A comparative study for degradation of RB5 dye using Ti/Ir_{0.15}–Ru_{0.15}–Sn_{0.6}–Sb_{0.1} electrodes fabricated by employing two different thermal decomposition methods

B. D. Soni¹ · U. D. Patel² · A. Agrawal³ · J. P. Ruparelia¹

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Abstract

A comparison of electrochemical degradation efficiency of Ir- and Ru-based mixed metal oxide electrodes fabricated by two different methods, i.e. polymeric precursor thermal decomposition (PPTD) and standard thermal decomposition (STD), was carried out on Reactive Black 5 (RB5) dye. The electrolysis experiments were performed with 100 mg/L RB5 at initial pH 2, a current density 50 mA/cm², and 4 mg/L NaCl dosage. The results of the study were evaluated in terms of reduction in colour, COD, and TOC. The result showed higher RB5 degradation rate constants obtained on the PPTD electrode during kinetic study, compared to the STD electrode. A better performance of the PPTD electrode compared to the STD electrode may be attributed to its higher Sn content and its different morphologies observed in characterization using SEM with EDX analysis. Although proven efficient, the service life of PPTD-coated electrode was found only ~76 h, compared to ~895 h of STD-coated electrode. Experimental results demonstrated that coating method influenced the performance and service life of the electrodes. A comparison of the MTC, ICE, and energy consumption of the two electrodes prepared by STD and PPTD methods demonstrated that PPTD-coated electrodes were more efficient with a shorter life-span.

Keywords Mixed metal oxides · RB5 degradation · Service life · Mass transport coefficient · Kinetic rate constant

1 Introduction

It is estimated that one million tons of dyes are produced every year around the world, to which azo dyes contribute almost 70% by weight [1, 2]. Usually, wastewater containing dye and dye intermediates is generated due to production losses and processing losses [3]. The impacted streams containing substantial amount of dyes and intermediates have become a clear concern since these compounds softened do not undergo natural attenuation by biological, chemical and physical processes [4]. Thus, polluted

streams consisting of colour and higher chemical oxygen demand (COD)/biochemical oxygen demand (BOD) ratio can create environmental concern and pose challenge to scientists for development of suitable approaches and technologies for the treatment of such wastewater prior to disposal [2–4].

Technologies reported in the literature for either colour or COD removal from dye wastewater are microbial consortia treatment [5], photocatalytic degradation [6], composite nanofiltration [7–9], combined process of coagulation/flocculation and nanofiltration [10] and

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✉ J. P. Ruparelia, jr@nirmauni.ac.in | ¹Department of Chemical Engineering, Institute of Technology, Nirma University, Ahmedabad 382481, India. ²Department of Civil Engineering, Faculty of Technology and Engineering, M S University, Baroda 390001, India. ³Department of Earth and Environmental Sciences, Wright State University, Dayton, OH 45435, USA.

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electrochemical treatment [1, 2, 11]. An electrochemical treatment by electro-oxidation employing mixed metal oxide (MMO) electrodes or dimensionally stable anodes (DSA) has been proved to be a promising alternative for the treatment of various kinds of wastewater [2, 11].

The main advantage of the electro-oxidation or electrochemical oxidation (EO) process, i.e. complete oxidation without producing sludge, is due to its mechanism where anodic oxidation reactions are accompanied by transfer of oxygen from water to the reaction products. The electro-oxidation process can be further classified into two processes: direct oxidation, and indirect oxidation (reversible) and indirect oxidation (irreversible)

In indirect oxidation, pollutants oxidize due to exchange of electron, but not directly. They exchange through the mediation of some electro-active species regenerated in situ. In the present investigation, all the experiments are conducted in the presence of NaCl. Therefore, the description of mechanism followed by DSA via indirect mechanism is described in detail.

During electrolysis in the presence of NaCl, chlorine will be in the form of chloride ion in an aqueous solution. Chlorine produces due to surface reaction of electrochemical oxidation of chloride ions at the anode according to Eq. (1) to (7)

At cathode, water decomposes [3] according to Eq. (3).

Chlorine and water decomposition in the bulk solution will form hypochlorous acid and hypochlorite ion. In acidic medium, reaction (4) takes place generating hypochlorous acid

If pH is neutral or alkaline, a reversible reaction takes place

Dye is then decolourized and degraded according to Eq. (6) and (7).

A variety of materials and methods have been employed for the fabrication of DSAs as reported in the literature [3, 4, 12]. Among all the methods reported, two thermal

decomposition methods, particularly polymeric precursor thermal decomposition (PPTD) [13] and standard thermal decomposition (STD) [14], are the two economical options for DSA fabrication. The efficiency and service life of DSA may not only be attributed to coating material but also to unique morphology and active surface area of coating, which results from the variation in fabrication methods and composition [1, 13, 14]. In the literature, numerous works have been reported for fabrication of DSA. The studies carried out either for fabrication or application of DSA are majority related to single-, two-, or three-dimensional morphology. Moreover, proper combination of catalyst with dopant and stabilizer also leads to higher service life. Studies have reported that mixing of IrO_2 [14] or RuO_2 [15] with SnO_2 – Sb_2O_5 during electrode fabrication can potentially increase the service life of the coating and therefore the coated anode, which makes the electrochemical process cost-effective. However, the results of IrO_2 and RuO_2 together with SnO_2 – Sb_2O_5 on degradation efficiency and service life have not been rigorously studied yet. Moreover, the effects of electrode fabrication methods on efficiency and service life have not been compared. The electrode's performance is simply reflection of the catalyst's activity, and it is to be estimated by chlorine evolution capacity or oxygen evolution capacity of individual metal catalyst. Chlorine evolution by electrode enhances degradation of dye via indirect oxidation [1, 2, 6] and proportion of Sb (dopant)/Ru (catalyst)/Sn (stabilizer/dispersing agent) :: 10:30:60 mol ratio which proved much higher current efficiencies for chlorine evolution [11]. Further, the literature also suggested different metals such as Ni, Co, Cu, Pt, Ir, Ta, Zr, Ru, Pb, La, and Ce as catalyst [3, 4, 12]; however, electrode with two best catalysts such as Ir and Ru with Sn and Sb is not rigorously tested.

Therefore, in this research the main objective was to fabricate $\text{Ti}/\text{Ir}_{0.15}\text{--}\text{Ru}_{0.15}\text{--}\text{Sn}_{0.6}\text{--}\text{Sb}_{0.1}$ electrode employing two different protocols, namely PPTD and STD. The novelty of the work is not only to fabricate an electrode with two different methods. The prime motive was to improve activity and efficiency of an electrode by introducing two catalyst metals along with appropriate stabilizer, dispersing agent and dopant as Sn and Sb, respectively. An improvement in pollutant degradation efficiency and electrode service life ultimately provides cost-effective effluent treatment employing EO process

In this type of electrode, Ir and Ru both act as catalysts with equal proportion keeping catalysts' proportion constant, i.e. 15 (Ir) + 15 (Ru) = 30 mol ratio. The fabricated electrodes are then applied for treatment of synthetic wastewater containing 100 mg/L Reactive Black 5 (RB5) dye as representative organic pollutant. The performance of the electrodes prepared by the two methods was compared for the reduction in colour, COD and total organic

carbon (TOC) during electro-oxidation of RB5 dye employing electrochemical treatment. In relation to measured parameters, the differences in instantaneous current efficiency (ICE), energy consumption, and service life of the electrodes prepared by the two methods were also evaluated. All the parameters were measured three times during the experiment, and their average values were considered for calculation. Further, the performance of electrodes was evaluated based on their surface morphology, surface structure, and surface composition and electrochemical activity.

2 Materials and methods

2.1 Electrode preparation

Mixed metal oxide-coated Ti/IrO₂-RuO₂-SnO₂-Sb₂O₅ electrodes were indigenously prepared using titanium substrate (99.9% pure, Grade-2, Steel Emporium, Mumbai) of similar size 75 mm × 50 mm × 3 mm (active area: 50 mm × 50 mm). The Ti substrates were further coated with mixed metal oxides having nominal molar ratio of Ir/Ru/Sn/Sb were 15:15:60:10 for total metal moles of 0.005 M. The complete procedure for preparation of electrodes is represented schematically in Fig. S1- Supplementary document, and detailed write-up for STD and PPTD methods is reported elsewhere [16].

2.2 Experimental procedure and set-up

Electro-oxidation experiments using batch reactor were performed on 500 mL synthetic wastewater prepared using tap water containing 100 mg/L RB5 ($\lambda_{\max}$ -597, Gayatri Colour Chemical, Ahmadabad). It is reported in the literature that NaCl performs better as an electrolyte compared to KBr and Na₂SO₄ [4]; therefore, in this study 4 g/L NaCl a supporting electrolyte (NICE, LR grade) was added to the synthetic wastewater and initial pH was adjusted 2-2.2 using appropriate amount of 1 M H₂SO₄ solution (Fig. S2) [14]. Indigenously prepared electrodes Ti/IrO₂-RuO₂-SnO₂-Sb₂O₅ by both methods were used as anodes in electrochemical oxidation process and stainless steel (SS-304) as cathodes in each experiment. The distance between working anode and cathode in the cell was kept at 8 mm [16]. Anode and cathode were connected to a DC power supply (LD-3205, Aplab India) for controlling the constant current density of 50 mA/cm². The batch reactor was equipped with stirring apparatus for homogeneous mixing at 150 rpm at room temperature (~ 35 °C), and all reaction parameters were chosen based on exhaustive literature search (Tables S1, S2, and S3). The samples were collected from batch reactor at appropriate

time intervals up to 2 h for COD and colour and up to 1 h for TOC analysis. The COD in the samples withdrawn from the reactors was analysed by standard closed reflux method [17] (Hach DRB200, COD reactor, USA), whereas colour was determined using UV-Visible spectrophotometer (UV-1800, Shimadzu, Japan) at wavelength range of 200-800 nm. Similarly, TOC in the samples before and after 1-hr electrolysis was determined using TOC Analyzer (TOC-Vcsh, Shimadzu, Japan). Fig. S2 depicts the effects of pH on (■) colour and (▨) COD reduction during electro-oxidation of synthetic wastewater containing 100 mg/L RB5 in batch reactor.

2.3 Electrode characterization

The electrodes were characterized using scanning electron microscopy (SEM)/energy-dispersive X-ray (EDX) (LEOs-440i, with Oxford Energy Dispersive X-Ray Analyzer 7060, Cambridge, England) and X-ray diffraction (XRD) (3000PTS, Seifert, Germany) techniques to acquire data related to surface morphology, composition of the thin oxide film, and coating microstructure, respectively. Cyclic voltammetry (CV) was performed on the electrodes with GAMRY Reference-600 potentiostat/galvanostat (USA).

2.4 Accelerated life test

It is reported that DSA can serve for many years under low current density in aqueous solutions. However, to reduce the testing time from years to hours, accelerated conditions are considered as the best option [15, 18, 19] for assessing the service life of electrodes. In this work, the life test of fabricated electrodes prepared by STD and PPTD methods was performed using two electrode cell systems connected to DC power supply. In this study, indigenously prepared electrodes were used as working electrodes, whereas readily available standard platinum electrode was used as counter electrode. The tests were performed at 400 mA/cm² constant current density in 0.5 M H₂SO₄ electrolyte. The cell potential with respect to time was monitored manually until it rose by 2 V with respect to the initial overall cell voltage, which is indicative of electrode deactivation [14].

2.5 Characterization of wastewater containing 100 mg/L RB5

In order to compare the degradation efficiency of indigenously prepared electrodes by two different methods, the study measured the reduction in COD, colour, and TOC with respect to time. For evaluation of colour reduction, the UV-Vis absorbance spectrum was recorded for the initial and treated wastewater samples containing RB5 dye

at 597 nm. The efficiencies for the removal of colour, COD, and TOC were calculated according to Eqs. (8) (9), and (10), respectively

$$\% \text{ Decolourization} = \frac{ABS_0 - ABS}{ABS_0} \times 100 \quad (8)$$

$$\% \text{ COD removal} = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (9)$$

$$\% \text{ TOC removal} = \frac{TOC_i - TOC_f}{TOC_i} \times 100 \quad (10)$$

The ICE, which represents the oxidation ability of the anode material, and E , the energy required for oxidation process at the operating condition were calculated using Eqs. (11), and (12), respectively.

$$ICE = \frac{[COD_t - COD_{t+\Delta t}]FV}{8/\Delta t} \quad (11)$$

$$E = \frac{UI\Delta t}{(COD_t - COD_{t+\Delta t})V} \quad (12)$$

All notations in Eqs. 8–12 have conventional meaning and reported elsewhere [2].

3 Results and discussion

3.1 Characterization of mixed metal oxide-coated electrodes

3.1.1 X-ray diffraction analysis

XRD characterization was used to identify the formation of metal oxides and their phases. The typical XRD patterns of $\text{IrO}_2\text{-RuO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$ thin film coated on titanium substrate prepared by STD and PPTD methods are presented in Figs. 1a, and 1b, respectively. The narrow shape of the peaks in Figs. 1a and 1b should indicate that the mixed oxide thin films prepared by STD as well as PPTD have good crystallinity. The diffraction peaks for IrO_2 , RuO_2 , Ti, and SnO_2 were clearly detected. Meanwhile, the peaks for Sb_2O_5 were difficult to find on XRD spectra; the reason for not finding Sb_2O_5 peaks is due to its similarity of lattice structure with SnO_2 , [20].

3.1.2 Surface composition analysis (EDX)

A quantitative chemical analysis of the thin film coated on the fabricated electrodes by PPTD and STD methods was accomplished through EDX analysis, and their results

Fig. 1 X-ray diffraction pattern for $\text{Ti/IrO}_2\text{-RuO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$ electrodes prepared by **a** STD and **b** PPTD methods, PCPDFWIN reference files for (triangle) SnO_2 (88–287), (diamond) IrO_2 (15–870), (circle) Ti (44–1294), (asterisk) RuO_2 (65–2824)

are summarized in Table 1, which shows the nominal and actual percentages of different elements. The representative results exhibit the composition of only the external part of the oxide layer, while the composition of the inner layers may be slightly different. However, the results in Table 1 may be taken as representative of the global composition of the oxide layer [21]. Table 1 indicates that after 15–16 cycles of film deposition, the overall metal oxide loading on the electrode plates was $\sim 1.5 \text{ mg/cm}^2$, even though Ti present in the substrate underneath ranged from 35 to 50% for both methods in EDX microanalyses. Montilla et al. [21] studied the relation between the amounts of titanium detected versus the number of successive deposition on electrodes and reported that a good surface coverage of the layer may be achieved only after ~ 20 deposition. In addition, Montilla et al. [21] suggested that if the number of depositions is < 20 , then Ti underneath the oxide layer may become detectable since the depth of EDX analysis is around $1 \mu\text{m}$; the authors argued that film thickness can be more than sampling depth by EDX if number of deposition is > 20 , but Ti may still be detected indicating detachment of deposited layer from substrate. Thus, in order to avoid detachment of the deposited layer and avoid exposure of Ti substrate, the deposition was completed by repeating 15–16 times. Therefore, it is speculated that Ti detected in this study may not be due to exposure of Ti metal, but may be due to the lesser thickness of the layer than the sampling depth of EDX.

The results of EDX analysis provided in Table 1 further indicate that the amount of Sn in the film coating is greater by the PPTD method than in the film by STD method, although the PPTD coating protocol follows a higher

Table 1 Surface composition of coated film by EDX analysis

Electrode	Ir (15%)	Ru (15%)	Sn (60%)	Sb (10%)	Ti substrate (0%)	Others (S, Si, Cl, Fe, Al) (0%)
Ti/IrO ₂ -RuO ₂ -SnO ₂ -Sb ₂ O ₅ (PPTD)	7.16	8.05	31.17	5.35	48.27	Not detected
Ti/IrO ₂ -RuO ₂ -SnO ₂ -Sb ₂ O ₅ (STD)	22.32	23.38	7.21	11.15	35.94	Not detected

Number in brackets shows nominal composition, while tabulated values are actual compositions of respective components in fabricated electrode

temperature than the STD protocol. The loss of Sn metal in from the film deposited by PPTD method is prevented due to polymeric reaction of citric acid and ethylene glycol, in which Sn atom can be fixed within the polyester chain formed during the resin preparation (Eq. 13) and thus prevent Sn loss during thermal decomposition [13, 22].

Therefore, the actual ratio of %Ir/%Sn is close to nominal value (0.25) in the PPTD method, whereas for STD method, the per cent loss value is much higher. Table 1 further shows that atomic% of all metals were not close to nominal values. A similar variation of the atomic percentages between measured versus nominal values has been reported by Forti et al. [23] and Profeti et al. [22], which could be due to the EDX results inclusive of Ti content, thus causing ambiguities in calculation of atomic percentages of metals, and thus its comparison with the nominal value on Ti-free base. However, similar observations have not been reported in recent studies. For Ti-free base, the observed atomic percentage is recalculated assuming the sum of Ru, Sn, Sb, and Ir metal percentage as 100% (Table 2), where the values may be closer to the nominal values. However, this issue was observed only when results of PPTD methods are examined, while the large variations between the measured and the nominal atomic percentage values in results from electrode by the STD method may be attributed mainly to losses of Sn from the oxide.

To predict the product formula, Table 2 and Fig. 1 are considered. From Fig. 1, it is concluded that the diffraction peaks for IrO₂, RuO₂, and SnO₂ were clearly detected. Table 2 data show that Ir/Ru/Sn/Sb :: 15:15:60:10 are actually 13.84:15.56:60.25:10.34 and

34.84:36.49:11.26:17.40 in PPTD and STD method, respectively. Therefore, the chemical formula of the final product Ti/Ir_{0.15}-Ru_{0.15}-Sn_{0.6}-Sb_{0.1} is fabricated finally with chemical formula Ti/Ir_{0.1384}-Ru_{0.1556}-Sn_{0.6025}-Sb_{0.1034} (PPTD) and Ti/Ir_{0.3484}-Ru_{0.3649}-Sn_{0.1126}-Sb_{0.1740} (STD).

3.1.3 SEM analysis

SEM was used to characterize the surface morphology of thin layer of IrO₂-RuO₂-SnO₂-Sb₂O₅ mixture coated on titanium substrate prepared by two different protocols, STD and PPTD. The presentative micrographs of the layer by the STD method at different magnifications, presented in Fig. 2a, c, revealed a typical dried mud-cracks and rough layer of mixed metal oxides with agglomerates seen distributed along ridges. This grain type of structure and depth of the layer increases from Ni, Ir, Ta, and Pt and gives higher surface area of the electrode. In comparison, the micrographs of the layer by the PPTD method at different magnifications, presented in Fig. 2b, d, revealed the presence of continuous flat layer consisting of small amounts of agglomerates distributed on the surface. It is observed that introduction of Ir made the surface smooth by decreasing plate-type structure. The difference in surface morphology of the electrodes prepared by STD and PPTD methods is evident in Fig. 2. It has been reported previously [23] that the cracked-mud aspect disappears and a more agglomerated surface is observed as Sn content increases in the coating mixture. The similar observation is made in this study (Fig. 2b, d) for PPTD coating with higher Sn content showing smooth agglomerated surface without cracked-mud structure.

Table 2 Surface composition of coated film by EDX analysis without considering Ti

Electrode	Type of coating	Sum of metals Ru, Sn, Sb, Ir	Ir (15%)	Ru (15%)	Sn (60%)	Sb (10%)
Ti/IrO ₂ -RuO ₂ -Sb ₂ O ₅ -SnO ₂	PPTD	51.73	(Ir) 13.84	15.56	60.25	10.34
Ti/IrO ₂ -RuO ₂ -Sb ₂ O ₅ -SnO ₂	STD	64.06	(Ir) 34.84	36.49	11.26	17.40

Fig. 2 Scanning electron micrographs of $\text{Ti/IrO}_2\text{--RuO}_2\text{--SnO}_2\text{--Sb}_2\text{O}_5$ electrodes prepared by **a** STD, **b** PPTD method, magnification 10.0 Kx and **c** STD, **d** PPTD method, magnification, 25.0 Kx

3.1.4 Accelerated life test

The service life of both the electrode types was measured as per the protocol. Fig. S3 shows the life of $\text{Ti/IrO}_2\text{--RuO}_2\text{--SnO}_2\text{--Sb}_2\text{O}_5$ electrodes fabricated by the PPTD and STD methods found to be 76 h and 895 h, respectively. A similar result of service life was reported by Forti et al. [23] for $\text{Ti/Ru}_{0.3}\text{Ti}_{(0.7-x)}\text{Sn}_x\text{O}_2$ electrode prepared by polymeric precursor, which was around 80 h. In the present study, the activity of an electrode prepared by PPTD method for electro-oxidation of RB5 was similar to that of STD method, but certain differences with respect to electrode characteristics were observed after the test. The differences in the electrodes prepared by STD and PPTD methods can be explained in terms of their surface properties. In particular, a cracked-mud-type morphology was notable for STD electrode, while a most flat morphology with particles was observed for the PPTD electrodes. It has

been reported previously that a cracked mud structure can prevent Ti substrate to come into contact with corrosive medium for longer time and thus service life of DSA can be improved [24]. In this study, a shorter service life was obtained with the PPTD electrode in comparison to the STD electrode, which may be attributed to higher Sn molar percentage compared to that of Ir, Ru, and Sb. A previous study demonstrated that electrode coated only with mixture of Sn and Sb [14] showed a much shorter activity (only 12 h) under anodic polarization, while incorporation of Ir or Ru increased the service life of the electrode significantly. Therefore, the increase in service life may be attributed to proper mixture of Sn and Sb with other metals such as Ru and Ir [22–24]. Further, in the case of electrode coated with STD method, the composition of Ru and Ir is greater compared to Sn and Sb, which may be responsible for long life of the STD electrode. A larger Ir and Ru metal content in the STD electrode may increase the crystalline

nature of the coating and therefore enhance its stability and service life [14]. Another possible reason for the observed differences in electrode behaviour may be due to improper adhesion of the polymeric coating on titanium substrate, which may have reduced the stability of the electrode prepared by PPTD method.

3.1.5 Cyclic voltammetry test

The confirmation of the redox transformation of RB5 dye on the electrode surface by CV has been reported elsewhere [16]. Cyclic voltammograms of Ti/IrO₂-RuO₂-Sb₂O₅-SnO₂ electrodes prepared by PPTD and STD methods are shown in Fig. 3(1), (2) in 0.5 M H₂SO₄ and RB5 solutions, respectively. In STD as well as in PPTD electrodes, no catalytic activity was observed for either electrode in 0.5 M H₂SO₄ solution; see Fig. 3(1). Only oxygen evolution points were found at 1.044 V and 0.988 V for PPTD and STD electrodes, respectively, expressing high oxygen potential of PPTD electrode compared to STD electrode.

Additionally, no oxidation or reduction of Ir or Ru metal peaks was observed in cyclic voltammograms(a) of the electrode coated with PPTD in RB5 solution (Fig. 3(2)), but the peaks related to chlorine reduction and hydrogen desorption were observed between the range of 0.5 to 0.7 V and -0.5 to -0.7 V, respectively [25]. The peaks shown in voltammograms (b) in Fig. 3(2) between 0.6 and 0.8 V have been attributed to the Ir(III)/Ir(IV) [19–21] transition, but there are no peaks for higher transition of Ir and Ru. In this reference, peaks corresponding to chlorine reduction and hydrogen desorption [26] were identified between 0.8 to 0.1 V and -0.5 to -0.7 V, respectively.

3.2 Decolourization of wastewater containing RB5 dye

Decolourization of wastewater containing RB5 is presented in Fig. 4 as a plot C_t/C_0 versus time. For the calculation of C_t/C_0 , UV-Vis spectra recorded (Fig. S4)

Fig. 4 C_t/C_0 versus time using Ti/IrO₂-RuO₂-SnO₂-Sb₂O₅ electrodes prepared by (diamond) STD and (square) PPTD methods at initial pH 2, current density 50 mA/cm in presence of 4 g/L NaCl

and calibration curve for different concentrations of RB5 dye ($\lambda_{\max} = 597$ nm) were used. As electro-oxidation progressed, the decolourization of 100 mg/L RB5 took place as depicted in Fig. 4 using electrodes prepared by PPTD and STD methods, respectively, within 10 min. For both the electrodes, the rate of decolourization was found almost similar. The decolourization is due to the absorption band disappeared at 597 nm after 10 min of oxidation with either electrode indicating 99.9% colour reduction at initial pH 2–2.2. It has been reported that in the presence of chloride ions, the oxidation of azo dyes takes effect mainly through the generation of ‘active chlorine’ due to indirect oxidation, although the direct anodic oxidation also occurs to some extent [2, 3, 27]. In the present work, the decolourization experiment began at acidic condition (initial pH 2–2.2), but during the electrolysis the pH rose from acidic to alkaline condition (Fig. S5) which is likely due to hydroxyl ion generated from water reduction on the cathode. Simultaneously, proton generation from water oxidation can coexist on the anode due to oxidation of the organic compound. However, as a consequence of the competing reaction, the proton generation rate is lower than that of hydroxyl anions. Overall, the generation

Fig. 3 Cyclic voltammograms of Ti/IrO₂-RuO₂-Sb₂O₅-SnO₂ electrodes coated by **a** PPTD **b** and STD method (1) in 0.5 M H₂SO₄ (2) and RB5 solution at 50 mV/s sweep (scan) rate

of protons only partially compensates for the cathodic hydroxyl ion generation that results into pH increase [3, 4, 27–29]. Further, an increase in solution pH was observed as electrolysis time increased (Fig. S4). The rate of decolourization of RB5 can be explained by taking into account the pH changes. Within 10 min after experiment began, the initial pH increased from ~2 to 8.5 and then stabilized. It has been suggested that change in pH may have a direct relationship with chlorine production [3, 29]. At acidic pH, chlorine is in the form of a hypochlorous acid (HClO) while at high pH it is converted into chlorate (ClO_3^-) and perchlorate (ClO_4^-). The hypochlorous acid/chlorine is the powerful oxidizing agent [28, 29]. It is well known that $-\text{N}=\text{N}-$ bonding is imparting colour in dye solution. Due to the production of hypochlorous acid/chlorine, oxidation of RB5 breaks the $-\text{N}=\text{N}-$ azo bonds, and decolourization can take place at lower pH. Therefore, in acidic condition, colour reduction is much faster than in alkaline condition while COD reduction is faster in slightly alkaline condition [3].

3.3 Effects of electrode preparation methods on COD reduction

The performance of the electrodes during RB5 degradation was measured in terms of %COD and %TOC reduction that were calculated using Eqs. (8) and (9), respectively. Initial COD and TOC of RB5 solution were 96 and 31 mg/L, respectively. Figure 5 shows COD reduction due to electro-oxidation of 100 mg/L RB5 synthetic wastewater using Ir-Ru containing mixed metal oxide electrodes prepared by both methods. Nominal difference was observed in COD reduction obtained by both electrodes for electro-oxidation of RB5 during 2 h of treatment. Apparently, iridium is a good catalyst for chlorine evolution as well as responsible for longer service life [14]. This study shows

Fig. 5 COD reduction (%) versus time using $\text{Ti}/\text{IrO}_2\text{--RuO}_2\text{--SnO}_2\text{--Sb}_2\text{O}_5$ electrodes prepared by (diamond) STD, (square) PPTD methods at initial pH 2, current density $50 \text{ mA}/\text{cm}^2$ in the presence of $4 \text{ g}/\text{L}$ NaCl

79% and 76% COD reduction from electro-oxidation of RB5 using $\text{Ti}/\text{IrO}_2\text{--RuO}_2\text{--SnO}_2\text{--Sb}_2\text{O}_5$ electrodes by PPTD and STD methods, respectively, within 1 h of treatment; however, no further COD reduction was observed thereafter up to 2 h (Fig. 5). A complete colour reduction was achievable by both electrodes but COD removal was observed up to a certain level, which is evident from UV-Vis spectra (Fig. S4), indicating that the electrodes were not capable of a complete destruction of the dye molecules. Further, it appears that the reaction intermediates that may have formed during the experiment were resistant to oxidative chlorine/hypochlorite attack [29]. The two common intermediates of RB5 breakdown, vinyl sulphone ($\lambda_{\text{max}} = 265 \text{ nm}$), and H-acid ($\lambda_{\text{max}} = 236 \text{ nm}$) were apparent not present in the experiment, as indicated by a different λ_{max} of the liquid containing degraded RB5 at the end of electro-oxidation. This confirms that the presence of the absorbance peak in the treated dye in the UV region is not from vinyl sulphone or H-acid formation but may be due to the formation of other by-products, such as carboxylic acid or other complex organic compounds [3, 4]. The COD reduction during RB5 degradation using the electrode by PPTD method is slightly higher than by STD method, which can be explained due to a higher Sn content in metal oxide coating. A higher SnO_2 content, due to the polymeric chain structure, can improve the performance of DSA-type electrodes resulting in an enhancement of electro-oxidation activity [23] and thus increase the overall electrode efficiency. The comparisons of obtained results for COD reduction with similar electrochemical systems found in the literature are presented in Table 3 (Table S1–S3). Result shows that compared to various electrodes used for COD reduction; the present study proved better.

3.4 Estimation of mass transport coefficient based on colour and COD reduction

Estimation of the mass transport coefficient during RB5 electro-oxidation in this experiment is considered important because the rate limiting step can be either under kinetic control or mass transport control, based on which the size of the reactor can be estimated [30]. For decolourization of RB5 using various electrodes, the mass transport coefficients (k_L) can be estimated under the conditions without pH control, according to Eq. (14) [29].

$$k_m = k_L = \frac{2.3 \log(C_0/C_t)V}{tA} \quad (14)$$

where all notations used have conventional meaning and they have been reported elsewhere [29].

Similar to Eq. (14), a relationship between the dye concentration (C_t) and the mass transport coefficient (k_m) can

Table 3 Comparison of COD reduction with similar electrochemical systems found in the literature

Sr. No	Electrochemical system	Treated component	COD reduction (%)	References
1	Ti/IrO ₂ -RuO ₂ -SnO ₂ -Sb ₂ O ₅ (PPTD)	RB5	79	Present study
2	Ti/IrO ₂ -RuO ₂ -SnO ₂ -Sb ₂ O ₅ (STD)	RB5	76	Present study
3	Commercially available DSA	RB5	73.5	[26]
4	Ti/RuO ₂	RB5	74	[27]
5	Diamond, aluminium, copper and iron-zinc alloy	RB5	65–67	[28]
6	Ti-Ta-Pt-Ir	RB5	90	[29]

be derived for degradation of RB5 assuming: (1) all components in the mixture are degraded at the same time, (2) the combustion of the compounds to CO₂ is rapid and significant, and (3) no intermediates are formed [12].

In relation to the kinetic model for BDD [31] based on the value of the COD [32, 33] under electrolysis regime, the limiting current density for electrochemical mineralization of organic compound can be estimated using Eq. (15) below:

$$i_{\text{lim}} = nFk_m C \quad (15)$$

All notations used in Eq. 15 have conventional meaning and reported elsewhere [32].

For a complete electrochemical mineralization of model pollutant, RB5, the number of electron (n) removed can be shown as the half-reaction in Eq. (16) [33].

For RB5, $n = 152$

For a chemical mineralization of RB5, the reaction can be expressed as Eq. 17 [4]:

The RB5 concentration, C (mol/m³), during electrolytic process is related to COD (mol O₂/m³) by the following relation.

$$C = \frac{4}{152} \text{COD} \quad (18)$$

Therefore, for electrochemical mineralization and from Eqs. (15–18):

$$\text{ICE} = \frac{i_{\text{lim}(t=t)}}{i_{\text{app}}} \quad (19)$$

where i_{lim} is limiting current density at time, t (min), and i_{app} is the applied current density in A/m².

But for RB5 (from Eqs. 15–18),

Fig. 6 Evaluation of ICE on Ti/IrO₂-RuO₂-SnO₂-Sb₂O₅ electrodes prepared by (triangle) STD and (diamond) PPTD methods at initial pH 2, current density 50 mA/cm², 4 g/L NaCl

$$i_{\text{lim}} = 152Fk_m C_{(t=t)} \quad (20)$$

And at $t = 0$.

$$i_{\text{lim}(t=0)} = 152Fk_m C_{(t=0)} \quad (21)$$

A characteristic parameter, α , of the electrolysis process can be defined in Eqs. (22, 23) [2].

$$\alpha = \frac{i_{\text{app}}}{i_{\text{lim}(t=0)}} \quad (22)$$

From Eqs. (12) and (15),

$$\text{ICE} = \frac{C_{(t=t)}}{\alpha C_{(t=0)}} \quad (23)$$

In Eq. (23), if $\alpha > 1$, the electro-oxidation will be under mass transport control, but if $\alpha < 1$, the electro-oxidation

process will be under current/kinetic control. According to Fig. 6, ICE values decrease exponentially, indicating RB5 oxidation under mass transport control [34].

Now colour reduction rate can (r) be expressed as,

$$r = -\frac{d(C)}{dt} = k(C)^a(Cl_2)^b \quad (24)$$

In Eq. (24), a and b are order of reaction with respect to concentrations of pollutant (C) and chlorine (Cl_2), while (k) represents the kinetics(rate constant) of reaction.

Apparent rate constant (k_{app}) for mass transport control in indirect oxidation can be written as [34],

$$-\frac{d(C)}{dt} = k_{app}(C)(t) = \frac{Ak_m}{V}C(t) \quad (25)$$

Integrating Eq. (25) gives,

$$\ln \frac{C_{(t=0)}}{C_{(t=t)}} = \frac{Ak_m}{V}t \quad \text{or} \quad \ln \frac{COD_{(0)}}{COD_{(t)}} = \frac{Ak_m}{V}t \quad (26)$$

Comparing Eq. (25 and 26)

$$k_{app} = \frac{k_m A}{V}t \quad (27)$$

As linear relation exists between absorbance and concentration, Eq. (26) can be modified to obtain Eq. (14). The k_m can be obtained either using Eq. (14) or from k_{app} , i.e. Equations (26) and (27) acquired from the slopes of plots $\ln C_{(t=0)}/C_{(t=t)}$ and $\ln COD_0/COD_t$ versus time for electrodes (Fig. 7). In the present study, the mass transport coefficient calculated as per Eq. (26) is shown in Table 4. The results indicate that there is no difference in mass transport coefficient obtained by the two electrodes for colour reduction. This indicates that both electrodes are equally efficient for complete decolourization of RB5-containing wastewater. For COD reduction, however, the mass transport coefficient of the electrode prepared by PPTD method is slightly higher than that by STD method [35], which may be attributed to differences in surface morphology.

3.5 Effects of electrodes on TOC reduction

Mineralization of RB5 can be written according to Eq. (16), and based on the TOC results, the mineralization efficiency can be estimated by Eq. (28) [34].

$$MCE = \frac{\Delta TOC_{exp}}{\Delta TOC_{theor}} \times 100\% \quad (28)$$

Fig. 7 Evaluation of kinetic rate constants based on **a** $\ln [COD_0/COD_t]$ versus time and **b** $\ln [C_0/C_t]$ versus time for Ti/IrO₂-RuO₂-SnO₂-Sb₂O₅ electrodes prepared by (circle) STD and (square) PPTD methods at initial pH 2 and current density 50 mA/cm² in the presence of 4 g/L NaCl

Table 4 Mass transfer coefficient of Ir-based mixed metal oxide-coated electrodes for colour and COD reduction and kinetic rate constants measured for electro-oxidation of RB5

Electrode	Preparation method	Colour removal efficiency (%)	Mass transfer coefficient for colour removal (cm/s)	Mass transfer coefficient for COD removal (cm/s)	Rate constant (k_{app}) for colour removal (min ⁻¹)	Rate constant (k_{app}) for COD removal (min ⁻¹)
Ti/IrO ₂ -RuO ₂ -SnO ₂ -Sb ₂ O ₅	PPTD	99	0.2266	0.0087	0.762	0.0268
Ti/IrO ₂ -RuO ₂ -SnO ₂ -Sb ₂ O ₅	STD	99	0.2264	0.0083	0.729	0.0251

where $\Delta(\text{TOC})_{\text{exp}}$ is the experimental value for TOC removal at time t and $\Delta(\text{TOC})_{\text{theor}}$ is theoretically calculated value of TOC removal, and can be calculated using Eq. (29) [34].

$$\Delta\text{TOC}_{\text{theor}} = \frac{(I \times t) / (n_e \times F) \times n_c \times M \times 10^3}{V} \text{ mg/L} \quad (29)$$

where I is current intensity (A), t is electrolysis time (s), F is Faraday constant, which is 96,485 C/mol, while in Eq. (17), n_e is electron transfer number, n_c is carbon number of the organic compound, M is carbon atomic weight, $M = 12$ g/mol, and V is volume of the sample solution (L). For RB5, n_e and n_c are 152 and 26, respectively (Eq. 15), and MCE, i.e. mineralization current efficiency, was calculated for both electrodes considering the duration of electrolysis to be 60 min. Table 5 (Table S4) shows $\Delta\text{TOC}_{\text{theor}}$ (mg/L) calculated according to Eq. (29), $\Delta\text{TOC}_{\text{exp}}$ (mg/L) (difference between Initial TOC and TOC after one hour of electrolysis), %TOC_{exp} reduction after 1 h electrolysis based on Eq. (10) and MCE according to Eq. (28).

Results indicate that the percentage TOC reduction of RB5 was higher on Ti/IrO₂-RuO₂-SnO₂-Sb₂O₅ electrode fabricated by PPTD method, i.e. 75% and 69%, for PPTD and STD, respectively, and mineralization current efficiency was less than 20% for both PPTD and STD. This result supports that a complete mineralization of RB5 did not occur on either electrode. Similar results for MCE was reported by Brillas et al. [36] for the removal of following herbicides: 4-chlorophenoxyacetic acid (4-CPA), 4-chloro-2-methylphenoxyacetic acid (MCPA), 2, 4-dichlorophenoxyacetic acid (2,4-D), and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), in aqueous medium at pH 3.0 by anodic oxidation using BDD electrode, where MCE was between 4.5 and 18.

Salazar et al. [33] reported the mineralization efficiency of 250 mg/L RB5 to be 74% and 94% by electro-Fenton and photoelectron-Fenton methods, respectively, after 70 min of operation. This indicates that a greater mineralization may be achieved by the advanced oxidation process versus electro-oxidation process; a higher efficiency by advanced oxidation could have been due to additional utilization of chemicals and UV light.

3.6 ICE and Energy consumption

The instantaneous current efficiency (ICE) and energy consumption were calculated according to Eqs. (10) and (11). Figure 6 shows the change in ICE with reaction time during electrochemical treatment using both types of electrodes. The ICE values for Ti/IrO₂-RuO₂-SnO₂-Sb₂O₅ electrode prepared by PPTD are slightly higher than that for the electrode prepared by STD method. Figure 6 also shows that ICE values for both electrodes are initially higher (~0.5) but they declined exponentially to less than 0.1 in about an hour, which indicates that the maximum COD reduction occurred during first 10 min of electrolysis with electrode [37].

The energy consumption, calculated based on Eq. (4) for both electrodes, shows an increase during COD reduction (Fig. 8). The results show that the energy requirement for COD reduction was initially low, but it started to increase after 40 min into the experiment. Further, after 60 min of electrolysis, a sharp rise in energy consumption was observed which coincided with no further COD reduction, which is also suggested by Eq. (10). Overall, the energy requirement for 1 h electrolysis of RB5 on the PPTD-coated electrode is 256.58 kWh/kg COD compared to 262.33 kWh/kg COD on the STD-coated electrode. The reported energy consumption for the treatment of paper mill wastewater using Ti/Co/SnO₂-Sb₂O₅ anode in batch process was in the range of 600–900 kWh/kg COD during 60 min electrolysis

Fig. 8 Energy consumption versus COD reduction (%) on Ti/IrO₂-RuO₂-SnO₂-Sb₂O₅ electrodes prepared by (triangle) STD and (square) PPTD methods at initial pH 2, current density 50 mA/cm² in presence of 4 g/L NaCl

Table 5 Mineralization efficiency of RB5

Electrode	$\Delta\text{TOC}_{\text{theor}}$ (mg/L)	$\Delta\text{TOC}_{\text{exp}}$ (mg/L)	%TOC _{exp} reduction after 1 h electrolysis	MCE
Ti/IrO ₂ -RuO ₂ -SnO ₂ -Sb ₂ O ₅ (STD)	191.47	21.39	69.07	11.17
Ti/IrO ₂ -RuO ₂ -SnO ₂ -Sb ₂ O ₅ (PPTD)	191.47	23.25	75.45	12.14

[37]. While the energy requirement reported for treatment of RB5 using commercial electrode was 450 kWh/kg COD for 1 h electrolysis [38], the energy requirement in the present study on the two different electrodes was much lower.

3.7 Kinetics of degradation

As reported previously, the presence of chloride generates a reversible Cl^-/ClO^- [2] redox couple and degrades the dissolved organics by indirect oxidation, in which chloride gets converted to chlorine and hypochlorite at the anode. The Cl_2 and ClO^- can oxidize the organic compounds and get reduced to chloride ion again. This process is repeated in a cyclic manner; hence, concentration of chlorine is assumed to be constant [29].

Assuming first-order kinetics, the electrochemical reaction of COD reduction can be written as follows:

$$-d[\text{COD}]/dt = k[\text{COD}]^a[\text{Cl}_2]^b \quad (30)$$

Assuming constant concentration of Cl_2 , Eq. (29) can be reduced to:

$$-d[\text{COD}]/dt = k_{\text{app}}[\text{COD}]^a \quad (31)$$

where

$$k_{\text{app}} = k[\text{Cl}_2]^b \quad (32)$$

k_{app} is the apparent degradation rate constant, and a , b are the order of reaction respect to $[\text{COD}]$ and $[\text{Cl}_2]$, respectively. Assuming $a = 1$ (pseudo-first-order reaction), Eq. (31) is written as follows:

$$\ln[\text{COD}]_0 = k_{\text{app}}(t) + \ln[\text{COD}]_t \quad (33)$$

where COD_0 and COD_t are values of COD at time 0 and at time, t . A plot of $\ln(\text{COD}_0/\text{COD}_t)$ versus t (time) gives k_{app} (rate constant for COD reduction in min^{-1}). In a same way with respect to concentration, a plot of $\ln(C_0/C_t)$ gives rate constant k_{app} (min^{-1}) for concentration (colour) reduction.

Figure 7a, b shows plots of $\ln[\text{COD}_0/\text{COD}_t]$ and $\ln[C_0/C_t]$ versus time for $\text{Ti}/\text{IrO}_2\text{-RuO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$ electrode prepared by STD and PPTD methods, respectively. As shown in figure, the colour (concentration) and COD reduction follow first-order decline (for zero- and second-order reaction kinetics, $R^2 < 0.92$). Table 4 shows that the rate constants for colour and COD removal on $\text{Ti}/\text{IrO}_2\text{-RuO}_2\text{-SnO}_2\text{-Sb}_2\text{O}_5$ electrode by PPTD method are 0.762 and 0.0268 min^{-1} , respectively, which were greater than those for the electrode by STD method, thus indicating a higher activity of the polymeric precursor coating on the titanium substrate by PPTD method. Higher

values of rate constant for colour reduction (Table 4) indicate that colour reduction is much faster than COD reduction on both the electrodes, mainly because a complete mineralization is expected to take longer. In comparison to this study, the rate constants for colour and COD reduction using commercially available titanium mesh coated with oxides of titanium, iridium, and ruthenium for RB5 removal reported by Rajkumar et al. [38] were 0.2771 and 0.0026 min^{-1} , respectively. Higher values of both kinetic rate constants obtained in the present work indicate better performance of fabricated electrodes compared to commercially available electrodes.

4 Conclusions

The electrochemical degradation of RB 5 was performed on indigenous electrodes prepared using two catalysts, i.e. Ru and Ir. Moreover, two different methods, STD and PPTD, were also adopted for fabrication of MMO electrode. The interesting results were observed while performing related to colour, COD, and TOC reduction. It was found that both the electrodes were equally efficient for decolourization of wastewater containing RB 5, while less difference was noted in COD and TOC reduction. In PPTD electrode, that reduction was higher. The COD reduction on electrodes by PPTD and STD methods was 79% and 76%, respectively. The higher degradation efficiency of PPTD electrode led to a higher mass transport as well as a kinetic rate constant than the STD electrode. It was further concluded that RB5 degradation using either electrode was under mass transport control rather than kinetic control. However, the mineralization efficiency of the electrodes was less than 20%, which may be due to formation of intermediates instead of its complete mineralization to CO_2 . Due to higher COD reduction, the energy requirement was much lower for both electrodes, compared to the reported values for RB5 removal. A large difference in result was observed in comparison with service life. The service life of the PPTD and STD electrodes during an accelerated test was 76 h and 895 h, respectively, which suggests that STD method of electrode preparation may be superior to PPTD method.

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Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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