



UNIVERSITI TEKNOLOGI MARA

**TREATMENT OF TARTRAZINE BY ELECTRO-FENTON
PROCESS USING USED BATTERIES**

AINA NASUHA BINTI ABDUL AZIZ

**BACHELOR OF SCIENCE (Hons.) CHEMISTRY WITH
MANAGEMENT
FACULTY OF APPLIED SCIENCES
UNIVERSITI TEKNOLOGI MARA**

AUGUST 2023

**TREATMENT OF TARTRAZINE BY ELECTRO-FENTON PROCESS
USING USED BATTERIES**

AINA NASUHA BINTI ABDUL AZIZ

**Final Year Project Report Submitted in
Partial Fulfilment of the Requirements for the
Degree of Bachelor of Science (Hons.) Chemistry with Management
in the Faculty of Applied Sciences
Universiti Teknologi MARA**

AUGUST 2023

This Final Year Report Project entitled “**Treatment of Tartrazine by Electro-Fenton Process using Used Batteries**” was submitted by Aina Nasuha binti Abdul Aziz, in partial fulfilment of the requirement for Degree of Bachelor of Science (Hons.) Chemistry with Management, in the Faculty of Applied Science, and was approved by

Nurhafizah Binti Mohd Selihin

Supervisor

B. Sc. (Hons.) Chemistry with Management

Center for Applied Sciences Studies

Universiti Teknologi MARA Cawangan Sarawak

93400 Kota Samarahan

Sarawak

Nurhafizah Binti Mohd Selihin

Project Coordinator

B. Sc. (Hons.) Chemistry with

Management

Center for Applied Sciences Studies

Universiti Teknologi MARA

Cawangan Sarawak

93400 Kota Samarahan

Sarawak

Ts. Dr. Siti Kartina Binti Abdul Karim

Head

Center for Applied Sciences Studies

Universiti Teknologi MARA

Cawangan Sarawak

93400 Kota Samarahan

Sarawak

Date: 8 August 2023

ACKNOWLEDGEMENTS

All praises to Allah, God Almighty, for granting me strength to power through this final year project. I would like to express heartfelt gratitude to my supervisor, Madam Nurhafizah binti Mohd. Selihin for her tremendous guidance and knowledge throughout the span of the project. I am also genuinely thankful to the dedicated and helpful lab staffs, Puan Fathymah, Cik Siti, and others as well. I got lucky as my fellow batch mates and my dear friends, Shafiqah, Kun, Melvina, Ria, and Irsyad were always cooperative and compassionate. Finally, I am forever grateful and thankful to my beloved parents and family who have recited prayers, encouragement, and support throughout this brief part of my academic journey.

(Aina Nasuha binti Abdul Aziz)

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENT	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF ABBREVIATIONS	ix
ABSTRACT	x
ABSTRAK	xi
CHAPTER 1 INTRODUCTION	
1.1 Background and problem statement	1
1.2 Significance of study	5
1.3 Objectives of study	6
CHAPTER 2 LITERATURE REVIEW	
2.1 Advanced Oxidation Process (AOP)	7
2.2 Electro-Fenton	9
2.2.1 Factors affecting Electro-Fenton process.	11
2.2.1.1 Electrodes	11
2.2.1.2 Catalyst	12
2.2.1.3 Optimal conditions	13
2.3 Azo Dyes	15
2.3.1 Tartrazine	17
CHAPTER 3 METHODOLOGY	
3.1 Materials	20
3.1.1 Chemicals	20
3.1.2 Apparatus	20
3.2 Experiment setup	21
3.2.1 Graphite electrodes	22
3.2.2 Electrolysis setup	23
3.3 Experimental design	24
3.3.1 Contact time	24
3.3.2 Concentration	25
3.3.3 Catalyst	25
3.3.4 Voltage	25
3.4 Analysis using UV-VIS Spectrophotometer	26
3.5 Kinetic study	28

CHAPTER 4 RESULTS AND DISCUSSION	
4.1 Effect of contact time.	29
4.2 Effect of initial concentration of dye.	33
4.3 Effect of concentration of catalyst.	35
4.4 Effect of voltage.	36
4.5 Kinetic study	38
CHAPTER 5 CONCLUSION AND RECOMMENDATIONS	40
CITED REFERENCES	42
APPENDICES	48
<i>CURRICULUM VITAE</i>	50

LIST OF TABLES

Table	Caption	Page
2.1	Summary of previous studies on various pollutants treatment using EF.	14
2.2	Summary of previous studies on tartrazine removal in wastewater.	19
3.1	Optimal Conditions Findings	26
4.1	Kinetic Analysis Table	38

LIST OF FIGURES

Figure	Caption	Page
2.1	Examples of common azo dyes.	16
2.2	Structure of Tartrazine.	17
3.1	Flow chart of the research process.	21
3.2	Used non-functioning batteries.	22
3.3	Graphite rods extracted from dry cells.	22
3.4	Electrode made from resin attached graphite rods.	22
3.5	EF setup.	23
3.6	EF setup powered by 1.5 V battery.	24
3.7	Electrodes submerged into beaker.	24
4.1	Decolourisation results over time.	29
4.2	Removal efficiency of TZN using EF for six hours contact time.	30
4.3	Structure of tartrazine (azo compound).	31

4.4	Percent removal against time for 10,20 and 30 ppm initial concentration of tartrazine.	33
4.5	Contamination due to rust.	34
4.6	Percent removal against time for various concentrations of catalyst.	35
4.7	Removal efficiency of tartrazine under 1.5,3 and 4.5 V current density.	36
4.8	Reaction order graphs.	39

LIST OF ABBREVIATIONS

AOP	:	Advanced Oxidation Process
COD	:	Chemical oxygen demand
EF	:	Electro Fenton
FeSO ₄	:	Iron (II) sulphate
H ₂ O ₂	:	Hydrogen peroxide
H ₂ SO ₄	:	Sulphuric acid
Na ₂ SO ₄	:	Sodium sulphate
OH [·]	:	Hydroxyl radical
ppm	:	Parts per million
TOC	:	Total organic compounds
TZN	:	Tartrazine
UV-Vis	:	Ultraviolet Visible Spectroscopy

ABSTRACT

TREATMENT OF TARTRAZINE BY ELECTRO-FENTON PROCESS USING USED BATTERIES

This study focuses on the use of Electro Fenton process for degradation of tartrazine, a type of azo dye. The degradation is achieved by reactions with hydroxyl radicals ($\text{HO}\cdot$) which are produced from Fenton reaction in a reactor consisting of 2 cm^2 of electrodes made of graphite cylinders from used batteries. Used batteries are one of the many types of hazardous wastes. They are scheduled wastes which means that they must be sent to recycling centres for proper treatment. Once they are improperly being discarded to the landfill, they pose a harmful threat towards the ecosystem. Utilizing these types of material is a driving factor towards sustainability and cost saving wastewater treatment. Electro Fenton utilizes the use of Fenton reagent as catalyst. The analysis of the experiment was done by using Ultraviolet Visible Spectroscopy (UV-Vis) to determine removal efficiency of tartrazine in wastewater. Variables studied were contact time, initial dye concentration, catalyst concentration and applied voltage. Color removal efficiency reached 97.87% for the three hours contact time, dye initial concentration of 10 ppm, Fe^{2+} catalyst = 0.3 mM at applied voltage = 4.5 V with equal sizes of electrodes. Under these conditions, kinetics study revealed that dye removal takes place through a second-order reaction.

ABSTRAK

RAWATAN TARTRAZIN MELALUI PROSES ELEKTRO-FENTON MENGUNAKAN BATERI TERPAKAI

Kajian ini memfokuskan proses Elektro Fenton untuk merawat dan melupuskan tartrazin iaitu sejenis pewarna azo. Keberhasilan perlupusan dicapai melalui pendedahan dengan radikal hidrosil ($\text{HO}\bullet$) yang terhasil daripada reaksi Fenton di dalam reaktor yang diletakkan 2 cm persegi elektrod diperbuat daripada silinder grafit daripada bateri terpakai. Bateri terpakai adalah termasuk dalam kategori sisa buangan berbahaya. Ia merupakan sisa buangan terjadual dimana ia hendaklah dihantar ke tapak pelupusan kitar semula untuk dilupus dengan kaedah yang betul. Apabila dibuang ke tapak pelupusan sampah dengan cara yang salah, ianya berpotensi besar untuk memberi impak buruk terhadap ekosistem. Menggunakan silinder grafit daripada bateri terpakai ini memberikan satu bentuk batu loncatan terhadap kelestarian dan penjimatan kos dari segi pengurusan sisa air kumbahan. Elektro Fenton menggunakan reagen Fenton sebagai pemangkin. Analisis eksperimen diperoleh menggunakan instrumen Spektroskopi Kelihatan Ultraungu (UV-Vis) untuk mengenal pasti kecekapan kelunturan tartrazin dalam sisa air kumbahan. Pemboleh ubah yang diteliti adalah tempoh rawatan, kepekatan permulaan pewarna, kepekatan pemangkin dan daya tenaga. Justeru, kecekapan kelunturan mencapai 97.87% selama tiga jam, kepekatan permulaan pewarna dengan 10 ppm, pemangkin $\text{Fe}^{2+} = 0.3 \text{ mM}$ serta voltan sebanyak 4.5 V dengan dua saiz elektrod yang sama. Di bawah kondisi ini, kajian kinetik kelunturan pewarna tercapai melalui tindak balas pesanan kedua.

CHAPTER 1

INTRODUCTION

1.1 Background and problem statement

Clean water is essential to the ecosystem. As the world population increases, there is increasing demand of clean water supply. On 15 November 2022, United Nations have estimated the citizens of the world to exceed 8 billion lives marking the day as 'Day of 8 billion' (United Nations, 2022). There are 2.1 billion communities who were unable to gain clean water supply with 3.4 million deaths occurred from water contamination issues (Quraishi *et al.*, 2022). World Health Organization (WHO) has reported that by considering low and middle-income families, one in four of them have lack access to clean water (Quraishi *et al.*, 2022).

Wastewater contains a lot of contaminants which are hazardous to the surrounding and for our consumptions. They flowed from various types of water such as at the surfaces, atmospheres, spaces, and groundwaters (Syahrani *et al.*, 2022). Common pollutants would be pesticides, pharmaceutical drugs, heavy metals, and dyes (Kadji *et al.*, 2021). Midassi *et al.*, (2020) stated that current Covid-19 pandemic eventually contributes to high contamination of chloroquine which is a type of antimalarial and antiviral drugs being prescribed to patients. Annually, about 70% of dyes

released contained azo group structures which are organics (Khan *et al.*, 2020). Synthetic dyes are preferable in the industry as they have low manufacturing cost, highly pigmented appearances as well as high stability properties (Albasher *et al.*, 2020). Synthetic dyes belong to the category of emerging pollutants as they are too hydrophilic to be in adsorption phase and have higher resistant to biodegradation (Benkhaya *et al.*, 2020; Silva & Fracacio, 2021). It is also due to aromatic amines produced from reduction of azo groups which can be hazardous (Albasher *et al.*, 2020).

Back then, it was easier to get access to the pristine waters from wells and streams. Archipelago communities in Makassar city are those who still uses classical tools of retrieving clean water through drilling wells and building water reservoirs (Syahrani *et al.*, 2022). However, this is not the case for many who now live in urbanization and populous cities. Water scarcity initiated the need for treatment of wastewater which produces the idea of building wastewater treatment plants with variety of approaches (Lucas *et al.*, 2021). Nowadays, conventional wastewater treatment processes include flocculation, reverse osmosis, adsorptions, activated sludges and many more (Khan *et al.*, 2020).

Recent studies have found that Advanced Oxidation Processes (AOPs) ensure effective water treatment method compared to conventional methods such as filtrations and coagulations (He & Zhou, 2017; Kadji *et al.*,

2021). In fact, its electrochemical prospect is found to be cheaper in terms of cost compared to chemical coagulation method (Zazou *et al.*, 2019). AOPs could produce large hydroxy radicals which ensure rapid and fast reactions to degrade organic pollutants (Midassi *et al.*, 2020). An example of AOPs is Electro-Fenton (EF) method. In EF, the electrolytic cell is composed of ferrous salt or Fenton reagent as catalyst with hydrogen peroxide being continuously supplied in acidic solution (Li *et al.*, 2022; Martone *et al.*, 2022).

Electro-Fenton process in this study focuses on treatment of tartrazine in wastewater by utilizing e-waste as the source of graphite electrodes. Firstly, tartrazine is a type of azo dyes with yellow colour that could somehow ended up in wastewater coming mainly from textile industries, food factories, cosmetics, and pharmaceutical industries (Albasher *et al.*, 2020; Sahin & O. I, 2021). Although less hazardous, it has mutagenic properties that contribute to jaundices, acute seizures, heart palpitations, vomiting, kidney failures and many more (Khan *et al.*, 2020; Wakrim *et al.*, 2022).

Then, increasing numbers of electronic wastes (e-wastes) being dumped on landfills becomes an alarming issue. E-wastes contain toxic heavy metals such as lithium, lead, cadmium, and mercury that could disrupt the food chains and quality of environment (Kadji *et al.*, 2021). Among the

highest sources of lead contaminations are from monitors, acid batteries and power circuits (Igbo *et al.*, 2022). These contaminants are accumulated in the leachate, which is extremely polluted with suspended particles of heavy metals and toxic substances massively undergoing microbiological and physical activities (Wdowczyk & Szymanska-Pulikowska, 2020). Zaini *et al.*, (2022) have studied the sample of leachate in a landfill located at Simpang Renggam, a town located in Johor, Malaysia and it was found that metal concentrations of arsenic (As) and lead (Pb) were 0.054 mg/L and 0.110 mg/L respectively, which exceeded the requirements in Environmental Quality Act 1974 (EQA 1974). Malaysia is the second largest country in Southeast Asia to produce e-wastes and only 10% are being recycled out of 50 million tonnes generated (Razip *et al.*, 2022). As countries in Asia were found to have low standardization for proper e-waste management, European countries such as Sutherland and Slovakia are among biggest example in implementing battery recycling activities where 60% used batteries are being recycled (Kadji *et al.*, 2021).

One of the prevention techniques that can be used to reduce the volume of toxicity contributed by e-waste at landfills is by reusing parts the materials that they contained. In Electro-Fenton process, the use of ideal electrodes is one of the parameters for effective degradation of azo dyes (Nordin *et al.*, 2019; Wdowczyk & Szymanska-Pulikowska, 2020). Material made of graphene is preferred as it has unique pi-interaction with metal species (An *et al.*, 2022). Apparently, commercial batteries are composed

of carbonaceous material (Zhang *et al.*, 2019). The term ‘urban mining’ can be described for this process as it is an effort to recover raw materials to be sent to landfills as there is 90% graphite incorporated to these used Lithium-ion batteries (Zensich *et al.*, 2022). Previously, exploration by Kadji *et al.*, (2021) has given confident result towards this sustainability effort due to success of degradation of amoxicillin; a type of medical waste, by using EF with used batteries have yielded 74% mineral efficacy with 95% degradation of said compound.

1.2 Significance of study

Establishment of optimal parameters for Electro-Fenton process could promote efficiency of wastewater treatment in the field of Environmental Chemistry. As there are increasing development of industrial zones in the world, unwanted components in discharged waters are at alarming rate and thus contribute to environmental issues (An *et al.*, 2022). Within AOPs principle, hydroxyl radicals produced are meant for larger impact for degradation of organic compounds. Thus, along with quite exceptional electrical energy needed, electrolysis of water is a straightforward system to foster hydrogen without contaminations from sulphur and carbons (Samsudeen *et al.*, 2020). Most importantly, parameters such as types of electrodes, current flows and pH values are crucial to be evaluated to ensure the effectiveness of EF application (Zazou *et al.*, 2019).

Recently, graphite becomes quite an expensive material due to the increasing demand of advancement of electric vehicles that require lithium-ion batteries as well as massive manufacturing of electronic devices (Natarajan *et al.*, 2022; Razip *et al.*, 2022). Therefore, in this study, our effort is to use used graphite which implies towards saving and utilizing the raw materials. Though this is indeed a micro scale project, it is hoped that it could be one of the many factors to enhance the pilot study in industry level.

1.3 Objectives of study

- I. To determine the removal efficiency of tartrazine when used batteries are being used as graphite electrodes in Electro-Fenton process.
- II. To investigate the optimal conditions of used batteries as graphite electrodes in Electro-Fenton process for tartrazine removal.

CHAPTER 2

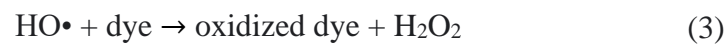
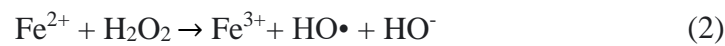
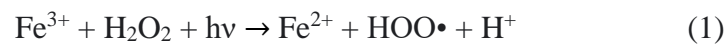
LITERATURE REVIEW

2.1 Advanced Oxidation Process (AOP)

Advanced Oxidation Process (AOP) is a process that utilizes hydroxy radicals, HO• to eliminate organic compounds in a solution. HO• is a powerful oxidizer to degrade and remove the existence of unwanted and hazardous organic compounds (Kord Forooshani *et al.*, 2020; Muzenda *et al.*, 2022). When there is a presence of hydroxy radicals from electrode potential, the free reactions with organic compounds would result in dehydroxylated and dehydrogenated products which means that the subject of interest is by right, becomes fully mineralized (Wakrim *et al.*, 2022). Upon mineralization, they could become by-products that will reduce water toxicity released to the ecosystem (Martini *et al.*, 2019). Generally, AOP is endorsed as tertiary treatment when there is only slight amount of chemical oxygen demand (COD) in wastewater (Rueda-Márquez *et al.*, 2020). In addition, AOPs cover several approaches which are H₂O/UV, photocatalytic, Fenton, electrochemical oxidation as well as ozonolysis (Selihin & Tay, 2022). AOP can be divided into two types of classes which are photochemical and non-photochemical. Akbari *et al.*, (2021) noted that the first type of AOP; photochemical, consists of homogenous and heterogenous processes while the latter include Fenton, wet air oxidation, ozonation cavitation and ozone-peroxides and more.

Fenton could be unconvincing since they possessed the oxidation process for metal ion Fe^{3+} to Fe^{2+} as a slow rate as well as very short $\bullet\text{OH}$ half-life evolution which is at 10^{-9} s. (He & Zhou, 2017; Kord Forooshani *et al.*, 2020). Therefore, modifications were made to carry upward the feasibility of the method such as applying photo-Fenton that introduces the uses of ultraviolet (UV) light (Kord Forooshani *et al.*, 2020). $\text{H}_2\text{O}/\text{UV}$ is one of the examples of photo-Fenton process.

Photo-Fenton is widely being applied by scientists alike. Khan *et al.*, (2020) has presented the mechanisms oxidation of dye using the said method as below:



From the equations (eq.1-3), hydroxy radicals are produced from hydrogen peroxides with $h\nu$, the light photon as inhibitor. Due to the addition of the radicals, azo dye degrades in line with the $-\text{N}=\text{N}-$ breaking moment in the compound (Khan *et al.*, 2020). Particularly, the metal ions are acting as coagulants that aids in disruptions of organic compounds (He & Zhou, 2017).

Besides that, ozonolysis has also made its way as a reassuring type of AOP due to its wide pH employability as well as cost effective treatment because unreacted ozone could decompose to oxygen (Bhad *et al.*, 2022). The equation (eq.4) below emphasis that reaction of ozone gas (O₃) with peroxide, H₂O₂ would produce highly reactive species of hydroxy radicals that could easily oxidized contaminants (Liu *et al.*, 2021).



This process can be simply conducted by channeling or bubbling ozone gas from generator to the water tank and expanded its further procedure through filtration systems (Bhad *et al.*, 2022). Since this study was conducting on only one AOP method, the next section discusses more on Electro-Fenton.

2.2 Electro-Fenton

In AOP, Electro-Fenton (EF) method is derived from the process of electrolysis and the application of Fenton reagent. Fenton reagent is made up of ferrous ion (Fe²⁺) and solution of hydrogen peroxide, H₂O₂ (Martone *et al.*, 2022). This process is taking up the usage of direct current (DC) ensuring the operation cycles for both oxidation and reduction onto graphite electrodes (He & Zhou, 2017; Divyapriya & Nidheesh, 2020). The need to have a continuous process towards degradation of unwanted chemical in the wastewater treatment has becoming a driven factor for scientists to develop something that could effectively eliminated those constituents. Sutherland

et al., (2020) justified that methods such as ultrafiltration (UF) and microfiltration (MF) would have far more energy requirement, scaling and facing limitation issues compared to electrolysis treatment. Besides, EF application utilizes transition metal catalyst, specifically iron-based, that implies on substrates while H₂O₂ are being generated in-situ (Liu *et al.*, 2020). EF is an indirect electro-oxidation (EO) because to oxidize pollutants, H₂O₂ must first be able to produce HO• in the presence of metal catalyst (Zazou *et al.*, 2019; Selihin & Tay, 2022). According to He & Zhou, (2017), the electrolysis using Fenton reagent is one of the most desired, inexpensive, safe, and effective method in AOP.

Below is the schematic equation on degradation of dyes from formation of hydroxy radicals generated by Fe²⁺ (Wakrim *et al.*, 2022).



Wakrim *et al.*, (2022) proposed that the condition for the electrolytic process is first, initiated in acidic medium with reduction of oxygen at cathode, as shown in (eq.5). Then, formation of peroxide H₂O₂, interacts with Fe³⁺ resulting towards the production of hydroxyl radicals at (eq.6). Only small amount of Fe²⁺ catalyst is required because the cathodic reduction of Fe²⁺ is associated with the generation of Fe²⁺ ion (eq.7). In

addition, acidic pH is also needed as in (eq.6), it could produce $\text{Fe}(\text{OH})_3$ that reduces the amount of active catalyst, Fe^{2+} (Selihin & Tay, 2022). Therefore, to perform excellent efficiency of EF process, few factors and parameters must be evaluated and determined to ensure its effectiveness.

2.2.1 Factors affecting Electro-Fenton process.

2.2.1.1 Electrodes

In terms of cathode preferences for electro-Fenton process, Kadji *et al.*, (2021) said that they must be able to have a proper cathode material, efficiently generates H_2O_2 , exhibit low catalytic activity for reduction and high prospect of evolution of hydrogen gas in acidic medium. Recent studies on graphite electrodes are becoming subjects of interest. For heterogenous EF reactions, Gao *et al.*, (2022) have studied on needle coke electrode; a type of grey solid carbon material with a metallic element, to have profound increase on efficiency when it shows increase from 42.2% to 63.1% COD removal when voltage is being increased from 6 V to 9 V. This corresponds to Faraday First Law because the increase of voltage increases the chemical activity on electrodes, which is in this case, contributes to H_2O_2 activation (Gao *et al.*, 2022). Next, according to Nordin *et al.*, (2019), electrodes with composites such as cobalt/graphite-polyvinyl chloride (Co47.5/C47.5-PVC5) allow synergistic effects that have caused high removal of pollutants such as chemical oxygen demand (COD) at 91.5% removal and removal of

biochemical oxygen demand (BOD) at 81.2%. Additionally, for Platinum (Pt) electrodes, Nair *et al.*, (2021) stated that they reduced the chances to degrade organic pollutants as they initially had strong interactions with H₂O₂ while highly electronegative atoms such as Fluorine doping could easily provide active sites for the desired radicals. In most cases, electrodes preferences in homogenous EF would be less dependent by Fenton reagent being used as compared to heterogeneous EF because no substrates are implemented in the catalyst system and thus eliminating mass transport perspectives (Liu *et al.*, 2020).

2.2.1.2 Catalyst

Elevating the amount of EF catalysts lead towards an increase of the pollutants' rate of degradation (Dugandžić *et al.*, 2018; Khan *et al.*, 2020). A study of amoxicillin degradation by EF from Kadji *et al.*, (2021) showed that when concentration of Fe²⁺ catalyst increased from 0.1 to 1 mmol. L⁻¹, the percentage of mineralization improves from 57% to 74% while further increase of concentration 1 to 2 mmol. L⁻¹ results in no improvement. Similar results were obtained by Adachi *et al.*, (2022) in which there is a decrease in dye removal efficiency from 93.09% to 92.01% when Fe²⁺ concentration is being increased form 0.2 mM to 0.3 mM. This is because excess ferrous ions may have generated undesired iron sludges which inhibited further degradation of organic pollutants (Adachi *et al.*, 2022). Although this study focuses more on homogeneous EF, the contribution towards success rate in heterogeneous EF process might as well due to

magnetite (Fe_3O_4) have properties that makes it suitable as EF enhancer when it possesses high rate of stability, ideal electrical properties and sustainability to ensure completion in EF cycle (Selihin & Tay, 2022). This has been proven by Muzenda & Arotiba, (2022) when aspirin removal efficiency achieved was 100% as they synthesized magnetic nanoparticles onto carbon felt cathodes.

2.2.1.3 Optimal conditions

In EF applications, parameters such as current density, contact time of electrolysis are needed to be evaluated to ensure desired efficiency (Zazou *et al.*, 2019). During electrolysis, continuous air is needed to ensure vigorous in-situ hydrogen peroxides being produced. Muzenda *et al.*, (2022) had employed bubbling air using air pump at the rate of $1 \text{ L}\cdot\text{min}^{-1}$. Wakrim *et al.*, (2022) studied that constant stirring must be applied during electrolysis to avoid precipitations of ferric hydroxides. Besides that, Adachi *et al.*, (2022) has concluded that increasing current density improves the efficiency of reaction. In addition, heterogenous EF would most likely works with various pH values (Jafari Rad, 2020; Muzenda *et al.*, 2022). Most studies have emphasized pH at the value of 3 would exhibit excellent efficiency of EF reaction as acidity promotes the reactions of H_2O_2 to produce hydroxyl radicals (Zazou *et al.*, 2019; Khan *et al.*, 2020; Liu *et al.*, 2020; Midassi *et al.*, 2020; Adachi *et al.*, 2022; Muzenda *et al.*, 2022; Wakrim *et al.*, 2022).

Table 2.1 Summary of previous studies on various pollutants treatment using EF.

Type of pollutants	Electrodes	Catalysts	Optimal conditions	Performance	References
Carmosine (Red Azo Dye)	Cathode: Pt-14 cm ² Anode: Graphite Carbon-3 cm ²	FeSO ₄ , 7H ₂ O (Fe ²⁺) Conc:0.2 mM	Current density: 200 mA cm ⁻² pH: 3	93% removal of dye in 1 contact hour.	Wakrim <i>et al.</i> , (2022)
Methylene Blue	Cathode: Carbon Fluoride CF-14 cm x 5.0 cm x 0.6 cm Anode: BDD on Niobium-10.0 cm x 4.0 cm x 0.2 cm	FeSO ₄ , 7H ₂ O (Fe ²⁺) Conc: 0.2 mM	Current density: 5 mA cm ⁻² pH: 3	94% TOC removal in 1 hour.	Zazou <i>et al.</i> , (2019)
Chloroquine drug, CLQ,	Cathode: Carbon cloth Anode: Boron Doped Diamond (BDD)	FeSO ₄ , 7H ₂ O (Fe ²⁺) / Na ₂ SO ₄ ,	O ₂ flow rate ¼ 80 mL/min Stirring rate:300 rpm pH: 3 Current density: 60 mA cm ⁻²	92% TOC removal at 2 contact hours.	Midassi <i>et al.</i> , (2020)
Antibiotic tetracycline	Carbon Nanotubes (CNT)	Gold Nanoclusters (AuNCs)	pH: 7.8 Potential difference (p.d.): 2.5 V	76.3% TC removal.	Liu <i>et al.</i> , (2020)
Tetracycline (Pharmaceutical pollutant)	Cathode: Graphite 23.5 cm × 5 cm x 0.5 cm Anode: Ti4O ₇ deposited on Titanium alloy 6 cm × 4 cm (HeteroEF)	Ilmenite (FeTiO ₃) nanoparticles (heteroEF process)	pH: 3 p.d.: 8 V	TOC removal: 61.4% in synthetic and 40% in real wastewater in 2 hours	Muzenda <i>et al.</i> , (2022)
Methyl Orange Azo Dye	Carbon graphite 1 cm x 1.5 cm x 10 cm, stainless-steel, 1 cm x 2.5 cm x 16 cm, (centre)	Fe ²⁺ : 0.232 mM 60 mg/L dye	pH: 3 I _c =80 mA MO = 60 mg/L	94.9% removal of dye during one hour process.	Adachi <i>et al.</i> , (2022)

2.3 Azo Dyes

The pollutant for this wastewater treatment research is a type of synthetic dye. The world will always be encapsulated and captivated with colours as they could give satisfactions and values. In addition, (Nordin *et al.*, 2019) stated that 100000 types of dyes were synthesized each year making it more than 0.7 million tonnes of world production. Dyes produced synthetically are 70% azo-type dye which means that it possesses N=N bond combined with aromatic ring (Khan *et al.*, 2020; Wakrim *et al.*, 2022). In the world of manufacturing, artificial colouring agents are constantly being used for enhancement and appearances for cosmetic products, food, pharmaceutical and many more. We obtained these colours through azo dyes. Dyes possesses aromatic and heterocyclic properties that could withstand surrounding threats such as temperatures, oxidation, decays and ozonation (Sahin & O. I, 2021). Next, they are produced from variety methods of diazotization and coupling conditions which determines their final yield, particle sizes and their appearances (Benkhaya *et al.*, 2020).

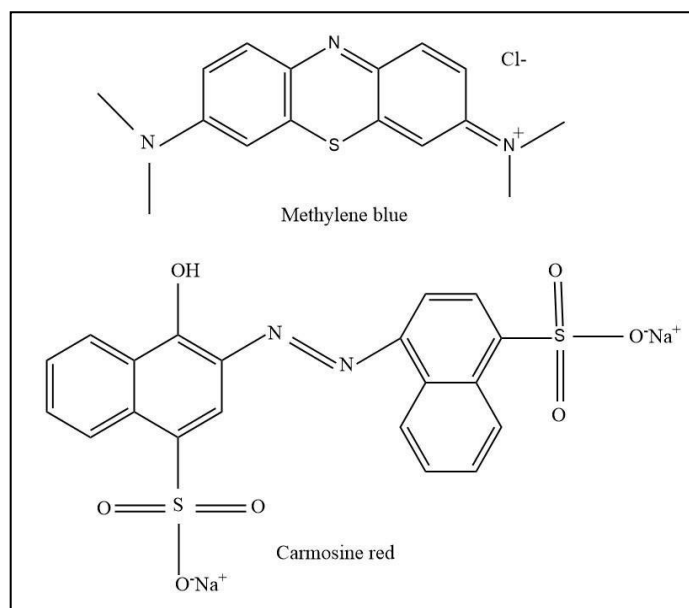


Figure 2.1 Examples of common azo dyes (Zazou *et al.*, 2019; Sahin & O. I, 2021).

Several studies on each type of azo dyes have been carried out. First, there is a common red colour dye called carmosine. Excess dose of this dye disrupts liver and downgrade enzymes that carry out metabolic activities (Sahin & O. I, 2021). Besides that, Sahin & O. I, (2021) also stated that it was proven to be true when they were able to increase some serum marker enzymes and lowered the activities of defensive genes in mice. As the release of azo dyes through streams are apparent to our naked eyes, it is also undeniable that they are affecting the aesthetics quality of water and capable to have profound effect to the aquatic ecosystem even in quantity as small as $<1 \text{ mgL}^{-1}$ (Nordin *et al.*, 2019). Thus, degradation of azo dyes is crucial to bring down their disadvantageous counterparts. Strength of azo dyes structure can be reduced upon reacting with peroxides, heat, or light (Benkhaya *et al.*, 2020).

2.3.1 Tartrazine

Tartrazine is an azo dye, notorious for its yellow colour. It has functionality of two sulphonic groups, a carboxylic group and an azo component, the N=N (Jafari Rad, 2020). The discovery of this compound is dating back to 1884 by Johann Heinrich Ziegler, a German scientist (May, 2018). Albasher *et al.*, (2020) indicated that they are widely found in sauces, energy drinks, candies and as well as skincare and beauty products. Recently, it has been regarded as cheaper substitute of pigment as compared to saffron and beta carotene pigments found in plants (Athira & Jaya, 2022). Besides that, Albasher *et al.*, (2020) had mentioned that since those of younger ages are prone to consume foods and drinks rich in colorants, they are among the risky generation to be exposed to this type of dye. Unfortunately, tartrazine has caused allergic reactions, destruction of DNA, severe asthmas and ADHD symptoms among children (Jafari Rad, 2020). Tartrazine has a chemical formula of $C_{16}H_9N_4Na_3O_9S_2$ and a molar mass of $543.40 \text{ g mol L}^{-1}$.

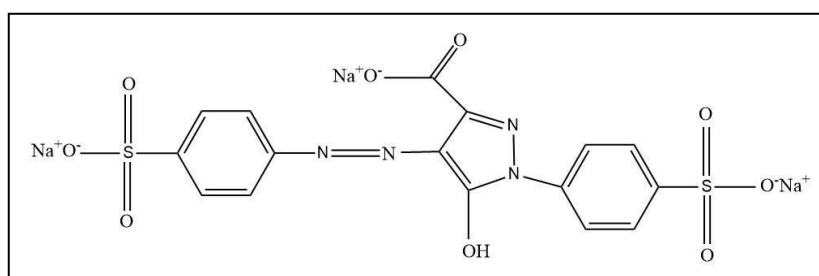


Figure 2.2 Structure of Tartrazine (May, 2018).

It gives colourless appearance once it is degraded or had undergo oxidation. Nevertheless, there are limited number of studies on EF treatment on this dye. A study by Dung *et al.*, (2022) concluded that decolorization efficiency of heterogenous EF, which peaked at 97% was higher towards tartrazine compared to homogenous EF, at 32.94% by using carbon felt (CF) electrodes while the latter used cobalt ferrite coated carbon felt ($\text{CoFe}_2\text{O}_4/\text{CF}$) as electrodes.

Next, Jafari Rad (2020) has found 98% removal efficiency of tartrazine using activated carbon as adsorbent and Copper Oxide (CuO) nanoparticles for effective treatment of the dye. Then, You *et al.*, (2022) have found tartrazine removal by the Zero-Valent Iron/Peroxymonosulfate (Fe^0/PMS) process to exhibit increase of efficiency from 43.1% to 75.4% when presence of chlorine ion as anion is employed in the system. Adsorption of tartrazine using Biochar-Mediated Zirconium Ferrite Nanocomposites in adsorption process produced highest removal percentage which peaked at around 80% at contact time 90 min when adsorption performance was observed during 15–480 min intervals (Perveen *et al.*, 2022).

Table 2.2 Summary of previous studies on tartrazine removal in wastewater.

Dye	Methods	Conditions	Removal efficiency	References
Tartrazine in wastewater	Removal Using Adsorption with Copper Oxide Nanoparticles on Activated Carbon	pH 2 Time: 60min Adsorbent: 0.5g	>80%	Jafari Rad (2020)
	Removal by the Zero-Valent Iron/Peroxymonosulfate Process	²⁻ , NO ³⁻ , HCO ³⁻ , and Cl ⁻ Cation: Ca ²⁺ , Cu ²⁺ , Mg ²⁺ , and Mn ²⁺	>50%	You <i>et al.</i> , (2022)
	Biochar-Mediated Zirconium Ferrite Nanocomposites	pH 2 Dose rate: 0.05 g Temperature: 30 °C Time: 360 min Conc: 100 mg/L	> 80%	Perveen <i>et al.</i> , (2022)

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Materials

3.1.1 Chemicals

Sulphuric Acid, H_2SO_4

Sodium Sulphate, Na_2SO_4

Iron sulphate, (FeSO_4)

Tartrazine, $\text{C}_{16}\text{H}_9\text{N}_4\text{Na}_3\text{O}_9\text{S}_2$

Used batteries (2 cm²)

3.1.2 Apparatus

Volumetric pipettes

Power supply

pH papers

Volumetric flasks

Fish Pump

Analytical balance

Distilled water

Cuvettes

Beakers

UV-Visible Spectrometer

3.2 Experiment setup

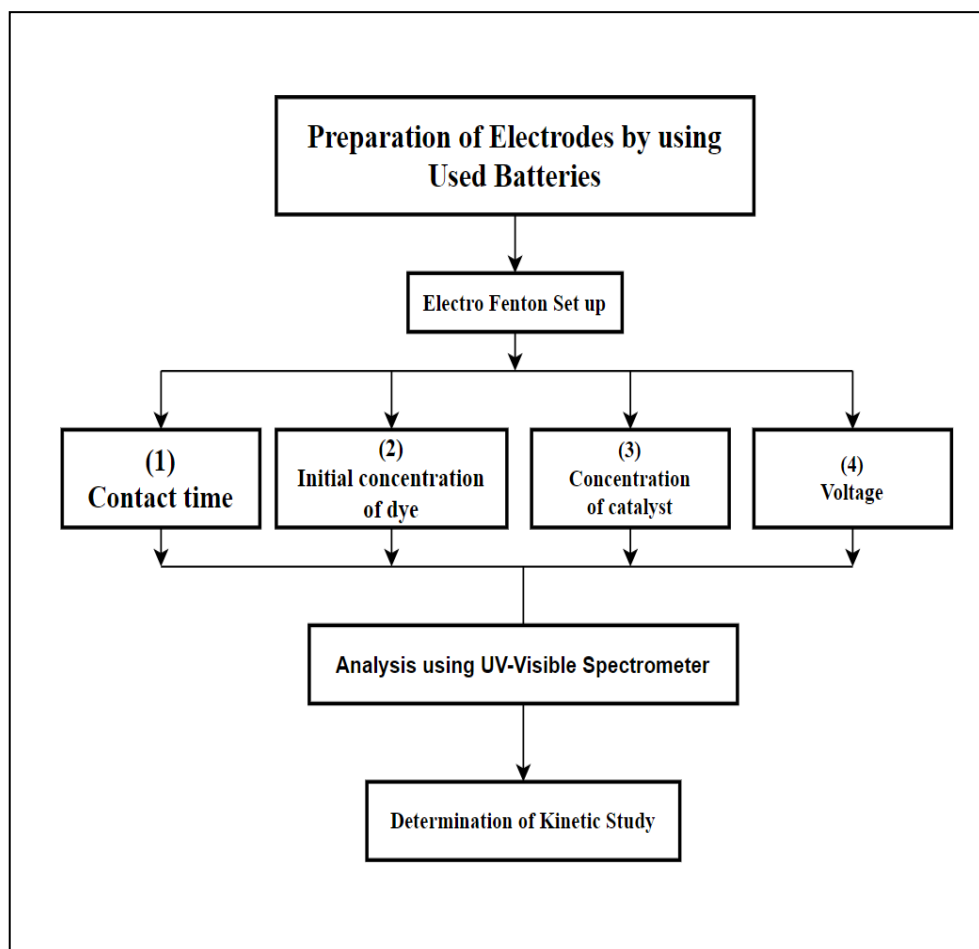


Figure 3.1 Flow chart of the research process.

3.2.1 Graphite electrodes

Carbon rod from used batteries were extracted by using pliers and gloves were used for safety precaution. Their sizes were modified into the area of 2 cm² as electrodes. Both were submerged into the beaker at approximately 1 cm distance with the surface area of 2 cm² (Cruz-González *et al.*, 2012).



Figure 3.2 Used non-functioning batteries.



Figure 3.3 Graphite rods extracted from dry cells

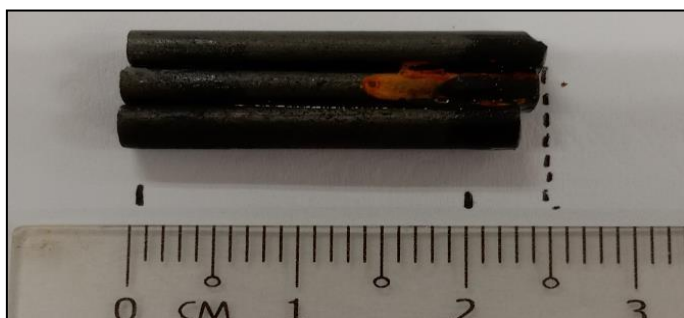


Figure 3.4 Electrode made from resin attached graphite rods.

3.2.2 Electrolysis setup

Commercially available fish pump was used to ensure continuous bubbles for rapid production of hydrogen peroxide (H_2O_2). Additionally, it could generate more O_2 , ensuring supply of hydrogen peroxide. Pump operation was kept run for 30 minutes prior to the starting of current flow. Besides that, the constant stirring effect will prevent precipitation of ferric hydroxides (Wakrim *et al.*, 2022). 10 ppm of tartrazine was prepared. The solution had been adjusted to pH 3 by addition of sulphuric acid, H_2SO_4 . After the addition of catalyst at 0.1 mM concentrations, 0.05 M Na_2SO_4 was added as a background electrolyte to induce conductivity. Then, electro-Fenton reaction will begin by starting the current flow.

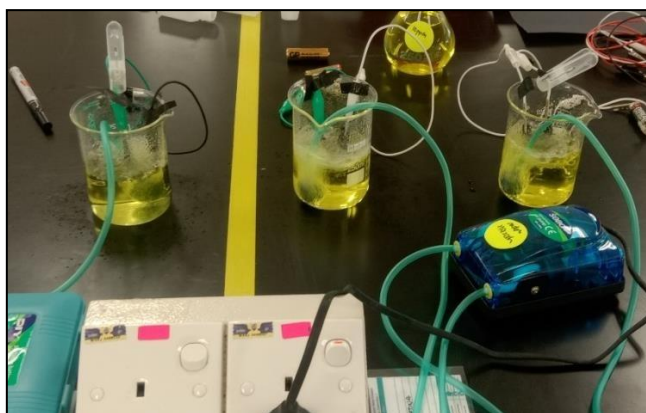


Figure 3.5 EF setup.



Figure 3.6 EF setup powered by 1.5 V battery.



Figure 3.7 Electrodes submerged into beaker.

3.3 Experimental design

3.3.1 Contact time

The initial conditions for electro-Fenton setup were fixed at 10 ppm dye, 1.5 V applied voltage, 25 °C (room temperature) and catalyst is 0.1 Fe^{2+} mM. The first cycle of this EF was evaluated for 6 hours. At each hour passed, sample was taken to measure the absorbance reading using UV-Vis Spectrophotometer. Optimal contact time (hour) was chosen at which the removal percentage is the highest (Moersidik *et al.*, 2020).

3.3.2 Concentration

Secondly, EF setup was started by using established optimal contact time at (3.3.1) followed by fixed conditions of 1.5 V, room temperature and catalyst Fe^{2+} (0.1 mM). Another two sets of setups for initial dye concentrations of 20 ppm and 30 ppm were also evaluated. Then, among 10,20 and 30 ppm dye concentration, optimal concentration was chosen from highest removal efficiency from absorbance readings.

3.3.3 Catalyst

Then, concentrations of catalyst were prepared at 0.1 mM, 0.2 mM, and 0.3 mM to determine which optimal concentration of catalyst which is the most optimal. Here, EF setup used optimal conditions at (3.3.1) and (3.3.2) followed by fixed voltage of 1.5 V and room temperature condition.

3.3.4 Voltage

After that, EF setup was optimized by considering the parameter values obtained from (3.3.1) - (3.3.3). Sets of voltages were tested at 1.5 V, 3.0 V and 4.5 V potential differences. At optimal time mentioned in (3.3.1), samples were taken to find the absorbance readings. Optimized voltage was obtained at highest removal efficiency.

Table 3.1 Optimal Conditions Findings

Parameters	Variables
Contact Time (hr)	1, 2,3,4,5,6
Concentration (ppm)	10,20,30
Catalyst (mM)	0.1,0.2,0.3
Voltage (V)	1.5,3.0,4.5

3.4 Analysis using UV-VIS Spectrophotometer

The samples were taken at every one hour for 6 hours interval to assess the removal of dye using absorbance measurement under UV-Vis spectrophotometer at λ max = 428 nm (Otavo-Loaiza *et al.*, 2019). From Beer's Lambert Law, unknown concentrations of samples was determined. The Beer-Lambert law describes a linear relationship between a solution's absorbance and its concentration, molar absorption coefficient, and optical coefficient.

$$\text{Absorbance (A)} = \epsilon lc$$

Where ϵ is molar absorptivity ($L \text{ mol}^{-1} \text{ cm}^{-1}$), l is sample path length (cm), c is concentration, mol L^{-1} .

(Hardesty & Attili, 2010)

When sets of standards of dye are made, absorbance readings could be obtained, and calibration curve was plotted. From the slope, concentrations were determined based on absorbance readings. From these

data, the removal percentage was obtained and the removal efficiency (%) were calculated as follows:

$$(\%) = (C_0 - C_t) / C_0 \times 100\%,$$

where C_0 is initial concentration of dye and C_t is concentration at time respectively.

(Cruz-González *et al.*, 2012)

3.5 Kinetic study

Lastly, kinetic study was concluded from the optimum conditions obtained to determine kinetic models. Pseudo-zero order, pseudo first-order and pseudo-second-order kinetic models were used to study the removal mechanisms of tartrazine using EF.

Zero-order kinetic model: $C_0 - C_t = kt$

First Order kinetic model: $\ln (C_t/C_0) = -kt$

Second Order kinetic model: $1/C_t - 1/C_0 = kt$

(Thor *et al.*, 2021).

Zero order will be independent of changes of reaction concentration, while first order implies proportional concentration to rate of reaction and second order constructs linearity between reciprocal rate of reaction to time (Moersidik *et al.*, 2020).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of contact time.

Results obtain from the first parameter is regarding contact time. The investigation was carried out for six hours duration of tartrazine removal using EF. Each variable in the system were prepared according to the proposed initial measurements. The initial setting of materials were 10 ppm tartrazine, 0.05 M Na_2SO_4 , 0.1 mM Fe^{2+} , pH 3 dye, 1.5 V applied voltage and room temperature condition. From the results, the optimum contact time was found to be three hours as it yielded 72.13 % removal of dye. The result seemed to be agreeable to most studies when EF is employed for organic dyes.

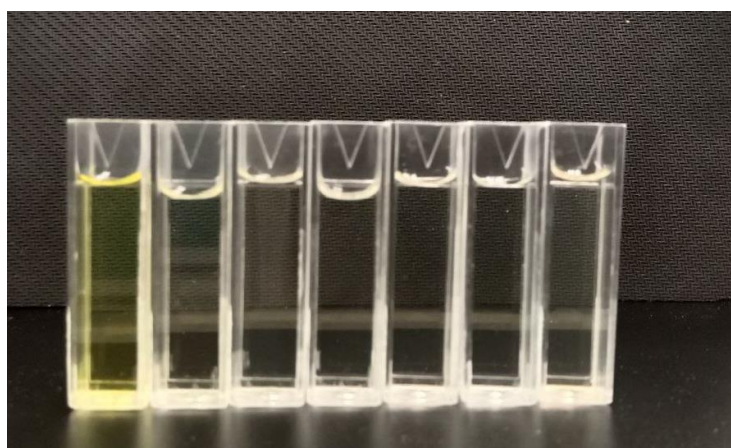


Figure 4.1 Decolourisation results over time.

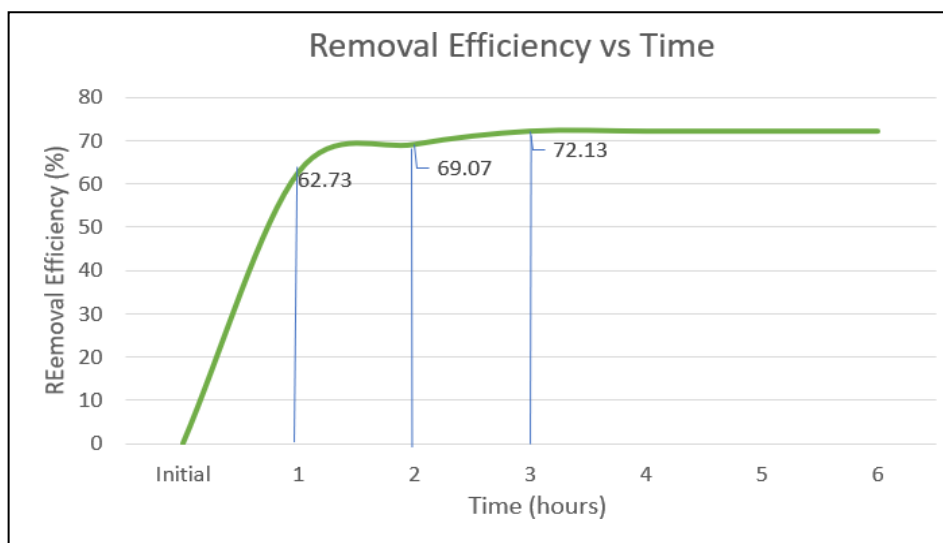
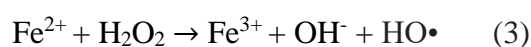
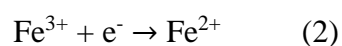
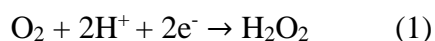


Figure 4.2 Removal efficiency of TZN using EF for six hours contact time.

During electrolysis, hydrogen peroxide, H_2O_2 was being released eq (1). Fe^{3+} undergoes reduction as a result of current flow to form Fe^{2+} . Hydroxy radical, $HO\cdot$ produced will be able to attack the aromatic rings of the azo compound with the presence catalyst Fe^{2+} eq (3). As a result, decolorization occurs over time.



(Kadji *et al.*, 2020; Wakrim *et al.*, 2022)

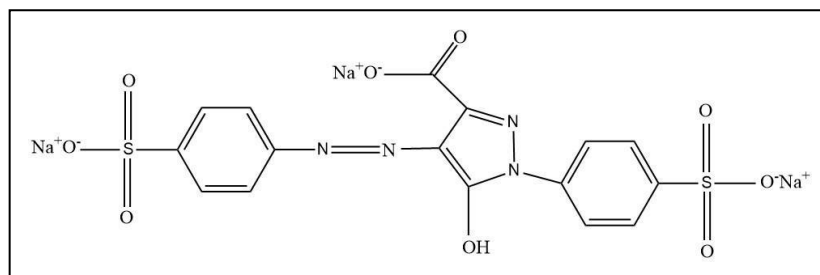


Figure 4.3 Structure of tartrazine (azo compound) (May, 2018).

Then, strong azo bond, (-N=N-) would be attacked by the radicals, making it mineralized in eq (4) (Khan et al., 2020; Omi *et al.*, 2022).



(Doumbi *et al.*, 2022)

Similarly, a study conducted by Omi *et al.*, (2022) using EF have shown removal efficiency of methyl orange (MO) dye at 89.9% within three hours. Menon *et al.*, (2021) also successfully showed three hours optimal contact time for removal of ammoniacal nitrogen from dye intermediate industrial wastewater using EF and achieved 65.5% removal efficiency. Besides that, surfactants removal efficiency using EF in waste-iron catalyzed MFC (WFe-MFC) was above 85% during contact time of three hours (Sathe *et al.*,2022).

In contrast, complete discoloration (100%) obtained after one hour contact time for EF removal of reactive red 195 from dyeing wastewater (Elbatea *et al.*, 2021). The same optimum contact time showed by the study conducted by Adachi *et al.*, (2022) with 94.9% decolorization for methyl orange dye. Both results have shorter time due to designated variables that have been improved and developed further from initial parameters. One thing that gives the most significant difference is the sizes of graphite electrodes being used. Elbatea *et al.*, (2021) have conducted the said study using graphite layer which had the surface area of 159.39 cm². Then, Adachi *et al.*, (2022) also used bigger graphite electrode which was 15 cm². Meanwhile in this study, we were only using 2 cm² of graphite electrodes which were much smaller in sizes, and thus limiting the rate of EF reaction.

4.2 Effect of initial concentration of dye.

Initial concentration of dye in EF, were carried out for 10,20 and 30 ppm had the removal efficiency of 72.13% &, 62.23% and 60.08% respectively in three hours contact time.

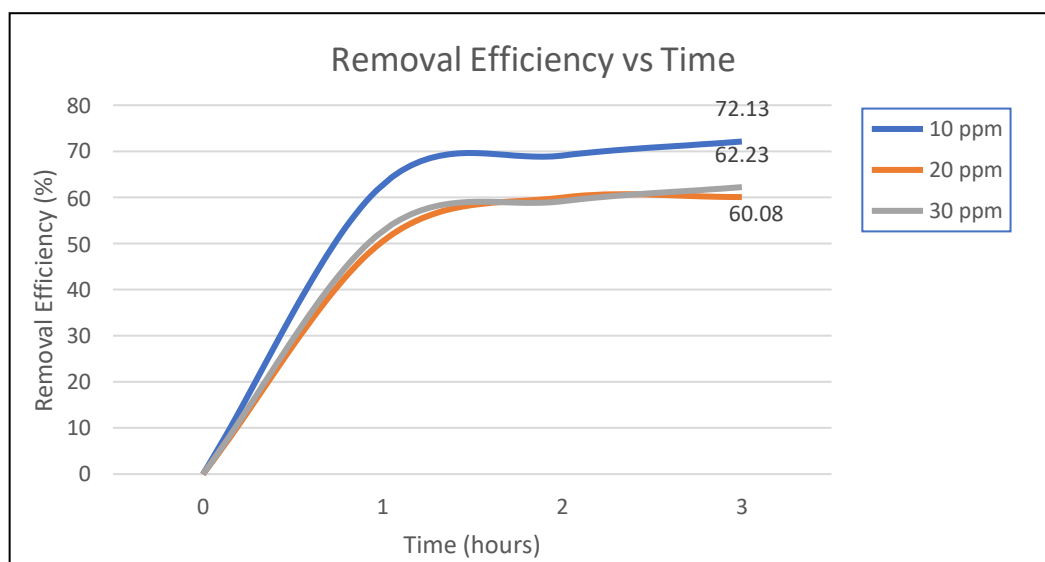


Figure 4.4 Percent removal against time for 10,20 and 30 ppm initial concentration of tartrazine.

Based on the results, the higher the initial concentration of dye, the lower removal efficiency. Besides, higher concentration was caused by competitive consumptive of the molecules undergoing oxidation process by hydroxyl radicals (An *et al.*, 2022). The mass transfer to the anode occurred at a slower rate due to increase in bulk concentration of dye (Mbaye *et al.*, 2022).

Nevertheless, the result of low in percentage might be because of contamination of dye as fast rusting crocodile clips were being used to submerge the graphite electrodes. As the setup were carried out after the first parameter, the crocodile

clips were not renewed causing rusts to develop faster during EF setup. According to Gao *et al.*, (2022) contamination of iron during degradation of organic compound could lead to precipitation being layered on the electrode surface which had hindered the removal efficiency of EF.



Figure 4.5 Contamination due to rust.

Most studies have shown that when the amount of initial concentration is being increased, removal efficiency decreases. Methyl orange dye had decolorized for 94% in one hour for initial concentration of 60 ppm using similar approaches (Zazou *et al.*, 2019). However, the reason for the efficacy is due to bigger sizes of electrodes used with an internal diameter of 6 cm and two electrodes. Another EF study was employed towards carmoisine with graphite carbon 3 cm² and the anode material was a platinum 14 cm² achieved 93% in one hour (Wakrim *et al.*, 2022).

4.3 Effect of concentration of catalyst.

Catalyst of Fe^{2+} were prepared according to different concentrations which are 0.1 mM, 0.2 mM and 0.3 mM and removal efficiencies obtained were 71.13%, 72.74% and 89.18% respectively.

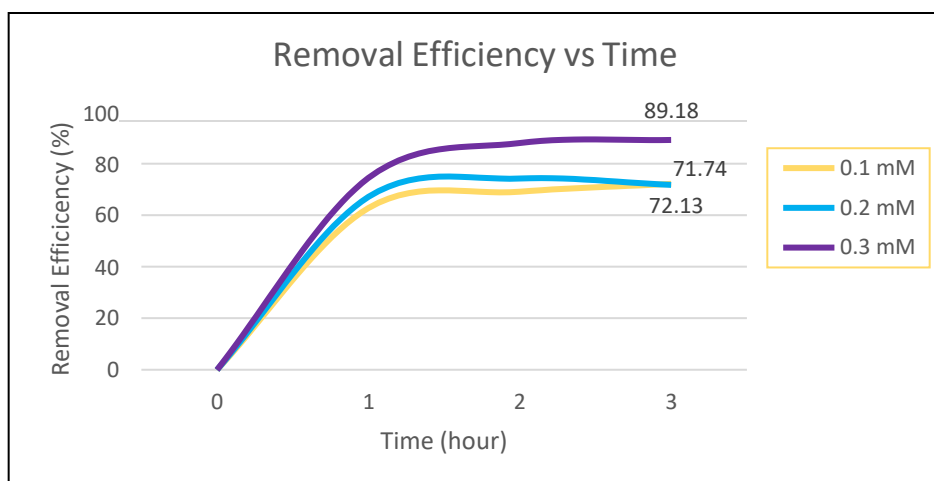
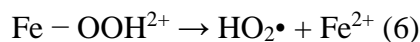
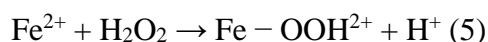
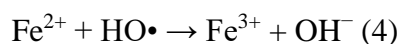


Figure 4.6 Percent removal against time for various concentrations of catalyst.

This proves that increase in concentration of catalyst could enhance removal efficiency in EF (Anil *et al.*, 2022).



(Anil *et al.*, 2022)

During EF process, when concentration of ferrous ions is high, hydrogen peroxide could achieve reduction of generated ferric species in eq. (4) to (5) (Dombi *et al.*, 2022). Excessive concentration of H_2O_2 has led to quenching of hydroxyl radicals over and over again eq. (6) (An *et al.*, 2022).

Similarly, carmosine removal in wastewater using EF achieved 93% for 0.2 mM in one hour (Wakrim *et al.*, 2022). For methylene blue, Zazou *et al.*, (2019) achieved 94% in one hour for 0.2 mM Fe catalyst.

4.4 Effect of voltage.

The decolorization efficiency was significantly affected by voltage in the range of 1.5V to 4.5 V. In three hours, the removal efficiencies are 72.13%, 82.74% and 97.87% for 1.5 V, 3 V and 4.5 V respectively.

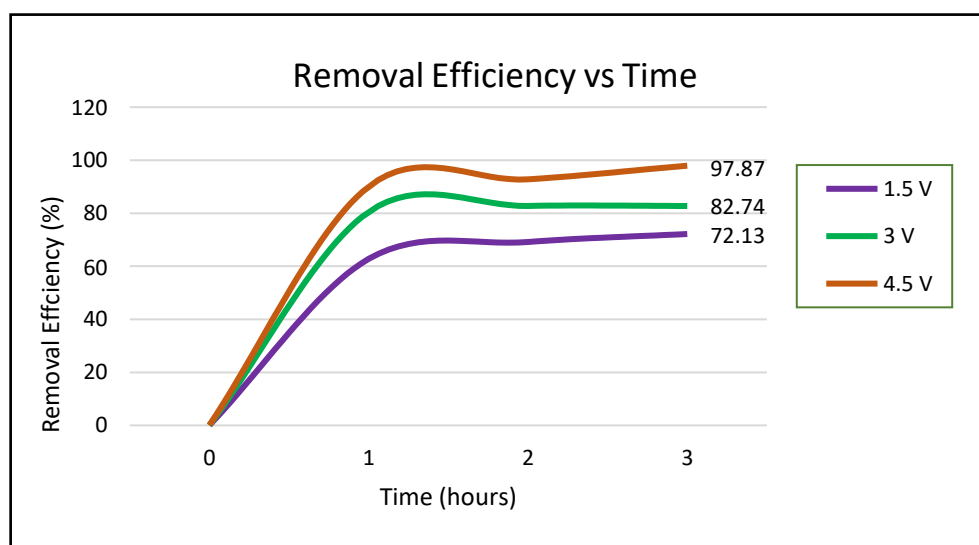


Figure 4.7 Removal efficiency of tartrazine under 1.5, 3 and 4.5 V current density.

A similar pattern shown by Menon *et al.*, (2021) on EF sonication for removal of ammoniacal nitrogen had shown 48.8% using 3 V and 45.2% for 4.5 V. Sometimes, a slight drop of removal percentage with increasing voltage due to oxidation reaction has slowed down (Menon *et al.*, 2021). One study showed acid orange 7 (AO7) degradation of dye increased from 92.23% to 96.2% when voltage was increased from 0.2 V to 0.5 V (Huang *et al.*, 2018). The distinct method was

that it used lignin; a type of wood waste incorporated as polymer networks in EF electrodes. In another study using EF, recorded removal efficiency for benzene in wastewater was found to be 72.59% using 2.85 V (Wang *et al.*, 2022).

The increasing efficiency with applied voltage is caused by generation of hydroxyl radical species by the application of higher voltage (Nordin *et al.*, 2019). Besides that, degradation of azo compound happened as the energy was enough to rupture the bonds that were used to form them (Benkhaya *et al.*, 2020). According to Faraday's First Law, as electric composition is proportional to mass of chemical changes on electrodes interfaces, more oxygen atoms were able to be generated and therefore lead to increase on production of H₂O₂ (Gao *et al.*, 2022). Kadji *et al.*, (2020) proposed that this linear increase of voltage with efficiency happened as there was an enhancement on electrons transfers activities on the cathode causing vigorous production of hydrogen peroxides molecules.

4.5 Kinetic study

The kinetic analysis tests were carried out under pH of 3, inter-electrode spacing of 1 cm and room temperature. The reaction time was set to 1, 2, and 3 hours. Table 4.1 summarizes rate constant, k values together with corresponding R² values for the whole set of studied parameters which are contact time, initial dye concentration, catalyst concentration and applied voltage.

Table 4.1 Kinetic Analysis Table

Parameters	Reaction orders	Zero Order		First Order		Second Order	
		k (M.h ⁻¹)	R ²	k (h ⁻¹)	R ²	k (M ⁻¹ h ⁻¹)	R ²
1) Contact Time (h)		-2.3461	0.7063	-0.3379	0.7854	0.0789	0.8769
2) Initial Dye Concentration	10 ppm	-2.3461	0.7063	-0.3411	0.7854	0.0789	0.8769
	20 ppm	-3.9595	0.7246	-0.3304	0.3096	0.0239	0.7881
3) Catalyst concentration	30 ppm	-6.5649	0.7251	-0.3068	0.7881	0.0155	0.8583
4) Voltage	0.1 mM	-2.3461	0.7063	-0.3411	0.7854	0.0789	0.8769
	0.2 mM	-2.2322	0.6494	-1.6407	0.2529	0.0842	0.7174
	0.3 mM	-2.6208	0.7507	-0.5978	0.8284	0.1763	0.8178
4) Voltage	1.5 V	-2.3461	0.7063	-0.2845	0.7854	0.0789	0.8769
	3.0 V	-2.4649	0.6219	-0.3636	0.2295	0.1529	0.7097
	4.5 V	-2.9821	0.666	-1.1869	0.9086	1.4095	0.8281

Moderately high correlation coefficient implies that the radical concentrations associated with organic matter concentration is feasible. From this table, it appears that the highest value of the k (1.4095 M⁻¹h⁻¹) was obtained for 4.5 V with removal efficiency of 97.87%. The higher the value, the faster the reaction in EF. By comparing the performance of initial and final conditions on designated parameters, reaction rate constant gave a significant distinct of values when k is 0.0155 M⁻¹.h⁻¹ removal efficiency 60.08 % of while the optimized conditions gave the highest value. This indicates that by employing the optimized values in the reactor, contaminants could be minimized in the sample.

According to the coefficient of determination (R^2 values) which are greater than 0.8, it can be concluded that the dye removal efficiency using EF follows the second order kinetic.

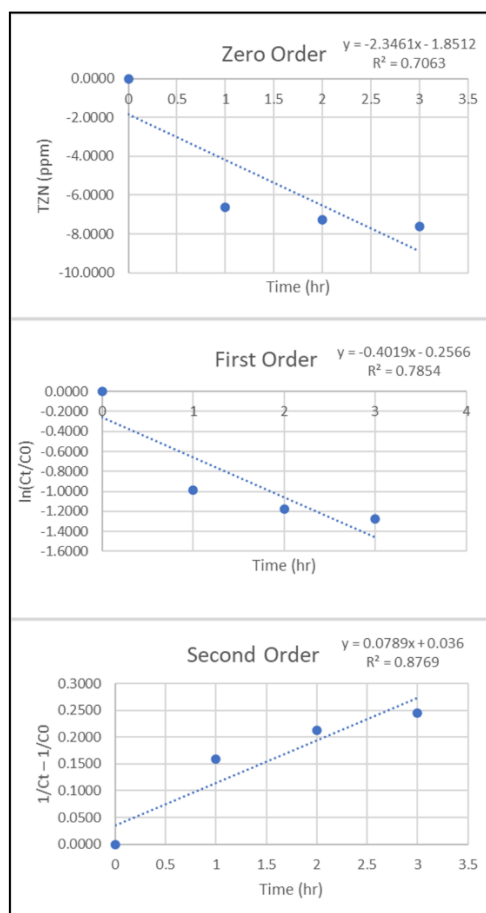


Figure 4.8 Reaction order graphs.

It has been identified that the parameters of contact time, initial dye concentrations, ferrous ion concentration and applied voltage are the key factors affecting both H_2O_2 generation and also the dye degradation. The experimental results shown in Fig. 4.8 demonstrated that the increase of the applied current density up to 4.5 V in the EF reaction could enhance the azo dye degradation significantly, since the higher rate of H_2O_2 generation was achieved at the higher applied voltage.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

This study explores the main active substance for tartrazine (TZN) removal in the process of wastewater treatment by using graphite electrodes from used batteries in Electro Fenton (EF) system. It is noteworthy that the electrodes used in this study are of lower cost and effective to treat pollutant in wastewater. Graphite is a strong and unique material which can be fully utilized to its full potential without harming the environment. Besides that, this study implied that the scale of experiment conducted has contributed to the effort towards reaching for a sustainable material in the wastewater treatment processes. In the EF system, the results show that the active substance produced by the cathode contribute to the removal of tartrazine. It was the $\cdot\text{OH}$ (hydroxyl radical), which is the most important active substance in the system, shows the strongest dye removal effect. The efficiencies of various effects to the removal of dye were analyzed under contact hours, initial dye concentrations, catalyst concentrations and different applied voltages. The result shows that the removal effect of the system is the best as it reaches 97.87 % when time=180 min, initial TZN = 10 ppm, $[\text{FeSO}_4]^0 = 0.3\text{mM}$ and applied voltage = 4.5 V. The contribution rate of $\cdot\text{OH}$ to the removal of TZN is found to be proportional to the removal ratio of TZN. Finally, the results of the study confirm the removal mechanism of the graphite electrodes from used batteries in electro-Fenton system for TZN in wastewater and the direction of reaction path

regulation which assists in the efficient removal of tartrazine in wastewater. This also provide a theoretical basis for the improvement of the current efficiency of the electro-Fenton system. Based on the experimental observations, a plausible mechanism and appropriate rate law has been deduced.

The main challenges faced during the EF process was the need for frequent replacement of the electrodes, especially for the treatment of real wastewater. The efficiency of the dye removal greatly depends on the cathode, and passivation of the cathode during treatment will negatively affect its efficiency. This is because the graphite is prone to rusts and the alternative for rust resistance is essential. Another challenge faced is associated with the variation in the behavioural properties of the catalyst during multiple synthesis. The need for pilot-scale research in dye polluted wastewater as well as extensive research on EF must be mentioned among educational institutions. Further studies require an increase in the efficiency of tartrazine in wastewater in terms of colour and COD, as well as TOC. The degradation of dye can also be found as a factor of time whether the optimized conditions will increase efficiency in extending the electrolysis time. Biological studies can be conducted to confirm the biodegradability of the wastewater after treatment. Next, the study on reusability of used batteries could induce further interest and approach towards reaching for sustainable materials. Besides, it could also minimize cost of operational processes of water treatment in the scale of the industry. Lastly, the effective treatment process could enable community to benefit more from clean and safe water supply for daily consumption.

CITED REFERENCES

- Adachi, A., Ouadrhiri, F. E., Kara, M., El Manssouri, I., Assouguem, A., Almutairi, M. H., Bayram, R., Mohamed, H. R. H., Peluso, I., Eloutassi, N., & Lahkimi, A. (2022). Decolorization and degradation of methyl orange azo Dye in Aqueous Solution by the Electro Fenton Process: Application of Optimization. *Catalysts*, 12(6), 665. <https://www.mdpi.com/2073-4344/12/6/665>
- Akbari, M. Z., Xu, Y., Lu, Z., & Peng, L. (2021). Review of antibiotics treatment by advance oxidation processes. *Environmental Advances*, 5, 100111.
- Albasher, G., Maashi, N., Alfarraj, S., Almeer, R., Albrahim, T., Alotibi, F., ... & Mahmoud, A. M. (2020). Perinatal exposure to tartrazine triggers oxidative stress and neurobehavioral alterations in mice offspring. *Antioxidants*, 9(1), 53.
- An, X., Hou, Z., Yu, Y., Wang, J., Lan, H., Liu, H., & Qu, J. (2022). Red mud supported on reduced graphene oxide as photo-Fenton catalysts for organic contaminant degradation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 640, 128461.
- Anil, G., Scaria, J., & Nidheesh, P. V. (2022). Removal of Synthetic Dye from Aqueous Solution Using MnFe₂O₄-GO Catalyzed Heterogeneous Electro-Fenton Process. *Water*, 14(20), 3350.
- Athira, N., & Jaya, D. S. (2022). Effects of tartrazine on growth and brain biochemistry of Indian major carps on long-term exposure. *Int. J. Adv. Biochem. Res*, 6(2), 25-33.
- Benkhaya, S., M'Rabet, S., & El Harfi, A. (2020). Classifications, properties, recent synthesis and applications of azo dyes. *Heliyon*, 6(1), e03271. <https://doi.org/https://doi.org/10.1016/j.heliyon.2020.e03271>
- Bhad, R. M., Das, A., & Kodape, S. M. (2022). Ozonation of procion blue reactive dye and its kinetics study. *Pollution*, 8(2), 529-541.
- Cruz-González, K., Torres-Lopez, O., García-León, A. M., Brillas, E., Hernández-Ramírez, A., & Peralta-Hernández, J. M. (2012). Optimization of electro-Fenton/BDD process for decolorization of a model azo dye wastewater by means of response surface methodology. *Desalination*, 286, 63-68.
- da Silva, J., & Fracacio, R. (2021). Toxicological and ecotoxicological aspects of tartrazine yellow food dye: a literature review. *Brazilian Journal of Environmental Sciences (RBCIAMB)*, 56(1), 137-151.
- Divyapriya, G., & Nidheesh, P. V. (2020). Importance of graphene in the electro-Fenton process. *ACS omega*, 5(10), 4725-4732.

- Doumbi, R. T., Noumi, G. B., & Ngobtchok, B. (2022). Tannery wastewater treatment by electro-Fenton and electro-persulfate processes using graphite from used batteries as free-cost electrode materials. *Case Studies in Chemical and Environmental Engineering*, 5, 100190.
- Dugandžić, A. M., Tomašević, A., Dabić, D. M., Šekuljica, N., Radišić, M., Petrović, S., & Mijin, D. (2018). Degradation of nicosulfuron using fenton and fenton-like reactions. *Chemical Industry & Chemical Engineering Quarterly*, 24(3), 201-208.
- Dung, N. T., Hoa, N. T., Thao, V. D., & Huy, N. N. (2022). A comprehensive study on the heterogeneous electro-Fenton degradation of tartrazine in water using CoFe₂O₄/carbon felt cathode. *Chemosphere*, 287, 132141.
- Elbatea, A. A., Nosier, S. A., Zatout, A. A., Hassan, I., Sedahmed, G. H., Abdel-Aziz, M. H., & El-Naggar, M. A. (2021). Removal of reactive red 195 from dyeing wastewater using electro-Fenton process in a cell with oxygen sparged fixed bed electrodes. *Journal of Water Process Engineering*, 41, 102042.
- Environmental Quality Act 1974 Environmental Quality (Scheduled Wastes) Regulations 2005 Arrangement of Regulations.
- Gao, X., Zhang, C., Wang, Y., Zhang, H., Zhao, M., Wang, Y., & Guo, Y. (2022). Treatment of membrane concentrated landfill leachate by a heterogeneous electro-Fenton process with an iron-loaded needle coke cathode. *Journal of Environmental Chemical Engineering*, 10(5), 108287.
- Hardesty, J. H., & Attili, B. (2010). Spectrophotometry and the Beer-Lambert Law: An important analytical technique in chemistry. *Collin College, Department of Chemistry*.
- He, H., & Zhou, Z. (2017). Electro-Fenton process for water and wastewater treatment. *Critical Reviews in Environmental Science and Technology*, 47(21), 2100-2131.
- Huang, H., Han, C., Wang, G., & Feng, C. (2018). Lignin combined with polypyrrole as a renewable cathode material for H₂O₂ generation and its application in the electro-Fenton process for azo dye removal. *Electrochimica Acta*, 259, 637-646.
- Igbo, J. K., Chukwu, L. O., Oyewo, E. O., Blum, J. L., Schanzer, A., Wirgin, I., Meltzer, G. Y., Roy, N. K., & Zelikoff, J. T. (2022). The Chemistry and Health Outcomes of Electronic Waste (E-Waste) Leachate: Exposure to E-Waste Is Toxic to Atlantic Killifish (*Fundulus heteroclitus*) Embryos. *Sustainability*, 14(18), 11304.
- Jafari Rad, A. (2020). Synthesis of copper oxide nanoparticles on activated carbon for pollutant removal in Tartrazine structure. *Journal of Composites and Compounds*, 2(3), 99-104. <https://doi.org/10.29252/jcc.2.2.6>

- Kadji, H., Yahiaoui, I., Garti, Z., Amrane, A., & Aissani-Benissad, F. (2021). Kinetic degradation of amoxicillin by using the electro-Fenton process in the presence of a graphite rods from used batteries. *Chinese Journal of Chemical Engineering*, 32, 183-190.
- Khan, J., Tariq, M., Muhammad, M., Haris Mehmood, M., Ullah, I., Khan, H. U., Raziq, A., Akbar, F., Saqib, M., & Niaz, A. (2020). Application of photo-fenton system (UV/H₂O₂/Fe²⁺) for efficient decolorization of azo-dye acid yellow 17 in aqueous solution. *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, 39(1), 127-140.
- Kord Forooshani, P., Pinnaratip, R., Polega, E., Tyo, A. G., Pearson, E., Liu, B., Folayan, T.-O., Pan, L., Rajachar, R. M., & Heldt, C. L. (2020). Hydroxyl radical generation through the fenton-like reaction of hematin-and catechol-functionalized microgels. *Chemistry of Materials*, 32(19), 8182-8194.
- Li, M., Chen, N., Shang, H., Ling, C., Wei, K., Zhao, S., Zhou, B., Jia, F., Ai, Z., & Zhang, L. (2022). An Electrochemical Strategy for Simultaneous Heavy Metal Complexes Wastewater Treatment and Resource Recovery. *Environmental science & technology*, 56(15), 10945-10953. <https://doi.org/10.1021/acs.est.2c02363>
- Liu, F., Liu, Y., Yao, Q., Wang, Y., Fang, X., Shen, C., Li, F., Huang, M., Wang, Z., & Sand, W. (2020). Supported atomically-precise gold nanoclusters for enhanced flow-through electro-Fenton. *Environmental science & technology*, 54(9), 5913-5921.
- Liu, Z., Demeestere, K., & Hulle, S. V. (2021). Comparison and performance assessment of ozone-based AOPs in view of trace organic contaminants abatement in water and wastewater: A review. *Journal of Environmental Chemical Engineering*, 9(4), 105599. <https://doi.org/https://doi.org/10.1016/j.jece.2021.105599>
- Lucas, M. S., Peres, J. A., & Li Puma, G. (2021). Advanced oxidation processes for water and wastewater treatment. *Water*, 13(9), 1309.
- Martini, J., Orge, C. A., Faria, J. L., Pereira, M. F. R., & Soares, O. S. G. P. (2019). Catalytic Advanced Oxidation Processes for Sulfamethoxazole Degradation. *Applied Sciences*, 9(13), 2652. <https://www.mdpi.com/2076-3417/9/13/2652>
- Martone, L., Minella, M., Minero, C., Sordello, F., & Vione, D. (2022). Effective degradation of ibuprofen through an electro-Fenton process, in the presence of zero-valent iron (ZVI-EF). *Journal of Cleaner Production*, 367, 132894. <https://doi.org/https://doi.org/10.1016/j.jclepro.2022.132894>
- May, Paul. "Tartrazine- Molecule of the Month - May 2018 (JSMol Version)." www.chm.bris.ac.uk, May 2018, www.chm.bris.ac.uk/motm/tartrazine/tartrazinejs.htm.

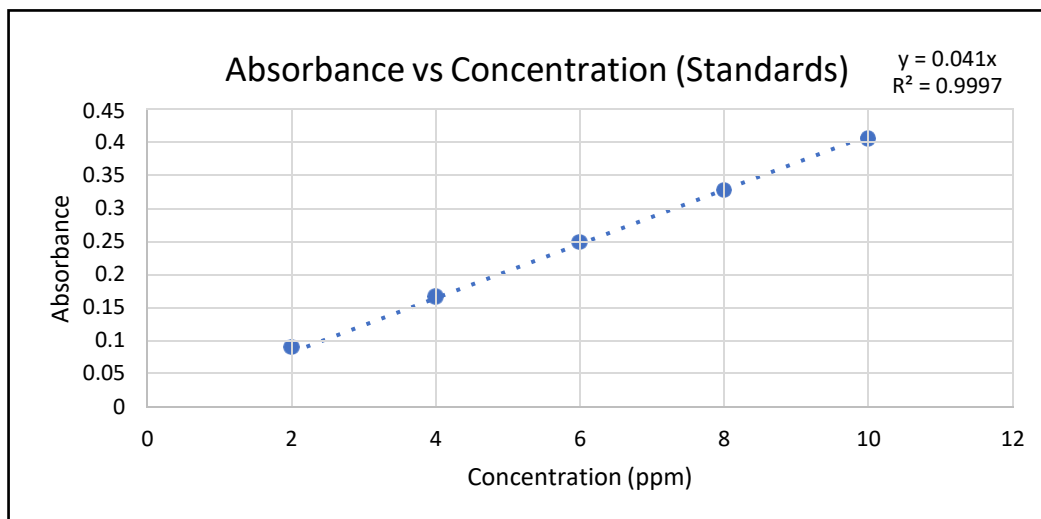
- Mbaye, M., Diaw, P. A., Mbaye, O. M. A., Oturan, N., Seye, M. D. G., Trelu, C., ... & Oturan, M. A. (2022). Rapid removal of fungicide thiram in aqueous medium by electro-Fenton process with Pt and BDD anodes. *Separation and Purification Technology*, *281*, 119837.
- Menon, P., Singh, T. A., Pani, N., & Nidheesh, P. V. (2021). Electro-Fenton assisted sonication for removal of ammoniacal nitrogen and organic matter from dye intermediate industrial wastewater. *Chemosphere*, *269*, 128739.
- Midassi, S., Bedoui, A., & Bensalah, N. (2020). Efficient degradation of chloroquine drug by electro-Fenton oxidation: Effects of operating conditions and degradation mechanism. *Chemosphere*, *260*, 127558.
- Moersidik, S. S., Nugroho, R., Handayani, M., & Pratama, M. A. (2020). Optimization and reaction kinetics on the removal of Nickel and COD from wastewater from electroplating industry using Electrocoagulation and Advanced Oxidation Processes. *Heliyon*, *6*(2), e03319.
- Muzenda, C., & Arotiba, O. A. (2022). Improved Magnetite Nanoparticle Immobilization on a Carbon Felt Cathode in the Heterogeneous Electro-Fenton Degradation of Aspirin in Wastewater. *ACS omega*, *7*(23), 19261-19269. <https://doi.org/10.1021/acsomega.2c00627>
- Muzenda, C., Nkwachukwu, O. V., & Arotiba, O. A. (2022). Synthetic Ilmenite (FeTiO₃) Nanoparticles as a Heterogeneous Electro-Fenton Catalyst for the Degradation of Tetracycline in Wastewater. *Industrial & Engineering Chemistry Research*, *61*(31), 11417-11428. <https://doi.org/10.1021/acs.iecr.2c01464>
- Nair, K. M., Kumaravel, V., & Pillai, S. C. (2021). Carbonaceous cathode materials for electro-Fenton technology: Mechanism, kinetics, recent advances, opportunities and challenges. *Chemosphere*, *269*, 129325. <https://doi.org/https://doi.org/10.1016/j.chemosphere.2020.129325>
- Natarajan, S., Divya, M. L., & Aravindan, V. (2022). Should we recycle the graphite from spent lithium-ion batteries? The untold story of graphite with the importance of recycling. *Journal of Energy Chemistry*, *71*, 351-369. <https://doi.org/https://doi.org/10.1016/j.jechem.2022.04.012>
- Nordin, N., Pital, M. A. F., Razman, N. I. H., & Jaafar, N. F. (2019). Electrochemical degradation of reactive blue 21 and synthetic textile effluent by using CO47. 5/C47. 5-PVC5 composite electrode. *Acta Chimica Slovenica*, *66*(2), 284-293.
- Omi, F. R., Rastgar, M., & Sadrzadeh, M. (2022). Synergistic effect of thermal dehydrating on the emerging contaminants removal via Electro-Fenton. *Journal of Cleaner Production*, *356*, 131880.

- Otavo-Loaiza, R. A., Sanabria-González, N. R., & Giraldo-Gómez, G. I. (2019). Tartrazine removal from aqueous solution by HDTMA-Br-modified Colombian bentonite. *The Scientific World Journal*, 2019.
- Perveen, S., Nadeem, R., Nosheen, F., Asjad, M. I., Awrejcewicz, J., & Anwar, T. (2022). Biochar-mediated zirconium ferrite nanocomposites for tartrazine dye removal from textile wastewater. *Nanomaterials*, 12(16), 2828
- Quraishi, U., Ali, H., Iftikhar, M., & Iftikhar, N. (2022). Factors Affecting Household Access to Clean Water Supply In Residential Areas Of Pakistan. *Bulletin of Business and Economics (BBE)*, 372-381.
- Razip, M. M., Savita, K. S., Kalid, K. S., Ahmad, M. N., Zaffar, M., Abdul Rahim, E. E., Baleanu, D., & Ahmadian, A. (2022). The development of sustainable IoT E-waste management guideline for households. *Chemosphere*, 303, 134767.
<https://doi.org/https://doi.org/10.1016/j.chemosphere.2022.134767>
- Rueda-Márquez, J. J., Levchuk, I., Manzano, M., & Sillanpää, M. (2020). Toxicity reduction of industrial and municipal wastewater by advanced oxidation processes (Photo-Fenton, UVC/H₂O₂, Electro-Fenton and Galvanic Fenton): a review. *Catalysts*, 10(6), 612.
- Sahin, O. I. (2021). Removal of azo dyes-tartrazine, carmoisine, and Allura Red- from wastewater using Spirulina biomass-immobilized alginate beads: equilibrium, kinetics, thermodynamics, desorption, and reusability.
- Samsudeen, N., Spurgeon, J., Matheswaran, M., & Satyavolu, J. (2020). Simultaneous biohydrogen production with distillery wastewater treatment using modified microbial electrolysis cell. *International Journal of Hydrogen Energy*, 45(36), 18266-18274.
- Sathe, S. M., Chakraborty, I., Doki, M. M., Dubey, B. K., & Ghangrekar, M. M. (2022). Waste-derived iron catalyzed bio-electro-Fenton process for the cathodic degradation of surfactants. *Environmental Research*, 212, 113141.
- Selihin, N. M., & Tay, M. G. (2022). A review on future wastewater treatment technologies: micro-nanobubbles, hybrid electro-Fenton processes, photocatalytic fuel cells, and microbial fuel cells. *Water Science and Technology*, 85(1), 319-341.
- Silva, J. d. (2021). *Toxicological and ecotoxicological aspects of tartrazine yellow food dye: a literature review*. Associação Brasileira de Engenharia Sanitária e Ambiental. http://rbciamb.com.br/index.php/Publicacoes_RBCIAMB/article/view/746
- Sutherland, A. J., Ruiz-Caldas, M.-X., & de Lannoy, C.-F. (2020). Electro-catalytic microfiltration membranes electrochemically degrade azo dyes in solution. *Journal of Membrane Science*, 611, 118335.

- Syahriani, N., Palutturi, S., Birawida, A. B., & Hidayanty, H. (2022). Clean Water Supply as an Indicator for Healthy Island in Makassar City. *Open Access Macedonian Journal of Medical Sciences*, 10(E), 320-325.
- Thor, S. H., Ho, L. N., Ong, S. A., Abidin, C. Z. A., Heah, C. Y., Nordin, N., ... & Yap, K. L. (2021). Discovering the roles of electrode distance and configuration in dye degradation and electricity generation in photocatalytic fuel cell integrated electro-Fenton process. *Separation and Purification Technology*, 278, 119652.
- United Nations. (2022, November 15). *Day of 8 Billion*. United Nations. <https://www.un.org/en/dayof8billion>
- Wakrim, A., Zaroual, Z., El Ghachtouli, S., Jamal Eddine, J., & Azzi, M. (2022). Treatment and Degradation of Azo Dye Waste Industry by Electro-Fenton Process. *Physical Chemistry Research*, 10(4), 495-504.
- Wang, Z., Qiao, H., Yu, Z., Yang, X., Tang, Z., Zhou, W., & Zhao, H. (2022). Source analysis of benzene degradability in floating cathode electro-Fenton system based on COD removal ratio. *Journal of Water Process Engineering*, 46, 102568.
- Wdowczyk, A., & Szymańska-Pulikowska, A. (2020). Differences in the composition of leachate from active and non-operational municipal waste landfills in Poland. *Water*, 12(11), 3129.
- You, W., Liu, L., Xu, J., Jin, T., Fu, L., & Pan, Y. (2022). Effect of Anions and Cations on Tartrazine Removal by the Zero-Valent Iron/Peroxymonosulfate Process: Efficiency and Major Radicals. *Catalysts*, 12(10), 1114.
- Zaini, M. S. I., Hasan, M., & Zolkepli, M. F. (2022). Urban landfills investigation for leachate assessment using electrical resistivity imaging in Johor, Malaysia. *Environmental Challenges*, 6, 100415. <https://doi.org/https://doi.org/10.1016/j.envc.2021.100415>
- Zazou, H., Afanga, H., Akhouairi, S., Ouchtak, H., Addi, A. A., Akbour, R. A., Assabbane, A., Douch, J., Elmchaouri, A., & Duplay, J. (2019). Treatment of textile industry wastewater by electrocoagulation coupled with electrochemical advanced oxidation process. *Journal of Water Process Engineering*, 28, 214-221.
- Zensich, M. A., Caballero, Á., & Tesio, A. Y. (2022). Multi-source recovered graphite and its use in electrodes for energy storage. *Current Opinion in Electrochemistry*, 101186. <https://doi.org/https://doi.org/10.1016/j.coelec.2022.101186>
- Zhang, W., Lv, W., Li, X., & Yao, J. (2019). Electrochemical oxidative degradation of indigo wastewater based on chlorine-containing system. *Pigment & Resin Technology*.

APPENDICES

APPENDIX A



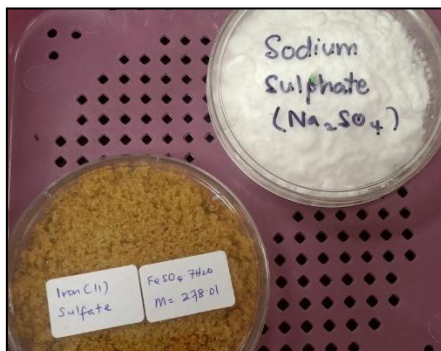
Calibration curve of TZN curve.

APPENDIX B



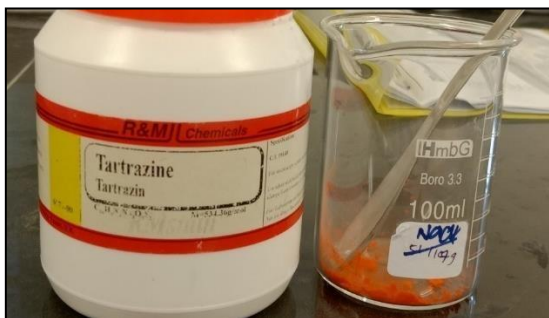
Preparation of 2,4,6,8,10 ppm standards of TZN.

APPENDIX C



FeSO_4 and Na_2SO_4 in powdered form.

APPENDIX D



Tartrazine dye powder.

APPENDIX E



Electrodes modified into 2 cm^2 area.

A. Personal Profile

Full name Aina Nasuha binti Abdul Aziz
National IC no 991022 13 6364
Birth Date 22 October 1999
Citizenship MALAYSIA
Place of birth Sarawak, Malaysia
Gender Female
Correspondence address Lot 632, Jalan Dato Muip,
Piasau Jaya Phase 1,
98000 Miri, Sarawak

Telephone no. (H) -
Telephone no. (HP) 011-31900656
Email address nasuha878@gmail.com



B. Hobbies and Interests

I enjoy baking for teatime and love to read non-fiction books such as memoirs themed because they depicted real, emotional and exhilarating reality. Besides that, scientific and fun trivial findings stories are among my favourites too.

C. Academic Qualifications

Degree	Area	Institution	Year Awarded
B.Sc. (Hons.)	Chemistry with Management	Universiti Teknologi MARA, Malaysia	2023
Diploma	Industrial Chemistry	Universiti Teknologi MARA, Malaysia	2020
S.P.M	Science	SMK Dato Permaisuri, Miri	2016
PT3	-	Kolej TDT Haji Bujang, Miri	2014

D. Work Experience

Post	Place	Year
Waitress	Warong Adek Kakak, Miri	2018-2019
F&B Assistant	Kenny Rogers Roasters, PICM, Miri	2019
Intern	Heartini's Spa, Miri	2020
Part-time Staff	Izzaf, Delights, Samarahan	2022

E. Related Experience

Post	Place	Year
Vice Secretary	CHEMISTS Faculty of Applied Sciences, UiTM	2021-2022
Exco Member	PRISMATICS (Degree), UiTM	2021-2022
Exco Member	CHEMISTS Faculty of Applied Sciences, UiTM	2020-2021
Volunteer	Beach Cleanup Day by Miri City Council	2020
Volunteer	Kenyalang Outreach UiTM Sarawak at Kampung Plaie	2019
Facilitator	Program Ajar Solat (Masjid Darul Ehsan)	2017