

**ELECTROCHEMICAL DEGRADATION OF  
REACTIVE RED 4 USING  
GRAPHITE/CHITOSAN-POLY(VINYL  
CHLORIDE) COMPOSITE ELECTRODES**

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**UNIVERSITI SAINS MALAYSIA**

**2021**

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CHLORIDE) COMPOSITE ELECTRODES**

by

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**Thesis submitted in fulfillment of the requirements  
for the degree of  
Master of Sciences**

**December 2021**

## ACKNOWLEDGEMENT

First of all, I would like to express my gratitude to the School of Chemical Sciences, Universiti Sains Malaysia (USM) for giving me the opportunity to conduct my research work in fulfillment of my Master degrees. My sincere gratitude to my main supervisor Dr. Norazzizi bin Nordin for the patience, enthusiasm, immense knowledge, motivation, and continuous support in completing my research. His guidance has helped me in all the time of research and writing of this thesis. I also would like to acknowledge the financial support provided by Ministry of Higher Education Malaysia through Fundamental Research Grant Scheme (FRGS) (FRGS/1/2020/STG04/USM/02/4) and Universiti Sains Malaysia through short-term grant (304/PKIMIA/6315104).

My special thanks to my co-supervisor Prof. Dr Rohana Binti Adnan for her encouragement and insightful comments. I also would like to thank Dr. Hairul Hisham Bin Hamzah for his guidance in using cyclic voltammetry. Not forgetting the technical staff from School of Chemical Sciences especially Mrs Norhayati, Mr Sujeyendran, Mr Zamri, Mr Fauzan, Mrs Ami Mardiana, Mr Siva, Mr Azhar, Mr Azizo, Ms Hasniza, and Mr Megat for the excellent services and kind assistance in using chemical instruments. My gratitude also goes to Mr Mutalib from Centre for Global Archaeological Research for the excellent services in FESEM and Mr Mustaqim from School of Physics for the excellent services in XRD analysis. Besides, my acknowledgement also goes to respective staff from Institute of Postgraduate Studies (IPS) for their kind guidance and assistance. Last but not least, my sincere gratitude to my parents, siblings, uncles, aunts, and friends for their financial assistance, love, trust, and moral support throughout my study.

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## LIST OF SYMBOLS AND ABBREVIATIONS

A	Ampere
Å	Angstrom (=10 <sup>-10</sup> meters)
AgCl <sub>2</sub>	Silver chloride
β	Beta
BET	Brunauer Emmet Teller
BOD	Biochemical oxygen demand
C	Graphite
Ce-PbO <sub>2</sub> /ZrO <sub>2</sub>	Cesium plumbum oxide zirconium oxide
Chi	Chitosan
Cl <sup>-</sup>	Chloride ion
Cl <sub>2</sub>	Chlorine
cm <sup>3</sup>	Cubic centimeter
CO <sub>2</sub>	Carbon dioxide
COD	Chemical oxygen demand
COOH	Carboxylic acid
Cr	Chromium
DC	Direct current
DSA	Dimensionally stable anodes
dm <sup>3</sup>	Cubic decimeter
e <sup>-</sup>	Electron
EAOPS	Electrochemical advanced oxidation processes
FTIR-ATR	Fourier-transform infrared spectrum-attenuated total reflectance
GC/MS	Gas chromatography/mass spectroscopy
H <sup>+</sup>	Hydrogen ion
H <sub>2</sub> O	Water molecule

HCl	Hydrochloric acid
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid
HOCl	Hypochlorous acid
IC	Ionic chromatography
Ir	Iridium
kWh	Kilowatt-hour
M	Molarity
mA	Milliampere
mg	Milligram
min	Minute (s)
mL	Millilitre
mm	Millimetre
NaCl	Sodium chloride
Na <sub>2</sub> CO <sub>3</sub>	Sodium carbonate
Na <sub>2</sub> SO <sub>4</sub>	Sodium sulphate
Nb/BDD	Boron-doped diamond on niobium substrate
Ni	Nickel
O <sub>2</sub>	Oxygen
O <sub>3</sub>	Ozone
OCl <sup>-</sup>	Hypochlorite ion
·OH	Hydroxyl radical
OH <sup>-</sup>	Hydroxide ion
ppm	Parts per million
Pt	Platinum
PVC	Poly(vinyl chloride)
RB5	Reactive black 5



RR4	Reactive Red 4
RSD	Relative standard deviation
rpm	Revolutions per minute
Ru	Ruthenium
SEM-EDX	Scanning electron microscopy-energy dispersive x-ray
SG	Seed germination
Si/BDD	Boron-doped diamond on silicon substrate
SO <sub>3</sub> H	Sulfonic acid
TGA	Thermal gravimetric analysis
TiO <sub>2</sub>	Titanium dioxide
Ti/PbO <sub>2</sub> -Sm <sub>2</sub> O <sub>3</sub>	Titanium/plumbum oxide-samarium oxide
TOC	Total organic carbon
UV-Vis	Ultraviolet visible-spectroscopy
μm	Micrometre
XRD	X-ray diffraction

## **LIST OF APPENDICES**

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# DEGRADASI ELEKTROKIMIA *REACTIVE RED 4* MENGGUNAKAN ELEKTROD KOMPOSIT GRAFIT/KITOSAN-POLI(VINIL KLORIDA)

## ABSTRAK

Dalam kajian ini, elektrod komposit grafit/kitosan-poli(vinil klorida) (C/Chi-PVC) telah digunakan sebagai anod untuk mengkaji degradasi *Reactive Red 4* (RR4) dengan kehadiran rod grafit dan natrium klorida (NaCl) masing-masing sebagai katod dan elektrolit penyokong. Menggunakan teknik voltammetri berkitar, lima elektrod dengan nisbah komposisi C:Chi yang berbeza telah diuji untuk menentukan komposisi elektrod terbaik untuk pengoptimuman parameter elektrolit 200 ppm RR4. Keputusannya, elektrod dengan nisbah komposisi 70:30 (dikenali sebagai C<sub>49</sub>/Chi<sub>21</sub>-PVC<sub>30</sub>) telah dipilih sebagai anod untuk degradasi RR4 pada kepekatan NaCl yang berbeza (0.01-1.0 M), voltan (1-20 V), masa elektrolisis (15-75 min), pH (2-12), dan suhu (30-70°C) bagi menentukan parameter elektrolisis yang optimum. Penemuan mendedahkan bahawa dengan kehadiran 0.4 M NaCl, voltan 5 V, masa elektrolisis 60 minit, pH larutan awal 6, dan pada suhu 30°C, kecekapan penyingkiran untuk warna, permintaan oksigen kimia (COD), dan jumlah karbon organik (TOC), adalah masing-masing 99.61%, 76.35%, dan 89.68%. Kajian lanjut mendedahkan bahawa penyingkiran RR4 mematuhi model kinetik tertib pertama. Pencirian menggunakan FESEM-EDX, FTIR-ATR, XRD, TGA, dan BET mendedahkan tiada perbezaan ketara dari segi morfologi permukaan, struktur molekul, kekristalan, penurunan peratusan dan keliangan elektrod dalam kedua-dua elektrod baharu dan terpakai. Menariknya, selepas 14 hari terdedah kepada sampel, RR4 yang dirawat mempunyai penilaian ketoksikan yang rendah dengan peratus percambahan biji benih sebanyak 60±0.40% berdasarkan ujian percambahan benih menggunakan kacang hijau

(*Phaseolus vulgaris* L.). Keputusan GC/MS membuktikan bahawa molekul RR4 telah didegradasikan menjadi sebatian jisim molekul rendah ((asid ftalik, 2-klorofil isobutil ester), (pirimidina, 5-metil), (asid karbonik, oktil fenil ester), (propanamida, N-(3-metoksifenil)-2,2-dimetil), (asid karbonik, isoheksil fenil ester), (benzena, (2,2-dimetilpropoksi)), (2-heptanol, 6-amino-2-metil), (propanoil klorida), (nitrogen), dan (karbon monoksida)) pada parameter yang dioptimumkan. Analisis BOD mendedahkan bahawa parameter elektrolisis yang dioptimumkan mempunyai peratusan tertinggi pengurangan BOD ( $92.99 \pm 0.01\%$ ). Menariknya, ujian kitar semula mendedahkan bahawa  $95.31 \pm 7.22\%$  penyingkiran warna telah dicapai menggunakan elektrod yang sama dalam proses berterusan sebanyak tiga kali tanpa membersihkan elektrod. Secara keseluruhan, elektrod yang dibuat menunjukkan ciri-ciri yang kuat dan tahan lama serta berkesan untuk digunakan dalam rawatan air sisa.

**ELECTROCHEMICAL DEGRADATION OF REACTIVE RED 4 USING  
GRAPHITE/CHITOSAN-POLY(VINYL CHLORIDE) COMPOSITE  
ELECTRODES**

**ABSTRACT**

In this study, graphite/chitosan-poly(vinyl chloride) (C/Chi-PVC) composite electrode was used as anode to investigate the degradation of Reactive Red 4 (RR4) in the presence of graphite rod and sodium chloride (NaCl) respectively as cathode and supporting electrolytes. Using the cyclic voltammetric technique, five electrodes with different C:Chi composition ratios were tested to determine the best electrode composition for the optimisation of electrolysis parameters of 200 ppm RR4. As a result, electrode with a 70:30 composition ratio (known as C<sub>49</sub>/Chi<sub>21</sub>-PVC<sub>30</sub>) has been chosen as the anode for RR4 degradation at different NaCl concentrations (0.01-1.0 M), applied voltages (1-20 V), electrolysis times (15-75 min), pH (2-12), and temperature (30-70°C) to determine the optimal electrolysis parameters. The findings revealed that in the existence of 0.4 M NaCl, an applied voltage of 5 V, an electrolysis time of 60 minutes, an initial solution pH of 6, and at 30°C, the removal efficiency for colour, chemical oxygen demand (COD), and total organic carbon (TOC) are 99.61%, 76.35%, and 89.68 %, respectively. Further investigation revealed that the RR4 removal obeyed the pseudo-first-order kinetic model. The characterisations using FESEM-EDX, FTIR-ATR, XRD, TGA, and BET revealed no significant differences in terms of surface morphology, molecular structure, crystallinity, percentage weight loss and the porosity of the electrode in both fresh and used electrodes. Interestingly, after 14 days of exposure to the sample, the treated RR4 solution had a low toxicity assessment with the germination percentage

of  $60\pm 0.40\%$  based on a seed germination test using green beans (*Phaseolus vulgaris* L.). Results of GC/MS proved that the RR4 molecule was degraded into low molecular weight compound ((phthalic acid, 2-chlorophyl isobutyl ester), (pyrimidine, 5-methyl), (carbonic acid, octyl phenyl ester), (propanamide, N-(3-methoxyphenyl)-2,2-dimethyl), (carbonic acid, isohexyl phenyl ester), (benzene, (2,2-dimethylpropoxy)), (2-heptanol, 6-amino-2-methyl), (propanoyl chloride), (nitrogen), and (carbon monoxide)) at optimised parameter. The BOD analysis revealed that the optimised electrolysis parameter has the highest percentage of BOD reduction ( $92.99\pm 0.01\%$ ). Surprisingly, the reusability test conducted without cleaning the electrode revealed that  $95.31\pm 7.22\%$  of colour removal was accomplished using the same electrode in a three-step continuous process. Overall, this fabricated electrode demonstrated robust and long-lasting characteristics and is efficient for application in wastewater treatment.

# CHAPTER 1

## INTRODUCTION

### 1.1 Water pollution

Water resources are some of the most crucial natural resources and most valuable on earth, which simultaneously facing the high demand. It is one of the basic essentials for sustaining life that highly important to human and other organisms on earth. Human needs water to drink, wash, and for other basic necessity that require the use of water. Rivers, lakes, glaciers, rainwater, groundwater, and so on are all examples of water sources. Physical, chemical, and biological parameters can be used to assess the quality of water in any specific area or source. These parameters' values are harmful to human health if they exceed the defined limits (Tyagi et al., 2013). In Malaysia, the suitability of water sources for human consumption and Water Quality Index (WQI) have been described by Ministry of Environment and Water as indicated in the Table 1.1.

**Table 1.1** Existing parameters and Water Quality Index (WQI) values (Idris et al., 2003; Akinbile et al., 2013)

Parameter	Class I	Class II	Class III	Class IV	Class V
Ammoniacal nitrogen	< 0.1	0.1-0.3	0.3-0.9	0.9-2.7	> 2.7
BOD	< 1	1-3	3-6	6-12	> 12
COD	< 10	10-25	25-50	50-100	> 100
Dissolved oxygen	> 7	5-7	3-5	1-3	< 1
pH	> 7	6-7	5-6	< 5	< 5
Total suspended solids	< 25	25-50	50-150	150-300	> 300
Water Quality Index	> 92.7	76.5-92.7	51.9-76.5	31.0-51.9	< 31.0

Class I -Conservation of natural environment

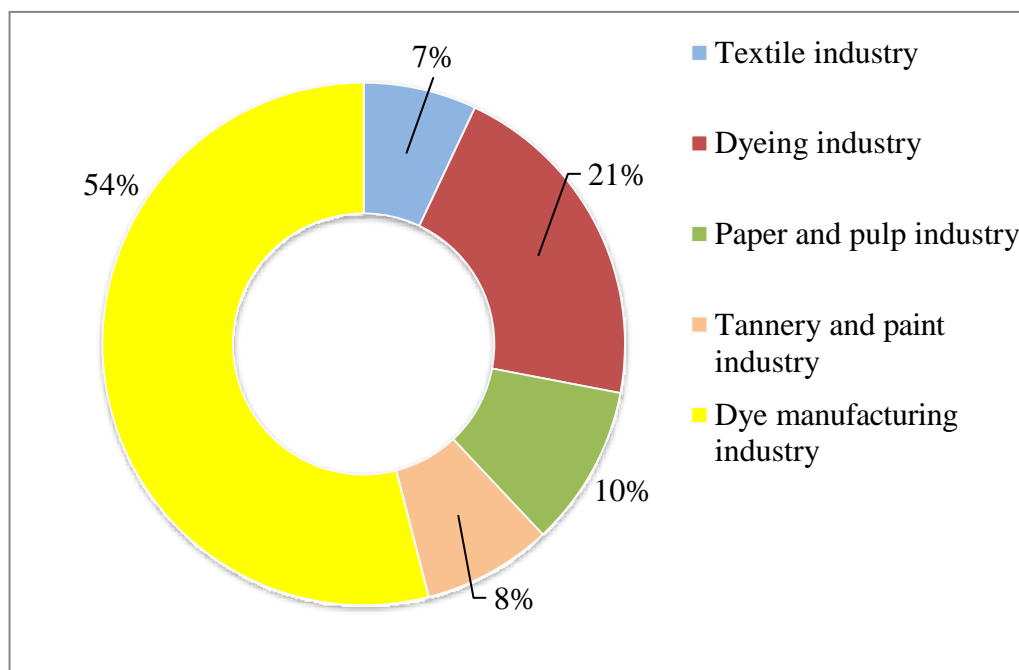
Class II-Conventional treatment required

Class III-Extensive treatment required

Class IV-Irrigation

Class V-None of the above

Many industries nowadays such as pharmaceutical companies processing personal care products (Kwarciak-Kozłowska, 2019) and textile industry (Samsami et al., 2020) have become the main source of water pollution. Textile industry is one of the industries that consumes high amount of water and produces highly polluted discharge water in huge amounts (Figure 1.1). Textile effluents are complex and difficult because they contain a variety of dyes. The organic unsaturated materials that consume light and provide colour for various applications are dyes (Benkhaya et al., 2020(b)). According to Kalra and Gupta (2020), over 100,000 different types and nearly 700,000 tonnes of synthetic dyes are used commercially around the world each year. Around 10 to 15% of these dyes end up in industrial wastewater streams as a result (Kalra & Gupta, 2020).



**Figure 1.1** Industries responsible for the present of dye effluent in the environment (Samsami et al., 2020)



Water pollution can be caused by heavy metal ions, phenolic compound, and dyes. There are more than 35 elements that can be categorised as heavy metals. The toxicity of these elements depends on the type of metal and its biological role in the lifespan. On the contrary, dye compounds are usually used in textile industry. Dyes are essentially chemical substances that can attach to fabrics or surfaces to instill colour. Because of their impenetrability, their discharge into bodies of water is a significant source of pollution. According to Katheresan et al. (2018), 85% dye effluent is removed from the dyeing process (Figure 1.2). Dyes are categorised in terms of colour, application method, and structure (Yagub et al., 2014). Dyes can be sorted into two categories which are natural and synthetic dye stuff. Synthetic dyes are classified by their application field namely basic, disperse, reactive, vat, mordant, metal complex, sulfur and acid dyes (Soon & Hameed, 2011).

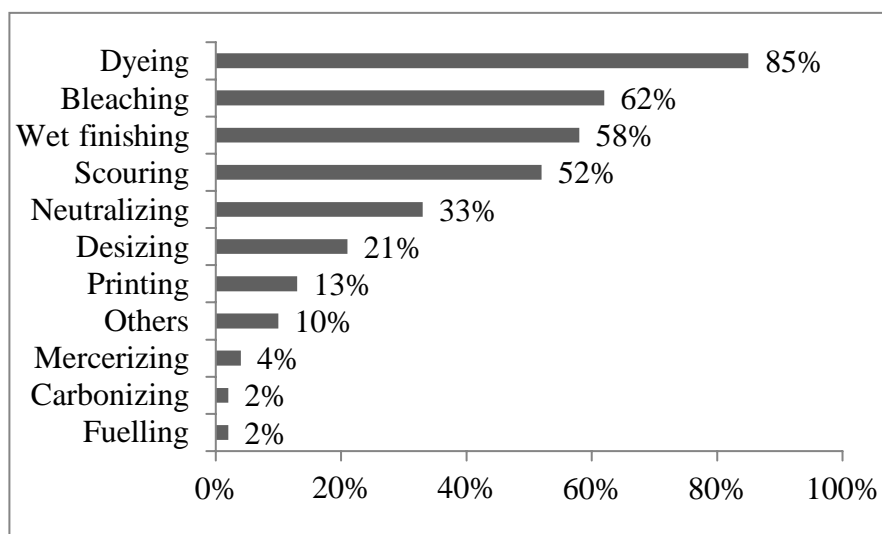


Figure 1.2 Discharge percentage of dye mixture from each process of textile industry

(Katheresan et al., 2018)

## **1.2 Wastewater treatment methods**

There are various methods need for the treatment that introduced by researcher in which consisted of biological, chemical, and physical. Biological treatments such as trickling filter and activated sludge are affordable and environmental-friendly (Haddad et al., 2018). A trickling filter is a common aerobic wastewater treatment process that uses microbes to remove organic matter and nitrogen at the same time. Because no aeration is required, these systems save energy. On the other hand, activated sludge process is an uninterrupted treatment that uses an accumulation of microbes supported in the wastewater in aeration tank to disintegrate and digest the organic pollutants. It is not cost effective and this process requires high-energy rate to provide the required oxygen (Khalaf et al., 2021).

The examples of physical method used by researchers to treat industrial wastewater are adsorption and membrane filtration. Adsorption is one of the most widely used wastewater treatment methods for removing organic and inorganic contaminants. Adsorption is well explained as the method of attracting and accumulating contaminants on the surface of an adsorbent. This process was found to be superior to other techniques in terms of design versatility and complexity, initial expense, resistance to contaminants, simplicity of handling, and lack of hazardous materials (Yagub et al., 2014). However, because of the low surface area of this method, the efficiency of these adsorbent materials is insufficient, as is the selectivity.

Membrane filtration is one of the methods that is broadly used in a variety of industrial fields, ranging from the water desalination and purification to the recovery of high value and fragile substances (Gifuni et al., 2020). It is a cutting-edge membrane technology with high separation efficiency, low toxicity, and low power

consumption that has been used in the field of wastewater treatment (Syahirah Kamarudin et al., 2020). However, this method causes two major problems which are poor removal of contaminants and serious membrane fouling problems (Ma et al., 2020).

On the other hand, chemical methods like electrochemical advanced oxidation processes (EAOPS) have been developed as a promising technology for the removal of persistent organic pollutants. These systems are associated with the formation of hydroxyl radical ( $\cdot\text{OH}$ ). The reaction produces organic radical and starts a radical chain including reaction with oxygen and formed reaction intermediates undergo further oxidation reactions with generated oxidising agents until the complete mineralisation of organic contaminants (Nidheesh et al., 2018). The advantages of this method are they use electron as reagent and is environmentally clean. However, this method uses high energy consumption (Duan et al., 2015).

### **1.3 Problem statements**

Azo dyes from textile industries are the major sources that cause water pollution. Dyes that absorb and scatter sunlight lead to the algae growth. Rapid growth of algae release toxin and takes up the oxygen content from water body that cause the death of aquatic life due to the lack of oxygen. Besides, dyes develop carcinogen that badly ruin human health (Huang et al., 2017). To overcome this problem, there are various treatments that have been introduced by researchers in which consist of biological, physical, and chemical method. Biological methods such as trickling filter and activated sludge are environmental-friendly and affordable. However, they are uneconomical for highly concentrated waste pollutants and sensitive to numerous environmental factors. Physical methods such as adsorption,

membrane filtration, and flocculation are ineffective on contaminants because of complex molecular structure of pollutants and pollutant's high degree of polarity. In the treatment of dyes, chemical methods such as electrochemical advanced oxidation processes (EAOPs) have been marked as a promising subclass of alternative water desalination. It can generate hydroxyl radicals indirectly or directly through electron transfer and degrade wastes that cannot be treated biologically. However, this technique is a bit difficult and not cost-effective. Composite electrode has larger surface area for adsorption, high porosity, and high stability than single electrode. Therefore, the electrochemical oxidation technique by using graphite/chitosan-poly(vinyl chloride) (C/Chi-PVC) composite electrodes has been introduced for the degradation of Reactive Red 4 (RR4).

#### **1.4 Research objectives**

The objectives of this research are:

1. to evaluate the efficiency of fabricated graphite/chitosan-poly(vinyl chloride) (C/Chi-PVC) composite electrodes in the electrochemical degradation of RR4;
2. to characterise the fabricated electrodes using Field emission scanning electron microscopy-elemental dispersive x-ray (FESEM-EDX), X-ray diffraction (XRD), Fourier transform infrared-attenuated total reflectance (FTIR-ATR), and electrochemical study to better understand the surface morphology, structural, and electrochemical behaviour of the electrode; and
3. to investigate the effect of electrolysis parameters (NaCl concentration, applied voltage, electrolysis time, pH, and temperature) on colour, Total organic carbon (TOC), and Chemical oxygen demand (COD) removal efficiency in RR4 degradation.

## 1.5 Outline of the thesis

The thesis consists of five chapters:

Chapter 1 emphasizes the thesis introduction. It points out the introduction of water and pollutant, treatment of water pollution, dyes, problem statements, research objectives, and outline of the thesis.

Chapter 2 is a detailed review of the literature on some basic knowledge of electrochemical oxidation reaction, electrode in electrochemical oxidation of dyes from previous studies, composite electrode, and chemical structure and properties of graphite and chitosan.

Chapter 3 outlines the general experimental technique and procedures for the preparation of C/Chi-PVC composite electrodes, electrochemical measurement by cyclic voltammetry and electrolysis of Reactive Red 4 (RR4), analysis of treated and untreated samples by using Ultraviolet-visible spectroscopy (UV-Vis), Total organic carbon (TOC), Chemical oxygen demand (COD), and seed germination test. The principles of the instrumental characterisation methods by field emission spectroscopy and energy dispersive X-ray (FESEM-EDX), Fourier transform infrared-attenuated total reflectance (FTIR-ATR), X-ray diffraction (XRD), Thermal Gravimetric Analysis (TGA), and Brunauer-Emmett-Teller (BET) surface area analysis are briefly discussed.

Chapter 4 summaries the composition of PVC used in C/Chi composite electrode and determining the best electrode by using cyclic voltammetry. Optimisation studies to determine the optimal parameters by electrolysis method

using different concentration of NaCl, applied voltage, electrolysis time, pH, and temperature of the solution by comparing the results of UV-Vis, TOC, and COD analysis were also stated. Besides, seed germination test was carried out to study the toxicity of treated water sample after electrochemical treatment using optimised parameter. On the other hand, Gas chromatography-mass spectrometry (GC/MS) was performed to propose the mechanism pathway of RR4 after the electrolysis reaction and Biological oxygen demand (BOD) was performed to analyse the percentage of BOD reduction for the optimised sample.

Chapter 5 is the conclusion of the findings and recommendations for further research.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Dyes

Dyes are oil-soluble or hydrophobic synthetic organic substances, whereas colourants are unsolvable and remain in granular form. The colour of dyes differs by various chromophore groups. Dyes can be classified in terms of their application and chemical structure (Varjani et al., 2021). There are two types of dyes which are natural and synthetic dyes. Dyes are classified as dispersed, direct, basic, reactive, vat, sulphur, or acid.

Dispersed dyes are established on azo structure despite blue and violet colours are frequently gained from anthraquinone by-product. These dyes, which are nonionic in nature, are usually insoluble in water. They are typically used on polyester, but have also been used on acrylic fibres, cellulose acetate, and nylon. Due to their non-biodegradable and recalcitrant nature, these dyes are classified as persistent. The examples of dispersed dyes are Disperse Yellow 7, Disperse Yellow 3, Disperse Red 82, and Disperse Blue 7, (Benkhaya et al., 2020(b)).

Direct dyes are primarily used to colour paper products. They are relatively cost effective. They are available in a wide range of colours but do not have a high level of colour brilliance. For instance, direct dyes are C.I. Direct Red 2, C.I. Direct Blue 86, Direct Black 38, and Direct Orange 40.

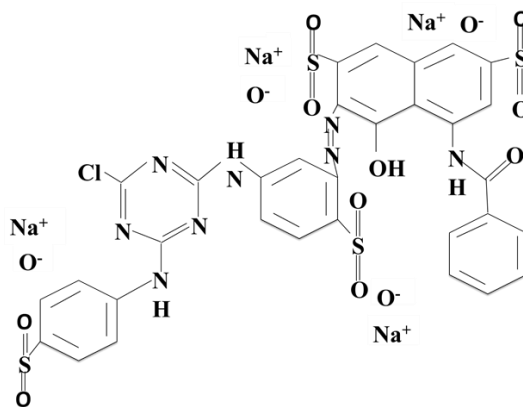
It has been disclosed that basic dyes can have either a positive charge on an ammonium group or a delocalized charge on the dye cation, which is found in many xantene, acridine, and triarylmethane dyes. These dyes are frequently used on nylon substrates, paper, and acrylic. The examples of basic dyes are Basic Red

monohydrochloride, Basic Brown 1, Basic Blue 11, and Basic Yellow 2 (Benkhaya et al., 2020(b)).

Reactive dyes become famous due to their brilliance, change in colour, and good light-fastness. These dyes are extensively used because of their reactive groups' ability to bind to the fibre, their processing conditions, and their stability. Examples of reactive dyes are Reactive Red 6, C.I. Reactive blue 19, C.I. Reactive Red 147, and C.I. Reactive Red 239, (Benkhaya et al., 2020(b)).

Reactive Red 4 (RR4) (Figure 2.1) is an azo and anionic dye that is widely used in printing, paper, cosmetic, pharmaceutical, and textile industries. Textile industries use a lot of water and chemicals. The chemicals used in this industry vary from inorganic compounds to polymers and organic products. As a result, the composition of wastewater is extremely complex and potentially toxic. Dyes are considered important pollutants in textile wastewater. RR4 is one of the most important dyes used in cellulosic fabrics. After the reactive dyeing process is completed, the amount of hydrolysed dye is greater than 800 mg/L. The fixation rate is in the 60 to 70 percent range. As a result, more than 40% of RR4 discharged in the effluent, resulting in highly coloured wastewater. Furthermore, RR4 is not easily biodegradable in both ordinary and hydrolyzed form and even after extensive treatments, the colour may still remain in the effluent (Foroozmehr et al., 2016). It is also an acidic and reactive molecule that can form a covalent bond with the amine group of proteins in textile fibres (Sung et al., 2005). It also has bright colour and better dyeing processing conditions.



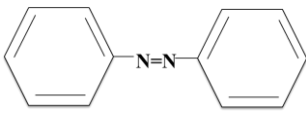
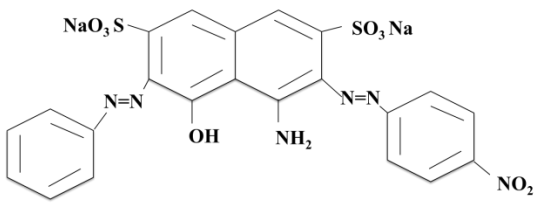
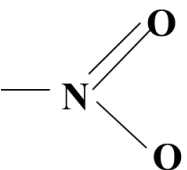
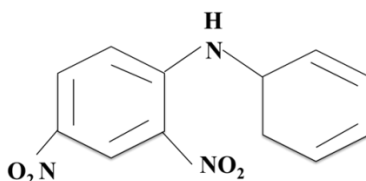
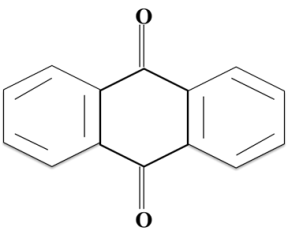
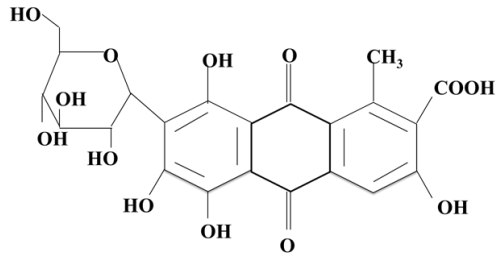
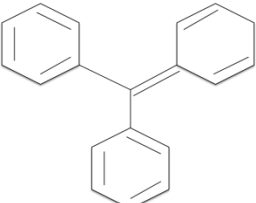
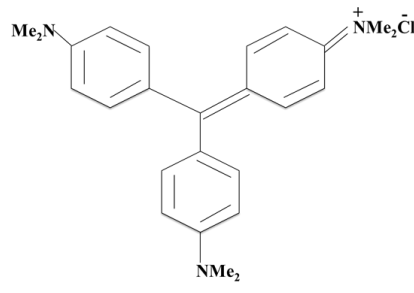


**Figure 2.1** Chemical structure of RR4

Vat dyes are known for good colour fastness, wet fastness properties, and characteristically excellent light. They are designed for used to cellulosic fibres. The examples of vat dyes are Vat Black 25, Indigo Carmine (IC), C.I. Vat green 1, and Vat Yellow 1. Sulfur dyes, on the other hand, are a type of vat dye. They are high molecular weight dyes produced by sulfurizing organic compounds. Sulfur dyes are not chlorine resistant and usually used for dyeing cellulosic fibres. The examples of sulfur dyes are Sulfur blue dye, Sulfur black, Phthalic anhydride, and Leuco Sulfur Black 1 (Benkhaya et al., 2020(b)).

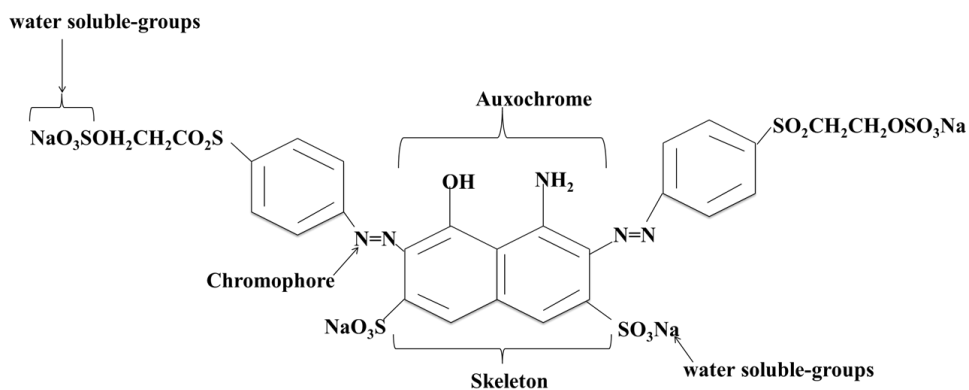
Acid dyes have one or more acid function ( $\text{SO}_3\text{H}$  and  $\text{COOH}$ ). Because of their high solubility and bright colours, these dyes are broadly used in printing, pharmaceutical, paper, leather, textile, and other areas. The examples of acid dyes are Acid Red 337, Acid Violet 17, Acid Yellow 36, and Acid Orange 7. Normally, acid dyes are broadly used on dyeing of silk, nylon fabrics, and wool under acidic conditions. Acid dyes can be structurally categorised as nitro dyes, triphenylmethane dyes, anthraquinone dyes, and azo dyes (Table 2.1).

**Table 2.1** Classification of textile dyes according to chromophore

Class	Chromophore	Dye example
Azo		 Naphthol Blue Black
Nitro		 C.I. Disperse Yellow 14
Anthraquinone		 C.I. Natural Red 4
Triphenylmethane		 Crystal Violet

Azo dyes which produce clear and strong colours, high molar extinction coefficient, and good dyeing performance most commonly used in textile industries (Cai et al., 2020). They are distinguished by one or more azo bonds (R-N=N-R) that allow the dyes to absorb visible light. The colour of azo dyes is resolute by the azo bonds and

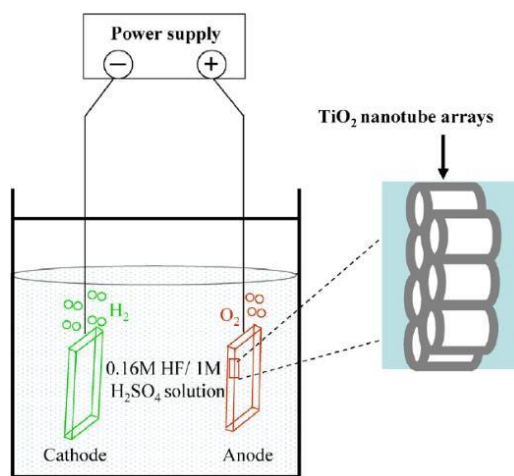
their related auxochromes and chromophores as shown in the figure below (Figure 2.2). The examples of other azo dyes that used in textile industry are Reactive Blue 19 (Rajkumar et al., 2007), C.I. Reactive Yellow 4 (Vahdat et al., 2012), Acid Red 88 (Bankole et al., 2018), and Direct Blue 2B (Cao et al., 2019).



**Figure 2.2** Structure of the azo reactive dye (Benkhaya et al., 2020(a))

## 2.2 Anodic Oxidation Technique

Anodic oxidation technique is carried out in a special reactors. This technique consists of at least two electrodes: a cathode, an anode, and an electrolyte-filled intermediate space (Figure 2.3). The electrical circuit is closed via a voltage source named as electrolysis cell. The anode undergoes oxidation reactions, whereas the cathode undergoes reduction reactions (Muddemann et al., 2019).

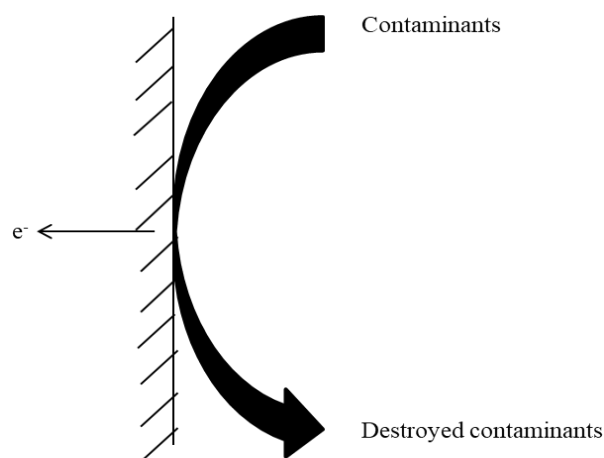


**Figure 2.3** Schematic diagram of anodic oxidation (Neupane et al., 2009)

There are some advantages using anodic oxidation which are sole use of electricity for contaminant removal without require adding chemical and operation at ambient temperature (Loos et al., 2018). According to Silva et al. (2020), anodic oxidation has lower sensitivity to matric effects and low cost in instrumentation. Another advantage of anodic oxidation is its robustness, which can be achieved by simply switching the power on and off or adapting the current density. Besides, they can degrade a wide range of inorganic and organic pollutants (Muddemann et al., 2019).

### 2.2.1 Direct anodic oxidation process

Direct anodic oxidation processes is the condition in which the contaminants are degraded on the anode surface. During direct oxidation process, there is only intervention of electron transfer without any materials, where the contaminants are directly destroyed by electron after the adsorption on anode surface (Jawad & Najim, 2018). The direct anodic oxidation of contaminant is takes place in two steps which are diffusion of contaminants from bulk solution and the oxidation of contaminants at the surface of anode (Figure 2.4).



**Figure 2.4** Direct anodic oxidation mechanism (Source: modified after Jawad & Najim (2018))

The adsorbed hydroxyl radical electrogenerated by water oxidises organic pollutants on the surface of anode.



For example, Stupar et al. (2017) investigated the direct anodic degradation of Acid Blue 111 (AB111) by using  $\text{IrO}_x$  anode. Organic compounds exchange electrons with the surface of the anode directly during the process of direct anodic reaction. The experiment was conducted in an open reactor at room temperature ( $25^\circ\text{C}$ ) with an electrolyte volume of  $200\text{ cm}^3$  with concentration of dye of  $100\text{ mg/dm}^3$ . A  $10\text{ cm}^2$  plate made of austenite 18Cr/8Ni stainless steel (series 304) is being used as the cathode, and the removal of AB111 was studied at pH levels of 3 and 12. The electrolyte  $\text{Na}_2\text{SO}_4$  was used to investigate the direct anodic oxidation of AB111. As shown in the equation below, the first reaction is the oxidation of water molecules ( $\text{H}_2\text{O}$ ) on the surface of electrode, which results in the formation of adsorbed hydroxyl radicals ( $\text{OH}$ ) (Eq. 2.2):



The active electrodes are distinguished by a charge transfer between the electrode (M) and (OH), resulting in the adsorbed OH forming so-called higher oxide (MO) at the anode (Eq. 2.3).



The redox couple MO/M then participates in the selective oxidation of organic compounds (R) without total incineration (Eq. 2.4).



As a result of the chemical decomposition of the higher oxide, the side reaction of oxygen evolution (Eq. 2.5) competes with the reaction in (Eq.2.4).



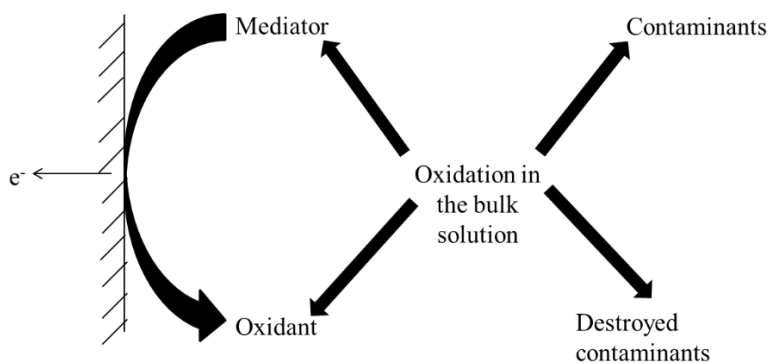
The result revealed that after 60 min of direct electrolysis, the removal percentage was found around 45% while TOC result showed only 24% of the dye was mineralized (Stupar et al., 2017).

Liu et al. (2019) used graphite electrodes to investigate the direct anodic oxidation of amine-containing pharmaceuticals (acetaminophen (ACT), dichlofenac (DIC), and sulfamethoxazole (SMX)). In electrolytic cells, direct anodic oxidation of contaminants took place on the electrode surface via direct electron transfer to the anode. The working electrode was graphite, the counter electrode was platinum, and the reference electrode was Ag/AgCl<sub>2</sub>. The electrochemical cell was performed with six graphite non-sacrificial electrodes (5 × 25 × 0.1 cm) apart, with a distance of 24 mm between each electrode. A double layered cylindrical container along with DC power supply was used to carry out the electrochemical oxidation experiments. The experiments were performed with a starting drug concentration of 15 µm and continuous stirring at 300 rpm. The results revealed that in a direct anodic system, 74.3%, 90.0%, and 81.6% of ACT, DIC, and SMX were eliminated after 60 min of reaction time, and 48.9%, 85.9%, and 68.2% of TOC were eliminated after reaction time under optimal conditions of current at 0.5 A (Liu et al., 2019).

### **2.2.2 Indirect anodic oxidation process**

Indirect oxidation process involves *in-situ* electrogeneration of chemical oxidant species with high oxidising power such as persulfate (SO<sub>4</sub><sup>2-</sup>), ozone (O<sub>3</sub>), active chloride (Cl<sup>·</sup>), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) which are able to aid the pollutant mineralization (He et al., 2019). To terminate oxidisable contaminants, anodically generated strong oxidising agents such as chlorine (Cl<sub>2</sub>) or hypochlorite (OCl<sup>-</sup>) ions

can be used. Besides, organic and inorganic contaminants can be degraded in the present of suitable amount of  $\text{Cl}^-$  as interpreted in the figure below (Figure 2.5).



**Figure 2.5** Indirect anodic oxidation mechanism (Source: modified after Jawad & Najim (2018)).

In indirect anodic oxidation, sodium or potassium chloride salts are added to the wastewater to increase conductivity and generate  $\text{OCl}^-$  ions. The anodic oxidation of chloride ion to form chlorine is shown below (Jawad & Najim, 2018).

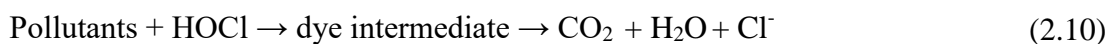


Anode reaction

The liberated  $\text{Cl}_2$  forms hypochlorous acid ( $\text{HOCl}$ ) in bulk solution,



And more associates to produce  $\text{OCl}^-$  ions.



According to Sivodia and Sinha (2020), the use of indirect anodic oxidation process with a graphite electrode has been used to investigate the removal of anticancer drug cytarabine. The effect of key parameters such as pH, current density,

and initial contaminant concentration on the performance of graphite electrode on cytarabine degradation has been investigated. After 60 minutes of electrolysis at 10 mA/cm<sup>2</sup>, the highest removal efficiency (98%) for 20 mg/L of initial cytarabine solution was obtained. The increase in cytarabine removal rate was caused by active Cl<sub>2</sub> species produced at the anode during electrolysis. The efficiency of graphite electrode was compared to that of copper electrode, and the results show that the *in-situ* generated •OH radical aided cytarabine degradation. The ability of anode material to generate reactive oxidation species is primarily determined by its oxygen evolution potential. •OH radicals are formed through a Fenton-like reaction with electrogenerated H<sub>2</sub>O<sub>2</sub> and a metal anode to oxidise organic contaminants. However, after 60 min of reaction at 15 mA/cm<sup>2</sup>, only 82% of the cytarabine was eliminated. As a result, graphite was discovered to be a more efficient electrode material for the removal of cytarabine than copper.

Bavasso et al. (2020) investigated electrochemically assisted ozone decomposition for diuron removal and mineralization. Diuron is a teratogenic herbicide that is harmful to humans and other living organisms. The experiments were conducted in a cylindrical glass reactor filled with 100 mL of diuron solution and outfitted with a ceramic microporous ozone diffuser. Ozone is a powerful oxidant that is extensively used in a variety of applications ranging from disinfection to sludge reduction and colour and odour removal. The electrochemically assisted ozone treatment was carried out with two distinct cathodic materials and a platinum wire anode. The effect of ozone alone on pH was investigated using both lower ozone rate (LOR) and higher ozone rate (HOR) regimes. In indirect oxidation of ozone reactions, the ozone molecules decompose to form free radicals (•OH) which



react quickly to oxidize the inorganic and organic compounds. The equation of indirect anodic oxidation of ozone is as below:



The results revealed that ozonation at alkaline pH and high ozone flow rate gives fast diuron degradation, with total removal achieved in only 20 min.

### 2.3 Electrodes in electrochemical oxidation of dyes

The application of environmental cleanup to treat industrial wastewater by using electrode had been one of most active areas in recent years. This is inspired by the ability of electrode for removal of organic materials in polluted wastewater. Many researchers have reported the use of different types of electrodes for wastewater treatment application such as boron-doped diamond electrodes (BDD) (Siedlecka et al., 2018), silver/carbon-poly(vinyl chloride) (AgC-PVC) electrode (Nordin et al., 2015), dimensionally stable anodes (DSA), boron-doped diamond (BDD) electrode (Soni et al., 2017), and sulfur/nitrogen co-doped activated carbon fibre (SN/ACF) (Ruan & Xie, 2020).

According to Nordin et al. (2015), the presence of two different elements in AgC-PVC electrode gave synergistic effect and active bifunctional catalyst which directly enhanced the electrode performance in the electrochemical oxidation and catalytic reaction of C.I. Reactive Orange 4 (RO4). The textile effluents were used for the electrochemical measurement and electrolysis using two-electrode system which consist of working electrode (AgC-PVC electrode) and counter electrode (Pt

plate) with NaCl solution as the supporting electrolyte. The stability of the prepared electrode was determined by cyclic voltammogram and Tafel plot was performed to determine the best composition electrode ( $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$  electrode) for the electrolysis reaction. The results showed that the best operating parameter was applied voltage of 10 V in the 1 M NaCl solution for 100 min of electrolysis time to decolourise the RO4 and textile effluents with removal percentage of more than 95%. The electrode was also able to decrease the COD, BOD, and surfactant contents of coloured solution during the treatment of textile effluents.

According to Soni et al. (2017), the use of dimensionally stable anodes (DSA) and boron-doped diamond (BDD) electrodes were studied for the degradation of RB5 in batch and continuous operation. The DSA electrodes that consist of  $\text{TiPtO}_x\text{-RuO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  were prepared by thermal deposition method. All experiments were carried out in a glass reactor with 500 mL of synthetic wastewater containing 100 mg/L RB5 in 4 mg/L of NaCl as a supporting electrolyte. The reactor was fully equipped with an anode of Nb/BDD or Si/BDD, and a cathode of stainless steel plates similar in size to BDD. The removal of RB5 by BDD electrodes was evaluated in terms of colours, TOC, and COD removal. The electrochemical behaviour of DSA and BDD electrodes was investigated using the voltammetry method. The high oxygen over potential of BDD electrodes may aid in the oxidation of organic pollutants, whereas complete oxidation is not possible on the DSA electrode due to oxygen evolution. The degradation efficiencies of RB5 on Nb/BDD and Si/BDD were very efficient, resulting in complete colour removal and a COD reduction of more than 85%. A similar treatment of RB5 in synthetic wastewater was investigated in a constant flow treatment system, with  $\text{TiPtO}_x\text{-RuO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$  used in the first two tanks and one of the BDD electrodes used in the third tank. The

results revealed that a high proportion of wastewater was treated in the continuous process, and that the dual effects of two different electrodes led to a higher TOC reduction.

Ruan and Xie (2020) studied that the sulfur/nitrogen co-doped activated carbon fiber (S/N-ACF) is conducted by thermal treatment of thiourea-bonded hydroxyl-rich carbon fiber, which can bond the decomposition products of thiourea via hydrogen bond interaction. The surface density and thickness of the carbon fibre (CF,  $1 \times 4 \text{ cm}^2$ ) were measured and found to be  $6.6 \text{ mg/cm}^2$  and  $2.0 \text{ mm}$ , respectively. The electrochemical activation of CF was carried out in a standard three-electrode cell with an electrolyte of  $3.0 \text{ M H}_2\text{SO}_4$ . The counter electrode was platinum, the working electrode was CF, and the reference electrode was saturated calomel electrode (SCE). The electrolyte for S/N-ACF was  $1.0 \text{ M H}_2\text{SO}_4$  solution. The dye sorption method was used to investigate the CF-OH, CF-O, and CF adsorption to methylene blue (MB). CF is electrochemically oxidised (CF-O), then reduced electrochemically to form CF-OH, followed by a high temperature treatment of CF, CF-O, and CF-OH impregnated with thiourea to produce S/N-CF, S/N-CFO, and S/N-ACF, respectively. S/N-ACF has a much higher S/N doping degree than S/N-CF, according to thermogravimetric analysis. S/N-ACF has a higher cycling durability than S/N-CF-O, with nearly 99.75% capacitance retention after 10,000 cycles. S/N-CF, S/N-CF-O, and S/N-ACF with high S/N doping levels have a highly active site to improve performance and a high delocalization electron to improve rate capability and conductivity.

## 2.4 Composite electrodes

Composite is a mixture of material which consists of conductor and insulator. Composite electrodes are materials that formed from the mixture of elements. It can often be fabricated with better flexibility in the shape and size of the substance and allowing easy adaptation to various kinds of electrode configurations. Besides, it has a greater signal-to-noise ratio and the versatility to supply a means of incorporating sensitivity or selectivity enhancers into the bulk electrode substance either through chemical modification of the conductors or the insulator phases (Silva et al., 2020).

In addition, composite electrode produces larger surface area for absorption of contaminant, high energy and power density, and high specific capacitance (Mousavi et al., 2017). Composite electrode has higher oxygen evolution overpotential and stability than single electrode (Yao et al., 2019). Several studies have found the application of composite electrodes in the degradation of pollutants such as titanium/plumbum oxide-samarium oxide (Ti/ PbO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub>) composite electrode (Zhang et al., 2019), expanded graphite based composite electrode (Liu et al., 2013) carbon black diamond composite electrode (Ajeel et al., 2017), cesium plumbum oxide zirconium oxide (Ce-PbO<sub>2</sub>/ZrO<sub>2</sub>) composite electrode (Yao et al., 2019), and TiO<sub>2</sub>/Ti composite electrode (Bennani et al., 2015) as listed in Table 2.2.

**Table 2.2** The performance of selected composite electrodes in the wastewater treatment from previous studies

No.	Composite electrodes	Pollutants	Parameters	Performances			Ref.
				Colours	TOC	COD	
1	Expanded graphite	Phenol	[A] <sub>0</sub> = 100 mg/L, [Na <sub>2</sub> SO <sub>4</sub> ] = 0.05 M, curr. dens. = 30 mA/m <sup>2</sup> , t = 150 min, pH = 7.7	77.8	-	-	Liu et al. (2013)
2	Carbon black diamond	Phenol	[Na <sub>2</sub> SO <sub>4</sub> ] = 0.25 M, curr. dens. = 30 mA/cm <sup>2</sup> , t = 360 min, pH = 3, T = 25°C	94	-	-	Ajeel et al. (2017)
3	Ce-PbO <sub>2</sub> /ZrO <sub>2</sub>	Acridine orange	[A] <sub>0</sub> = 30 mg/L, curr. dens = 50 mA/cm <sup>2</sup> , t = 90 min, pH = 5.0, T = 30°C	100	-	76	Yao et al. (2019)
4	TiO <sub>2</sub> /Ti	Phenol	Curr. dens = 8.4 × 10 <sup>-2</sup> mA/cm <sup>2</sup> , t = 240 min, pH = 7	62	-	-	Bennani et al. (2015)

\*[A]<sub>0</sub> = Initial concentration, Curr. dens = current density, [ ] = electrolyte concentration, t = electrolysis time, T = temperature, Ce-PbO<sub>2</sub>/ZrO<sub>2</sub> = Cesium plumbum oxide zirconium oxide, TiO<sub>2</sub> = Titanium dioxide

Zhang et al. (2019) investigated how a titanium/plumbum oxide-samarium oxide (Ti/PbO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub>) composite electrode with high electrocatalytic activity was successfully fabricated and analysed for electrochemical degradation of alizarin yellow R (AYR) wastewater using the electrodeposition method. The crystal structure of PbO<sub>2</sub> and PbO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> coating particles was determined using XRD. The AYR was electrocatalytically degraded using a Ti/PbO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> composite electrode as anode and stainless steel as cathode, with 0.25 M Na<sub>2</sub>SO<sub>4</sub> as the supporting electrolyte. The AYR wastewater concentration was 80 mg/L, the pH was

adjusted to 5 with 1.0 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M NaOH, and the plate space between anode and cathode was 3.0 cm. COD was used to investigate the effect of electrode on COD removal efficiency. The results showed that the Ti/PbO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> composite electrode has high stability and excellent electrocatalytic activity, and it can successfully degrade AYR with a COD removal efficiency of 79.90% and a degradation efficiency of 80.00% under optimal conditions (0.25 M Na<sub>2</sub>SO<sub>4</sub> electrolyte concentration, plate space 3.0 cm, initial pH 5, cell voltage 3.0 V, and electrolysis time 150 min).

Umukoro et al. (2017) studied the photo-assisted electrochemical degradation of 2-nitrophenol using tungsten trioxide-exfoliated graphite (WO<sub>3</sub>-EG) composite electrode. FTIR analysis was used to study the existence of functional groups and chemical interactions among the prepared tungsten trioxide (WO<sub>3</sub>) and exfoliated graphite (EG). The electrochemical behaviour of EG and WO<sub>3</sub>-EG was investigated using voltammetry. The results showed that WO<sub>3</sub>-EG had a higher peak current than EG electrode due to an increase in electrode active surface area, which improved the conductivity of the WO<sub>3</sub>-EG composite electrode. Electrochemical process was performed using WO<sub>3</sub>-EG as anode and platinum foil as cathode. It was performed in a 100 mL reactor containing 20 mg/L of 2-nitrophenol and 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution as the supporting electrolyte, with a current density of 10 mA/cm<sup>2</sup>, a time of 180 min, and a pH of 6. UV and TOC analysis were used to study the removal efficiency of 2-nitrophenol. Compared to EG electrode (54% of removal), WO<sub>3</sub>-EG demonstrated higher removal efficiency (82%) and TOC removal (69%).

Yu et al. (2021) investigated the electrocatalytic degradation of sulfamethazine (SMT) by using iridium oxide-ruthenium oxide (IrO<sub>2</sub>-RuO<sub>2</sub>) composite electrode. The surface micromorphology of the electrode was studied