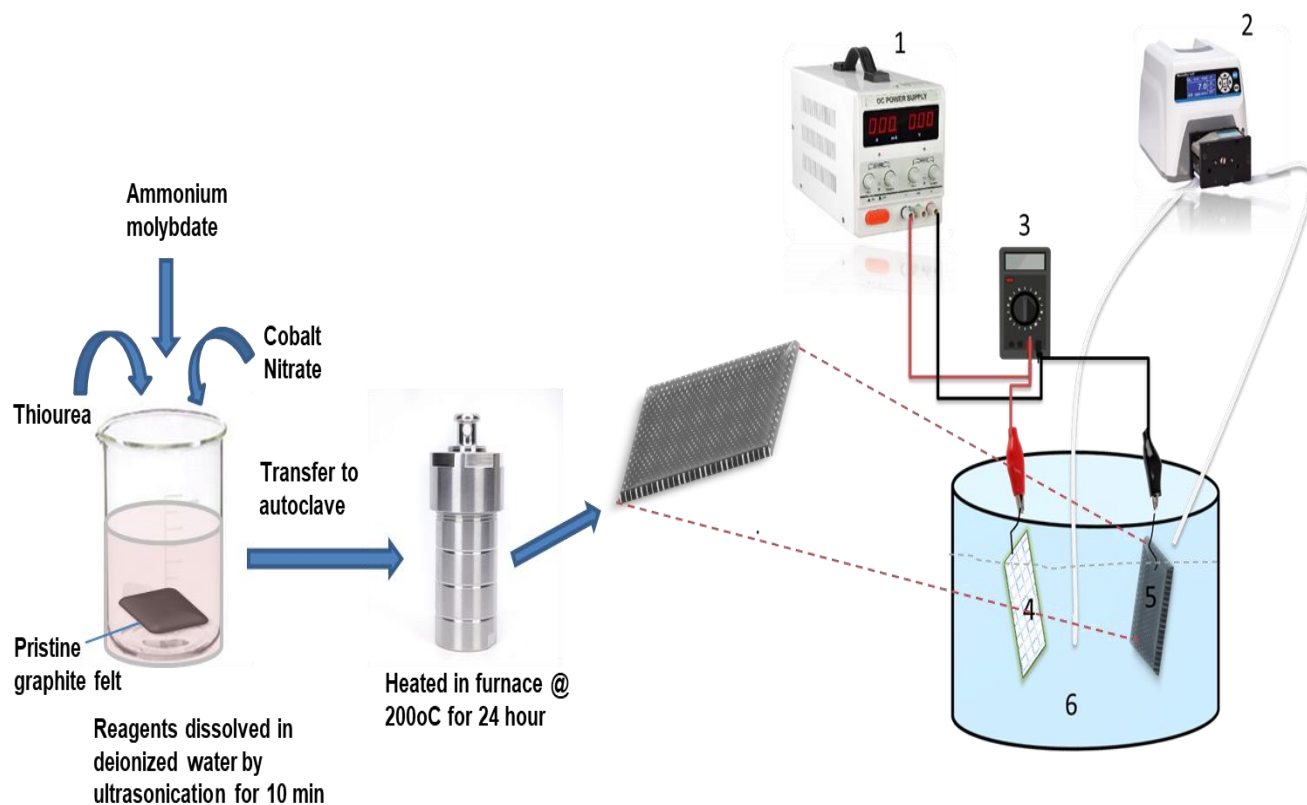


Figure 3.1 :Schematic diagram of the electrode preparation process and electrolytic reactor setup (1: DC power supply, 2: peristaltic pump, 3: multimeter, 4: platinum mesh as the counter electrode, 5: prepared CoMoS₂-GF electrode, 6: Sealed cylindrical reactor)

For the reactor setup, the prepared CoMoS₂-GF was employed as the cathode electrode, and a platinum mesh (dimension 6 cm²) was used as the anode electrode. The electrodes were placed parallel to each other at 3-cm space apart, and 1-cm distance spacing between the bottom of the cell to the bottom tip of the electrodes was maintained. An aqueous solution of 10 mM of Na₂SO₄ (inert electrolyte) was prepared and purged with nitrogen gas for 30 min to remove dissolved oxygen. For the electrolysis experiment, 210 mL volume of the purged Na₂SO₄ solution spiked with an appropriate amount of the mixed DBPs standard to give a concentration of 500 -1500 ng/L was prepared and introduced into the electrolytic cell. A constant current (5-30 mA) was supplied to the electrodes with the aid of a DC power supply (EZ Digital GP-4303A) and was monitored with a digital multimeter (Fluke). During the electrolysis experiment, the solution was continuously recycled at a 60 mL/min flow rate, and aliquot samples of 10 mL were collected at a predefined interval (5-120 min). To determine the degradation efficiency, the collected samples were extracted for the DBPs using pentane as the extraction solvent. The extraction procedure involves adding 500µL of pentane to 10 mL of the collected sample in a corked volumetric flask (10 mL). The mixture was agitated and sonicated for 10 min, and the top organic layer was carefully collected in a 1 mL GC-MS vial for analysis. To ensure the results' reproducibility, all the degradation experiments were performed in triplicate and at room temperature. Besides, the prepared solutions were maintained at near-neutral pH values (6-7) reminiscent of environmental samples.

3.2.6 Analytical Method

The extracted DBPs and the formed byproducts were quantified using a gas chromatography/mass spectroscopy system (GC-MS) (QP2010 Shimadzu (Kyoto, Japan)). The extracted sample

was injected with an autosampler (Shimadzu AOC-20s) to the GC column (Rxi-5 Sil MS, 0.25 μm width, 30.0 m length, and 0.25 mm diameter) (Restek, PA, USA). High purity helium gas (99.999%) at a 1.00 mL/min flow rate was used as the carrier gas. The GC injection port temperature of 180°C and a GC-MS interface temperature of 220°C were maintained. For the ion source, a temperature of 200°C was maintained. The GC column oven was ramped to 180°C at 10°C/min, and held for 4 min; after that, it was increased to 210°C at 2°C/min, and kept for an additional 4 min; and finally, it was increased to 231°C at 3°C/min. The qualitative and quantitative analysis was performed in scan mode with a split ratio of 1:10. The quantity of halides (Cl^- and Br^-) ions generated from the electroreduction experiments was determined with Dionex ICS-3000 Ion Chromatography (Thermo Scientific, USA). The employed Ion Chromatography consists of an electrolytic eluent generator (for KOH production), a dual-piston pump with vacuum degassing, two six-port injection valves fitted with two loops in series (25 and 250 μL), heated conductivity cell, column heater, and a post-column reaction system.

The removal efficiency (%) was evaluated based on the concentration of the halogenated organic compounds before (C_o) and after (C_i) the degradation process, as shown in equation 1.

$$\text{Degradation efficiency} = \left(1 - \frac{C_i}{C_o}\right) * 100 \quad \dots\dots\dots (1)$$

The coulombic current efficiency (CE) of the dehalogenation process that denotes the ratio of possible amount halogenated organic reduced to the amount of charge passed during the electrolysis process was determined according to the expression provided in equation 2.

$$CE (\%) = \frac{(n_1C_1 + n_2C_2 + n_3C_3 + n_4C_4 + n_5C_5) * F * V}{Q} * 100 \quad \dots\dots\dots (2)$$

Where, $C_{i=1-5}$ represent the change in concentration (mol L^{-1}) of DBPs (CHCl_3 , CCl_4 , CHBr_2Cl , CHBr_3 , $\text{C}_3\text{H}_5\text{Br}_2\text{Cl}$) degraded at time t during the electrolysis process, while $n_{i=1-5}$ ($n_1 = 6$, $n_2 = 8$, $n_3 = 6$, $n_4 = 6$, $n_5 = 6$) denotes the corresponding theoretical electron transfer required for full reduction of the compounds. F represents the Faradays constant (96486 C mol^{-1}), n is the number of electrons transferred, V denotes the volume of the solution in the cell (Litres), and Q is the amount of electric charge applied for a specified time t .

3.3 Results and Discussion

3.3.1 Material Characterization

Several of the Co-MoS₂-GF catalyst electrodes were prepared, and the amount of the loaded catalyst on the GF was found to be around 14.2 mg/cm^2 area (2-sided area) of the electrodes on average. Figure 3.2 provides the FESEM images of the bare GF and the Co-MoS₂-GF electrode after the CoMoS₂ catalyst's deposition. As shown in Figure 3.2 (a), the bare GF exhibits an intertwine fibre-like structure with a relatively smooth surface. After the hydrothermal synthesis and deposition process, it was apparent that the GF was coated with a thin layer sheet of the catalyst, as revealed in Figure 3.2(b). Higher magnification of this image shown in Figure 3.2 (c) reveals the CoMoS₂ layer's deposition longitudinally on each of the GF fibers. This individual coating of the fibers ensures that the GF material's porosity was maintained after the deposition process.

TEM measurement and XRD analysis were carried out to elicit the phase composition of deposited CoMoS₂ catalyst. HRTEM images of deposited catalysts in Figure 3.2 (c & d) show lattice fringes with a measured interlayer spacing of 0.325 nm that corresponds to the crystalline phase of MoS₂ [58]. Figure 3.3 (a) shows the XRD patterns acquired for both GF and CoMoS₂-

GF samples. The patterns indexed to 2H-MoS₂ and CoS₂ reference standard (JCPDS Card No. 65-3322 & 73-1508), as depicted, showed that most of the X-ray reflection was due to the GF support. The two diffraction peaks located at 25.9° and 44.7° in both samples were associated with (002) and (100) planes of graphitic carbon of the graphite felt [59]. Besides, the appearance of new peaks with low intensity at 36.9° (210) and 57.6° (110) in the Co-MoS₂-GF sample indicates the deposition of a thin layer of the composite catalyst on the GF surface. These new peaks at the planes (210) and (110) correspond to the CoS₂ phase [60] and MoS₂ phase [40,60], respectively.

As revealed from the TGA result, the thermal stability of the Co-MoS₂-GF and bare GF is shown in Figure 3.3 (b). As expected, the GF was highly stable up to the temperature of 600°C before a gradual weight decline was noticed. A weight loss of approximately 35 % was observed for the GF, attributed to graphite decomposition. On the other hand, the Co-MoS₂-GF electrode presented two characteristics region weight loss. At the temperature range of 100 – 600 °C, a steady decline in weight (15 %) was noticed and was followed by a sharp reduction (75 %) in weight at 600 – 995 °C. This observation signifies that the GF incorporated catalyst resulted in composite material formation that exhibited different thermal properties.

The surface chemical structure of Co-MoS₂-GF and bare GF, as inspected by the Surface Enhanced Raman Spectroscopy is presented in Figure 3.3(c). The two samples show characteristics of graphite peaks at 1350 cm⁻¹ and 1590 cm⁻¹ that correspond to the D and G bands. The A_{1g} vibrational out of plane mode resulting from catalyst deposition can be seen at 450 cm⁻¹ in the spectra of Co-MoS₂-GF [60].

To further characterize the surface elemental composition of the loaded CoMoS₂ catalyst, X-ray photoelectron spectroscopy (XPS) analysis was performed, as shown in Figure 3.4. The resulting XPS survey scan (Figure 3.4a) shows the incorporation of molybdenum (Mo), cobalt (Co), and sulfur (S) elements onto the catalyst electrode in addition to the carbon and oxygen composition of the graphite felt. The high-resolution scan of the Mo spectrum (Figure 3.4b) reveals two doublet peaks at 233 eV and 228 eV, which was attributed to Mo 3d_{3/2} and Mo 3d_{5/2} binding energies, respectively, thus, suggests the existence of Mo in the +4 oxidation as MoS₂ [60]. Cobalt spectrum shows two peaks of Co 2p₁ and Co 2p₃ at 802 eV and 780 eV, respectively, that are characteristic of cobalt in +2 oxidation state due to CoS₂ formation [61]. The sulfur (S 2p) spectrum (Figure 3d) shows the appearance of S 2p_{3/2} peak at 168 eV that reveals the presence of sulfur in the -2-oxidation state. The XPS result described above confirms the formation of hybrid CoS₂-MoS₂ composite material on the GF surface during the hydrothermal synthesis process.

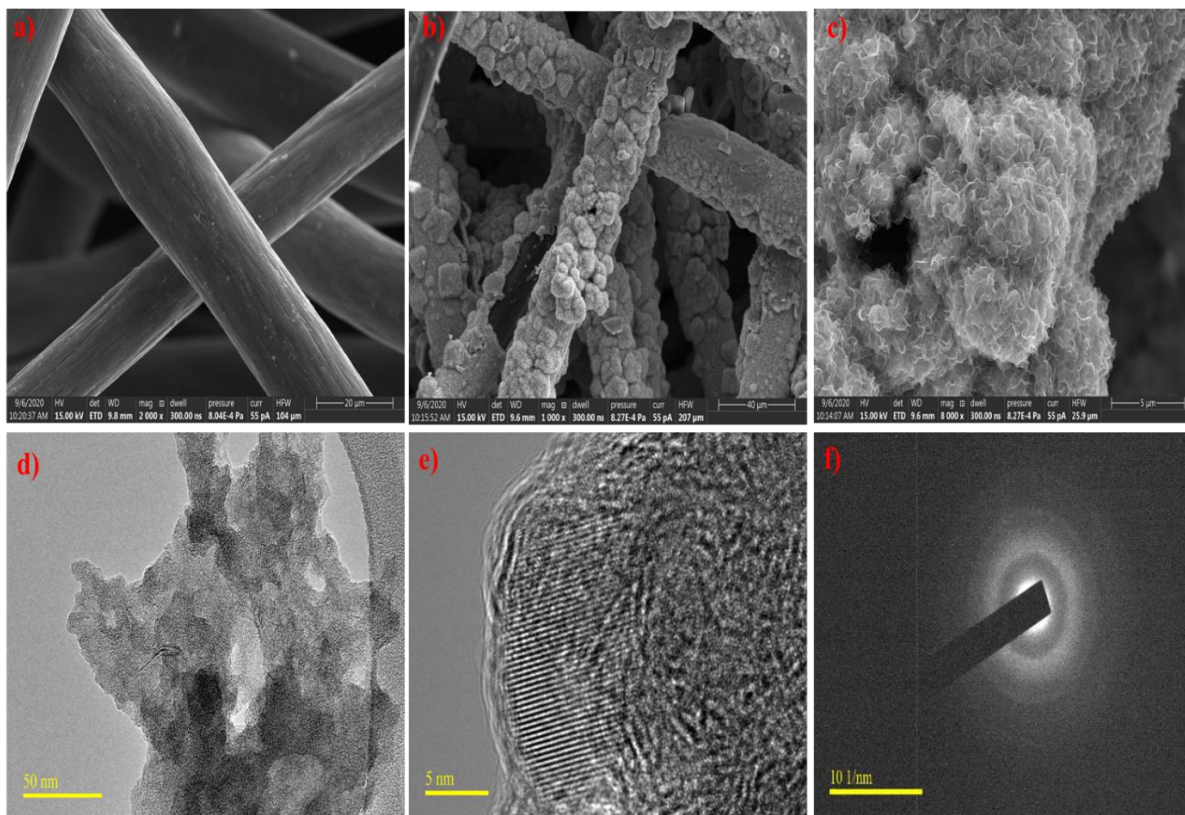


Figure 3.3 : SEM micrograph of the bare graphite felt (a) and after the deposition of CoMoS₂ catalyst (b) & (c) and TEM & HRTEM image of the synthesized Co-MoS₂ (d, e, f) deposited on the graphite felt

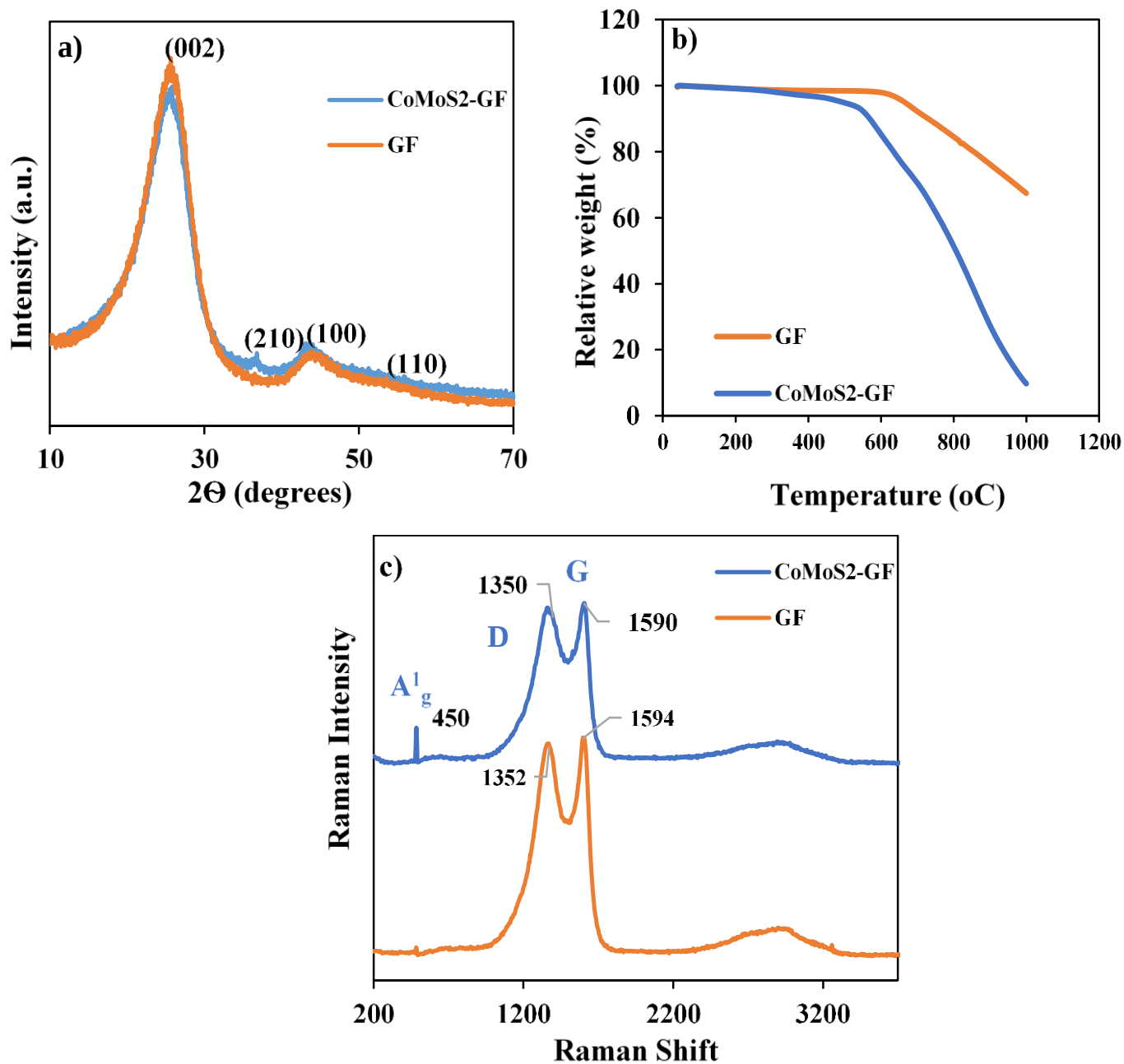


Figure 3.3: XRD patterns (a), TGA result (b), and Raman spectra (c) of bare graphite felt and CoMoS₂ loaded graphite felt

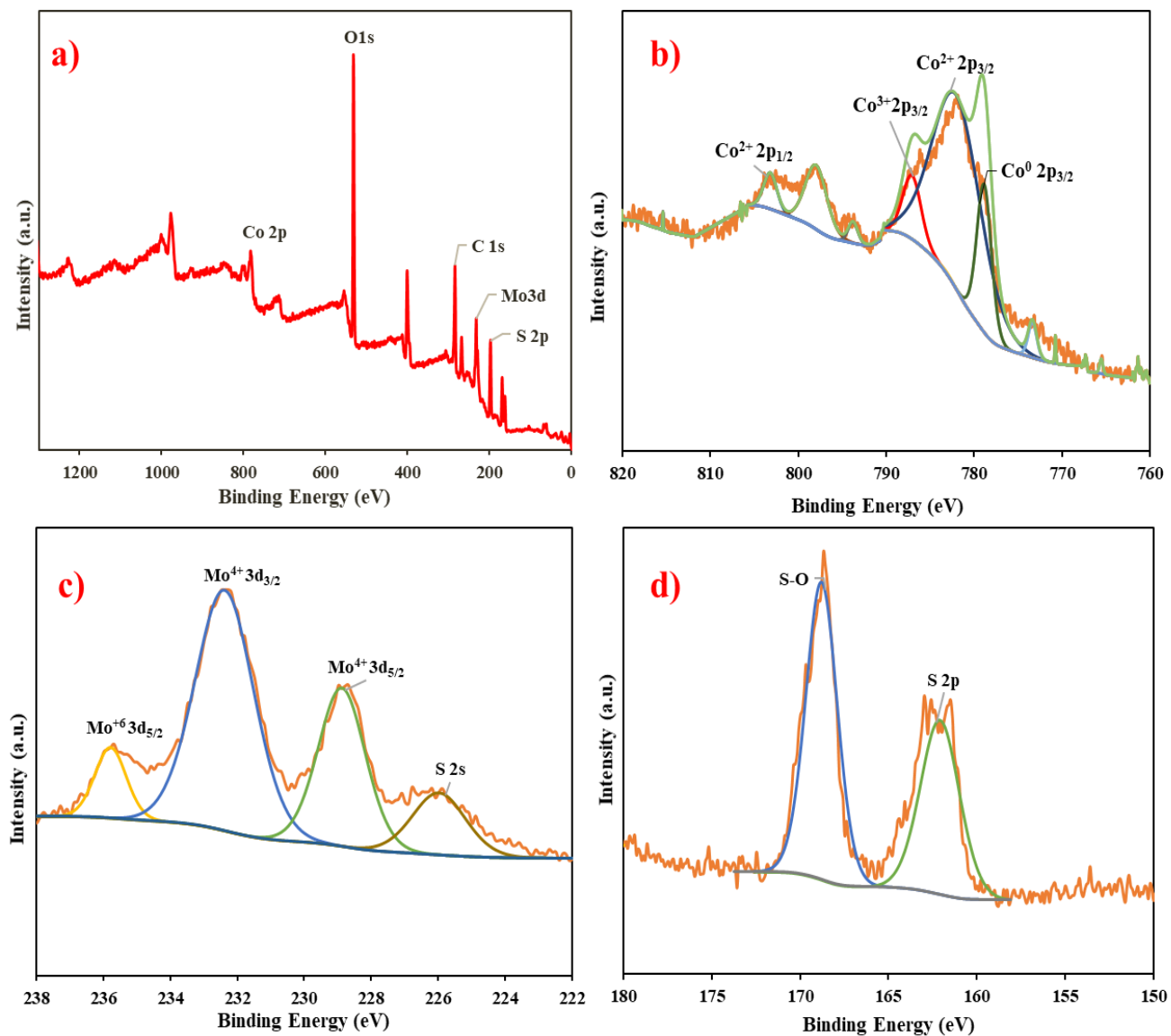


Figure 3.34: XPS spectra of Co-MoS₂ deposited on the graphite felt showing survey spectra (a) and high-resolution spectra of (b) Mo3d (c) Cop3 and (d) S 2p

3.3.2 Electrochemical performance of the CoMoS₂-GF cathode

Electrocatalytic activity of the electrodes (bare GF and CoMoS₂-GF) towards the reduction of one of the selected DBPs at high concentration (0.5 M CCl₄ in acetone water mixture- as the substrate) was investigated via cyclic voltammetry as shown in Figure 3.5 (a & b). A significant reduction peak (-0.3 V/_{Ag-AgCl}) was observed with the CoMoS₂-GF cathode towards the substrate reduction as compared to the bare GF (Figure 3.5 (a)), suggesting its enhanced catalytic ability towards the halogenated organic. Moreover, a lower water reduction peak (-0.2 V/_{Ag-AgCl}) detected with the same electrode in the absence of the substrate suggests that the increased current displayed was due to the halogenated organic reduction during the cyclic voltammetry scan. Figure 3.5 (b) shows the cyclic voltammograms acquired for the CoMoS₂-GF cathode towards the substrate reduction at different scan rates (10-200mV/s). The resulting different voltammetry responses illustrated at different scan rates specify that the reduction process was not controlled by the electron mass transfer mechanism and was likely due to the generation of surface adsorbed atomic H* reductant [45].

To compare the CoMoS₂-GF catalyst electrode's performance to that of the bare GF, several electrochemical reduction experiments were performed with the mixed DBPs at low concentrations (500 µg/L). For these experiments, the effect of the operational variables that include applied current, electrolysis time, and current efficiency were all investigated. Figure 3.6 (a) shows the degradation efficiencies of the organics with both the CoMoS₂-GF and bare GF electrodes. As shown, the GF electrode displayed a lower degradation for each organic at the fixed condition (30 mA applied current, a recirculation flow rate of 60 mL/min, and 30 min time). While CoMoS₂-GF, on the other hand, exhibited an exceptional high degradation of more than

70 % for each of the compounds in the same condition. Based on this finding, it can be speculated that the CoMoS₂-GF electrode offers an indirect reduction approach to the organic through atomic H^{*} generation. At the same time, the GF aided reduction likely resulted from direct cathodic electron transfer.

An open circuit (OC) experiment was performed to determine the impact of volatilization and adsorption on the decrease in the DBPs concentration during operation. The OC experiments were performed using the CoMoS₂-GF electrode with a relatively higher concentration of the organic halides (1000 µg/L). The prepared solutions were recycled through the reactor for 2 hours. A decrease in the amount of each of the DBPs by less than 15 % was noted in the absence of applied current, which indicates that the volatilization and adsorption effect on the degradation process was not highly significant. Nevertheless, to ensure the impact of these factors were captured, degradation efficiencies of the DBPs reported in this work was ascribed to be inclusive of both volatilization and adsorption process.

Based on the assumption that complete dehalogenation of the organics took place during operation (depicted in the GC/MS-chromatogram (Figure 3.7) before and after treatment), the current efficiencies of the two electrodes at 30 mA applied current was estimated as shown in Figure 5 (b). The Co-MoS₂-GF electrode displayed a much higher current efficiency (~13 %) than the bare GF (~2 %), signifying its high selectivity for reducing the DBPs. This decrease in current efficiency with time could be attributed to the decrease in the organic halide concentration resulting from continuous degradation.

The effect of applied current to the Co-MoS₂-GF electrode shows an increasing trend toward organics degradation (Figure 3.8 (a)). An increase in current from 5mA to 30 mA leads to a

significant increase in degradation from 5 % or less to 75 % or more for the organics after 30 min of electrolysis. It can be implied that at high cathodic current ample amount of atomic H^* was generated on the active sites of the Co-MoS₂-GF cathode, which was able to expedite the degradation process. On increasing the current above the 30 mA for the same duration (not included), a similar degradation efficiency was noted with accelerated hydrogen evolution. This suggests that only a portion of atomic H^* generated on the Co-MoS₂-GF surface has been exploited for the organic reduction and the rest interacting to form hydrogen via the HER Tafel step ($2H^*_{\text{Cathode}} \rightarrow \uparrow H_2$).

The reaction time was investigated, as displayed in Figure 3.8 (b). The DBPs show a progressive increase in removal with time. The result shows that brominated organics were readily degraded compared to the chlorinated organics at the onset of electrolysis. At 5 min of electrolysis time, a significant degradation of more than 60 % was recorded for CHBr₂Cl (78 %), C₃H₅Br₂Cl (76 %), CHBr₃ (71 %), CHCl₃ (65 %), and CCl₄ (61 %), respectively. Moreover, at a higher electrolysis time, an enhanced degradation efficiency of more than 90 % was achieved for all the compounds. The fast degradation rate noted for the brominated compounds can be attributed to the carbon-Br bond property and the size of the molecules. The report has shown that brominated aliphatic organics possess lesser bond strength than their chlorinated counterparts [62]. As such, it is expected that lesser energy and time will be required to break their bonds during electrolysis. Successful reduction of the DBPs compounds was confirmed via the timed measurement of bromide (Br⁻) and chloride (Cl⁻) ions generation, as shown in Figure 3.8 (c). A marginal increase in the concentration of both anions with time can be observed, with chloride formation being substantial due to the numerous chlorinated compounds in the standards. It is worth knowing that the results presented above were consistent with findings in the published literature [63].

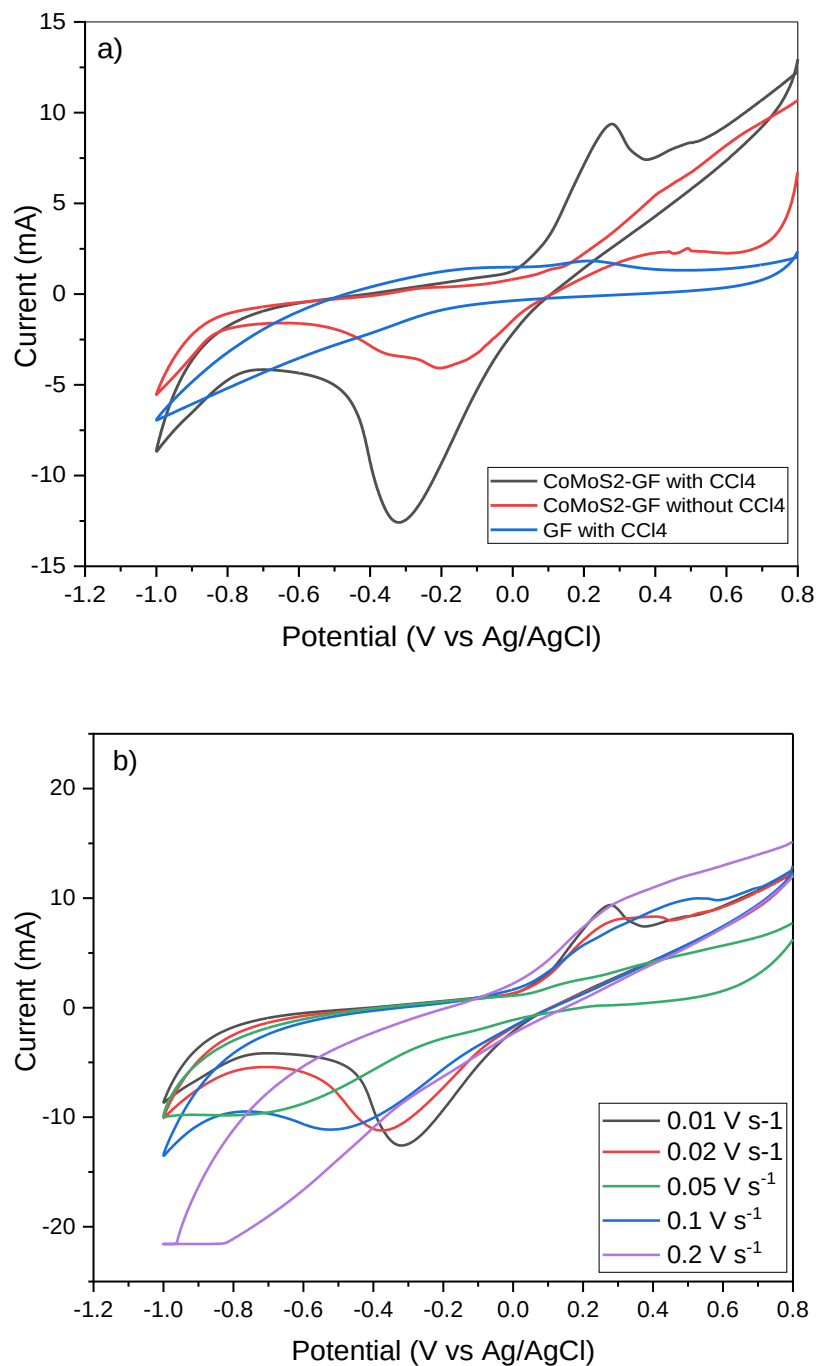


Figure 3.3 : Cyclic Voltammogram recorded for (a) bare GF and CoMoS₂-GF electrodes in 0.5 M Na₂SO₄ solution in the presence (black & blue lines) and absence (red line) of 0.1 M CCl₄, and (b) CoMoS₂-GF electrodes in 0.5 M Na₂SO₄ solution with 0.1 M CCl₄ at different scan rate (10-200mV/s)

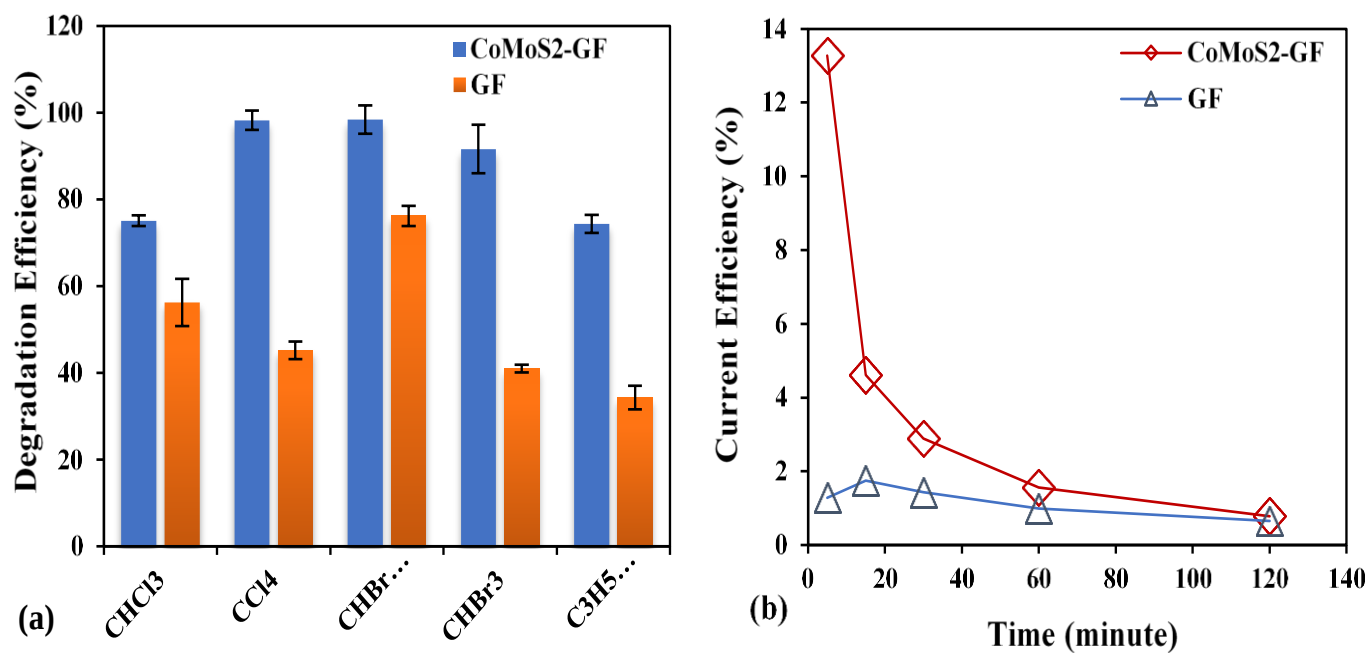


Figure 3.36: Comparison of the (a) degradation efficiency of the DBPs and (b) current efficiency of CoMoS₂-GF and bare GF electrodes

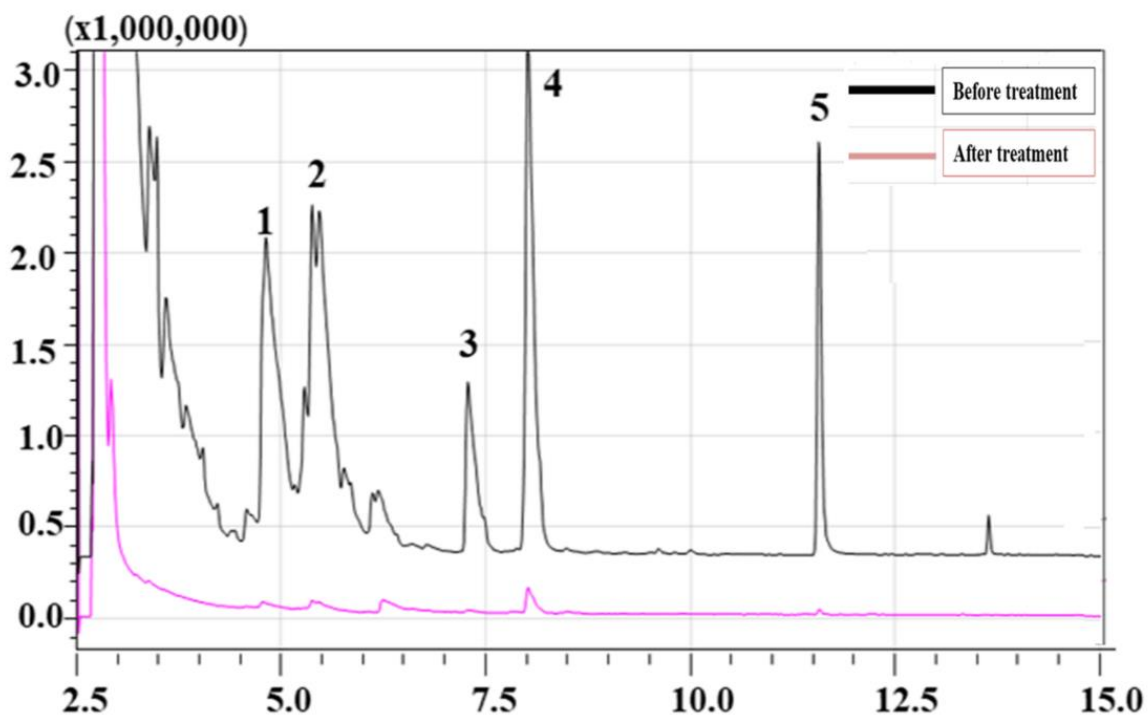


Figure 3.37: GC/MS Chromatogram of the extracted halogenated DBPs before and after treatment. (1- Chloroform (CHCl_3), 2- Carbon tetrachloride (CCl_4), 3- Dibromochloromethane CHBr_2Cl) 4- Bromoform (CHBr_3), 5- 1,2-Dibromo-3-Chloropropane ($\text{C}_3\text{H}_5\text{Br}_2\text{Cl}$), DBPs conc: $500\mu\text{g/L}$, applied current: 30mA, time: 30min)

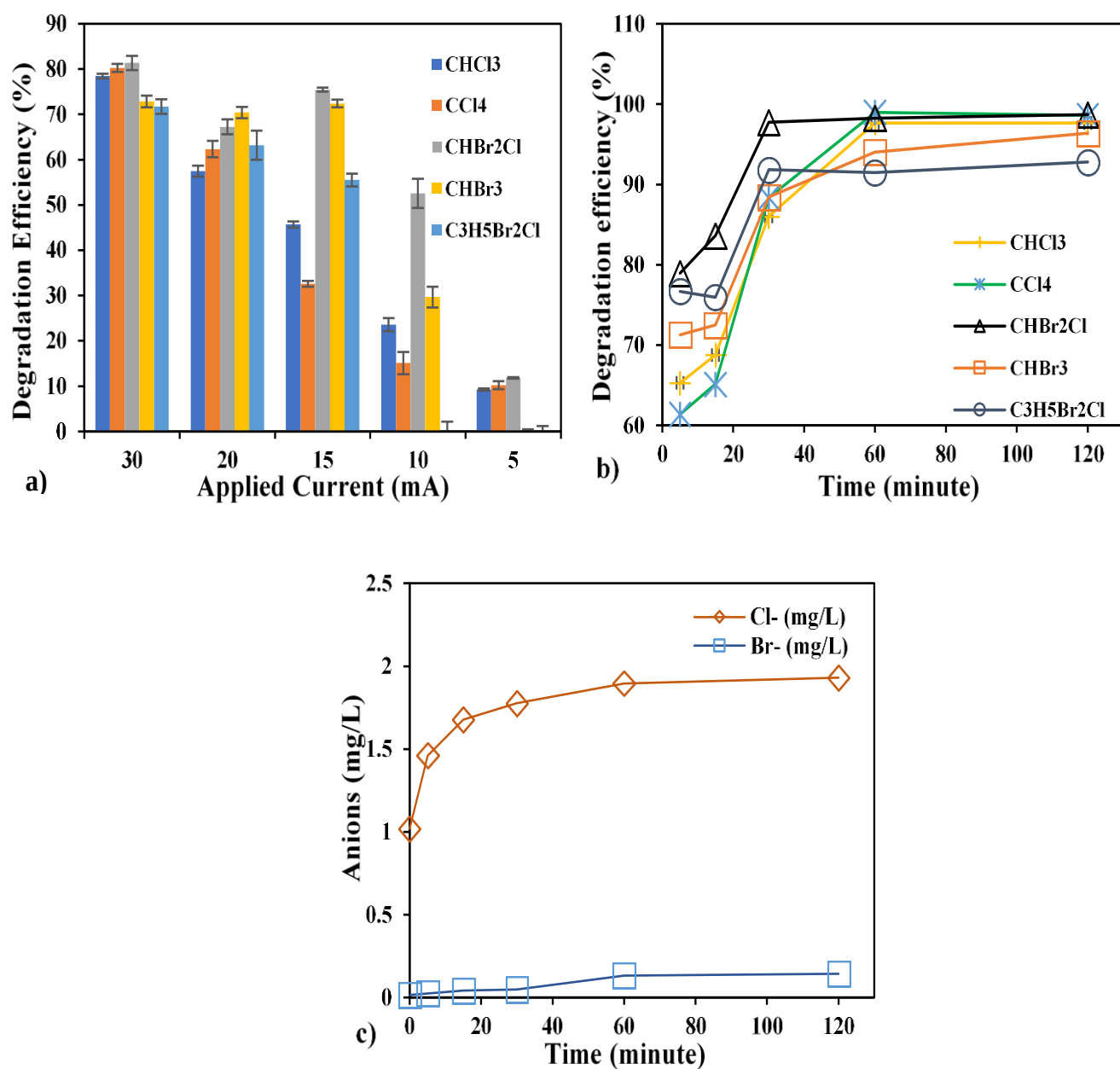


Figure 3.3: The effect of (a) applied current (b) degradation time and (c) anions generation from CoMoS₂-GF application for the DBPs reduction.

Table 3.1 : Comparison of different electrodes applied for degradation of halogenated DBPs reported in literature

Electrode	Cell type	DBPs	Electrolyte	Applied Current/ Potential	Time (min)	Degradation/ Conversion Efficiency (%)	Ref
Graphite	Divided Cell	CCl ₄	DMF + 0.1 M Et ₄ NClO ₄	-2.9 V	-	8.3	[64]
Silver		(10 mM)		-2.2 V	-	18	
Resin Impregnated Graphite Block	Divided Cell	CHCl ₃ , CHBr ₃ , CHBr ₂ Cl (65.3-129.7µg/L)	H ₂ PO ₄ /K ₂ HPO ₄ (buffer)	-700 mV	-	32-70	[23]
Palladium/polymeric pyrrole-nickel foam	Divided Cell	CHCl ₃ (2mg/L)	0.05M Na ₂ SO ₄	20 mA	180	50.6	[65]
Palladium/nickel foam						37.6	
Palladium thin films on glassy carbon	Undivided Cell	CCl ₄ (30mg/)	0.5M H ₂ SO ₄	-0.2V	15	89.3	[66]
Zero valent iron	Undivided Cell	CCl ₄ (0.05M)	0.05 H ₂ SO ₄	-0.62V	30	79.2	[67]
Activated carbon-based column electrode	Divided Cell	CHCl ₃ , CHBr ₂ Cl, CHBr ₃ . (500 nmol)	100mM H ₂ PO ₄ /K ₂ HPO ₄ (buffer)	-1000 mV	360	CHCl ₃ : 40; CHBr ₂ Cl, CHBr ₃ : > 90	[22]
Stainless steel electrode (contact glow discharge electrolysis)	Undivided Cell	CHBr ₃ (0.4mM)	0.01M Na ₂ SO ₄	100 mA	60	68	[68]
Co-MoS ₂ -Graphite Felt	Undivided Cell	CHCl ₃ , CCl ₄ , CHBr ₃ , CHBr ₂ Cl, C ₃ H ₅ BrCl (500µg/ L)	10mM Na ₂ SO ₄	30 mA	60	> 90 for each compound	Current study

In general, the CoMoS₂-GF electrode offered a satisfactory chemical dehalogenation reaction for the diverse type of organic halides investigated and showed an immense potential comparable to noble metal electrodes. A comparison of the prepared CoMoS₂-GF electrode performance with those reported in the literature for halogenated DBPs degradation is shown in Table 3.1. It is evident from the comparison that the CoMoS₂-GF electrode shows an excellent electrocatalytic performance than some of the reported electrodes.

3.3.3 Electrode Stability and reusability

The stability and durability of the prepared electrode are vital for its use in the produced water samples. Thus, the prepared electrode (freshly made) was repetitively used for the degradation of the same concentration of mixed DBPs, as shown in Figure 3.9. As illustrated, there were no significant changes in the organic degradation efficiencies even after ten cycles of repeated electrode usage. This finding demonstrates that the prepared electrode is satisfactorily stable and durable for electrochemical dehalogenation reactions. To further corroborate the electrode's stability, Raman spectra of the electrodes before and after ten cycles of repeated usage were compared, as shown in Figure 3.10. The intrinsic A_g¹, D, and G Raman bands of the CoMoS₂-GF electrode at 450 cm⁻¹, 1350 cm⁻¹, 1590 cm⁻¹, respectively, shifted slightly to 453 cm⁻¹, 1342 cm⁻¹, 1593 cm⁻¹ after ten cycles of use for the organic's degradation. This non-significant shifting or broadening Raman bands even after the repetitive degradation reactions, suggests excellent structural stability and reusability potential.

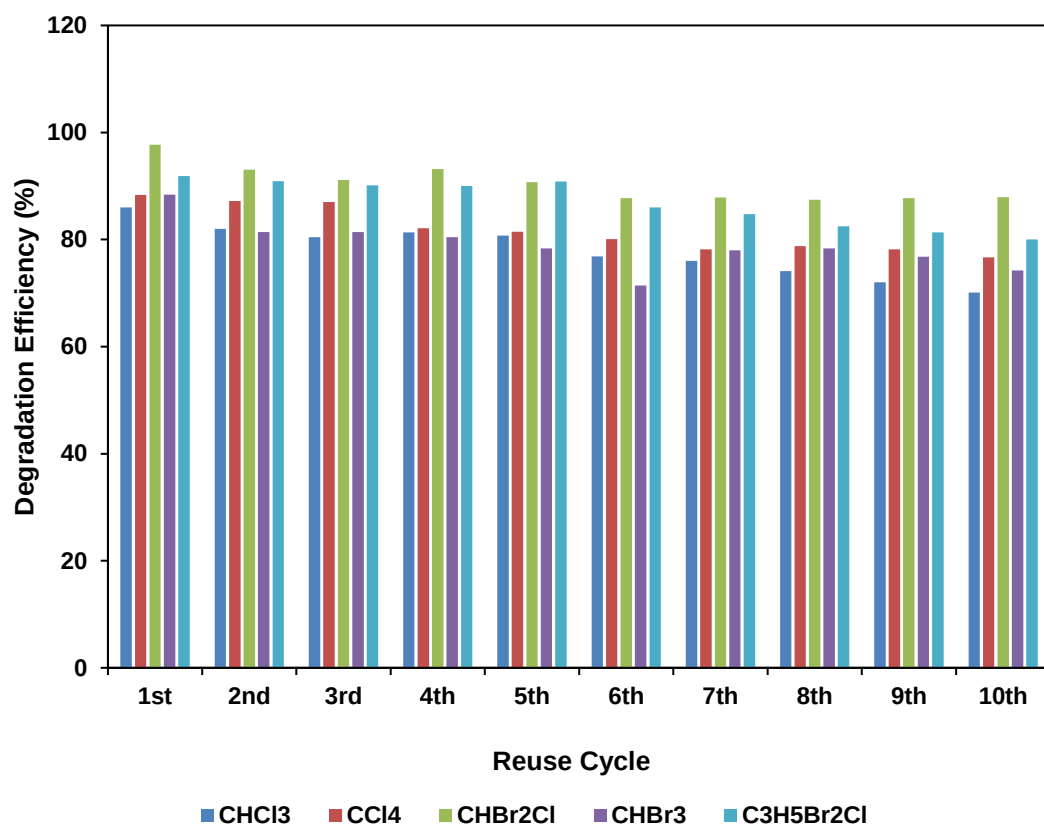


Figure 3.9: Organic halide degradation with the electrode at different cycle number

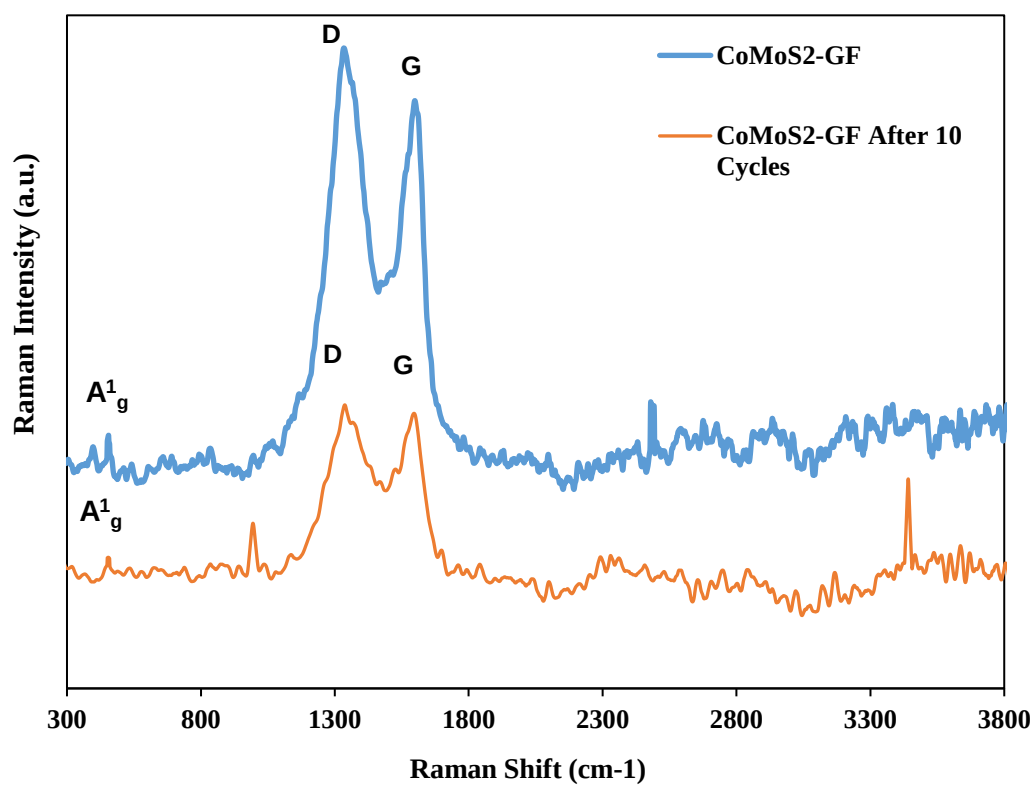


Figure 3.3: Raman Spectra of the CoMoS₂-GF before and after 10 cycles of use

3.3.4 Proposed Mechanism of Degradation

Generally, the electrochemical dehalogenation reaction mechanism proceeds via direct cathodic electron-induced reduction or indirect reduction by cathodic surface generated atomic $\text{H}^{\bullet}$. For catalytic electrodes like the one employed in this study, the dehalogenation reaction is mainly directed by the latter through atomic $\text{H}^{\bullet}$ mediated reduction [13,16,23,69]. In consideration of this, the formation of $\text{H}^{\bullet}$ and its effect on the DBPs reduction were explored by electrochemical technique and the use of $\text{H}^{\bullet}$ radical scavenger. In the electrochemical technique, a linear sweep voltammetry (LSV) study of the electrode in an aprotic organic electrolyte medium and with a proton source (acetic acid) was performed to provide more evidence of $\text{H}^{\bullet}$ formation. As illustrated in Figure 3.11 an increase in reduction current was observed in the presence of proton compared to its absence, which indicates that the organic reduction was due to the formed reductive species ($\text{H}^{\bullet}$) generated via faradaic reduction and not from direct electron transfer. It is worth noting that this finding was corroborated by Lee et al. [53] in their study.

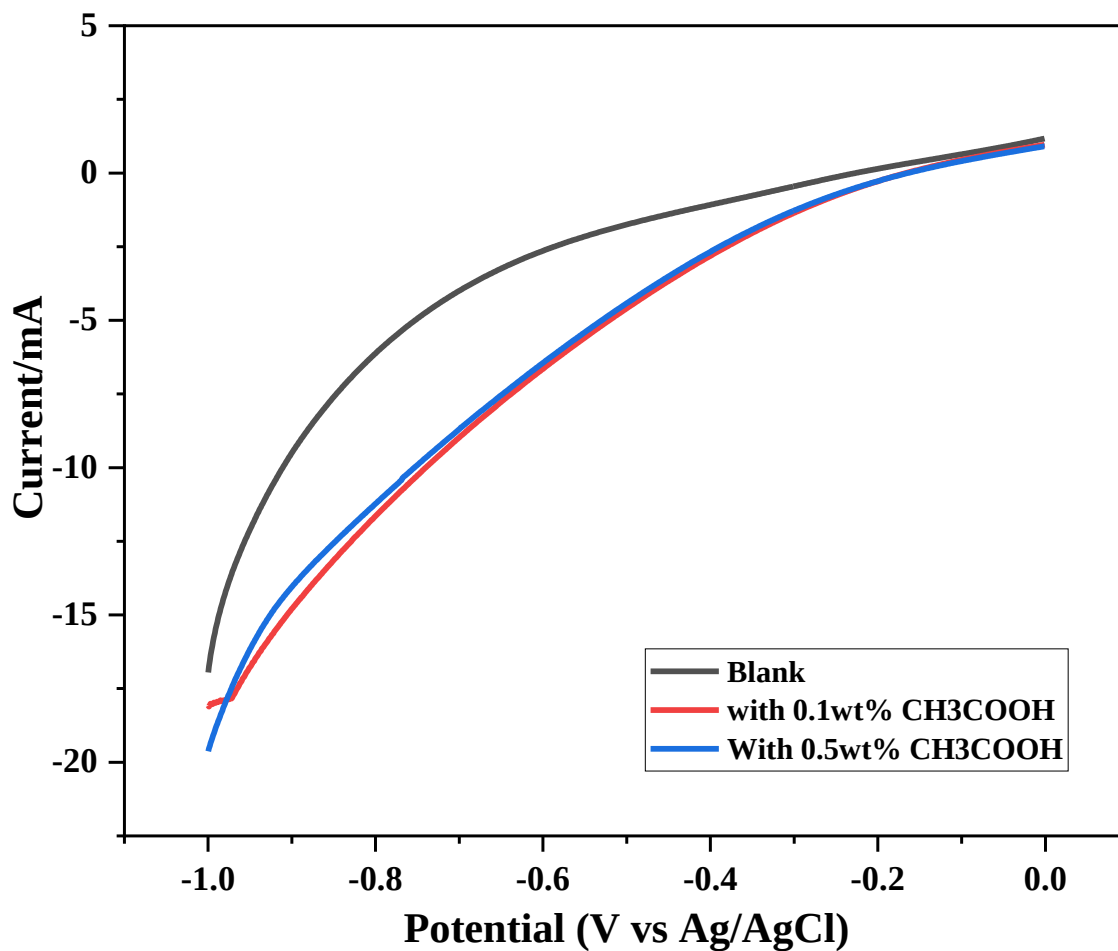


Figure 3.11 : Linear sweep voltammogram (black line) CCl_4 in N_2 - Purged 0.1M TBAC (Tetrabutylammonium chloride) in DMF (Dimethylformamide). The Linear sweep voltammogram of CCl_4 in N_2 - Purged 0.1M TBAC in DMF with 0.1wt.% (red line) and 0.5 wt.% (blue line) acetic acid.

Furthermore, the impact of the atomic $\cdot\text{H}$ towards the degradation of the organic as explored with the radical scavenger is shown in Figure 3.12. TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) was chosen as the radical scavenger due to its high affinity for atomic $\cdot\text{H}$ [70]. As shown in the Figure, the degradation of the organic was inhibited to a certain degree in the presence of TEMPO compared to its absence, indicating the contribution of atomic $\cdot\text{H}$ to the degradation process. Moreover, it could also be argued that the nature of the reactor set-up, which is an undivided cathode and anode configuration, might have contributed to organic degradation via anodic reaction. Considering the above, the mechanism of the organic halide's degradation by the $\text{CoMoS}_2\text{-GF}$ was proposed to involve the following; (i) adsorption of the organics onto the $\text{CoMoS}_2\text{-GF}$ surface, (ii) electrocatalytic reduction of organic halides on the $\text{CoMoS}_2\text{-GF}$ surface mediated by surface-bound atomic $\cdot\text{H}$ generated by water reduction, (iii) direct electrooxidation of the organics or its reduced intermediate at the platinum anode.

Based on the GCMS analysis, the primary product of degradation was 1,2-propanediol that was likely formed during the anodic oxidation of acetone used as a solvent of DBPs.

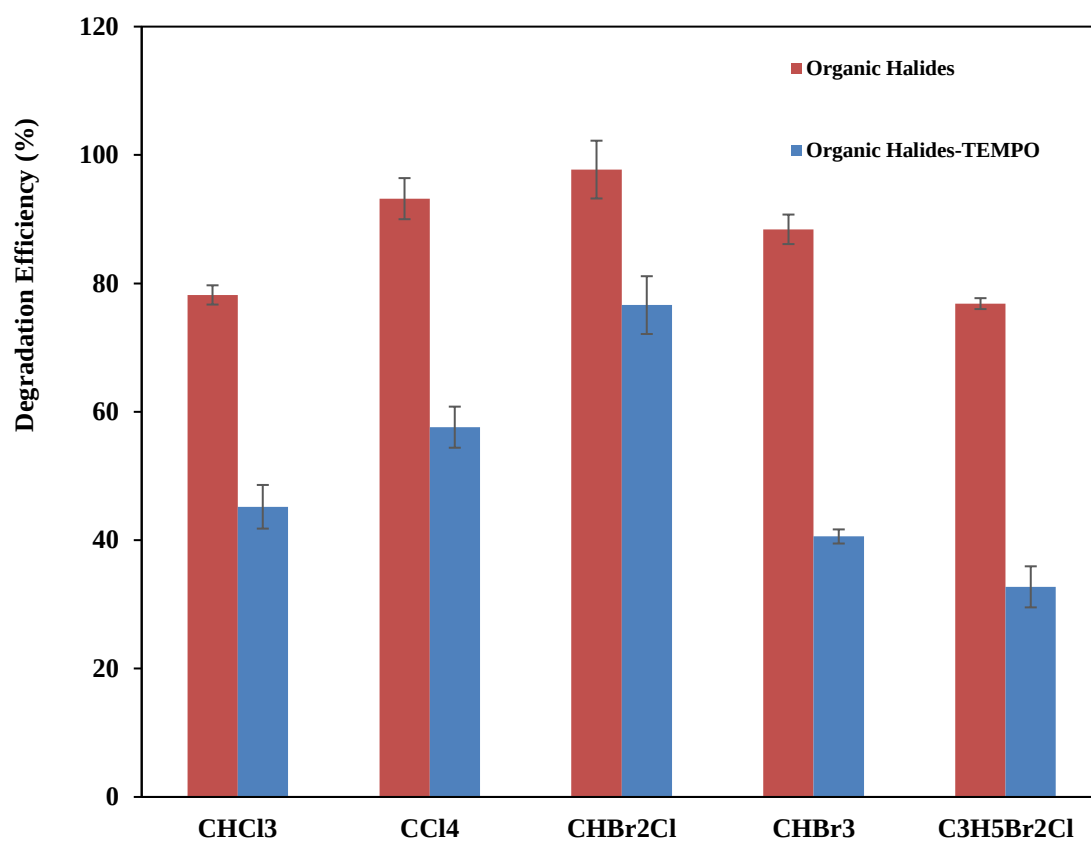


Figure 3.12: Effect of atomic $\cdot\text{H}$ radical scavenger towards the halogenated organic degradation

3.4 Summary

The presented work shows that Co-MoS₂ is an active and durable electrocatalyst that enhances the electrochemical performance of graphite felt support towards the reductive degradation of DBPs. To conclude, the Co-MoS₂ catalyst was successfully synthesized and deposited on the graphite felt via hydrothermal synthesis procedure. The surface characterization techniques confirm that the synthesized electrocatalyst was composed of a hybrid CoS₂ and MoS₂ nanosheet. The FESEM analysis revealed that the Co-MoS₂ catalyst was loaded along the fiber strand of the graphite felt material, ensuring it retains most of its pore structure after the deposition process. Moreover, the Co-MoS₂-GF electrode was proven to possess superior electrocatalytic activity. It exhibits a sizeable current peak at a negative potential of -0.3 V/Ag-AgCl when compared to the bare graphite felt. The performance of the Co-MoS₂-GF for the reductive degradation of 5 selected organic halides includes CHBr₂Cl, C₃H₅Br₂Cl, CHBr₃, CHCl₃, and CCl₄ was evaluated in terms of degradation efficiency. All the DBPs exhibited a degradation efficiency of more than 90 % after 60 min of electrolysis. The enhanced degradation noted was attributed to the synergetic relationship between CoS and MoS₂ that accelerated the cathodic Volmer step of hydrogen evolution reaction (HER). The accelerated HER ensures that ample atomic hydrogen *H were generated and utilized towards the organic reduction. The stability and reusability of the electrode were evaluated, and the results demonstrated an insignificant reduction in degradation efficiency after ten cycles of operation. The finding from this study demonstrated that Co-MoS₂-GF is an effective and stable electrode that shows immense potential for application in treating real halogenated DBPs contaminated water.

Chapter 4

Degradation Kinetics and Mechanism of Polychloromethanes Reduction at Co-MoS₂/Graphite Felt Electrode

Abstract

In this study, electrochemical dechlorination of different polychloromethanes (CCl₄, CHCl₃ and CH₂Cl₂) on Co-MoS₂ graphite felt cathode was investigated. The Co-MoS₂ catalyst was synthesized hydrothermally and deposited in situ on the graphite felt support. Characterization of the prepared catalyst reveals the formation of hybridized CoS_x and MoS₂ nanosheet deposited along the fiber strand of the graphite felt support. The performance of the electrode during the reduction of each of the organochloride and the influence of the process parameters that include applied current density, pH, and initial concentration on the dechlorination rate were investigated. It was noted that the prepared electrode exhibited excellent catalytic activity towards the reduction of each of the organochlorides with high selectivity towards the higher order organochloride. A significant capacitive reduction current density peak of approximately 1mA/cm² was noted for CCl₄ at a potential of 0.3 V (vs AgCl). The mechanism of dechlorination was attributed to the stepwise hydrogenolysis mechanism that involves the organochlorides bond cleavage by H^{*} insertion. Moreover, the dechlorination rates for each of the compounds were suited to the first-order kinetic model and the estimated apparent rate constants shows the dechlorination in the following sequence CH₂Cl₂ ($k_3 - 1.54 \times 10^{-4} \text{ s}^{-1}$) < CHCl₃ ($k_2 - 2.40 \times 10^{-4} \text{ s}^{-1}$) < CCl₄ ($k_1 - 1.63 \times 10^{-3} \text{ s}^{-1}$).

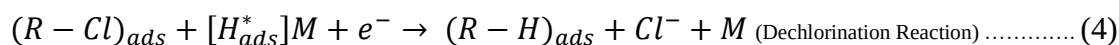
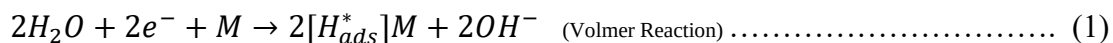
4.1 Introduction

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 [71]. These compounds have been discharged into the environment because of their extensive use as organic solvents by several industrial processes [11]. Due to their toxicity and persistence in nature, several dehalogenation treatment approaches [29,72–74] have been offered towards 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 [73]. This treatment approach, referred to as hydrochlorination, 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 [75]. Hydrodechlorination reaction is highly sought for its effectiveness towards the cleavage of the C-X bonds (X: Cl, Br, F) of organic halides at mild reaction conditions [76]. Despite its broad appeal, its application has been restricted due to its limitations that bother on catalysts aggregation and deactivation, reducing agent requirement (hydrogen donor), which can be expensive, and its inability to offer a complete reduction for some organic halides. To circumvent these perceived limitations and to provide a robust hydrodechlorination treatment approach, the electrocatalytic dehalogenation approach was advanced as a simple, fast, and environmentally friendly approach for organochlorides reduction. 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 [71]. In this approach, the reductive species is continuously generated in situ via water dissociation and does not require the addition of a hydrogen donor. When compared to 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 electrocatalytic dehalogenation reaction has been demonstrated to involve the following sequence of reactions provided in equations 1-4.



Where M denote the catalyst metal, $(R-Cl)_{ads}$ is the adsorbed organochloride on the catalyst surface and $[H]_{ads}$ represent the chemisorbed atomic 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 in addition to supplying the needed electrons for water dissociation. Hence, electrode material with superior catalytic activity to generate sufficient H^* is required for rapid and effective dechlorination reaction [77].

Several studies have demonstrated the excellent catalytic activities of noble metals-based catalyst electrodes that include Palladium (Pd) and Silver (Ag) towards the complete dechlorination of several types of organic halides [64,78–83]. It has been shown that Pd possesses lower hydrogen

overpotential compared to other metals when employed as a cathode electrode for dechlorination reaction [78]. 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 [27]. 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 [45,49,61,84] of Co-doped MoS_2 for H^* formation, which can be used to reduce organochloride effectively. It was reported that the hybridized CoS_x and MoS_2 formed during Co doping of MoS_2 (Co- MoS_2) leads to the formation of catalytic active surface edges sites that enables the accelerated surface-bound H^* formation [40]. Despite the successful application of Co- MoS_2 for reductive treatment of organochloride, the true nature and mechanistic detail of the electrode reaction is still lacking in the literature. Moreover, the knowledge of 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 electro reductive dechlorination of selected polychloromethanes CCl_4 , $CHCl_3$ and CH_2Cl_2 on Co- MoS_2 catalyst supported on graphite felt electrode. The Co- MoS_2 catalyst was prepared through the hydrothermal synthesis route and was deposited on the graphite felt in situ. More so, reports have shown that the rate of dechlorination reaction is highly dependent on the operating conditions [78,85]. For this reason, we investigated the influence of operating parameters that includes

solution pH, applied current densities and reaction time to elicit their effect on the organochloride's reduction by the electrode.

4.2 Materials and Methods

4.2.1 Materials

The following lists of chemicals supplied by Sigma Aldrich Co. were employed in the study; Cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), thiourea ($\text{CH}_4\text{N}_2\text{S}$), ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$), sodium sulfate (Na_2SO_4), chloroform (CHCl_3), carbon tetrachloride (CCl_4), Dichloromethane (CH_2Cl_2), and pentane (C_5H_{12}). PAN-based graphite felt (100 x 100 x 5 mm) was purchased from Jiangsu Sutong Carbon Fibre Co. Ltd (China) and used as the support for the catalyst deposition. Deionized water (resistivity 18.2 M Ω) prepared from the Millipore system was used for preparing the supporting electrolyte solution.

4.2.2 Electrode preparation and characterization

Before the catalyst deposition, the graphite felt (GF) with the dimension of 2 * 3 cm was heated in a muffle furnace (300 °C) for 2 hours to remove its hydrophobic groups. Consequently, the Co-MoS₂ catalyst was deposited hydrothermally on the GF surface according to the synthesis procedure described in our previous study [84]. Briefly, a combined solution containing 300 mg of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, 300mg Co (NO_3)₂·6H₂O, and 900 mg of C₂H₅NS was prepared with 50 mL of deionized water (Milli-Q). The pre-treated GF was immersed in the solution, and the resulting mixture 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 hours. After cooling, the Co-MoS₂ loaded GF was thoroughly rinsed with deionized water to remove the

unattached residue. 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 hours.

Field emission scanning electron microscopy analysis (FESEM -TESCAN, Czech Republic) was employed in examining the surface morphology of the catalyst electrode. The crystalline composition of the electrode was verified through the Transmission Electron Microscopy (JEOL, JEM-F-200). X-ray photoelectron spectroscopy (XPS) analysis was used to characterize the loaded catalyst's chemical composition and structure. The XPS spectra were collected using a Thermo scientific Escalab 250Xi spectrometer at a high vacuum with a monochromatic Al K α (1486.6 eV) X-ray source.

4.2.3 Electrochemical characterization

The effectiveness of the prepared Co-MoS₂-GF electrode towards the reduction of the selected polychloromethanes (CCl₄, CHCl₃ and CH₂Cl₂) and the formation of H^{*} were verified through the Cyclic voltammetry (CV) measurements. The CV studies were conducted using an undivided electrolytic cell with a three-electrode system (CoMoS₂-GF-working electrode, platinum mesh counter electrode, and Ag/AgCl reference electrode) and a computer-controlled CHI 760E Potentiostat. Prior to the CV measurements, the supporting electrolyte solutions were bubbled with nitrogen gas for a duration of 20 min to remove dissolved oxygen. The electrolyte was composed of 0.2 M Na₂SO₄ solution and was spiked with 5mM concentrations of each of the organochlorides. The CV scans were performed in the presence and absence of the compounds and at a scan rate of 10mV/s with an applied potential range of −1.0 to 1.0 V.

4.2.4 Electrolysis Experiments

Dechlorination of the polychloromethanes was conducted using an undivided electrolytic cell (500 mL) with two electrodes system (the prepared Co-MoS₂-GF as the cathode and Platinum mesh as the anode). For the supporting electrolyte, 10 mM of Na₂SO₄ solution (inert) was prepared and deaerated with nitrogen gas for 20 min. The synthetic solution of each of the compounds, CCl₄, CHCl₃ and CH₂Cl₂ (1 - 5 mM concentration), was prepared by spiking approximately 20 -100 μ L of the organochlorides in 250 mL volume of the deaerated Na₂SO₄ solution to give the desired concentration. The resulting mixture kept in the sealed volumetric flask is continuously stirred with a magnetic stirrer until the organic is completely dissolved. Afterwards, the prepared 250 mL solution of organochlorides was introduced into the electrolytic cell, and the electrolysis was performed under galvanostatic conditions. A constant current was supplied to the electrodes with the aid of a DC power supply (EZ Digital GP-4303A), and the current was monitored with a digital multimeter (Fluke). To avoid concentration polarization in the cell during electrolysis, the solution was continuously recycled using a peristaltic pump to ensure adequate mixing.

The influence of the operational factors that include solution pH (3-11), organochloride concentration (1-5 mM), electrolysis time (5-120 min), and applied current density (2.5-15 mA/cm²) were investigated. During the electrolysis experiment, aliquot samples of 10 mL were collected at a predefined time, and the organochloride was extracted with pentane (extraction solvent). The extraction procedure involves adding 500 μ L of pentane to 10 mL of the collected sample in a corked volumetric flask (10 mL). The mixture was agitated and sonicated for 10 min, and the top organic layer was carefully collected in a 1 mL GC-MS vial. To determine the

degradation efficiency of each of the organochlorides, the extracted samples were analysed using GC-MS analysis. At the same time, the dechlorination efficiency was determined from chloride measurement with Ion Chromatography.

4.2.5 Analytical Method

The concentration of CCl_4 , CHCl_3 and CH_2Cl_2 from the extracted samples were quantified using gas chromatography/ mass spectroscopy system (GC-MS) (QP2010 Shimadzu (Kyoto, Japan)). The GC-MS system has a column with the following features: Rxi-5 Sil MS, 0.25 μm width, 30.0 m length, and 0.25 mm diameter) (Restek, PA, USA). For the analysis, high purity helium gas (99.999%) at a flow rate of 1.00 mL/min was used as the carrier gas. The analysis method was composed of the GC injection port temperature of 180°C and a GC-MS interface temperature of 220°C. Ion source temperature was kept at 200°C was maintained. The GC column oven was ramped to 180°C at 10°C/min, and held for 4 min; after that, it was increased to 210°C at 2°C/min, and kept for an additional 4 min; and finally, it was increased to 231°C at 3°C/min. The qualitative and quantitative analysis was performed in scan mode with a split ratio of 1:10.

The amount of chloride (Cl^-) generated from the electroreduction experiments was determined using Dionex ICS-3000 Ion Chromatography (Thermo Scientific, USA). The employed Ion Chromatography consists of an electrolytic eluent generator (for KOH production), a dual-piston pump with vacuum degassing, two six-port injection valves fitted with two loops in series (25 and 250 μL), heated conductivity cell, column heater, and a post-column reaction system.

The degradation efficiency ($D\%$) of the organochlorides was evaluated based on the concentration before (C_o) and after (C_i) the degradation process, as shown in equation (5).

$$D \% = \left(1 - \frac{C_i}{C_o}\right) * 100 \dots\dots\dots (5)$$

While the dechlorination efficiency (ratio) was determined according to the following relation

$$R \% = [Cl_{max}^-]/[Cl_o^-] * 100 \dots\dots\dots (6)$$

Where $[Cl_{max}^-]$ represents the maximum amount of chloride species formed during electrolysis and $[Cl_o^-]$ denotes the initial concentration of chloride in the solution before electrolysis.

The coulombic current efficiency (CE) of the dechlorination process that denotes the ratio of the possible amount of chloride generated to the amount of charge passed during the electrolysis process was determined according to the expression provided in equation 7.

$$CE (\%) = \frac{(n_i C_i) * F * V}{Q} * 100 \dots\dots\dots (7)$$

Where C_i represents the change in concentration (mol L^{-1}) of organochloride degraded at time t during the electrolysis, while n_i denotes the corresponding theoretical electron transfer required for full reduction of the compounds ($n_1 = 8, 6, 4$ for CCl_4 , CHCl_3 and CH_2Cl_2 , respectively). F represents the Faradays constant (96486 C mol^{-1}), V denotes the volume of the solution in the cell (Litres), and Q is the amount of electric charge applied for a specified time t .

4.3 Results and Discussion

4.3.1 Material Characterization

The morphological features of the prepared Co-MoS₂-GF electrode were acquired through the FESEM analysis, as illustrated in Figure 3.2 (a, b, & c). The FESEM micrograph of the bare GF

shows a smooth surface with a 3-D interlaced structure before the catalyst deposition, as presented in Figure 3.2 (a). After the deposition process, an agglomerated particulate with active edges sites that signifies the formation of hybrid Co-MoS₂ nanosheet was seen aligned along each of the GF's fibers as revealed in the figure. To gain more insight into the morphology and phase composition of the synthesized Co-MoS₂ catalyst, TEM analysis was performed as depicted in Figure 3.2 (d, c, &e). As illustrated, the TEM image in Figure 1 (d) shows a layered corrugated structure that is characteristics of MoS₂ crystalline phases[47,86]. Moreover, the HRTEM image in Figure 1(e) shows the presence of orderly spaced lattice fringes with an inter-planar distance of 0.35nm that corresponds to the crystalline phase of Co- MoS₂ [87]. In addition, the selected area electron diffraction (SAED) pattern acquired for the catalyst supports the presence of hybrid CoS₂ and MoS₂ lattice phases from the pattern of the bright ring [88].

The surface elemental composition of the loaded CoMoS₂ catalyst was determined through X-ray photoelectron spectroscopy (XPS). The XPS survey scan in Figure 3.4 (a) confirms the formation of the Co-MoS₂ composite based on the presence of molybdenum (Mo), cobalt (Co), and sulfur (S) elements. To confirm the chemical state of each element in the Co-MoS₂ composite, their individual high-resolution spectrum was deconvoluted, as revealed in Figure 2 (b, c, &d). For Mo, its spectrum (Figure 3.4b) presents two paired peaks at 233 eV and 228 eV binding energies assigned to Mo 3d_{3/2} and Mo 3d_{5/2} oxidation states, respectively [60]. In the case of Co, its spectrum shows two peaks of and at 802 eV and 780 eV binding energies, respectively, attributed to Co +2 (Co 2p₁ & Co 2p₃) oxidation state [89]. On the other hand, the sulfur spectrum reveals a significant peak at 168 eV (Figure 3.4d) that suggests the existence of sulfur in the S-2-oxidation state (S 2p_{3/2}). These findings from the XPS analysis were able to

substantiate the formation of hybrid CoS₂-MoS₂ composite material on the GF surface during the hydrothermal synthesis process.

4.3.2 Electrode Cyclic Voltammetric Analysis

Cyclic voltammetry (CV) analysis was employed in verifying the catalytic property of the prepared Co-MoS₂-GF electrode towards H^{*} formation for the dechlorination reaction. The CV was recorded in the presence and absence of the substrate (polychloromethanes), as illustrated in Figure 4.1. In the absence of the substrate (blank-background electrolyte), the voltammogram shows a minimal reduction peak at 0.2 V (vs. AgCl) attributed to water dissociation. This small capacitive current peak displayed in the absence of the substrates indicates apparent H^{*} formation on the active sites during water reduction. Moreover, the significant peaks observed in each of the substrates' presence suggests the potential contribution of formed H^{*} towards the reduction of the compounds. Among the organochlorides, CCl₄ displayed the highest reduction peak at approximately 0.3 V (vs AgCl) with a capacitive current density of ~1mA/cm², indicating the higher-order electrode selectivity organochloride. While CH₂Cl₂ and CHCl₃ showed moderate peaks at the same 0.3 V (vs. AgCl) potential. More so, it can be inferred from the Figure 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-MoS₂-GF cathode in the CV scan could be exemplified as a hydrogenolysis mechanism that involves the organochlorides bond cleavage by H^{*} insertion [90]. This is based on the significant reduction peak displayed by each of the compounds at the same potential. It is worthy to note that this finding corroborates reports [26,65,91] that present

a hydrogenolysis mechanism for these organochlorides based on the formation of significant peaks as revealed on the CV scan.

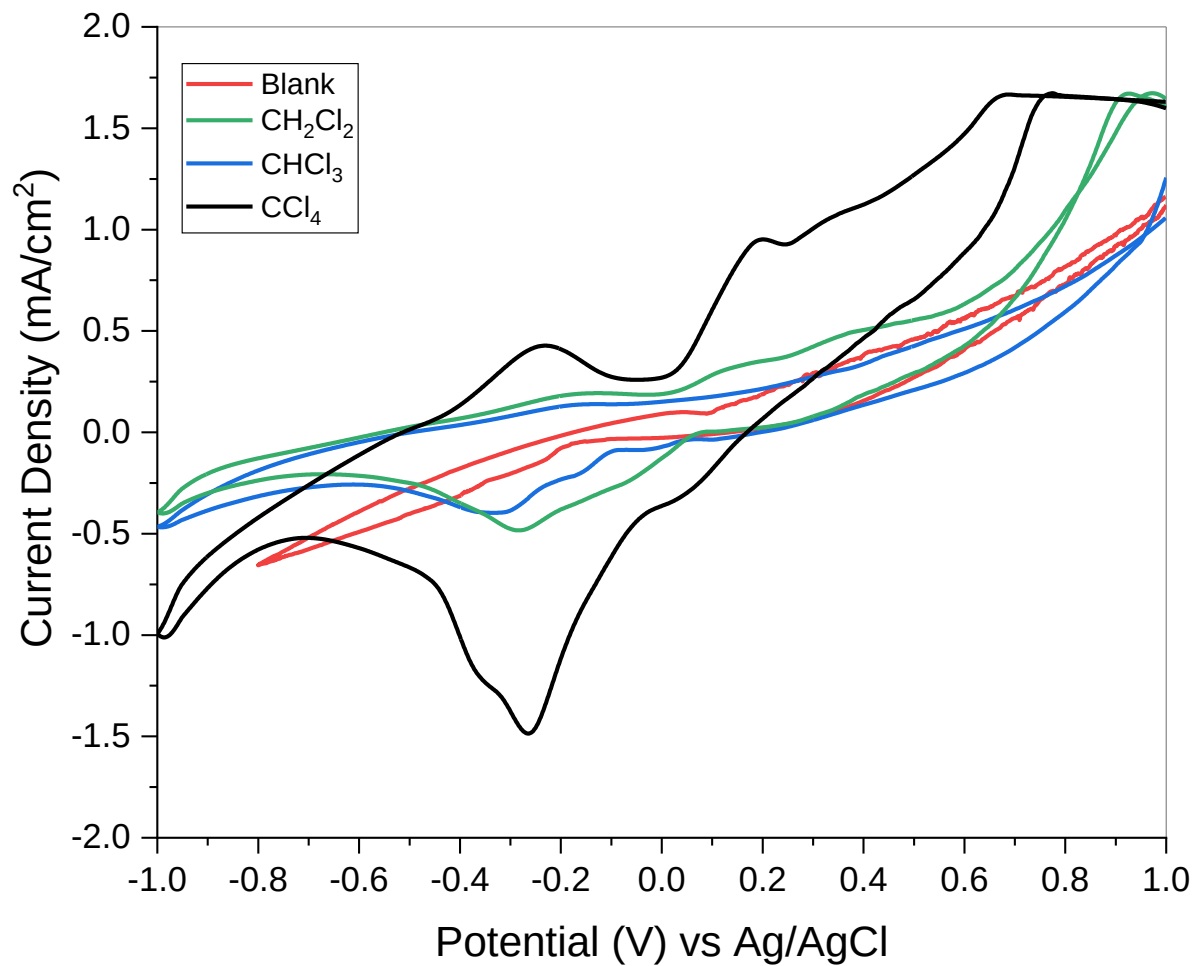


Figure 4.1: Cyclic Voltammetry scan for the Co-MoS₂-GF cathode in the absence (blank-
-background electrolytes- 0.5 M Na₂SO₄) and presence of 5mM of each of the CCl₄,
CHCl₃ and CH₂Cl₂. Scan rate 10mV/s

4.3.4 Influence of operational parameters

4.3.4.1 Effect of applied current density

Current density is an important electrolysis parameter that controls the electron transferability of the electrode to the substrates[92]. Therefore, in this study, the influence of current density variation from 2.5 to 15mA/cm² on the reduction efficiencies of CCl₄, CHCl₃ and CH₂Cl₂ was investigated, as shown in Figure 4.2. As illustrated, all the compounds showed a positive trend in dechlorination as the current density was raised from 2.5 to 15 mA/cm². CCl₄ presents a significant reduction of 60 % at 2.5 mA/cm², which increases to around 85 % at 10mA/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 around 75 to 80 % range at higher current densities.

Figure 4.3 shows the effect of applied current density towards the electrode faradaic current efficiency for each of the organochlorides. As illustrated in the Figure, the electrode exhibits a decreasing trend in current efficiency 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. An explanation to this downward trend in current efficiency could be due to the dominance of hydrogen evolution reaction (HER) over dechlorination reaction (as evidenced by increased H₂ bubble formation), where the majority of generated H* are recombined towards H₂ formation according to Tafel step in HER catalyzed reaction [93].

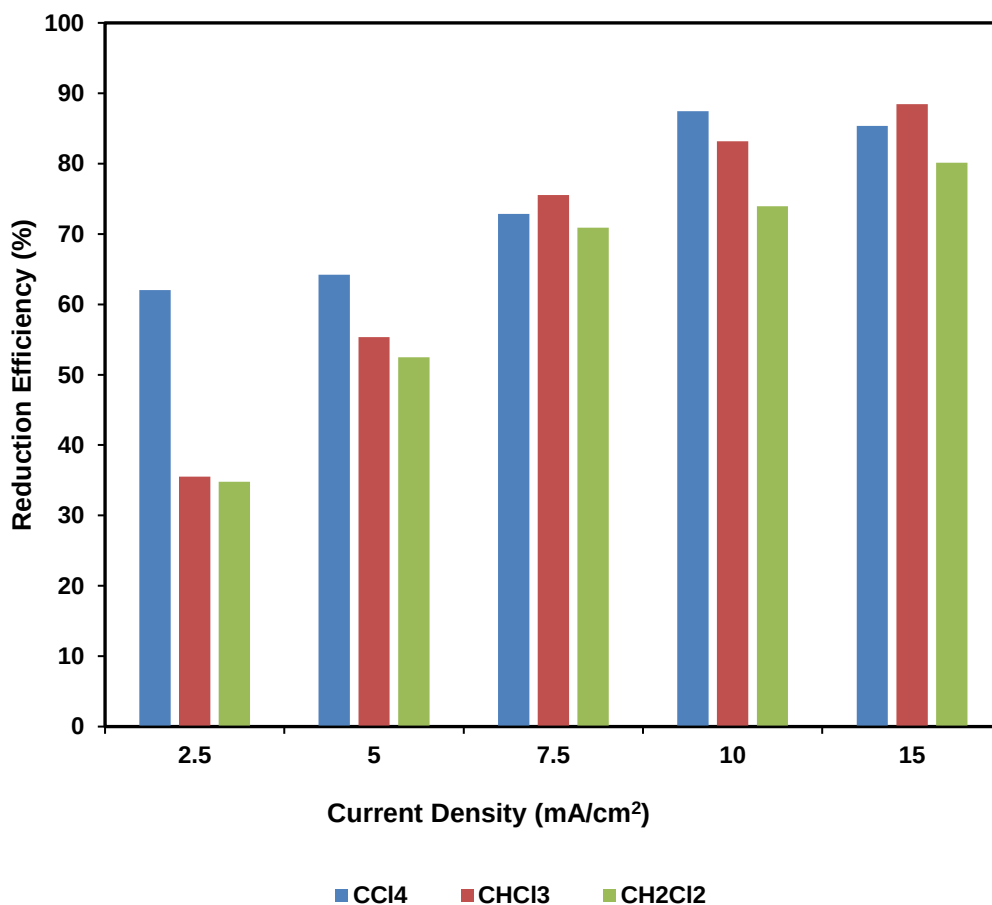


Figure 4.2 : Current Density variation on the reduction efficiency of the organochlorides (electrolysis conditions: time- 30 min, solution pH-6.4, 5mM concentrations of CCl₄, CHCl₃ and CH₂Cl₂)

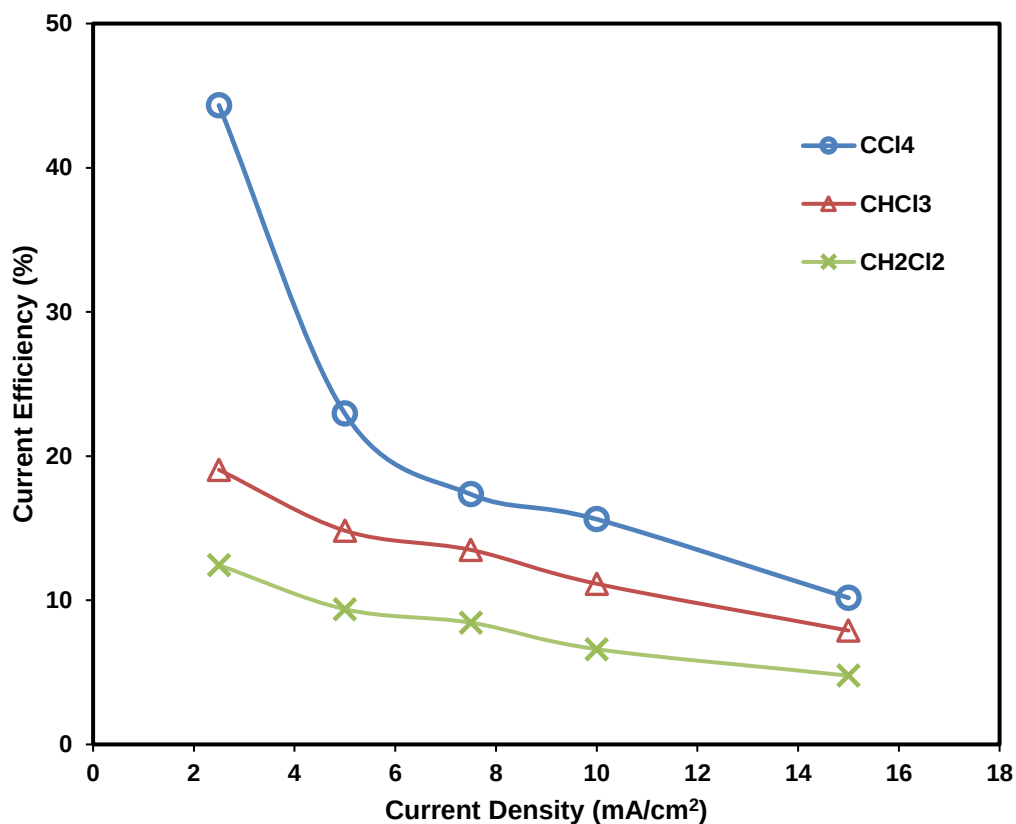


Figure 4.3 : Effect of current density variation on the electrode current efficiency for the organochlorides dechlorination

In general, the electrode showed high selectivity for CCl₄ dechlorination at a lower current density than CHCl₃ and CH₂Cl₂ but presented a relatively close dechlorination rate at higher current density for all compounds. Moreover, the high organochloride dechlorination observed at high current density was attributed to the high amount of charge loading to the electrode surface that facilitated the enhanced generation of H^{*} (from water dissociation).

4.3.4.2 Effect of Solution pH

Solution pH is an important parameter that affects the reaction conditions at both the anode and cathode in electrochemical processes. For this reason, the effect of pH variation from acidic (pH 3) to neutral (7) and basic (pH 12) conditions on the dechlorination of each organochloride is presented in Figure 4.4. All the organochlorides showed a decreased dechlorination efficiency as the pH was varied from acidic to basic medium. Also, a slight decrease in final pH is noted for all the pH values (not included) after electrolysis suggesting the formation of chloride ions during electrolysis. As illustrated, significant dechlorination of around 75 %, 68 %, and 50 % was noted at pH 3 for CCl_4 , CHCl_3 and CH_2Cl_2 , respectively, after 30 min of electrolysis time. Whereas, at the neutral condition - pH 7, a slight decrease in reduction efficiencies were noted for each of the compounds. Moreover, at the basic condition of pH 12, all the compounds presented a meagre reduction in the range of 30 to 10 %.

Generally, reports have demonstrated that at acidic conditions, electrocatalytic dechlorination reaction is usually enhanced because of the presence of significant protons (H^+) in the solution, which is easily converted to H^* at the electrode surface [94]. Hence, it is proposed that 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. More so, 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 [95].

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

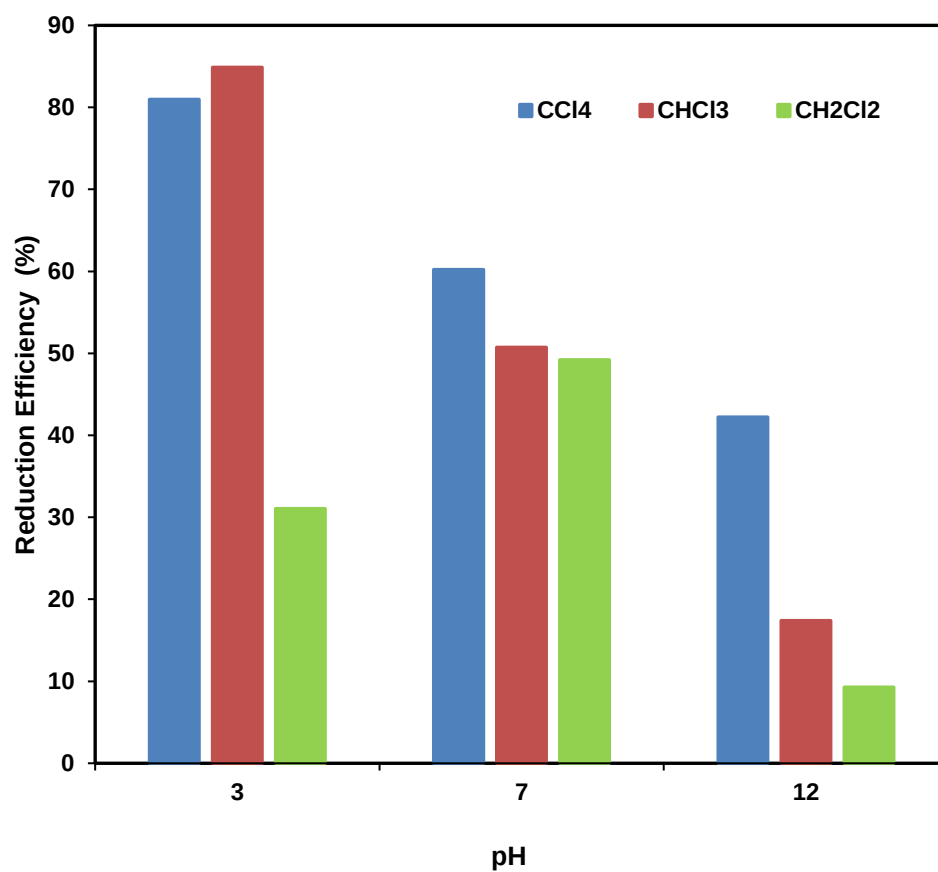


Figure 4.4 : pH variation on the dechlorination efficiency of the organochlorides
(Experimental conditions: 5mM concentration of CCl₄, CHCl₃ and CH₂Cl₂, electrolysis time: 30 min, current density: 15mA/cm²)

4.3.5 Kinetic Modelling and Mechanism of Degradation

To further elucidate the mechanism of reduction of the organochlorides, degradation of the individual compound, carbon tetrachloride (CCl_4), chloroform (CHCl_3) and dichloromethane (CH_2Cl_2) were conducted. Figure 4.5 shows the kinetic degradation profile for each organohalide. As illustrated, all the compounds showed a rapid and progressive increase in degradation efficiency with the passage time in the following order $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$. More so, the concentration variation for each of the organochlorides from 1 to 5 mM was evaluated towards their dechlorination rates. The degradation efficiencies for the organochlorides were observed to be highly dependent on their initial concentration. CCl_4 showed a final degradation rate of 98 %, 92 % and 85 % at the respective concentrations of 5 mM, 2mM and 1mM. Similarly, CHCl_3 presented the same trend in degradation rates (90 %, 88 % and 80%) for the same concentrations but with a slightly lower degradation efficiency. CH_2Cl_2 , on the other hand, presented a much lower final degradation rate of < 72 % for all the initial concentrations investigated.

Based on these, we propose a stepwise reduction mechanism of organochlorides, as shown in Figure 4.6.

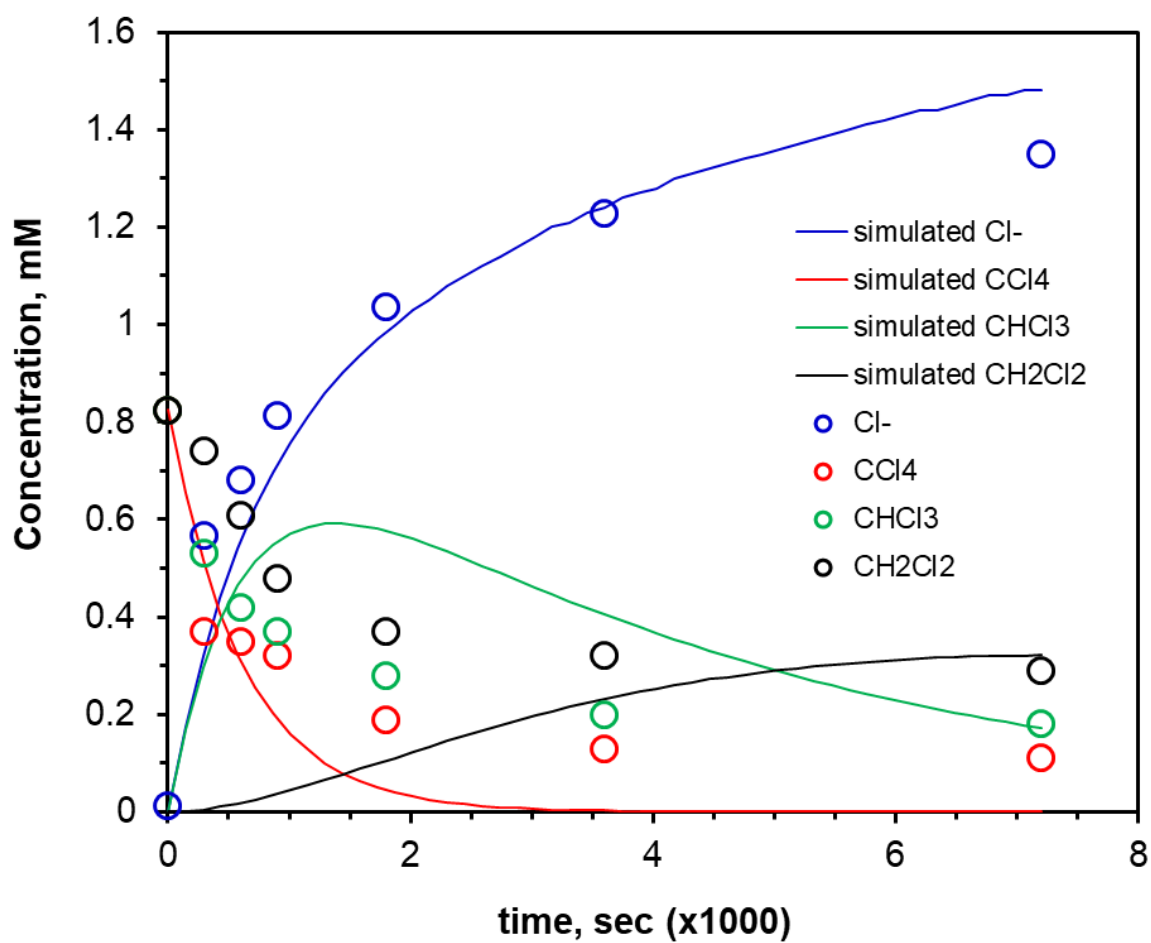


Figure 4.5 : Concentration variation on dechlorination rate of CCl_4 (red) CHCl_3 (green) CH_2Cl_2 (black) and measured chloride ion (blue) for each of the 0.825 mM concentrations of the organochlorides after electrolysis

The first-order reaction kinetics was fitted to the stepwise electroreduction (as shown in Figure 8) of CCl_4 , CHCl_3 and CH_2Cl_2 as well as the formation of Cl^- with the reaction time using equation (8)

$$[\text{C}]_t = [\text{C}]_0 e^{(-kt)} \quad (8)$$

where $[\text{C}]_0$ initial concentrations and $[\text{C}]_t$ are the concentrations (M) at times t (sec), k is the rate constant (sec^{-1}), respectively.

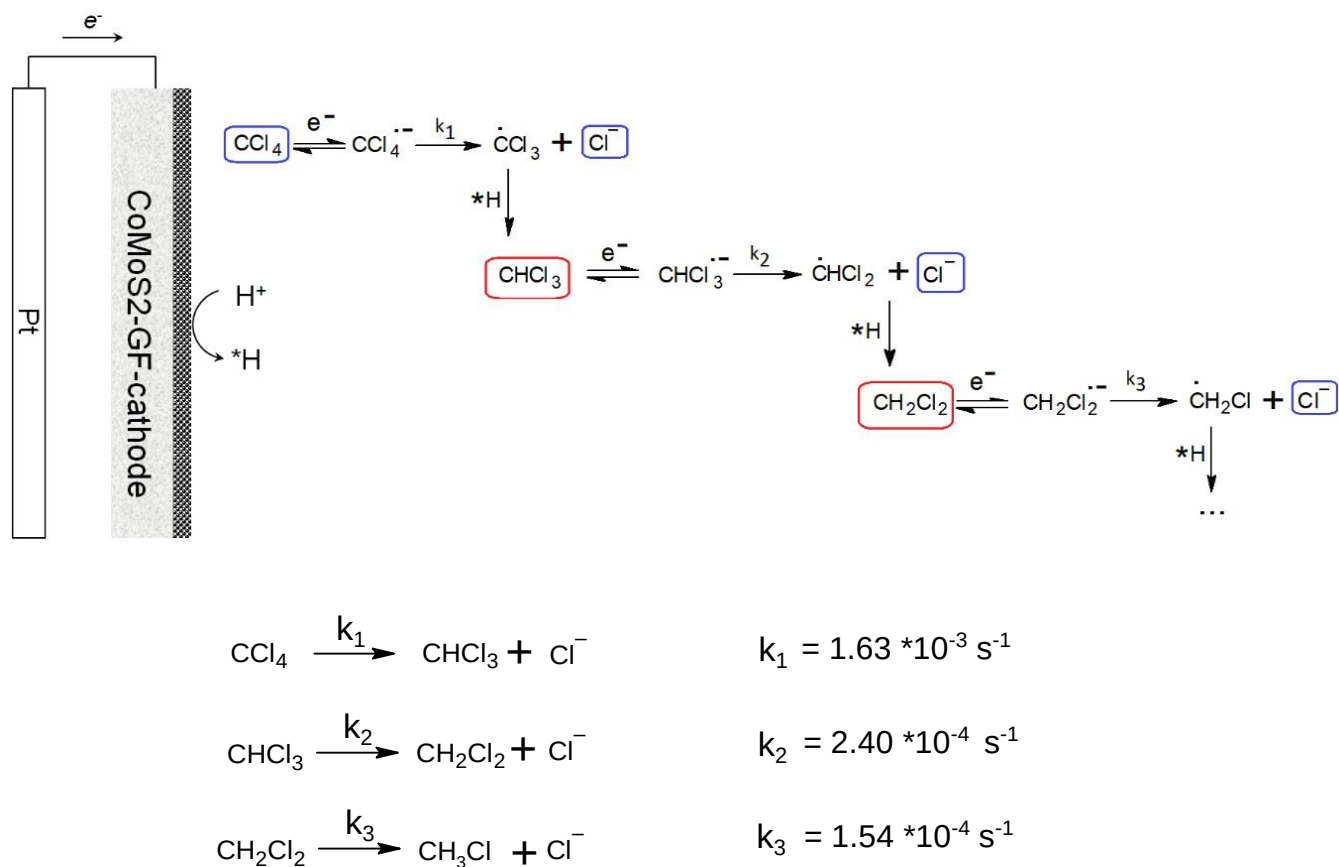


Figure 4.6 : Schematic representation of the electrocatalytic reduction of organohalides at Co-MoS₂/Graphite Felt Electrode and rate constants for each dechlorination step.

It is evident from the kinetic profiles and the simulated rate constants that the rate of degradation increases as follows $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$. The trend shows that a higher number of halogens possess a more considerable electron affinity of organohalides, pointing to the increased reactivity with the number of halogen atoms in organohalides. Therefore, these observations suggest the stepwise degradation of higher-order halogenated organohalides via intermediate organohalides subsequently formed during the electroreduction processes. Additionally, these observations further suggest the indirect reduction by cathodic surface generated atomic $\cdot\text{H}$. Schematically the proposed mechanism is shown in Scheme 1.

4.4 Summary

In summary, electrochemical dechlorination of different polychloromethanes (CCl_4 , CHCl_3 and CH_2Cl_2) in the aqueous sample by Co-MoS₂ graphite felt cathode was demonstrated. The dechlorination rate of individual polychloromethane was found to be influenced by different operational parameters that include solution pH, applied current density, and initial concentration. For the studied parameters, the increase in current density (2.5 to 15mA/cm²) and initial concentration (1 to 5 mM) both had a positive impact on the dechlorination process, while 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 increase in the following sequence $\text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$. To conclude, observed findings from the dechlorination rates at different concentrations and the obtained kinetic model parameters showed that the dechlorination process displayed in the study was likely controlled by the mass transfer limitation of the electrode. This is supported by the rapid and high dechlorination rate achieved for the higher concentration of the compounds than the lower concentration.

Chapter 5

Bimetallic Bismuth-Copper/GF electrode for enhanced degradation of halogenated aromatic organic compounds

Abstract

In this study, a bimetallic Bi-Cu composite electrocatalyst was synthesized by a facile co-electrodeposition approach and was used for electrochemical degradation of halogenated aromatic organic compounds in an aqueous medium. The prepared electrocatalyst exhibited a moss-like morphological structure with microcavities and present a stable Bi-Cu composite crystalline particle. The prepared bimetallic Bi-Cu electrode showed an improved catalytic activity compared to the Bi-electrode, suggesting that the bimetallic composition confers a favourable synergistic property on the electrode performance. Anodic electrochemical oxidation of the three selected halogenated aromatic organics (2,4-dichlorophenoxyacetic acid, 4-chloro-3-methyl phenol and 4-bromophenol) was carried out to evaluate the performance of the electrode. A central composite experimental design was employed to investigate the effect of the operational factors. It was noted that all the factors (Concentration, applied current, reaction time and pH) had a significant impact on the degradation efficiency of each of the organic halides. A degradation efficiency of more than 90 % was achieved for each of the organic halides at the upper level of the chosen factors.

5.1 Introduction

Halogenated aromatic compounds are ubiquitous in the environment because of their wide use in several household products such as herbicides, pesticides, and disinfectants[96]. These organic halide compounds have attracted considerable attention as an environmental pollutant because of their adverse effect on both human health and the environment [97]. Polychlorinated biphenyls, which were previously used as an insulator in electrical equipment and have been discharged into the environment are a typical example of these types of water pollutants. Others include 2,4-Dichlorophenoxyacetic acid (2,4-D) used as a herbicide and chlorinated phenols as antiseptics. As with most organic halides, halogenated aromatic compounds are toxic and bio-refractory which implies they are not easily amenable to the conventional biological treatment approach.

In recent years, electrochemical treatment technique has emerged as a versatile treatment approach for the removal of these classes of organic compounds from polluted water. Electrochemical processes offer an appealing alternative to other conventional approaches owing to their inherent advantages, such as robust performance, ease of setup and operation, and do not require any additional chemical reagents nor does it generate waste[8]. However, electrochemical treatment is not without flaws, since it has some major drawbacks that bother on the potential for harmful by-products to be generated in the treated water and the relatively high cost of the special electrodes required to achieve an efficient treatment process.

To overcome the harmful by-product formation during electrochemical treatment of organic halides, a highly efficient electrocatalytic electrode based on noble metals such as platinum (Pt), silver (Ag), and palladium (Pd) are often employed. The use of these electrodes enhances the formation of oxidant (hydroxyl radical $\cdot\text{OH}$) or reductant (hydrogen anion $\cdot\text{H}$) required for the

conversion of the target pollutants to its less harmful product either by complete reduction to its primary compound or complete mineralization via oxidation. However, the high cost of these noble metals has served as a limitation toward the wide adoption of electrochemical treatment methods. The quest for an inexpensive and highly efficient electrode has led to the development of other metal-based catalytic electrodes that can provide similar activity to those of noble metals. One of such transition metals that have been found to possess excellent catalytic activity for both oxidation and reduction reaction is Bismuth. Bismuth metal and its oxide component (Bi_2O_3) have been widely explored as an electrode material for chemosensor analysis [98,99], carbon dioxide reduction[100], and for oxidation of various organic compounds [101] due to their intrinsic catalytic activity. Although the electrocatalytic of Bismuth has been widely investigated for other applications, it was observed that its application for the degradation of organic halides has rarely been reported in published literature. Considering the above, the present study aims to investigate the electrocatalytic behaviour of Bismuth towards the degradation of selected halogenated aromatic organic compounds that include 2,4-dichlorophenoxy acetic acid, 4-chloro-2-methyl phenol, and 4-bromophenol in an aqueous medium. A preliminary experiment conducted to test the feasibility of the Bismuth electrode showed that it is well suited to the oxidation of the organic halides as it exhibited poor performance in the reduction process.

Meanwhile, in heterogeneous catalysis, it is well established that bimetallic catalyst often displays excellent activity compared to their mono-metallic counterparts [102]. This is because bimetallic composition often confers the electrocatalyst with synergistic properties. In this study, Copper (Cu) was chosen as a dopant to enhance the electro-oxidation activity of Bismuth towards the degradation of the organic halides. The effect of operational parameters affecting the treatment process was investigated through statistical experimental design (central composite

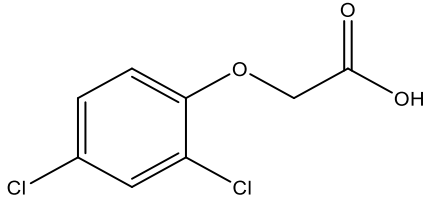
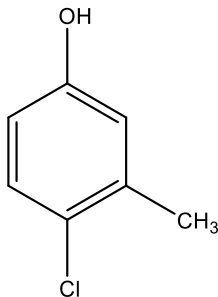
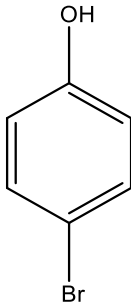
design) based on response surface methodology, and the performance of the electrode was thoroughly evaluated.

5.2 Experimental Section

5.2.1 Materials and Chemicals

The chemicals used for the bimetallic catalyst preparation include the following; Bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Trisodium citrate dehydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), Urea ($\text{CH}_4\text{N}_2\text{O}$), Ethylenediaminetetraacetic acid (EDTA), Sodium formate (CHNaO_2). Sodium sulfate (Na_2SO_4) was used as the electrolyte. The selected halogenated aromatic organics are presented in Table 5.1. PAN-based graphite felt (3.2 cm x 3.2 cm x 5 mm) was purchased from Jiangsu Sutong Carbon Fiber Co. Ltd (China) and used as the support for the catalyst deposition. Deionized water (resistivity 18.2 M Ω) prepared from the Millipore system was used for solution preparation.

Table 5.1: Chemical Structure of the selected halogenated aromatic organics

Compound	Short Name	Chemical Structure	Molecular weight (g/mol)
2,4-Dichlorophenoxy acetic acid	2,4-D		221.04
4-Chloro-3-methyl phenol	CMP		142.58
4-Bromophenol	BP		173.01

5.2.2 Electrode Preparation

In this study, the bimetallic bismuth-copper electrocatalyst was prepared by a facile co-electrodeposition method as described by [103] with a slight modification. Before the electrode preparation, the graphite felt support was pre-treated in an oven at 300 °C to improve its hydrophilicity. Next, a mixed 100mL solution of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (2.5 g), $\text{CH}_4\text{N}_2\text{O}$ (0.45 g) and EDTA (0.54 g) were prepared in a beaker. Subsequently, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.96 g), $\text{Cu}(\text{NO}_3)_2$.

3H₂O (0.12 g) and CHNaO₂ (0.6 g) were added in succession, and the resulting mixture was stirred for 30 min to give a clear plating solution. Furthermore, the co-electrodeposition of the metallic components from the solution was carried out in a two-electrode system where the pre-treated graphite felt was used as the working electrode and a platinum mesh as the counter electrode. The electrolysis was carried out at a high current density of 500 mA for a duration of 10 min. Finally, the resulting bismuth-copper coated graphite felt electrode labelled as Bi-Cu-GF was rinsed with an ample amount of distilled water to remove any unattached residue and further dried in an oven at 60 °C for 6 hours. To understand the role of copper doping in the performance of the electrode, a mono-metallic bismuth electrode was also prepared according to the described approach, except for the exclusion of copper precursor in the plating solution.

5.2.3 Electrode Characterization

The morphology of the prepared electrocatalyst was investigated by field emission scanning electron microscopy analysis (FESEM -TESCAN, Czech Republic). The elemental distribution was acquired through the energy dispersive X-ray spectroscopy (EDS). The crystalline structure of the electrocatalyst was by X-ray diffractometer (XRD) with Benchtop Bruker D2 Phaser Diffractometer (USA) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The chemical composition and the electron states of the elements in the prepared samples were examined by Raman spectroscopy (LabRAM HR Evolution, Horiba Japan) and X-ray photo electron spectroscopy (XPS, Thermo scientific Escalab 250Xi spectrometer).

Electrochemical characterization of the electrode was performed through the Cyclic Voltammetry (CV) studies to understand their catalytic activity. For this purpose, a three-electrode system made up of Bi-Cu-GF as the working electrode, platinum mesh as the counter electrode, and

Ag/AgCl as the reference electrode was used in an undivided electrolytic cell. The supporting electrolyte was 0.5 M Na₂SO₄, and the substrate was 100 mg/L individual or a mixed solution of organic halides. The CV measurements were performed with a CHI 760E Potentiostat in the presence and absence of the substrates (only electrolyte).

5.2.4 Electrochemical Performance of the Electrode

In this study, three organic halides; 2,4-D, CMP, BP were chosen as representatives of the halogenated aromatic organic compound to evaluate the electrochemical performance of the Bi-Cu-GF. The degradation of the three organic halides was carried out in a flow-through divided electrochemical cell (ElectroCellTM (USA)) with a cation exchange membrane (NafionTM N324) separating the cathodic and anodic compartments. In the anodic compartment, a specific concentration of the organic halides in 100 mL 50mM Na₂SO₄ solution as the electrolyte was employed as the catholyte, while the cathode electrode with prepared Bi-Cu-GF electrocatalyst. In the case of the anodic compartment, a 100 mL 50mM solution of the Na₂SO₄ was used as the catholyte and the anodic electrode was a titanium-iridium metal plate. The effective surface area for each of the electrodes was around 10 cm² and both the catholyte and anolyte were continuous recycle in their respective compartments to minimize concentration polarization. The electrochemical experiments were conducted under a galvanostatic condition powered by a Kenwood DC power supply, and the applied current was monitored with a fluke multimeter.

A composite experimental design (CCD) based on response surface methodology was used to investigate the effect of operational factors affecting the degradation of organic halides. The CCD allows for the determination of an ideal factors combination via statistical analysis that will give the optimum value of the desired response. More so, with the statistical analysis, the effect of

each of the factors and their interactions (synergistic) on a response can be evaluated. In this study, the investigated factors (independent variables) include the initial concentration of the organic halides, applied current, reaction time and pH as shown in the experimental design in Table 5.2. While the degradation efficiencies for each of the organic halides were chosen as the responses. According to the standard face-centred CCD with four factors, a total number of 30 experimental trials were created using the statistical software Design Expert V12. The relationship between the responses and the factors was modelled by a linear polynomial function as presented in equation 5.1.

$$y = \beta_o + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} x_i x_j + \varepsilon \quad (5.1)$$

For this expression, β_o , β_i , β_{ii} , β_{ij} , represents the constant, linear, square and interaction coefficients, respectively. While X_i and X_j denote the factors considered and y is the degradation efficiency in percentage for each organic halide.

Table 5.2: Central Composite Design for the degradation experiment

Factor	Code Level	Values of coded levels		
		-1	0	1
Concentration (mg/L) (A)	X ₁	100	200	300
Applied Current (mA) (B)	X ₂	100	200	300
Reaction time (min) (C)	X ₃	20	30	40
pH (D)	X ₃	5	7	10

5.2.5 Analytical Method

The concentration of the organic halides was determined using Ultra-high-performance liquid chromatography (LC, Shimadzu). The analysis condition is defined as follows; 15 mM ammonium formate (A) and acetonitrile (B) were used in the mobile phase, which was administered at a flow rate of 0.5 mL/min. The gradient program used was 0 min 30% B, 0–15 min 90% B, 15–20 min 30% B, 20–25 min 30% B, with a 20-L injection volume.

The degradation efficiency for each organic halide was determined based on equation 5.2 as provided.

$$\text{Degradation efficiency: } D \% = \left(1 - \frac{C_i}{C_o}\right) * 100 \quad \dots\dots\dots (5.2)$$

Where C_i represents the change in concentration (mol L⁻¹) of the organic halide degraded at time t during the electrolysis and C_o- represent the initial concentration of organic halides.

5.3 Results and Discussion

5.3.1 Synthesis of Bi-Cu-GF electrode and characterization

The prepared electrocatalyst's surface morphology is of interest because the size and uniformity of the bimetallic coating can significantly alter the conductive properties of graphite felt support, and thus the resulting electrode effectiveness. As shown in Figure 5.1, the morphology of the prepared bimetallic composites revealed a moss-like crystalline structure with microcavities that covers each of the fiber of the graphite felt support. The electrodeposited method allows for the vertical growth of Bi-Cu crystalline composites along the fiber strand of each of the support without the need for a binder. It is envisaged that the moss-like structure of the bimetallic composites would provide an ample surface site for its interaction with the organic halides during electrolysis. As expected, the composition of elements in the prepared electrode as revealed from the single site EDS analysis shows Bi, O and C as the major constituents with 95 % composition and Cu as the minor constituent.

The crystalline phase of the bimetallic composition of the as-prepared electrodes was investigated by XRD analysis. The XRD spectra of the pristine GF, monometallic Bi-GF and bimetallic Bi-Cu-GF electrodes were acquired as shown in Figure 5.2. The two prominent broad diffraction peaks for the GF at 25.3° and 43.6° were assigned to (002) and (100) planes of graphitic carbon of the graphite felt [104]. It should be noted that these broad peaks were also noticeable in both the Bi-GF and Bi-Cu-GF samples. In the case of monometallic Bi-GF, the diffraction peaks due to the bismuth metal are observed at 27.02° , 38.24° and 39.32° , which are associated with (012), (104) and (110) planes respectively [103].

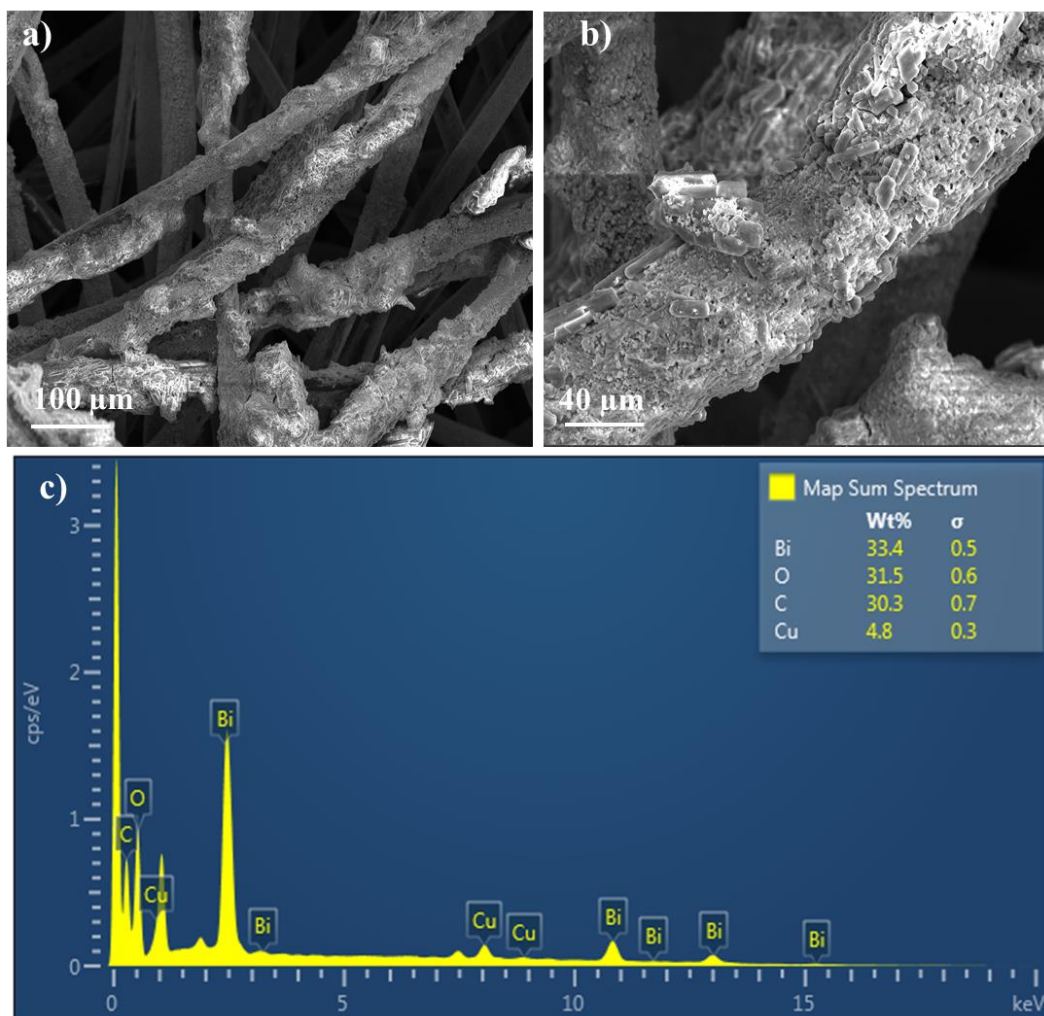


Figure 5.1: SEM image (a, b) and EDS result (c) of the prepared Bi-Cu-GF electrode

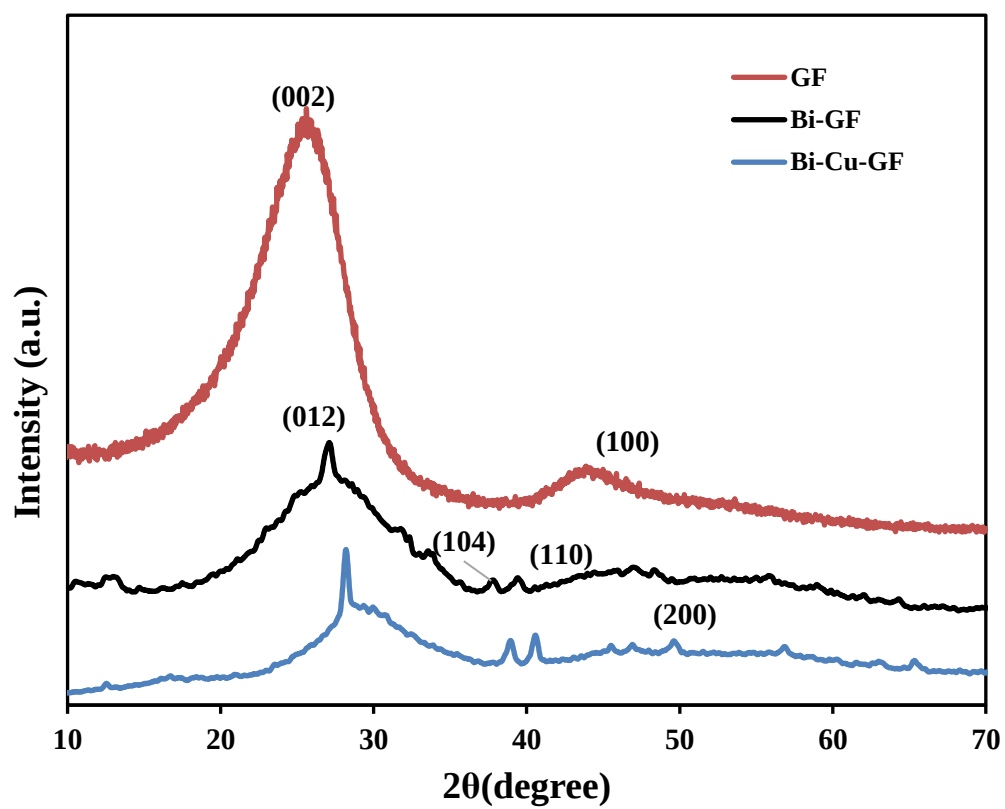


Figure 5.2 : XRD spectra of the prepared electrode

As for the bimetallic Bi-Cu-GF, its diffraction pattern also presented the same peaks associated with bismuth metal and an additional peak at 49.45° that corresponds to (200) plane of metallic Cu [105]. These findings confirm the growth of Bi and Cu crystals separately on the GF supports forming a stable composite material.

The chemical states of the elements in the prepared electrode were investigated by the XPS analysis as shown in Figure 5.3. The survey spectrum (Figure 5.3 a) shows the presence of Bi4f, O1s and Cu2p3 that signifies the formation of oxides of Bi and Cu. The high-resolution Bi4f spectrum shows two prominent peaks at 165 eV and 162 eV, which were assigned to Bi4f_{5/2} and Bi4f_{7/2}, respectively, and thus, signifying the presence of Bi as Bismuth metal and Bi₂O₃ [106]. The peaks at 935 eV and 954 eV in the Cu2p spectrum have been assigned to Cu2p_{3/2} and Cu2p_{1/2}, respectively, and thus indicate Cu 2+ bonded to oxygen [103]. As for the O1s spectrum, the 530 eV peak was assigned to lattice oxygen in metal oxide[107]. The above findings were able to substantiate the formation of individual Bi and Cu oxides during the electrodeposition process which was fused on the GF surface to form a stable Bi-Cu composite.

The electrocatalytic activity of the electrode was evaluated through cyclic voltammetry studies (Figure 5.4) performed in the presence of each of the organic halides (2,4-D, CMP, and BP). Figure 5.4 (a) shows the CV scan of both the Bi-GF and Bi-Cu-GF in the presence of reference electrolyte solution. It can be observed that both electrodes presented considerable reduction and oxidation current peaks in the electrolyte solution which demonstrate their electrocatalytic activities. It is worth noting that the bimetallic Bi-Cu-GF electrode showed a much higher oxidation current peak than the Bi-GF electrode, thus, indicating its better electro-oxidation activity.

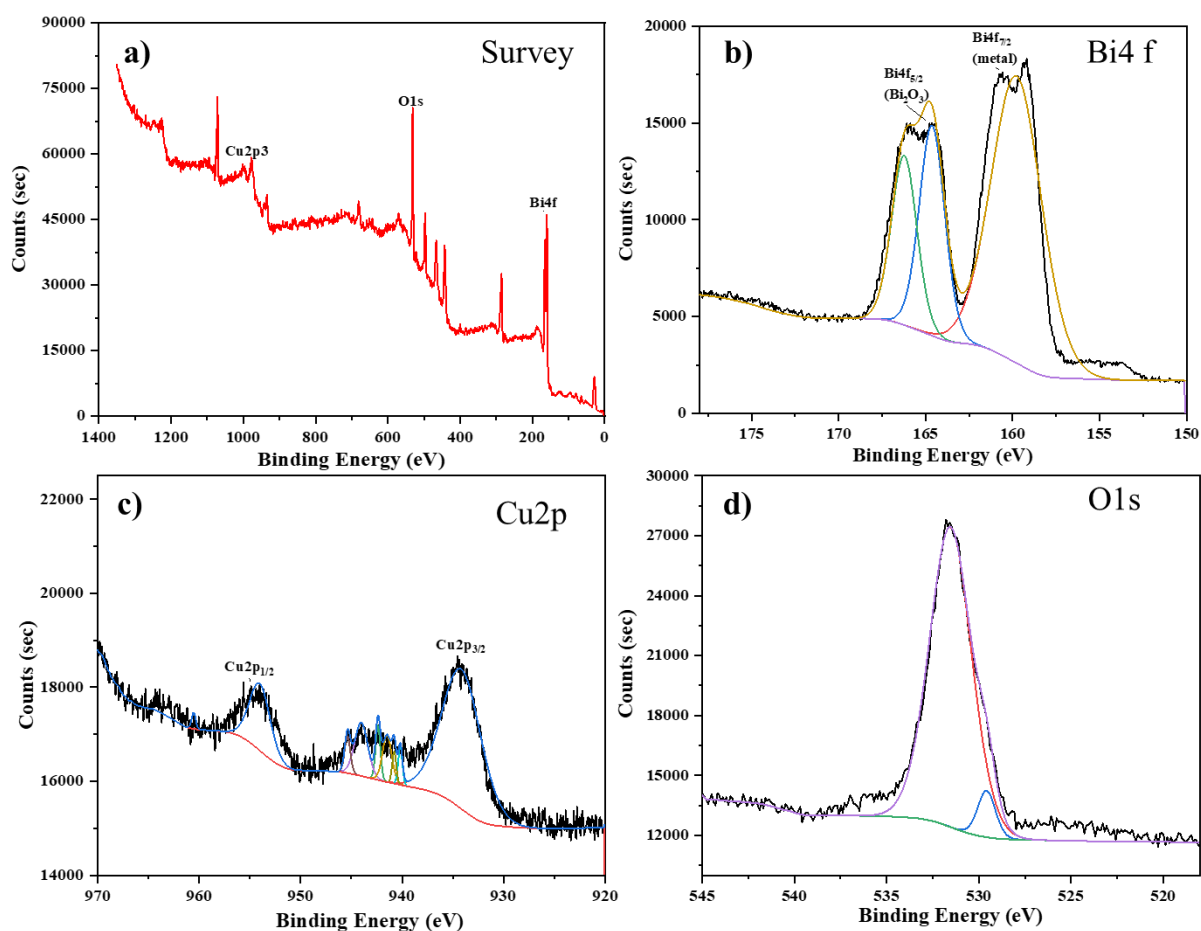


Figure 5.3 : XPS spectra of the Bi-Cu-GF electrode showing (a) Survey scan (b) $\text{Bi}4f$ (c) $\text{Cu}2p$ and (d) $\text{O}1s$

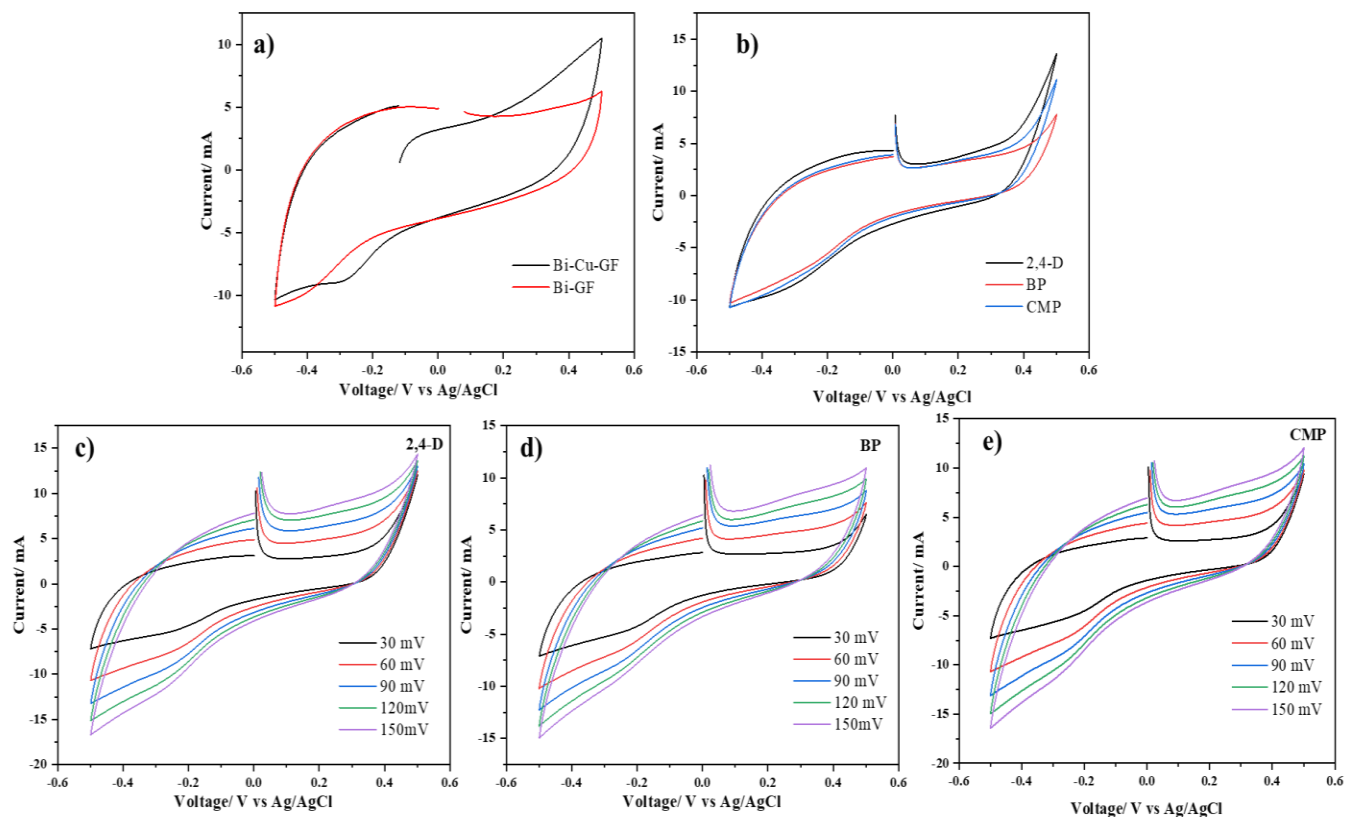


Figure 5.4 : CV studies for (a) Bi-GF and Bi-Cu-GF electrodes in reference electrolyte (0.5 M Na₂SO₄), (b) Bi-Cu-GF electrode for each of the organic halides (100 mg/L solution, 0.5 M Na₂SO₄ as electrolyte, and scan rate 50 mV) (b) Bi-Cu-GF electrode for each of the organic halides at different scan rate (same condition as (b)).

It was averred that the high oxidation current displayed by the Bi-Cu-GF in the electrolyte medium is due to high oxygen evolution induced by the presence of Cu in electrode composition, which is beneficial towards the formation of hydroxyl radical (*OH).

The CV scan of the Bi-Cu-GF electrode in the presence of each of the organic halides is illustrated in Figure 5.4b. As depicted, the electrode displays a significant current response for each of the organic halides at the lower potential of 0.4 V, which demonstrates its high oxidation activity. Moreover, the current response due to the oxidation of the compounds was in the following order; 2,4-D (14 mA) < CMP (12 mA) < BP (7 mA). To gain a better understanding of the likely mechanism of organic halide oxidation by the electrode, a CV at different potential scan rates was performed for each of the compounds, as shown in Figure 5.4(c, d, e). It can be observed that an increase in the scan rate led to a corresponding increase in both the oxidation and reduction current peaks. Furthermore, the variation in the slope of each of the CV scans oxidation peaks at different scan rates suggests that the electrooxidation is reminiscent of an irreversible oxidation process mediated by the formation of *OH radicals [102].

5.3.2 RSM Modelling using CCD

To investigate the effect of the operational factors affecting the performance of Bi-Cu-GF electrode towards the degradation of the three selected organic halides (in multi-solute solution), an experimental design based on CCD was employed. Table 5.3 presents the result of the CCD design matrix showing the various factor combinations and corresponding experimental responses. Using the Design Expert software, the degradation efficiencies for each of the organic halide (responses) was fitted to a two-factor interaction model (equation 1) based on the coded factor values as presented in equations 5.3 – 5.5.

The fitted models were validated by the normal probability plots of residual as illustrated in Figures 5.5 - 5.7. Based on the linear regression model's assumption that the error terms are normally disturbed, and this can be verified if the residuals' normal probability plot is linear. It can observe that experimental responses were approximately normally distributed, as illustrated by the residual's plots showing a nearly straight line. Another important diagnostic tool for validating the fitted models is the plot of externally studentized residual versus the actual predicted responses as shown in Figure 5.8 – 5.10 for each of the organic halide degradations. These plots are used in detecting the existence of non-linearity, unequal error variance, and the presence of an outlier. It can be observed from the plots that the residuals are distributed randomly around the zero line which indicate that the linearity assumption is valid.

Furthermore, the statistical relevance and adequacy of the fitted models were elicited through the Analysis of Variance Test (ANOVA) as presented in Table 5.4 & 5.5. Parameters from the ANOVA test that include probability value (p-value), lack of fit test value, correlation coefficient (R^2), adjusted R^2 , and predicted R^2 were used in confirming the predictive capabilities of the models. As shown, the models' P-values were found to be less than 0.05 ($p\text{-value} < 0.05$), indicating that they were all statistically significant. Moreover, the lack of fit tests for each of the models was observed to be insignificant based on their p-values > 0.05 . Thus, proving the models can provide a satisfactory prediction of the responses. The obtained R^2 and adjusted R^2 values for all the models (Table 5.5) were close to unity (1). In addition, a good agreement between the adjusted R^2 and the predicted R^2 for all the models was also observed (occurs when their difference is less than 0.2). Adequate precision value, a measure of signal to noise ratio, with a value of 4 indicating an adequate signal for a model with good predictive capability. The adequate precision values for all the models were greater than 4. In summary, all the above analyses were

able to provide considerable prove of the adequacy of the models and indicate their good predictive capability for the experiment responses.

$$\begin{aligned} \text{2,4-D degradation (\%)} = & 63.2833 + -3.55556 * A + 15.1667 * B + 6.51667 * C + 2.97778 * D + \\ & -3.34375 * AB + 0.54375 * AC + 3.20625 * AD + 0.91875 * BC + \\ & 3.10625 * BD + 4.89375 * CD \dots\dots\dots (5.3) \end{aligned}$$

$$\begin{aligned} \text{CMP degradation (\%)} = & 71.6267 + -0.188889 * A + 12.3944 * B + 5.53333 * C + 1.1 * D + - \\ & 3.84375 * AB + 1.43125 * AC + -1.60625 * AD + 1.43125 * BC + - \\ & 0.18125 * BD + 7.69375 * CD \dots\dots\dots (5.4) \end{aligned}$$

$$\begin{aligned} \text{BP degradation (\%)} = & 74.5567 + -1.98889 * A + 13.1167 * B + 6.47222 * C + -1.05 * D + - \\ & 1.56875 * AB + 0.46875 * AC + -0.20625 * AD + -1.09375 * BC + \\ & 1.90625 * BD + 6.26875 * CD \dots\dots\dots (5.5) \end{aligned}$$

The effects of the organic halide concentration (A), applied current (B), reaction time (C) and pH (D) as predicted by the fitted models are shown in the 3D- response surface plots in Figures 5.11- 5.13. The 3D plots allow for the graphical representation of the factor's interactions, from which, valuable information about them can be deduced. As depicted from the plots, all the studied factors appear to display a significant effect (positive/negative) on the degradation efficiencies of the organic halides.

The degradation of the organic halides was found to be current dependent as evidenced by the high removal efficiencies observed at higher current values. When the applied current was increased from the low value of 50 mA (coded value: -1) to 300 mA (coded value: +1), a noteworthy upward trend in the degradation efficiency was observed. The above finding proves that complete or near-complete mineralization of compounds can be attained upon increasing the applied current to a specific optimum value. Moreover, the observed trend can be attributed to a rapid formation of the *OH radicals at the Bi-Cu-GF electrode interface at higher current values.

On the contrary, the effect of the organic halide concentrations was found to display an antagonistic effect as its increase led to a decrease in the degradation efficiencies. As illustrated, the organic halides were removed more efficiently at a lower concentration (50 mg/L) than the higher concentration (300 mg/L), which showed a moderate removal. The effect of the solution pH on the degradation process was observed to elicit a negative impact at a lower value (acidic) and a positive one at a higher value. As illustrated, the highest degradation of each of the organics occurred at pH 10 (coded value: +1), while a moderate degradation was noted at the neutral pH 7 (coded value : 0). The observed trend shows that the Bi-Cu-GF electrode can be effectively employed for the treatment of the organic halide at neutral to basic pH range conditions. Lastly, the effect of the reaction time also showed a positive impact on the degradation process as it increases led to significant removal of the organic halides.

Table 5.3: Factors combination and responses

STD	Run	A- Conc. (mg/L)	B-Applied current (mA)	Reaction time (min)	pH	2,4-D (%)	CMP (%)	BP (%)
18	1	1	0	0	0	32.3	50.2	54.4
3	2	-1	1	-1	-1	72.3	85.6	88.4
10	3	1	-1	-1	1	53.8	63.4	58.5
23	4	0	0	0	-1	30.5	40.2	58.6
14	5	1	-1	1	1	64.2	70.7	66.5
6	6	1	-1	1	-1	53.5	75.6	74.6
2	7	1	-1	-1	-1	47.5	67.8	63.3
11	8	-1	1	-1	1	81.8	78	84.9
24	9	0	0	0	1	75.2	82.5	87.4
16	10	1	1	1	1	85.8	92.6	92.9
13	11	-1	-1	1	1	59.3	75.6	78.7
21	12	0	0	-1	0	35.6	44.6	42.2
29	13	0	0	0	0	68.2	75.7	80.2
8	14	1	1	1	-1	72.3	82.5	85.4
5	15	-1	-1	1	-1	46.6	40.2	59.3
28	16	0	0	0	0	68.5	74.7	80.6
27	17	0	0	0	0	68.3	74.3	80.1
19	18	0	-1	0	0	20.7	32.1	34.2
4	19	1	1	-1	-1	67.6	88.4	90.1
9	20	-1	-1	-1	1	22.1	39.8	34.6
12	21	1	1	-1	1	67.2	63.5	70.5
1	22	-1	-1	-1	-1	72.2	75.7	80.2
30	23	0	0	0	0	68.2	75.7	80.1
22	24	0	0	1	0	82.2	90.5	91.2
15	25	-1	1	1	1	90.1	94.2	93.8
25	26	0	0	0	0	68.2	75.6	80.4
7	27	-1	1	1	-1	83.4	84.5	86.3
26	28	0	0	0	0	68.1	75.4	80.3
17	29	-1	0	0	0	80.4	84.5	85.3
20	30	0	1	0	0	92.4	94.7	94.2

Table 5.4: ANOVA analysis result

2,4-D						
Source	Sum of Squares	df	Mean Square	F-value	p-value	Comment
Model	6191.24	10	619.12	2.41	< 0.0477	significant
Residual	4887.52	19	257.24			
Lack of Fit	4887.43	14	349.10	18373.79	0.1391	not significant
Pure Error	0.0950	5	0.0190			
Cor Total	11078.76	29				
CMP						
Model	4629.59	10	462.96	2.04	< 0.0469	significant
Residual	4310.85	19	226.89			
Lack of Fit	4309.09	14	307.79	877.74	0.0832	not significant
Pure Error	1.75	5	0.3507			
Cor Total	8940.44	29				
BP						
Model	4691.51	10	469.15	2.45	0.0445	significant
Residual	3636.20	19	191.38			
Lack of Fit	3636.01	14	259.72	6895.09	0.2782	not significant
Pure Error	0.1883	5	0.0377			
Cor Total	8327.71	29				

Table 5.5 : Important features of the models

Parameters	2,4-D	CMP	BP
Std. Dev.	16.04	15.06	13.83
Mean	63.28	71.63	74.56
C.V. %	25.34	21.03	18.55
R ²	0.9426	0.9764	0.9439
Adjusted R ²	0.9091	0.9902	0.8861
Predicted R ²	0.7846	0.8069	0.8550
Adeq Precision	6.6894	6.1549	7.1528

Color points by value of
2,4-D degradation:
20.7 92.4

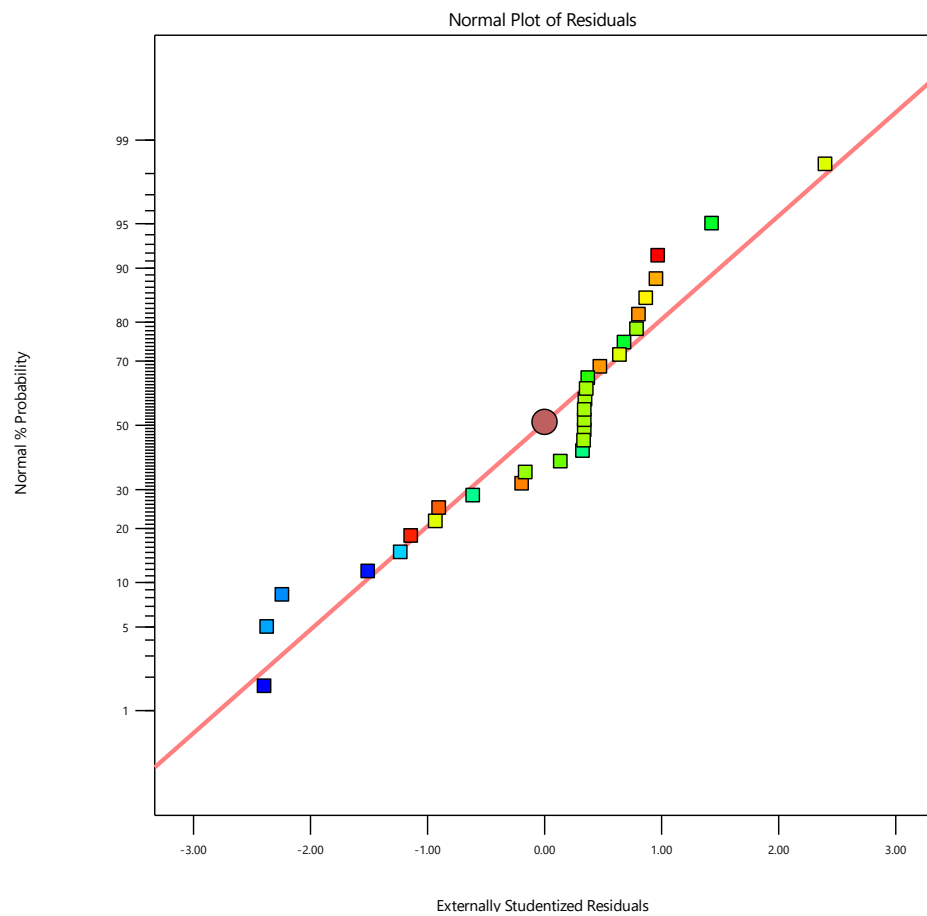


Figure 5.5 : Normal plot of residual for 2,4-D degradation

Color points by value of
CMP degradation:
32.1 94.7

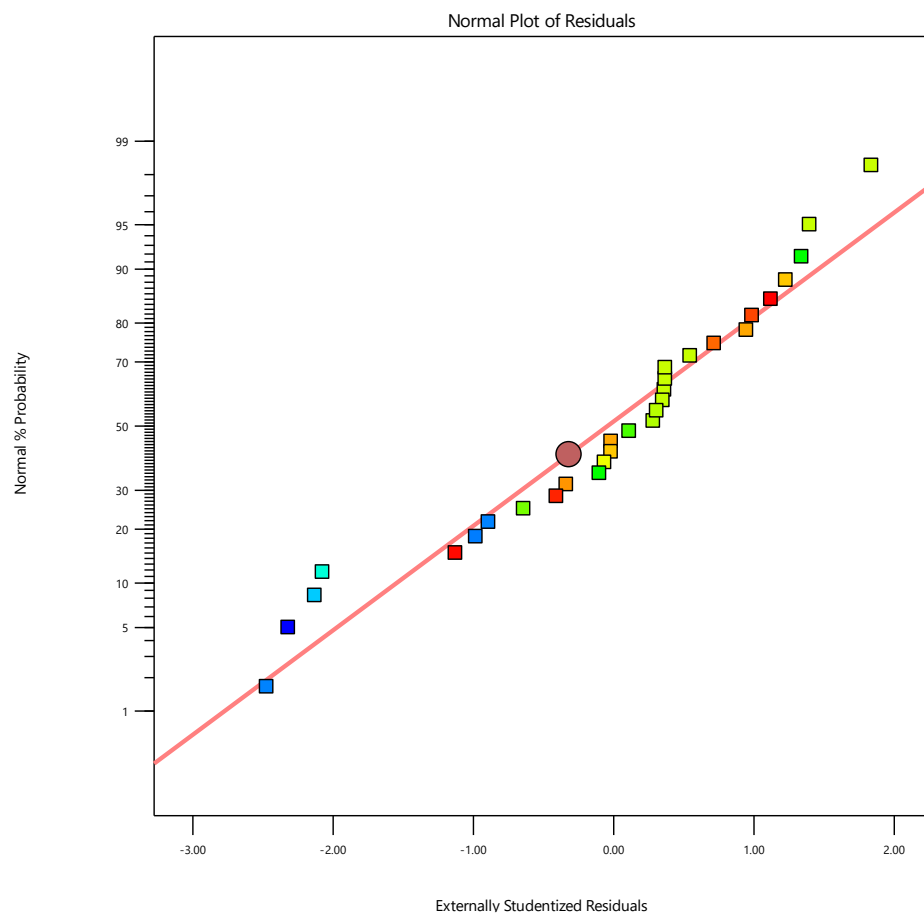


Figure 5.6 : Normal plot of residual for CMP degradation

Color points by value of
BP degradation:
34.2 94.2

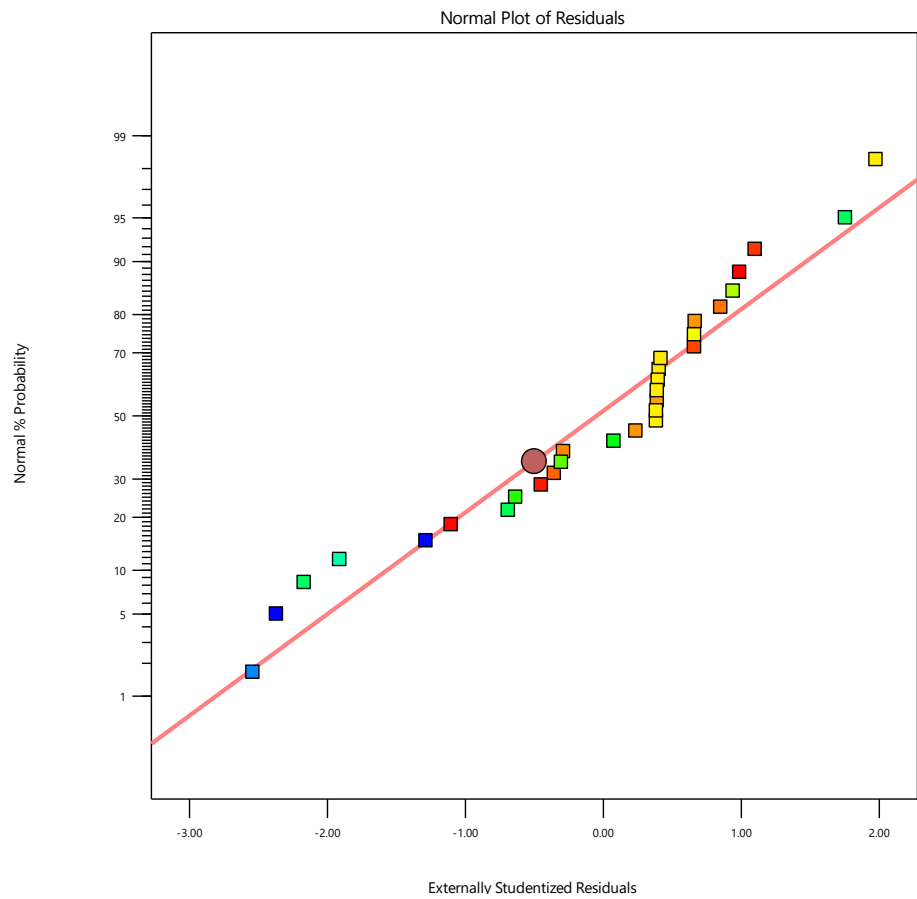


Figure 5.7: Normal plot of residual for BP degradation

Color points by value of
2,4-D degradation:
20.7 92.4

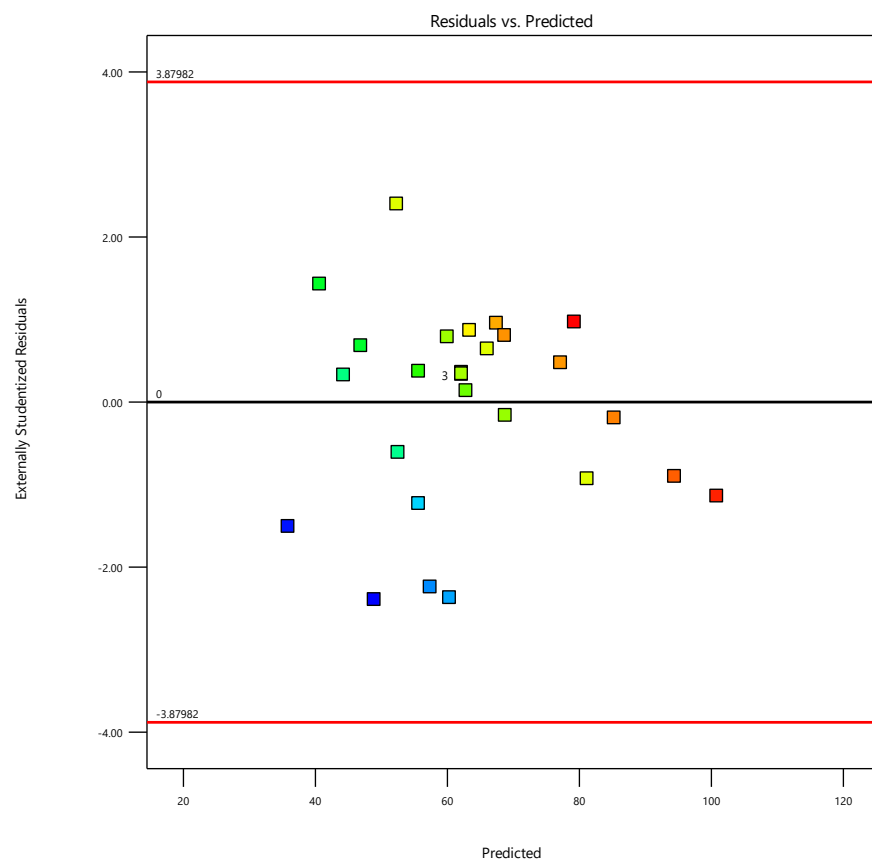


Figure 5.8 : Externally studentized residual versus predict plot for 2,4-D degradation

Color points by value of
CMP degradation:
32.1 94.7

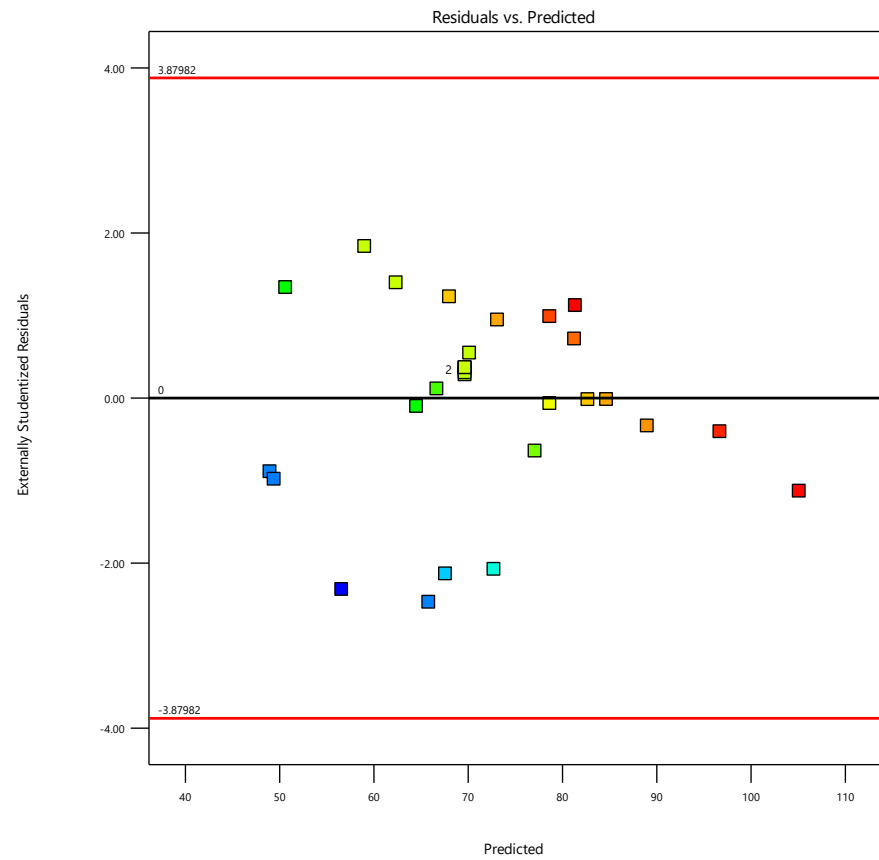


Figure 5.9 : Externally studentized residual versus predict plot for CMP degradation

Color points by value of
BP degradation:
34.2 94.2

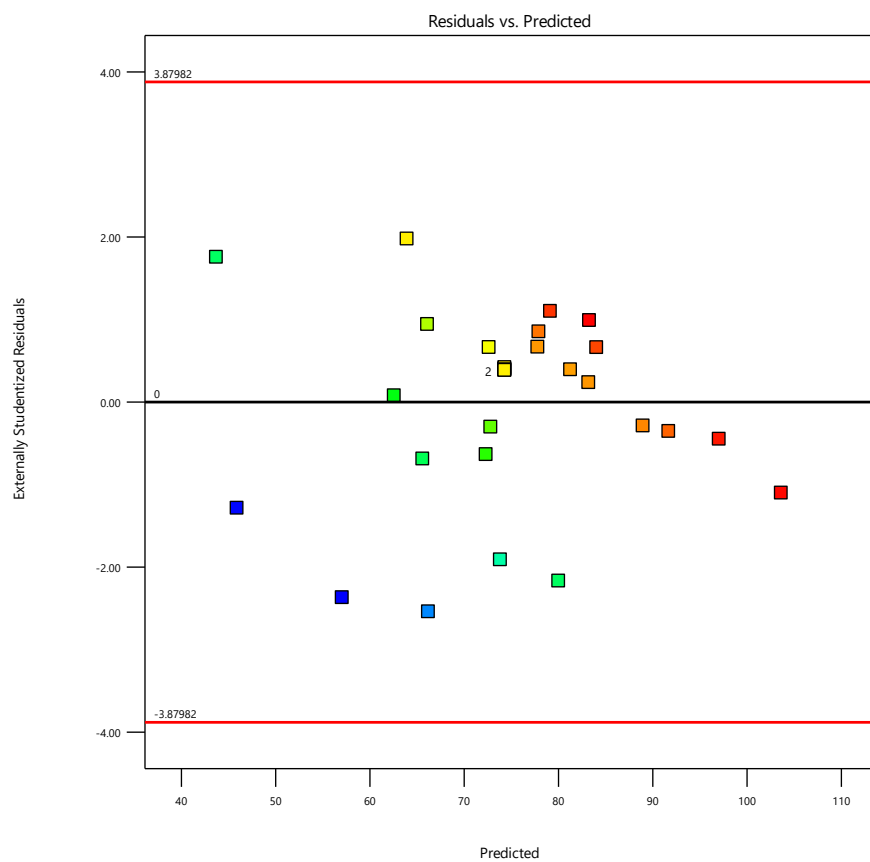


Figure 5.10 : Externally studentized residual versus predict plot for BP degradation

Factor Coding: Actual

Design Points:

● Above Surface
○ Below Surface
20.7 92.4

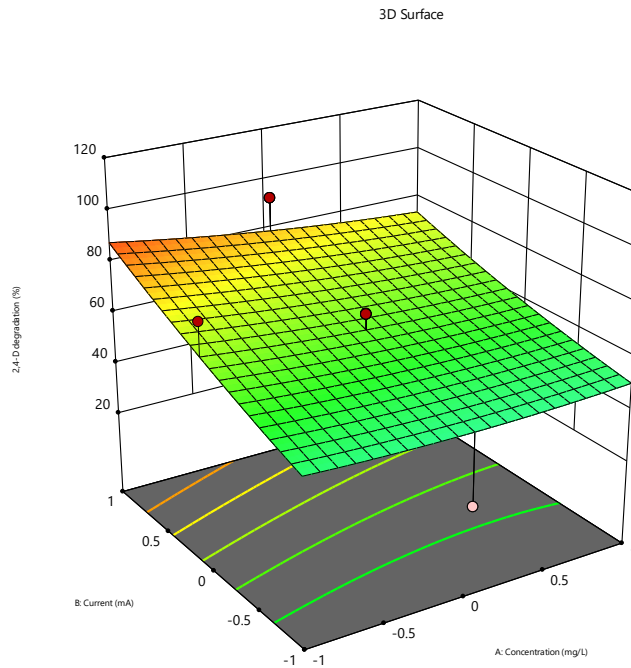
X1 = A

X2 = B

Actual Factors

C = 0

D = 0



Factor Coding: Actual

Design Points:

● Above Surface
○ Below Surface
20.7 92.4

X1 = B

X2 = C

Actual Factors

A = 0

D = 0

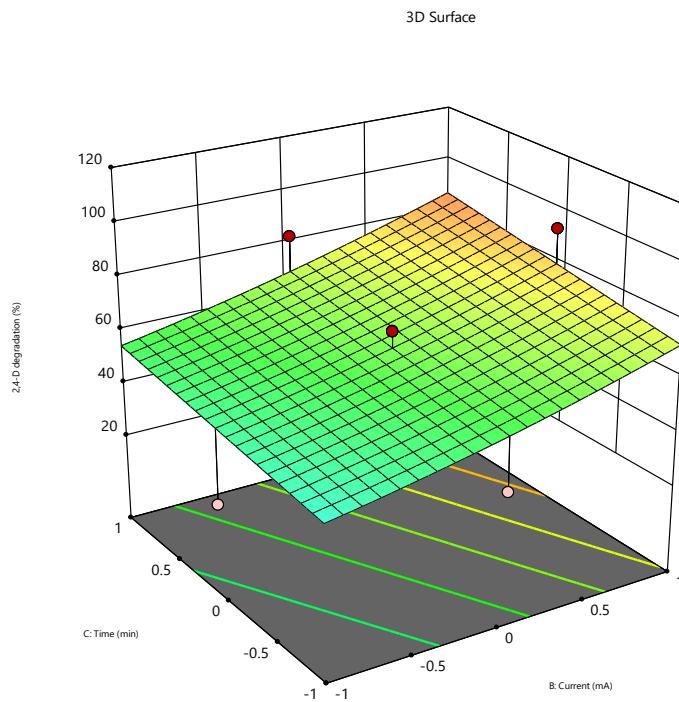


Figure 5.11: Effect of (a) applied current vs Concentration (b) Time vs Current on 2,4-D degradation

Factor Coding: Actual

Design Points:

● Above Surface

○ Below Surface

32.1 94.7

X1 = A

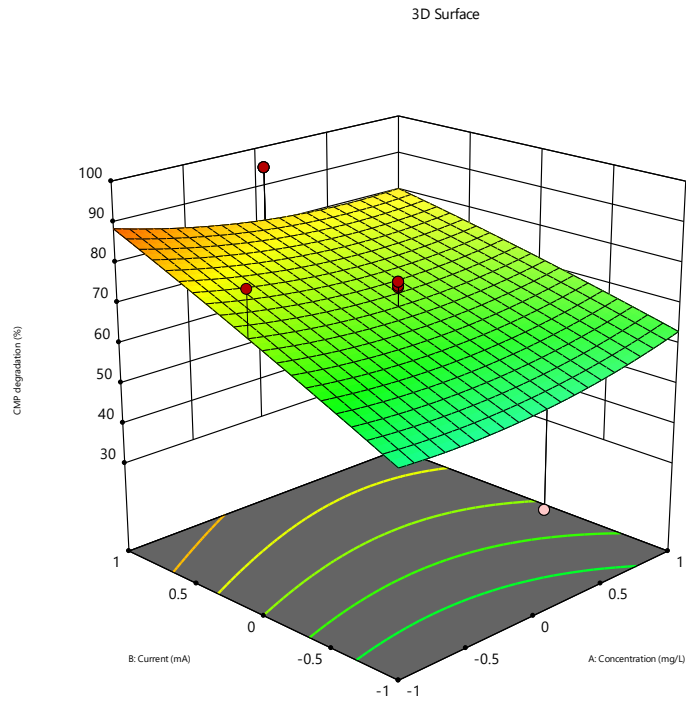
X2 = B

Actual Factors

C = 0

D = 0

a)



Factor Coding: Actual

Design Points:

● Above Surface

○ Below Surface

20.7 92.4

X1 = C

X2 = D

Actual Factors

A = 0

B = 0

b)

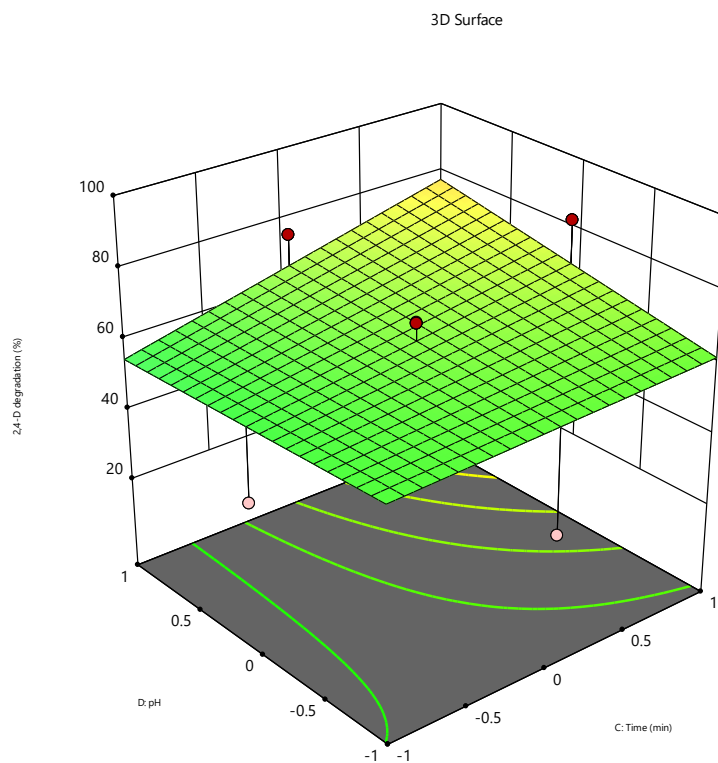


Figure 5.12 : Effect of (a) applied current vs Concentration (b) Time vs Current on CMP degradation

Factor Coding: Actual
Design Points:

● Above Surface

○ Below Surface

34.2 94.2

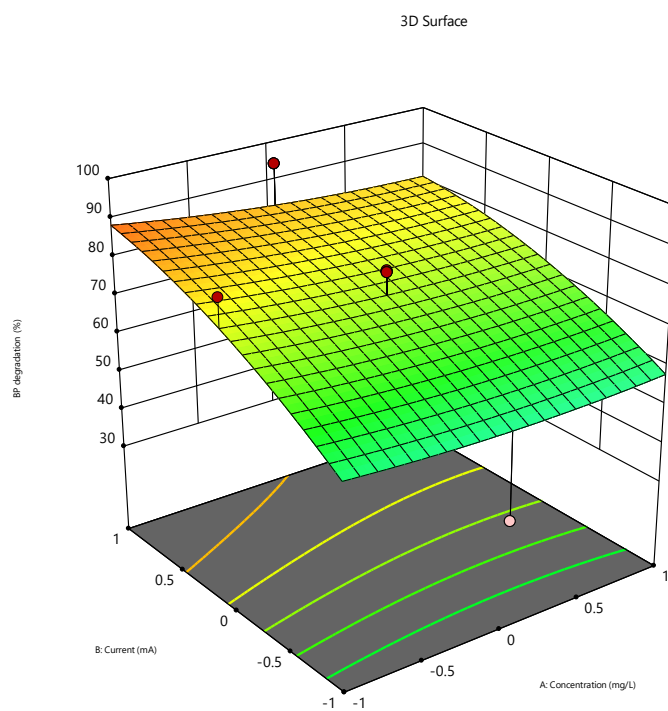
X1 = A

X2 = B

Actual Factors

C = 0

D = 0



Factor Coding: Actual
Design Points:

● Above Surface

○ Below Surface

34.2 94.2

X1 = C

X2 = D

Actual Factors

A = 0

B = 0

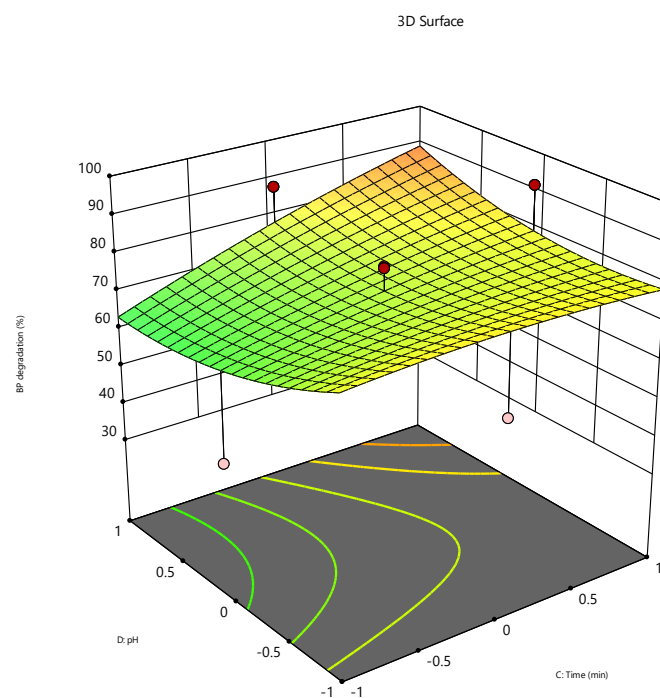


Figure 5.13 : Effect of (a) applied current vs Concentration (b) Time vs Current on BP degradation

5.3.3 Kinetic Study

The degradation kinetics for each of the organic halides was studied at the optimum conditions to better understand the underlying degradation mechanism. Figure 5.14 shows the trend in concentration decrease for each of the compounds with reaction time. As illustrated, an exponential decrease of the initial concentration of the compounds was observed that demonstrate a degradation by $\cdot\text{OH}$ radicals generated on the electrode surface[108]. Furthermore, the presented kinetic profiles for each compound were found to be consistent with previous literature that report $\cdot\text{OH}$ radicals mediated degradation for these organic halides[109,110].

The experimental kinetic data were modelled using the pseudo-first-order kinetic model provided in equation 5.7. The model application was based on the following assumptions as highlighted in the published literature: (1) The degradation of the organic halides occurs at the electrode surface and is solely caused by the produced $\cdot\text{OH}$ radicals. (2) The mass transport of the organic halides from the bulk solution to the electrode surface was rapid, and their adsorption onto the active sites of the electrode surface aided the reaction.

Pseudo First Order Kinetic Model

$$\frac{d[C]}{dt} = -k_1 [C] \quad (5.6)$$

By integrating the expression and applying the initial conditions, at $t = 0$, $[C] = [C_0]$. The final expression is given as follows;

$$[C_t] = [C_0] e^{-k_1 t} \quad (5.7)$$

Where C_0 - is the initial concentration of the organic halides, C_t - is the sampled concentration at time- t , and k_1 - is the apparent or observed pseudo first-order rate constant.

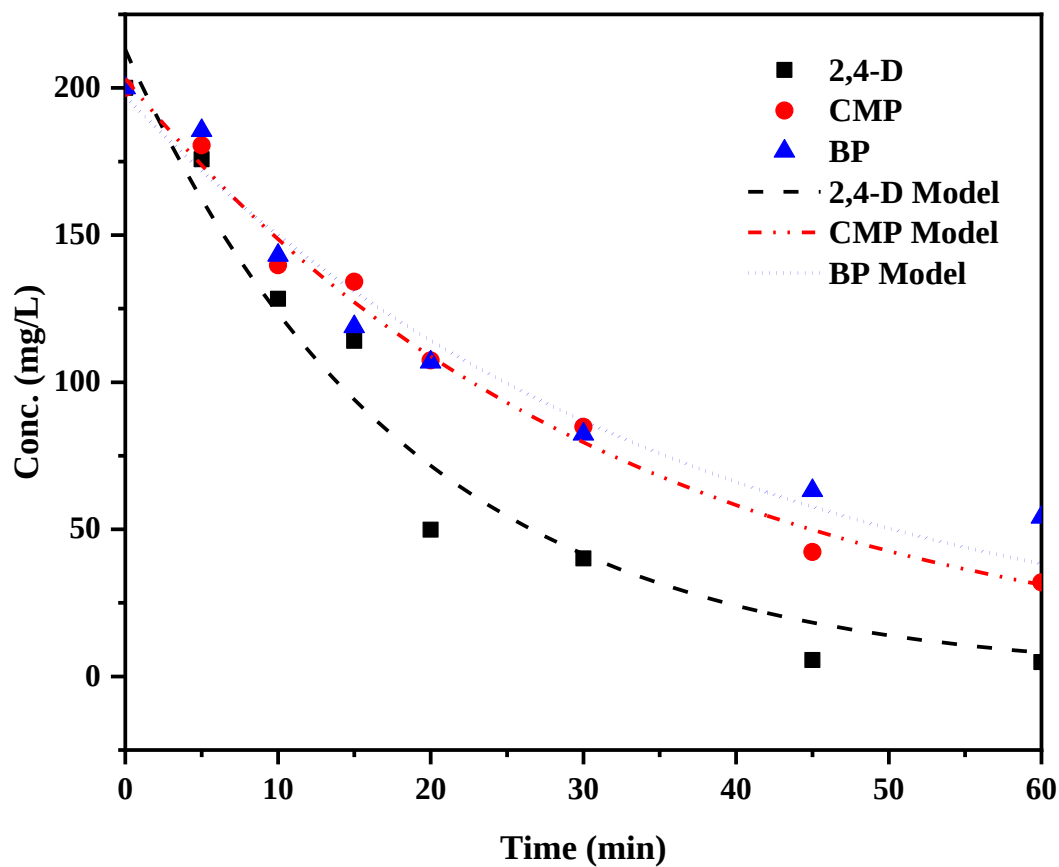


Figure 5.14 : Degradation kinetics of the organic halides (Experimental condition: 200 mg/L concentration of the organic halides, applied current- 500 mA, pH- as prepared solution)

The kinetic data were fitted to the equation using the non-linear regression method (Fig. 5.14) and from the fitted curves, the kinetic parameters were estimated as shown in Table 5.6. As presented, a good correlation between the experimental and model-fitted values was observed, indicating that the degradation process is of first-order nature. Furthermore, the high R^2 values (> 0.96) and adjusted R^2 (0.95) obtained for the fitted curves provide additional validation to the strong correlation between the data.

According to the calculated apparent rate constants (Table 5.6), the rate of the organic halides degradation was found to be in the following order: 2,4-D (0.054 s^{-1}) $<$ CMP (0.031 s^{-1}) $<$ BP (0.027 s^{-1}) which was also consistent with the anodic current response displayed by each of the organic halides during the CV scans. Out of the three organic halides, 2,4-D showed the highest degradation rate that implies its rapid conversion to intermediates/product compounds by the generated $\cdot\text{OH}$ radicals. More so, the moderate degradation rate displayed by CMP and BP also supports their significant conversion to intermediates/products compounds.

Table 5.6: Kinetics Parameters

Component	Pseudo first order rate constant (s^{-1})	Fit Parameters	
		R^2	Adj. R^2
2,4-D	0.054 ± 0.0067	0.9644	0.9584
CMP	0.031 ± 0.0018	0.9895	0.9877
BP	0.027 ± 0.0027	0.9638	0.9577

5.3.4 Degradation Mechanism

Given the significant degradation achieved for each of the organic halides as revealed by the HPLC analyses results, the samples were further subjected to mass spectroscopy (MS) analysis to precisely identify the formed intermediates/products of the reactions. Based on the identified products from the MS analysis, the pathway for the degradation of the organic halides was proposed. Figures 5.15-5.17 show the acquired MS spectra for each of the compounds (2,4-D, CMP, and BP) after the degradation experiments and the proposed degradation pathway. The mass spectrum of 2,4-D (Fig. 5.15) shows the presence of acetic acid (m/z - 60), glycolic acid (m/z -77.1) and benzoquinone (m/z -110) as the main products together with other organic fragments (m/z : 91, 97, 181.2). As for CMP, its mass spectrum (Fig. 5.16) shows the formation of acetic acid (m/z - 59.1), glycolic acid (m/z -74.2), hydroquinone (m/z -114.2) , and methylbenzene-1,4-diol (m/z - 129.2) as the degradation products. Similarly, BP mass spectrum shows the formation of acetic acid (m/z - 60), glycolic acid (m/z -77), hydroxyquinone (m/z - 124.2) and hydroquinone (m/z - 110) as the main products together with other organic constituents (m/z : 84, 96.8, 195, 205, 221, 283, 229.5).

Based on the presented results, the pathway of the organic halides degradation is likened to involve dehalogenation reaction, hydroxylation reaction, and the decomposition of the C=C bonds of the aromatic rings of the compounds all mediated by the generated $\cdot\text{OH}$ radicals. 2,4-D was broken down to glycolic acid (m/z - 77) and dichlorophenol intermediate (not detected) by hydroxylation from $\cdot\text{OH}$ radical attack. Subsequently, the chlorine atoms were cleaved from the produced intermediate compounds to afford the formation of quinones. The formed quinone undergoes further oxidation that cleaved its C-C bond and opened its aromatic ring structure

finally resulting in the formation of acetic acid (m/z - 60). CMP was dechlorinated by hydroxylation from *OH attack to form benzene derivatives which were further oxidized to yield aromatic by-product quinones. The C-C bonds of the generated quinones were further cleaved through ring-opening by *OH attack to afford low molecular weight carboxylic acids that include acetic acid and glycolic acid. In the case of bromophenol, an oxidative hydroxylation of the aromatic group by *OH radicals led to its debromination and the formation of quinones by-products. Further oxidation of the quinones by *OH attack led to the aromatic C-C bond breaking the formation of oxalic acid which also undergoes further oxidation to form the relatively stable acetic acid and glycolic acid.

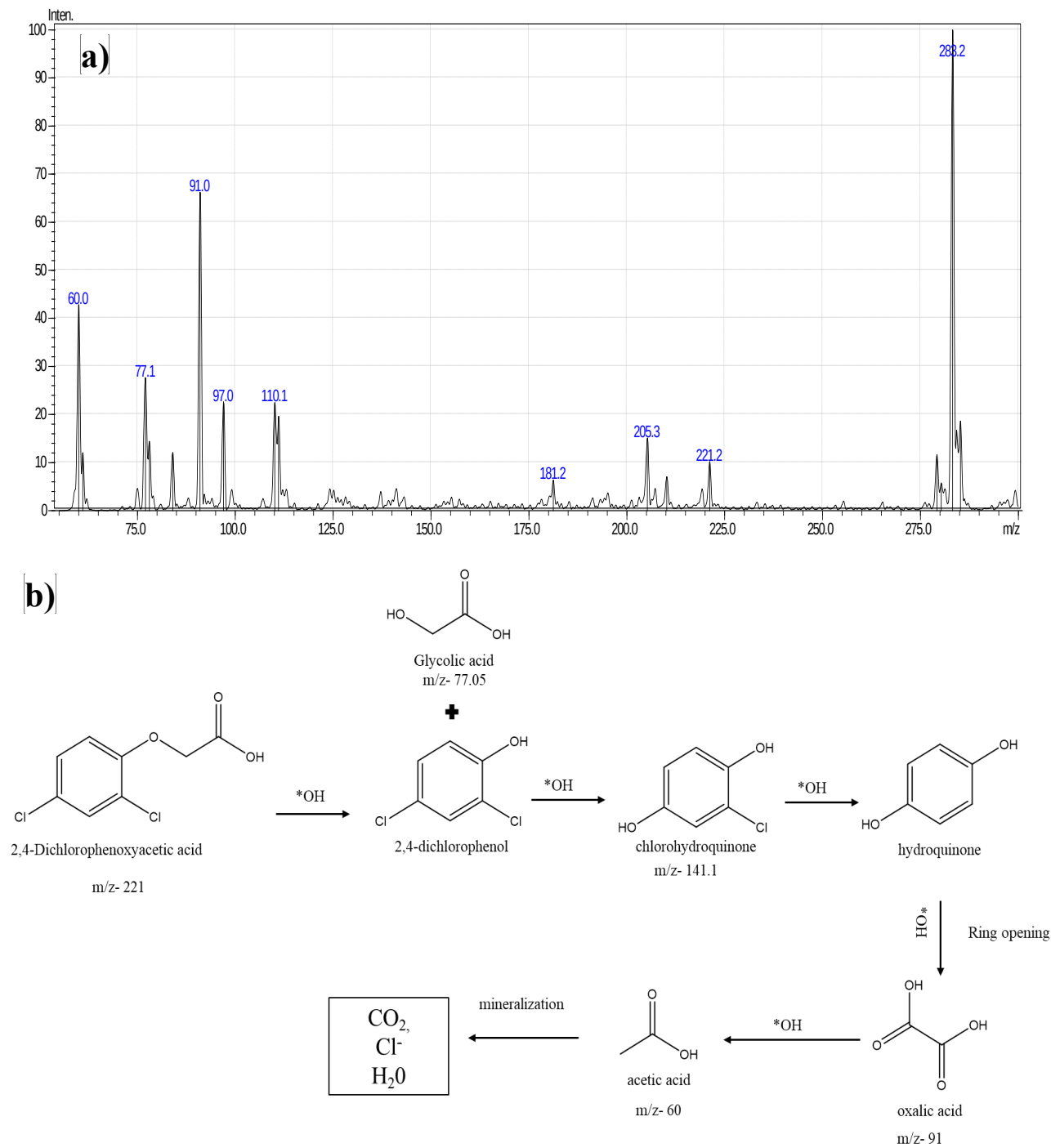


Figure 5.15: (a) Mass Spectra of 2,4-D after degradation and (b) the proposed degradation scheme

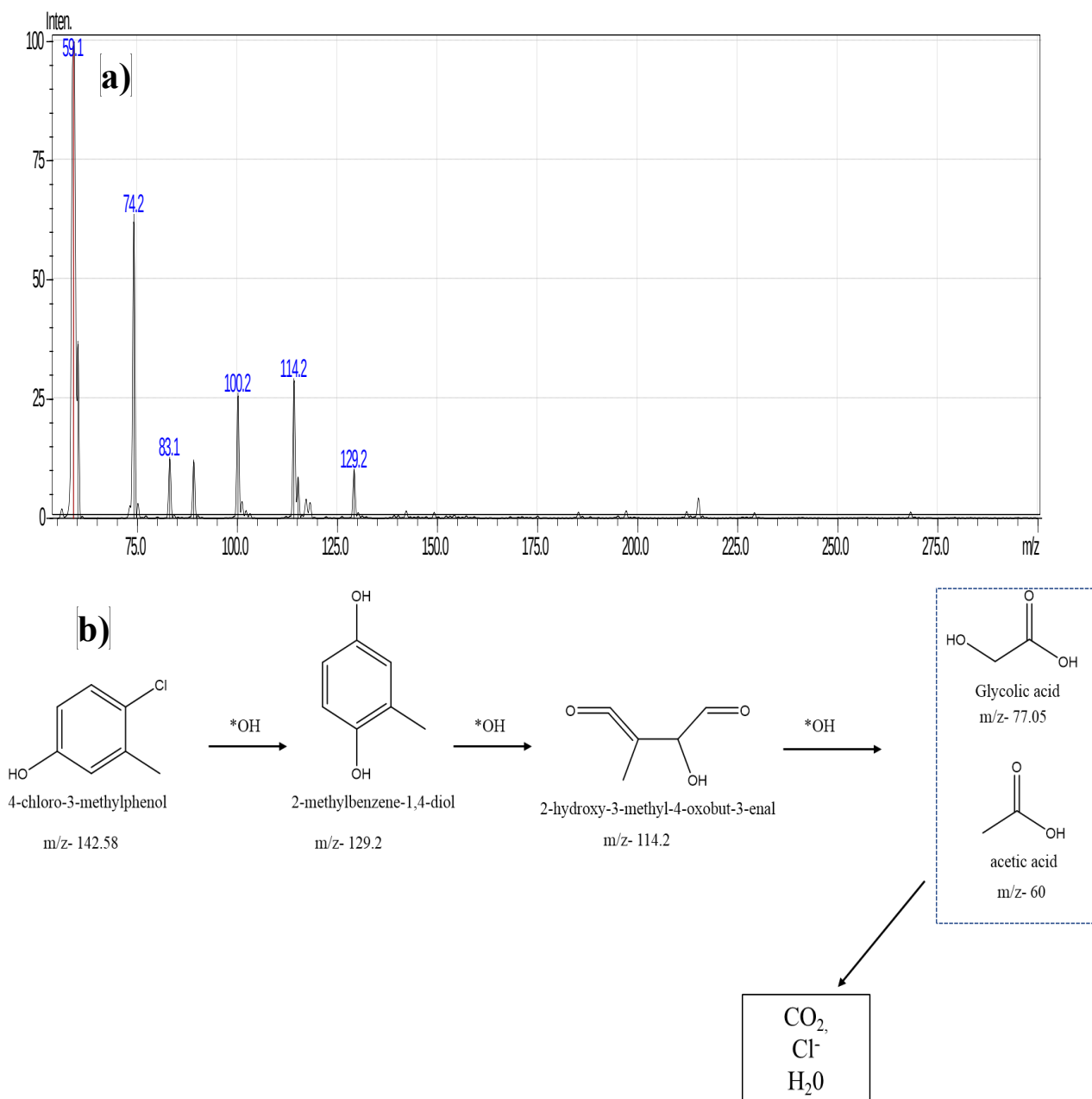


Figure 5.16: (a) Mass Spectra of CMP after degradation and (b) the proposed degradation scheme

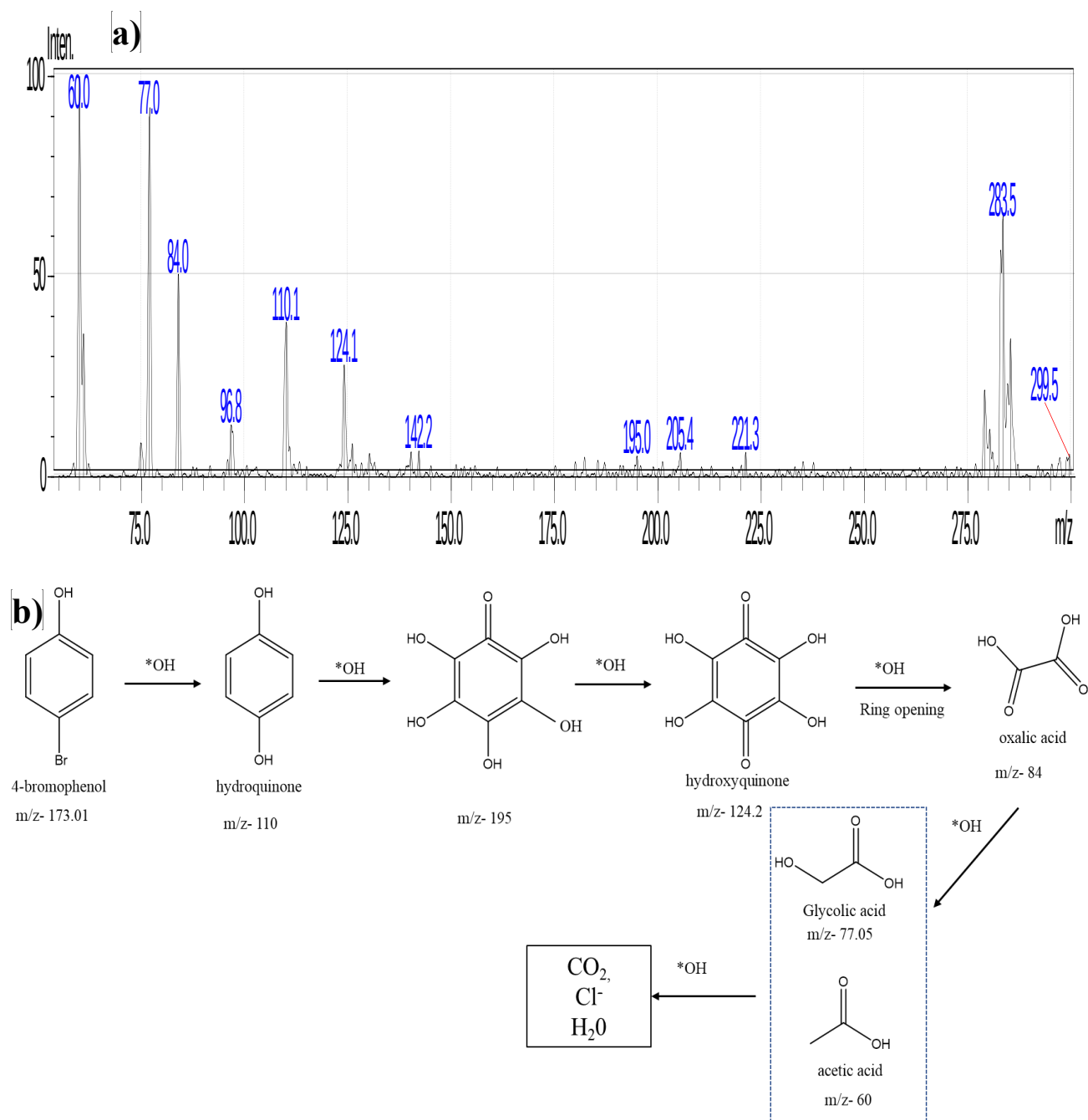


Figure 5.17: (a) Mass Spectra of BP after degradation and (b) the proposed degradation scheme

5.3.5 Electrode Stability

The long-term stability of the Bi-Cu-GF electrode was examined through chronoamperometry study with an applied potential of 50 mV (Ag/AgCl) for 18000 sec (5 hours) as shown in Figure 5.16. The chronoamperometry study was carried out using a mixed solution of organic halides as a substrate. The analysis results showed that the Bi-Cu-GF electrocatalyst underwent a significant current decay at the onset of the analysis and thereafter a steady-state current condition was reached. The rapid decrease in current consumption with time was associated with the complete oxidation of organic halides in the solution. Moreover, the electrode performance was not significantly affected due to its use for this analysis, suggesting it enhanced stability.

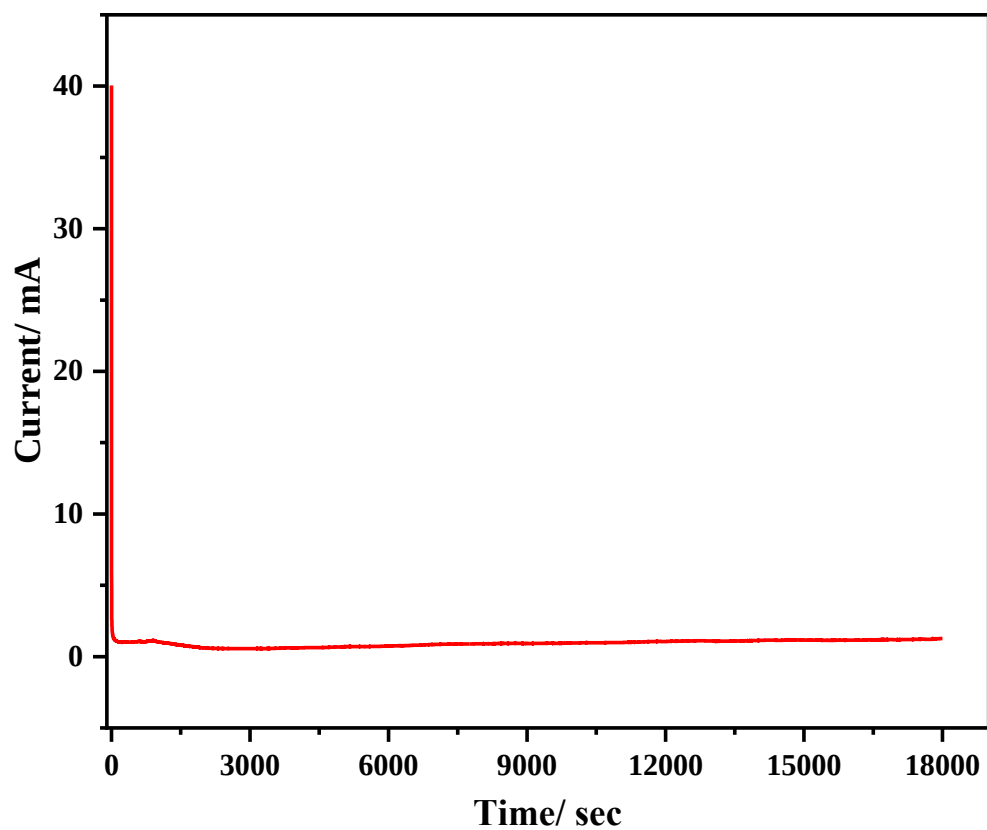


Figure 5.18: Chronoamperometry study of the Bi-Cu-GF electrode

5.4 Summary

In summary, a bimetallic Bi-Cu electrocatalyst grown on the surface of graphite felt support was successfully synthesized by a facile co-electrodeposition approach. The prepared electrode showed excellent electrocatalytic activity towards the degradation of the three selected halogenated aromatic organics (2,4-D, CMP and BP). The electrode enhanced performance was attributed to the synergistic role of its bimetallic Bi-Cu composition. The performance of the electrode towards the degradation of organic halides was investigated using a central composite experimental design and through this, the effect of the operational factors was examined. It was noted that all the operational factors (Concentration, applied current, reaction time and pH) had a significant impact on the degradation efficiency of each of the organic halides. Based on mass spectroscopy analysis, the mechanism of organic halide degradation was proposed to involve a sequence of dehalogenation reactions, hydroxylation reactions, and the decomposition of the aromatic rings' C=C bonds mediated by $\cdot\text{OH}$ radical attack.

CHAPTER 6

Bimetallic Co-Ag-MOF Catalyzed Electroreduction of halobenzene in the aqueous phase and the formation of biaryls via Suzuki coupling

Abstract

In this study, a new cathodic promoted Suzuki coupling for the synthesis of biaryls using cobalt-silver-based MOF as an electrocatalyst has been demonstrated. The MOF catalyst prepared by a solvothermal approach and grown in situ on a copper foam support showed a fused ball-like morphological structure with a hybrid Co-Ag crystalline particle. The electrocatalyst exhibited superior performance in catalyzing the reductive coupling of the three aryl halides (chlorobenzene (1a), bromobenzene (1b), and iodobenzene (1c)) with phenylboronic acid in an aqueous medium. The coupling reactions were highly influenced by the presence of a base, as lower coupled-product yields (biphenyl) were noted at neutral pH conditions compared to the basic condition. In a basic reaction medium, aryl halide conversion efficiency of 98%, 90%, and 70% was achieved for (1a), (1b), and (1c), with corresponding biphenyl yields of 90%, 80%, and 60%, respectively. In addition, the proposed reductive Suzuki coupling approach was able to tolerate a variety of functional aryl boronic acids, transforming them to their respective biaryls products. The cobalt-silver-based MOF exhibited significant stability and recycle potential through its insignificant decrease in reactivity even after ten cycles of repetitive use.

6.1 Introduction

The application of electricity for the selective synthesis of valuable chemical products has gained wide attention in the past decade. This synthesis approach termed electrochemical synthesis or as short electrosynthesis has offered a versatile and sustainable protocol for producing myriads of organic compounds[111,112]. Electrosynthesis utilizes only electrical current to initiate the required oxidation/reduction reactions for the chemo-selective transformation of a substrate(s) to products or intermediates[113]. When compared to the conventional chemical synthesis method that requires a stoichiometric amount of the oxidant/reductant, this approach presents a remarkable advantage in terms of both economic and environmental implications [114,115]. Furthermore, electrosynthesis also benefits from operating at mild reaction conditions, and can be easily scaled, and does not present uncontrollable reaction conditions typical of the conventional chemical synthesis route because it can be stopped immediately [115].

In recent years, biaryl units have emerged as an important structural component in synthetic organic chemistry due to their wide use in pharmaceuticals and agro-industrial fields[116]. The transformative C-C cross-coupling reactions, notably the Suzuki-Miyaura and Negishi reactions have provided a convenient approach for the synthesis of these organic moieties. Typically, these reactions proceed via the interaction of leaving groups with an organometallic partner in the presence of palladium (Pd) complexes or Pd salts as catalysts [117]. The advent of highly efficient homogenous Pd complex catalysts with electron-rich ligands has revolutionized the versatility of these reactions in the synthesis of various biaryl compounds. Studies have shown that Pd complexed with bulky ligands such as biaryl phosphine and carbapalladacycles tend to offer enhanced catalytic activities compared to Pd salts or metallic counterparts in promoting cross-

coupling reaction [118–120]. It was noted that the high catalytic activities exhibited by these Pd complexes were due to the electron-rich active sites of the attached ligands that facilitate their interaction with the substrates in solution.

Despite the numerous advantages homogeneous Pd complexes catalysts provide in facilitating cross-coupling reactions, their widespread application is limited by their high cost and potential toxicity [121]. More so, their application in a continuous flow condition presents a major challenge considering the difficulty in separating the catalysts from the reaction medium, and their likelihood of contaminating the reaction products. Consequently, intensive research effort has been devoted towards developing heterogeneous Pd catalysts or exploring other alternative low-cost, eco-friendly approaches to achieving C-C cross-coupling reactions. In the case of heterogeneous catalysts, studies have demonstrated that the well-known homogeneous catalysts may be heterogenized by attaching them to a porous material or organic polymers. [122–125]. Despite their apparent benefits over homogeneous Pd complexes, heterogeneous Pd catalysts have been found to have stability issues as a result of their decomposition to Pd metallic components after several cycles of use.[117] The catalyst breakdown is said to be caused by chemical stress produced during its mechanistic cycle (redox conversion of the metallic component). Although the produced Pd metallic catalysts could still induce C-C cross-coupling reactions, their intrinsic catalytic activity was found to be much lower than that of the complexed metallic catalysts.[117,126,127].

Recently, electrochemically mediated cross-coupling reaction has attracted much attention as a versatile approach for biaryls synthesis. This approach can circumvent some of the major limitations encountered in both the homogenous and heterogenous catalysis-driven C-C cross-coupling reaction. Electrochemical C-C bond formation via anodic or cathodic mediated cross-

coupling reactions provides a straightforward means for the preparation of various biaryls units as it utilizes only electrons as the active reagent. In addition, the use of transition metal catalyst as a catalytic electrode for this approach can aid in the in-situ formation of metallic ions with a favourable oxidation state (zero valent) at the electrode surface. These metal ions coupled with the formation of redox mediators either in the solution or at the electrode surface can promote the construction of diverse types of C-C bonds.

Meanwhile, metal-organic frameworks (MOFs) have emerged in recent years as a promising material for heterogenous catalysis-driven reactions, which is inclusive of cross-coupling reactions [128]. MOFs are a new class of highly porous crystalline material made of metal ions or metal ions cluster anchored to an organic functional group (linker) via a coordination bond. MOF metal ions have an exchangeable coordination position due to their unique coordination bond, which allows them to function as Lewis' acid or redox sites in catalytic reactions.[117,129,130]. Furthermore, MOFs' enormous surface area, high metal content, and electron-rich functional groups (carboxyl groups) have been discovered to be beneficial in promoting cross-coupling reactions. The electron-rich functional group of MOFs can facilitate their interaction with the substrate while promoting the redox conversion of the metallic species (from a +2 oxidation state to 0) in a similar fashion to the organic ligands in transition metal complex catalyst [131]. There are precedents in the literature that show several successful attempts at preparing Pd-based MOFs [131,132] or anchoring Pd onto other metallic MOFs [133,134] and exploring their uses as a catalyst/electrocatalyst for promoting the Suzuki-Miyaura cross-coupling reaction. However, since Pd is an expensive noble metal, it will be important and economically attractive to explore other affordable transition metals-based MOFs for the Suzuki-Miyaura cross-coupling reaction.

In this study, we present a new bimetallic cobalt-silver-based MOF as an active electrocatalyst for promoting Suzuki-Miyaura cross-coupling of aryl halides with phenylboronic acids in an aqueous medium. The goal of this study is to leverage the intrinsic catalytic activity of cobalt-silver MOF (high metal contents and active sites) with applied electricity to develop an efficient protocol for the synthesis of biaryl compounds.

6.2 Experimental

6.2.1 Materials

Aryl halides (Chlorobenzene-1a, Bromobenzene-1b, Iodobenzene-1c), boronic acids (phenylboronic acid-2a, 4-hydroxyl phenylboronic acid-2b, 4-acetyl phenylboronic acid-2c, 4-methoxy phenylboronic acid-2d, 4-cyano phenylboronic acid-2e, carboxylphenylboronic acid-2f), Cobalt (II) hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Silver nitrate (AgNO_3), 1,3,5-Benzenetricarboxylic acid-BTC ($\text{C}_9\text{H}_6\text{O}_6$), Dimethylformamide (DMF), Methanol, Ethanol, and Pentane were purchased from Sigma Aldrich (USA). Copper foam (2 x 3 cm) used as the catalyst support was supplied by Henan Zion New Material Co. (China). All the chemical reagents were used as received without further purification.

6.2.2 Synthesis of Bimetallic Co-Ag-MOF and Co-MOF

In this study, bimetallic Cobalt-Silver MOF was synthesized by the one-pot hydrothermal procedure that allows for its direct deposition on copper foam support. Briefly, Solution A containing a 30 mL mixture of 917 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 928 mg of AgNO_3 was prepared in a beaker. While in a separate beaker, 324 mg of $\text{C}_9\text{H}_6\text{O}_6$ was dispersed in a 30 mL solution of

ethanol and DMF (a ratio of 1:1) to make solution B. Afterwards, solutions A and B were mixed in a separate beaker and ultrasonicated for 10 minutes to ensure the complete dissolution of the solids. The resulting, pink-colored mixture was transferred into a 100 mL Teflon-sealed autoclave. A piece of copper foam pretreated in a 0.5 M solution of HCl to remove its oxide layer was added to the solution in the autoclave. The autoclave was sealed, kept in an oven, and heated at 160 °C for 24 hours. After cooling, the resulting Co-Ag-BTC solid and Co-Ag-MOF coated copper foam were collected and washed thoroughly with DMF and methanol. Next, the samples were dried in an oven at 60 °C for 24 hours to obtain the final products. While employing the same preparation procedure, Co-MOF coated copper foam was prepared without adding AgNO₃ to ascertain the influence of Ag addition on the MOFs' catalytic properties.

6.2.3 Prepared Electrocatalyst Characterization

The surface morphological feature of the prepared Co-Ag-MOF catalyst was examined through the field emission transmission electron microscopy (FESEM, QuattroS, ThermoScientific, USA) coupled with Energy-dispersive X-ray spectroscopy (EDS) analysis. The phase composition and crystalline structure were analyzed via X-ray diffraction spectroscopy (XRD). The XRD spectra were collected using Benchtop Bruker D2 Phaser Diffractometer (USA) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The chemical composition and structure of the MOF catalyst were analyzed using Raman spectroscopy. The Raman spectra were collected with a LabRAM HR Evolution Raman spectrometer (HORIBA, Japan) that was equipped with a HeNe Laser at a wavelength of 634nm. Furthermore, to verify the chemical state of each of the elements in the synthesized MOF, X-ray Photoelectron spectroscopy (XPS) analysis was conducted. The X-ray photoelectron spectra were taken at high vacuum using a monochromatic Al K (1486.6 eV) X-ray source with

the Thermoscientific Escalab 250Xi spectrometer instrument. The specific surface area and pore size distribution were characterized by a surface area analyzer with Micrometric ASAP 2020 PLUS (UK). The specific surface area was determined based on the multipoint BET (Brunauer-Emmett-Teller) method.

Electrochemical characterization of the prepared electrodes by Cyclic Voltammetry (CV) measurements was carried out to understand the electrode's electrochemical activity. An undivided electrolytic cell equipped with a three-electrode system that consists of a MOFs catalyst as the working electrode, platinum mesh as the counter electrode, and Ag/AgCl as the reference electrode was utilized. A prepared solution of 0.5 M Na₂SO₄ was used as the supporting electrolyte and 10mM equimolar concentrations of 1a and 2b were used as the substrates. The CV measurements were recorded using a CHI 760E Potentiostat in the presence and absence (only electrolyte) of the substrates.

6.2.4 General Procedure for Electrochemical Suzuki Coupling Reaction

A divided electrochemical flow cell purchased from ElectroCell™ (USA) was utilized for this electrochemical synthesis. The flow cell has an anode and cathode chamber each with an active electrode area of 10 cm², which are separated by a proton exchange membrane (Nafion 324). The schematic diagram of the reaction setup with an included photograph is shown in Figure 6.1. As depicted, the cathode electrode was made of the prepared Co-Ag-MOF copper foam electrode bonded to a copper plate with the aid of double-sided carbon tape, and the anode electrode was a stainless-steel plate. In a similar classical Suzuki coupling approach, the aryl halides (1a, 1b, 1c) were used as the substrates and the boronic acids (2a, 2b, 2c, 2d, 2e) were chosen as the coupling partner for this electrochemical synthesis. A 500 mL volume of 50 mM Na₂SO₄ solution was

prepared as the supporting electrolyte and was purged with nitrogen for a duration of 30 min. In a 250 mL volume of this solution, an appropriate amount of aryl halides and boronic acids were dissolved via ultrasonication for 30 minutes to give a resulting concentration of 10mM for each of the reagents. Due to the low solubility of iodobenzene (1c), an appropriate amount of methanol was used for its dissolution. This resulting mixture was used as the catholyte for the reaction, while the anolyte was the remaining 250 mL volume of electrolyte. Preparative electrolysis experiments were carried out under galvanostatic conditions (constant current) with a Kenwood DC power supply and the current was monitored with a Fluke Multimeter. All experiments were carried out in triplicates and at room temperature (25°C).

During the experiments, both the catholyte and anolyte solutions were continuously recycled, and a 20 mL aliquot sample was collected from the catholyte at a specific time interval for analysis. The collected samples were divided into two portions to identify the product formation. The first portion was extracted with Pentane and analyzed by Gas Chromatography Mass Spectroscopy (GC-MS, Shimadzu Japan) analysis, while the second portion was filtered and subjected to High Performance Liquid Chromatography (HPLC, Shimadzu Japan) analysis. It should be noted that the GC-MS analysis was used to qualitatively verify the formation of the reaction intermediates and products (Biphenyl, Benzene, and Phenol), and the HPLC analysis was employed for their quantification.

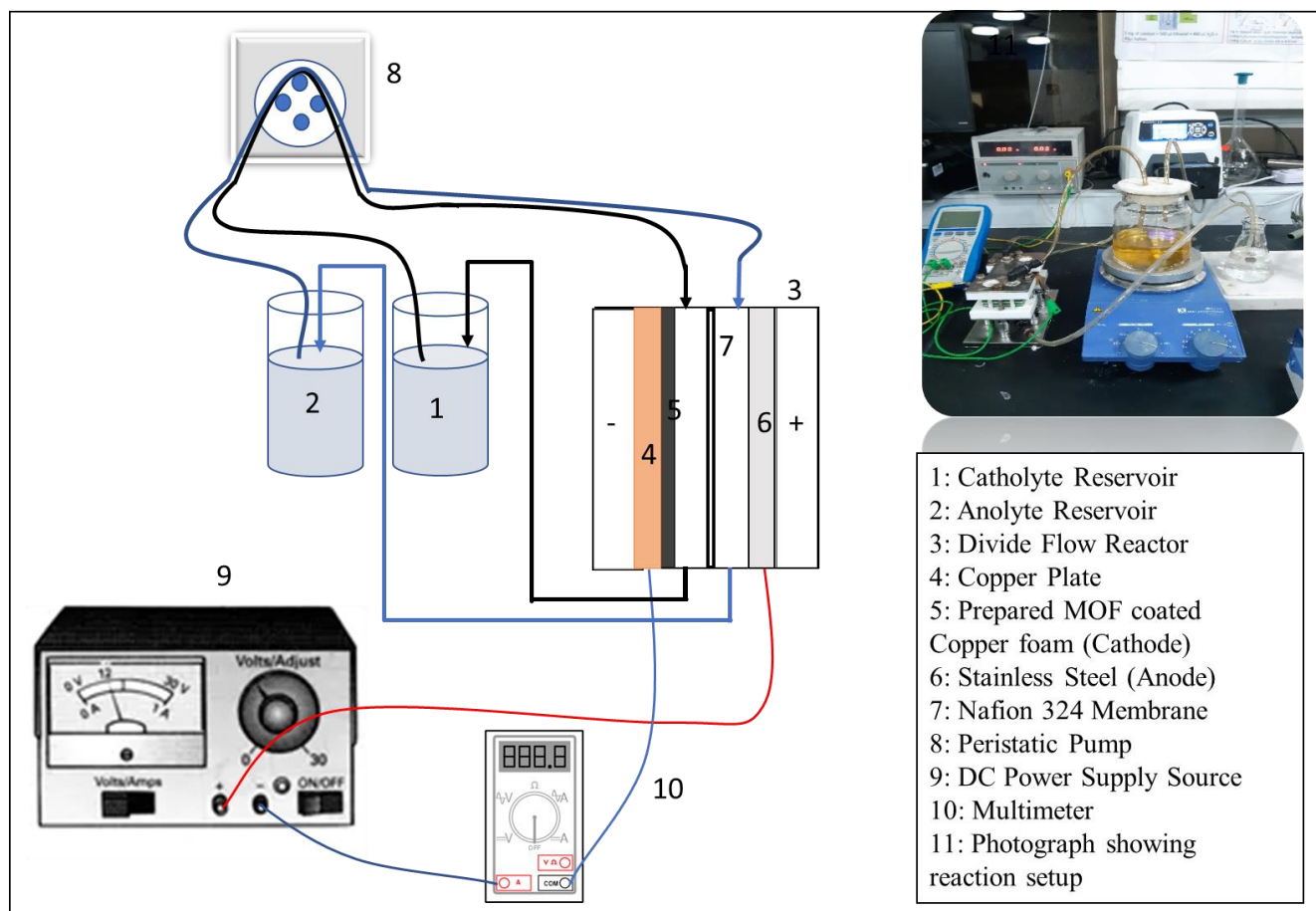


Figure 6.1 : Schematic diagram of the reaction setup.

The GC-MS analysis was carried out at the following temperatures: 180°C, 220°C, and 200°C for the GC injection port, GC-MS interface, and ion source, respectively. The temperature of the GC column oven was increased at a rate of 10 °C/min from the starting temperature to 180 °C, which was maintained for 4 minutes, and then increased at a rate of 3 °C/min to 231 °C. The qualitative analysis was carried out in scan mode with a 1:10 split ratio. The following conditions were used to conduct the HPLC analysis: 15 mM ammonium formate (A) and acetonitrile (B) were used in the mobile phase, which was administered at a flow rate of 0.5 mL/min. The gradient program used was 0 min 30% B, 0–15 min 90% B, 15–20 min 30% B, 20–25 min 30% B, with a 20- μ L injection volume.

All the experiments were carried out in triplicates and the conversion of the aryl halides, selectivity of the reaction, and yield of the formed products were determined through the following expression:

$$\text{Conversion (\%)} = \frac{C_0 - C_t}{C_t} * 100 \% \quad (6.1)$$

$$\text{Selectivity (\%)} = \frac{C_p}{C_0 - C_t} * 100 \% \quad (6.2)$$

$$\text{Yield (\%)} = (\text{Conversion(\%)} * \text{Selectivity (\%)}) * 100 \% \quad (6.3)$$

Where C_0 (mM/L) is the initial concentration of the starting substrates, and C_t (mM/L) is the residual concentration of the substrates at a certain time. C_p (mM/L) denotes the concentration of the formed products (biphenyl).

6.3 Results and Discussion

6.3.1 Electrocatalyst Synthesis and Characterization

In this study, bimetallic Co-Ag-MOF was successfully synthesized by the one-step hydrothermal method and deposited directly on copper foam support as a catalytic electrode. The surface morphology and structural details of the prepared MOF electrodes were examined by the FESEM/EDS analysis as presented in Figure 6.2. The pristine copper foam (Fig. 6.2(a)) exhibits a characteristic smooth surface with interconnected porous structures. In contrast, the Co-Ag-MOF electrode (Fig. 6.2 (b & c)) reveals a thoroughly coated copper foam with the synthesized MOFs sheet that shows an agglomerated ball-like structure. The fused prismatic components of the crystalline particles were responsible for the ball-like formations as indicated by the high-resolution FESEM picture (Figure 6.2 c-inset). Furthermore, the agglomerated surface structure of the MOF particles led to its small surface area, as will be further supported by the BET surface area analysis. The results of Co-Ag-MOF surface elemental mapping obtained from the EDS analysis are also shown in Figure 6.2 (d-h). Both Ag and Co elemental mapping were evident throughout the MOFs particles, as revealed in Figure 6.2 (e-h). Their composition in the Co-Ag-MOF particles was different, with Ag and Co sharing 56% and 16% composition, respectively. The large percentage of Ag in the final product confirms that Ag had a higher reactivity preference with the BTC than Co during the MOF crystallization process because an equal mass ratio (1:1) of Ag and Co was employed during the synthesis procedure.

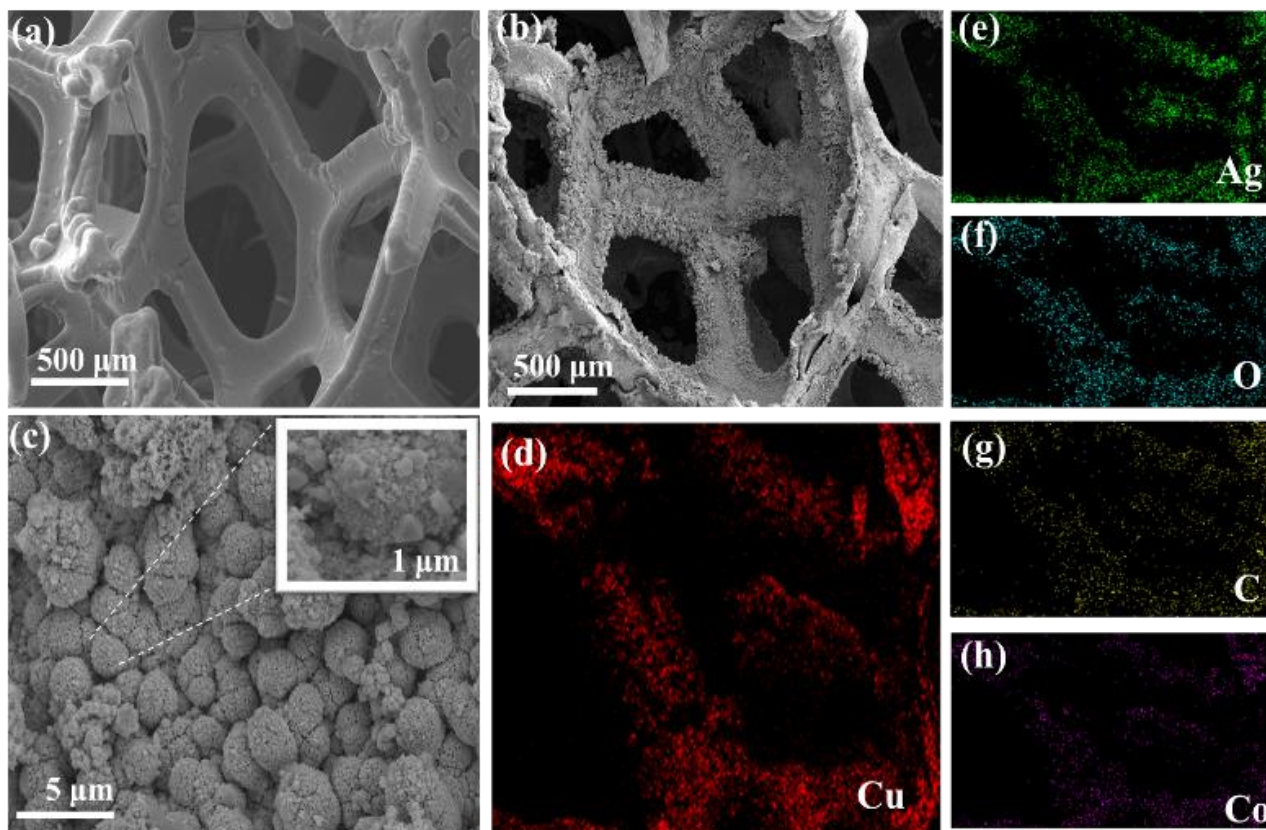


Figure 6.2 : FESEM images of (a) copper foam and (b, c, d) Co-Ag-MOF coated copper foam and (e, f, g, h) EDS surface elemental mapping.

The chemical composition and state of the elements in the Co-Ag-MOF were examined through the XPS analysis as presented in Figure 6.3. The survey scan spectra of Co-Ag-MOF (Figure 6.3a) shows the presence of Ag, Co, O and C elements in its composition that were consistent with the EDS analysis result. The high resolution Ag3d spectrum (Figure 6.3b) shows two distinct peaks at 367.5 eV(Ag3d_{5/2}) and 373.5 eV (Ag3d_{3/2}) that signifies the presence of metallic silver [135,136]. Moreover, the 6-eV binding energy separation between the two Ag3d peaks affirm the existence of Ag⁰ oxidation state in the Co-Ag-MOF [136]. As for the emission due to Co2p (Figure 6.3c), its spectrum shows two prominent peaks at 780.78 eV and 796.18 eV binding energies that indicate the presence of cobalt species in +2 oxidation states [137].

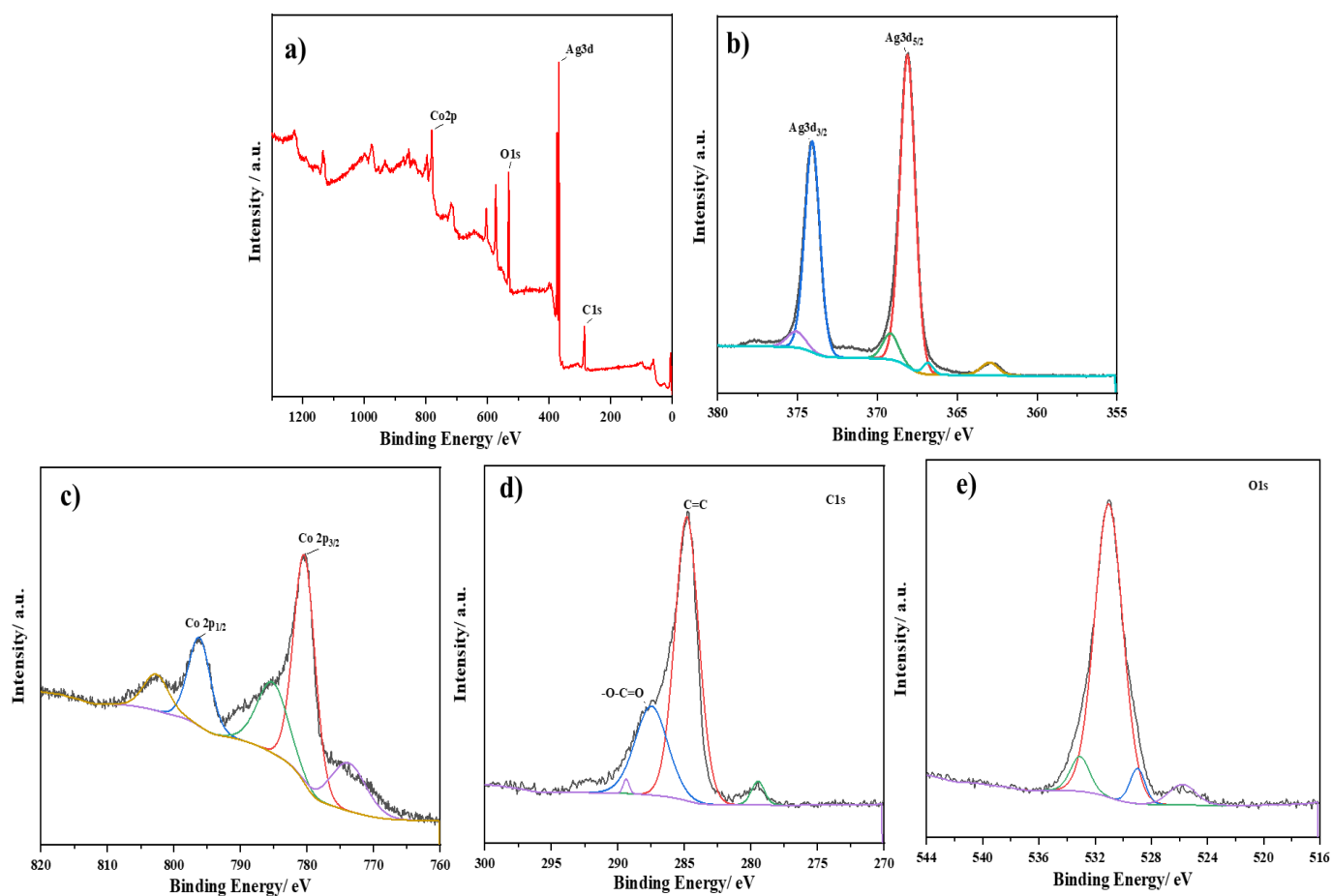


Figure 6.3 : XPS spectra of the Co-Ag-MOF(a) survey scan (b) Ag_{3d} (c) Co_{2p} (d) C_{1s} and (e) O_{1s}

The high resolution C1s spectrum shows two peaks at 284.88 eV and 287.68 eV which were linked to C=C and O-C=O of the BTC ligand. The O1s emission spectrum shows a distinct peak at 531.08 eV that is likely due to metal-oxygen bond [136]. In general, the XPS results was found to be consistent with previous literature findings and affirm the successful synthesis of the Co-Ag-MOF composites and.

The Raman and XRD spectra of the produced MOF materials are shown in Figure 6.4 (a and b). The spectra of both MOFs (Co-Ag-MOF and Co-MOF) are shown here to highlight how silver inclusion modifies the composition of the Co-MOF. For the Raman analysis (Fig. 6.4a) The observed characteristic peaks in the band range of $350 - 1800 \text{ cm}^{-1}$ in both materials were compatible with recent studies on Co-MOF synthesis [138,139]. In the case of Co-MOF, the aromatic and carboxylate groups of the BTC produce multiple peaks at 974, 1132, and 1335 cm^{-1} , which were ascribed to C-O-C stretching, C-C stretching, and C-H in-plane bending vibration, respectively[139]. In the case of Co-Ag-MOF, the broad peak in the band range of $750 - 1100 \text{ cm}^{-1}$ was associated with the C-C stretching vibration, while the peaks at 1172, 1598 cm^{-1} were assigned to C-O-C, C = O stretching vibrations, respectively [140]. Moreover, the peak band at 375 cm^{-1} (Co-MOF) and 359 cm^{-1} (Co-Ag-MOF) in the samples were attributed to Co-O and Co-Ag-O, respectively. The intensity of the peak caused by Co-Ag-O at band 359 cm^{-1} was significantly greater than the one caused by Co-O at band 375 cm^{-1} , as shown in the Figure. This result validates the incorporation of Ag into the MOF structures and confirms the successful synthesis of the bimetallic Co-Ag-MOF particles. Moreover, the notable shift in Raman bands of Co-Ag-MOF in comparison to Co-MOF indicates that Ag inclusion had a significant impact on the MOF structural property.

The acquired XRD spectra of the MOF particles are shown in Figure 6.4 b. The diffraction peaks exhibited by each of the MOF particles match well with previously reported spectra for Co-MOF and Ag-MOF [141–143]. As illustrated, the addition of Ag significantly affected the crystallinity of resulting MOFs particles as shown by the sharp diffraction peaks of Co-Ag-MOF in comparison to that of Co-MOF. Co-Ag-MOF shows a sharp diffraction peak at 2θ values of 37.85° and 44.03° that corresponds to (1 1 1) and (2 0 0) lattice planes of Ag, respectively [141]. Furthermore, the appearance of peaks at 2θ values of 25° , 33° , and 65° validates the presence of Co [143] and confirms the successful formation of Co-Ag bimetallic crystalline particles.

The N_2 adsorption-desorption isotherm for Co-Ag-MOF was carried out as shown in Figure 6.5, from which the BET surface area of $18.66 \text{ m}^2/\text{g}$ was obtained. The plot shows a type III adsorption isotherm property, indicating a non-porous or macro-porous structure with low adsorption energy [144]. It is worth noting that a similar low BET surface area was reported in previous studies on cobalt/silver based-MOFs synthesis [145,146].

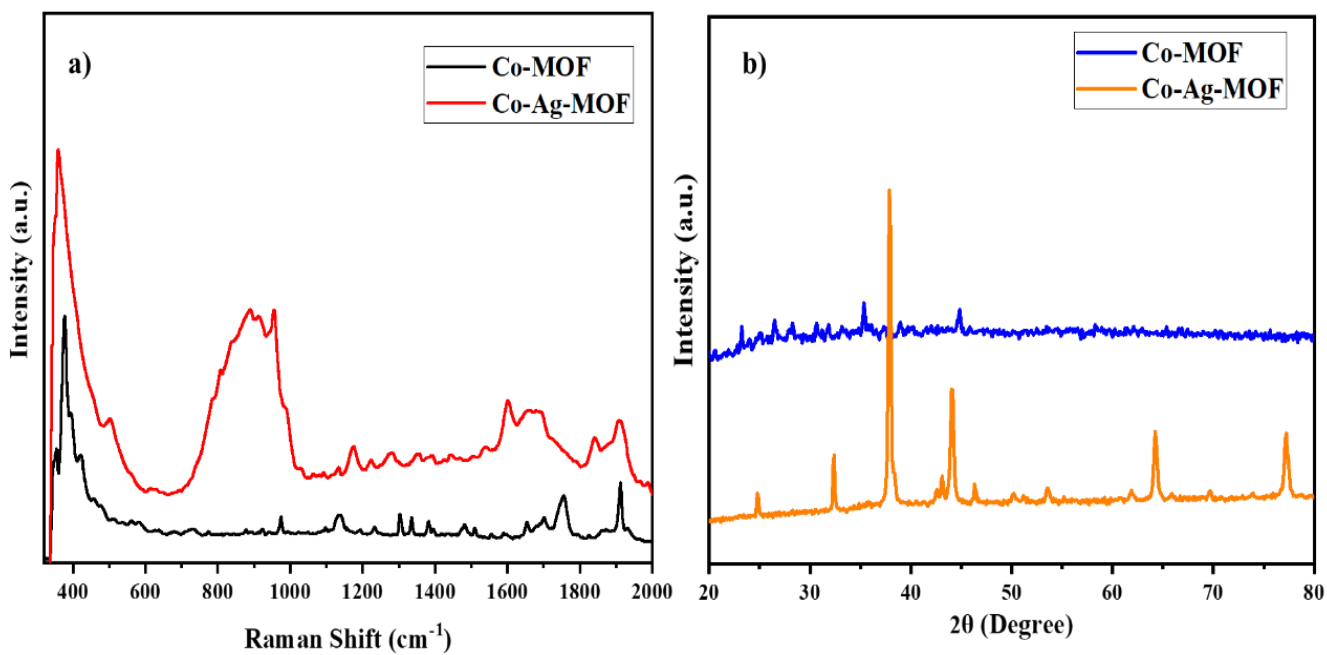


Figure 6.4 : (a) Raman spectra and (b) XRD spectra of prepared MOFs.

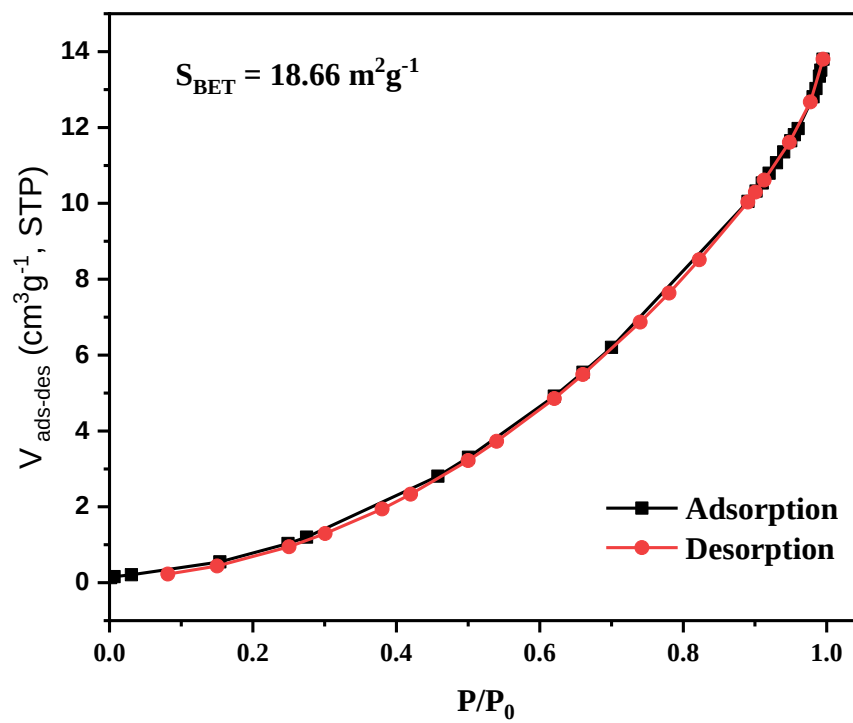


Figure 6.5 : N₂ adsorption-Desorption Isotherm Plot

6.3.2 Cyclic Voltammetry Studies

The electrocatalytic activity of the prepared Co-Ag-MOF electrode was investigated through cyclic voltammetry studies. Figure 6.6(a) shows the cyclic voltammograms of the Co-Ag-MOF/Copper foam electrode and the Copper foam electrode in the presence of substrates (chlorobenzene and phenylboronic acid). The voltammogram of Co-Ag-MOF displays a significant cathodic current response that was much higher than that of a pristine copper foam electrode, which implies its high catalytic activity towards the reduction of the substrate in the solution. The high cathodic response displayed by the Co-Ag-MOF could be linked to the reduction of the C-Cl bond of (1a) at the electrode surface via an electron transfer mechanism. Moreover, the variation in the slope of the voltammogram at different potential scan rates (Fig. 6.6 b) indicates that the electrochemical process is directed by an electron transfer mechanism[147]. This finding led us to postulate that the cathodic reduction of the aryl-halide substrate by a single electron insertion at the electrode surface would generate an unstable aryl radical, which would subsequently displace the coupling partner's boronic group by a nucleophilic substitution reaction to form the biaryls unit. More details about the proposed coupling reaction mechanism and the catalytic role of the Co-Ag-MOF electrode are discussed in the later section of the manuscript.

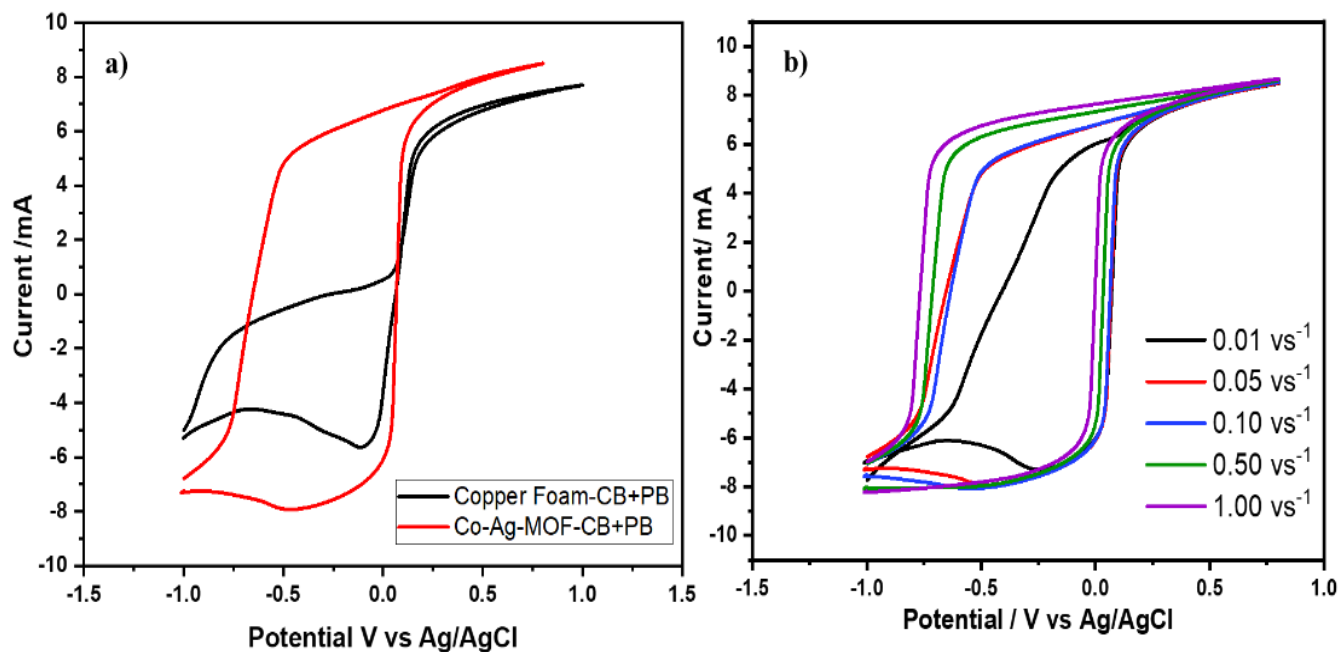
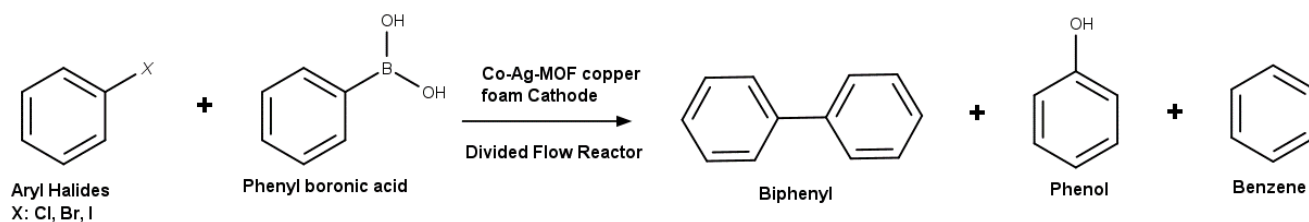


Figure 6.6: Cyclic Voltammetry measurement recorded for (a) Copper foam and Co-Ag-MOF copper foam and (b) Co-Ag-MOF at a different scan rate.

6.3.3 Electrochemical Suzuki Coupling with Co-Ag-MOF Electrode

Based on our investigations in this study, the proposed reaction pathway for the electrochemical reductive cross-coupling of the aryl's halides with aryl boronic acid in the aqueous medium is exemplified in scheme 1. Initially, we probed the reductive conversion of (1a) as a model substrate with each of the electrodes to discern the electrode's performance and the reaction pathway. The reactions were carried out in an aqueous medium with Na_2SO_4 as the stable electrolyte.

As shown (Figure 6.7), the Co-Ag-MOF/copper foam outperformed both the Co-MOF/copper foam and the pristine copper foam in the conversion of (1a) to biphenyl and phenol (low yield), demonstrating its high catalytic activity. (1a) conversion efficiency of more than 70% was achieved for the Co-Ag-MOF/copper foam electrode with an applied current density of $30\text{mA}/\text{cm}^2$ and a reaction time of 30 minutes. Based on this outcome, biphenyl and phenol formation were identified as the possible side reactions that could hinder the performance of the electro reductive cross-coupling of the substrates in the aqueous medium.



Scheme 1: Electrochemical Suzuki coupling of aryl halides and aryl boronic acid in aqueous medium

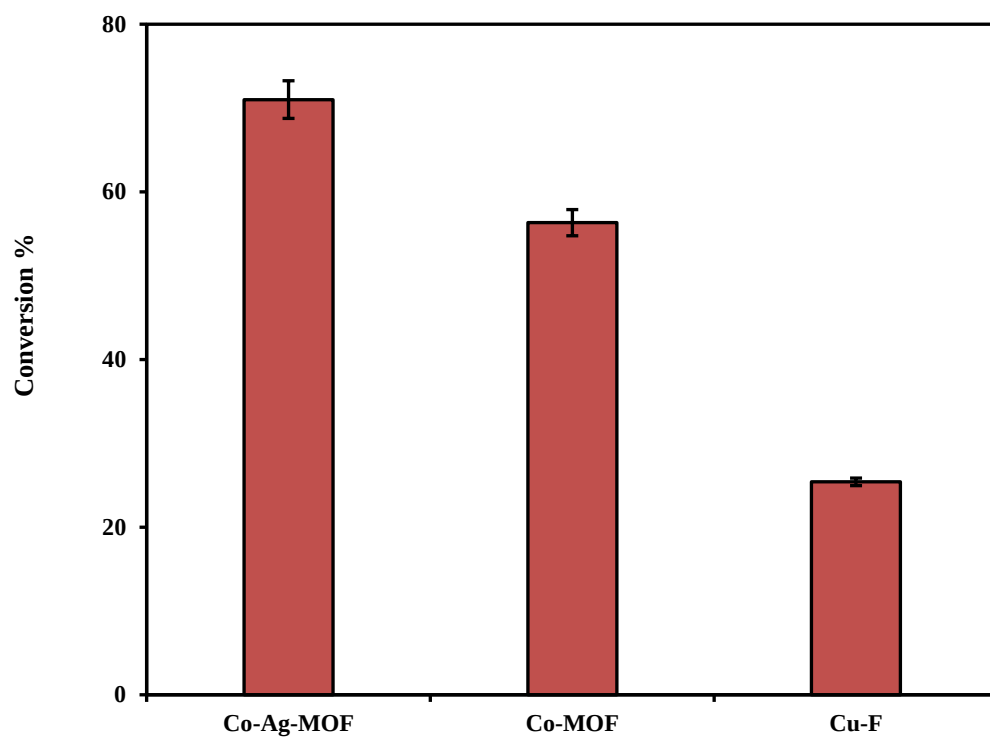


Figure 6.7 : Chlorobenzene conversion with the MOFs coated copper foam and pristine copper foam electrodes (applied current 180mA, reaction time 30 min, 10mM concentration of Chlorobenzene)

6.3.4 Effect of applied current density

Subsequently, we explored the reductive cross-coupling of (1a) with (2a) using Co-Ag-MOF/copper foam as the cathodic electrode in a divided flow reactor. For this purpose, we tested the effect of applied current density variation on the substrate's conversion and yield of the coupled product. An increasing trend in both (1a) conversion and biphenyl formation was observed with an increase in current density. The results in Figure 6.8 shows the yields of the coupled product-biphenyl and that of the intermediates compounds produced (benzene and phenol) during the reductive conversion of the substrates. Around 50% (1a) conversion was achieved at $5\text{mA}/\text{cm}^2$, yielding 40 % benzene with a meagre biphenyl yield of 4%. While at the higher current density of $30\text{mA}/\text{cm}^2$, 80% (1a) conversion was noted with a corresponding benzene yield of more than 65% and biphenyl formation of around 30%. For all the current density values investigated, the observed biphenyl yields were lower in comparison to the significant (1a) conversion achieved. This poor product yield to higher conversion ratio could be due to the over-reduction of the reduced (1a) intermediates to benzene and phenol as confirmed from the GC-MS analysis. This overreduction was likely facilitated by the hydrogenation of these intermediates achieved through the $\cdot\text{H}$ (hydrogen atom) radicals produced during cathodic water reduction at the electrode interface.

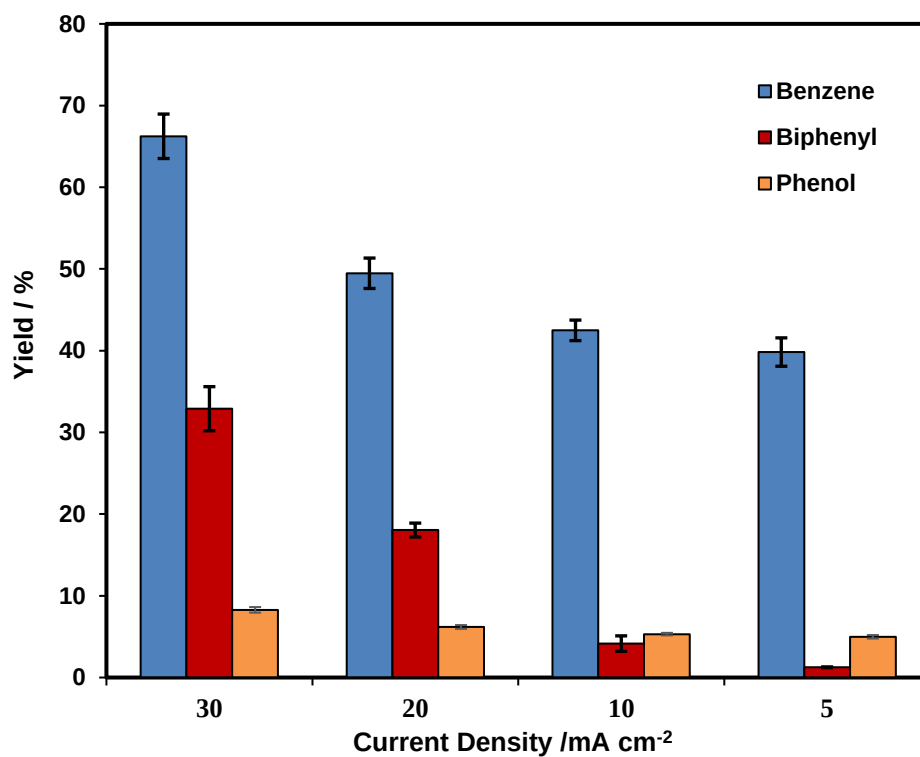


Figure 6.8 : Effect of applied current density on the yield of detected products during electrochemical reductive coupling of chlorobenzene and phenylboronic acid (reaction time- 30 min, 50mM Na₂SO₄ electrolyte, 10mM concentration of chlorobenzene, 10mM phenylboronic acid).

6.3.5 Effect of reaction time

Next, the influence of different reaction durations was examined to understand the reaction kinetic and the probable cross-coupling mechanisms as shown in Figure 6.9. All the aryl halides (1a, 1b, and 1c) were tested for the cross-coupling reaction with the 2a to understand the influence of the starting aryl halide in these experiments. More so, we assessed the influence of a basic reaction medium on the conversion and the product yield. Figure 6.9 (a1, b1, and c1), illustrate the results of the time dependence of the concentration of the starting substrates (aryl halides and phenylboronic acid) and the concentration of the formed products in the typical Na_2SO_4 electrolyte medium.

As shown, the aryl halides-coupling partner pairs showed a decreasing trend in concentration with reaction time that indicate their rapid conversion in the aqueous medium. In addition, the conversion of the two substrates was followed by a progressive increase in the formation of the reaction products. As illustrated (Fig. 6.9- a-1, a-2, and a-3), both (1a) and (1b) showed a similar fast conversion from the initial concentration of 10mM to 1.5 mM (> 90%) after 120 min of reaction time.

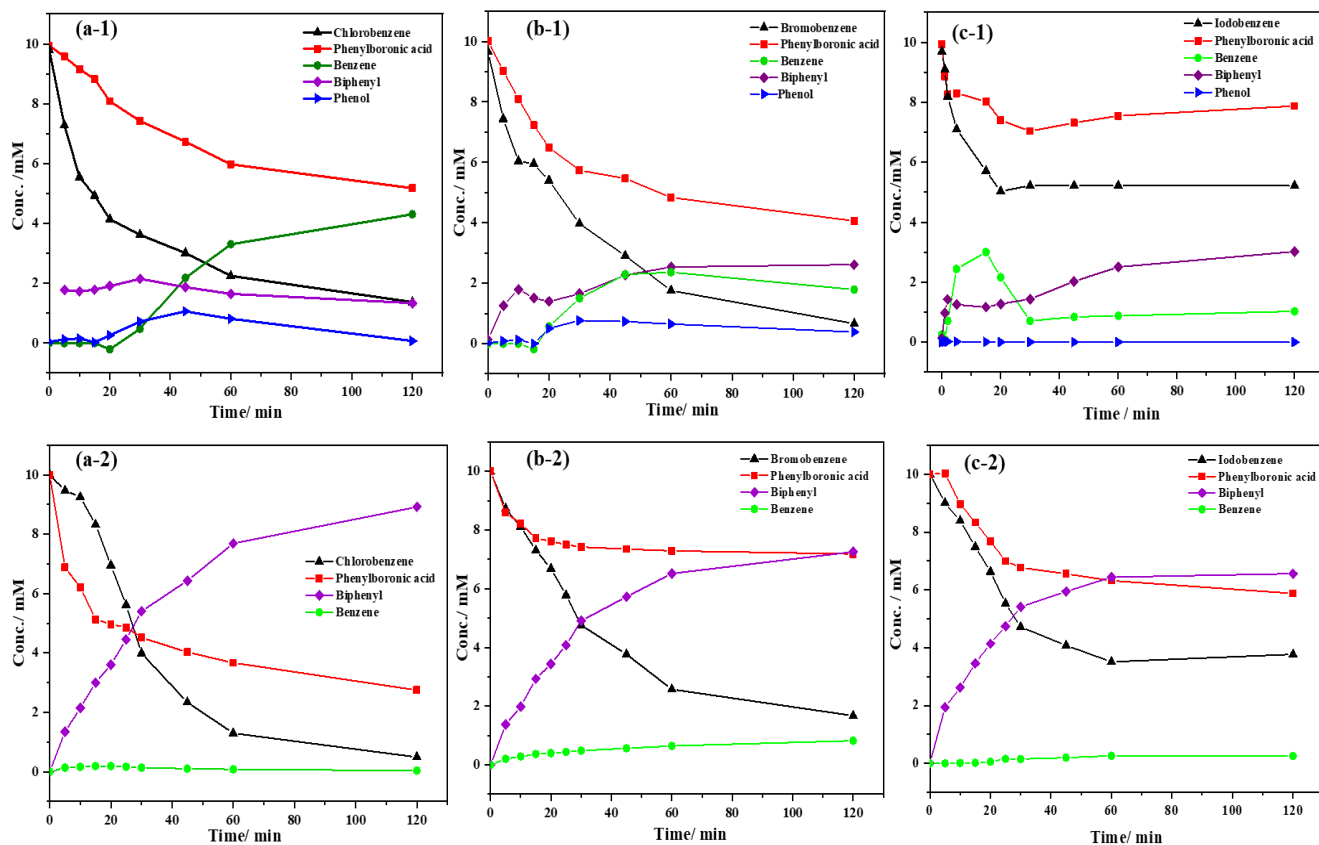


Figure 6.9 : Effect of reaction time on aryl's halides conversion and yield of the products (a) 50 mM Na₂SO₄ electrolyte (b) 0.5 M NaOH as electrolyte (10 mM concentration of aryl halides, 10 mM phenylboronic acid, applied current density-30 mA/cm²).

While (1c) exhibits a rapid conversion from the reaction onset up to 20 min with a concentration decrease from 10 mM to 5.2 mM (>50%), its concentration afterwards remains constant for the entire reaction duration of 120 min. Similarly, (2a) conversion in the presence of each of the aryl halides showed a progressive decrease in its initial concentration, achieving 40%, 50%, and 20% conversion in the presence of (1a), (1b), and (1c), respectively, for the entire reaction duration. Meanwhile, the lower conversion of (1c) may be attributed to its low aqueous solubility, which might have hindered its interaction with the electrode. This assertion is supported by previous reports [148,149] that showed excellent conversion of (1c) in coupling reactions due to the weaker carbon-iodine bond.

In the case of (1a) and (2a) reactions in Figure 6.9 (a-1), benzene was identified as the major product alongside biphenyl in moderate yield and lower phenol yield. While (1b) with (2a) reaction (Figure 6.9(1-b)) afforded a considerable biphenyl yield in comparison to benzene and phenol formation. Interestingly, (1c) and (2a) reactions also yielded a fair amount of biphenyl despite its lower (1c) and (2a) conversion, as shown in Figure 6.9 (1-c). Since these reactions were carried out in an aqueous medium, the concurrent cathodic water reduction generating atomic hydrogen (H^*) could have mediated the excessive conversion of aryl halides to benzene via hydro-dehalogenation as observed in this study.

Even for a stronger carbon-halogen bond such as (1a), which is rarely reported, its transformation alongside (1b) and (1c) to biphenyl in this investigation, albeit at lower yields, are enough proof to substantiate the catalytic performance of the Co-Ag-MOF electrode in promoting reductive cross-coupling reaction. It is suggested that the neutral pH condition of these reactions might have been the stumbling block favouring the side reaction of benzene formation through cathodic

water reduction. For this reason, we investigated the reductive cross-coupling of the aryl halides with phenylboronic acid in a basic reaction medium.

Figure 6.9 (2-a, 2-b, 2-c) shows the time dependence of the concentrations of the starting substrates and the formed products for these reactions carried in a basic medium. Interestingly, the results reveal an enhanced biphenyl yield for each of the aryl halides, with a negligible benzene formation. The (1a) and (2a) reaction (Figure 6.9 (2-a)) reveals a rapid conversion that was followed by an increase in biphenyl production, yielding more than 90 % after 120 minutes of reaction time. Similarly, (1b) and (1c) reactions with the (2a) (Figure 6.9 (2-b, 2-c)) reveal a significant (1a) conversion with increased biphenyl production achieving 80% and 60% for (1b) and (1c), respectively. However, the lower (2a) conversion in these reactions indicates that biphenyl formation is likely dominated by the homocoupling of the reduced (1b), and (1c) intermediates and not entirely from cross-coupling with (2a). Furthermore, the inhibition of benzene formation (side reaction) in these investigations were attributed to the deprotonation of the reaction system, where hydrogenation reaction is suppressed, and the substrate reduction occurs solely through electron transfer.

6.3.6 Kinetic study

The kinetic modelling of the experimental data was carried out with respect to the starting aryl halides (reactant) and biphenyl (product) to gain a deeper understanding of the coupling mechanism. The data were fitted to the first-order kinetic model as illustrated in Figure 6.10 using equations 6.4 and 6.5 for the reactant and product, respectively.

$$C_t = C_o e^{-kt} \quad (6.4) [150]$$

$$C_{t-\text{biphenyl}} = C_o (1 - e^{-kt}) \quad (6.5) [150]$$

Where, C_o and C_t represent the initial concentration and concentration at time (t), respectively for reactants (aryl halides, phenylboronic acid), $C_{t\text{-biphenyl}}$ is the concentration of formed product (biphenyl), t- denotes the reaction time and k- represent the rate constant of the reaction. From the fitted models, the reaction rate constants were estimated as shown in Table 6.1. The fitted model reactions conform to the first-order kinetic behaviour based on the high R^2 (coefficient of determination) and adjusted R^2 values. It should be noted that the time concentration dependence of phenylboronic acid was found to conform to zero-order kinetic behaviour (not included), which is consistent with previous reports[121,151]. The rate constants for the aryl halides conversion were in the following sequence: chlorobenzene > bromobenzene > iodobenzene, which matches the trend of their halide electron affinities ($Cl^- > Br^- > I^-$). Similarly, the corresponding rate constant for biphenyl formation also follows the same trend. It is suggested that the high reactivity preference exhibited by the chlorobenzene compared to the other aryl halides is likely due to its halide high electron affinity which facilitated its enhanced conversion. Based on the observed first-order rate constants, the mechanism of the coupling reaction is proposed to involve the direct cathodic reduction of the aryl halides to an aryl radical through an electron transfer which is likely the rate-determining step. Subsequently, the interaction of aryl radical with the phenylboronic acid through a rapid nucleophilic substitution reaction yielded the corresponding coupled product- biphenyl.

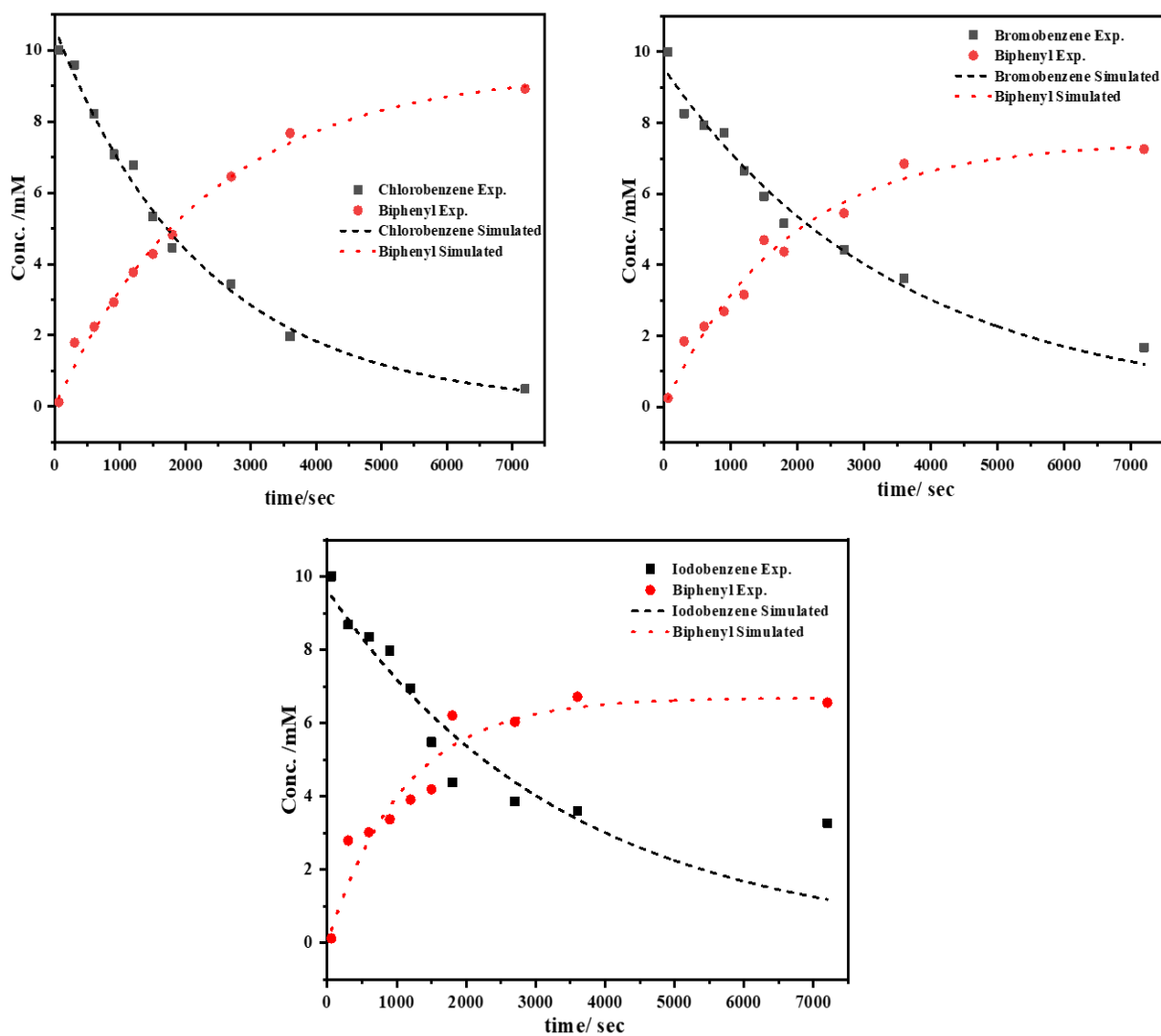


Figure 6.10 : First order kinetic curve fitting with respect to the aryl halides conversion and Biphenyl

Table 6.1: Kinetic parameters for the first order model fit for the reactant and product

Entry	Reactant/Product	First order rate constant (k- s ⁻¹)	Fit parameters	
			R ²	Adj. R ²
1	Chlorobenzene,	Chlorobenzene	0.0264	0.9996
	Phenlyboronic acid	Biphenyl	0.02565	0.9999
2	Bromobenzene,	Bromobenzene	2.873x10 ⁻⁴	0.9749
	Phenlyboronic acid	Biphenyl	5.474x10 ⁻⁴	0.9718
3	Iodobenzene,	Iodobenzene	2.911x10 ⁻⁴	0.9690
	Phenlyboronic acid	Biphenyl	9.041x10 ⁻⁴	0.9651

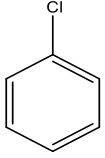
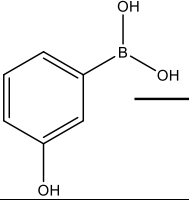
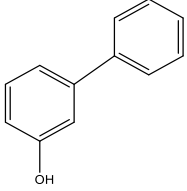
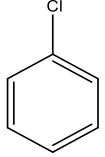
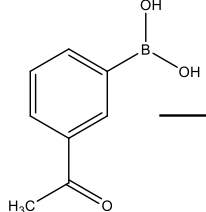
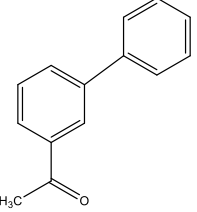
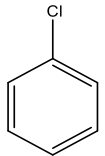
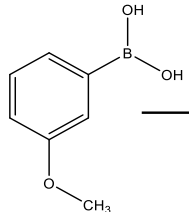
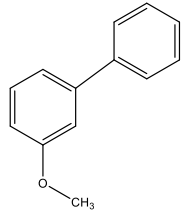
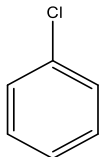
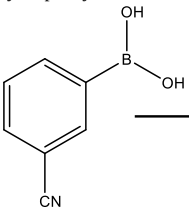
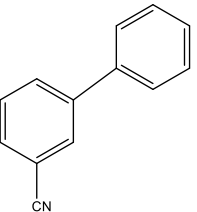
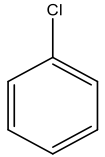
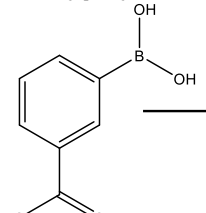
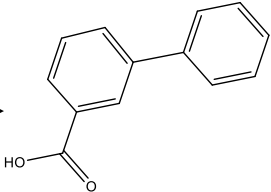
6.3.7 Effect of different boronic acids

To extend the scope of the proposed cross-coupling approach, we investigated the cathodic cross-coupling of (1a) with different functional boronic acids as shown in Table 6.2. As with the case with (2a), the cross-coupling reaction of (1a) with hydroxyl phenylboronic acid (2b) having an electron-donating group (OH) afforded a much higher yield of 95 % for the coupled Hydroxylbiphenyl product. Furthermore, electron-withdrawing functional boronic acids such as acetyl phenylboronic acid (2c), methoxy phenylboronic acid (2d), cyano phenylboronic acid (2e) and carboxyl phenylboronic acid (2f) provided moderate yields for their coupled products. However, in comparison to (2b), their yields were relatively low, which is likely due to the steric hindrance of these functional groups.

6.3.8 Electrode Stability

The reusability of the Co-Ag-MOF electrode was evaluated through a repetitive use for the reductive cross-coupling over ten cycles of operation. The result in Figure 6.11 shows that the electrode was fairly stable providing a decent conversion for the substrate even after the 10th cycle of use. A significant (1a) conversion of more than 90 % was accomplished at the first cycle which decreases fairly in the subsequent cycles to around 80% for the 10th cycle. Similarly, the formation of biphenyl due was also significant in the first cycle and was found to decrease to 70 % in the 10th cycle. The observed decrease in the electrode activity with each cycle of use might be due to the interaction of the MOF Ag particles with the formed chloride ions generated from (1a) reduction. The outcome is substantiated by the thin black film observed on the electrode surface after each cycle of use that indicates the formation of AgCl.

Table 6.2 : Cathodic cross-coupling of the aryl halide with different phenylboronic acids

Aryl halide	Coupling Partner	Formed Product	Substrate Conversion	Yield (%)
 Chlorobenzene	Hydroxyphenyl boronic acid 	 Hydroxybiphenyl	98	95
 Chlorobenzene	Acetylphenylboronic acid 	 Acetylbiphenyl	95	85
 Chlorobenzene	Methoxyphenylboronic acid 	 Methoxybiphenyl	90	82
 Chlorobenzene	Cyanophenylboronic acid 	 Cyanobiphenyl	92	72
 Chlorobenzene	Carboxylphenylboronic acid 	 Carboxybiphenyl	81	52

Experimental Conditions: 0.5 M NaOH electrolyte, current density-30mA/cm², reaction time-120 min, equimolar concentration of the substrates-10mM

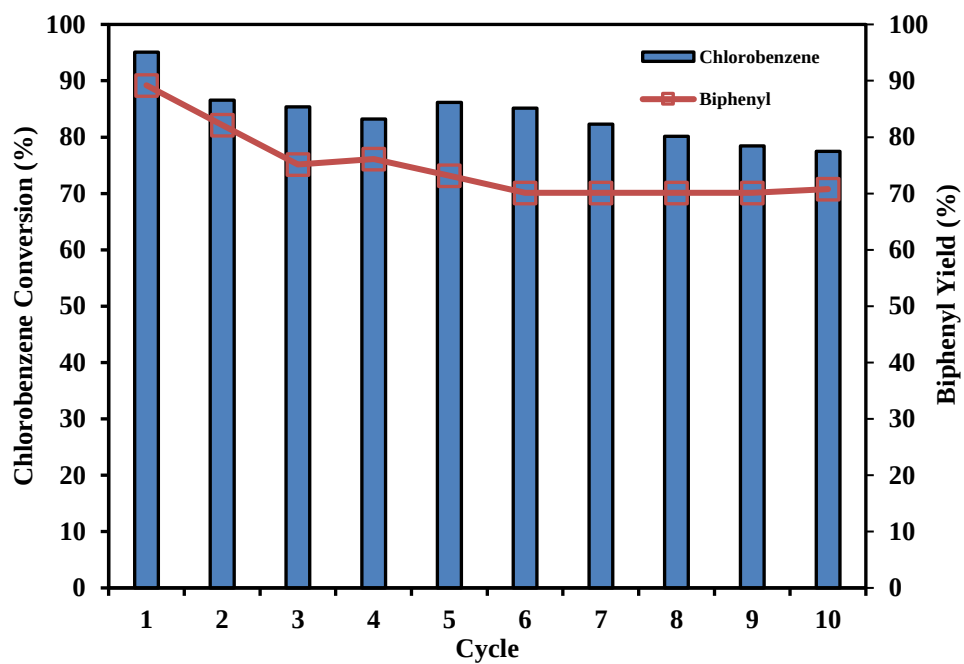
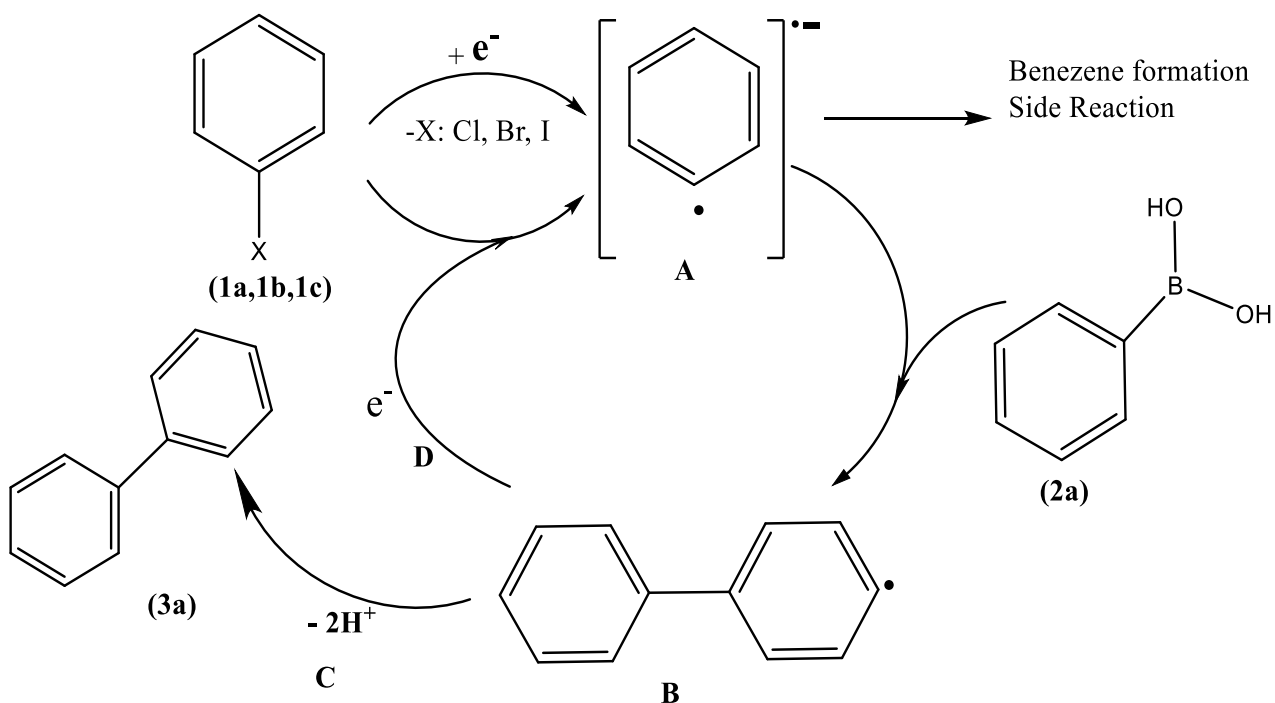


Figure 6.11 : Cyclic experiment for the Co-Ag-MOF electrode (Experimental Conditions: 0.5 M NaOH electrolyte, current density-30mA/cm², reaction time-120 min, equimolar concentration of the substrates (chlorobenzene, phenylboronic acid)-10mM)

6.3.9 Mechanism of Electrochemical Reductive Suzuki Coupling

The proposed mechanism of electrochemical reductive coupling with the Co-Ag-MOF cathodic electrode is presented in scheme 2. The mechanism is based on reported precedents in literature and the results achieved in this current study. The interaction of the substrates with the Co-Ag-MOF electrode occurs took place via surface adsorption process. The carboxylate functional groups of the MOF linker likely facilitated this interaction. Through cathodic action, the aryl halide (1a, 1b, 1c) is reduced to an aryl radical (product **A**) via a single electron insertion approach. The produced aryl radical can further undergo a hydrogenation reaction to form benzene and phenol as a side reaction in the absence of a base. Otherwise, in a basic medium, the aryl radical being a nucleophile would interact with the coupling partner (2a) through a nucleophilic substitution reaction to form an intermediate radical **B**. Finally, the intermediate radical is transformed to the coupled product (biaryls) via an electron loss (**D**) with two protons (H^+) **C**.



Scheme 2: Proposed mechanism of electrochemical reductive cross-coupling of the aryl halides with the aryl boronic acid

A comparison of the developed electro-reductive Suzuki coupling approach with reported literature was carried out (Table 6.3) to establish the superiority of the proposed method. It can be observed from the Table that the current study showed the highest biphenyl yield ever presented for the electro-reductive synthesis approach. Moreover, the proposed method also showed a comparable biphenyl yield with lower reaction time and mild reaction conditions to the previously reported MOF catalyzed biaryls synthesis approach.

Table 6.3: A comparison of biaryls synthesis with MOFs Catalysis and Electroreductive synthesis approach

Entry	Catalyst/Electrocatalyst	Substrates/experimental conditions	Products	Yield (%)	Ref.
Heterogenous MOFs Catalysts					
1	Pd- MOF	p-Bromoanisole and Phenylboronic acid solvent- o-xylene, K ₂ CO ₃ -base, temperature -150 °C, time – 6 hours	Methoxybiphenyl	99	[131]
2	Zeolites based MOF (MIL-101) supported Pd Catalyst	Chlorobenzene, phenylboronic acid, solvent- water, base- NaOMe, TBAB, 80 °C temperature, reaction time- 20 hours	Biphenyl	97	[152]
3	Pd nanoparticle supported on amino functionalized MOF (MIL-53(Al)-NH ₂)	Bromobenzene ^a , Iodobenzene ^b , phenylboronic acid, solvent- water/ethanol (2:1), base- Na ₂ CO ₃ , temperature- 40°C, reaction time- 30 min	Biphenyl	92 ^a , 94 ^b	[153]
4	Pd supported on cobalt MOF	Chlorobenzene ^c , Iodobenzene ^d , phenylboronic acid, solvent- water, base- K ₂ CO ₃ , temperature- 70°C, reaction time- 6 hours	Biphenyl	60 ^c , 98 ^d	[154]
Electro-reductive synthesis approach					
5	Magnesium electrode	Bromobenzene, Benzyldehyde, solvent- THF with LiClO ₄ electrolyte, ambient condition, reaction time- not provided	Biphenyl	62.3	[155]
6	Platinum Electrode	Iodotoluene, Benzonitrile, solvent- DMF, base- NaOt-Bu, temperature- 25°C, reaction time- 24 hour	3a [*]	38	[156]
7	Co-Ag-MOF electrode	Chlorobenzene ^a , Bromobenzene ^b , Iodobenzene ^c , Phenylboronic acid, solvent- water, base- NaOH, ambient reaction condition, reaction time – 2 hours	Biphenyl	98 ^a , 80 ^b , 60 ^c	Current study

6.4 Summary

In conclusion, we have demonstrated the use of Co-Ag- MOF as an active electrocatalytic electrode in promoting the reductive Suzuki coupling of aryl halides with aryl boronic acid in an aqueous medium in the study. This reductive coupling method proceeds under a mild reaction condition without the need for palladium catalyst and a bulky ligand while achieving excellent biaryls yields. The yield of the biaryls was highly influenced by the presence of a base. The proposed coupling approach was able to accommodate the transformation of a variety of aryl boronic acids with different functional groups to their corresponding biaryls. Furthermore, the Co-Ag-MOF electrode showed excellent stability, presenting a moderate decrease in reactivity even after times of repetitive use. |

CHAPTER 7

CONCLUSIONS AND RECOMMENDATION

7.1 Conclusions

The formation of disinfection by-products (DBPs)/ halogenated organic compounds in water during disinfection processes have received widespread attention in recent years, due to the adverse health effects these compounds pose to humans. Since most of the formed DBPs in product water (treated) are usually a product of halogens (disinfectants) and organic compounds interaction (halogenated-organics), the degradation (cleavage) of these halogenated-organic bonds using electrochemical methods is sought as an efficient treatment approach for these classes of water pollutants. In this dissertation, electrochemical degradation of selected DBPs/ halogenated organics (aliphatic and aromatic halogenated organics) was carried out in an aqueous medium using different inexpensive transition metal catalyst electrodes. The presented work has described the synthesis, characterization, and applications of the following supported transition metal electrocatalysts for DBPs/ halogenated organics degradation in various electrochemical cell configurations: Co-MoS₂, bimetallic Bi-Cu, and Co-Ag-MOF. The performance of the prepared electrocatalysts was thoroughly evaluated, and possible degradation mechanisms were proposed. Based on the outcomes of this dissertation work, the following sets of conclusions were reached.

1. It has been discovered that Co-MoS₂ is an active and stable electrocatalyst that can promote the reductive degradation of different aliphatic halogenated DBPs compounds that include chloroform, dichloromethane, and carbon tetrachloride.

2. The superior electrocatalytic activity displayed by Co-MoS₂ was due to its hybrid CoS and MoS₂ nanosheet that promoted the cathodic Volmer step of hydrogen evolution reaction (HER). The promoted HER ensures that enough atomic hydrogen *H is produced and used in the organic reduction process.
3. pH, applied current density, reaction time, and initial DBPs concentration were the key influencers of the mechanisms of aliphatic DBPs reduction with the Co-MoS₂ electrode within the range of the levels of experimental parameters investigated.
4. Based on the kinetic study, electrochemical characterization tests and the use of radical scavenger, the mechanism of the aliphatic DBPs reduction with the Co-MoS₂ electrode is proposed to involve a stepwise degradation of higher-order halogenated DBPs via intermediate organohalides subsequently formed during the electroreduction processes. Moreover, it was speculated that the reduction of DBPs on the CoMoS₂-GF surface was also promoted by surface-bound atomic *H generated by water reduction.
5. The prepared bimetallic Bi-Cu electrode was inefficient towards the reduction of selected halogenated aromatic organic compounds (2,4-dichlorophenoxy acetic acid, 4-chloro-3-methylphenol, 4-bromophenol). However, it was found to be highly efficient in promoting the electro-oxidation of the organic compounds
6. Excellent combined electro-oxidation of the halogenated aromatic organic compounds was achieved in the multi-components solution with the bimetallic Bi-Cu electrode.
7. The applied CCD experiment design based on response surface methodology was found to be an adequate tool for modelling the degradation process and for comprehending the operational factors affecting the process.
8. The prepared novel cobalt-silver MOFs electrocatalyst was highly stable and exhibited excellent catalytic properties towards the reduction of aromatic halogenated organic

compounds that include Chlorobenzene, Bromobenzene and Iodobenzene in an aqueous medium. Considering the superior performance displayed by the electrode towards the reduction of the organic halides, the scope of the study was extended to investigate the formation of biaryls compounds via reductive Suzuki coupling of the organic halides with phenyl boronic acid.

9. The reductive Suzuki coupling of the organic halides with the phenyl boronic acid proceeded under a mild reaction condition and was found to be highly influenced by a basic reaction medium.
10. The cobalt-silver MOFs electrocatalyst was highly efficient in promoting the Suzuki reaction and was able to accommodate the transformation of a variety of aryl boronic acids with different functional groups to their corresponding biaryls.

7.2 Recommendations

Based on the findings of this study, the following sets of recommendations for future work in advancing electrocatalytic halogenated organic degradation are presented.

- The development and application of carbon-based materials as catalytic electrode can be explored as an alternative to the transition metals utilized in the current study. This suggestion is based on the high abundance and inexpensive nature of carbon materials compared to these metals.
- It is suggested that an advanced characterization tests for the prepared electrocatalysts be carried out before, after and during application to further understand the underlying mechanism of degradation at microscale or atomic level.

- A detailed kinetic modelling and a theoretical modelling of the interfacial interactions of the electrocatalyst with the substrates through density functional theory (DFT) simulation can be explored to further elicit the degradation mechanism.
- Application of the prepared electrode for the treatment of real halogenated organic contaminated water in a pilot scale process can be explored to test the industrial feasibility of the treatment process.

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PUBLICATIONS

- **Mohammed Dauda**, Chanbasha Basheer, Muhammad H. Al-Malack, Bimetallic Cobalt-Silver MOF Catalyzed Electro-reductive Suzuki Coupling in a Continuous Flow Reactor. (Under Review)
- **Mohammed Dauda**, Chanbasha Basheer, Muhammad H. Al-Malack, Bimetallic Bismuth-Copper/GF electrode for enhanced degradation of halogenated aromatic organic compounds. (Under Review)
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