

Application of Ti/RuO₂-SnO₂-Sb₂O₅ Anode for Degradation of Reactive Black-5 Dye

Jayesh P. Ruparelia, and Bhavna D. Soni

Abstract—Electrochemical-oxidation of Reactive Black-5 (RB-5) was conducted for degradation using DSA type Ti/RuO₂-SnO₂-Sb₂O₅ electrode. In the study, for electro-oxidation, electrode was indigenously fabricated in laboratory using titanium as substrate. This substrate was coated using different metal oxides RuO₂, Sb₂O₅ and SnO₂ by thermal decomposition method. Laboratory scale batch reactor was used for degradation and decolorization studies at pH 2, 7 and 11. Current density (50mA/cm²) and distance between electrodes (8mm) were kept constant for all experiments. Under identical conditions, removal of color, COD and TOC at initial pH 2 was 99.40%, 55% and 37% respectively for initial concentration of 100 mg/L RB-5. Surface morphology and composition of the fabricated electrode coatings were characterized using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) respectively. Coating microstructure was analyzed by X-ray diffraction (XRD). Results of this study further revealed that almost 90% of oxidation occurred within 5-10 minutes.

Keywords—Electrochemical-oxidation, RB- dye, Decolorization.

I. INTRODUCTION

PROTECTION of the environment is one of the most challenging and pressing task for mankind due to industrial development [1]. Furthermore, it is a fact that the dyes industries are one of the most polluting industries in the world causing grave damage to the environment [2]. Dyes are extensively used in textile industries [2, 3, 4, 5], paper industries [6], food technology and also in agricultural research. Therefore, wastewater of above listed industries contain large amount of dye pigments. Synthetic organic dyes contain toxic material such as organic compounds and color pigments. Due to their strong color, they are visible even at low concentration in wastewater. These organic compounds are responsible for high chemical oxygen demand (COD) level in wastewater and create serious problems in the environments.

Conventional methods for dyes wastewater treatment include physico-chemical, electro-coagulation and biological treatment. Dyes usually shows high stability under sunlight and resistance to microbial attack and temperature, conventional wastewater treatment methods are unable to degrade majority of these compounds [7]. Therefore, methods for decontamination and decolorization of effluents from dyes and textile industries have received considerable attention in recent years. Advanced oxidation process, microbial and

enzymatic decomposition, ozonation, membrane separation and adsorption are some of the known methods for decolorization and decontamination of wastewater from textile and dyes industries [7]. Due to various advantages over other methods electrochemical processes considered as very effective method for removal of petroleum hydrocarbons from produced water (refinery wastewater)[8], synthetic organic dyes from wastewater[9,10,11] treatment of mixed industrial waste water[10] and treatment of wastewater from wood furniture industries [12]. There are various types of dyes available in the market. Among them RB-5 is found to be widely used for textile dyeing and paper industries. RB-5 is azo type of dye, which is difficult to degrade compared to other dyes. Therefore in this work, for application of electrochemical process, RB-5 has chosen as model compound.

It is reported that electrode is a crucial part in electrochemical process. Right choice of an electrode material makes process very effective and improves its efficiency because mechanism driven by the process as well as degradation product depends upon the anode material. Suitability of an electrode is dependent on three requirements [13]. High efficiency; high stability and low production cost are the most desirable properties of electrodes. Several anode materials have been tested and reported to make an electrode effective for complete degradation of organic pollutants. But some of them are either very costly, not efficient for degradation, present a rapid loss of activity, some release toxic ions or shows a limited service life [14]. Aluminum, iron and stainless steel are electrodes useful for electro-coagulation [15, 16, 17, 18]. Dimensionally stable electrodes (DSA) are titanium based electrodes containing conductive metal oxide coating. These electrodes have some desirable properties such as high surface area, high electrical and mechanical strength and excellent electro-catalytic properties [19]. Fabrication of DSA type electrodes [20, 21, 22] can be done by using transition metals such as ruthenium, tantalum, iridium, tin, antimony etc. This type of electrode generally gives partial oxidation of organics. Boron doped diamond (BDD) [23, 24, 25, 26], lead oxide are the material useful to give complete oxidation of pollutants [12].

It is evident from literature that, different pollutant requires different combination of material for fabrication of electrodes. Therefore, the major objective of this study was to indigenously prepare DSA electrode for electrochemical process and check its potential for degradation of RB-5 dye in acidic, neutral and alkaline medium.

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II. EXPERIMENTAL

A. Chemicals

Reactive Black -5 ($\lambda_{\text{max}}=597$) dye chosen for experiments was provided by local dye industry (Gayatri Color Chemical, Ahmadabad). Sulphuric acid and NaOH were procured from S D Fine chemicals and proper solutions employed for adjustment of pH. Sodium chloride (NICE make LR grade) was used to increase conductivity of solution. Oxalic acid (NICE make LR grade) was used as etchant for titanium. $\text{RuCl}_3 \cdot \text{XH}_2\text{O}$ (99.9%, Aldrich), SbCl_3 (98.5%, CDH) and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (98% Aldrich) were used to prepare precursor solution for coating on selected substrate. Iso-propanol (99.8% CDH, AR- grade) and hydrochloric acid (37%, CDH) were used as solvent for precursor solution in electrode fabrication.

B. Preparation of Anodes

Three stage procedures were followed for preparation of electrodes as reported in literature [27, 28].

- (1) Surface of titanium metal cleaning
- (2) Precursor preparation
- (3) Electrode coating

Titanium metal piece (75 mm \times 50 mm \times 3mm) was polished with Sic paper (400–200 grit) and etched in 10 % oxalic acid at 80 °C for 1 hr and then rinsed with deionized water before thermal decomposition process [28]. Precursor solution was prepared by dissolving 0.161 g $\text{RuCl}_3 \cdot \text{XH}_2\text{O}$, 0.171 g SbCl_3 and 1.227 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in a solvent consisting of 10 mL iso- propanol and 0.5 mL hydrochloric acid .This precursor solution was prepared with molar ratio 15 : 15 : 70 :: Ru : Sb : Sn [29,30].

Freshly prepared precursor solution was brushed on pre-treated titanium substrate at room temperature, dried at 80 °C for 5 min to allow the solvents to vaporize and then heated at 550 °C for 5 min. This process was repeated about 15 times to provide proper coating on metal which can be ensured by measuring increase in weight of substrate for oxide loading. After oxide loading on substrate achieved about 2-3 mg/cm² the electrode was heated at 550 °C in muffle furnace for an hour and cooled in desiccator up to room temperature.

C. Apparatus and Instruments

The batch unit consists of a 1.0 L electrochemical glass reactor with reaction mass 500 mL. Both the electrodes used have same dimensions 75mm \times 65mm \times 3mm. Ti/RuO₂-SnO₂-Sb₂O₅ was employed as anode and stainless steel as cathode in all experiments. The distance between two electrodes was kept 8mm in all the experiments. The applied potential was maintained constant by means of a D.C. power supply (Aplab India, LD-3205). For each run COD and color was measured before and after treatment to find percentage reduction in pollution levels. COD was determined by standard closed reflux method [29] using COD reactor (HACH DRB200, COD reactor, USA). Color was determined using UV-Vis spectrophotometer (UV-1800, Shimadzu, Japan) for wavelength range 200-800 nm. TOC of the samples were also

determined using TOC analyzer (TOC-VCSH, Shimadzu, Japan).

D. Experimental Protocols

The dye solutions were prepared by dissolving appropriate dyes in tap water to make 100 mg/L solution. The initial COD of synthetic dye solution was about 172.8 mg/L. Further, to increase conductivity of solution NaCl (2 g/L) was added as electrolyte in solution. The pH of the solutions was measured by pH meter and adjusted by adding NaOH or H₂SO₄ solutions. Titanium electrode (Ti/RuO₂-SnO₂-Sb₂O₅) was used as anode and stain less steel (304) was used as cathode in each experiment. Both the electrodes were connected to a DC power supply (Fig. 1) for controlling the constant current density (50 mA/cm²). Magnetic stirring was done at 150 rpm to achieve homogeneous dispersion. All the runs were performed at room temperature. In each run, 500 mL of the dye solution was decanted into the electrolytic cell. After starting electro-oxidation, samples were drawn for different interval of time for COD, UV and TOC analysis. Above procedure was repeated for pH 2, 7 and 11 to find optimum one.

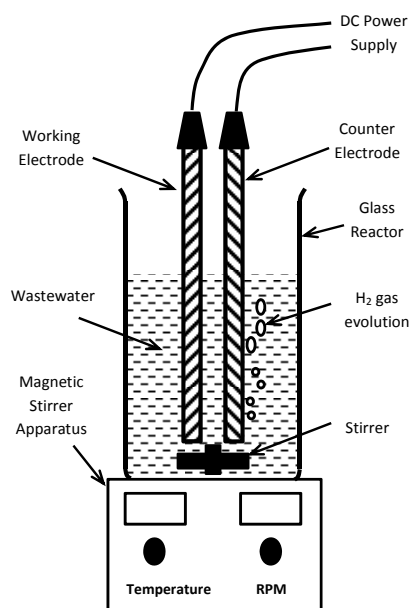


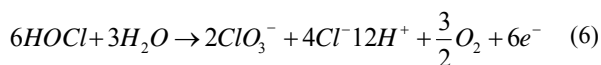
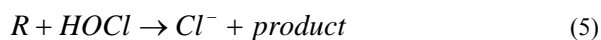
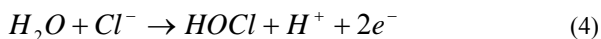
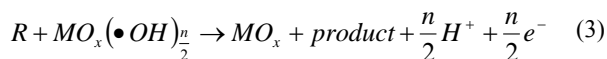
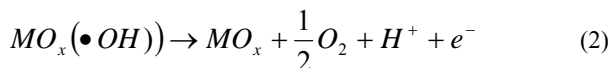
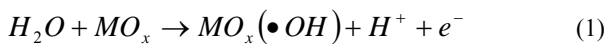
Fig. 1 Schematic diagram of experimental batch reactor

E. Mechanism of Electrochemical Oxidation of RB-5

Decolorization with DSA type electrode is obtained due to electrochemical oxidation using non-soluble anodes. The degradation product of dyes are different but in general they are carbon dioxide, nitrogen, sulphate compound with possible formation of esters, phenols, aromatic carboxylic acids, cyclic and aliphatic hydrocarbons, aromatic amines etc. [11].

Degradation mechanism of dyes usually depends on their strength and reactive group. Reactive dyes contains -N=N- (azo group) derivative which are responsible for imparting

color. Oxidation taking place on the electrode (anode) breaks this derivative, and therefore degradation of wastewater becomes possible. COD reduction is possible due to mineralization of organic compounds in to simple compounds such as carbon dioxide; water etc. Reaction sequence is represented as under for generalized electrochemical process [7].



Reaction (1) indicates electrolytic discharge of water carried out due to metal oxide (MO_x) to form metal oxide hydroxide complex ($MO_x(\bullet OH)$) and hydrogen. Reaction (2) is for decomposition of metal oxide hydroxide complex results in evolution of oxygen and hydrogen gas giving partial oxidation of pollutants. Complete oxidation of pollutants (R) where no oxygen gas generated is given by reaction (3). Thus reaction (3) is a desirable reaction. In presence of active chlorine, reaction (4) and (5) takes place for degradation of pollutants (R) [20]. As per these reaction, hypochlorous acid produces due to presence of free chlorine and water molecule [7]. At high pH reaction takes place as shown in (6) generating perchlorate which reduces oxidation efficiency.

The COD, colour and TOC were chosen as parameters in order to evaluate the effect of electrochemical treatment. Dyes concentrations were determined from their absorbance characteristics in the UV with the calibration method. The calculation of color removal efficiency after electro chemical treatment was performed using Eq. (7) [12, 30, 31].

$$\%Decolorization = \frac{ABS_0 - ABS}{ABS_0} \times 100 \quad (7)$$

Here ABS_0 and ABS are absorbance values before and after electrolysis of dye at maximum visible wavelength (λ_{max}) of the wastewater.

The decontamination of dyes wastewater was monitored from the abatement of chemical oxygen demand (COD) measured for examining water and wastewater. From these data, the percentages of COD decays are calculated from Eq. (8) [12, 30,31].

$$\% COD \text{ removal} = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (8)$$

Where COD_i and COD_f , are initial and final (after electrolysis) values of COD. Same way TOC decays are calculated from Eq. (9)

$$\%TOCremoval = \frac{TOC_i - TOC_f}{TOC_i} \times 100 \quad (9)$$

Instantaneous current efficiency (ICE) i.e. oxidation ability of the anode material was also calculated using equation Eq. (10) [12].

$$ICE = \frac{[COD_t - COD_{t+\Delta t}] F V}{8 I \Delta t} \quad (10)$$

Where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the COD values at t and t+ Δt time (seconds) in ($g O_2 dm^{-3}$), respectively, I is the applied current (ampere), F is the Faraday constant ($96487 C mol^{-1}$), V is the volume of the electrolyte solution (m^3), 8 is a dimensional factor for unit consistence [12, 30, 31].

Cost of energy was calculated using Eq. (11) [12, 30, 31].

$$E = \frac{U I \Delta t}{(COD_t - COD_{t+\Delta t}) V} \quad (11)$$

Where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the COD values at t and t+ Δt time (hr) in ($g O_2 dm^{-3}$), respectively, U is the average cell potential(V), I is the applied current (ampere), and V is the volume of the electrolyte solution (L), to get energy consumption in kWh/mg of COD reduction.

F. Electrode Characterization

Characterization of Ti/RuO₂-SnO₂-Sb₂O₅ electrode was done for its surface morphology and composition of the coatings using Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) respectively (SEM-EDX, LEOs- 440i With Oxford Energy Dispersive X-Ray Analyzer 7060). Coating microstructure was analyzed by X-ray diffraction (XRD, 3000PTS, Seifert).

III. RESULTS AND DISCUSSION

A. Importance of DSA Type Electrodes

DSA type electrodes use conductive precious metal oxides as electro catalysts. This oxide has excellent activity in Cl₂ evolution [29]. This Cl₂ helps in degradation of organic pollutants [32]. In this experiment Ti/ RuO₂-SnO₂-Sb₂O₅ electrode was fabricated and tested for RB-5 degradation in acidic, neutral and alkaline condition.

TABLE I
COMPARISON OF REDUCTION OF COD, TOC AND COLOR ON 100 PPM REACTIVE BLACK -5 DYE WITH Ti/ RuO₂-Sb₂O₅-SnO₂ ELECTRODE

Electrode	Time (minutes)	Current Density mA/cm ²	pH	NaCl added in g/L	COD reduction	Color reduction	TOC reduction
Ti/RuO ₂ -Sb ₂ O ₅ -SnO ₂	60	50	7-8	2	47	99	35
	60	50	2-3	2	55	98	37
	60	50	11-12	2	34	85	not measured

Table I shows results of Ti/ RuO₂-SnO₂-Sb₂O₅ at different pH. In this electrode oxide mixture is mixture of three metal oxides. In this oxide mixture RuO₂ serves as a catalyst, SnO₂ serves as a dispersing agent and Sb₂O₅ serves as a dopant. RuO₂ also increases service life of an electrode while SnO₂ increases coating stability [32, 33].

B. Effects of pH

Degradation of synthetic organic 100 mg/L RB-5 dye was carried out at pH 2, 7 and 11 with Ti/ RuO₂-Sb₂O₅-SnO₂ electrode and influence of the initial pH on the reduction of COD concentration, color and TOC with respect to time was observed. It was observed that at initial pH 11, less color and COD reduction was taken place. At neutral pH, degradation and decolorization took place but COD and TOC reduction was lesser compare to results obtained at initial pH 2. Means decolorization and decontamination was best carried out at pH 2. So, the initial pH plays important role in the oxidation of pollutants. The oxygen evolution reaction takes place at high pH as secondary reaction parallel to electro-oxidation [34]. Higher oxygen evolution leads to less degradation [34, 35]. Means reaction (3) is preferable instead of reaction (2). Secondly if pH is high reaction proceeds as per equation (6) rather than equation (5), means as per reaction (4-5) hypochlorous acid will form and further dissociated to give hypochlorite ion. This ion acts as main oxidizing agent in the pollutant degradation. Reactions (3, 4, 5) are favorable in acidic media only. Fig. 2 is UV spectra of 100 mg/L untreated and treated reactive black-5 dye solution. Fig. 2 (a) shows peaks in visible range while in Fig. 2 (b) peaks disappeared in visible range means color has been removed, however it shows some peaks in UV range which may be due to production of intermediates, probably related with the formation of the vinyl sulfone or hydroxyethyl sulfone derivative [36] as result of the hydrolysis of the sulfatoethyl sulfone groups of the RB-5.

C. Degradation and Mineralization

Ti based three dimensional electrodes includes anodic oxidation process. This oxidation takes place due to simultaneous electro generated active oxygen and chlorine complex as per reaction (3, 4) close to electrode could also remove the pollutants. COD reduction with respect to time for RB-5 dye with Ti/RuO₂-SnO₂-Sb₂O₅ for 100 mg/L concentration is shown in Fig. 3. Maximum COD reduction

was possible within ten minutes only and then there was not much reduction of COD.

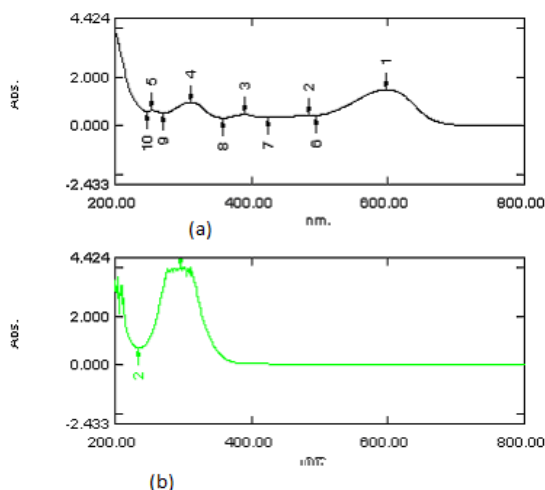


Fig. 2 UV spectra of (a) 100ppm Reactive Black-5 dye sample (b) sample treated with Ti/ RuO₂-SnO₂-Sb₂O₅ after five minutes at pH 2

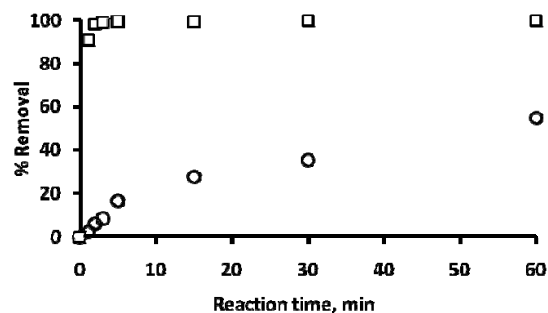


Fig. 3 Evolution of color (□) and COD (o) removal in % with time

Here Fig. 3 depicts removal of color with respect to time. As can be seen from figure, maximum color reduction was possible within five minutes only and then minor reduction of color took place.

D. Instantaneous Current Efficiency (ICE)

It is reported that when the applied current exceeds limiting current, organic pollutants are completely converted to CO₂, H₂O and secondary reaction (oxygen evolution or electrolyte decomposition) starts resulting decreases in instantaneous

current density[12,31,32]. Fig. 4 presents ICE decreases maximum within ten minutes, which reflects maximum oxidation takes place within this time only.

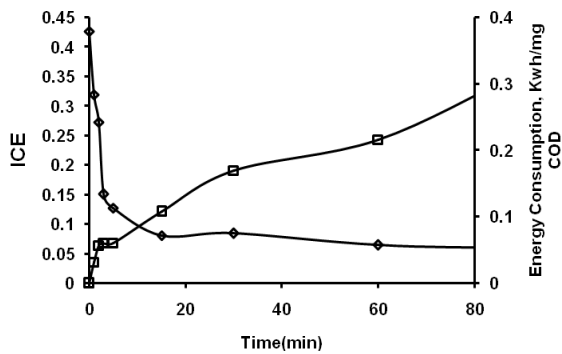


Fig. 4 Evolution of ICE and energy consumption with time

E. Energy Consumption

Energy consumption was calculated using equation (10). Fig. 4 shows that as time increases electrical energy required for mineralization of organic compounds also increases. Energy consumption was less i.e. up to 10 Kwh/mg COD for 45% reduction. Then there was rise in energy consumption for COD reduction from 40-55% COD. This is shown by Fig. 5.

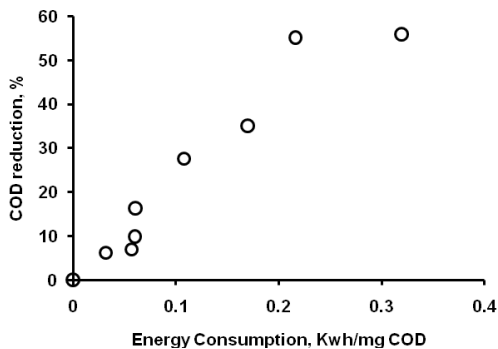


Fig. 5 Evolution of COD reduction with energy consumption

IV. CHARACTERIZATION OF Ti/RuO₂-SNO₂-SB₂O₅ ELECTRODE

A. XRD Measurement

Fig. 6 depicts XRD pattern of RuO₂-Sb₂O₅-SnO₂ film coated on a flat titanium substrate. In addition to the Ti metal peaks from the substrate, new and noticeable peaks corresponding to RuO₂ and SnO₂ did appear. Indicating that layer of RuO₂ and SnO₂ has formed on metal piece. Corresponding to Sb₂O₅ rich peaks were not detected. These facts reveal that Sb₂O₅ has been highly intermixed with other oxides [37]. This could be concluded from some unidentified peaks. These peaks would be a mixture of RuO₂-Sb₂O₅-SnO₂ in form of a solid solution. Some peaks are wide and some are narrow shape indicating mixture of crystalline and amorphous nature of the sample [30].

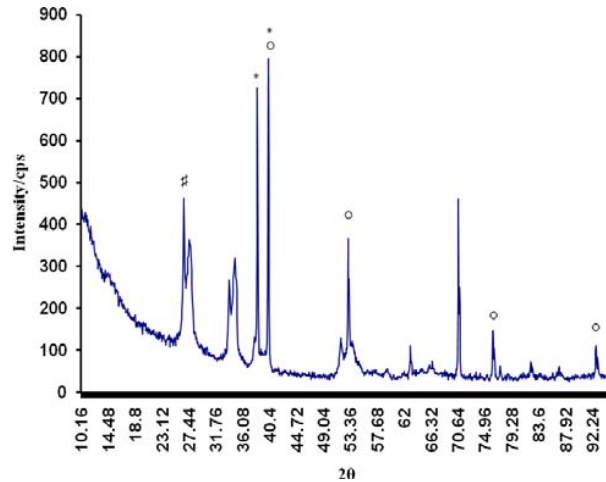


Fig. 6 XRD spectra of Ti/ RuO₂-Sb₂O₅-SnO₂, o(titanium), # (SnO₂), *(RuO₂) (Phases: 88-322 (RuO₂); 44-1294 (Ti); 88-287, (SnO₂))

B. SEM and EDX Analysis

The morphology of the outer layer film of Ti/ RuO₂-Sb₂O₅-SnO₂ has been analyzed by SEM in Fig. 7. Fig 7 (a, b) shows outer layer film consisting of layer of mixture RuO₂-Sb₂O₅-SnO₂ relatively crystalline and rough. Crystals of Cl⁻ are clearly visible (Fig. 7ba) on an electrode because that electrode was used for treatment of RB-5 dye containing 2 gm of NaCl. Such types of crystals were not found in (Fig. 7a) as it was unused electrode. The RuO₂-Sb₂O₅-SnO₂ film had cracks. This indicates porous structure of the film.

Surface morphology of both electrodes (Fig-7 a, b) is different due to reaction occurred on outer layer of an electrode (Fig. 7a) in case of used electrode.

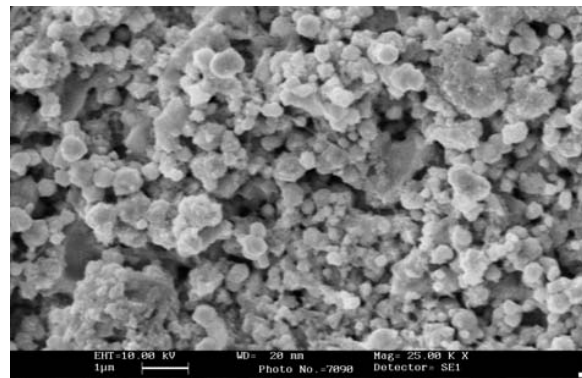


Fig. 7 (a)

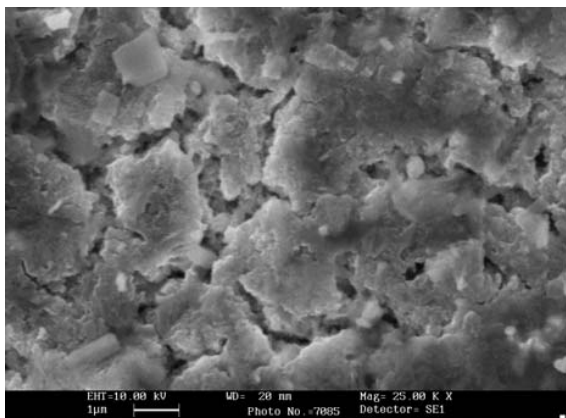


Fig. 7 (b)

Fig. 7 Scanning electron micrographs of the outer layer surface of (a) unused Ti/ RuO₂-Sb₂O₅-SnO₂ electrode (b) used Ti/RuO₂-Sb₂O₅-SnO₂ for RB-5 treatment, magnification 25000 x

In Fig. 8, EDX analysis gives molar ratio of the oxide in the mixture. Result indicates molar ratio as Ru (25.55%), Sn (31.72%) and Sb (14.71%).

Here molar percentage of Sn is less compare to theoretical data because in thermal decomposition process, during oxides preparation, Sn loss could reach up from 40 to 80 percentages [38]. There for the actual molar ratio of SnO₂ in electrode coating is much lower than the nominal composition in the precursor solution. In other words RuO₂ molar percentage in the film is higher than actually added in precursor solution.

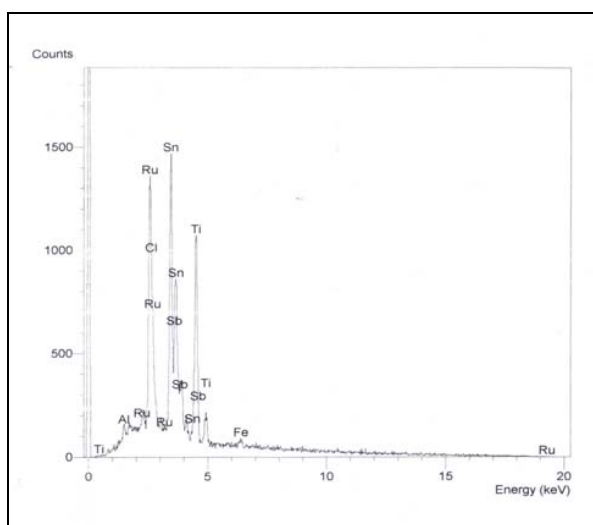


Fig. 8 EDX analysis of RuO₂-Sb₂O₅-SnO₂ film coated on titanium substrate

V. CONCLUSION

Titanium electrode prepared by coating of oxide metals like RuO₂, SnO₂, and Sb₂O₅ on titanium substrate gave substantially good results. For Reactive black-5 color removal was possible up to 99%. COD and TOC reduction was 55% and 37% respectively at pH 2. At neutral pH color, COD and

TOC reduction was found less. It was also found that almost 90% of oxidation occurred within 5-10 minutes only. This is proved by instantaneous current density (ICE) plot. Instantaneous current density drastically decreases within five minutes represents that the maximum degradation occurs during first ten minutes of treatment and it is responsible for color, COD and TOC reduction.

Energy consumption is also less up to five minutes of reaction. It suggests that optimum time for mineralization is considered to be five minutes. Existence of Ruthenium, Tin and Antimony oxides in EDX as well as XRD spectra indicates that substrate is completely covered with solid metal oxide film.

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