Baghdad International Journal of Engineering (BIJE)
Volume 2025, pp. 48-74, December 2025
Received September 2025 / Accepted October 2025

Research Article

Study of the Electrochemical Removal of Bromophenol Blue using a Titanium Electrode Modified with a Mixture of Iridium and Ruthenium Oxides

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Abstract: In this study, the anode is a titanium electrode modified with a mixture of iridium and ruthenium oxides and is used to remove bromophenol blue dye. This anode is highly effective in removing this type of dye from aqueous samples due to its high ability to decompose complex organic pollutants in water, such as bromophenol blue dye. These electrodes consist of a thin layer of IrO2-RuO2 on the surface of titanium. The special features of these electrodes include high corrosion resistance in harsh environments, including acidic, alkaline, and saline solutions. The SEM, EDS, and EDS-MAP images show that titanium, ruthenium, iridium, and oxygen elements are distributed non-uniformly on the surface of the sample. The strong titanium peaks in the EDS indicate the predominant presence of this element in the sample. The strong oxygen peak indicates the presence of oxides of these elements in the coating. The results also showed that the best removal coefficient was achieved at a concentration of bromophenol blue dye = 30 mg/L, two-electrode chronoamperometry technique, applied voltage 5 V, pH = 4, and KCl = 0.1 M. The removal efficiency of bromophenol blue dye was achieved when using chronoamperometry on three electrodes and chronoamperometry on two electrodes, but the best removal efficiency was when using chronoamperometry on two electrodes, where it was (41.81%, 74.62%, 85.40%, 98.92%, 100%) at 6 minutes, and the removal efficiency increased to (61.01%, 83.44%, 100%, 100%, 100%) after 10 minutes when applying a current of (2.0, 3.5, 4, 4.5, 5.0) V, respectively. This means that the higher the applied current and the longer the contact time between the electrodes, the higher the removal efficiency. These electrodes require regular maintenance to maintain their optimal performance. These electrodes are more expensive than other electrodes, but their long life and high efficiency make them a worthwhile investment in the long run. These electrodes provide excellent performance and high efficiency in a wide range of industrial applications, such as the chlor-alkali industry, electrolyte industry, water treatment, battery industry, and organic electrolysis.

Keywords: Iridium and ruthenium oxides, Bromophenol blue, Electrochemical oxidation.

1. Introduction

Water pollution from industrial waste is a major global environmental challenge. The increasing speed of industrialization has led to an increased use of color chemicals, such as dyes. Nearly 40,000 dyes and pigments have been documented, each exhibiting more than 7,000 distinct chemical compositions [1]. Globally, the annual production of dyes and pigments exceeds 700,000 tons, with India alone producing nearly 80,000 tons [2, 3]. Every year, more than 10,000 distinct types of dyes and pigments are manufactured worldwide [4]. These dyes have high chemical and biological stability, making them highly resistant to disinfection [5]. Synthetic dyes are used in various sectors such as textiles, leather, food, cosmetics, paper, and pharmaceuticals. In particular, the textile sector uses a lot of dyes and pigments and generates wastewater after the dyeing process. For example, the daily waste volume from a typical factory producing 60 × 104 m of fabric is approximately 1.5 million liters, which is released into natural water sources [5]. This wastewater contains various pollutants in addition to dyes, such as solvents, salts, and detergents, many of which are hazardous. The removal of dyes from wastewater requires special attention due to their significant environmental impact. Even at low levels, dyes aesthetically pollute the environment as well as affect aquatic life and the food chain. High levels of dyes in textile wastewater, averaging 300 mg L-1, can impede light penetration, disrupt photosynthetic activity, and negatively affect symbiotic processes within water sources. Through the food chain, the harmful and toxic properties of dyes cause physiological problems in aquatic life. Some azo dyes have been linked to bladder cancer and chromosomal aberrations in mammalian cells. Standard wastewater treatment systems often fail to remove dyes effectively due to their high persistence and resistance to microbial activity and temperature changes. Therefore, research focuses on practical treatment procedures for removing pollution from dyes. Dyes are organic materials characterized by three main groups in their structure: chromophore, auxochrome, and matrix [6]. Light energy is absorbed by the chromophore, which is the active part of the dye. Synthetic dyes are quickly replacing natural optical adjuncts as the preferred chromophore-containing molecule in surgical procedures [6]. The most popular chromophores are: nitro (─NO2), azo (─N═N─), carbonyl (─C═O), and alkenes (─C═C─) [6]. A molecule containing a chromophore named chromogenic [7]. Nevertheless, the chromogenic molecule's staining capabilities are only achieved through the incorporation of other atom groups, which are referred to as auxochromes [7]. The auxochromic groups in dyes fix and alter their color, while the remaining atoms form the matrix, the third component of the dye. Bromophenol blue (BPB) (Fig. 1.) roles as a pH indicator, in the range of 3 to 4.6. BPB appears yellow in its acidic form and purple in its basic media. It is widely utilized in spectrophotometric analyses, including as a colorimetric sensor to detect ammonia in gaseous form [8], an association reagent for the solvent extraction of NH4+ ion [9], and in applications involving drugs [10], surfactants [11], liposomes [12], proteins [13], and monitoring of solid-phase peptide synthesis [14]. BPB also reacts with soil carbonates and amino acids [15]. As a triphenylmethane derivative, BPB, along with similar compounds like fluoresceins and xanthenes, is broadly used in different industrial applications [16, 17].

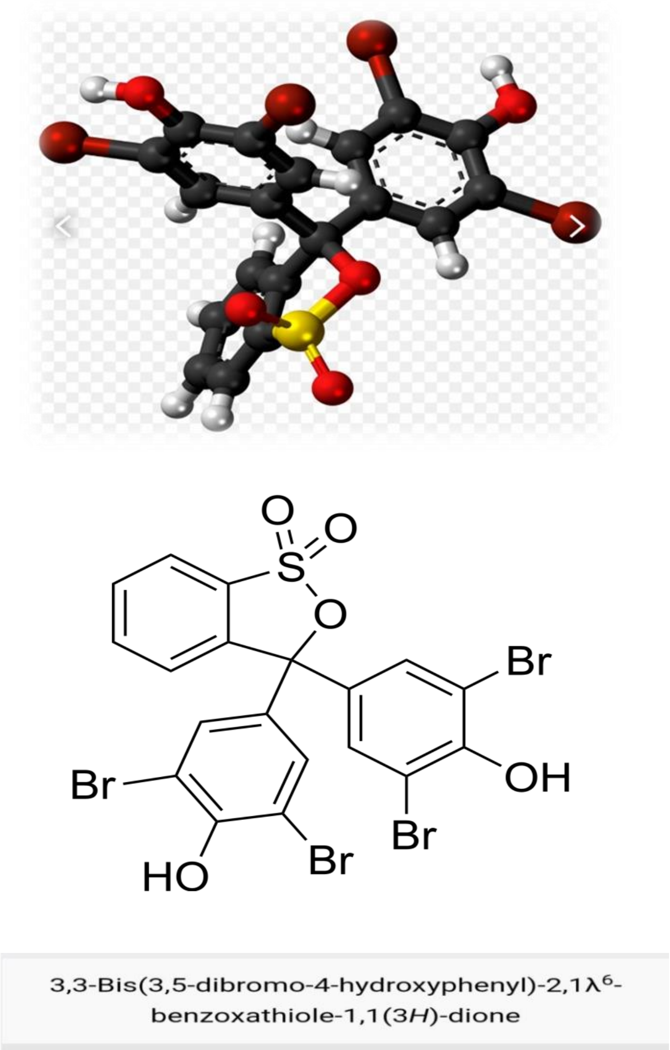


Figure 1. BPB structure

Standard wastewater treatment systems often fail to effectively remove dyes due to their high stability and resistance to microbial activity and temperature changes. Consequently, researches are focused into the practical treatments procedures for dyes decontamination [18, 19].

Electrochemical oxidation that is also referred to as anodic oxidation (AO), is the most commonly applied electrochemical method for treating contaminants in wastewater. Comninellis [20] detailed a well-known method for aqueous solution organic pollutant oxidation (Figure. 2). This classification is based on the type of anode and active compounds that exhibit surface physicochemical behavior.

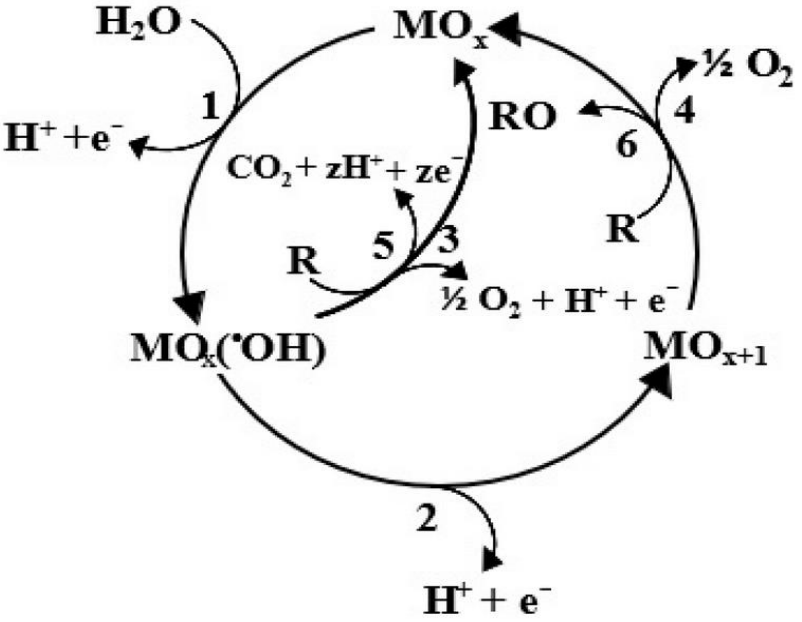


Figure 2. Mechanism of Anodic oxidation for decontamination of organic materials

Anodes of the active type (numbers 1, 2, 4, and 6 in Figure 2) are shown to release water in order to produce OH radicals, as shown in Equation (1).

$$MOx + H2O \rightarrow MOx(\bullet OH) + H+ + e- \qquad (1)$$

In order to produce the surface site MOx+1 for superoxide (Equation (2)), the adsorbed •OH radical interacts with the MOx [21].

$$MOx(\bullet OH) \rightarrow MOx+1 + H+ + e- \qquad (2)$$

Afterwards, as presented in Equation (3), MOx+1 site undertake organic oxidation [20].

$$R + MOx+1 \rightarrow MOx + R \qquad (3)$$

Since the active anode predominantly interacts with the reactive surfaces, it can only partly oxidize organic pollutants (R) to (RO). This restriction is due to the intense contact between •OH radicals and the anode's surface. As demonstrated in Equation (4), side reactions may also occur, resulting in spontaneous deactivation. The deactivation process may potentially limit the overall efficacy of organic degradation processes.

$$MOx+1 \rightarrow 1/2\ O2 + MOx \qquad (4)$$

Furthermore, active anodes' low O2 evolution over potential leads them to oxidize fast, producing water. These electrodes are often made of metal oxides (MOx), which may form a surface MOx+1 site and have a limited potential for O2 evolution. Pt, IrO2, and RuO2 substrates are some cases of active anode [21]. Anglada et al. [22] found that active anodes typically have O2 evolution potentials below 1.9 V, resulting in the O2 evolution reaction occurring in the anodic zone. As a result, since the bubbles generated might impede the anode surface, which lowers the formation of •OH radicals, active anodes are not well suited for EO treatments of organic contaminants [23]. A suggested solution for this issue is to apply a lower current density to hinder the O2 evolution reaction; however, this results in undesirably long treatment times [24]. Alternatively, non-active anodes (1, 5, and 3 in Figure 1) have a weak contact between •OH radicals and their surfaces, enabling easier interactions with organic molecules. Based on Equation (5), •OH species on the anode surface can quickly break down pollutants [21].

$$R + MOx(\cdot OH) \rightarrow M + mCO2 + nH2O + nH+ + ne- \tag{5}$$

As a result, CO2 and H2O are produced when R undergoes full oxidation. On the other hand, Equation (5) may be thrown off by unsavory side reactions (Equations (6) and (7)) [20].

$$MOx(\cdot OH) \rightarrow MOx + 1/2O2 + H+ + e- \tag{6}$$

$$2M(\cdot OH) \rightarrow 2MO + H2O2 \tag{7}$$

Electrochemically produced radicals on inert anodes are physisorbed onto the electrode surface and exhibit poor attachment [25]. Furthermore, the oxygen evolution potentials of inactive anodes are greater than those of active electrodes. Typical potential levels versus SHE for inactive electrodes are between 1.9 and 2.6 V [22]. Boron-doped diamond (BDD), TiO2, PbO2, SnO2, and Ti4O7 are among the most often utilized non-active anodes. More potential is needed for these substrates to overcome the activation energy required to create molecular oxygen, which increases the formation of •OH radicals [26, 27].

The review of the literature review reveals a variety of results regarding the impact of pH on the AO and AO-H2O2 processes. Several investigations indicate that the mineralization rate is not affected by pH within the ranges of 2.0–6.0 or 4.0–10.0 [28]. In contrast, others have demonstrated higher process efficiency at pH 3.0 [29]. This facilitates explaining the competitive electro-generation of oxidizing agents that are less potent, such as superoxide anion radicals. Hamza et al. [30], however, observed slightly faster mineralization at pH 7.4 than at pH 3.0. Other authors have recorded maximal and comparable mineralization rates within various pH ranges, such as 2.0–4.0 [31], 2.0–3.0 [32], 3.0–4.0 [33], and 3.5–4.0 [23].

Belal et al. (2021) investigated the efficacy of an IrO2/Ti meshed electrode in the decolorization of BY28 dye. According to the research, the ideal parameters were as follows: pH levels of 2.5 for Na2SO4 and 6.5 for NaCl; current density of 0.03 A cm−2; and electrolyte levels of 0.08 M for Na2SO4 and 0.03 M for NaCl. With Na2SO4 and NaCl, the color removal of BY28 was 92.9% and 93.3%, respectively, after 15 minutes. Additionally, the research indicated that NaCl was a more effective supportive electrolyte than Na2SO4 [34].

Singh et al. (2016) studied the EC oxidation of MG dye in various pH media using RuO2–TiO2 and Pt-coated Ti electrodes. Active areas on the electrode surface facilitated the production of •OH. The generation of •OH was facilitated by the active sites on the electrode surface. In order to clarify the oxidative degradation mechanism of EC with both types of electrodes, a variety of analytical techniques were implemented, including gas GC–MS, HPLC, color removal, and COD. The study found that acidic pH conditions promoted efficient dye degradation. Under optimized conditions, complete decolorization of MG dye and 98% COD removal were achieved by EC method. In accordance with the identification of intermediates and by-products, the degradation of MG dye was attributed to processes that involved the disintegration of the conjugated structure and N-methylation [35].

In this paper, the simulated solution of BPB was decomposed by a porous composite electrode of IrO2-RuO2. The electrochemical decomposition of BPB was studied using IrO2-RuO2 porous composite electrodes as anodes. The effects of initial BPB concentration, current density, initial pH values, and supporting electrolyte concentration on the BPB processing efficiency were investigated in order to determine the optimal electrochemical conditions. Meanwhile, the electrochemical decomposition process and a small number of intermediates formed during the decomposition process were monitored by UV-Vis spectra.

2. Experimental

Materials

Commercial bromophenol blue dye was provided by Hopkin & Williams. Each solution was prepared using deionized water and used as a simulant solution. This dye is often used as a visual indicator to monitor chemical changes. The color of this type of dye changes with pH changes and thus helps in determining reaction end points with high accuracy. Also, the chemicals used in this study, KCl and Na_2SO_4, were supplied by Merck (Germany). The IrO_2-RuO_2 electrode was supplied by Erfan Chemical Company in Iran.

Instruments

The evolution of bromophenol blue dye concentrations was monitored by an ultraviolet/visible spectrophotometer (UNICO, UV-Vis Spectrometer) at a wavelength range of 500-650 nm. There are two important techniques in electrochemistry. The potentiostatic technique keeps one electrode's potential constant and monitors the current flow. This helps in understanding the reaction kinetics and electrode processes. On the other hand, the galvanostatic technique keeps the current constant and monitors the change in potential. It is useful in studying battery performance and corrosion rates.

Electrochemical set up

The experiments were conducted in a 0.2 L tank cell at laboratory scale. In all studies, the solution was vigorously stirred at 700 rpm using a magnetic stir bar to ensure complete mixing of the organic materials and efficient mass transfer to and from the electrodes. Solutions containing 30 mg L-1 of BPB dye, along with KCl or Na_2SO_4, were hydrolyzed at pH 4.0 using electrochemical oxidation. The effect of applied voltage on the performance of each EAOP was investigated. In the EOx processes, the IrO_2-RuO_2 electrode based on Ti electrode was the anode electrode, and the cathode electrode was Ti. Also, the distance between the electrodes was 1 cm.

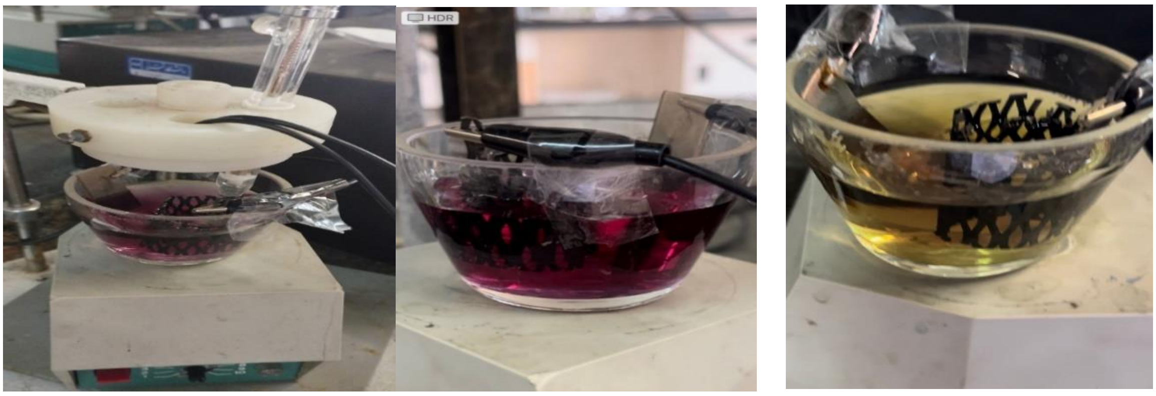


Figure.3 Electrochemical cell decolorization stages.

3. Preparation of the simulation solution (Bromophenol blue dye with KCl solution)

1- Several initial concentrations (20, 25, 30, 35, and 40) mg/L of bromophenol blue dye were prepared and studied to know and choose the appropriate concentration according to which other variables are verified.

2- An initial concentration of bromophenol blue dye at 30 mg/L. We Prepare 0.03 g of bromophenol blue dye. In the next chapter, the reason for choosing this initial concentration was studied.

3- Preparation of a concentration of 0.1 M potassium chloride, we weigh 0.7455 g of it, then the prepared weights are mixed in (2,3) and the volume is completed to 100 ml of distilled water and the pH should be 4. So we have a solution that can be studied as a simulation solution and an indicator of organic pollutants.

4. Analytical Procedures

Using a spectrophotometer, the absorbance (A) at the visible spectrum's peak wavelength was measured in order to follow the dye's color removal. Equation (2-1)was used to calculate the color removal percentage.

$$\text{Color Removal }\%=\left(\frac{A0-At}{A0}\right)\times 100 \qquad \textbf{Equation (8)}$$

Where A_0 and A_t are the initial and final absorbance times, respectively.

After determining the parameters and preparing the simulated solution, the techniques that will be used are tested, which are techniques (Two-electrode system chronoamperometry, three -electrodes system chronoamperometry, and three-electrodes system chronopotentiometry) to study the concentrations used for the dye in this study.

After studying and applying these techniques and with applied voltages and potentials that were chosen, which we will discuss in the next chapter, we found that the concentrations used (20 mg, 25 mg, 30 mg, 35 mg, 40 mg) have similar removal results and there is no significant difference between them, so a concentration of 30 mg/L was chosen as the best concentration for the study.

The best pH 4 was also chosen for removing Bromophenol blue dye because it changes its color based on the acidity level, which is optimal for removing the color from blue to yellow. This color change helps in determining the point at which the dye is removed effectively.

After determining the pH, 30 mg/L dye concentration, the two electrolyte solutions, KCl and Na_2SO_4, were compared under the same conditions, where it was found that the efficiency of KCl is better.

After applying the techniques used in this study through the Potentiostatic and Galvanostatic device verifying the process and monitoring the color removal with the UV/Vis spectrophotometer, it was found that the best technique used is Two-electrode system chronoamperometry, which will be studied in the next chapter. As shown in the (figure 3.) a 150 ml electrolytic cell was used, and a 50 ml sample of the dye was transferred with the previously prepared electrolyte solution, which was adjusted to pH = 4. This ensures that the maximum surface of the anode (IrO_2 -RuO_2) and cathode (Ti) electrodes is immersed. There is a space of 1 cm between them, with using a magnetic stirrer to maintain the homogeneity of the electrolyte concentration. After operating the selected technique and applying the voltage or potential, several samples are taken, the first before operating the selected technique and the rest of the other samples after it and at specific time intervals, after which they are read on a UV/Vis spectrophotometer to monitor the progress of color removal. The electrodes are polished and cleaned under water and rinsed with distilled water to eliminate any interference and ensure the possibility of reproducing the surface during analysis.

5. Results and discussion

Structure and characterization of electrode

The strong titanium peaks in the EDS spectrum indicate the predominant presence of this element in the sample. This is the same underlying titanium layer that we expected. Ruthenium peaks are also clearly visible, indicating the presence of this element in the coating. The presence of iridium peaks confirms that this element is also part of the coating. The strong oxygen peak indicates the presence of these element oxides in the layer. This is consistent with ruthenium and iridium oxides forming on the titanium surface.

Scanning electron microscopy (SEM) provides high-resolution, three-dimensional images of a sample surface, allowing for the observation of very fine details. SEM can also be used to analyze the chemical composition of a sample surface by analyzing the X-ray radiation emitted from it.

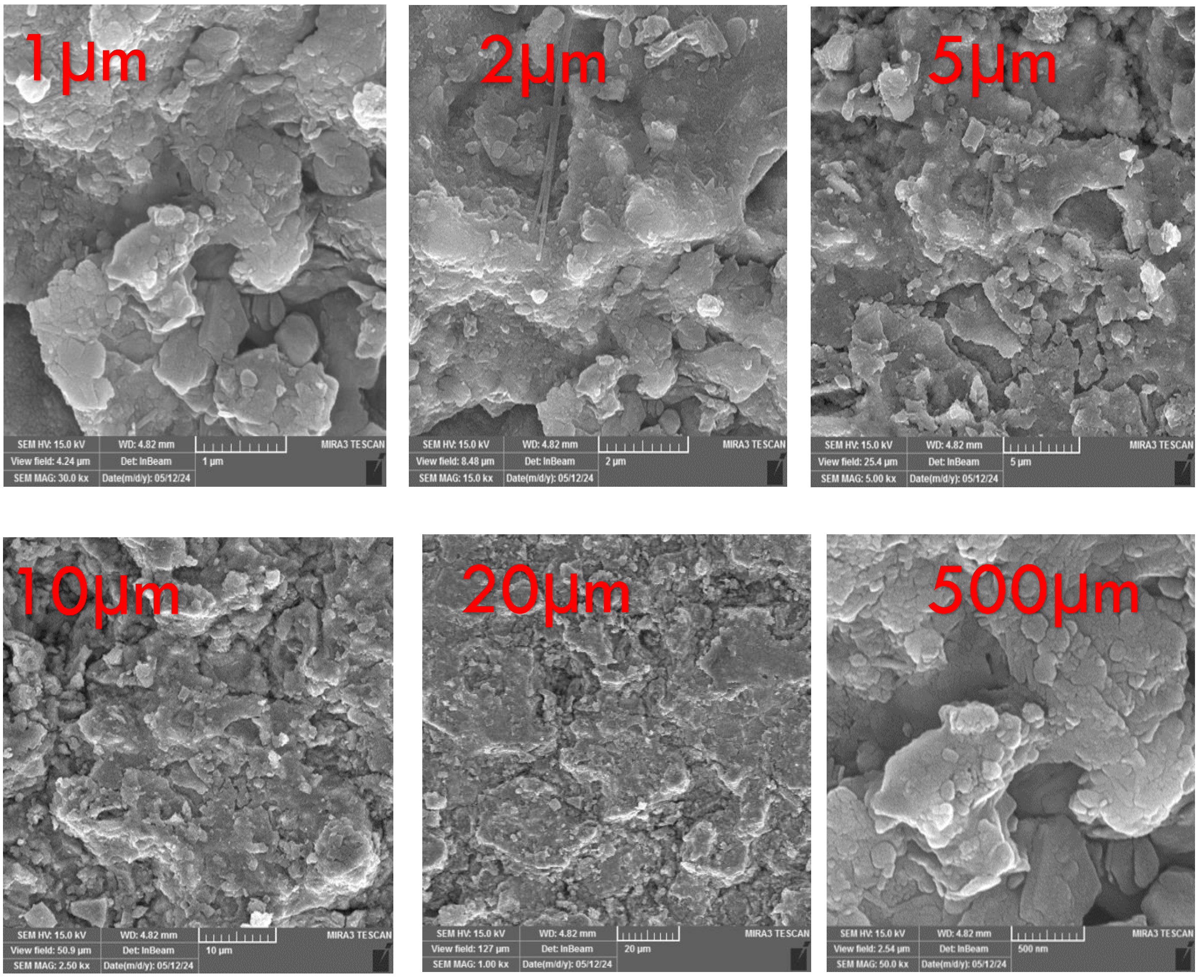


Figure 4. Scanning electron microscopy (SEM).

various elements, internal stresses, or non-uniform coating conditions. The pores and cracks are likely due to the release of gases during oxidation, internal stresses, or defects in the coating. The spherical particles may also be due to the agglomeration of fine oxide particles or impurities present in the raw materials.

The SEM image and EDS data together show that the surface of the titanium sample is covered with a rough and porous layer of ruthenium and iridium oxides. This coating has a non-uniform distribution of elements and contains numerous pores and cracks. These characteristics can affect the mechanical, chemical, and electrical properties of the coating.

EDS mapping images provide us with valuable information about the spatial distribution of elements in the sample. By comparing these images with the SEM image, we can better understand the relationship between the surface structure and the chemical composition of the sample.

(Figure 5) shows the MAP analysis of the fabricated IrO_2-RuO_2 based on Ti electrodes. Based on the results, Ti, Ru, O, and Ir are the main components of IrO_2-RuO_2 based on the Ti electrode.

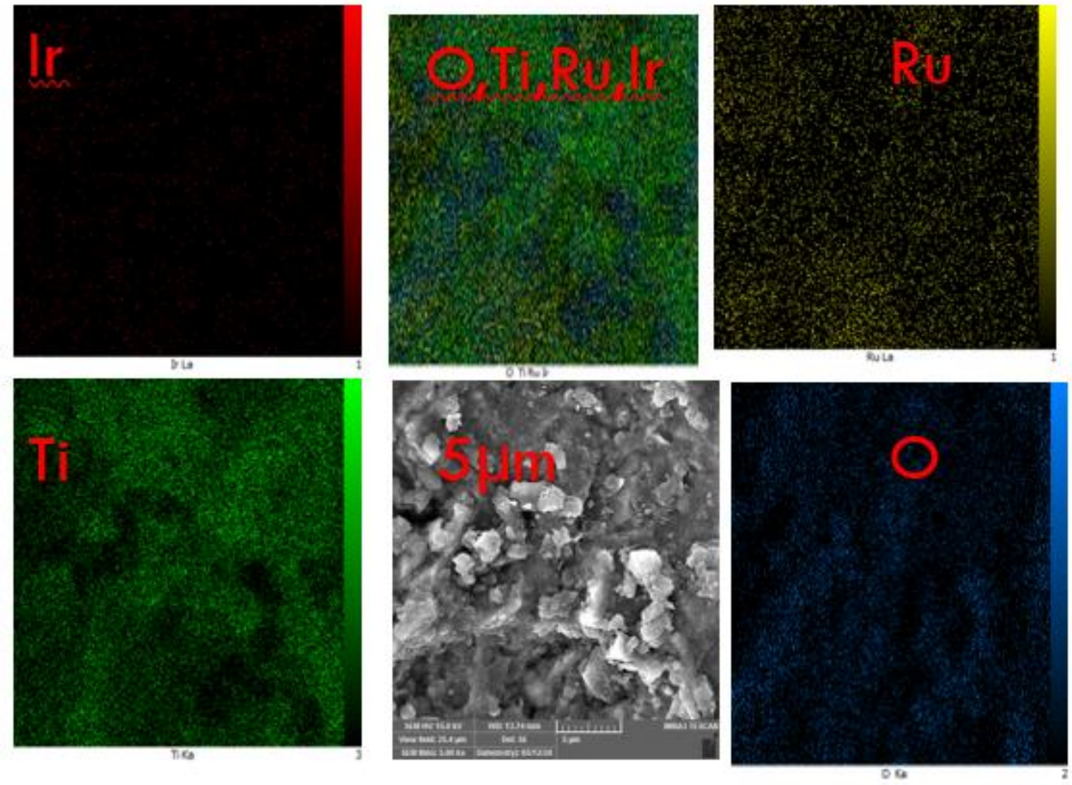


Figure 5. MAP analysis of the IrO2-RuO2 based on Ti electrode. Ti, Ru , Ir mixed element, O, 1-MAP 5µm

Also, based on the SEM images, EDS data, and EDS mapping, we can reach the following conclusions:

EDS mapping images show that titanium, ruthenium, iridium, and oxygen elements are distributed non-uniformly on the sample surface. Some areas are rich in titanium, indicating the presence of the titanium substrate. Other areas are rich in ruthenium and iridium oxides, indicating the presence of the coating on the titanium surface. The presence of areas with high oxygen concentrations indicates severe oxidation in some areas.

6.Optimization of parameters

Effect of initial concentration.

The results of the investigation into the effect of varying initial concentrations of Bromophenol blue dye on the removal efficiency of this dye are shown in (Figure 6.) Based on the results, a removal efficiency of about 100% was obtained for

Bromophenol blue dye at a concentration of 20 mg/L in 5 min. In addition, the kinetic results in (Figure. 4) show that the removal efficiency of this dye decreases with increasing initial concentration. Specifically, the removal rates were 71.8%, 63.9%, 62.9%, 65.9%, and 79.7% for dye concentrations of 20, 25, 30, 35, and 40 mg/L, respectively, in One minutes. However, the removal rates changed to 100%, 100%, 99.83%, 99.89%, and 99.69% for dye concentrations of 20, 25, 30, 35, and 40 mg/L at 5 minute. According to the table.1. Since there was no significant difference between the removal efficiencies of the concentrations mentioned in the table and based on the recommendations of previous studies Zhang, L., Wei, F., Zhao, [36]. The concentration of 30 mg/L was chosen as the optimum. Concentration for continuous improvement in the study of the remaining variables in this study.

Table 1. The concentration with time and removal Efficiency

Time/min	20mg/L	25mg/L	30mg/L	35mg/L	40mg/L
0	0	0	0	0	0
1	71.89%	63.98%	62.92%	65.99%	79.74%
2	97.92%	81.10%	79.04%	83.06%	80.51%
3	98.63%	96.14%	88.42%	89.42%	91.23%
4	99.52%	99.82%	95.61%	95.99%	97.24%
5	100%	100%	99.83%	99.80%	99.69%

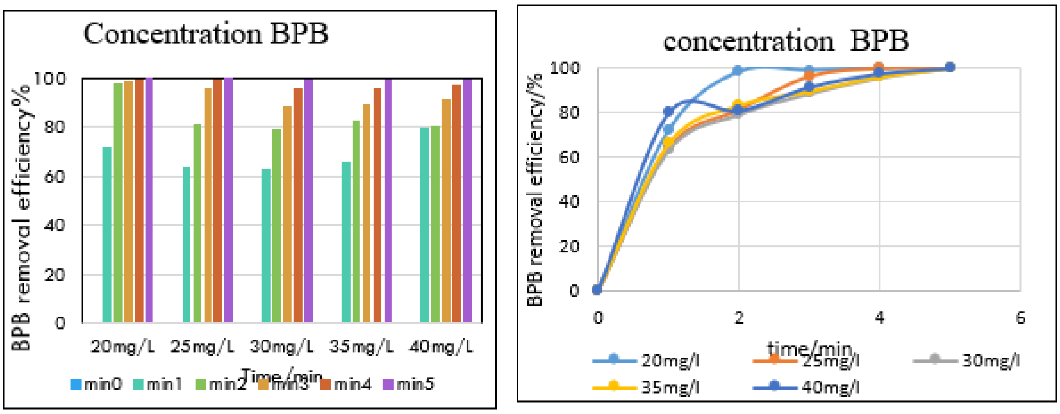


Figure 6. Removal percentage of BPB using two electrode chronoamperometry system Conditions: 5V, pH=4 and KCl=0.1 M.

Applied Current in chronoamperometry technique

- **Three electrodes system chronoamperometry.**

The chronoamperometry technique is used to measure the current passing through an electrochemical cell over time when a constant voltage is applied. The current is recorded with respect to time, which helps in studying the dynamics of oxidation, reduction, and surface reactions at the electrodes.

By studying the three-electrode chronoamperometry system and based on the practical results obtained, we note that the removal efficiency increases with increasing contact time between the electrodes between the anode electrode IrO_2-RuO_2 and the cathode electrode Ti. After applying the three-electrode chronoamperometry system and increasing the current, we note that when applying each current and after starting the electrochemical oxidation process, the removal efficiency of bromophenol blue dye will increase, where it is in the first minute of operation (11.67%, 6.20%, 68.27%, 73.39%, 52.65%, 57.60%) when the applied current is (1.0, 1.2, 1.4, 1.6, 1.8, 2.0) V, respectively under Conditions [BPB]=30 mg/L, pH=4, KCl=0.1.

When the time was increased to achieve greater removal of bromophenol blue dye, we found that the removal efficiency increased to 43.97%, 61.57%, 98.14%, 100%, 87.74%, and 88.22%) after 6 minutes from the start of the electrochemical oxidation process, as shown in Table 2. After 7 minutes from the start of the electrochemical oxidation process, the removal efficiency of bromophenol blue dye was (43.88%, 65.60%, 100%, 100%, 90.73%, 91.23%) when applying current (1.0, 1.2, 1.4, 1.6, 1.8, 2.0) V, respectively. At minute 10, we note that the removal efficiency was (52.12%, 73.97%, 93.51%, and 97.62%) when applying current (1.0, 1.2, 1.8, 2.0) V, respectively.

Table 2. Removal efficiency %, Time/minute and apply current to three electrodes system chronoamperometry.

Time/min	1.0V	1.2 V	1.4V	1.6V	1.8V	2.0V
0	0	0	0	0	0	0
1	11.67%	6.20%	68.27%	73.39%	52.65%	57.60%
2	19.44%	27.22%	80.48%	85.46%	69.57%	71.10%
3	27.98%	45.04%	89.09%	93.81%	75.45%	76.69%
4	34.34%	50.80%	95.42%	95.70%	80.66%	81.32%
5	41.84%	54.80%	97.20%	99.35%	84.48%	85.44%
6	43.97%	61.57%	98.14%	100 %	87.74%	88.22%
7	43.88%	65.60%	100 %		90.74%	91.23%
8	45.64%	69.13%			90.23%	93.56%
9	46.26%	71.61%			90.59%	95.88%
10	52.18%	73.97%			93.51%	97.62%

When applying some current, such as (1.2, 1.0, 1.8, and 2.0) V, we notice that the removal process may take longer than possible. The difference in the applied current may lead to the production of O2 or other products on the surface of the electrode instead of consuming bromophenol blue dye. Previous studies showed that the higher increase in the applied current values on electrochemical oxidation often causes an increase in the rate of decomposition of the pollution with the production of more oxidized species during a certain period, as shown by Boye, B., Dieng, M.M., and Brillas [37]. However, there is a limit to increasing the current because it can enhance parasitic reactions, which leads to a decrease in the efficiency of the current and a decrease in the removal rates of pollutants compared to low current values. From this, we conclude that the best removal efficiency of bromophenol blue dye when using the three-electrode chronoamperometry system was (98.1%, 100%) in 6 minutes when applying current (1.4, 1.6) V, respectively, and (100%, 100%) in 7 minutes when applying voltages (1.4, 1.6) V, respectively. We notice there is noise at the wavelength between (551-553) nm, and this is due to the challenges that Beir Lambert put and the deviations that the operation may accompany.

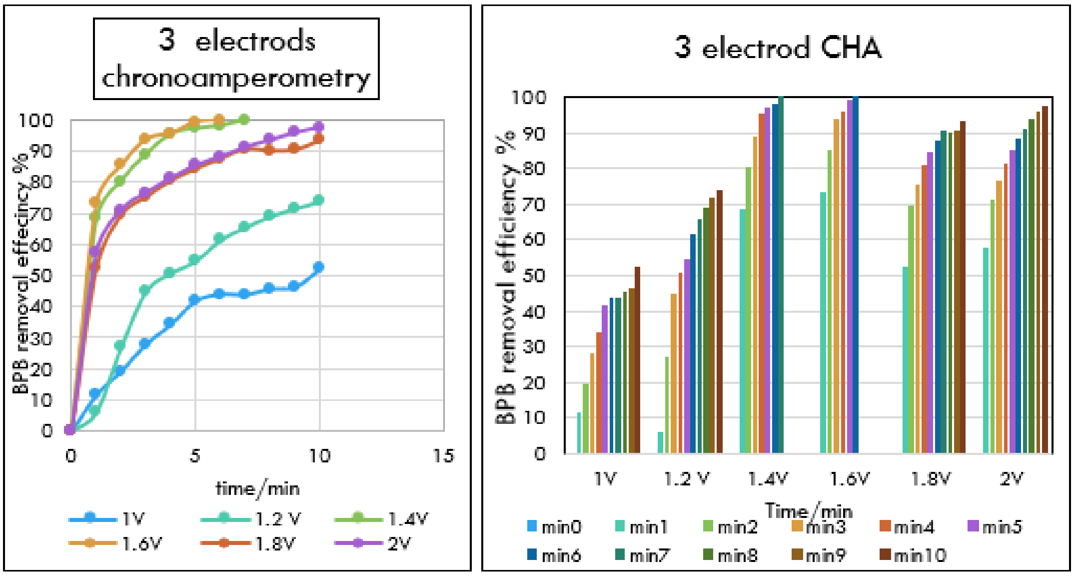


Figure 7. Removal percentage of BPB at different applied current for three-electrode chronoamperometry system Conditions: 30 mg L-1 BPB, pH=4 and KCl=0.1 M.

- **Two-electrode system chronoamperometry.**

Previous experiments were repeated by using the emulator solution for bromophenol blue dye with two-electrode chronoamperometry instead of a three-electrode system when used by applied current (2.0, 3.5, 4.0, 4.5, and 5.0) V. After starting electrochemical oxidation operation on the electric electrodes in the electrochemical cell, using the operating conditions KCl = 0.1 M, pH = 4, [BPB] = 30 mg/L. We found that the removal efficiency of bromophenol blue was as follows: 41.81%, 74.62%, 85.40%, 98.92%, and 100% at the 6th minute. While the efficiency of the removal of this dye in the 7th minute was as follows: (47.53 %, 77.86 %, 90.5%, 100%, and 100%). While the efficiency of the removal of this dye was in the 10th minute as follows: (61.01%, 83.44 %, 100%,100%, and 100%). When using applied current (2.0, 3.5, 4.0, 4.5, 5.0) V, respectively.

By comparing the technology of two-electrode chromatoamperometry and three-electrode chromatoamperometry, we find that the process of removing the bromophenol blue dye in minutes (6, 7) and with an efficiency of 100% removal. this means that the effect of parameters used in chronoamperometry was fixed under Conditions: 30 mg/L BPB, pH = 4, and KCl = 0.1 M

Table 3. Removal efficiency %, Time/minute and apply Current Two – electrodes system chronoamperometry.

Time/min	2.0V	3.5V	4.0 V	4.5V	5.0V
0	0	0	0	0	0
1	9.05%	11.99%	54.84%	65.89%	62.92%
2	13.05%	54.90%	65.83%	76.83%	79.04%
3	24.71%	63.45%	75.05%	84.53%	88.42%
4	32.37%	67.95%	82.53%	91.25%	95.61%
5	39.82%	72.30%	82.61%	95.91%	99.83%
6	41.81%	74.62%	85.40%	98.92%	100%
7	47.53%	77.86%	90.57%	100%	
8	54.30%	80.88%	94.98%		
9	56.43%	82.31%	98.54%		
10	61.01%	83.44%	100%		

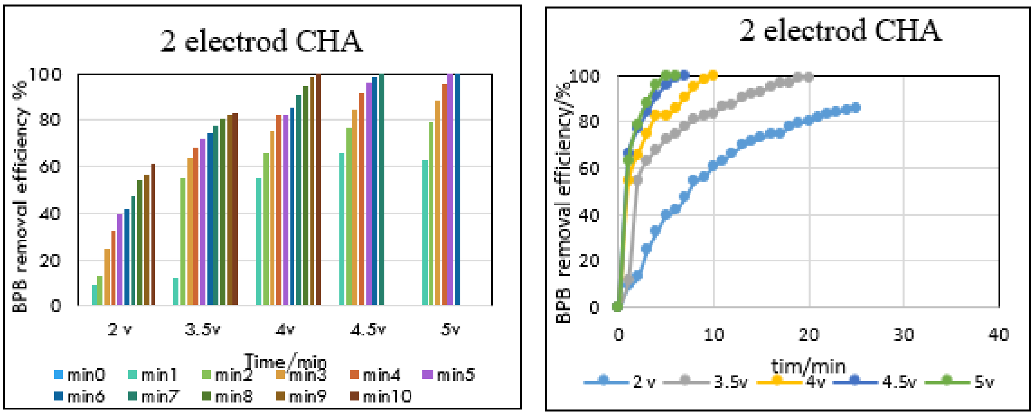


Figure: 8. Removal percentage of BPB at different applied current for two electrode chronoamperometry system, Conditions: 30 mg L-1 BPB, pH=4 and KCl: 0.1 M

- ## Three electrode chronopotentiometry technique.

Chronopotentiometry technique is used to measure the voltage with respect to time when a constant current is applied. When a specific current is applied to an electrochemical cell, the change in voltage with time is recorded. This technique is useful for understanding the mechanisms of oxidation and reduction, studying surface reactions, and the behavior of electrodes. The previous experiments were repeated on the Chronopotentiometry three electrodes technique and through practical experiments and after using the parameters that were fixed in the previous experiments in Chronoamperometry three electrodes, Chronoamperometry two electrodes, to comparing this technique with The previous technique was found that the results obtained after determining the values of the applied voltage (1.0, 1.5, 2.0, 2.5) mA, where the removal efficiency of Bromophenol blue dye was as follows: in the sixth minute (59.6%, 66.3%, 73.5%, 84.7%). While the removal efficiency in the seventh minute was (63.6%, 74.4%, 80.4%, 92.1%). The removal efficiency in the tenth minute was (79.5%, 89.8%, 95.2% 99.5%)

Table 4. Removal efficiency %, Time/minute and apply voltage Three electrode chronopotentiometry technique.

Time/min	1.0 mA	1.5 mA	2.0 mA	2.5 mA
0	**0**	**0**	**0**	**0**
1	**5.93%**	**5.12%**	**6.18%**	**10.53%**
2	**25.84%**	**26.56%**	**32.03%**	**42.01%**
3	**42.73%**	**38.57%**	**44.74%**	**47.17%**
4	**51.57%**	**49.81%**	**56.02%**	**54.99%**
5	**55.72%**	**61.99%**	**65.37%**	**67.32%**
6	**59.60%**	**66.39%**	**73.50%**	**84.78%**
7	**63.66%**	**74.43%**	**80.40%**	**92.10%**
8	**68.43%**	**80.54%**	**87.78%**	**98.23%**
9	**73.61%**	**85.45%**	**94.67%**	**99.33%**
10	**79.57%**	**89.81%**	**95.24%**	**99.55%**

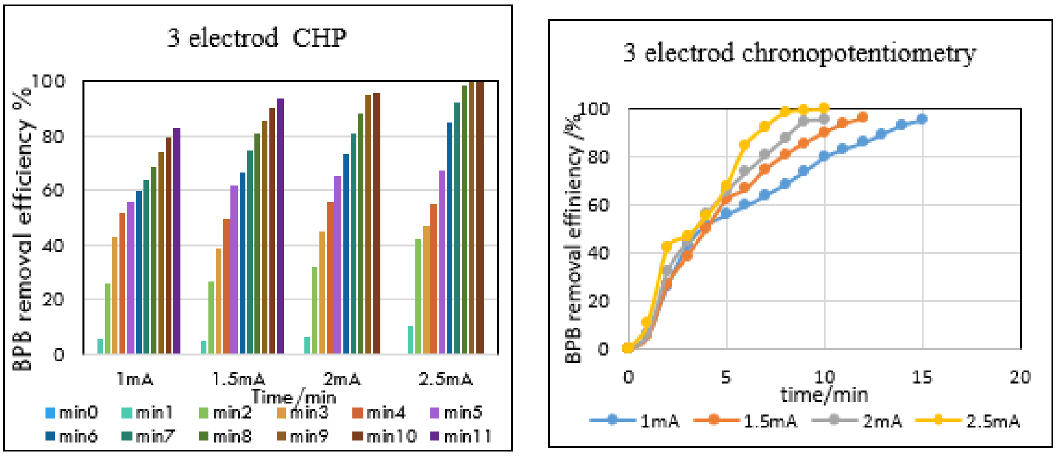


Figure 9. Removal percentage of BPB at different applied voltage for three electrode chronopotentiometry system ,Conditions: 30 mg L-1 BPB, pH=4 and KCl: 0.1 M.

Table 5 the comparison shows the best removal efficiency of the three techniques with time**.**

Time/min	Chronoamperometry three electrodes (1.0,1.2,1.4,1.6,1.8,2.0) V	Chronoamperometry two electrodes (2.0,3.5,4.0,4.5,5.0) V	Chronopotentiometry three electrodes (1.0,1.5,2.0,2.5)mA
6 minute	43.97%, 61.57%, 98.14%, 100%, 87.74%, 88.22%	41.81 %, 74.62 %, 85.40 %, 98.92 %, 100 %	59.6%, 66.3%, 73.5%, 84.7%
7 minute	43.88%, 65.60%, 100%, 100%, 90.73%, 91.23%	47.53 %, 77.86 %, 90.57 %, 100 %, 100 %	63.6%, 74.4%, 80.4%, 92.1%

10 minute	52.12%, 73.97%,100%, 100%, 93.51%, 97.62%	61.01 %, 83.44 %, 100 %, 100%, 100 %	79.5%, 89.8%, 95.2%, 99.5%

By comparing the best removal efficiency of Bromophenol blue dye with the three techniques over time and under the same conditions with a change in the applied voltage and current, it was as depicted in Table 5. we note that the removal efficiency of Bromophenol blue dye increases with increasing contact time between the electrodes when operating the electrochemical oxidation process. This efficiency also increases with increasing applied voltage or current, but within limits, because the increase may cause parasitic reactions that cause a decrease in the current efficiency and thus a decrease in the removal efficiency. It was also noted that the best technique that achieved the best removal efficiency is Chronoamperometry two electrodes, Chronoamperometry three electrodes.

- **Effect of pH**

Affects pH the electrochemical oxidation process by titanium-based mixed metal oxides (IrO_2 and RuO_2) ,electrochemical oxidation is an important process in many industrial applications, such as water treatment, chlorine production, and chemical synthesis. Mixed metal oxides, especially titanium-based ones such as IrO_2 and RuO_2, play a crucial role in this process due to their excellent electrochemical properties. However, the efficiency of this process is greatly affected by various factors, including the pH of the solution.

Different pH values including 4, 6 and 10 were investigated after selecting the best two electrode chronoamperometry technique. After determining the parameters under the conditions obtained from experimental tests, our laboratory experiments showed that pH = 4 provided the maximum removal efficiency of bromophenol blue dye at 6 min. The removal efficiency was (100%, 96.68%, 94.53%) at pH values (4.0, 6.0 and 10.0), respectively.as depicted table .7. This means that the best removal efficiency occurred at pH = 4. In an acidic environment, hydroxyl radicals are formed and radicals are more active in this environment. Therefore, it can improve the decomposition effects, but it also causes corrosion of the IrO_2-RuO_2 composite electrode and shortens the service life. Therefore, pH = 4.0 was selected as the appropriate value.

- **Effect of pH on surface structure**:

The surface structure of metal electrodes changes with changing pH, affecting their ability to adsorb ions and facilitate redox reactions.

In acidic media, oxide or hydroxide layers may form on the surface of the electrode, changing its electrochemical properties.

In alkaline media, dissolution of the metal oxide may occur, leading to deterioration of the electrode performance.

- **Effect of pH on oxidation-reduction reactions:**

The activation energy of oxidation-reduction reactions is affected by pH, which affects the reaction rate and electrochemical efficiency.

Changes in pH may lead to a change in the reaction mechanism, which affects the final products.

- **Effect of pH on bubble formation:**

The process of gas bubble formation resulting from electrochemical reactions is affected by pH, which affects the charge transfer efficiency and current distribution on the electrode surface.

- **Effect of pH on IrO_2 and RuO_2 oxides:**

IrO_2 is one of the best-modified electrodes for electrochemical oxidation in acidic and alkaline media.

In acidic media, IrO_2 exhibits high electrochemical oxidation activity, due to the presence of a stable thin oxide layer on its surface.

In alkaline media, partial dissolution of IrO_2 may occur, which leads to a decrease in its electrochemical activity.

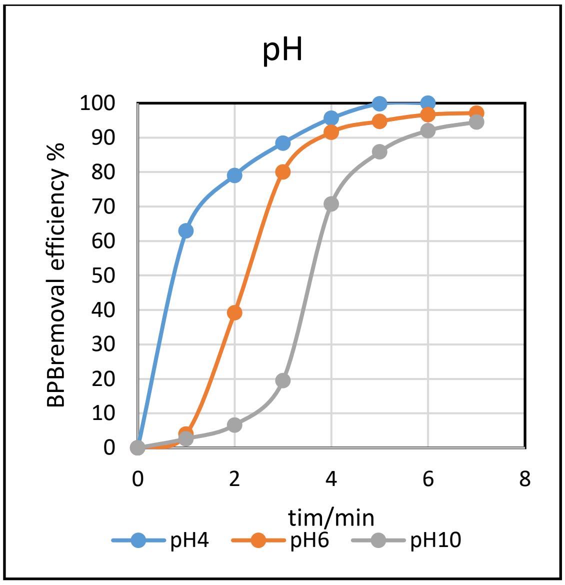
RuO_2 is also a good modified electrode for electrochemical oxidation, but it shows greater sensitivity to pH changes than IrO_2.

In acidic media, RuO_2 shows good electrochemical activity, but it may corrode over time.

In alkaline media, rapid dissolution of RuO_2 may occur, which limits its use in these media.

Table 6. Removal efficiency %, Time/minute and pH Two – electrodes system chronoamperometry.

Time/min	pH4	pH6	pH10
0	0	0	0
1	62.92%	3.95%	2.63%
2	79.04%	39.14%	6.63%
3	88.42%	80.06%	19.50%
4	95.61%	91.57%	70.76%
5	99.83%	94.72%	85.86%
6	100%	96.68%	92.05%
7		97.14%	94.53%



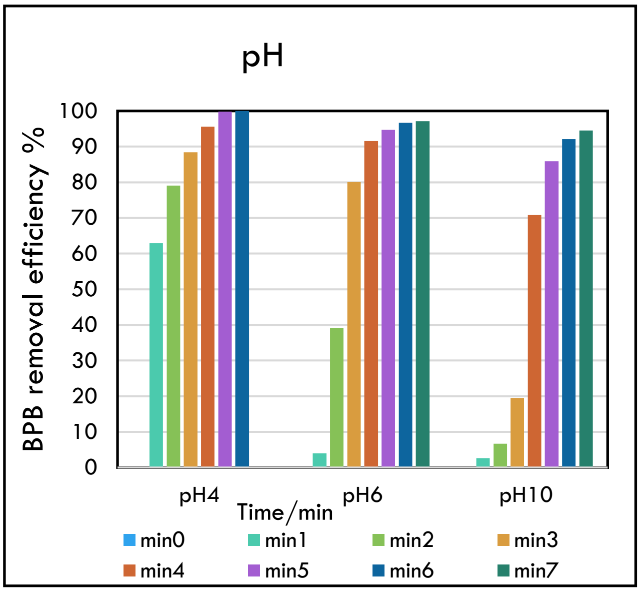


Figure 10. Removal percentage of BPB at different applied voltage for two electrode chronoamperometry system. Conditions: 30 mg L-1 BPB, I=5V and KCl 0.1 M.

The Result:

The pH greatly affects the electrochemical oxidation process by mixed metal oxides IrO_2 and RuO_2. The appropriate pH for a particular application should be selected based on the properties of the electrode and the material being oxidized. hydroxyl radicals to oxidize organic matter, which is a competitive reaction with the oxygen evolution reaction of electrodes. In an acidic environment, the oxygen evolution potential of the electrode is high, and the oxygen evolution reaction is difficult to carry out. At this time, the reaction occurring in the system is mainly based on the reaction of hydroxyl radicals with organic molecules. In an alkaline environment, the oxygen evolution potential of the electrode is low, and the oxygen evolution reaction is more likely to occur, which competes with the electro catalytic oxidation reaction of organic matter. Furthermore, electrolytes would be consumed excessively, and the conductivity of the solution would be reduced. Thereby, the electrical oxidation speed and effect are weakened, significantly reducing BPB and COD removal efficiency. In addition, in an acidic environment, hydroxyl radicals have higher oxidation activity and are more susceptible to oxidizing contaminants in solution, which is conducive to improving the degradation effects [38].

However, peracid electrolytes can cause corrosion to the IrO_2_RuO_2 composite electrode and shorten its service life. Therefore, pH = 4 was selected as the most suitable ,degradation condition.

Effect of type and concentration of supporting electrolyte.

Electrochemical oxidation uses supporting electrolytes to assist the flow of electrical current during the decomposition of the model compound. This improves the flow of electrical current and helps generate strong oxidizing agents—such as active chlorine species—electrochemically. Common

Supporting electrolytes include Na_2SO_4, NaCl, KCl, $NaClO_4$, $NaNO_3$, and Na_2CO_3. The choice of supporting electrolyte greatly affects the kinetics of

The decomposition. For example, direct oxidation of chloride at the anode can generate strong oxidants, including active chlorine species. This can lead to the formation of complexes with iron, such as iron sulfate and iron-chloro complexes.

After studying the removal process, it was found that the efficiency of potassium chloride electrolyte solution in transferring electrons in the electrochemical cell is better than using sodium sulfate under the same variables. Based on previous studies, the higher the concentration of the electrolyte solution, the more corrosion may be caused to electrodes, which reduces the life of the electrode used, so a concentration of 0.1 M was chosen.

Table 7. Removal efficiency %, Time/minute and pH4, KCl= (0.1, 0.3) M, Two – electrodes system Chronoamperometry

Time/min	**0.1 M**	**0.3 M KCl**
0	0	0
1	62.92%	82.22%
2	79.04%	98.56%
3	88.42%	
4	95.61%	
5	99.83%	

Based on the results, the removal efficiency of bromophenol blue dye when using a supporting electrolyte solution was (62.92%, 82.22%) in the first minute, then this efficiency increased to (99.83%, 100%) in the fifth minute when using KCl concentration (0.1, 0.3) M, respectively. From this we conclude that the more the supporting electrolyte solution in the electrochemical cell, the more electrons are transferred across the electrodes, but this causes corrosion of the electrodes used. Therefore, the KCl concentration = (0.1) M was used in the experimental tests. As for the electrolyte Na_2SO_4, it was used for the purpose of comparison with the KCl electrolyte solution, where the removal efficiency of bromophenol blue dye was zero%. Then the removal efficiency reached 68% at 14 minutes under the same conditions. By observing the figure Na_2SO_4, we notice a deviation from the absorption peak, and this is due to the mechanical deviations that Pierre Lambert determined in the tools or devices, as we mentioned earlier.

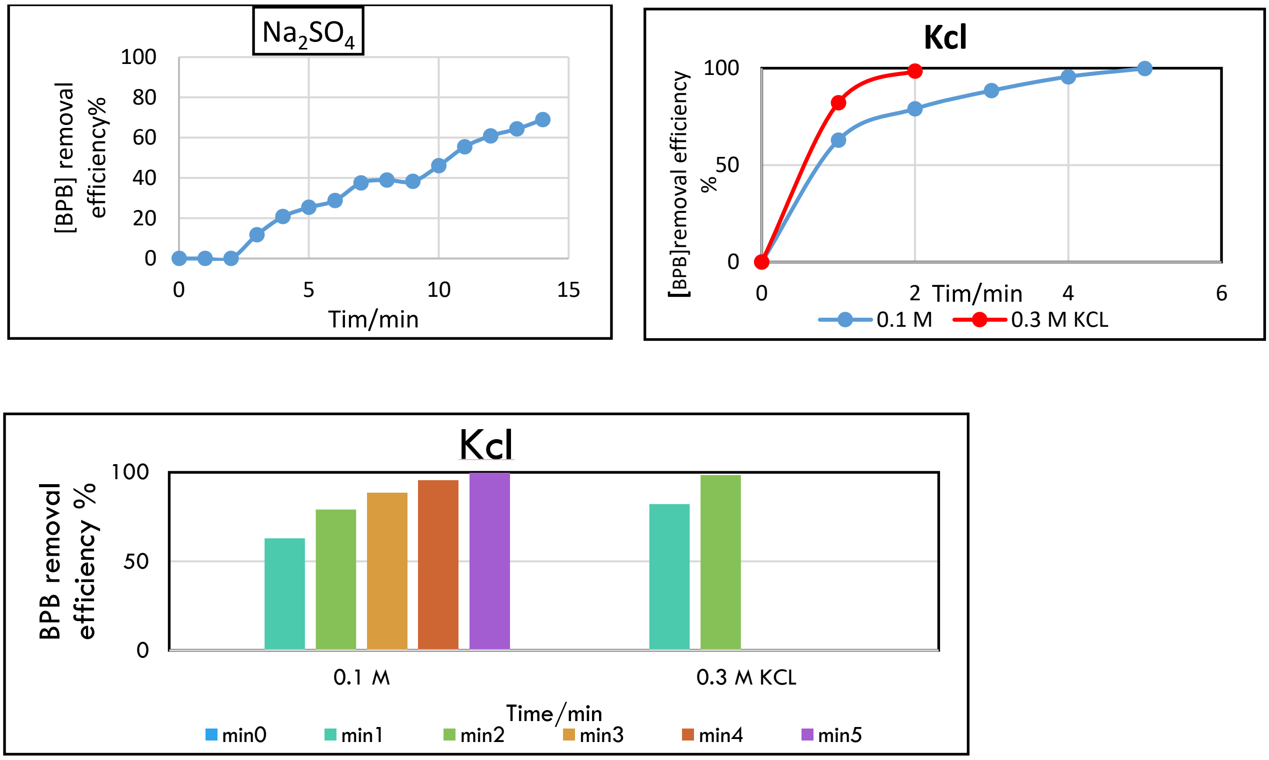


Figure 11. Removal percentage of BPB at different KCl concentration for two electrode chronoamperometry system KCl=0.1 M, KCl=0.3 M ,Na2SO4=0.1 M ,removal percentage versus time for Na2SO4. ,Electrolyte mixed curves of removal percentage versus time for KCl concentration for 0.1 M, KCl. Conditions: 30 mg L-1 [BPB], pH=4, 5V.

Potassium chloride (KCl) solution affects the electrochemical oxidation process by titanium-based mixed metal oxides (IrO_2 and RuO_2) .Potassium chloride (KCl) is a commonly used electrolyte in many electrochemical applications, including those using mixed metal oxides as electrodes. The type and concentration of the electrolyte plays a crucial role in determining the efficiency of the electrochemical oxidation process, as it affects several factors such as:

Charge transfer: The electrolyte acts as a medium for charge transfer between the electrode and the solution.

Formation of an electrical double layer: An electrical double layer is formed at the electrode/solution interface, which affects the electrical potential distribution and redox reactions.

Solubility of reactants: The electrolyte affects the solubility of reactants and products, and thus affects their concentration on the electrode surface.

Effect of Inter-Electrode Distance on Color Removal Efficiency

The inter-electrode distance of 1 cm produced the highest color removal for all processes. The larger the inter-electrode distance, the lower the removal efficiency. The electrical resistance increases with increasing the inter-electrode distance, leading to a decrease in current flow and less production of hydroxide ions, which results in a decrease in color removal. Consequently, high energy consumption as the electrochemical oxidation process takes longer. The shorter the inter-electrode distance, the lower the resistance and thus the lower the specific energy consumption and cost of organic water treatment. Effect of the internal distance between electrodes in the electrochemical oxidation process .The distance between electrodes in an electrochemical cell is one of the critical factors that affect the efficiency of the electrochemical oxidation process, especially when using iridium oxide and ruthenium oxide electrodes based on titanium. This effect is directly reflected in the distribution of electric current, the resistance of the solution, and the formation of oxide layers on the surface of the electrodes.

Mechanism of influence:

- Electrical current distribution:

Close distance: The proximity of the electrodes leads to an inhomogeneous distribution of electric current, as the current is concentrated in the area

Adjacent to the electrodes, which leads to an increase in the local current density and the formation of gas bubbles that may hinder the oxidation process.

Long distance: Increasing the distance between the electrodes results in a more uniform distribution of current, but may also increase the resistance of the solution, which reduces the efficiency of the process.

- Solution resistance:

Close distance: Close distance reduces the resistance of the solution, which facilitates the transfer of ions between the electrodes and increases the efficiency of the process.

Far distance: Distance increases the resistance of the solution, which reduces the efficiency of the process and leads to a decrease in the reaction rate.

- Formation of oxide layers:

Close distance: Inhomogeneous distribution of current may lead to the formation of heterogeneous oxide layers on the surface of the electrodes, affecting their physical and chemical properties.
Far distance: It may lead to the formation of more homogeneous oxide layers, but the formation rate may be slower.

Effect of distance on iridium and ruthenium oxide electrodes:

Increased stability: The appropriate distance between the electrodes helps to distribute corrosion uniformly on the surface of the electrodes, which

Increases their operating life.

Improved efficiency: The optimum distance leads to improved efficiency of the oxidation process, as a balance is achieved between the current distribution and the resistance of the solution.

Minimizing Bubble Formation: The appropriate distance helps to minimize the formation of gas bubbles on the surface of the electrodes, which improves the transfer of material between the liquid and the electrode.

Factors affecting the choice of distance:

Nature of the solution: The concentration of ions and the viscosity of the solution affect the resistance of the solution and the current distribution.

Current density: The higher the current density, the more important is the homogeneous current distribution.

Electrode dimensions: The size and shape of the electrodes affect the distribution of the electric field between them.

Type of electrochemical reaction: The type of reaction affects the reaction rate and transfer resistance.

The Result:

Choosing the appropriate distance between the electrodes in the electrochemical oxidation process using iridium and ruthenium oxide electrodes is crucial to achieve the best performance. There must be a balance between the current distribution, solution resistance, and the formation of oxide layers.

Effect of chemical reaction kinetics on electrochemical oxidation process with mixed metal oxides (IrO_2 and RuO_2) based on titanium

In addition to the effect of pH, chemical reaction kinetics plays a crucial role in determining the efficiency of the electrochemical oxidation process in which mixed metal oxides such as IrO_2 - RuO_2 are used. This kinetics determines the rate of occurrence of reactions on the surface of the electrode and thus affects the efficiency of charge transfer and the amount of oxidant per unit time.

Effect of reaction kinetics on IrO_2 - RuO_2 electrode

IrO_2 is characterized by its high ability to catalyze oxidation reactions, but the reaction kinetics may be affected by the presence of impurities or a change in the surface structure.

RuO_2 is an effective oxidation catalyst, but the reaction kinetics may be affected by pH and the presence of chloride ions.

Factors affecting reaction kinetics in electrochemical oxidation

Nature of the electrode: The reaction kinetics varies depending on the type of material from which the electrode is made, its area, and its surface structure.

Nature of the solution: The composition of the solution, including the type and concentration of ions, affects the reaction kinetics.

Current density: The current density applied to the electrode affects the reaction rate, where increasing the current density increases the reaction rate until it reaches a specific value.

Temperature: Increasing the temperature increases the activation energy of the molecules, which increases the reaction rate.

Importance of studying reaction kinetics

Studying the kinetics of reactions in electrochemical oxidation helps in:

Improving the efficiency of the processes: Understanding the kinetics of the reactions can help in designing more efficient electrochemical systems.

Developing new electrode materials: New electrode materials with better catalytic properties can be designed.

Understanding the reaction mechanisms: Studying the kinetics of the reactions helps in understanding the mechanisms of the complex reactions that occur on the surface of the electrode.

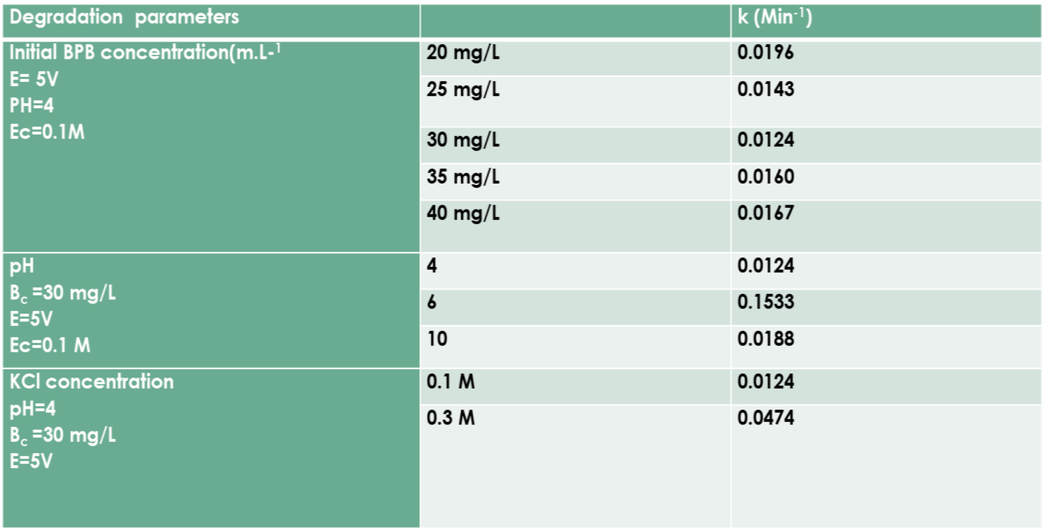
Conclusion: The kinetics of chemical reactions play an important role in determining the efficiency of the electrochemical oxidation process using mixed metal oxides such as IrO_2 - RuO_2. By understanding the factors affecting this kinetics, the performance of these electrodes can be improved and new applications can be developed for them.

Kinetic results

The results of kinetic data for BPB degradation for different parameters including initial BPB concentration, pH and KCl concentration. Bromophenol blue dye removal efficiency was represented by following Pseudo-First-Order as presented in Equation 9.

$$\mathrm{Ln}\ (C_0/C_t) = kt \qquad \textbf{Equation(9)}$$

Table 9. Kinetics data for the BPB degradation at different parameters.



Degradation parameters		k (Min^{-1})
Initial BPB concentration(m.L-^{1} E= 5V PH=4 Ec=0.1M	20 mg/L	0.0196
	25 mg/L	0.0143
	30 mg/L	0.0124
	35 mg/L	0.0160
	40 mg/L	0.0167
pH B_c =30 mg/L E=5V Ec=0.1 M	4	0.0124
	6	0.1533
	10	0.0188
KCl concentration pH=4 B_c =30 mg/L E=5V	0.1 M	0.0124
	0.3 M	0.0474

Bc = initial Bromophenol blue dye Concentration (mg/L),
E =potential (V)
pH=pH
Ec= supporting electrolyte concentration (mol/L)
Ln (C0/Ct) =kt
This equation represents the basic relationship in first-order reactions in chemistry.

To clarify the equation,

Ln: natural logarithm.

C_0: initial concentration.

Ct: concentration at time t.

K: rate constant.

T: time.

Equation Meaning:

First-order reaction: means that the reaction rate is directly proportional to the concentration of one reactant only.

Ln (C_0/Ct): This part represents the percentage change in concentration over time. The longer the time, the lower the value of Ct, and thus the higher the value of the ratio ln (C_0/Ct).

Kt: This part represents time multiplied by the rate constant. The longer the time or the higher the rate constant, the higher the value of kt.

In other words, the equation expresses the relationship between the change in concentration of the reactant over time and the rate constant.

Uses:

Calculating the rate constant: If we draw a curve representing the relationship between ln (C_0/Ct) and time, the slope of this curve is equal to -k.

Determining half-life: Half-life is the time it takes for the concentration of a reactant to decrease by half. It can be calculated from this equation.

Studying the rate of chemical reactions: This equation helps us understand how the rate of a reaction changes with concentration and time.

8. Conclusion:

1. IrO_2-RuO_2 based on Ti modified electrode is very effective in removing Bromophenol blue dye from aqueous samples as simulated markers due to its high ability to decompose organic pollutants in water.
2. These electrodes have important advantages in terms of increasing the electrode area and stability, the contact surface area of the electrode with the solution, and the electrochemical properties.
3. According to the information and results obtained after studying each of the initial concentrations of Bromophenol blue dye, pH, supporting electrolyte solution, voltages, and currents applied using Chronoamperometry three electrodes, Chronoamperometry two electrodes, Chronopotentiometry three electrodes, we found that the best initial concentration of Bromophenol blue dye used in this study is 30 mg/L, pH = 4, KCl=0.1 M, The removal efficiency of Bromophenol blue dye was achieved when using three chronoamperometry electrodes, and two chronoamperometry electrodes, but the best removal efficiency was when using two chronoamperometry electrodes, where it was (41.81%, 74.62%, 85.40%, 98.92%, 100%) at 6 minutes, and the removal efficiency increased to (61.01%, 83.44%, 100%, 100%, 100%) after 10 min when applying a current of (2.0, 3.5, 4, 4.5, 5.0) V, respectively. This means that the higher the applied current and the longer the contact time between the electrodes, the higher the removal efficiency.

These electrodes provide excellent performance and high efficiency in a wide range of industrial applications such as the chlor-alkali industry, electrolyte industry, water treatment, battery industry, and organic electrolysis.

Parameter	Value - Case 1	Value - Case 2
Parameter 1 (N)	12.3	1.5
Parameter 2 (kg)	34.50	12.00
Parameter 3 (mm)	25	9

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Funding

The authors had no institutional or sponsor backing.

Conflicts Of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgment

The authors have no acknowledgments to declare.

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