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Statistical Optimization of Electrooxidation Process for the Removal of Paracetamol from Synthetic Wastewater

BY

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Approval Page

This is to certify that the thesis prepared by Ms. Bereket Adinow entitled "**Statistical Optimization of Electrooxidation Process for the Removal of the Paracetamol from synthetic wastewater**" and submitted as a partial fulfillment to the requirements for the award of the degree of master of science in chemical engineering (environmental engineering stream) compiles with the regulations of the university and meets the accepted standards with respect to content, quality, and originality.

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Abstract

Over the past few decades, there has been a growing interest among researchers and scientists worldwide in removing toxic substances from wastewater. Micro pollutants, in particular, have become a major public concern due to their ability to accumulate in the environment, their carcinogenic properties, and their harmful effects even at low concentrations. In this particular study, the focus was on degrading and mineralizing paracetamol, a commonly found micro pollutant, in synthetic wastewater using the electro oxidation process. To achieve this, a Ti/IrO2 coated anode and a stainless-steel cathode were utilized, and the efficiency of paracetamol removal was measured by analyzing changes in absorption spectra using a UV-VIS spectrophotometer. The researchers conducted preliminary experiments to understand the impact of various operating parameters, such as pH, paracetamol concentration, electrode distance, and current density, on the efficiency of paracetamol removal. Once the individual effects were studied, the interaction effect of these parameters and optimized them using a statistical tool called central composite design (CCD), which is a type of response surface methodology (RSM). This allowed them to determine the optimal conditions for the electro oxidation process. Based on the findings of this study, it can be concluded that the electro oxidation process using a Ti/IrO2 anode and a stainless-steel cathode presents a viable alternative treatment technology for mitigating the environmental issues caused by paracetamol contamination. The oxidation process was carried out within a pH range of 3-5, a current density range of 5-7 mA/cm2, an electrode distance range of 1-2 cm, and an initial paracetamol concentration range of 20-50 mg/L. Through the optimization process, it was found that 97.3% of paracetamol could be removed at an optimum pH of 3.7, a current density of 6.47 mA/cm2, an electrode distance of 1.12 cm, and an initial paracetamol concentration of 21.14 mg/L. However, even under these optimized conditions, only 60% of the average total organic carbon (TOC) could be removed after 40 minutes of electrolysis.

Keywords: Electro oxidation; Micropollutants; Paracetamol; Optimization; Electrolysis; Total organic carbon ; UV-VIS Spector Photometer.

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Abbreviations and Acronyms

AOP	Advanced Oxidation Process
ANOVA	Analysis of Variance
BDD	Boron Doped Diamond
CCD	Central Composite Design
ECs	Emerging Contaminants
EO	Electro Oxidation
EPs	Emerging Pollutants
HPLC	High Performance Liquid Chromatography
NF	Nano filtration
PC	Paracetamol
RO	Reverse Osmosis
RSM	Response Surface Methodology
TOC	Total Organic Carbon
UV	Ultraviolet
WHO	World Health Organization

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1. Introduction

1.1 Background

Water pollution is a pressing problem that affects communities worldwide, especially in developing countries. Many water sources and treatment plants are connected to sewage systems and receive pollutants from medical facilities, mining operations, and chemical industries, posing a significant threat to their quality and safety (Kodom et al., 2021). Currently, a variety of harmful organic and inorganic compounds have been detected in surface water, wastewater, and groundwater. This pollution is primarily caused by the use of herbicides, fertilizers, pesticides, industrial chemicals, heavy metals, detergents, soaps, pathogens, textile dyes, pharmaceuticals, and organic solvents, which all make their way into water sources (Adisu et al., 2022). The removal of toxic substances from wastewater has become a major focus of researchers and scientists worldwide in recent decades. Among these toxic contaminants, emerging pollutants are a particularly concerning issue due to their ability to accumulate in organisms, their carcinogenic properties, their persistence in the environment, and their harmful effects even at low concentrations (Castro-Castro et al., 2020; Rout et al., 2021).

Depending on the duration and dosage of exposure, paracetamol can have detrimental effects on human health. These effects include the potential to cause sexual disorders in both males and females, prolonged time to conception, reduced male fertility, increased miscarriage rates, disruptions in the development of male and female reproductive organs, and even the stimulation of breast cancer cell growth, as well as prostate and testicular abnormalities (Rout et al., 2021). These toxic effects are generally attributed to the presence of reactive oxygen species, which can lead to a range of harmful outcomes, such as protein denaturation, lipid peroxidation, and DNA damage (Kashif et al., 2021). With the anticipated increase in the consumption of paracetamol and other pharmaceutical active compounds in the future, it is imperative to develop and implement new technologies capable of effectively removing these chemicals at low concentrations before they are released into the environment (Rios-Miguel et al., 2022). Among the various types of micro pollutants, pharmaceutical products like analgesics and antibiotics are notable examples, as they have been detected in wastewater and even in drinking water. These pharmaceutical compounds produce metabolites within the body that are excreted along with their residual active ingredients (Periyasamy & Muthuchamy, 2018). Consequently, a number of pharmaceutical compounds are now being detected at low concentrations in water bodies worldwide, posing risks to both the environment and human health. One such pharmaceutical compound is paracetamol, also known as acetaminophen, which is commonly prescribed as an analgesic and antipyretic to alleviate pain in humans and animals (Ghanbari et al., 2021). Paracetamol is widely consumed globally and, as a result, its concentration in wastewater and surface water is among the highest of all pharmaceutical micro contaminants. In wastewater treatment plant effluents, its concentration can exceed 100 µg/L, and in rivers, it can reach over 100 ng/L (Rios-Miguel et al., 2022). Emerging pollutants, which encompass pharmaceuticals, personal care products, phthalates, flame retardants, and hormones, have the potential to cause significant and chronic harm to aquatic life, as well as human and animal health, when exposed over extended periods of time (Kashif et al., 2021). In recent decades, micro pollutants have emerged as a growing global concern, as they can have adverse effects on both the environment and human well-being. These pollutants originate from a variety of sources, including industrial activities, agricultural practices, hospitals, and domestic households, ultimately finding their way into water supplies (Rout et al., 2021).

Industrial wastewater, such as effluents, must undergo proper treatment to ensure that it meets the acceptable limits before being discharged into the environment (Adisu et al., 2022). Traditional treatment methods, including chemical precipitation, membrane separation, ion exchange, flocculation, and coagulation, have been developed but have proven ineffective in removing emerging contaminants from contaminated water (Kashif et al., 2021). In recent years, advanced oxidation processes, particularly electro oxidation, have emerged as highly significant treatment methods for the removal of emerging pollutants (Rout et al., 2021). Electro oxidation, in particular, has proven to be a highly effective method for treating wastewater that contains emerging pollutants, specifically paracetamol. Compared to conventional treatment methods, electro oxidation offers numerous advantages such as high efficiency, rapid reaction rates, and easy implementation. Furthermore, it requires minimal chemical consumption and does not produce secondary pollutants (Kouadio et al., 2021). The effectiveness of the electrochemical oxidation treatment process primarily relies on the properties of the electrode used, particularly the anode in electrolysis. In this specific study, Ti/IrO2 coated anode and stainless-steel cathode electrodes were utilized to degrade paracetamol, an emerging pollutant, from synthetic wastewater due to their exceptional optical, electronic, and mechanical qualities (Kouadio et al., 2021)..

1.2 Statement of the Problem

Pharmaceutical compounds, which make up the largest category of emerging micro pollutants, have raised significant public health alarms. These substances have been commonly identified and quantified in a range of settings, including water sources, wastewater, soil, sediments, and more. Additionally, the existence of pharmaceutical compounds, even at low levels, in the environment has negative impacts on the health of humans, animals, and microorganisms (Ghanbari et al., 2021).

Paracetamol, a commonly prescribed pharmaceutical compound, holds a prominent position in the world of medicine. However, it is important to note that overdosing on paracetamol can lead to several adverse effects, including the growth of breast cancer cells and the development of sexual disorders in both males and females (Rout et al., 2021). In an effort to address the presence of paracetamol in wastewater, various conventional treatment methods have been utilized over the years. These methods include chemical precipitation, membrane separation, ion exchange, coagulation, flocculation, and adsorption processes, all aimed at removing emerging pollutants such as paracetamol (Kashif et al., 2021). Despite their widespread use, these technologies are not without their limitations. Challenges associated with incomplete pollutant removal, high costs of equipment, substantial energy requirements, and the generation of secondary byproducts have been identified (Bahadur et al., 2019; Kashif et al., 2021). Therefore, there is a need for further advancements in wastewater treatment technologies to overcome these drawbacks and ensure the effective removal of paracetamol from wastewater.

In order to address the limitations of traditional approaches for eliminating paracetamol from wastewater, there is a need to create and implement a novel and environmentally conscious removal technique. The electro oxidation method, which falls under the category of advanced oxidation processes, has emerged as a highly effective technology for breaking down paracetamol in wastewater. When it comes to treatment methods, the electrooxidation treatment stands out due to its numerous advantages. Firstly, it boasts high efficiency, allowing for a more effective removal of pollutants. Secondly, the reaction process is rapid, ensuring a quicker treatment turnaround time. Moreover, the implementation of electrooxidation treatment is straightforward and uncomplicated. Furthermore, this method requires minimal usage of chemicals, resulting in cost savings and minimizing chemical waste. Lastly, electrochemical oxidation processes do not generate any secondary pollutants, making it an environmentally friendly option (Kouadio et al., 2021). The success of the electrochemical oxidation treatment process is primarily determined by the characteristics of the electrode utilized as the anode during electrolysisIn a recent research study conducted by Kouadio et al. (2021), an innovative approach was adopted to tackle the issue of degrading the emerging pollutant paracetamol from synthetic wastewater. The researchers utilized Ti/IrO2 coated anode and stainless-steel cathode electrodes, which were chosen due to their exceptional electronic properties, cost-effectiveness, and mechanical durability. This experimental approach aimed to find a sustainable and efficient solution for the removal of paracetamol, a commonly used pharmaceutical compound, from wastewater.

1.3 Objective

1.3.1 General Objective

The general objective of this study was to investigate and optimize selected operational parameters on the application of Ti/IrO_2 electrodes for the removal of paracetamol from aqueous solution using electro oxidation process.

1.3.2 Specific Objectives

- To investigate the individual and interaction effect of pH, electrodes distance, paracetamol concentration, and current density on removal efficiency of paracetamol by electrochemical oxidation using Ti/IrO_2 coated anode and stainless-steel cathode electrodes;
- To optimize the selected optimization parameters (distance of electrodes, initial paracetamol concentration, initial pH of the solution, and current density) on the degradation of paracetamol using electro oxidation to give the best paracetamol removal efficiency;
- To analyze and confirm the selected optimizing operational parameters on removal of the paracetamol.

1.4 Significance of the Study

The significance of this study was to show that the degradation of the emerging pollutant which is paracetamol using the green electro oxidation removal method is more advantageous than the conventional methods. Due to the inability and high cost of conventional treatment methods of the emerging pollutants removal; this study has focused to investigate the electro oxidation of paracetamol from wastewater using Ti/IrO_2 coated anode and stainless-steel cathode electrodes. This electrolysis process contributes a lot to environmental pollution control since conventional removal methods are costly and generate secondary pollutants. Localities will benefit from this study output, keeping them living in a healthy environment. Industrialists are also highly beneficial because they can reduce sludge production which was a problem for disposal and treatment. Generally, it has great significance in terms of showing directions for pollution prevention and resource utilization. In addition to this, the research can be used as input for further studies to explore more about the removal technologies for the emerging pollutants.

1.5 Scope of the Study

This research focused on the breakdown and transformation of paracetamol in artificial wastewater using an electro oxidation process. The process involved the utilization of a titanium/iridium oxide coated anode and a stainless-steel cathode in a batch-wise manner. Several factors, including the pH of the solution, distance between the electrodes, current density, and initial concentration, were thoroughly examined and analyzed. The study also investigated the interaction effects of these parameters using response surface methodology to optimize the process. The degradation of paracetamol was monitored and evaluated by means of a UV visible spectrophotometer, and the total organic carbon (TOC) degradation was measured both before and after electro oxidation at the optimal conditions

2. Literature Review

2.1 Water Pollution

Environmental pollution, particularly water contamination, has become one of the most significant challenges faced by the global community (Barrios et al., 2016). The pollution of water is a critical issue on a global scale, demanding immediate attention and the development of comprehensive strategies to address and resolve this problem (Geissen et al., 2015). The alarming increase in the volume of wastewater produced and the contamination levels observed internationally can be attributed to various factors such as population growth, economic progress, expansion of agricultural practices, and urbanization (Asfaha et al., 2021). Water pollution occurs when the natural environment is unable to absorb the excessive amounts of pollutants that are discharged into water bodies (Geissen et al., 2015).The main pollutants contained in water and wastewater can be categorized into traditional pollutants (e.g., heavy meals) and emerging pollutants (e.g., pharmaceuticals). Traditional pollutants such as heavy metals have been studied by many researchers and can be easily removed using conventional and existing technologies .But removal of the emerging micro pollutants such as personal care products, pharmaceuticals etc. Is poorly studied and it needs to develop new and advanced technologies that can remove these pollutants effectively.

2.2 Emerging Pollutants

The rapid increase in human activities over the past few decades has led to the introduction of a wide range of new chemical compounds into the environment, known as "emerging pollutants" (Jari et al., 2022). These emerging pollutants, also referred to as micro pollutants, are substances that are not commonly monitored in the environment but have the potential to enter and have harmful effects on both ecosystems and human health (Geissen et al., 2015). Examples of emerging pollutants include pharmaceuticals, personal care products, phthalates, flame retardants, and hormones. The presence of micro pollutants is a growing global concern (Jari et al., 2022). These substances, such as pesticides, endocrine disruptors, pharmaceuticals, and their byproducts, can have significant impacts on human health and the environment due to their ability to persist and accumulate in organisms (Barrios et al., 2015; Geissen et al., 2015). Emerging pollutants can enter the environment through various sources, including agricultural runoff, industrial waste, and leaks from domestic and municipal wastewater treatment facilities (Jari et al., 2022).Over the past several years, there has been a growing focus on pharmaceutical residues as a potential environmental pollutant, particularly due to their abundance of bioactive chemicals. These compounds, classified as micro contaminants in wastewater, are currently either unregulated or in the process of being regulated. Emerging pollutants, including pharmaceuticals, are being released into the environment through various pathways such as wastewater, surface water, groundwater, and even drinking water, typically at concentrations between 0.1 and 20 mg/L (García-Montoya et al., 2015). Pharmaceuticals, which are organic compounds utilized in medications for disease prevention and treatment, have the potential to contaminate water bodies through human excretion, runoff, and industrial discharges (Jari et al., 2022).

2.3 Environmental Impact of Emerging Pollutants

On a global scale, the ongoing and uninterrupted introduction of emerging pollutants into the environment is significantly and alarmingly compromising the quality of water resources. Numerous studies conducted worldwide have directed their attention towards these pollutants in an effort to gain a comprehensive understanding of their toxicity, their impact on the environment, and how they behave in diverse marine environments. Persistent compounds stemming from various industries, pesticides, pharmaceuticals, and agricultural activities find their way into water bodies through multiple pathways, often surpassing permissible levels and accumulating over time. This accumulation, in turn, leads to detrimental consequences for both the environment and human communities (Jari et al., 2022. The continuous release of emerging contaminants, their persistent nature, tendency to form complex compounds, and potential for bioaccumulation can have severe and long-lasting effects on aquatic life, human health, and the environment. Over time, these contaminants can lead to chronic illnesses in both animals and humans. Depending on the duration and amount of exposure, these micro pollutants can contribute to various sexual disorders such as polycystic ovaries, reduced male fertility, difficulties in conceiving, higher rates of miscarriages, and abnormalities in the development of reproductive organs in both males and females. Moreover, they have been linked to the development of cancers in the prostate, testicles, and breasts. Additionally, when taken in excessive amounts, paracetamol can have harmful effects, particularly in promoting the growth of breast cancer cells. This toxicity is typically attributed to the presence of reactive oxygen species, which can cause a range of detrimental effects such as the denaturation of proteins, the peroxidation of lipids, and damage to DNA.

2.4 paracetamol

Paracetamol, also known by its chemical name N-acetyl-4-amino-phenol, is a commonly used medication for relieving pain and reducing fever. It is widely utilized for its analgesic and antipyretic properties in the medical field. . Paracetamol, also known as acetaminophen, is a widely used medication that is prescribed and taken by millions of people worldwide (Jari et al., 2022). It falls under the category of an acylated aromatic amide and is commonly used to alleviate symptoms such as headaches, joint pain, chronic pain associated with cancer, and fever in both adults and children (Periyasamy & Muthuchamy, 2018). With a chemical formula of $C8H9NO_2$ and a molecular weight of 151.16 $gmol^{-1}$, paracetamol is classified as a weak acid and exhibits high solubility in water, specifically 14000 mg/L at a temperature of 20 °C. It is important to note that paracetamol has the potential to transform into a harmful substance. The presence of paracetamol, along with other pharmaceuticals, in the environment stems from various sources, including human excretion of drugs or their metabolites that are not fully absorbed, remnants from pharmaceutical manufacturing processes, and agricultural activities (Jari et al., 2022; Periyasamy & Muthuchamy, 2018)..

Paracetamol, a widely used analgesic and anti-inflammatory drug, is commonly administered to both humans and animals worldwide. Its occurrence has been extensively examined in various sources such as hospital effluents, treatment plants, surface water, and groundwater, with concentrations ranging from 29 to 246 mg/L (García-Montoya et al., 2015). The presence of paracetamol in wastewater poses a potential environmental hazard, making it a significant concern among the numerous active pharmaceutical compounds found in hospital wastewater (Al-Itawi, 2019)..

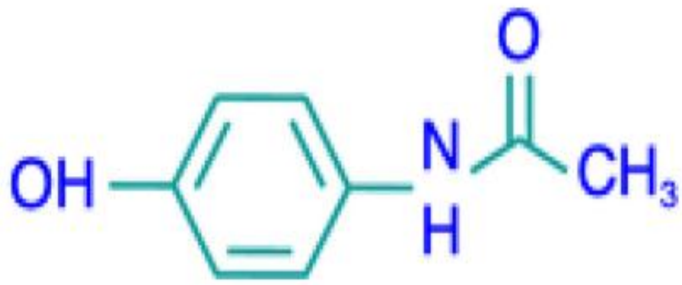

Figure 1. Paracetamol molecule

2.5 Removal Methods of Emerging Pollutants

Over the past few decades, the discovery of newly identified compounds in the marine environment, whether they are man-made or naturally occurring, has become a global issue that is causing increasing concern for the environment (Rout et al., 2021). These contaminants are primarily organic in nature and are typically found in very small concentrations, ranging from parts per trillion to parts per billion. The presence of various chemicals and particles in water, including nutrients, heavy metals, microorganisms, and priority pollutants, plays a significant role in determining water quality. However, there has been a recent focus on organic pollutants, also known as emerging contaminants, as they have been found to not only have a negative impact on water quality but also present challenges for existing water treatment systems in terms of effectively removing them (Kashif et al., 2021).

There have been numerous advancements in treatment technologies designed to tackle the issue of micro pollutants and their harmful impact on both human health and the environment (Asfaha et al., 2021). These treatment methods can be broadly categorized into three main groups: physicochemical, biological, and advanced oxidation processes (Jari et al., 2022). The effectiveness of these technologies in removing micro pollutants is heavily influenced by various physicochemical properties such as functionalities, hydrophobicity, charge, size, morphology, dissociation constant, and the nature of the specific contaminants being targeted. Traditional treatment methods like ion exchange, chemical precipitation, membrane separation, flocculation, and coagulation have proven to be inadequate in effectively eliminating emerging contaminants from polluted water sources (Kashif et al., 2021). Biological wastewater treatment methods rely on the utilization of microorganisms in either aerobic or anaerobic conditions to break down toxic substances that are resistant to biodegradation. However, these microorganisms are not very efficient when it comes to eliminating emerging pollutants. Alternative treatment technologies, such as activated carbon adsorption, membrane filtration, and ozonation, have also been proven effective in removing micro pollutants. Nevertheless, ozonation can lead to the creation of byproducts through oxidation, activated carbon adsorption is not as successful in deactivating bacteria, and membrane filtration faces difficulties in disposing of concentrated waste, in addition to requiring high levels of energy and capital investment.

In recent years, advanced oxidation processes have emerged as the most widely used and extensively studied advanced treatment methods for removing emerging pollutants from wastewater among the various technologies available for wastewater treatment. This trend has been observed in the research and application of wastewater treatment technologies (Rout et al., 2021). The electrooxidation process, a highly sophisticated method of oxidation, has proven to be highly effective in eliminating wastewater that contains emerging pollutants. The extent to which it successfully removes these pollutants largely hinges upon the characteristics and composition of the electrodes employed as either an anode or cathode during the electrolysis process (Kouadio et al., 2021). In recent times, there has been a growing interest in the use of electrochemical oxidation as a means of removing micropollutants due to its versatility, energy efficiency, environmental friendliness, and cost-effectiveness. This method also offers the advantage of automation, as highlighted by Angl et al. (2020a). Compared to traditional methods, electrochemical treatment stands out for its high efficiency, quick reaction times, and ease of implementation. Furthermore, this process requires minimal chemical usage and does not generate any harmful secondary byproducts, as noted by Kouadio et al. (2021).

Table 1. Overview of different treatment technologies used for the removal of emerging pollutants (paracetamol) from wastewater (Boshir et al., 2016; Jari et al., 2022; Kashif et al., 2021; Khan et al., 2019).

Treatment technologies	Advantages	Drawbacks
Membrane separation	Requires less space	High capital cost, fouling and disposal issues
Adsorption	Ease operation, high quality	High cost of commercial adsorbents, desorption issues
Ion exchange	Low sludge production	High operational cost
Fenton's process	Degradation and mineralization of emerging pollutants	Decrement of •OH due to formation of chloro and sulfato-Fe (III)
Ozonation	High affinity to pollutants in the presence of H_2O_2	Requires high energy, formation of oxidative by products
Advanced oxidation process (AOP)	Short degradation rate, Selective oxidant favoring disinfection and sterilization properties	High energy consumption, issues of maintenance and operational cost
Nanofiltration (NF)	Useful for treating saline water and wastewater	High energy consumption, fouling of membrane issues
Reverse osmosis (RO)	Can remove personal care pharmaceutical pollutants	High energy demand, membrane fouling issues
Micro or ultrafiltration	Low cost, can remove pathogens, stable and catalyst recovery	Not effective to remove some emerging pollutants as the pore is 100 to 1000 times larger than the micropollutants

2.3 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) are a type of treatment technology that operates in a water-based environment. These processes aim to remove pollutants by utilizing highly reactive substances. Examples of these substances include strong oxidizing agents like peroxide and ozone, as well as catalysts such as manganese, iron, or titanium dioxide. In addition, high energy radiation, such as UV irradiation, is often used to enhance the effectiveness of AOPs. One of the key outcomes of AOPs is the generation of hydroxyl radicals (•OH), which are extremely powerful and non-selective oxidizing species. These radicals play a crucial role in oxidizing the targeted organic pollutants, leading to the formation of biodegradable intermediates. Ultimately, these intermediates are further degraded into harmless byproducts like carbon dioxide, water, and inorganic salts.

Over the past few decades, there has been extensive research conducted on electrochemical advanced oxidation processes (EAOPs) within the field of wastewater treatment (Feng et al., 2013). These EAOPs offer numerous advantages in addressing and resolving issues related to wastewater. One notable advantage is the use of electrons as a clean reagent, which contributes to the overall cleanliness of the process. Additionally, EAOPs boast high energy efficiency and require simple equipment, making them easy to handle. They can also be easily automated and do not necessitate the use of chemical reagents. Moreover, EAOPs are free from secondary pollution and are considered safe as they operate under mild conditions, such as room temperature and pressure. Furthermore, their versatility is noteworthy as they can be successfully applied to effluents with chemical oxygen demand (COD) levels ranging from 0.1 to 100 g L−1 (Chen et al., 2021; Kashif et al., 2021)

Among these methods, anodic oxidation is the most commonly employed technique. It operates by generating oxidizing agents through the use of specific anode materials. This method shows promise in resolving environmental issues arising from the discharge of emerging effluents. One of its key advantages is its simplicity in terms of equipment, as well as its ability to prevent sludge formation. Additionally, it requires lower temperature conditions and is easy to operate (López Zavala & Jaber Lara, 2018). A variety of electrochemical technologies have been utilized in the treatment of wastewaters, including electro-Fenton, photoelectron-Fenton, anodic oxidation, sonoelectro-Fenton, electrochemical oxidation, electro floatation, and UV ozonation. These technologies have proven to be effective in addressing environmental concerns by facilitating effluent treatment and implementing integrated production processes (Amouzgar & Salamatinia, 2015; Sánchez et al., 2022; Khan et al., 2020; Orimolade et al., 2020).

2.4 Electrochemical Oxidation

In today's world, electrochemical processes are widely recognized as highly effective methods for treating wastewater due to their ability to eliminate pollutants without the need for additional chemical additives. These processes rely solely on the introduction of electrons to initiate reactions (Karungamye, 2020). The electrochemical oxidation process works through two main mechanisms. Firstly, pollutants are attracted to the anode where they undergo degradation through electron transfer reactions. Secondly, pollutants can also be degraded through indirect oxidation in the liquid bulk, facilitated by oxidants generated during the electrochemical process (Karungamye, 2020; Ouarda et

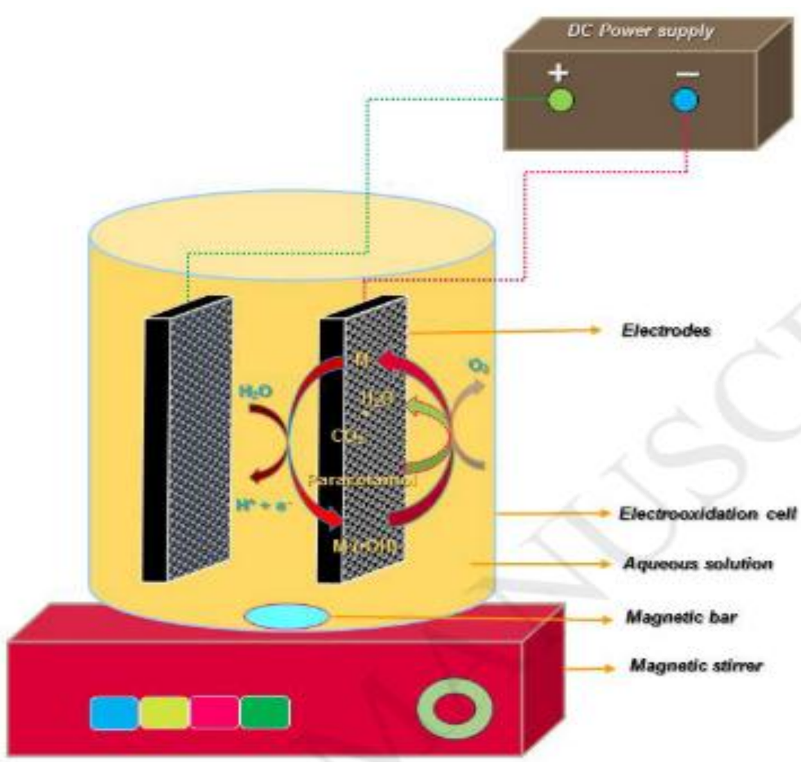

Figure 2. Experimental setup for electrochemical oxidation process (Periyasamy & Muthuchamy, 2018).

2.5 Working Principle of Electrooxidation Process

The degradation of emerging pollutants through electrochemical means can be achieved using two different techniques, namely direct and indirect anodic oxidation processes. Anodic oxidation, also known as AO, is an advanced electrochemical oxidation process that holds great potential as a cutting-edge technology for effectively treating emerging pollutants. This process involves the oxidation of organic compounds by either directly transferring electrons from these compounds to the surface of the anode, or by generating hydroxyl radicals (•OH) through the oxidation of water on the electrode surface. It is worth noting that the latter reaction occurs with high O2 overvoltage, as highlighted in a study by Trellu et al. (2017).

2.5.1 Direct Anodic Oxidation

The direct anodic oxidation process involves the diffusion of pollutants from the bulk solution to the surface of the anode electrode before they are adsorbed and degraded through an anodic electron transfer reaction. This process, illustrated in Figure 3, sees organic pollutants oxidized on the anode surface by hydroxyl radicals (•OH) generated by water, as depicted in equation (1) (Angl et al., 2020b).

$$2H_2O \rightarrow 2HO^{\bullet} + 2H^{+} + 2e^{-} \quad (1)$$

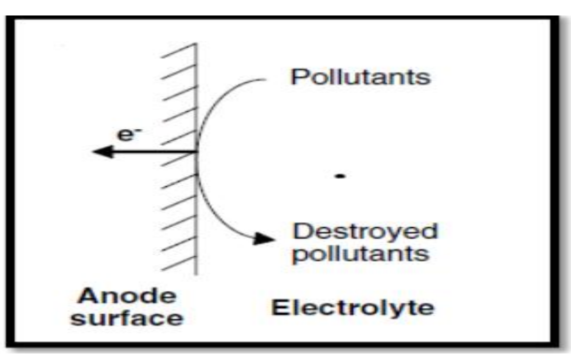

Figure 3. Direct oxidation process

2.5.2 Indirect Anodic Oxidation

As HCl was introduced to regulate the pH levels of the solutions, chloride ions became present in the solutions as a result of the dissociation of HCl into H+ and Cl-. In this environment, acetaminophen underwent electrooxidation by reactive chlorine species. The Cl- ions were oxidized directly at the anode, leading to the production of soluble chlorine (Cl2) according to reaction (2) (Angl et al., 2020b). The potent oxidizing agents like chlorine and/or hypochlorite that were created at the surface of the anode could be utilized to eliminate substances that can be oxidized.

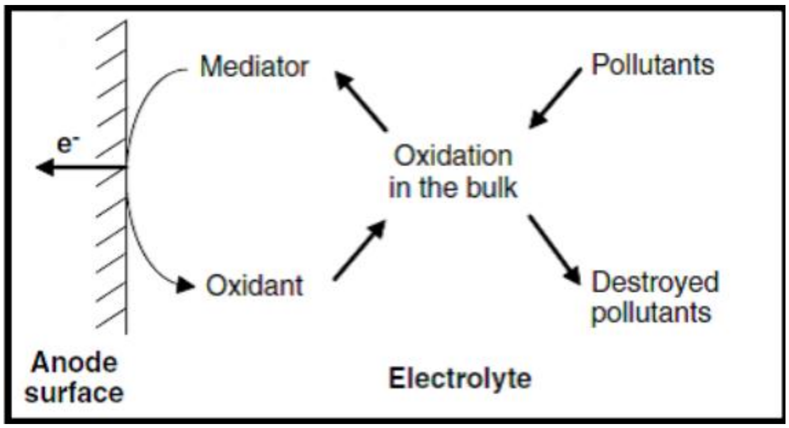

Figure 4. Indirect oxidation process.

In the process of indirect electro-oxidation, sodium or potassium chloride salts are introduced into the wastewater to enhance electrical conductivity and facilitate the production of hypochlorite ions. This method aims to improve the efficiency of the oxidation process by utilizing these salts as catalysts for the generation of reactive species that can effectively degrade contaminants in the wastewater..

$$2Cl^{-} \rightarrow Cl_2 + 2e^{-} \qquad (2)$$

The generated chlorine in reaction (2) is used to form hypochlorous acid at bulk solution reaction system.

$$Cl_2 + H_2O \rightarrow HOCl + H^{+} + Cl \qquad (3)$$

$$Cl^{-} + H_2O \rightarrow HOCl + H^{+} + 2e^{-} \qquad (4)$$

In addition, the hypochlorous acid that is produced further breaks down into hypochlorite ion by undergoing reaction (5). This hypochlorite ion, also known as OCl-, is then utilized to break down the paracetamol (PC) pollutant into carbon dioxide and water through reactions (6) and (7).

$$HOCl \rightarrow H^{+} + OCl^{-} \tag{5}$$

$$OCl + PC \rightarrow \quad \text{intermediate} \ \rightarrow CO_2 + H_2O + Cl^{-} \tag{6}$$

$$HOCl + PC \rightarrow CO_2 + H_2O + HCl \tag{7}$$

2.6 Factors that Affect the Removal of Paracetamol by EO Process

Electrochemical treatment methods are widely used for the investigation of electroactive compounds in pharmaceutical firms like paracetamol due to their simple, rapid, and environmentally friendly (Periyasamy & Muthuchamy, 2018). According to traditional electrochemistry and recent study, electrolytic effects could be influenced by electrolyte concentration (conductivity), pH, temperature, electrolysis time, type of electrode, inter electrode distance, pollutant concentration, steering speed and electric voltage.

2.6.1 Effect of pH of Solution

The pH level of a solution plays a critical role in determining how effectively the electrochemical process operates, according to Angl et al. (2020a). It significantly impacts the performance of Electrooxidation (EO), particularly in terms of the electrolysis mechanism, as it dictates the types of hydrolyzed metal species formed in reactive environments and influences the dominant EO mechanisms. Periyasamy et al. (2018) conducted a study on the impact of pH changes during EO of paracetamol with graphite electrodes, finding that the removal efficiency was enhanced in acidic conditions.

2.6.2 Effect of Electrolyte Concentration

The conductivity of a solution is a significant aspect when it comes to facilitating the flow of electrical current. This is due to the fact that a higher concentration of ions in the solution increases the likelihood of electron transport, which in turn contributes to a more efficient degradation rate. Additionally, the conductivity of both the surface and wastewater is typically influenced by the quantity of total dissolved solids present. In the context of electrochemical oxidation (EO) experiments, sulfate ($SO4\ 2\ ^{-}$) is commonly used as an electrolyte to provide support and is commonly found in both natural and wastewater environments (Saha et al., 2022).

2.6.3 Effect of Electrolysis Time

The duration of electrolysis plays a crucial role in the electrochemical oxidation process. According to a research study conducted by Tahir in 2017, it was found that as the time of electrolysis increases, both the effectiveness of removing contaminants and the amount of energy consumed also increase. However, it is important to note that the increase in energy consumption surpasses the improvement in removal efficiency after a certain point. In general, when the current density remains constant, the production of metal hydroxide also rises with longer electrolysis times

2.6.4 Effect of Inter Electrode Distance

The diffusion rate of the target pollutant in the electrochemical oxidation system is influenced by the distance between the electrodes, and this in turn affects the efficiency of its degradation. It is important to consider the inter electrode distance in order to determine the most effective distance for the electrodes. Numerous studies have demonstrated that the optimized distance between electrodes is a crucial parameter in the electrochemical oxidation process. For instance, research conducted by Liu et al. (2012) and Periyasamy & Muthuchamy (2018) have shown that a distance of 1 cm between electrodes is more ideal for promoting effective mixing compared to distances of 5cm and 7cm..

2.6.5 Effect of Applied Current Density

The significance of current density cannot be overstated in the electrooxidation process, as it plays a crucial role in regulating the rate of reaction in various electrochemical processes (Periyasamy & Muthuchamy, 2018). It is widely believed that the acceleration of applied current density leads to a more rapid and efficient degradation of paracetamol, primarily because it triggers the production of oxidizing radicals on the anode surface (Angl et al., 2020b). This underscores the pivotal role that current density plays in enhancing the efficiency and effectiveness of electrochemical processes.

2.6.6 Effect of Stirring Speed

The primary goal of adjusting the stirring speed is to ensure that the coagulant matter is evenly distributed throughout the reactor, which is created by the electrode solution. When the coagulant matter is not properly dispersed in the reactor, it can lead to non-uniformity in the reactor content and potential regional variations (Bayar et al., 2011). Excessive stirring speeds can break apart the flocs that have formed in the reactor, resulting in the formation of smaller, more difficult-to-remove flocs in the water

2.6.7 Effect of Paracetamol Concentration

The level of pollutants present has a major impact on how effectively the electrochemical process works. It is crucial to study how the starting concentration of paracetamol affects the efficiency of the electrochemical oxidation process used to remove pollutants. Research indicates that breaking down and completely removing paracetamol is more successful at lower concentrations compared to higher concentrations. This is because higher concentrations of paracetamol result in more pollutant molecules, but not an increase in hydroxyl radical concentration, leading to a decrease in the efficiency of degradation (De Luna et al., 2014).

2.6.8 Effect of Electrode Type

The choice of electrode materials is a crucial aspect of the electrolysis process, which holds significant importance in the electrochemical oxidation process. This directly impacts the efficiency, selectivity, and energy consumption of the electrolysis process (He et al., 2019a). Therefore, when selecting electrodes for the electrooxidation process, it is essential that they possess favorable properties such as physical and chemical stability, good electrical conductivity, selective reactivity, and affordability (He et al., 2019b; Zhang et al., 2022). Various electrode anode materials are utilized for the electrochemical oxidation and reduction of organic compounds, including boron doped diamond (BDD) anodes, titanium meshes coated with mixed metal oxides, carbon-based electrodes such as graphite, and composites of titanium with lead dioxide (Ti/PbO2), titanium with iridium dioxide (Ti/IrO2), and carbon nanotubes (Thamaraiselvan et al., 2021). These materials have proven effective in facilitating the electrochemical reactions involved in the oxidation and reduction of organic compounds. Similarly, the cathode material also plays a crucial role in the electrochemical oxidation of wastewater. From a practical standpoint, materials such as titanium, copper, and stainless steel can be chosen as cathode materials for their suitability in this process.

This research utilized a Ti/IrO2 coated anode and stainless-steel cathode electrodes to facilitate the degradation of paracetamol in synthetic wastewater. These electrodes were chosen for their ability to operate effectively with minimal over potential, simplicity in operation, cost-effectiveness, energy efficiency, and resistance to corrosion..

2.7 Summary of Some Previous Studies on Paracetamol Removal from Wastewater

In a similar vein, Ghanbari et al. (2021) utilized an ultrasound-assisted heterogeneous electro-Fenton process with hematite nanoparticles to degrade paracetamol in aqueous solution. Their results demonstrated a 98.9% degradation of paracetamol under specific conditions, including pH, current density, initial concentration, and electrolysis time. Additionally, Kouadio et al. (2021) investigated the removal of paracetamol through electro-oxidation using boron-doped diamond electrodes. They found that oxidation of paracetamol was more effective in acidic media. Within the field of literature, numerous researchers have delved into the topic of removing the emerging pollutant known as paracetamol from wastewater. They have explored various treatment technologies and investigated the treatment process under different operating parameters. For example, Periyasamy and Muthuchamy (2018) conducted a study in which they successfully removed paracetamol from synthetic wastewater using an electrochemical oxidation process with a graphite anode. By examining the effects of electrolyte concentration, current density, and initial pH, they were able to achieve a 90% removal efficiency of paracetamol at optimized parameter

3. Materials and Methods

3.1 Materials

3.1.1 Chemicals and Reagents

All of the chemicals and reagents utilized in this study were obtained from local chemical suppliers located in Addis Ababa, Ethiopia. The study involved the use of various chemicals and reagents, including Paracetamol (a powder with a purity level of 99%), which was utilized to create synthetic wastewater. Additionally, Hydrochloric acid (HCl) and Sodium hydroxide (NaOH), both with a purity level of 99%, were employed for the purpose of adjusting the pH levels. Furthermore, Na2SO4 was utilized as an electrolyte medium during the electrolysis process. It is important to note that all of these chemicals were of analytical grade and were utilized in their original form without any further purification

3.1.2 Apparatus and Equipment

In this research study, a variety of equipment was utilized. One essential tool was the hot plate magnetic stirrer, which was responsible for thoroughly mixing the solution throughout the entire process. To detect the degradation of paracetamol, a UV visible spectrophotometer (UV/V/S/NIR-England) was employed. Additionally, several other instruments were utilized, including an analytical balance (HS220S), a pH meter (UK,3505), an ultrapure water distiller, various beakers, another analytical balance, a DC power supply (SN-022343), and a TOC analyzer (ELTR HELIOS CS-580A). All of these pieces of equipment played a crucial role in conducting this thorough and comprehensive research study.

3.2 Methods

3.2.1 Electrochemical Oxidation Experimental Setup and Procedures

For this study, experiments were carried out in a batch-wise using undivided cylindrical glass cell with a working volume of 300 ml equipped with two electrodes. The solutions during the experiment were continuously stirred using a magnetic bar stirrer revolving at 300 rpm for efficient mass transfer of the mineralization of paracetamol from wastewater. Ti/IrO_2 coated anode and stainless-steel cathode electrodes have been taken as working anode-cathode electrodes for the degradation of paracetamol and this assembly was connected to a DC power supply under galvanostatic mode to control and monitor the electrolysis conditions during the experiments. The dimension of Ti/IrO_2 and stainless-steel electrodes was 3cm ×3 cm ×1mm thickness with the effective surface area of $9cm^2 \times 2cm^2$. The mineralization and degradation of the paracetamol was monitored and detected with the help of UV visible spectrophotometer. During the electrolysis process Na_2SO_4 solution was used as supporting electrolyte solution. Initial trials were carried out to investigate the impact of different factors on the process, such as varying the current density (ranging from 2 to 7 mA/cm2), adjusting the pH levels (between 2 and 7), changing the distance between electrodes (1 to 3.5 cm), and manipulating the concentration of paracetamol in the solution (from 20 to 95 mg/L). The pH of the solution was controlled by using 0.1 molar solutions of NaOH and HCl.

3.2.2 Analytical Method

The study focused on evaluating the effectiveness of removing paracetamol from wastewater by analyzing changes in absorption spectra. This was done by utilizing a UV-VIS spectrophotometer to measure absorbance at a specific wavelength of 300 nm. The absorbance values obtained were then converted into residual concentrations through a calibration curve. Subsequently, the efficiency of paracetamol removal from the wastewater was determined using a specific equation

$$\text{Removal efficiency (\%)} = \frac{Co - Cf}{Co} * 100 \qquad (8)$$

Where Co is the initial concentration of paracetamol (mg/L), C_f is final concentration of paracetamol after degradation (mg/L).

Similarly, the percent removal of total organic carbon (%TOC) of the paracetamol solution was calculated using the following equation (9).

$$\%\text{TOC} = \frac{TOCi - TOCf}{TOCi} * 100 \quad (9)$$

Where, TOC_i (mg/L) is the total organic carbon present in the paracetamol solution before electrooxidation process, and TOC_f (mg/L) is the total organic carbon present in the paracetamol solution after the electrooxidation process.

3.3 Experimental Design and Data Analysis

The research study involved the use of experimental design and data analysis through design expert software (version 13), specifically utilizing central composite design (CCD) as part of response surface methodology (RSM). Prior to statistical optimization and analysis of the electrooxidation process for paracetamol degradation, preliminary experiments were conducted to assess the impact of various operating process variables including current density (ranging from 2 to 7), pH levels (ranging from 2 to 7), electrodes distance (ranging from 1 to 3.5 cm), and paracetamol concentration (ranging from 20 to 95 mg/L). The interaction effects of these parameters were then examined using response surface methodology (RSM). Subsequently, statistical optimization and validation of experiments were carried out using tools such as ANOVA, coefficient of determination (R2), probability (P-value), and Fisher value (F-value). The selection of factor levels for studying interaction effects, statistical optimization, and experiment analysis was based on the individual factor effects observed in the electrooxidation process. Finally, the degradation of total organic carbon in the paracetamol solution was assessed through three trial experiments conducted at the optimized oxidation parameters.

3.3.1 Individual Parameter Effects on the Electrochemical Oxidation Process

Initial experiments were carried out to test various factors on the degradation of paracetamol. These factors included the applied current density, pH levels, distance between electrodes, and the initial concentration of paracetamol. Each variable was tested individually while keeping the others constant. The range of each parameter and its impact on the degradation of paracetamol can be seen in Table 2.

Table 2. Parameters and their levels for OVAT analysis

Parameters	Unit	Levels					
pH	-	2	3	4	5	6	7
Current density	mA/cm^2	2	3	4	5	6	7
Electrodes distance	Cm	1	1.5	2	2.5	3	3.5
Concentration	mgL^{-1}	20	35	50	65	80	95

3.3.2 Study of Parameter Interaction Effect and Model Evaluation Using RSM-CCD

Following the analysis of how specific factors impact the breakdown of paracetamol, researchers conducted further experiments to explore how these factors interact with one another during electrolysis. These factors included current density, pH levels, electrode distance, and the initial concentration of paracetamol. The results from these initial experiments were crucial in determining the optimal range for each parameter and in designing subsequent experiments using Response Surface Methodology (RSM). The Central Composite Design (CCD), a form of RSM, was employed as a statistical analysis tool to create models from experimental data of varying complexities.

In the initial experiments conducted by OVAT, a total of four parameters were chosen for further investigation of their interaction effects and for evaluating the model. These parameters were varied at three different levels each, as outlined in Table 3. To ensure accuracy and reliability, multiple trials were carried out and the average results were recorded for analysis. Subsequently, a mathematical model was constructed to establish the relationship between the independent parameters and the response variable of removal efficiency. Regression analysis was then applied to the quadratic model, which is represented by equation (9) below.

$$\text{Removal efficiency (\%)} = \beta + a_1A + a_2B + a_3C + a_4D + b_1AB + b_2AC + b_3AD + b_4BC + b_5BD + b_6CD + c_1A^2 + c_2B^2 + c_3C^2 + c_4D^2 \quad (10)$$

Where β is an intercept constant, a_1–a_4 is coefficients of main effects, b_1–b_6 is coefficients of parameters interaction, c_1–c_4 is coefficients of quadratic effects, and A–D is experimental variables.

Table 3. Independent parameters and their coded levels for CCD experiments

Parameters	Symbol	Unit	Levels		
			Low (-1)	Medium (0)	High (+1)
pH	A	-	3	4	5
Current density	B	mA/cm^2	5	6	7
Electrodes distance	C	Cm	1	1.5	2
Concentration	D	mgL^{-1}	20	35	50

As stated by Chopra and Kumar in their 2020 study, the formula to determine the necessary number of experimental runs is 2n + 2n + c, where n represents the independent factor and c denotes the number of center points. Therefore, in the case of four independent factors, a total of 30 experiments were carried out to investigate the removal efficiency of paracetamol through electrooxidation in an aqueous solution, as detailed in Table 4. Each experiment was conducted in duplicate, and the results were averaged for further analysis

Table 4. CCD design matrix for four variables

Run	pH (-)	Current density (mA/cm^2)	Distance of electrodes (cm)	Initial concentration (mg/L)
1	4	6	1.5	35
2	3	7	2	50
3	4	6	1.5	35
4	3	7	2	20
5	5	5	1	50
6	5	7	2	20
7	4	8	1.5	35
8	4	6	1.5	35
9	5	5	1	20
10	5	7	2	50
11	4	6	1.5	65
12	3	5	2	50
13	4	6	1.5	5
14	5	7	1	50
15	3	7	1	50
16	4	6	1.5	35
17	4	6	2.5	35
18	4	6	1.5	35
19	5	5	2	50
20	5	5	2	20
21	2	6	1.5	35
22	3	5	1	50
23	4	6	1.5	35
24	3	5	2	20
25	6	6	1.5	35
26	3	5	1	20
27	5	7	1	20
28	3	7	1	20
29	4	4	1.5	35
30	4	6	1.5	35

3.3.3 Optimization of Process Parameters and Statistical Analysis

The process variables, including current density, pH, electrodes distance, and initial paracetamol concentration, were optimized using Design-Expert-13 software. The goal was to achieve the best possible result in terms of paracetamol removal through the electrochemical oxidation process. To assess the effectiveness and importance of the model, a statistical analysis tool called ANOVA was utilized. This analysis considered factors such as the coefficient of determination (R2), probability (p-value), and Fisher value (F value). Furthermore, the optimized parameters were used to conduct experiments and validate the model. The obtained results were then compared with the predicted outcome.

3.3.4 Study of the Degradation of Total Organic Carbon (TOC)

Investigating the complete degradation of organic carbon in relation to the removal of paracetamol from wastewater is a necessary area of research in environmental science and wastewater treatment (P. Kaur et al., 2023). To investigate the degradation of total organic carbon in paracetamol, the experiment was conducted with optimized electro oxidation process parameters in three trials, and TOC was measured and analyzed by a TOC analyzer.

4. Results and Discussion

4.1 Experimental Study of Electrochemical Oxidation of Paracetamol

A series of batch experiments were conducted in a 300 ml working volume of beakers. The electrolyte solution was continuously stirred using a hot plate magnetic stirrer, which was set to rotate at a speed of 300 rpm. These experiments took place at room temperature. To investigate the degradation efficiency of the Ti/IrO2 anode and stainless-steel cathode electrodes for paracetamol from an aqueous solution, a preliminary experimental study was conducted. This study employed the principle of one variable at a time and also examined the interaction effect of the electrochemical oxidation process parameters, namely current density, pH, distance of electrodes, and initial concentration of pollutant. The purpose of this study was to determine the impact of each individual parameter on the electrochemical oxidation process, in order to identify the optimal levels of these variables. By understanding the effects of each parameter, the range for each electrolysis variable was determined. It is recommended to investigate the interaction effects of the process variables by simultaneously changing them all. Once the electro oxidation process was complete, the final concentration of paracetamol was measured using a UV-visible spectrophotometer.

4.2 Effect of Individual Variables on the Electrochemical Oxidation of Paracetamol

In this particular study, we aimed to investigate how various individual factors contribute to the degradation process of paracetamol. To achieve this, we manipulated one parameter at a time while keeping all other variables constant. The preliminary experiment involved altering the pH levels within a range of 2 to 7, adjusting the current density between 2 to 7 mA/cm2, changing the distance of the electrodes from 1 to 3.5 cm, and varying the initial concentration of the pollutant from 20 to 95 mg/L.

4.2.1 Effect of pH of Solution

The pH level of a solution plays a crucial role in the breakdown of micro-pollutants. In this particular study, the impact of pH on the oxidation of paracetamol was investigated. The pH of the solution was varied between 2 and 7, while keeping the electrolysis time constant at 40 minutes, the current density at 6 mA/cm2, the concentration of paracetamol at 35 mg/L, and the concentration of the supporting electrolyte at 0.1 M Na2SO4. The results, as depicted in Figure 5, showed that the highest efficiency in removing paracetamol, reaching 97.25%, was achieved at a pH of 3. However, as the pH of the solution increased from 4 to 7, the removal efficiency dropped to 45%. Additionally, when the pH was lowered to 2, the degradation of paracetamol only slightly decreased from 97.25% to 96.5%. This decrease can be attributed to the fact that in strongly acidic conditions, hydrogen ions can scavenge hydroxyl radicals, thereby suppressing the degradation process. It is worth noting that under similar experimental conditions, the maximum removal efficiencies of paracetamol were observed in an acidic environment (Periyasamy & Muthuchamy, 2018). The presence of an acidic medium potentially increases the generation of S2O82- radicals from the supporting electrolyte, thereby improving the rate at which organic compounds are eliminated. The acidic environment likely hinders the process of oxygen evolution, which ultimately boosts the efficiency of paracetamol degradation.. In a highly acidic setting, the presence of •OH radicals leads to heightened oxidation, resulting in the most effective breakdown of paracetamol molecules in a water-based solution (Ghanbari et al., 2021). Conversely, when the pH levels are elevated, the number of •OH radicals diminishes due to the deactivation of the catalyst (Xu et al., 2022a). This shift in conditions ultimately impacts the degradation process of paracetamol

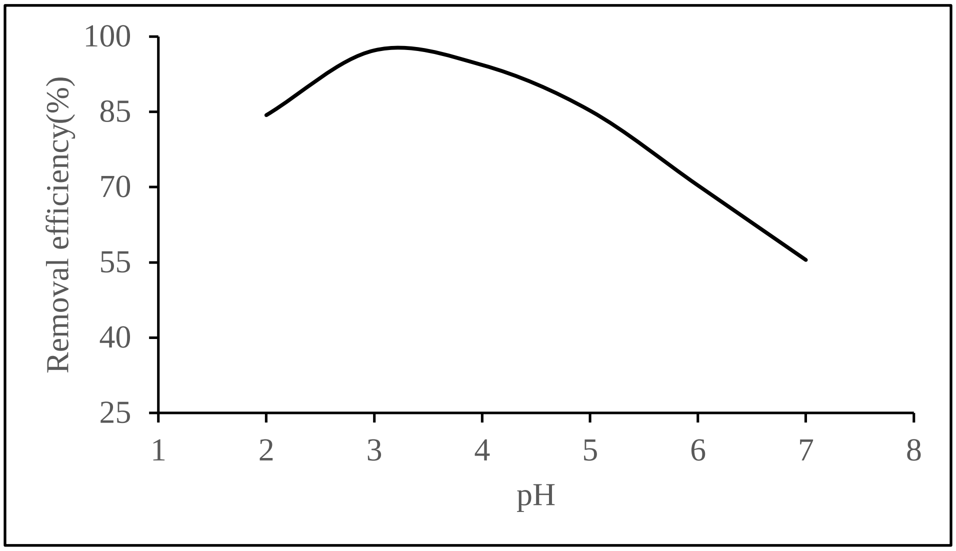

Figure 5. Effect of pH on the degradation of paracetamol

4.2.2 Effect of Current Density

The observed increase in removal efficiency with higher current density can be attributed to the formation of oxidizing radicals. These radicals are generated on the surface of the anode when a higher current density is applied, leading to enhanced degradation of the paracetamol micro-pollutant (Henrique et al., 2020). Therefore, it is expected that paracetamol oxidation will be more effective at higher applied current densities. The current density, which refers to the applied current per unit area of an electrode, is a crucial factor in electrolysis processes. It plays a significant role in controlling the reaction rate during electro oxidation. A study conducted by Ghanbari et al. (2021) aimed to investigate the impact of different current densities on the degradation of paracetamol. The experiments involved varying the current density from 2 to 7 mA/cm2, while keeping the concentration of paracetamol at 35 mg/L, using 0.1 M Na2SO4 as a supporting electrolyte, and maintaining an acidic pH of 3. The results, as shown in Figure 6, revealed that the maximum removal efficiency of paracetamol, reaching 96.25%, was achieved at a current density of 7 mA/cm2. However, as the current density decreased from 7 to 2 mA/cm2, the removal efficiency also decreased. However, it is important to note that increasing the current density also has some negative effects. Firstly, it results in an increase in the operating voltage, which can create challenges related to oxygen evolution. The higher current density exacerbates the production of oxygen on the electrode, which in turn hinders the mass transfer of organic molecules and reduces the removal efficiency (Ghanbari et al., 2021). In conclusion, the current density plays a critical role in the electro oxidation process for the degradation of paracetamol. Higher current densities lead to increased removal efficiency due to the formation of oxidizing radicals. However, the increase in current density also brings challenges related to oxygen evolution and inhibits the mass transfer of organic molecules. Further research is needed to optimize the current density to achieve the most efficient and cost-effective degradation of paracetamol in electrolysis processes.

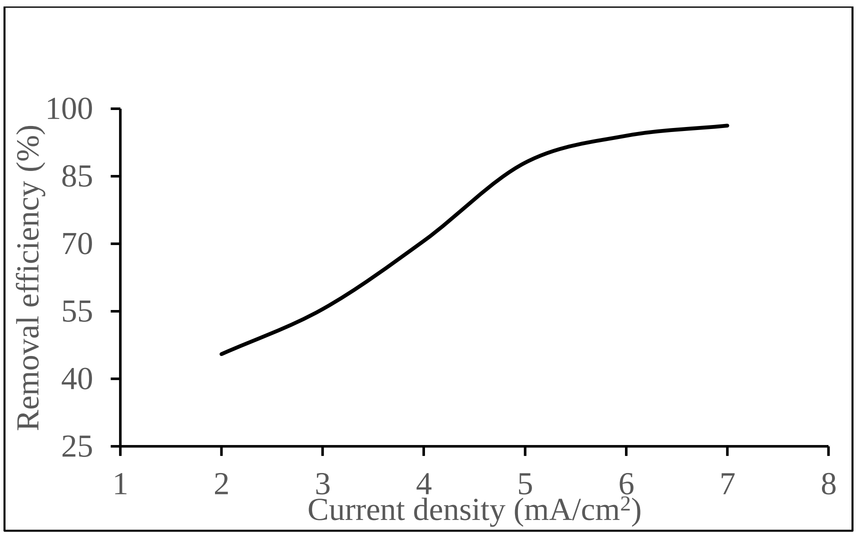

Figure 6. Effect of current density on the degradation of paracetamol

4.2.3 Effect of Distance of Electrodes

The diffusion rate of the target pollutant in the electro oxidation system is influenced by the distance between the electrodes, which in turn affects the efficiency of its degradation. To investigate the impact of electrode distance, the study varied the distance between the electrodes at 1, 1.5, 2, 2.5, 3, and 3.5 cm. The experimental conditions included a pollutant concentration of 35 mg/L, a 0.1 M concentration of Na2SO4 as a supporting electrolyte solution, and an acidic media with a pH of 3. The results showed that at an electrode distance of 1 cm, the maximum removal efficiency reached 97.25%. Figure 7 illustrates that the degradation of paracetamol decreases as the distance between the electrodes increases. These findings are consistent with previous studies conducted by (Sastrawidana and Sukarta in 2018).

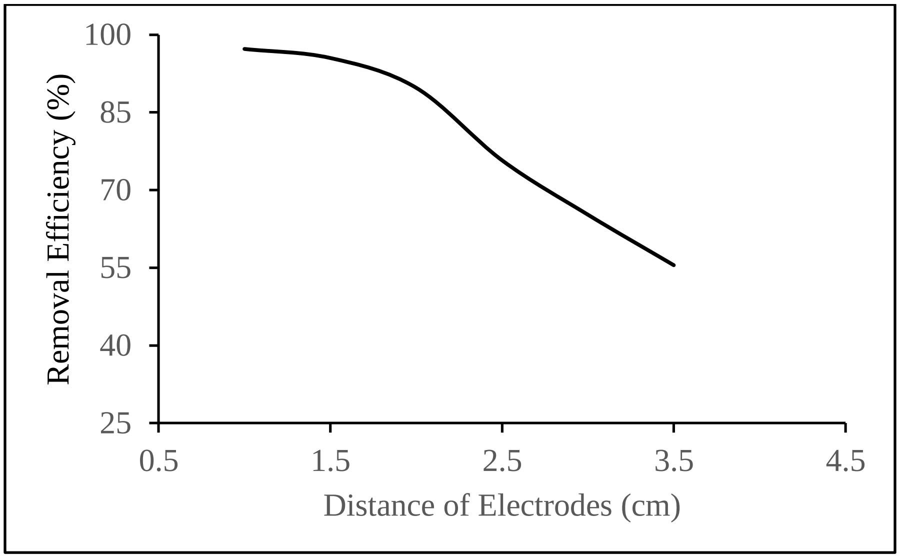

Figure 7. Effect of distance of electrodes on the degradation of paracetamol

4.2.4 Effect of Concentration of Paracetamol

The degradation of paracetamol decreased from 98.5% to 55% as the initial concentration of paracetamol increased from 20 mg/L to 95 mg/L. This suggests that higher concentrations of pollutants require higher levels of oxidizing agents to effectively degrade the pollutant in the electrooxidation system (Ghanbari et al., 2021). Similar findings have been reported by Xu et al. (2022b) concerning this phenomenon. The concentration of micro-pollutants at the beginning of the electrochemical oxidation process is a crucial factor that directly impacts the efficiency of degradation. To investigate the influence of the initial concentration of the emerging pollutant (paracetamol) on the degradation process, the concentration was varied at 20, 35, 50, 65, 80, and 95 mg/L. The pH was maintained at 3, current density at 6 mA/cm2, electrodes distance at 1 cm, and a 0.1M concentration of Na2SO4 as the supporting electrolyte solution. Figure 8 illustrates the results

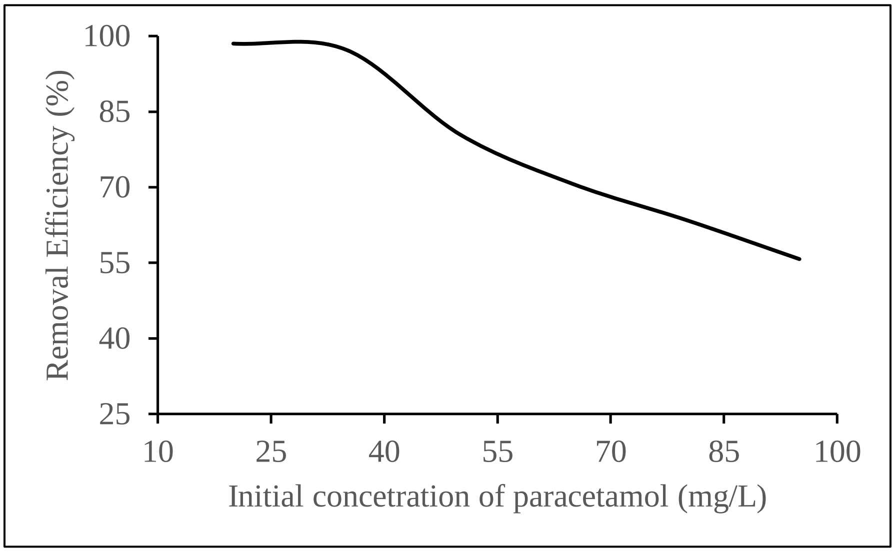

Figure 8. Effect of initial concentration on the degradation of paracetamol

4.3 Interaction Effect of Parameters and Optimization Using RSM

Response surface methodology (RSM) is a statistical technique used to establish a relationship between independent process parameters and the desired outcome by creating a mathematical model (Chopra & Kumar, 2020; Genawi et al., 2020). In this particular study, a Central Composite Design (CCD), a type of RSM, was employed to explore how the electrooxidation process variables interact and impact the desired response. The goal was to develop a mathematical model, assess the significance of the process parameters, and visualize the data using 3D surface graphs for a more comprehensive analysis of the electrolysis system. Through preliminary experiments, the researchers identified the range and levels of the process variables, which were then analyzed using RSM. The study focused on understanding how pH (3-5), current density (5-7 mA/cm2), distance between electrodes (1-2 cm), and initial concentration of paracetamol (20-50 mg/L) interacted to affect the removal efficiency. A series of thirty experimental runs were conducted to evaluate their impact on the response, optimize the process, and validate the results

4.3.1 Model Fitting and Analysis of Variance using ANOVA

A mathematical model was created using Deign Expert Software version 13 in order to establish a connection between the response (removal efficiency) and the independent process variables. This model was then utilized to optimize and analyze the parameters of electrolysis. To determine the validity of the model equation, statistical analysis was performed on the generated mathematical model, taking into account the considered process parameters. Statistical parameters such as Probability (p-value), coefficient of determination (R2), and Fisher value (F-value) were used to assess the significance of the model. A model with a p-value below 0.05 and R2 close to one indicates a significant model. Consequently, this suggests that the response predicted by the model closely aligns with the experimental results.

$$\text{Removal efficiency (\%)} = 96.4083 - 0.882083A + 1.80708B - 0.327917C - 1.71125D + 0.773125AB - 0.564375AC - 0.608125AD - 1.67687BC + 0.941875BD - 0.504375CD - 0.954896A^2 - 1.8674B^2 - 0.548646\,C^2 - 0.692396\,D^2 \quad (11)$$

Where, A is pH, B is current density (mA/cm^2), C is distance of electrodes (cm), and D is initial pollutant concentration (mg/L).

In a similar manner, the significance and influence of the main factors and the other interactive terms were analyzed statistically using statistical parameters of P-value and F-value. From the statistical analysis, all the main, interactive, and quadratic terms were significant with < 0.0001 p-values as shown in Table 5.

Table 5. Analysis of variance (ANOVA) for the quadratic model

Source	Sum of squares	Df	Mean square	F-value	P-value	
Model	366.65	14	26.19	301.38	< 0.0001	Significant
A	18.67	1	18.67	214.89	< 0.0001	
B	78.37	1	78.37	901.91	< 0.0001	
C	2.58	1	2.58	29.7	< 0.0001	
D	70.28	1	70.28	808.78	< 0.0001	
AB	9.56	1	9.56	110.06	< 0.0001	
AC	5.1	1	5.1	58.65	< 0.0001	
AD	5.92	1	5.92	68.09	< 0.0001	
BC	44.99	1	44.99	517.74	< 0.0001	
BD	14.19	1	14.19	163.34	< 0.0001	
CD	4.07	1	4.07	46.84	< 0.0001	
A^2	25.01	1	25.01	287.81	< 0.0001	
B^2	95.65	1	95.65	1100.7	< 0.0001	
C^2	8.26	1	8.26	95.01	< 0.0001	
D^2	13.15	1	13.15	151.32	< 0.0001	
Residual	1.3	15	0.0869			
Lack of Fit	1.16	10	0.1156	3.93	0.072	not significant
Pure Error	0.1471	5	0.0294			
Cor Total	367.95	29				

The mathematical model developed through the use of Design Expert software has been determined to be statistically significant based on the P- and R2values. This indicates that the model is reliable. When a model is significant, it is expected that the predicted removal efficiency (response) from the mathematical model will closely match the values obtained from actual experiments. In this particular study, both the predicted and actual values for removal efficiency are similar, with R^2, adjusted R^2, and predicted R^2 values of 0.9965, 0.9932, and 0.9813 respectively (refer to Appendix B, Table B-2). Table 6 displays the actual and model-predicted responses for the electrooxidation process used in paracetamol degradation, considering the four process parameters

Table 6. Experimental design matrix generated by CCD for the degradation of paracetamol using electro oxidation process

Run	A: pH	B: Current density (mA/cm^2)	C: Distance of electrodes (cm)	D: Initial concentration(mg/L)	Removal efficiency (%)	
					Actual	Predicted
1	4	6	1.5	35	96.25	96.41
2	3	7	2	50	89.5	89.81
3	4	6	1.5	35	96.5	96.41
4	3	7	2	20	93.75	93.57
5	5	5	1	50	85.75	85.43
6	5	7	2	20	93.25	93.27
7	4	8	1.5	35	92.35	92.55
8	4	6	1.5	35	96.35	96.41
9	5	5	1	20	88.5	88.51
10	5	7	2	50	92.35	91.94
11	4	6	1.5	65	90.25	90.22
12	3	5	2	50	89.5	89.21
13	4	6	1.5	5	96.85	97.06
14	5	7	1	50	95.5	95.83
15	3	7	1	50	96.35	95.96
16	4	6	1.5	35	96.65	96.41
17	4	6	2.5	35	93.5	93.56
18	4	6	1.5	35	96.5	96.41
19	5	5	2	50	87.88	88.25
20	5	5	2	20	93.45	93.35
21	2	6	1.5	35	94.25	94.35
22	3	5	1	50	88.35	88.65
23	4	6	1.5	35	96.2	96.41
24	3	5	2	20	96.75	96.74
25	6	6	1.5	35	90.75	90.82
26	3	5	1	20	94.25	94.17
27	5	7	1	20	95.35	95.14
28	3	7	1	20	97.75	97.7
29	4	4	1.5	35	85.35	85.32
30	4	6	0.5	35	94.75	94.87

Further analysis was conducted on the predicted and experimental values of the model by visually representing them in a graph. The graph in Figure 9 illustrates that the actual and predicted values are quite similar, with a high R^2value of 0.9965. This indicates that the developed model is highly reliable in predicting the efficiency of paracetamol removal using both Ti/IrO2 anode and stainless-steel electrodes, even under challenging process conditions that are difficult to regulate

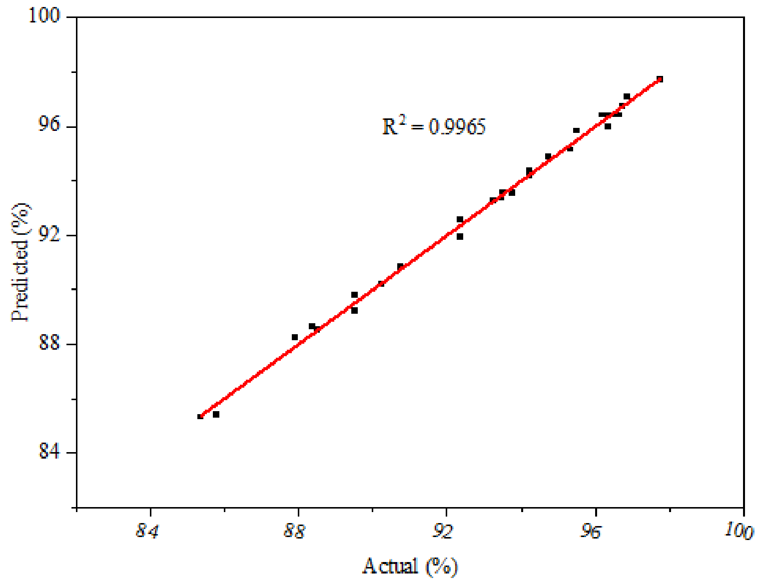

Figure 9. Experimental and model predicted paracetamol removal efficiencies

4.3.2 Interaction Effect of the Electrooxidation process Variables

The variables involved in the electrolysis process are quantities that play a crucial role in determining the state of a specific physical phenomenon. These variables have a direct impact on each other and the overall process itself. The interaction between these parameters is extensively studied to assess the effectiveness of the process. Various factors with varying degrees of influence are responsible for shaping processes in the physical world. In the case of electrooxidation, the levels of parameters such as pH of the solution, applied current density, distance between electrodes, initial concentration of paracetamol, and to some extent temperature and agitation speed significantly determine the outcome of the process.

Similarly, Figure 10 (b) showcases the interaction between the pH and the distance between the electrodes. The removal efficiency is measured at a constant current density of 6 mA/cm2 and an initial paracetamol concentration of 35 mg/L. The 3D graph reveals that the removal efficiency increases as the pH decreases from 5 to 3, and as the distance between the electrodes decreases from 2 cm to 1 cm. The interaction effect between the pH of the solution and the applied current density on the electrooxidation of paracetamol is demonstrated in Figure 10 (a). This figure illustrates how the pH and current density interact with each other when the distance between the electrodes is kept constant at 1.5 cm and the initial concentration of the pollutant is 35 mg/L. By examining the 3D surface plot, it becomes evident that the efficiency of removing paracetamol increases as the pH decreases from 5 to 3, and as the applied current density increases from 5 mA/cm^2 to 7 mA/cm^2.

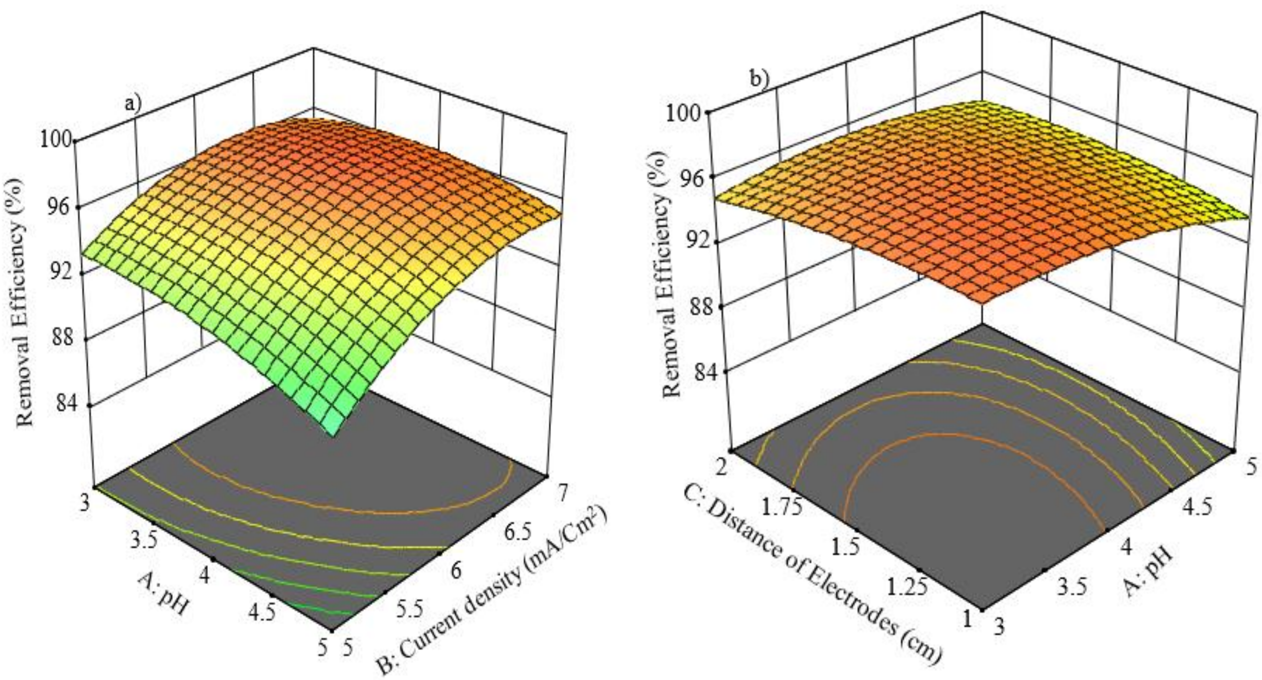

Figure 10. Interaction effect of a) pH and applied current (distance: 1.5 cm, initial concentration: 35mg/L) b) pH and distance of electrodes (current density: 6 mA/cm^2, initial concentration: 35mg/L on the oxidation of paracetamol.

Furthermore, the interaction effect of applied current density and the distance between electrodes was investigated at a pH of 4 and an initial paracetamol concentration of 35 mg/L. The results, depicted in the 3D graph of Figure 11 (b), revealed that the removal efficiency increased as the current density increased from 5 mA/cm^2 to 7 mA/cm2. This can be explained by the fact that as the current density increases, the production of oxidizing radicals also increases, resulting in the maximum degradation of the emerging paracetamol. The interaction between pH and initial paracetamol concentration has been examined in Figure 11 (a), specifically focusing on its impact on the electrooxidation of paracetamol. It was found that as the initial concentration of paracetamol increased from 20 mg/L to 50 mg/L, the efficiency of its removal decreased. This can be attributed to the fact that higher concentrations of the pollutant require a larger number of oxidizing agents for effective degradation. On the other hand, it was observed that the removal efficiency of paracetamol decreased as the distance between electrodes increased from 1 cm to 2 cm. Similarly, the removal efficiency of paracetamol was found to increase as the pH of the solution decreased. This increase can be attributed to the inhibition of the oxygen evolution reaction as the acidity of the solution decreases, leading to an enhancement in the degradation efficiency of paracetamol. This decrement is because as distance of electrodes is increased electrolysis resistance is also increased with fixed applied current density.

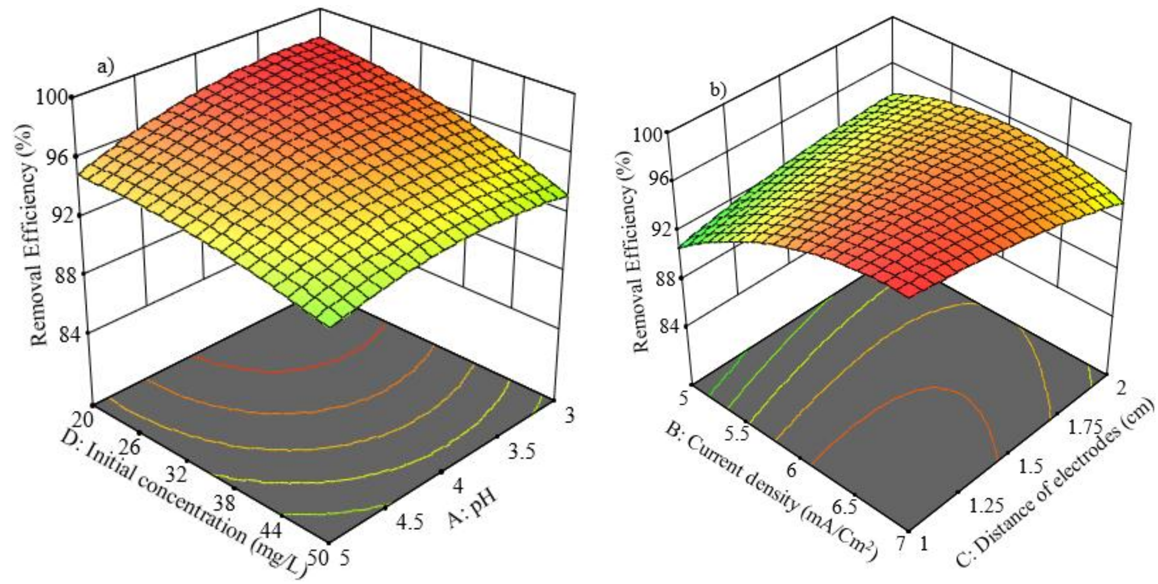

Figure 11. Interaction effect of a) pH and initial concentration (distance:1.5, current density: 6 mA/cm^2) b) current density and distance of electrodes (pH: 4, initial concentration:35mg/L on the oxidation of paracetamol.

In Figure 12 (b), the interaction effect of electrode distance and initial concentration on the mineralization of paracetamol is illustrated. It was noted that the removal efficiency improved as both the electrode distance and initial concentration decreased from 2 cm to 1 cm and 50 mg/L to 20 mg/L, respectively. The coded equation of the response variable revealed that the interaction effect of initial paracetamol concentration and electrode distance had a negative impact on the removal efficiency, with a coefficient of -0.5044 (as shown in equation 10). In Figure 12 (a), the 3D surface graph depicts the interaction effect of current density and initial concentration of paracetamol on the electro oxidation process at a constant pH of 4 and electrode distance of 1.5 cm. It was observed that the removal efficiency of paracetamol increased as the current density increased from 5 mA/cm2 to 7 mA/cm2, and the initial concentration decreased from 50 mg/L to 20 mg/L. Both the applied current density and initial concentration had a significant impact on the degradation of paracetamol, with a P-value of less than 0.0001 (see Table 5 for details).

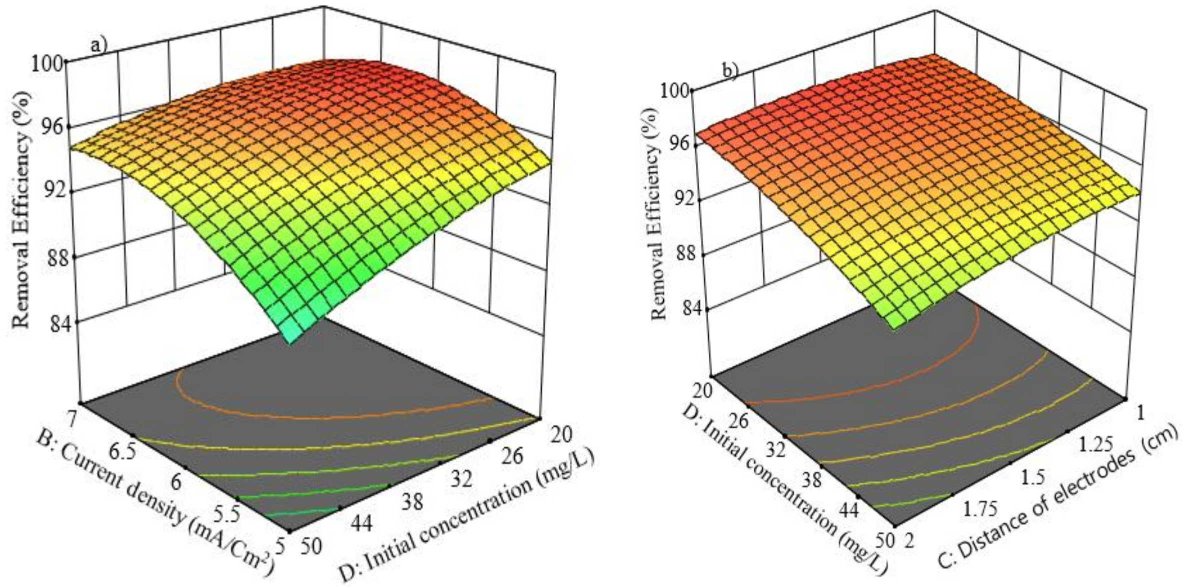

Figure 12. Interaction effect of a) current density and initial concentration (distance:1.5, pH:4) b) initial concentration and distance of electrodes (pH: 4, current density: 6 mA/cm^2 on the oxidation of paracetamol.

4.4 Optimization and Validation of Experiment

After conducting a study on the interaction effect of various variables in the electrolysis process, the next step was to optimize the parameters for the electro oxidation of paracetamol. This involved using a Ti/IrO2 anode and stainless-steel electrodes. As discussed in section 4.3.2, different process parameters have varying effects on the removal efficiency. The pH, electrodes distance, and initial concentration all decrease the removal efficiency, while the applied current density increases it. To achieve the best conditions for the electrolysis process, optimization was necessary. The parameters were adjusted within the range studied and the goal was to maximize the percent removal of paracetamol. Table 7 provides a summary of the optimization process conditions, including the ultimate goals and the lower and upper limits of the factors affecting the response (removal efficiency of paracetamol). The optimal process parameters were selected based on the highest removal efficiency values obtained from the solutions generated using design expert software.

Table 7. Working conditions of process variables and response for optimization

Variables	Unit	Goals	Lower limit	Upper limit
pH	-	In a range	3	5
Current density	mA/cm^2	In a range	5	7
distance of electrodes	Cm	In a range	1	2
Initial concentration	mg/L	In a range	20	50
Removal efficiency	%	Maximize	85.35	97.75

The model's predicted optimal results were confirmed through three repeated experiments carried out at the identified optimum parameters from the numerical optimization process. The actual removal efficiency observed in the experiments closely matched the predicted values from the model, with only a slight deviation of 0.664% as indicated in Table 8. This demonstrates the accuracy and reliability of the model in predicting the response variable, leading to the conclusion that the fitted model is both significant and trustworthy.

Table 8. The model predicted and experimental responses at optimum conditions

Parameters	pH	Current density (mA/cm^2)	Distance of electrodes(cm)	Initial concentration (mg/L)	Removal efficiency (%)
Predicted	3.71	6.47	1.12	21.14	97.96
Observed	3.71	6.47	1.12	21.14	97.3

4.5 Analysis of Total Organic Carbon (TOC)

In electro-oxidation process was effective in reducing the total organic carbon content in paracetamol, although it was not as efficient as the removal of the paracetamol compound itself. This study was conducted by Pan and Qiao in 2019 (Pan & Qiao, 2019). In order to examine the extent of degradation of total organic carbon in paracetamol, an experiment was conducted using the electro oxidation process. The parameters for this process were carefully optimized, with a pH level of 3.71, a current density of 6.47 mA/cm2, an electrode gap of 1.12 cm, and a reaction time of 40 minutes. This experiment was performed three times to ensure accuracy. Interestingly, despite the lower removal percentage of total organic carbon, the electro-oxidation process still achieved an impressive removal efficiency of over 97% within the 40-minute timeframe. This finding highlights the fact that the elimination of total organic carbon was noticeably slower compared to the removal of paracetamol itself. Prior to the electro-oxidation process, the paracetamol solution had an average total organic carbon content of 50.7%. However, after subjecting it to the 40-minute electro-oxidation, this carbon content decreased significantly to 19.86%. This suggests that only 60% of the total organic carbon present in the paracetamol was successfully removed using the optimized parameter

4.6 Comparison of this Study with Some Previous Related Works

Table 9 presents a comprehensive analysis of the optimal operating conditions and effectiveness of different oxidation methods for eliminating emerging pollutants, specifically paracetamol. This comparison is crucial in highlighting the importance of utilizing a Ti/Iro2 coated anode and stainless-steel cathode electrodes for the electro oxidation process of paracetamol. By examining previous studies, researchers can gain valuable insights into the most efficient parameters for removing this particular pollutant

Table 9. Comparison of this study with some previous works

Treatment technology	Operating conditions	Reference
Ultra -sound assisted electro-Fenton process	pH: 5 Initial paracetamol concentration: 20 mg/L Current density: 230 mA/cm^2 Removal efficiency: 98.9%	(Ghanbari et al., 2021)
Electrochemical oxidation with graphite anode	pH: 4 Initial paracetamol concentration: 20 mg/L Current density: 5.1 mA/cm^2 Removal efficiency: >90%	(Periyasamy & Muthuchamy, 2018)
Electro-catalytic oxidation using Ti/RuO_2 anode	pH: 7 Initial amoxicillin concentration: 50 mg/L Current density: 5.88 mA/cm^2 Removal efficiency: 60%	(R. Kaur et al., 2019)
Electrochemical oxidation using BDD electrodes	pH: 3 Initial paracetamol concentration: 40 mg/L Current density: 70 mA/cm^2 Removal efficiency: 97%	(Kouadio et al., 2021)
Electro oxidation process using Ti/IrO_2 coated anode	pH: 3.71 Initial paracetamol concentration: 21.14 mg/L Current density: 6.47 mA/cm^2 Electrodes distance: 1.12 cm Removal efficiency: 97.296%	This study

5. Conclusion and Recommendations

5.1 Conclusion

In this particular study, the utilized an electro oxidation process to effectively remove or degrade paracetamol from synthetic wastewater. They employed a Ti/IrO2 coated anode and stainless-steel electrodes to aid in this process. To better understand the electro oxidation of paracetamol, preliminary experiments were conducted using a one factor at a time approach. These experiments helped determine the range and impact of various electrolysis parameters on the degradation process. After analyzing the results of the preliminary experimental study, four key factors (pH, current density, distance of electrodes, and initial concentration of the pollutant) were chosen for further investigation and optimization using the Response Surface Methodology (RSM) method. The ANOVA analysis revealed that these four factors had a significant influence on the electro oxidation of paracetamol. Specifically, the applied current density had a positive effect on the process, while the pH, distance of electrodes, and initial concentration had negative effects. A mathematical model was then developed based on the data gathered, and it was found to be statistically significant with a P-value of less than 0.0001. The R2 value of 0.9965 and adjusted R2 value of 0.9932 further supported the accuracy and validity of the model..

The Central Composite Design (CCD) was utilized to investigate the interaction effect and optimization of the process parameters. The results indicated that all factors had a significant impact on the removal efficiency of paracetamol. Specifically, it was found that higher values of current density and lower values of pH, distance of electrodes, and initial concentration led to the maximum removal efficiency. Through numerical optimization using CCD, the optimal electrolysis parameters were determined to be a pH of 3.71, current density of 6.47mA/cm2, electrodes distance of 1.12 cm, and concentration of 21.14 mg/L. At these optimized parameters, a remarkable 97.3% removal of paracetamol from synthetic wastewater was achieved. However, it is worth noting that only 60% of the average total organic carbon present in the wastewater was eliminated.

In recent studies, it has been found that utilizing a Ti/IrO_2 anode in combination with stainless steel electrodes during the electro oxidation process shows great potential in the treatment of paracetamol pollutants. This technology offers a more effective and cost-efficient solution compared to traditional methods, as evidenced by experimental data.

5.2 Recommendations

The purpose of this study was to utilize the electro oxidation process, specifically employing a Ti/IrO2 anode and stainless-steel electrodes, for the removal of paracetamol. In order to further expand on this research, it is important to consider the following points. During the electrooxidation process, synthetic wastewater was used. However, it is important to note that synthetic wastewater does not contain any other impurities that could potentially hinder the oxidation process. Therefore, it is highly recommended to conduct investigations using real industrial wastewater that contains paracetamol, as this will provide more accurate and effective results. The current study primarily focused on the impact of four operating parameters: pH levels, electrode distance, paracetamol concentration, and current density. These parameters were found to have a significant effect on the oxidation of paracetamol. However, several other factors such as electrolysis time, steering speed, different electrode types, and the kinetics of degradation have not yet been evaluated in relation to this aspect. Thus, it is crucial to conduct a systematic study in order to thoroughly examine the effects of these factors on the degradation of paracetamol pollutants.

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Appendices

Appendix A: Individual Effect of Process Variables on the Electro oxidation of Paracetamol

Table A-1. Effect of pH on the percent removal of paracetamol from the synthetic wastewater

pH (-)	Final concentration 1 (mg/L)	Final concentration 2 (mg/L)	Final concentration 3 (mg/L	Average concentration (mg/L)	Removal efficiency (%)
2	5.4772	5.4777	5.4776	5.4775	84.35
3	0.9622	0.9626	0.9627	0.9625	97.25
4	1.9777	1.9772	1.9776	1.9775	94.35
5	5.1622	5.1627	5.1626	5.1625	85.25
6	10.3777	10.3776	10.3772	10.3775	70.35
7	15.572	15.577	15.576	15.575	55.5

Table A-2. Effect of current density on the percent removal of paracetamol from the synthetic wastewater

Current density (mA/cm^2)	Final concentration 1 (mg/L)	Final concentration 2 (mg/L)	Final concentration 3 (mg/L	Average concentration (mg/L)	Removal efficiency (%)
2	19.077	19.076	19.072	19.075	45.5
3	15.572	15.576	15.577	15.575	55.5
4	10.2726	10.2727	10.2722	10.2725	70.65
5	3.9	4.4	4.3	4.2	88
6	2.3	2.2	1.8	2.1	94
7	1.3127	1.3126	1.3122	1.3125	96.25

Table A-3. Effect of distance of electrodes on the percent removal of paracetamol from the synthetic wastewater

Distance of electrodes (cm)	Final concentration 1 (mg/L)	Final concentration 2 (mg/L)	Final concentration 3 (mg/L	Average concentration (mg/L)	Removal efficiency (%)
1	0.9622	0.9626	0.9627	0.9625	97.25
1.5	1.577	1.576	1.572	1.575	95.5
2	3.5876	3.5877	3.5872	3.5875	89.75
2.5	8.4872	8.4877	8.4876	8.4875	75.75
3	12.1626	12.1622	12.1627	12.1625	65.25
3.5	15.577	15.576	15.572	15.575	55.5

Table A-4. Effect of initial concentration on the percent removal of paracetamol from the synthetic wastewater

Initial concentration (mg/L)	Final concentration 1 (mg/L)	Final concentration 2 (mg/L)	Final concentration 3 (mg/L	Average concentration (mg/L)	Removal efficiency (%)
20	0.527	0.526	0.522	0.525	98.5
35	0.9626	0.9622	0.9627	0.9625	97.25
50	6.827	6.822	6.826	6.825	80.5
65	10.2722	10.2727	10.2726	10.2725	70.65
80	12.776	12.777	12.772	12.775	63.5
95	15.4877	15.4872	15.4876	15.4875	55.75

Appendix B: Data from Design Expert Software and Model Fitting Analysis

Table B-1. Model fit summary for electrooxidation of paracetamol

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.0029	< 0.0001	0.3757	0.244	
2FI	0.0748	< 0.0001	0.5262	0.4872	
Quadratic	**< 0.0001**	**0.072**	**0.9932**	**0.9813**	**Suggested**
Cubic	0.9015	0.0105	0.9898	0.7009	**Aliased**

Table B-2. Fit statistics for electrooxidation of paracetamol

Std. Dev.	0.2948	**R^2**	0.9965
Mean	93.16	**Adjusted R^2**	0.9932
C.V. %	0.3164	**Predicted R^2**	0.9813
		Adequate Precision	59.3867

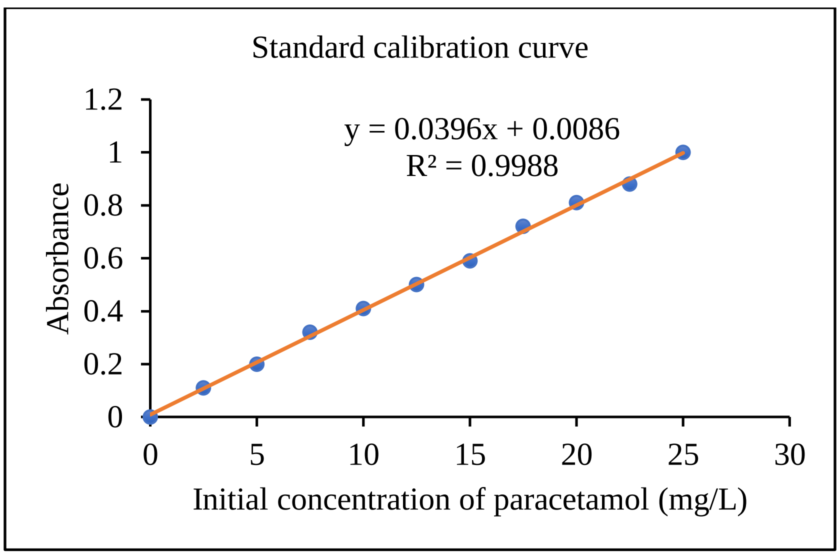
Table B-3. Sequential model sum of squares

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Mean vs. Total	2.60E+05	1	2.60E+05			
Linear vs. Mean	169.91	4	42.48	5.36	0.0029	
2FI vs. Linear	83.83	6	13.97	2.32	0.0748	
Quadratic vs. 2FI	**112.91**	**4**	**28.23**	**324.83**	**< 0.0001**	**Suggested**
Cubic vs. Quadratic	0.3936	8	0.0492	0.3785	0.9015	Aliased
Residual	0.9099	7	0.13			
Total	2.61E+05	30	8690.62			

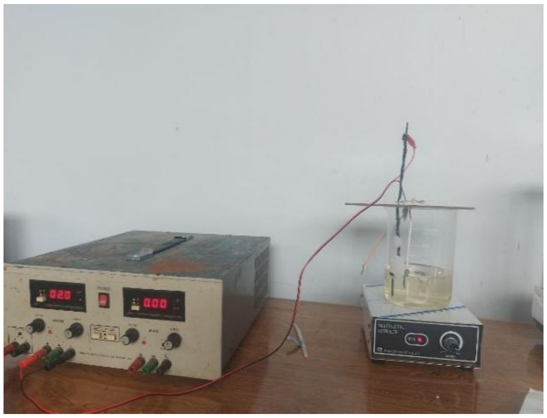
Appendix C: Experiments of TOC analysis

Run	Initial TOC (%)	Average initial TOC (%)	Final TOC (%)	Average final TOC (%)	%TOC removal	Average %TOC removal
Trial-1	50.11		21.61		56.88	
Trial-2	50.62		20.52		59.46	
Trial-3	51.38	50.71	18.64	19.85	63.7	60

Appendix D: Standard Calibration Curve of Concentration of Paracetamol Versus Absorbance

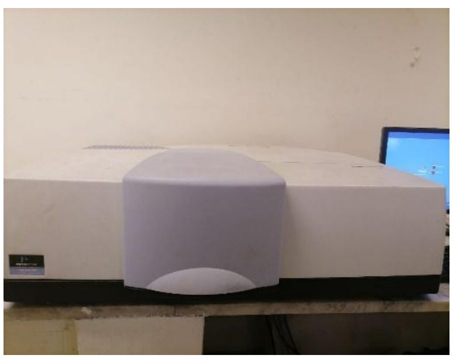


Appendix E: Some Experimental Photos



Electrooxidation of paracetamol

Analytical balance



UV visible spectrophotometer

Magnetic stirrer