



# Efficient indirect electrochemical degradation of bromothymol blue and methyl red from aqueous phase at $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anode

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## Abstract

This contribution describes the indirect electrochemical oxidation of wastewater laden with bromothymol blue and methyl red dyes using a laboratory-scale electrochemical reactor with a  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  anode and stainless-steel cathode. The influence of current density, pH, and electrolyte concentrations on the oxidative degradation pattern of the dyes in the wastewater was also investigated by coupling the electrochemical reactor with an Ultraviolet–Visible spectrometer. By indirect oxidation, 97% of the bromothymol blue at  $10 \text{ mA cm}^{-2}$  current density and pH 3.0 and 98% of the methyl red at  $2 \text{ mA cm}^{-2}$  current density at pH 3.0 were indirectly oxidized in 10 min. Initial concentrations of each were 200 ppm. During the degradation of the dyes, electrochemically generated chlorine and hypochlorite ions ( $\text{OCl}^-$ ) played pivotal roles. Under the aforementioned ideal circumstances, the minimum energy consumption values for bromothymol blue and methyl red were  $0.2025$  and  $0.0636 \text{ kW h m}^{-3}$ , respectively. The anode exhibited an excellent service life for treating dye wastewater, and repeated tests and surface analysis revealed no evident passivation. In this way, a variety of dyes in effluents can be cheaply degraded by electrolyzing with a  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  anode, utilizing readily available electrolytes and with minimal electricity requirements.

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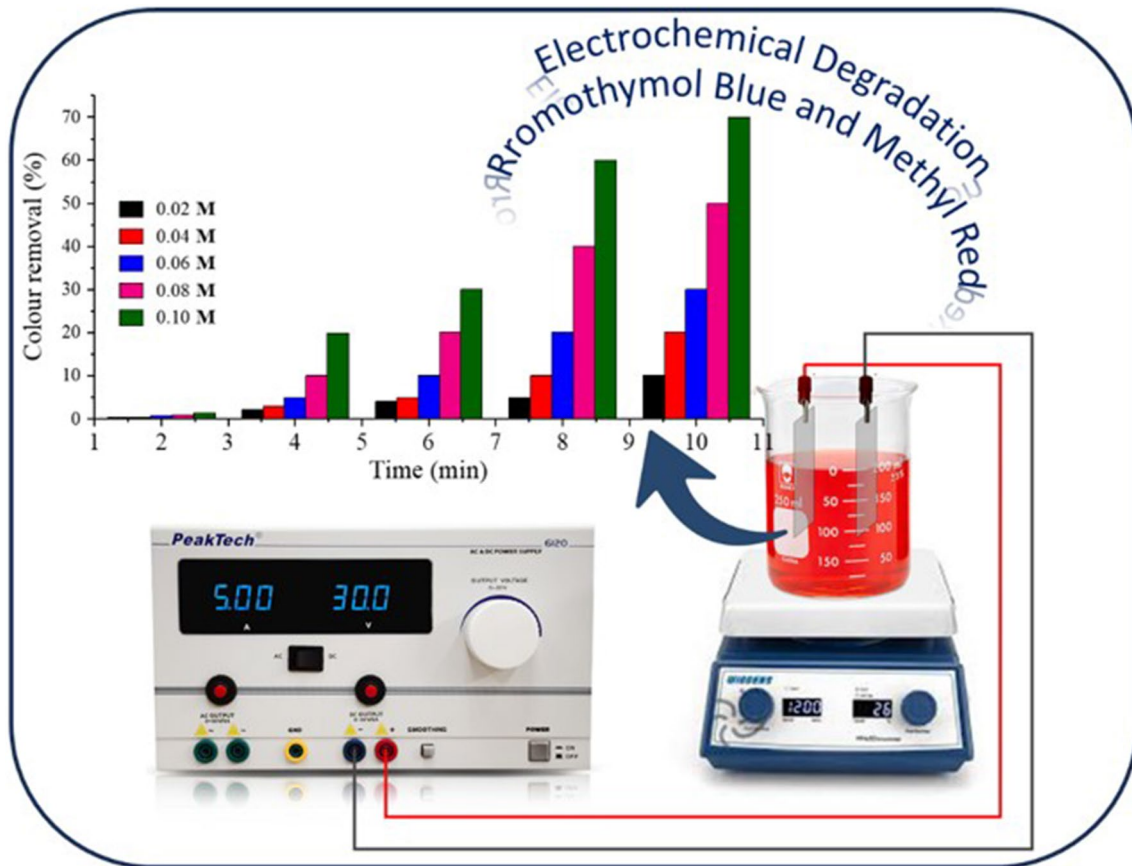
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## Graphical abstract



**Keywords** Current density · Degradation · Dyes · Electrochemical oxidation · Energy consumption · Wastewater

## Introduction

Water is a vital natural resource and is a basic need of living organisms. Due to human activity, population increase, climate change, urbanization, and industrialization, water quality is deteriorating day by day. Life on Earth is currently seriously threatened by water contamination. Natural organic matter is the principal pollutant in surface waters that is used for both agriculture and drinking (Andersson et al. 2020), but it is not the only pollutant. A variety of industries, including textiles, leather, paper, plastic, pharmaceutical, ink, ceramics, and food processing, use dyes to color their products and increase their value (Donkadokula et al. 2020). Tons of synthetic organic dyes are produced each year, according to estimates (Chequer et al. 2013). Textiles account for a significant portion of the developing world's industrial landscape. Large amounts of water are used in textile processing for washing and dyeing. As a result, textile manufacturers pollute water bodies with effluents that contain dyes employed at various stages of the

textile manufacturing process. Dye-containing effluents are widely established to have a deleterious impact on aquatic bodies. Insoluble dyes have been shown to leave a residue color that is very resistant to biological activity (Rápó and Tonk 2021). Bromothymol blue (BTB) a type of sulfonphthalein dye is an unrestricted textile dye derivative and is used as a pH indicator (Steinegger et al. 2020; Maamar et al. 2015). BTB can damage target organs when exposed over an extended period since it can irritate the eyes, skin, and respiratory system, attack the lungs and mucous membranes, and cause respiratory tract infections (Prakash et al. 2018). The colouring of paper, textiles, leather, cosmetics, inks, ceramics, and food-processing goods uses azo dyes of the methyl red (MR) type (Cockerham et al. 2022). The presence of MR in aquatic bodies causes an aesthetic issue and may be harmful to public health due to the production of aromatic amines, which are thought to be mutagenic or carcinogenic when they are broken down. If eaten or inhaled, MR may irritate the digestive tract and sensitize the skin and eyes (Iqbal et al. 2022; Takkar et al. 2017).



Treatment of water contaminated with harmful chemicals such as dyes, herbicides, insecticides, pharmaceuticals, detergents, etc., is crucial since these substances pose a major threat to the local flora and wildlife (Al-Nuaim et al. 2023). Various methods including physical methods (adsorption, sedimentation floatation, etc.) (Kavindra et al. 2011; Zeb et al. 2020; Gul et al. 2022), chemical (Lin and Chen 1997), and biological processes (Takkar et al. 2017), are being employed for wastewater treatment. Other methods such as ozonation (Venkatesh et al. 2017), photocatalytic oxidation (Khan et al. 2020; Sartaj et al. 2020), and electrochemical oxidation (Hussain et al. 2021; Brito et al. 2018; Pieczyńska et al. 2019; Muhammad et al. 2020) are being employed by scientists which can be effective against textile dyes. Each of these approaches has distinct merits and demerits (Crini et al. 2019). Unfortunately, most of the treatments used currently use chemicals that are prohibitively expensive in most countries, have little effectiveness, and negatively impact the environment. Therefore, more sophisticated and economical water treatment technologies for desalination and water reuse are needed in order to boost water supplies. Green technologies have been emphasized as a long-term plan for preserving natural resources, lowering harmful effects on the environment, and accelerating social and economic development (Niknejad et al. 2023). In order to meet the growing demand for clean water and reduce adverse environmental effects, membrane-based technologies such as microfiltration, ultrafiltration, nanofiltration, and forward- and reverse-osmosis membranes are now being viewed as viable alternatives to traditional water and wastewater remediation techniques (Shehata et al. 2023). Although these technologies have many benefits, but they also have some significant drawbacks, such as expensive startup and high operating costs. Many water and wastewater treatment applications involve a variety of pollutants, such as pesticides and prescription medications that are challenging to eliminate using only physical, chemical, or biological methods. Due to their microscopic size, these contaminants are classified as micro-pollutants. They are very challenging to remove from water and wastewater using specific methods, in part because of their size alone. Advanced oxidation processes (AOP) are necessary for the removal of small-sized pollutants. These processes produce strong oxidizing agents, such as hydroxide ( $\text{OH}^-$ ) or its neutral variant, the hydroxyl radical ( $\bullet\text{OH}$ ), in sufficient quantities to degrade organic and some inorganic pollutants. These agents are produced by Ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and ultraviolet light (UV). Numerous advantages of AOP include its quick reaction times, small footprint, and ability to remove heavy metals, ability to convert organic materials in water into stable inorganic compounds like carbon dioxide and water, and lack of sludge production. It also does not introduce new hazardous substances

into the water. AOP does, however, have certain drawbacks, such as relatively high startup and operating/maintenance costs, complex chemistry that necessitates customization to particular pollutants, and a problem with residual peroxide removal (Priyadarshini et al. 2022). The sequencing batch reactor (SBR) system is another useful method for treating landfill leachate and wastewater contaminants because of its cost-effectiveness, simplicity, tolerance to shock loads, and adaptability in terms of reaction time according to influent water quality. Long treatment cycles, frequent changes in the water's entry and exit, and a high need for equipment automation are some drawbacks of SBR (Jagaba et al. 2021). For the treatment of wastewater, various other methods are used, each with advantages and disadvantages, including membrane filtration, membrane bioreactors, membrane PC-reactors, ballasted coagulation, sedimentation & filtration, sequencing batch bioreactors and sequencing batch PC-reactors, magnetic ion exchange (MIEX), coagulation, sedimentation and filtration, sequencing batch ion exchange, pre-ozonation, dissolved air flotation (DAF), and filtration (Wang and Wang 2023).

The electrochemical oxidation method either direct (Zeb et al. 2018) or indirect (Zhang et al. 2014) oxidation is a potentially green technology that is extensively used for the depletion of dyes and other contaminants from industrial or domestic wastewater. The electrochemical oxidation of dyes from wastewater has shown promising degradation results to eradicate these contaminants in a short period when compared to conventional methods (Rodríguez-Narváez et al. 2021; Wang et al. 2020; Pieczyńska et al. 2019; Martínez-Huitle and Panizza 2018). In the direct oxidation method, the pollutant is first adsorbed on the anode and then oxidized by a powerful oxidant such as the hydroxyl radical or chlorine/hypochlorite ion through the transmission of the anodic electron (Stupar et al. 2017; Zhang et al. 2014; Panizza and Cerisola 2009). Several research has been conducted based on the current literature to remove synthetic colored dyes from water using an electrochemical technique at various electrodes. The electrochemical decontamination of the dye Chromotrope 2R is carried out by Du et al. (2017) on a boron-doped diamond (BDD) anode. Fajardo et al. (2017) used individual or assembling of flow cells with Ti/Pt and Ti/Pt-SnSb anodes for the electrochemical abatement of amaranth dye solutions. Electrochemical degradation of methylene blue dye was carried out by Saadia et al. (2017) using the  $\text{PbO}_2$  electrode of a lead-acid battery, Indigo Carmine by Labiadh et al. (2017) using  $\text{PbO}_2$  and TiRuSnO<sub>2</sub> anode, Acid yellow 36 by Aguilar et al. (2017) on Ir-Sn-Sb anode, etc.

Electrochemical degradation of methyl red has been reported by Ahmad et al. (2022) on zinc hydroxide and zinc oxide thin films and by Panizza and Cerisola (2008) on BDD and  $\text{PbO}_2$  anodes. Morais et al. (2013) studied



the direct electrochemical degradation of methyl red using  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  using cyclic voltammetry and achieved a total color removal by applying 20 and 30  $\text{mA cm}^{-2}$  while, at 10  $\text{mA cm}^{-2}$ , only 78% was obtained. We did the indirect electrochemical degradation of the MR dye at  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  anode and achieved 99% color removal.

Maamar et al. (2015) report the electrochemical oxidation of Bromothymol blue in an aqueous medium ( $\text{pH} = 3$ ) by the electro-Fenton process (EFP). Maamar and Bellakhal (2017) have reported the treatment of a Tunisian textile effluent containing BTB dye using anodic oxidation on a Boron-doped diamond electrode. In most of the literature, photocatalytic degradation of BTB is reported (Al-Asfar et al. 2018; Fui et al. 2016; Khan et al. 2016).

In the current study, BTB and MR (Fig. 1) were indirectly electrochemically oxidized (EO) by using a composite anode,  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ , and a cathode made of stainless steel. The influence of several parameters such as the pH of the solution, current density, electrolyte concentration, and nature of supporting electrolyte during the process were assessed. To the best of our knowledge, a  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  anode has not previously been employed for the indirect electrochemical oxidative degradation of BTB and MR dyes from wastewater effluents. Seema Sartaj et al. 2020 have reported the use of a titanium ruthenium oxide anode for the electrochemical degradation of Allura red and erythrosine dyes. Our study significantly diverges from the reported work by addressing distinct dyes (bromothymol blue and methyl red), utilizing a  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  anode, and establishing novel optimal degradation conditions. The work of Seema Sartaj et al. 2020 is basically focused on comparing of Photolytic degradation and electrochemical degradation of two food dyes namely Allura red and Erythrosine, they applied statistical approaches to optimize the variables. Whereas our research emphasizes experimental optimization of electrochemically influence parameters for the degradation of pH indicator dyes (Bromothymol blue

and methyl red). As current density, NaCl concentration and pH are fundamental parameters for any electrochemical process and both work study the influence of these variables. These aspects collectively delineate a considerable departure from the previous study, underscoring our contribution in advancing the understanding and practical application of electrochemical degradation processes for dye-laden wastewater treatment.

#### Date and location of the research:

A part of this research work was carried out in 2019 and due to COVID-19 closures, the remaining experimentation was carried out in 2020–21 at the Institute of Chemical Sciences, University of Peshawar Khyber-Pakhtunkhwa, Pakistan. Currently, in July 2023, some experiments were re-conducted at the Faculty of Materials and Chemical Engineering, Ghulam Ishaq Khan (GIK) Institute of Engineering Sciences and Technology Topi, Khyber-Pakhtunkhwa, Pakistan.

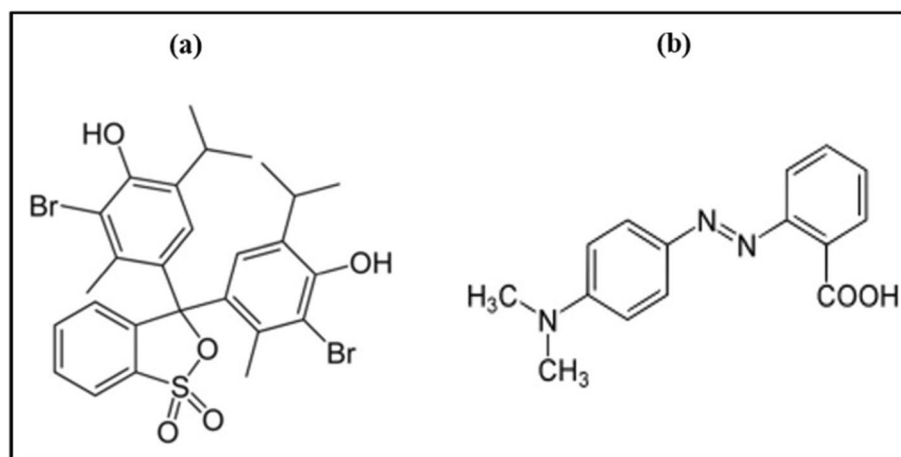
## Materials and methods

### Materials

All of the compounds were of analytical quality when they were received, and they were all used without any additional purification. BTB (> 95.0%), MR (> 95.0%), NaCl (> 99.5%), and  $\text{Na}_2\text{SO}_4$  (> 99.0%) were purchased from Merck Millipore and  $\text{NaNO}_3$  (> 99.0%) and  $\text{H}_2\text{SO}_4$  (97–98%) were from Sigma Aldrich.

The titanium/ruthenium–titanium oxide,  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  composite electrode was obtained from De Nora Brazil. The electrode was electrochemically characterized using cyclic voltammetry and matched characterization first seen by co-authors of this article (Zeb et al. 2018).

**Fig. 1** Molecular structure of **a** BTB (Klotz et al. 2011) and **b** MR (Das et al. 2012)



## Instruments used

A power supply DAZHENG DC model ps-303D, China was employed for the quantification of voltage and current, and a double beam UV–VIS spectrophotometer model UV 1602, USA was used to measure the concentration of the dyes.

## Solutions preparations

All the solutions for the experiment were prepared in double distilled de-ionized water. To make a 200 ppm solution, 0.1 g each of the dyes BTB, and MR was dissolved in distilled water and then diluted up to 500 mL. This was used as a stock solution from which various samples of variable concentrations were prepared. The absorbance of these solutions was determined by using a UV–VIS spectrophotometer. The data is taken in triplicate and the average data is reported and the percent error bar ( $\pm 5\%$ ) is applied to each data.

## Electrochemical debasement

Using a Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> composite anode, aqueous solutions of the BTB and MR dyes were subjected to electrochemical degradation in a Pyrex glass reactor. The current and voltage were measured using the aforementioned DC power supply. A 400 mL of a 200 ppm mixture of each of the BTB and MR solutions was electrolyzed in the presence of various electrolytes in each test. The effect of pH and electrolyte concentration as well as of the current density on the degradation of the dye from their aqueous solutions was studied. At various time intervals, 1 mL of the aliquots were taken out of the solutions and analyzed via a UV–VIS spectrophotometer at an ambient temperature and pressure. The % electrochemical degradation of the dyes was calculated using an Eq. (1).

$$\%degradation = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where  $A_t$  is the absorbance at the lambda maximum (max) after  $t$  minutes of the experiment, and  $A_0$  is the absorbance at  $t = 0$  min. Equation (2) provided the estimation of energy consumption for both dyes.

$$\text{Energy consumption (kW h)} = \frac{I \times V \times t}{V_s} \quad (2)$$

where  $I$  denotes the applied current (A),  $V$  denotes the average voltage (V),  $t$  is the oxidation time (h), and  $V_s$  denotes the solution volume (400 mL).

## Results and discussion

### Wavelength of maximum absorbance ( $\lambda_{max}$ ) and calibration curves

Figure 2 displays a wavelength versus absorbance plot for (a) BTB and (b) MR dyes. The absorbance of the dyes is measured at different wavelengths by passing UV–visible light from a definite concentration of the two dye solutions ( $20 \mu\text{g mL}^{-1}$  solution of BTB and  $20 \mu\text{g mL}^{-1}$  solution of MR) using a UV–VIS spectrophotometer. Examining the absorbance of BTB and MR over the visible spectrum, it can be seen from the figure that the highest absorbance for BTB and MR occurs at 615 and 515 nm, respectively. This wavelength at which the highest absorbance occurred is called the wavelength of maximum absorbance or the absorbance maximum or  $\lambda_{max}$  and is read as lambda max.

At the  $\lambda_{max}$  of BTB ( $\lambda_{max} = 615$  nm) and MR ( $\lambda_{max} = 515$  nm) absorbance for different concentrations (20–50 ppm solutions for BTB and 2–20 ppm solutions for MR) was discovered at max for the working curve of BTB and MR) of these dyes were measured and plotted as the concentration (in ppm on the x-axis) and the absorbance for both the dyes and are shown in the inset of Fig. 2a for BTB and Fig. 2b for MR. The plot is known as a working curve or calibration curve which was linear for both the dyes confirming Beer–Lamberts law. As can be seen from the plots when the concentration (i.e. the amount of solute) increased for each of the dye solutions, more light was absorbed following Beer–Lamberts law. These calibration curves were used to calculate the unknown concentrations of each dye solution using their known absorbance values from the linear plot.

### Electrochemical degradation

On the rate of electrochemical oxidation of BTB and MR dyes, the effects of various working parameters, such as current density, electrolyte concentration, and pH, were investigated.

### Influence of current density on the degradation of BTB and MR dyes

The production of oxidative species like aqueous chlorine,  $\text{ClO}^-$ , and  $\text{HOCl}$  are critical for the oxidative degradation of dyes using a DSA anode. These species are generated at the anode surface and move into the bulk of the solution to degrade organic pollutants, therefore the current density is expected to be a key factor in the process. The data is plotted as % color removal versus time (minutes) and shown in Fig. 3a at a range of current densities. The



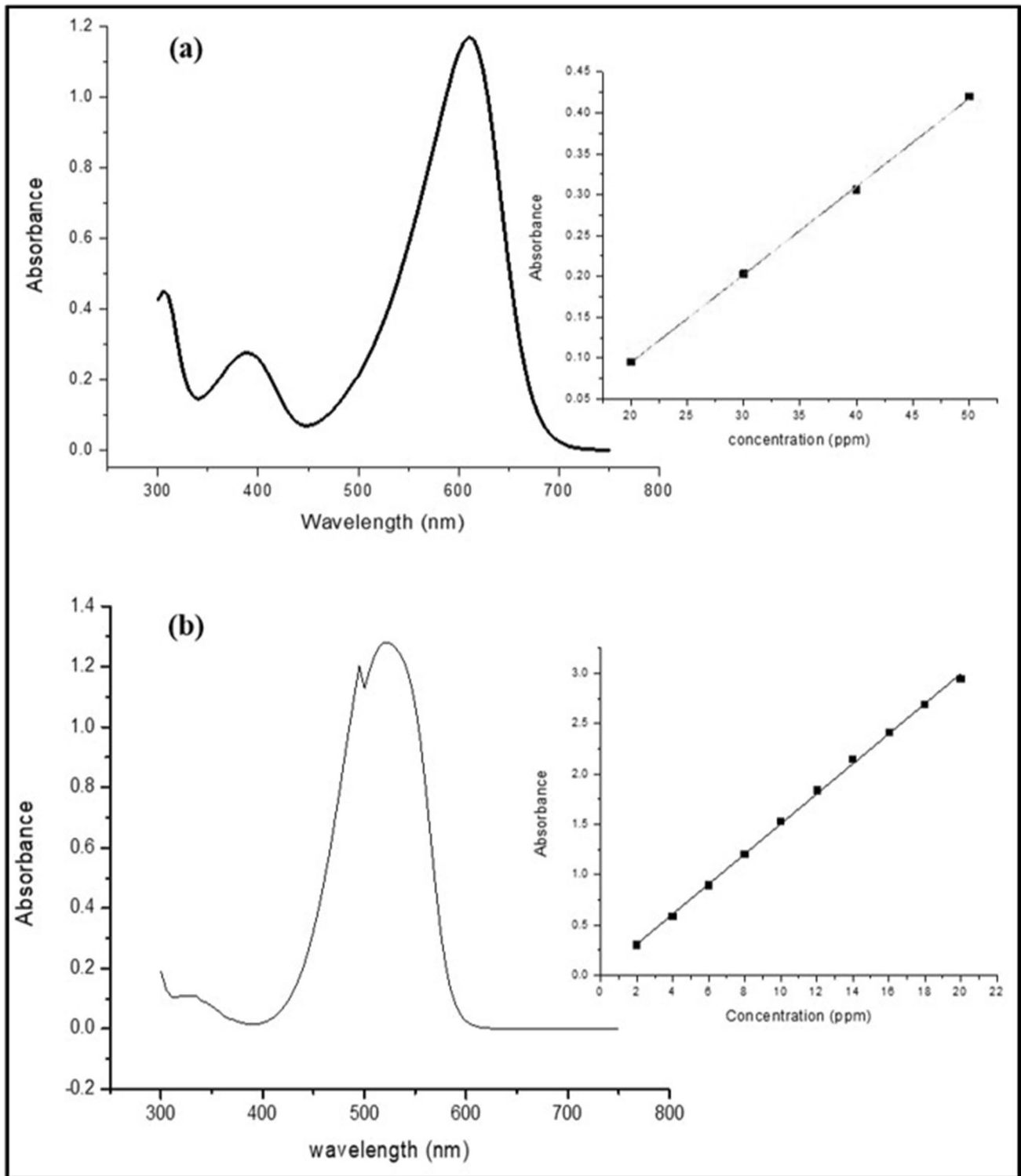
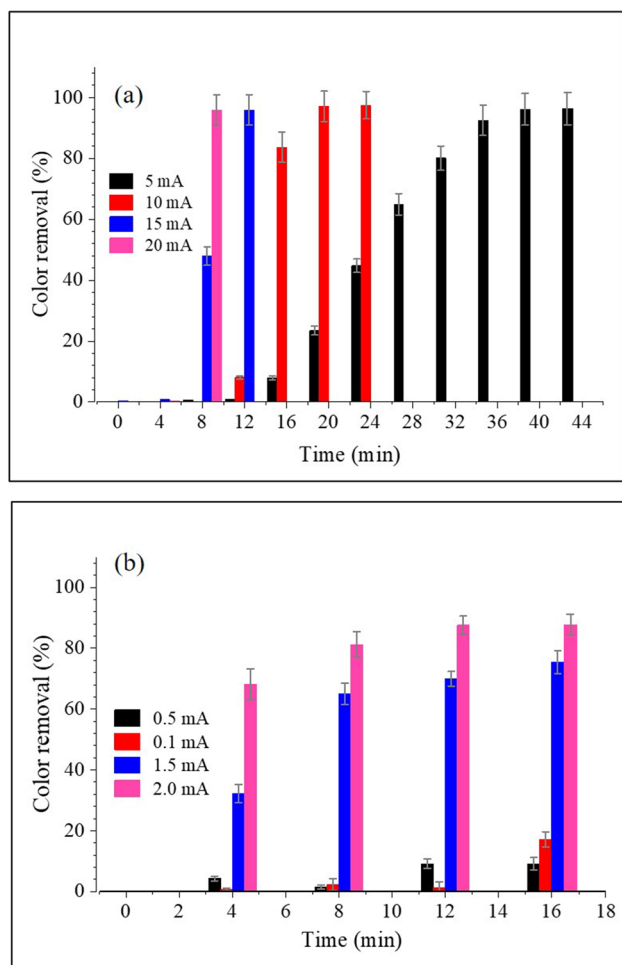


Fig. 2 UV-VIS spectra showing  $\lambda_{\max}$  along with the working curves for **a** BTB at  $\lambda_{\max} = 615$  nm and **b** MR at  $\lambda_{\max} = 515$  nm

electrochemical debasement of BTB was carried out at 5, 10, 15, and 20  $\text{mA cm}^{-2}$  current densities with 0.1 M of NaCl electrolyte at a pH of 3. At a current density of 5  $\text{mA cm}^{-2}$ , a degradation of 97% occurred in 44 min while

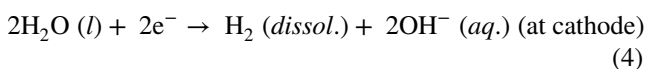
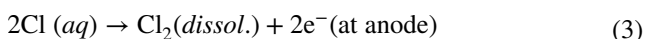
a degradation of 95% took place in 8 min at a current density of 20  $\text{mA cm}^{-2}$ . This shows that as current densities rise, more chlorine, hypochlorite ions (OCI) as well as



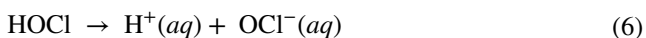


**Fig. 3** Current effect on the removal of **a** BTB and **b** MR

•OH radicals are generated, which speeds up the process of color removal as per reactions (3–6).



In the bulk solution:



It is also obvious from Fig. 3a that more than 97% of dye degraded at  $10 \text{ mA cm}^{-2}$  in just 20 min of electrolysis. Therefore, a current density of  $10 \text{ mA cm}^{-2}$  was selected, as it showed the most promising results in terms of cost and color eradication. Further increases in current density had no appreciable impact on the effectiveness of dye degradation.

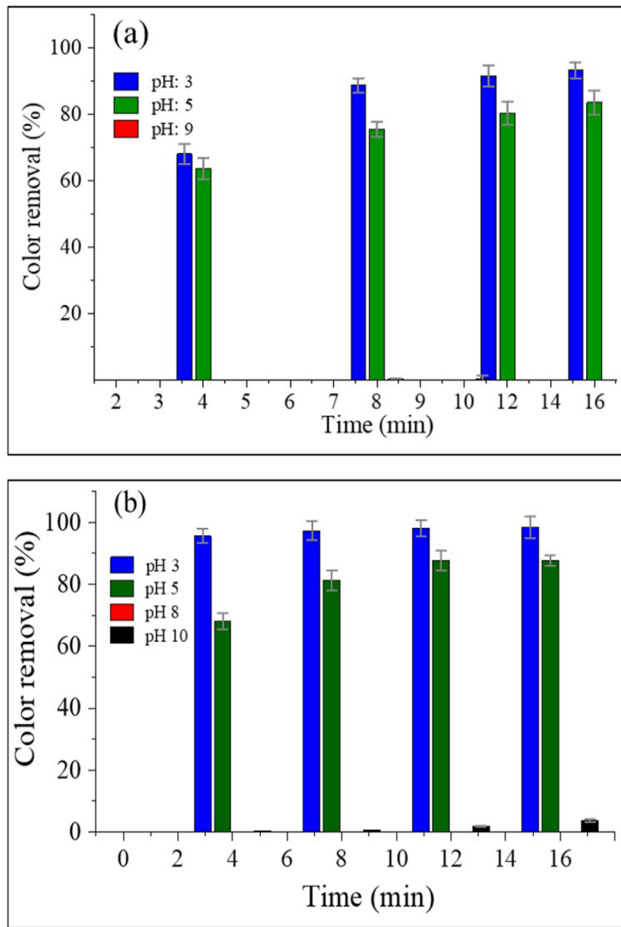
By comparison, the removal of reactive blue 19 dye at a titanium-based DSA anode investigated by Rajkumar and Kim (2006), resulted in a linear increase in the debasement of the dye rose at current densities range,  $7.22\text{--}36.10 \text{ mA cm}^{-2}$ , in the presence of NaCl.

The degradation of MR was also investigated, this time at current densities of 0.5, 0.1, 1.5, and  $2.0 \text{ mA cm}^{-2}$  and a pH of 3.0. We can see in Fig. 3b that the Methyl Red dye degradation is small at a low current density, as we increase the current density the removal of MR dye increases. 16 min of electrolysis at  $2 \text{ mA cm}^{-2}$  resulted in MR being oxidized up to 87%. The enhancement of degradation depends on the current density and subsequently on the generation of •OH radicals/OCl<sup>-</sup> ions. The optimum current density was determined to be  $2 \text{ mA cm}^{-2}$  to remove the most color for minimum cost. Similar tests were conducted for acid blue and basic brown dyes by Awad and Galwa (2005) using a Pb/PbO<sub>2</sub> electrode, and they found that after 30 min of electrolysis, almost a complete removal had been achieved in the presence of NaCl at  $30 \text{ mA cm}^{-2}$ .

#### The impact of different pH levels on BTB and MR deterioration

Methyl Red and Bromothymol Blue are both pH indicators that change color as we change the pH of the solution. The colors and lambda max of these indicators vary at different pH ranges. Therefore the concentration of BTB was measured at different wavelengths i.e. 430 nm for the acidic solution and 615 nm for the basic solution and for MR 515 nm and 425 nm were used to quantify the residual concentration in the treated solution. The acidity and basicity of both dye solutions were maintained constant during electrolysis by adding NaOH and HCl and putting the pH electrode in the electrochemical reactor. Figure 4 illustrates how pH affects (a) BTB and (b) MR's oxidative degradation. By adding NaOH or H<sub>2</sub>SO<sub>4</sub> the pH of the dye solution was adjusted from 3 to 10. In the case of BTB electrolyte also contained 0.1 M NaCl, and a  $10 \text{ mA cm}^{-2}$  current density was applied during electrolysis. With rising pH from 3 to 9 the removal of color diminished (Fig. 4a). At pH 3, the dye was degraded by >90% after 15 min. More alkaline solutions were less effective for dye removal as we can observe that degradation of BTB at pH 9 is negligible. Alves et al. (2010) attained 70% degradation of industrial dye. For MR dye removal four different pH was tested, i.e. 3, 5, 8, and 10, and Fig. 4 displays the findings from the 15-min examination of MR oxidation while maintaining constant current density and electrolyte content. Figure 4b shows that acidic condition (pH 3 and pH 5) is more favorable for dye removal, and up to 97% removal was achieved in just 8 min of electrolysis. However, pH 8 and 10 did not show any degradation. The data represent that the rate of color removal per cent



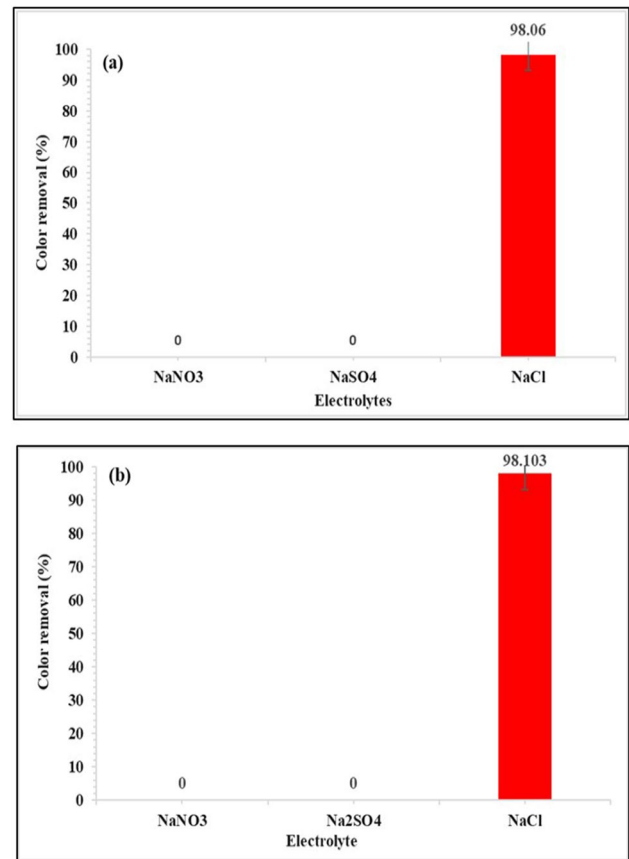


**Fig. 4** A plot of % degradation versus time of exposure at different pH values for **a** BTB and **b** MR dyes

increases as pH decreases, indicating that more acidic media are more favorable for MR oxidation. At acidic conditions, chlorine exists as a hypochlorous acid, with a higher oxidation potential (1.49 V) compared to hypochlorite (0.94 V) (Hussain et al. 2015). As a consequence, this led to high degradation of dye molecules.

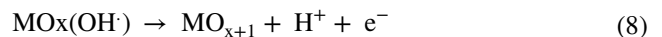
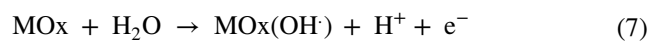
#### Effect of electrolytes on the oxidative degradation BTB and MR

Figure 5 shows the impact of different electrolytes on the oxidation of BTB, Fig. 5a, and MR, Fig. 5b. Using 200 ppm solutions of BTB at pH 3 and with a 10 mA cm<sup>-2</sup> current density, and MR solutions of 200 ppm at pH 3 and a 2 mA cm<sup>-2</sup> current density, degradation was only observed in NaCl solutions, and not NaNO<sub>3</sub> or Na<sub>2</sub>SO<sub>4</sub> containing solutions. In the presence of sulphate and nitrate, the oxidation process takes place directly on the electrode surface. The H<sub>2</sub>O molecule is simply electrolyzed in the direct anodic mechanism, and the OH radical physically adsorbs on the



**Fig. 5** Effect of various electrolytes on the oxidation of **a** BTB and **b** MR

anode surface as shown in the equation reported by Zhang et al. (2014) and is shown below. The metal oxide is designated as MO<sub>x</sub>, and the physisorbed hydroxyl radical generates the chemisorbed active oxygen (oxygen in the lattice, MO<sub>x+1</sub>).



MO<sub>x+1</sub> oxidizes the organic pollutants found in wastewater. However, we observed no evidence of this process taking place. Likely, the electrodes displayed poor electrocatalytic activity due to either the formation of an adherent film on the anode surface or the creation of stable intermediates that could not be directly oxidized in this conductive electrolyte (Ghalwa et al. 2013). Additionally, it was shown by Do and Yeh (1996) that the O<sub>2</sub> evolution was the primary anodic process due to the absence of chloride. The production of O<sub>2</sub>





does not help degrade the dyes, and negligible performance was observed in the  $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_3$  electrolytes. However, 87% of the color was removed by electrolysis using NaCl as the supporting electrolyte. This is due to the working anode surface's formation of chlorine and hypochlorite species, which ensures indirect oxidation. In indirect oxidation, chloride-containing wastewater transforms into electrically generated HOCl oxidant species on the anode surface.

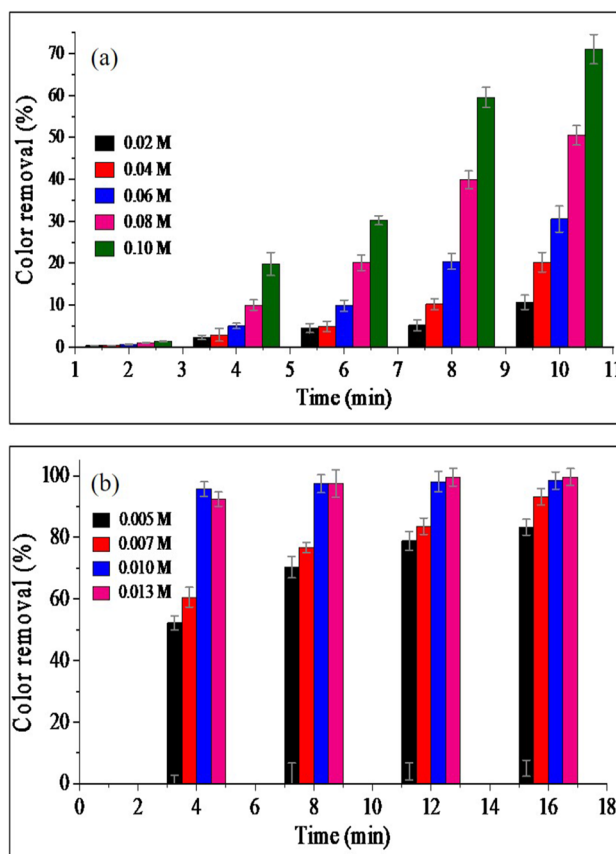
The discussion above has shown that NaCl was thought to be the best electrolyte because a degradation of almost 87% was accomplished in just 16 min. By contrast, in solutions of  $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_3$  no degradation was observed. Therefore, it was found that 0.1 M NaCl worked the best for BTB and MR electrochemical oxidation. Similarly, Miwa et al. (2006) described how, within 60 min of electrolysis, pesticides completely degrade in 0.1 M NaCl.

### Effect of NaCl concentrations on the degradation of BTB and MR

Based on the degradation performance of various electrolytes, NaCl exhibits a superior removal of dyes, therefore it is essential to investigate the influence of NaCl concentration on the electrochemical removal of dyes. The electrochemical oxidation of BTB dyes was investigated for 10 min at  $10 \text{ mA cm}^{-2}$  constant current density and with various concentrations of NaCl studied in this work (0.02–0.1 M NaCl), as depicted in Fig. 6a. It is clear from the figure that as the concentration of the electrolyte NaCl in the dye solution increases, its ability to remove color also increases. Indeed, ~70% of the degradation of the dye was achieved in 10 min for BTB at a concentration of 0.1 M of NaCl. Similarly, the MR degradation was also determined at 0.005–0.013 M NaCl at a constant current density of  $2 \text{ mA cm}^{-2}$ . The degradation of MR dye was fast as compared to BTB, and it was observed that increasing the NaCl concentration enhances the oxidation of MR dye, and only 8 min of electrolysis is required to completely remove the MR dye from the solution. This is due to the high rate of generation of  $\text{Cl}_2/\text{OCl}^-$  species at the anode, which ensures indirect oxidation. The higher concentration of NaCl results in an increased chlorine concentration at the anode surface causing greater degradation of the dyes<sup>26</sup>. The optimal concentration of NaCl in this work was 0.1 M.

### Energy consumption for the degradation

Electric energy plays a crucial role in all processes relying on electrical potential. The consumption of energy was deduced from the degradation data using Eq. (2), which demonstrates as electrical energy in  $\text{kW h m}^{-3}$  is required to degrade dye from waste solution. Figure 7 shows plots of the energy consumption (EC) versus current densities

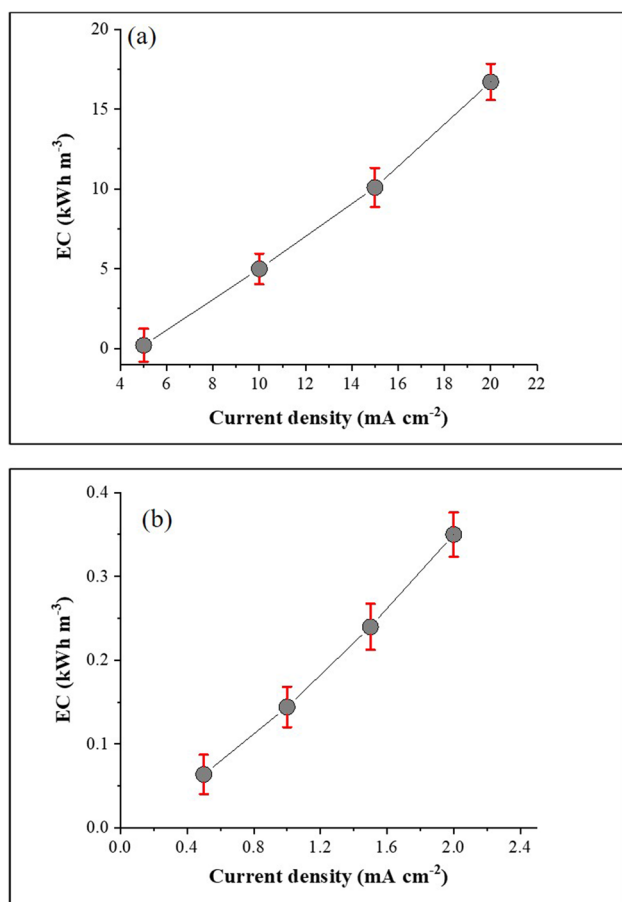


**Fig. 6** Influence of concentration of NaCl on the removal of **a** BTB **b** MR

for the electrochemical degradation of (a) BTB and (b) MR dyes from a 200 ppm solution each. EC increased from 0.2025 to  $16.704 \text{ kW h m}^{-3}$  as the current densities rose from 5 to  $20 \text{ mA cm}^{-2}$  for BTB (Fig. 7a) demonstrating that the energy expenditure at  $5 \text{ mA cm}^{-2}$  is much lower in comparison to  $20 \text{ mA cm}^{-2}$ . However, the dye degradation process becomes more rapid as the current densities increase. As a result, it can be shown that the calculated energy consumption was  $4.992 \text{ kW h m}^{-3}$  at  $10 \text{ mA cm}^{-2}$ .

The electrical energy required for the electrochemical degradation of MR dye at 200 ppm versus current densities is also shown in Fig. 7b. Similar to the BTB data, the degradation of the dye increased as the current density increased, and the energy cost rose from 0.0636 to  $0.349 \text{ kW h m}^{-3}$ . Compared to  $2 \text{ mA cm}^{-2}$ ,  $0.5 \text{ mA cm}^{-2}$  has a lower energy consumption but a slower rate of dye degradation is observed at  $0.5 \text{ mA cm}^{-2}$ . In the same way, Sartaj et al. (2020) reported that the Allura red dye had a minimum electrical energy consumption of  $0.196 \text{ kW h m}^{-3}$  and the erythrosine dye had a minimum electrical energy consumption of  $0.941 \text{ kW h m}^{-3}$  at a current density of  $5 \text{ mA cm}^{-2}$  at pH 5.0 and  $8 \text{ mA cm}^{-2}$  at pH 6.0, respectively.





**Fig. 7** A plot of EC versus current density for electrochemical degradation of **a** BTB and **b** MR each with 200 ppm concentration

## Conclusion

The results show that wastewater containing BTB and MR dyes can be successfully degraded by an indirect electrochemical oxidation method using a  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  composite anode under optimal conditions. The degradation was highly efficient in  $\text{NaCl}$  solutions, but not observed in  $\text{NaNO}_3$  or  $\text{Na}_2\text{SO}_4$  solutions. It has been shown that the rate of color loss increases as  $\text{NaCl}$  concentration increases, current density increases and solution pH decreases. When  $\text{NaCl}$  is used as the electrolyte, the  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  anode has a good capacity to produce chlorine species such as hypochlorite,  $\text{OCl}^-$  that have strong oxidative power, and which contribute to the removal of more than 90% of the dyes from wastewater while requiring little electricity. The electrochemical oxidation of organic pollutants is advantageous because of it is a low-cost, versatile, and environmentally benign method with excellent energy efficiency.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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