Application of Electrochemical Advanced Oxidation Process for Treatment of Recalcitrant Wastewater

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Declaration

This is to certify that

1. The thesis comprises my original work towards the degree of Master of Technology in Environment Process Design at Nirma University and has not been submitted elsewhere for a degree.
2. Due acknowledgement has been made in the text to all other material used.

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I, Nidhi Mehta, 14MCHE06, give undertaking that the major project entitled “**Application of Electrochemical Advanced Oxidation Process for Treatment of Recalcitrant Wastewater**” submitted by me, towards the partial fulfillment of the requirements for the degree of master of technology in Environment Process Design of Nirma University, Ahmedabad is the original work carried out by me and I give assurance that no attempt of plagiarism had been made. I understand, that in the event of any similarity found subsequently with any published work or any dissertation work elsewhere, it will result in severe disciplinary action.

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Abstract

Textile and dyeing industries are one of the dominant industrial sectors for producing colored wastewater. The effluents so produced from these industries are tricky to treat due to their recalcitrant nature. Conventional treatment techniques are not suitable to treat this effluent due to presence of high amount of non-biodegradable compounds. Electrochemical advanced oxidation technique is gaining tremendous attention due to its high potential to treat recalcitrant organic compounds into environmentally acceptable end products. Mixed Metal Oxides (MMOs) are emerging to be most preferable anode to treat wastewater containing recalcitrant organic compounds due to their excellence performance.

The foremost aim of present work is to compare and analyze performance of various Mixed Metal Oxides (MMOs) for the treatment of synthetic wastewater containing two single dyes i.e. RR2, RR195. Effect of various parameters on mineralization efficiency of dye was also analyzed and optimum operating conditions were finalized based on it. Effectiveness of process was analyzed on the basis of %color, COD and TOC removal. Energy consumption was also calculated for optimized electrode based on unit mass of COD removal.

Keywords- Electrochemical oxidation, Mixed Metal Oxide, Color removal, COD removal, TOC removal, Energy Consumption, Life Test.

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Textile and pigment industries are considered to be one of the most crucial industrial classes producing high strength colored wastewater. Dyeing and finishing processes consumes huge amount of water and in turn end up generating large amount of wastewater [1-3].

A dye is a colored substance that has an affinity to the substrate to which it is being applied. It is an ionizing and sweet-smelling natural compound. The dye is for the most part connected in a fluid arrangement, and may require a mordant to enhance the quickness on the fiber. Dyes are fundamentally ionizing and fragrant mixes; they have chromophores present in them. Their structures have an Aryl ring that has delocalized electron frameworks [4]. These structures are said to be in charge of the assimilation of electromagnetic radiation that have fluctuating wavelengths, based upon the energy of the electron mists.

Different types of dyes are being used in various sectors of textile and pigment industries such as azo, anthraquione, sulfur, indigo, tri phenyl methyl and phthalocyanine derivatives [5, 6].

Textile dyes and pigment industry is a large sector which comprises almost 8000 different compounds with more than 40,000 commercial names. Reactive dyes are most widely being utilized in textile industry, mainly for dyeing cellulose fibers. Reactive dyes have drawn attention due to its good technical characteristic, however it is found to be very toxic and carcinogenic not only to humans but also to the environment. Along with dyes the chemicals which are utilized in dyeing industry are toxic in nature.

Dyes are classified on the basis of source from which it is being produced. It is classified as followed [7]:

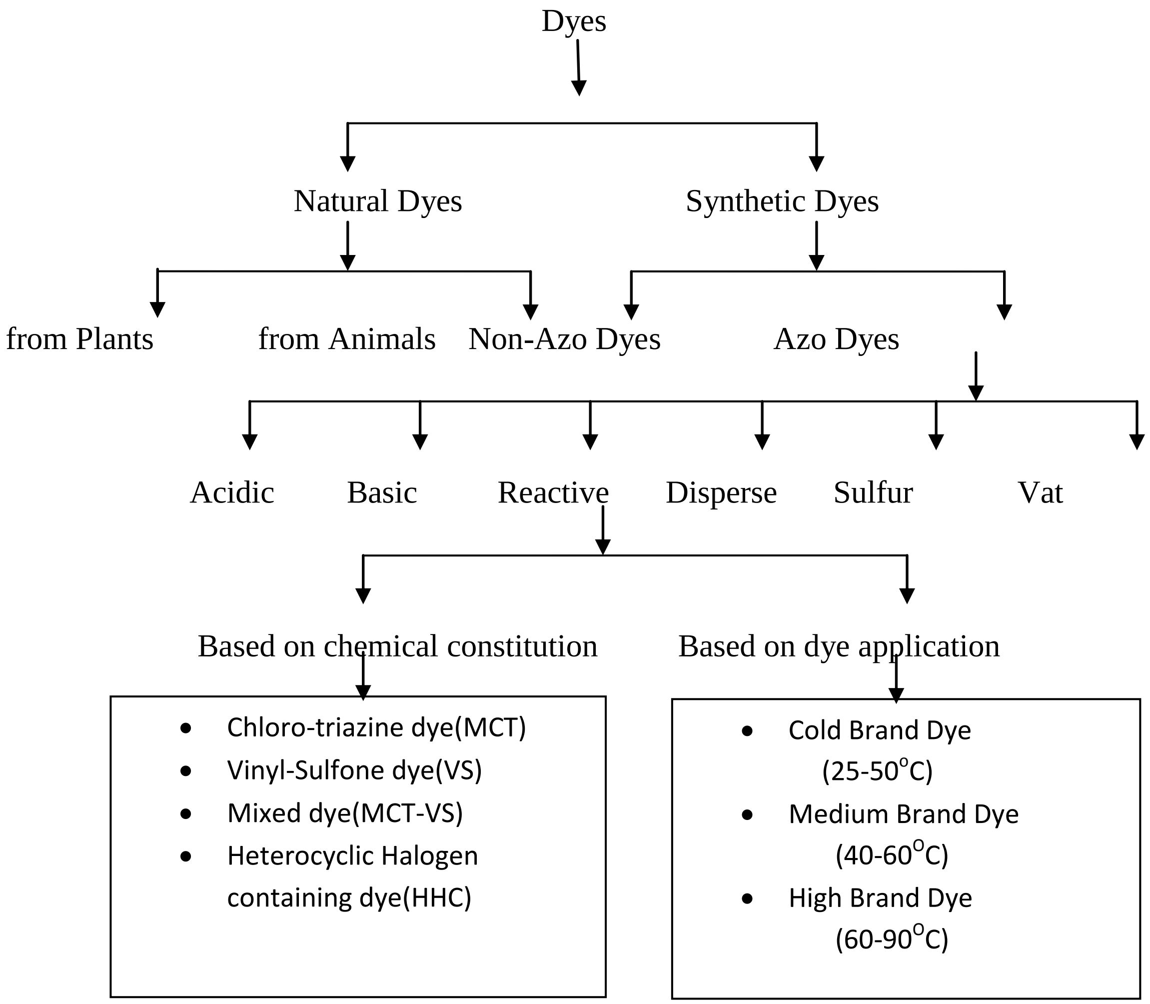
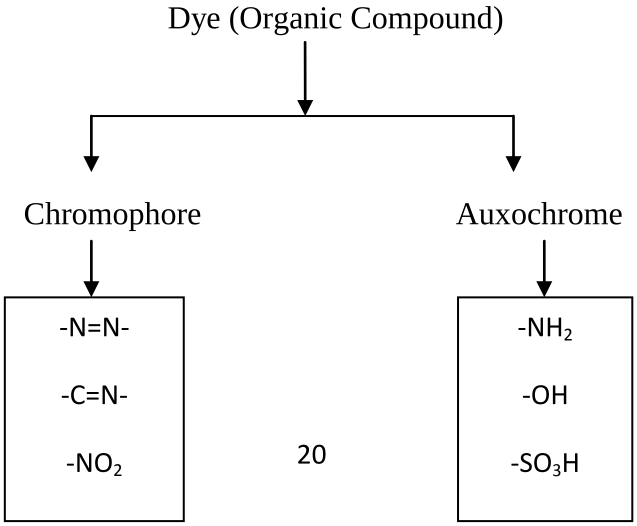


Table I. Major dyes and chemicals used in synthetic textile mills [1]

SrNo.	Chemicals	Quantity Kg/month
1	Acetic Acid	1611
2	Ammonium Sulphate	858
3	P V Acetate	954
4	Wetting Agent	125

5	Caustic Soda	6212
6	Softener	856
7	Organic Solvent	247
8	Organic Resin	5115
9	Formic Acid	1227
10	Soap	154
11	Hydrosulphites	6563
12	Hydrochloric Acid	309
13	Hydrogen Peroxide	1038
14	Leveling & Dispersing Agent	547
15	Solvent 1425	321
16	Oxalic Acid	471
17	Polyesthylene Emulsion	1174
18	Sulphuric Acid	678
19	Disperse Dyes(Polyester)	1500
20	Vat Dyes (Viscose)	900
21	Sulphur Dyes	300
22	Reactive Dyes	45

Dyes are very toxic in nature and as a result of this it is considered to be very problematic to human health as well as to environment. It is very difficult to determine the characteristic of any dye because each synthetic dye which is developed is basically a new compound due to which its complete risk is not known. Synthetic dyes are organic compounds and are difficult to treat as they are recalcitrant in nature. Dye is composed of two basic group auxochrome and chromophore. Chromophore is group present in dye which is basically responsible for providing color to the dye. It consist of various groups such as –N=N-, -C=N-, -NO_2 which are very stable and are recalcitrant in nature, hence it is very difficult to remove them or treat them to environmentally acceptable end products [8].



1.2 Mixed Metal Oxides

Mixed metal oxides (MMOs) has drawn tremendous attention for utilizing as anode material for treating wastewater containing recalcitrant organic matters using electrochemical oxidation method. MMOs have been widely used for heterogeneous catalysis. A combination of different valve metal based oxides has been tested to fabricate electro catalytic coating on the working electrode. The electrodes so developed are very stable and active electrodes in multiple dimensions. They are considered to be very effective in degrading the recalcitrant organic compounds on the working electrode which include contaminants of dyes and intermediates, pharmaceuticals, pesticides and herbicides, phenolic compounds, plasticizers and landfill leachets. Electrochemical oxidation is an efficient method employed for wastewater treatment. Anodes used in this process are prepared by doing coating of mixture of various metal salts. Wastewater released from textile and dyeing, pulp and paper, printing, pharmaceuticals and food industries are considered to contain high amount of dye, toxic organic and inorganic molecules, pesticides, surfactants, etc [9, 10].

The stringent government rules have made it compulsory to treat the wastewater before disposing it into water bodies. Various physical, chemical and biological treatments are employed to treat wastewater [11-13]. Electrochemical treatment method has drawn a lot of attention in last few years as it is economical process, easy to construct and operator friendly, highly efficient and environmental friendly [14-16]. Electrodes provide active site for the oxidation of organic matter [13]. Electrochemical method is more preferable over chemical method as it does not require any chemicals or reagents. Sometimes electrolyte need to be added if wastewater is not sufficiently conducting. Many times electrolytes are being added to enhance the degradation process. Electrolyte also plays an important role as it directly influences the efficiency of the process. Electrode used is utmost important in this process as it will govern the degradation and mineralization of organic matter or recalcitrant organic compounds.

Metal oxide comes under the category of solid catalysts [17]. It is used for heterogeneous catalysis mainly due to its redox and acid-base properties. Mixed metal oxides (MMOs) are mixture of two or more metal oxides. To produce new and stable compound with significantly improved catalytic activity different metal oxides are being mixed in different proportions [14]. Improved catalytic activity may be due to some modifications or enhanced surface area, addition of new energetic acidic or basic sites or may be due to some alteration in its chemical states of metal ions. Few significant applications of MMOs in terms of heterogeneous catalyst are Al_2O_3 supported MMOs for $(CH_3)_2S_2$ degradation [18], Ti$O_2 - ZrO_2$ for non oxidative dehydrogenation of ethylcyclohexane [19], Mg-V-Al MMOs for oxidative dehydrogenation of propane [20, 21], V-Sb-Nb MMOs for ammoxidation of propane [22], LaNiO_3 for ethanol reforming [23] and RuO_2-IrO_2-SnO_2 for chloral-kali process [24]. MMOs are not only utilized as catalysts, but have extensive applications in semiconductors, sensors, photoconductive thin films, electrode materials for lithium battery, fuel cell and environmental application [25]. Various researches have been done and still going on to utilize MMO as anode for treating recalcitrant organic compounds with the help of electrochemical oxidation process. [25, 26].

Literature reveals that various studies have been conducted in the past for utilizing MMO anodes for treating recalcitrant organic compounds by electrochemical oxidation process. Thin layer of MMOs is deposited on inert substrates such as titanium, carbon, stainless steel etc to for MMO anode. Increasing efforts are being made to utilize MMOs for treating various recalcitrant organic matters such as, dyes, pesticides, phenolic compounds, plasticizers, surfactants and derivatives, chelating agents and microcrystal toxins.

1.3 Mechanism of Electrochemical Oxidation

Electrochemical oxidation is an advanced oxidation process which can be done in either of the two ways- by direct oxidation or by indirect oxidation [14, 27]. In direct oxidation electrons are directly exchanged with the anode surface whereas in case of indirect oxidation some active species or mediators are being produced which helps to degrade the pollutants. Both the mechanisms are shown in figure. 1. In direct oxidation process electrons are directly exchanged between anode and the organic matter at the electrode solution interface. This reaction is feasible at potentials well below oxygen evolution over potential. However major drawback accompanied to this process is passivation of anode surface due to adsorption of organic matter. The reaction rate for direct oxidation has low kinetics and it depends on the electro catalytic activity of the anode. To accomplish high electrochemical rates noble metals are used such as Pt, Pd and metal oxides such as iridium dioxide, ruthenium- titanium dioxide, and iridium-titanium dioxide [26].

On the other hand, major issue confronting to electrochemical oxidation is reduction in catalytic activity due to generation of polymer layer on the surface of anode, which is also known as poisoning effect. In case of aromatic organic compounds such as chlorophenols, naphthol and pyridine poisoning effect is more emphasized due to its adsorption properties on the anode surface and its concentration.

Indirect electrochemical oxidation process can either be reversible or irreversible process. In this process exchange of electrons takes place through some mediators of electro active species generated there, which perform as agent for transferring electrons between the electrode and the organic matters.

In the reversible process, Reaction scheme for the same is shown below:

$$MO_X + H_2O \rightarrow MO_X(\bullet OH) + H^+ + e^- \tag{1}$$

$$MO_X(\bullet OH) \rightarrow MO_{X+1} + H^+ + e^- \tag{2}$$

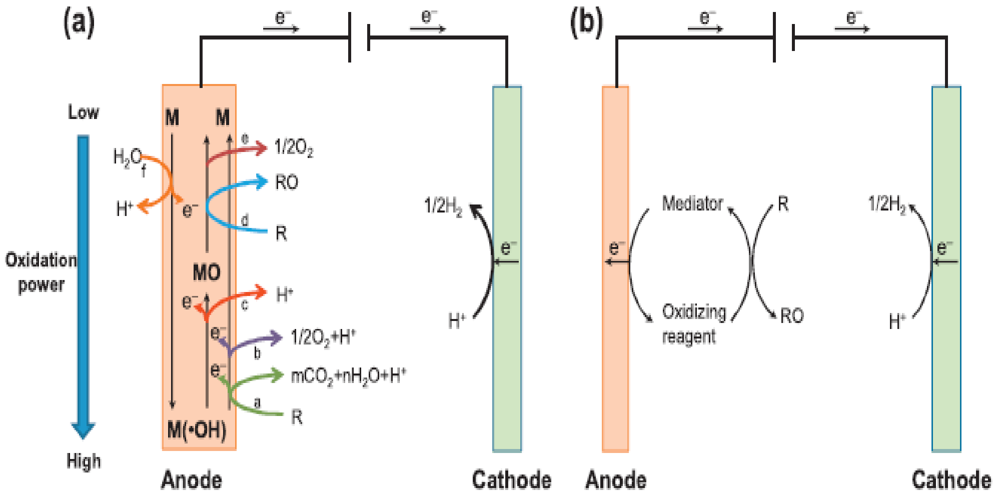
The formation of H$^+$ ions is accompanied due as a result of interaction of hydroxyl radical ($\bullet OH$) with the anode, as well as accessibility of higher oxidation state for the anode metal. In indirect oxidation, hydroxyl radical species generated by the discharge of water or other active oxidants known as mediators are consumed in the oxidation of organics in the bulk of the electrolyte.

$$MO_X(OH) + RH \rightarrow MO_X + H_2O + R \tag{3}$$

$$MO_X(OH) + R \rightarrow MO_X + CO_2 + H_2O \tag{4}$$

$$MO_{X+1} + R \rightarrow MO_X + Intermediate \tag{5}$$

Several Mixed Metal Oxides electrodes have been used in industrial effluent treatment. However it is worthy to note from literature that most of these are the derivatives of various metals like Ru, Rh, Sn, Ti, Pt, Ta, Pb, etc [10].



Note: R – target pollutants;
M - MMO;
MO - MMO with chemisorbed active oxygen;
M(•OH) - MMO with physically adsorbed active oxygen.

Figure 1.1 Mechanism scheme for (a) direct (b) indirect electrochemical oxidation process [26].

1.4 Various parameters affecting electrochemical oxidation efficiency

There are number of operating parameters that can affect the electrochemical oxidation of organic pollutants by MMO anodes, they are listed as,

1.4.1 Effect of pH

pH plays most vital role in electrochemical oxidation process using MMO anodes [28, 29]. Literature reveals that lot of work has been done confronting effect of pH on anodic oxidation. Though results are assorted and may be clashing some times to each other. The reason for this diversity in result is may be due to types of dye used, targeted pollutants, types of supporting electrolyte or MMO used. Generally according to literature lower pH enhances the removal efficiency of organic pollutants by electrochemical oxidation, with a few exceptions.

Exceptions may be explained by perspective of thermodynamics, considering the fact that oxidation of organic matter is highly dependent on pH of solution.

From oxidation of water molecules HO• generation takes place

$$H_2O \rightarrow HO\bullet + H^+ \tag{6}$$

In view of the fact that HO• at lower pH shows higher oxidative potential and as a result of this it removal efficiency of organic pollutants is enhanced. Accordingly it is always favored to carryout oxidation of organic pollutants at lower pH range. Electro migration mass transfer is also accompanied to pH. Literature reveals that solubility of cationic dyes is enhanced at lower pH range, which will consequently improve diffusion of dyes and decrease the resistance to mass transfer.

1.4.2 Effect of Temperature

Temperature is another parameter which affects electrochemical oxidation process as it not only alters degradation rate of organic molecules but also helps to improve adsorption capacity of HO• in the MMO anode surface. Literature has diverse findings as some studies revealed that increasing the temperature will consequently increase the degradation rate of organic molecules whereas on contradictory to this according to some studies there are some organic pollutants which remains unaffected by change of temperature [29, 30]. Electrochemical oxidation of maleic acid at Ti/IrO_2-Ta_2O_5 anode and p-methoxyphenol at Ti/SnO_2-Sb anode is unaffected by any change in temperature.

In indirect oxidation process the degradation effectiveness of organic matters is increased by increase of temperature due to generation of active species such as reactive chlorine, peroxodisulfate, etc [31].

Taking into account additional cost of operation at high temperature, electrochemical oxidation of organic pollutants is generally carried out at ambient temperature. On the other hand, there are arguments that high temperature is favorable for electrochemical oxidation at MMO anodes. Literature also reveals that as electro chemical oxidation is exothermic reaction so cost of maintaining high temperature can be satisfactorily achieved. Also, according to literature MMOs are highly stable at elevated temperature than other anodes like BDD, and also give higher removal efficiency at high temperatures [32].

1.4.3 Effect of Current Density

For electrochemical oxidation, current density is considered to be one of the vital parameter taking into account both the factors mechanistic study as well as cost effectiveness. In general electron transfer ability as well as generation of oxidizing agents depends on the applied current density. However, as current density increases the electrochemical oxidation. It should also be taken into account that increasing the current density will additionally increase the operating cost of the process, so it is very important to optimize the current density which will not only give better degradation of organic pollutants but also need to be economically feasible [28, 29, 33, 34].

1.4.4 Effect of Supporting Electrolyte

To increase the conductivity of solution supporting electrolyte are being used for electro chemical oxidation of organic pollutants. Various studies have been conducted to determine the effect of types and concentrations of supporting electrolytes. Salts such as neutral salts ($NaClO_4$, Na_2SO_4, NaCl and $NaNO_3$) and reducing salts ($NaSO_3$ and $NaNO_2$) contributes to form supporting electrolytes. Literature reveals the superiority of NaCl as electrolyte specially for treating dye wastewater. The only disadvantage of using NaCl as electrolyte is generation of organochlorine compounds (RCl), which can be more recalcitrant than their parent compound. On the other hand, literature revealed that RCl could be rapidly utilized before the end of electrolysis. Additionally electrolyte will help to enhance the conductivity, helps to reduce resistance of system and also contributes to lower the energy cost of process [28-30].

CHAPTER 2

INTRODUCTION TO MIXED METAL OXIDES ELECTRODES

2.1 General Introduction:

Mixed metal oxides (MMOs) in electro chemical oxidation process are most widely used for heterogeneous catalysis. MMOs has acknowledged lot of attention as anode materials for treating waste water containing recalcitrant organic compounds using electrochemical oxidation method. MMOs have been widely used for heterogeneous catalysis [17]. A combination of different valve metal based oxides has been tested to fabricate electro catalytic coating on the working electrode. The electrodes so developed are very stable and active electrodes in multiple dimensions.

2.2 Mixed Metal Oxide Anode:

2.2.1 Bulk MMO anode:

MMO anodes are of two types bulk mixed metal oxides or supported mixed metal oxides. Bulk mixed metal oxide corresponds to MMO anode whose surface layer consist of mixed metal oxides. Bulk mixed metal oxide can be prepared using any of the following methods such as, thermo chemical decomposition, electrodepostion, chemical vapor deposition (CVD) and physical vapor deposition (PVD). Precursor solution is prepared which contain mixture of corresponding metal oxides, and this precursor solution is evenly applied onto the surface of substrate so as to get a uniform layer of mixed metal oxide. This method gives a uniform and homogeneous deposition of metal oxide layer. The MMO can be binary, ternary or quaternary system depending on the number of metal cation involved. Figure 2.1a shows the surface composition in a binary metal oxide anode system. MMO components will provide active sites for electro catalytic reactions. For removal of recalcitrant organic compounds from wastewater most commonly used bulk MMO includes Sn-Sb binary MMO anodes, Ir-Ru binary MMO anodes, Ir-Ta binary MMO anodes, Ti-Ru binary MMO anodes, Ti-Bi binary MMO anodes, Ir-Ru-Sn ternary MMO anodes, Ce-Ru-Sn ternary MMO anodes and Ru-Ir-Sn-Ti quaternary MMO anodes. Surface of solid electrodes is described on the basis of various parameters such as roughness, porosity, or thickness of MMO layer. It is really important to get complete insight regarding surface sights and internal sites and also possible reactions taking place.

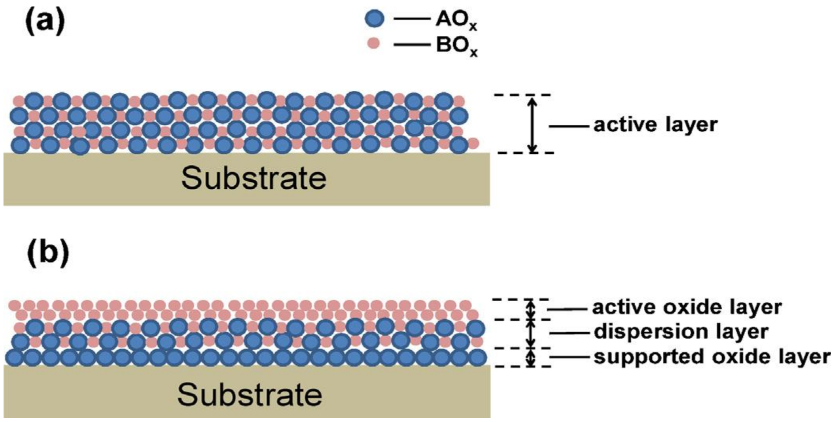


Figure 2.1Structure of MMO on substrate (a) binary MMO anode; and (b) supported MMO anode.

2.2.2 Supported MMO anode

To improve the performance as well as for prolonged service life of electrode, metal oxides are being mixed and coated in the surface layer of MMO. On the other hand sometimes this can be achieved by coating the film of active metal oxide over the supported metal oxide. The anodes prepared by above methods are termed as supported MMO anodes. A dispersion layer formed by mixing different metal oxides salts will be formed. For preparing supported metal oxide anodes the calcinations process is required which is accompanied by high temperature usually ranges from 400◦C to700◦C. Figure. 2 b represents structure of MMO on substrate.

Supported oxide layer never straightly contribute in reaction occurring at surface of anode which include oxidation of organic matter and oxygen evolution, it helps to improve the working of MMO anode by: (1) enhancing the electrocatalytic activity of the surface layer , (2) improving firmness of the surface, and thus extend the life of MMO anode, (3) increasing the conductivity and (4) provides greater active surface area and hence considerably increases rate of reaction[9-10, 18].

Table II : Function of dopants in MMO anodes. [22]

Dopant	Anode Material	Function	References
Sb(V)	SnO_2	Enhances conductivity.	22
F(-I)	SnO_2	Extend service life of electrode Catalyzes organic degradation.	
Bi(III)	PbO_2	Enhances oxidation of organic pollutants.	22
Ce(IV)	PbO_2	Improves stability.	22
La(III)	SnO_2	Catalyzes organic degradation.	22
Sb/SnO_2	TiO_2	Provides chemical and electrochemical stability, Improved electrical conductivity, Shows high potential for oxygen evolution	36
Pt	Ti/SnO_2-Sb	Helps to improve service life	36
RuO_2& IrO_2	Ti/TiO_2	Cost effective, Commercially available	37
RuO_2	Ti/TiO_2	Enhances service life of anode	38
SnO_2	Ti/TiO_2	Improves stability of coating	38

CHAPTER 3

MIXED METAL OXIDES ELECTRODES

3.1 Application of MMO’s in waste water treatment

Electrochemical treatment for wastewater can be carried out using various mixed metal oxides, but literature reveals that most of the MMOs are derivative of SnO_2, PbO_2, RuO_2 and IrO_2, and therefore present chapter provides detailed characteristics and use of these MMO electrodes.

3.1.1 SnO_2

The performance of SnO_2 is affected by modification in its structures, nature, and type of doping into the crystal lattice. The oxygen vacant sites are accountable not only for conductivity but are also responsible for determining the ratio of MO_{X+1} and MO(•OH) on the anode surface. The unoccupied locations of the crystal lattice are chemically occupied by hydroxyl radical so as to form MO_{X+1}. MO_{X+1} which converts organic matter into intermediate agents, while MO(•OH) entirely decomposes the organic matter into environmentally acceptable end products, i.e. CO_2 and H_2O. The electro catalytic activity of Ti/SnO_2 electrode is superior as compared to that of PbO_2 and RuO_2/IrO_2 MMOs. Additionally, it is relatively cheaper compared to those noble metal oxide fabricated MMO electrodes and effortless to construct [39-40].

F-block elements have vacant electron orbits and therefore used in metal oxide coating so as to favor transfer of electron from the substrate. Doping also improves electro catalytic activity of the MMO anode [40]. The property of electrode is influenced by dopant and its molar ratio. Compared with number of dopants (B, Bi, Ce, F, Fe, Gd, Ir, La, Ni, Pt, Ru, and Sb) utilized to improve the characteristics of the SnO_2, Sb has shown noteworthy impact.

Dopants such as La and Ru are beneficial in transforming the characteristics of an electrode. On doping SnO_2-Sb with La and Ru, alteration property led to the obstruction in the crystal growth and the crystallite size was reduced. The smaller crystallite size not only increases the surface area, but also increases the number of active sites on the surface of the anode [41].

3.1.2 PbO_2

PbO_2 helps in mineralization or electrochemical degradation of organics due to high O_2 overvoltage material [39, 42]. PbO_2 are of two types, Orthorhombic α- PbO_2 (brown color) and tetragonal β- PbO_2 (black color). Orthorhombic shows low resilience towards surface corrosion and tends to generate secondary pollutants Pb^{2+}, which are highly toxic in nature [42]. β- PbO_2 is a disordered close packed structure, have higher conductivity and higher over potential for oxygen evolution are highly preferred. β- PbO_2 is a non-active anode, highly conducting, chemically inert, cheaper than noble metals, and possesses high oxygen evolution over potential and high catalytic activity for the production of oxidants. This MMO can be used for direct oxidation of organic molecules on the anode surface. Thermal decomposition and electro oxidation are the techniques used for fabrication of PbO_2 electrodes [41] and

$$PbO_2 + H_2O \leftrightarrow PbO(OH)_2 \leftrightarrow H_2PbO_3 \tag{7}$$

3.1.3 Ruthenium oxide and Iridium oxide

RuO_2 and IrO_2 based anodes are active anodes, known for their electrocatalytic activity for oxygen and chlorine evolution.RuO_2 and IrO_2 are gaining more importance due to their outstanding mechanical and chemical properties which offers resistance even at extreme conditions of current density and acid media [39, 42]. IrO_2 is one of the cheapest dimensionally stable anodes and shows low chlorine and oxygen evolution over potential used in the generation of active chlorine species. Both IrO_2 -RuO_2 and -coated Ti anodes undergo dissolution in basic medium on anodization [41]. Ti/RuO_2 undergoes corrosion during electrolysis on prolonged usage. However, the service life of RuO_2 enhances on doping with Ir .The electrochemical properties of iridium ($Ti_{0.6}Ir_{0.4}O_2$/Ti) and ruthenium ($Ti_{0.6}Ru_{0.4}O_2/Ti$) oxide anodes, prepared by sol–gel method. They found that the iridium oxide shows enhanced catalytic activity for both oxygen and chlorine evolution and stability against corrosion as compared to ruthenium oxide. These electrodes provide only small range of operating potential within hydrogen and oxygen evolution reactions. It is difficult to realize the direct oxidation of variety of organics on these anodes within this potential range [41]. Hence, practical relevance of these anodes in the wastewater treatment on large scale is unacceptable. However, few research teams have successfully degraded the organic pollutants using these anodes.

The low chlorine evolution over-potential on these anodes is advantageous in the production of active chlorine species in wastewater containing chloride ions. The addition of NaCl as supporting electrolyte improves the removal efficiency, indicating that electrochemical treatment using Ti/IrO_2 and Ti/RuO_2 involves both direct and indirect oxidation [43]. Enhancement in the COD removal efficiency was observed due to oxidation mediated by electrochemically generated oxidants in the presence of chloride ions using Ti/RuO_2 anode in olive mill wastewater treatment. The degradation process involves the formation of intermediates followed by further oxidation to CO_2 and water [41].

Table III: Performance of different anodes on various pollutants.

S.No	Dye	Electrode Specifications	Operational Conditions	Performance	References
1	Alphazurine A (αzA)	Working Electrodes (Anode)- Ti/IrO_2 Pb/PbO_2 Cathode- Zirconium. Dimensions of Electrode- Square	Media- $0.5 mol Na_2SO_4$ Current Density- 30 & 60 mA/cm^2	COD Removal- 60% removal by Ti/IrO_2 & 90% removal by Pb/PbO_2 Current	4

		electrodes with 10 cm^2 surface area.		Efficiency- 3% for Ti/IrO_2 & 24% for Pb/PbO_2 Energy Consumption - for 30 mA/cm^2 is 254 KWh/m^3 for Ti/IrO_2 & 124 KWh/m^3 for Pb/PbO_2	
2	Acid Blue and Basic Brown	Working Electrodes (Anode)- Pb/PbO_2 Cathode- Austenitic Stainless Steel.	Case-1:2g/l Acid(H_2SO_4) Dye concentration- 100mg/l Temperature-25° pH- 2 Current Density- 30 mA/cm^2 Time- 30 min Case-2 : 2g/l Base(NaOH) Dye concentration- 100mg/l Temperature-25° pH- 8 Current Density- 30 mA/cm^2 Time- 30 min Case-3 : 2g/l of Salt(NaCl) Dye concentration- 100mg/l Temperature-25° pH- 3 Current Density- 30 mA/cm^2 Time- 30 min	Dye removal efficiency- For Acid Blue- 42% for H_2SO_4, 78% for NaOH, 98% for NaCl. For Basic Brown- 50% for H_2SO_4, 80% for NaOH , 98% for NaCl. COD removal efficiency- For Acid Blue- 37.5% for H_2SO_4 ,76% for NaOH, 96.5% for NaCl. For Basic Brown- 45% for H_2SO_4 ,77.5% NaOH, 97.5%	5

				NaCl.	
3	Acid Orange 7	Working Electrode BDD, Ti/IrO_2-Ta_2O_5	Media-0.035M Na_2SO_4 Current Density- 0- 160 A/m^2	COD removal- 76%	46
4	Reactive Red 195	Working Electrode Ti/SnO_2-Sb/PbO_2 Cathode- Nickle	Media- 0.1 M Na_2SO_4 Current Density- 0-40 mA/cm^2 pH- 10-13	COD removal- 48%	46
5	Acid Orange 7	Working Electrode Pt/Ti, Graphite, ACFa, ACFb, ACFc Cathode- Stainless Steel	Current Density- 3.3- 13.3 mA/cm^2 Time- 40 min	Color removal efficiency- ACFc>ACFb >ACFa> Pt/Ti> Graphite	27

CHAPTER 4

FABRICATION METHODSOF MMO ELECTRODES

4.1 Introduction

The metal oxide anodes are inexpensive and simple to construct. It is very complicated and difficult task to construct an electrode as per desired composition. To obtain thin film metal oxide coating solution phase and gas phase chemical methods are being employed. The solution phase method comprises of dip coating, spin coating, painting, spray pyrolysis, and sol–gel techniques, in which a precursor solution is needed. The gas phase methods are chemical vapor deposition (CVD) and atomic layer deposition (ALD). Electrochemical anodization and deposition method are commonly used to prepare or fabricate MMO electrodes [17].

4.1.1 Dip Coating

Dip coating is done using a precursor solution which is prepared by dissolving known quantity of metal salts in a solvent or mixture of solvents. The solution so obtained is known as precursor and is applied on the surface of a substrate using appropriate coating techniques dip coating, spin coating, or painting.

4.1.2 Spin Coating

To obtain uniform coating on a flat substrate spin coating technique is used. Generally, if surface of substrate is uneven than it is preferable to use dip coating or painting. For spin coating a process cycle of coating precursor on substrate surface followed by drying is repeated until desired thickness of coating is achieved. Annealing is carried out at the end to accomplish better morphological characteristics.

4.1.3 Spray Pyrolysis

Spray pyrolysis is an aerosol process. It is comparatively easy and economical process. In this process atomization of precursor is done followed by conversion of these droplets into solid particles by heating.

The MMO surface obtained by this process is highly dependent on the transformations undergone by the droplets. There are various factors which affects the transformation undergone by the droplets such as temperature gradient between the spraying nozzle and the substrate, the carrier gas and precursor solution flow velocity, and shape and nature of the substrate.

4.1.4 Sol- gel Method

Sol–gel method is extensively employed for preparing MMO anodes. pH and viscosity are basically two important parameters affecting coating in sol-gel method. Normally, for preparing precursor, salts are hydrolyzed by mixing them in proper media and stirring it for certain aging time. The formation of solid phase particles of the sol from hydrolyzed precursor is dependent on ageing time. Electrodes prepared at different ageing time differ in their electrochemical behavior [16].

4.1.5 Electrochemical Deposition Method

To obtain the desired thickness of metal oxide coating along with uniform film layer electrochemical decomposition method is adopted. In this method, a pretreated metal substrate is anodized in a suitable electrolytic bath. A uniform coating with desired thickness is obtained on the surface of the anodized metal. In this process, precursor salt which is dissolved in the electrolytic bath, are electrodeposited on the substrate. To obtain uniform coating of desired thickness this method is most beneficial.

4.1.6 Gas Phase Techniques

Another method for fabricating MMO is gas phase technique, but it requires sophisticated instruments and is relatively costly. In CVD method reaction chamber is maintained at optimum temperature and pressure, precursor gases are pumped into the reaction chamber and then these gases adsorb and react with the substrate to form a thin film. To obtain thin film with high uniformity this technique is being used but major drawbacks of this process are complexity of the process, high temperature, and toxic gases. However literature reveals that solution method is most preferable for fabrication of MMO electrode.

4.2 Characterization of MMO anodes

It is evident from the past studies that various characterization techniques have been introduced so as to carryout crystal studies of metal-based catalysts, in addition to compare its reaction rates quantitatively. Though, somehow there is not much development in the field of catalysis science of MMO, this is attributed due to following reasons: (1) MMO catalysts is complex in nature (e.g. they may exist in different oxidation states, simultaneous bulk and surface phases existence,) and (2) there is need to develop new techniques to determine such structural details. In present, a variety of characterization techniques have been implemented to study the physiochemical, electrochemical and crystallochemical properties of MMO anodes. These extensively practical techniques comprises of: X-Ray diffraction(XRD), Raman spectroscopy, X-ray adsorption spectroscopy (XAS),thermal gravimetric analysis (TGA), scanning electron microscopy and transmission electron microscopy (SEM and TEM), energy-dispersive X-ray spectroscopy (EDS), cyclic voltammeter (CV),scanning electrochemical microscopy (SECM), electrochemical impedance spectroscopy (EIS), UV–vis diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and Fourier-transform infrared (FTIR) spectroscopy [16].

XRD examines the crystal phase and it gives complete structural phase analysis of the surface of MMO anode coatings. Since the metal oxides can be mixed or laid in different manners, the XRD patterns of MMO anodes compared to that of single component metal oxide differs in various ways. However in supported metal oxide systems, the surface layer behaves as electro-catalytic active layer and its XRD pattern is not influenced by the property of the inner layer, which shows perfect and identical surface crystal structure.

On the other hand, in MMO, XRD pattern is influenced by the presence of metal oxides in surface layer as (1) supplementary diffraction peaks may appear due to formation of new crystal phase and (2) visible difference on the half-width and intensity of diffraction peaks, due to the expansion of metal oxide lattice through incorporation of other elements.

XPS is a method used to determine the oxidation states and quantitative atomic composition of surface elements. XPS makes it mainly helpful to study the doped MMO anodes. In MMO anodes, the binding energy peaks of O1s include two parts: the main peak with lower binding energy value (∼530 eV) is attributed to the lattice oxygen, while the peak with high binding energy value (531–532 eV) is believed to be the adsorbed oxygen. For MMO anodes, dopants are usually in their highest oxidation states, but there are exceptions if the MMO anodes are calcined at low temperatures or the dopants are at high doping level [21].

EIS is a method for the characterization of electrochemical systems. Electrochemical impedance is usually measured by applying a small AC amplitude sinusoidal potential to the system and measuring the response current. The response current will be a sine wave at the same frequency but its phase shifted. Therefore by varying the frequency of signal, the impedance of the system can be determined as a function of frequency.

TGA analysis is done to so as to obtain exact physical and chemical changes of the precursor solution during pyrolysis. In case of precursors containing single metal chloride, initial mass losses took place between0 and 200◦C, followed by sharp mass losses at 400◦C. They were attributed to the evaporation of solvent and decomposition of chloride ions respectively. A thermal curve obtained for the three mixed metal chlorides showed a similar behavioral pattern to that of single metal chloride, indicating that polymerization occurred between the three mixed metals.

4.3 Recent Developments in MMO’S

4.3.1 Deposits with nano- and microstructure

Literature reveals that MMO anodes with nano structured deposits have drawn a lot of attention in the recent past. The foremost objective of utilizing nano structure in MMO is to increase its surface area along with enhancement of its reaction rate. It is reported that the anodic oxidation of Ti substrate to get vertically aligned TiO_2 -NTs. They can serve as the tubular template where in metal oxides are implanted aiming to have improved loading capacity of Ti substrate. The mean pore diameters of the TiO_2-NTs range between 100 and 220 nm, according to the different anodization condition. PbO_2 is reported to be directly deposited into the TiO_2-NTs by pulse electro-deposition and photoelectron deposition.

4.3.2 Doped MMO anodes

Past study reveals that, various efforts have been made to develop doped MMO electrodes so as to obtain improved characteristics (e.g. electrocatalytic activity, photo electrocatalytic activity, corrosion resistance and conductivity) or desired properties (e.g. hydrophilic–hydrophobic properties). The doped components, or dopants, can be simply introduced to MMO anodes by including dopant ions into the precursor solution or electro-deposition bath, or by more complicated methods (e.g. grafting). It is evident that the performance of the MMO doped anodes is significantly enhanced after doping. It depends on the type and characteristics of dopants that to which extent it can improve the property of anode material. Furthermore, the extent of dopants and doping conditions are equally important and it also affects the physicochemical property and oxidation performance of MMO anode.

Fluoride ions are non-metallic dopants that have been widely used to improve the conductivity of SnO_2or improve the adhesion and stability of PbO_2. In Ti/PbO_2-Co-F MMO anode, the fluoride ions are found to inhibit the incorporation of Co into the surface film. Ti/Ni-Sb-SnO2anode with fluorine doped tin oxide (FTO) interlayer, and the ser-vice lifetime of the modified MMO anode was improved by a factor of 6. Bi(III)-doped MMO anodes are very practical for catalyzing the oxidation of organic compounds.

4.3.3 Polymer composites

Polymers are additional type of material which are utilized to initiator improve specific properties of MMO anodes. Polypyrrole and PbO_2 were co-electrodeposited on Ti/SnO_2/PbO_2 substrate, and the modified electrode had hydrophobic surface, which demonstrates a significant improvement in oxidizing hydrophobic organic compounds due to the strong hydrophobic interaction between the electrode surface and organic substrates described a novel PbO_2 electrode with electrodeposited poly tetra fluoro ethylene (PTFE) layer, and it is found to have a good resistance to corrosion and excellent electro-catalytic activity to degrade nitrophenol. The

PTFE customized MMO anodes are accounted to be competent to display complete electrochemical oxidation of some organic pollutants. On the whole, MMO anodes with deposited polymer composites are considered to have hydrophobic property and they are capable for degrading recalcitrant organic compounds by electrochemical oxidation.

CHAPTER 5

EXPERIMENTAL WORK

Phase- I

5.1 Materials and Methods

5.1.1 Chemicals

Reactive Red 2 dye was used as a model pollutant. The dye was received as a free sample from Vatva GIDC. Sodium chloride (NaCl) was used as supporting electrolyte. The combinations of various metal salts were used in different proportion for making MMO electrodes. Ce- 4D electrode was used as working electrode, which was combination of Cerium, Ruthenium, Tin and Antimony. So the respective metal salts were taken according to their calculated proportion.

5.1.2 Experimental Set-up

The experiments were conducted using Ce- 4D ($Ti/CeO-RuO_2-SnO_2-Sb_2O_5$) DSA (Dimensionally Stable Anode) type electrode was made by applying respective coating of mixed metal oxides over Titanium substrate. Stainless Steel (SS 304) was used as cathode. The distance between anode and cathode was kept 8 mm. A constant DC Power supply was used (Aplab India, LD-3205).

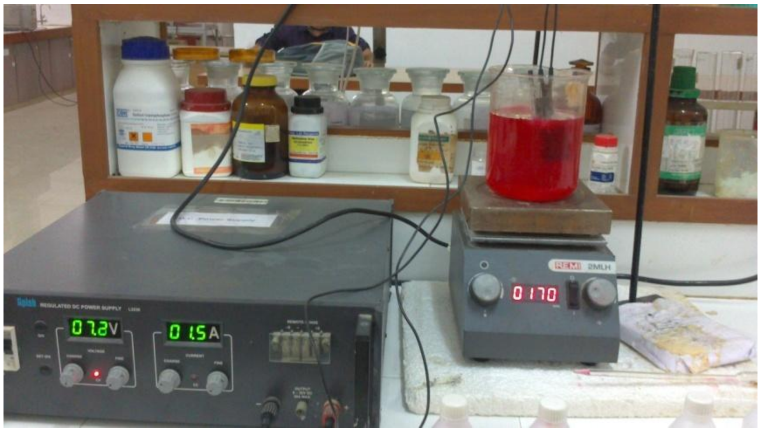


Figure 5.1 Experimental set-up

5.1.3 Electrode Fabrication Method

Ti/ CeO-RuO_2-Sb_2O_5-SnO_2 MMO electrode was used as working electrode and it was fabricated by thermal decomposition method. Titanium metal piece (50mm x 75mm x 3mm) was polished with sand paper. After polishing it was then etched with 10% Oxalic acid solution at 80°C for about 1 hour. Etching helped to remove all the impurities from the surface and pores of titanium metal piece. Precursor solution was prepared by dissolving 1.863gm of $CeCl_3.7H_2O$, 0.169gm of $RuCl_3H_2O$, 0.114 gm of $SbCl_3$, 1.052 gm of $SnCl_4.5H_2O$ in a solvent consisting of 10mL isopropanol and 0.5mL hydrochloric acid(HCl). Precursor solution was then applied to the pretreated titanium metal piece with the help of brush. It is then put into hot air oven at 100°C for about 5min so as to allow the propanol to vaporize and after that it is kept in muffle furnace at 550°C for the next 5 min. The same procedure was repeated for about 8 to 10 times to get proper and uniform coating of mixed metal oxide. After final coating the electrode was kept in muffle furnace at 550°C for 60 min. It is then placed into desiccators so that its temperature falls slowly and uniformly to room temperature.

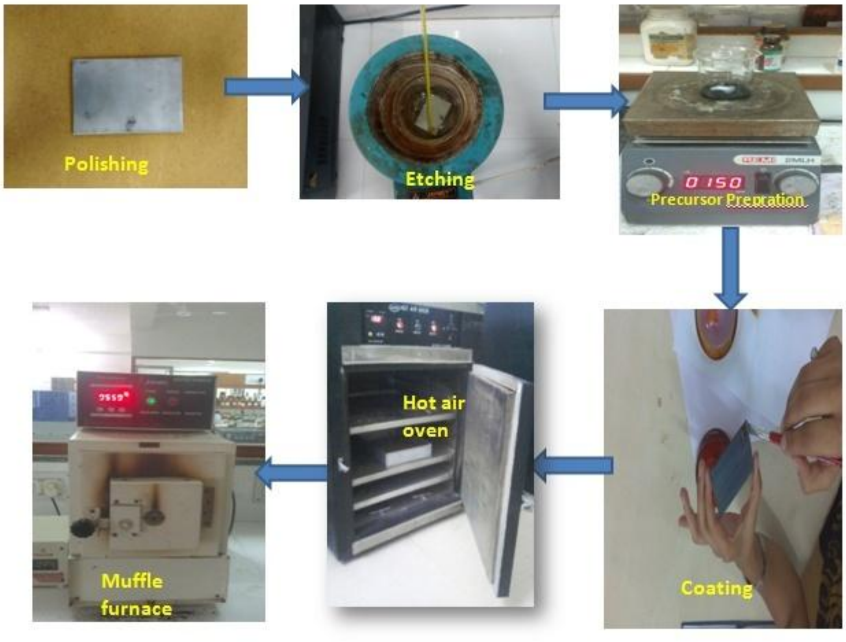


Figure 5.2 Procedure for preparing MMO electrode

5.2 Methodology

Experiments were conducted at a concentration of 200ppm of Reactive Red 2 dye. Operating parameters such as pH, salt concentration and current density were varied so as to obtain the best optimized condition for carrying out further experiments. Various experiments have been carried out by changing the operating parameters to determine its effect on the efficiency of Ce-4D electrode. The results were generated in terms of % TOC removal and % color removal.

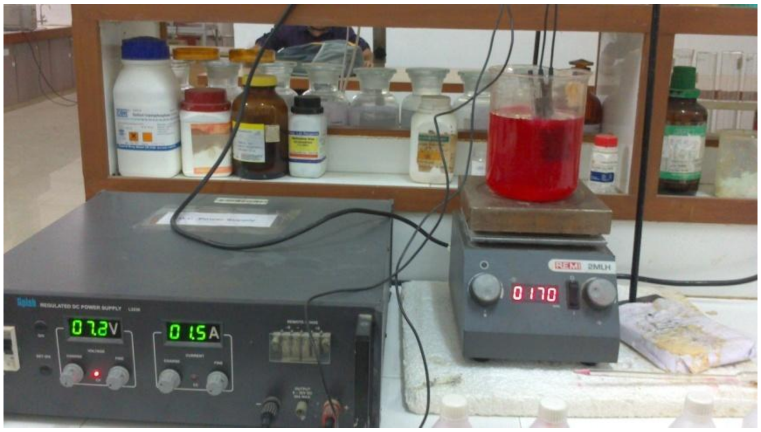


Figure 5.3 Experimental Setup.

5.3 Calculations

Color removal was measured from the initial concentration and dye concentrations at time t (A_0 and A_f respectively) by measuring the absorbance at the visible maximum dye absorption wavelength

$$\%Decolorization = \frac{A_0 - A_f}{A_0} \tag{8}$$

The UV scans of the samples were done using UV-visible spectrophotometer at 200 nm to 800 nm.

The removal of organic matter was measured from TOC measurements as follow

$$\%\text{ TOC removal } = \frac{TOC_0 - TOC_f}{TOC_0} \tag{9}$$

Where, TOC_0 corresponds to the initial value and TOC_f is the value at time t. TOC was measured by TOC Analyzer TOC-$V_{CPH/CPN}$ supplied by Shimadzu Corporation.

5.4 Observations

Table IV: Effect of various operating parameters on Ti/ CeO-RuO_2-Sb_2O_5-SnO_2 MMO electrode.

S.No	Salt Concentration g/l (NaCl)	Current Density (mA/cm^2)	Current (A)	pH	% TOC Removal	% Color Reduction
1	2	20	0.7	7.2	32.51	99.36
2	2	40	1.4	7.31	51.5	99.3
3	2	60	2.1	7.21	32.73	99.46
4	4	20	0.7	7.22	20.61	99.36
5	4	40	1.4	3.08	34.8	99.69
6	4	40	1.4	7	40.33	99.96
7	4	40	1.4	11	37.89	96.63
8	4	60	2.1	7.4	52.78	99.99
9	6	20	0.7	7.32	13.88	97.44
10	6	40	1.4	7.58	16.89	99.13
11	6	60	2.1	7.38	34.71	98.86

5.4 Results and Discussions

5.4.1 Effect of Current Density on TOC reduction

It is evident from the given results that current density plays an important role for the removal of Total Organic Carbon (TOC). Figure 5.4 shows the %TOC removal at different current densities, with constant salt concentration of 2 g/l and pH 7. Result shows that at constant salt concentration of 2 g/l the current density 40 mA/cm^2 gives 57% TOC reduction.

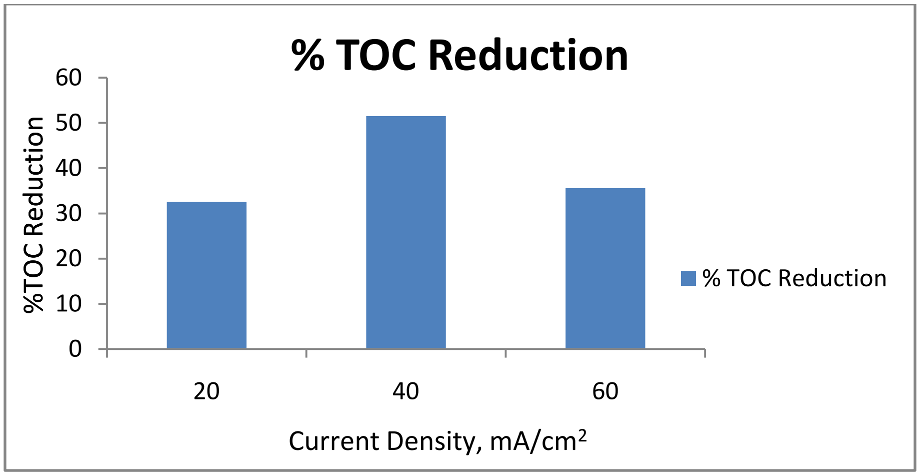


Figure. 5.4 Current Density vs % TOC Reduction at 2g/l salt concentration

The experiments were also conducted at constant salt concentration of 4 g/l, pH 7 and by varying the current densities. Figure 5.5 shows that as the current density increase the % TOC reduction also increases by keeping all other parameters like pH and salt concentration constant.

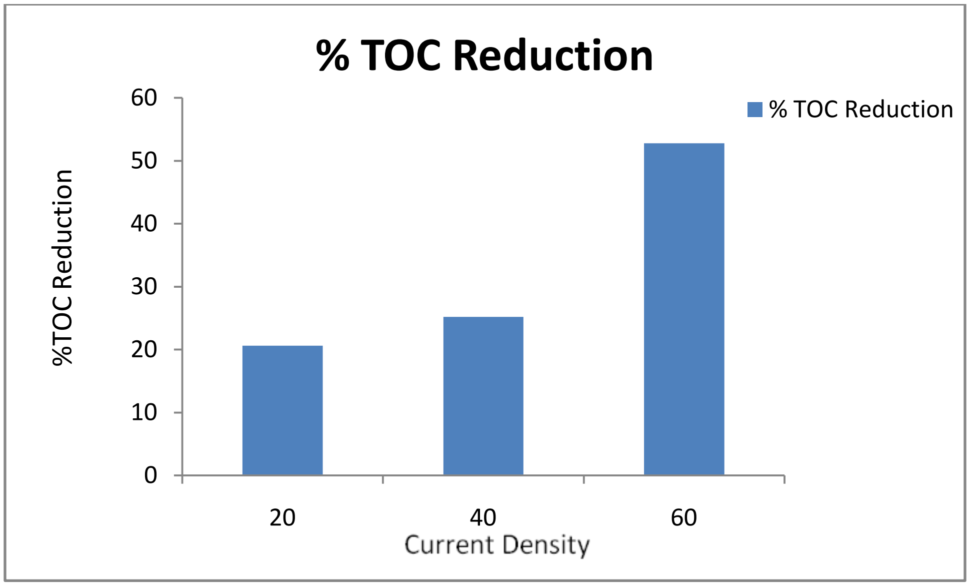


Fig.5.5 Current Density vs % TOC Reduction at 4g/l salt concentration

At constant salt concentration of 6g/l and pH of 7 when the current densities are changed, trend shown in Figure.5.6 was observed for % TOC removal.

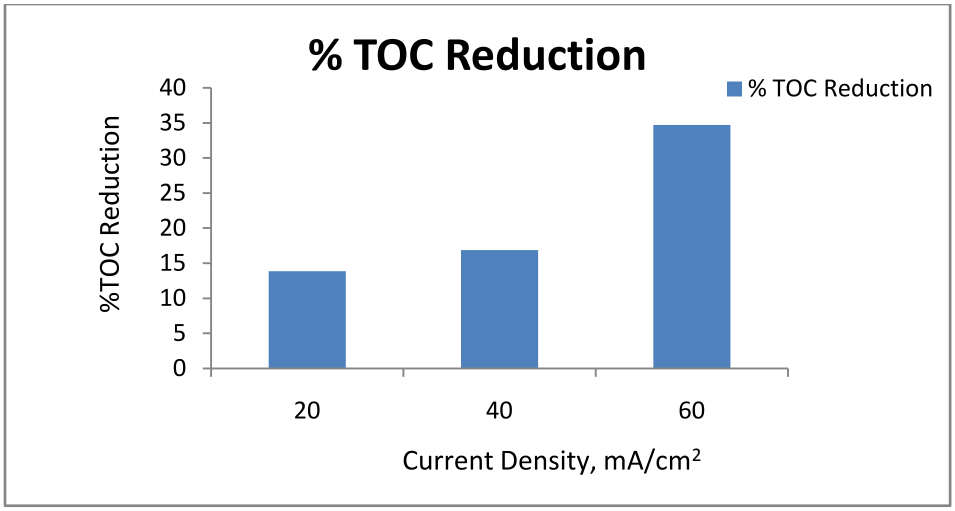


Figure. 5.6 Current Density vs % TOC Reduction at 6g/l salt concentration

5.4.2 Effect of pH on % TOC reduction

pH also plays an important role as operational parameter in electrochemical oxidation process. The effect of pH generally varies on the basis of type of pollutant required to be treated. Fig.5.6 shows the effect of pH on TOC reduction at constant current density and salt concentration. It can be concluded from the given results of Figure 5.7 that at pH 7, 41% of TOC removal of RR 2 dye was achieved.

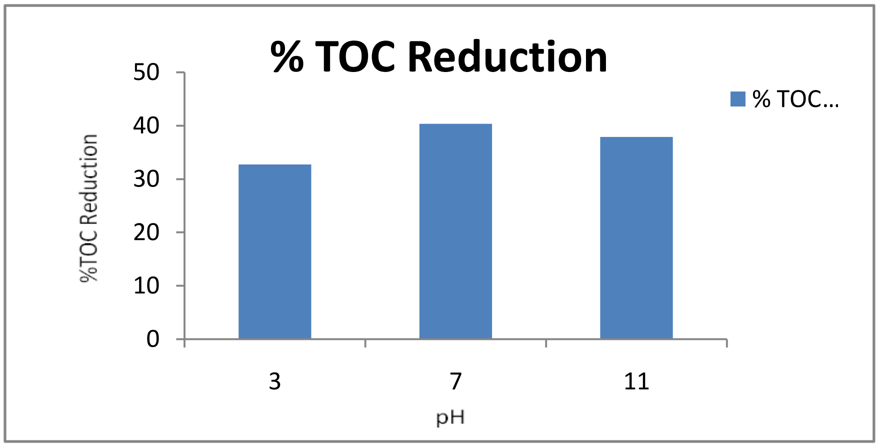


Figure .5.7 pH vs % TOC Reduction

5.4.3 Effect of Salt Concentration

Experiments were also conducted at different salt concentration to determine the effect of salt concentration on TOC reduction. Figure.5.8 shows the % reduction of TOC at different salt concentration.

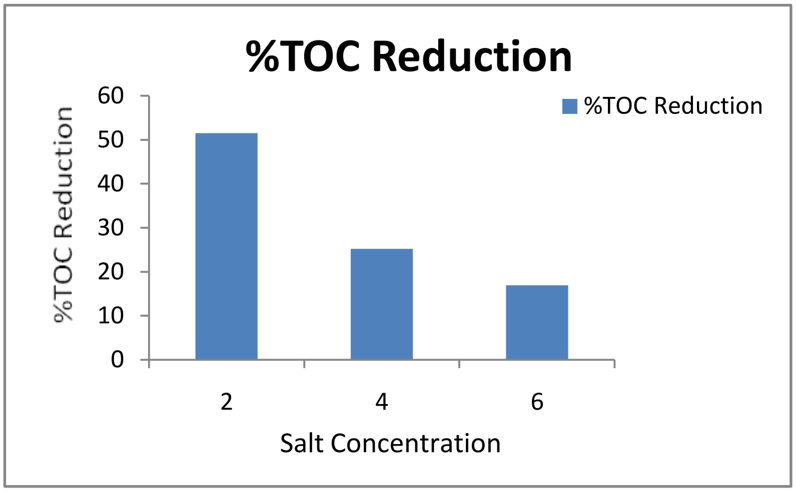


Figure.5.8 Salt Concentration vs %TOC Reduction

5.4.4 Effect of Current Density on Color Removal

Current density plays a vital role in removal of dye by electrochemical oxidation method. Increase in current density increases the removal or degradation efficiency of dye from the wastewater through electrochemical oxidation method. Figure.5.9 shows that 99.48% color removal was achieved at current density of 60mA/cm^2.

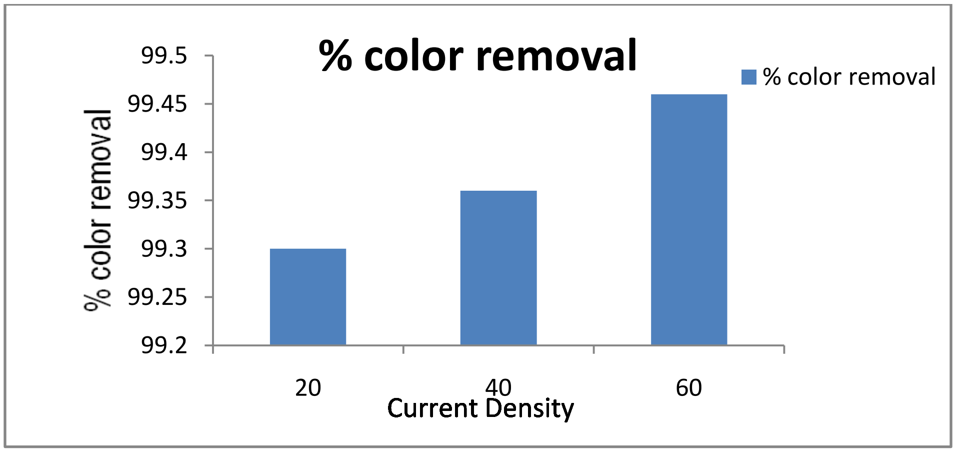


Figure.5.9 Current Density vs % Color Removal

5.5 Conclusions

On the basis of results of the experiments it can be concluded that color removal efficiency of Reactive Red 2 by electrochemical oxidation method increases with the increase in current density. It is also noticeable that pH 7 gives best result for Reactive Red 2 dye. TOC reduction with reference to constant salt concentration shows that as current density increases TOC reduction potential also increases.

Phase- II

5.6 Materials and Methods

5.6.1 Chemicals

Reactive Red2 and Reactive Red195 dye were used as model pollutants. The dyes were procured from GIDC Vatva. Sodium chloride was used as supporting electrolyte. In phase II of the study, four different MMOs have been used for which their respective metal salts such as Nickel Chloride Hexahydrate ($NiCl_{2.}6H_2O$), Ruthenium trichloride ($RuCl_3xH_2O$), Antimony Chloride ($SbCl_3$), Tinchloride pentahydrate ($SnCl_4.5H_2O$) were purchased from respective vendor and used without further purification. Isopropanol (99.8% CDH) and hydrochloric acid (37% CDH) were used as solvents to prepare the precursor solution.

5.6.2 Experimental Set-up

All the experiments were conducted in the laboratory unit of 1L capacity. Experiments were conducted using four different electrodes and two different dyes. MMO electrode was made by applying respective coating of mixed metal oxide over titanium substrate and it was used as a DSA type anode, Stainless Steel (SS 304) is used as cathode. The distance between anode and cathode was 8 mm. A constant DC Power supply was applied (Aplab India, LD-3205). All the four electrodes were fabricated using thermal decomposition method as discussed in Phase I.

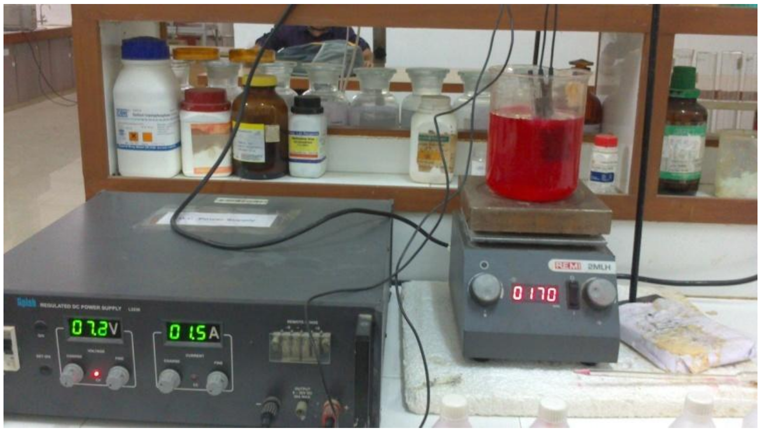


Figure.5.10 Experimental set-up

5.6.3 Methodology

All the experiments were conducted at optimized conditions obtained from Phase I of this study, salt concentration of 4g/L, pH of 7, and current density of $40mA/cm^2$. For RR195 experiments were conducted at pH 3, 7 and 11 to obtain the optimized condition of pH for RR195. The dye concentration was maintained at 200 ppm.

5.7 Observations

Table V: Comparison of various electrodes for mineralization of RR2 and RR195

S.No	Dye Used	Electrode Used	pH	%Color Removal	%TOC Removal	%COD Removal	Remarks
1	RR2	$Ti/NiO-RuO_2-SnO_2-Sb_2O_5$	7	100	69.08	84.48	No sludge

2	RR2	Ti/CeO-RuO_2-SnO_2-Sb_2O_5	7	100	63.79	83.36	No sludge
3	RR2	Ti/CeO- RuO_2	7	99.93	59.89	32.78	Minimum amount of sludge
4	RR2	Ti/Sn-Sb	7	100	42.47	23.33	Minimum amount of sludge
5	RR195	Ti/NiO-RuO_2-SnO_2-Sb_2O_5	7	100	42.47	84	No Sludge
6	RR195	Ti/NiO-RuO_2-SnO_2-Sb_2O_5	3	100	21.57	22.08	Sludge formation was observed
7	RR195	Ti/NiO-RuO_2-SnO_2-Sb_2O_5	11	100	17.75	11.66	Large quantity of sludge is produced
8	RR195 (without salt)	Ti/NiO-RuO_2-SnO_2-Sb_2O_5	7	26.83	44.6	22	Sludge formation was observed and high voltage was needed to maintain constant current.
9	RR195	Ti/CeO-RuO_2-SnO_2-Sb_2O_5	7	100	26.83	45	No Sludge
10	RR195	Ti/CeO- RuO_2	7	99.66	24.11	38	Minimum amount of sludge generated
11	RR195	Ti/Sn-Sb	7	25.34	30.41	25	Sludge formation was observed after 10 min

5.8 Results and Discussions

5.8.1 Treatment performance of Ti/NiO- RuO_2-SnO_2-Sb_2O_5

The effect of using Ti/Ni-4D electrode for degradation and mineralization of synthetic wastewater containing RR2 and RR195 dye respectively is analyzed in terms of color removal, %TOC removal and %COD removal.

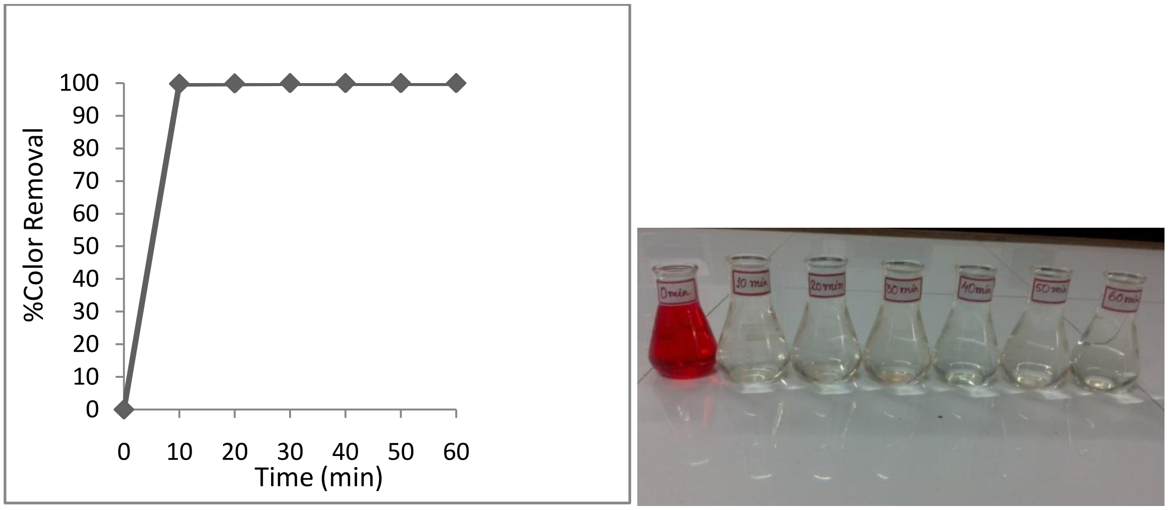


Figure 5.8.1 a Effect on color removal of RR2 wrt time using Ti/NiO- RuO_2-SnO_2-Sb_2O_5

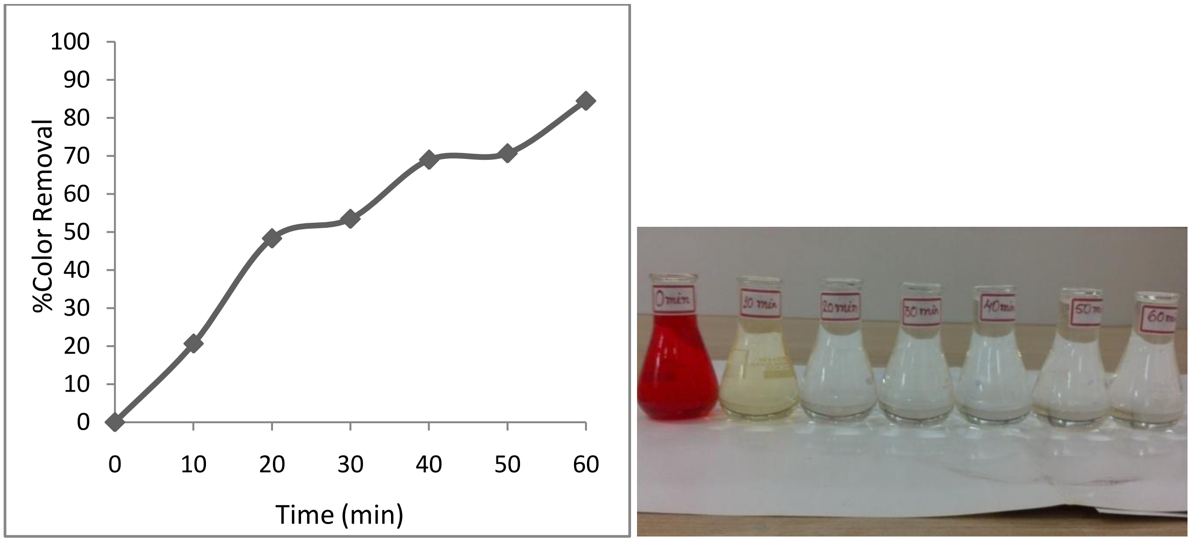


Figure 5.8.1 b Effect of color removal on RR195 uaing Ti/NiO- RuO_2-SnO_2-Sb_2O_5

Figure 5.8.1 a and b represents performance of Ti/Ni-4D electrode on color removal of RR2 and RR195 respectively. Figure depicts that almost 100% color is removed in both the cases.

However in case of RR2 100% color removal is achieved only on 10 min whereas it took almost 60min in case of RR195 for complete color removal.

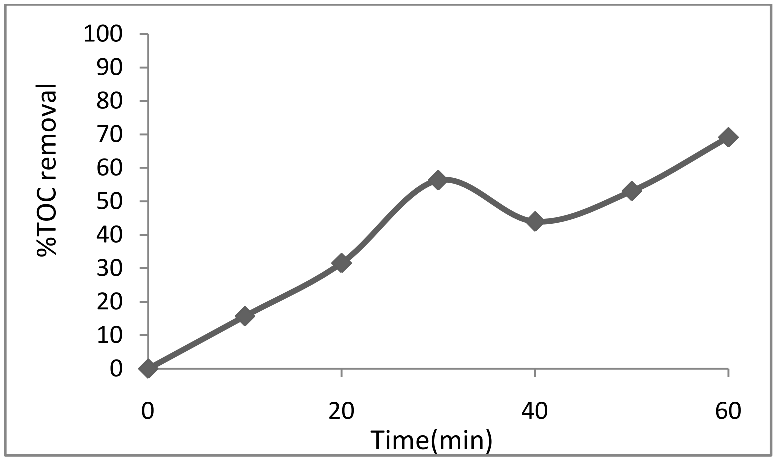


Figure 5.8.1c %TOC removal for RR2 using Ti/NiO- RuO_2-SnO_2-Sb_2O_5

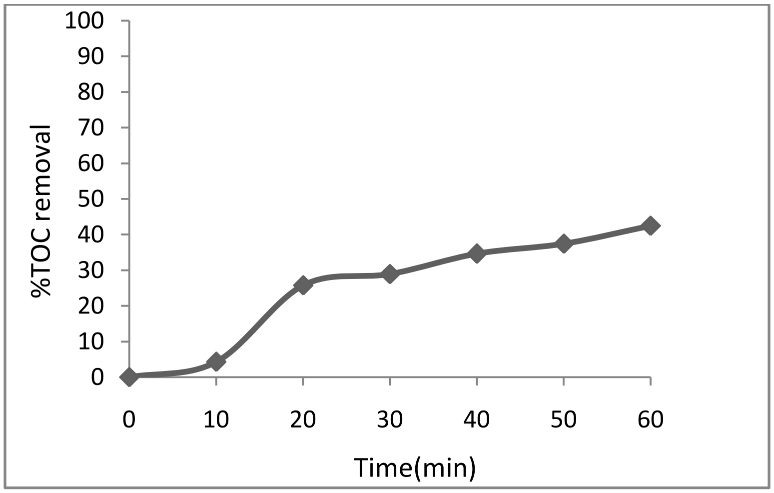


Figure 5.8.1 d % TOC removal for RR195 using Ti/NiO- RuO_2-SnO_2-Sb_2O_5

The above figure 5.8.1 c and d represents the performance assessment of Ti/Ni-4D electrode for RR2 and RR195 in terms of % TOC removal respectively. It can be observed from above graph that in case of RR2 dye %TOC removal is 38.52% higher than that of RR195 dye.

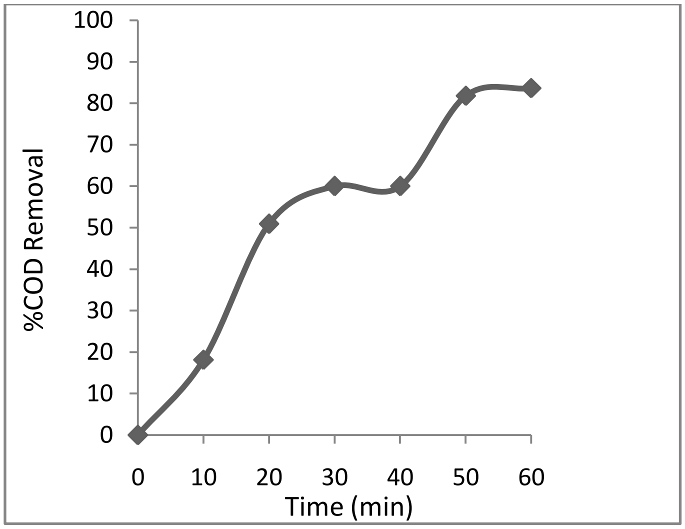


Figure 5.8.1 e %COD removal in RR2 using Ti/NiO- RuO_2-SnO_2-Sb_2O_5

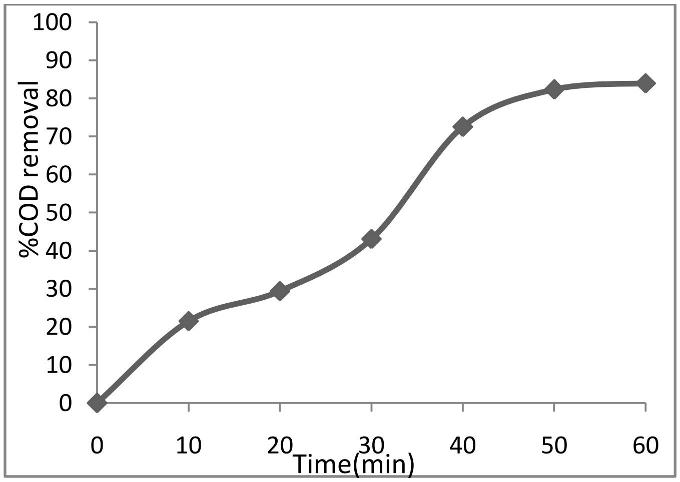


Figure5.8.1 f %COD removal in RR195 using Ti/NiO- RuO_2-SnO_2-Sb_2O_5

The above figure 5.8.1e and f represent the performance of Ti/Ni-4D electrode in terms of COD removal for RR2 and RR195 respectively. It can be observed from the graph that for both the dyes Ti/Ni-4D gives almost similar COD reduction.

5.8.2 Treatment performance of Ti/CeO-RuO_2-SnO_2-Sb_2O_5

The effect of using Ti/Ce-4D electrode for degradation and mineralization of synthetic wastewater containing RR2 and RR195 dye respectively is analyzed in terms of color removal, %TOC removal and %COD removal. Figure 5.8.2 a and b represents % color removal for both the dye RR2 and RR195 respectively and it can be observed that in both the cases almost complete color removal is achieved at the end of experiment.

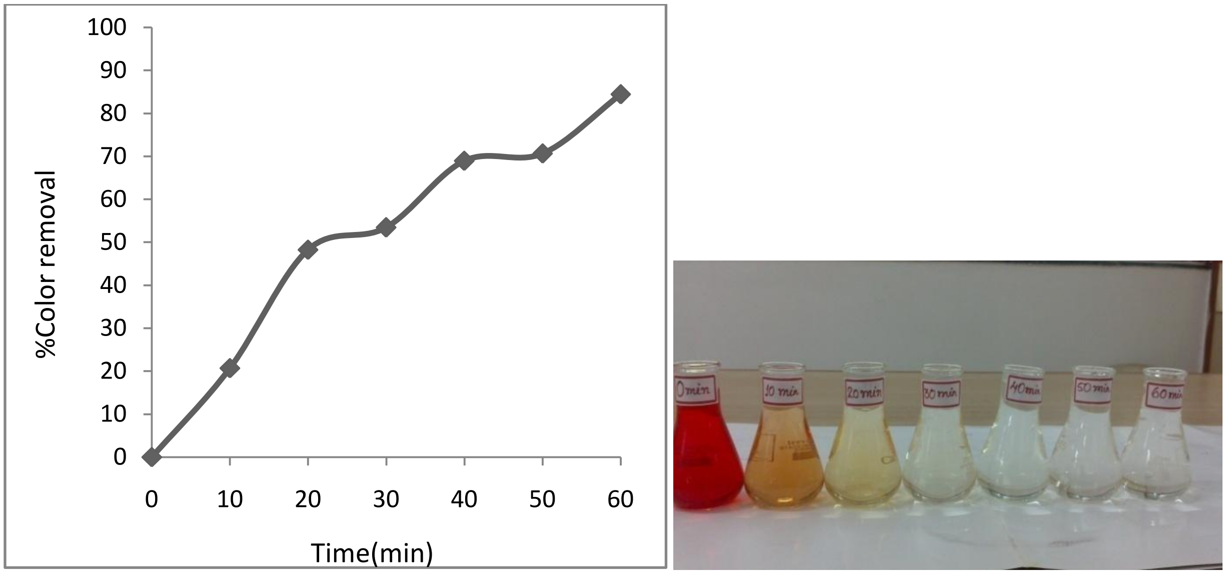


Figure 5.8.2 a %Color removal on RR2 using Ti/CeO-RuO$_2$-SnO$_2$-Sb$_2$O$_5$

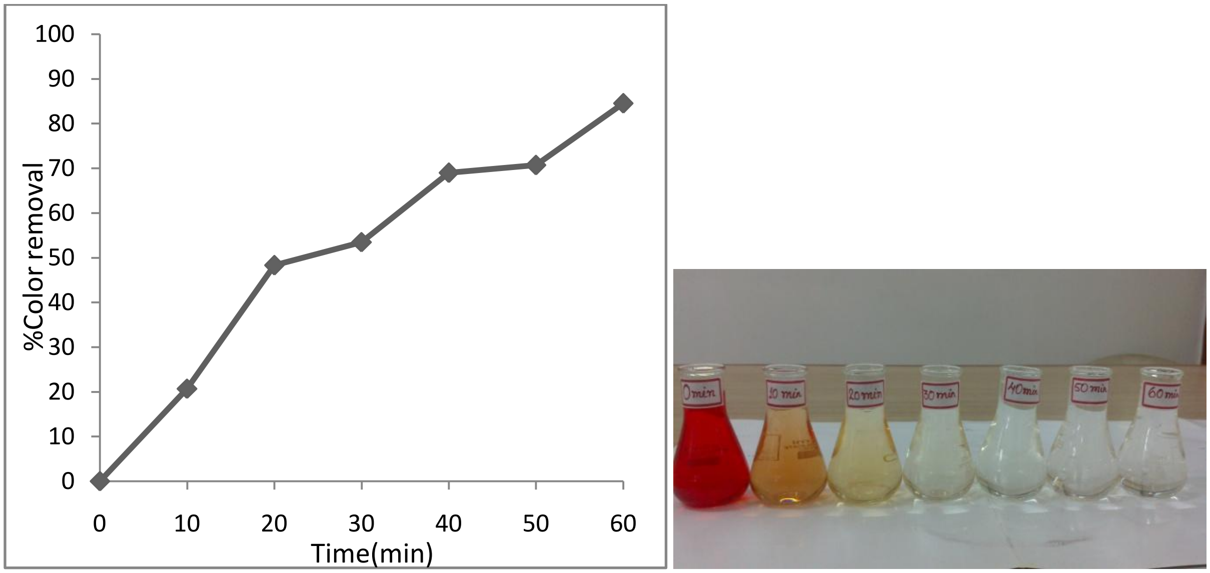


Figure 5.8.2 b %Color removal on RR195 using Ti/CeO-RuO$_2$-SnO$_2$-Sb$_2$O$_5$

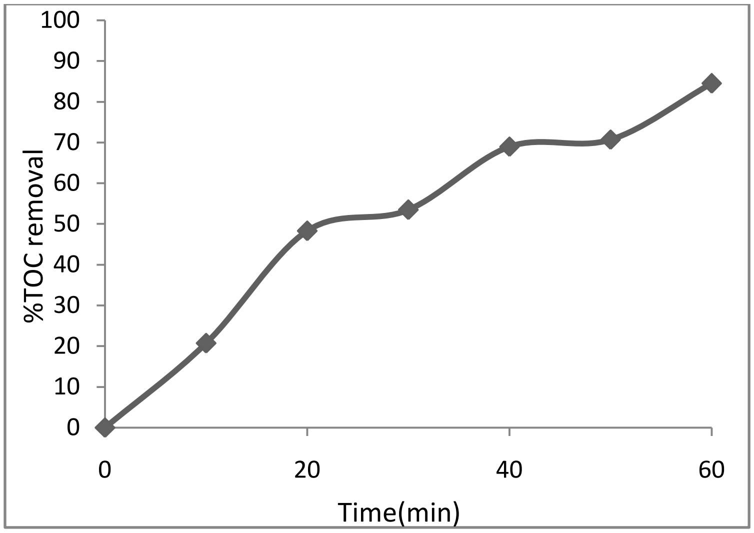


Figure 5.8.2c %TOC removal for RR2 using Ti/CeO-RuO$_2$-SnO$_2$-Sb$_2$O$_5$

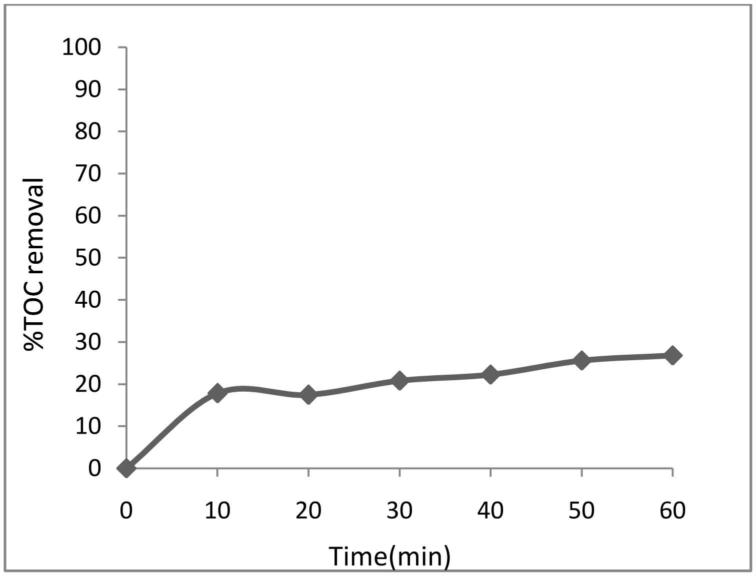


Figure 5.8.2 d %TOC removal for RR195 using Ti/CeO-RuO$_2$-SnO$_2$-Sb$_2$O$_5$

From the above figure 5.8.2 c and d it can easily be seen that in case of RR2 dye %TOC removal is 46.19% higher than that of RR195. Ti/Ce-4D electrode gives better TOC removal for RR2 dye as compared to RR195 dye. Also, additional sludge is noticed in case of RR195 dye, whereas in case of RR2 dye no such sludge is found.

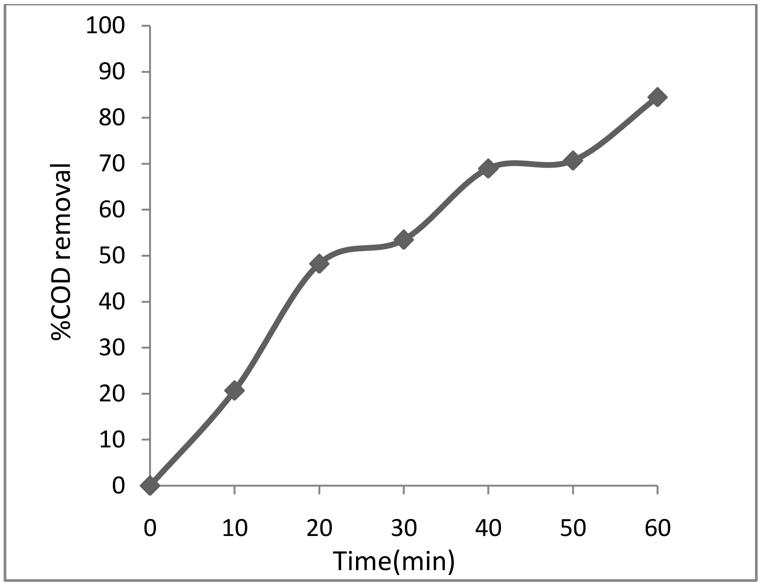


Figure 5.8.2 e % COD removal vs time for RR2 using Ti/CeO-RuO_2-SnO_2-Sb_2O_5

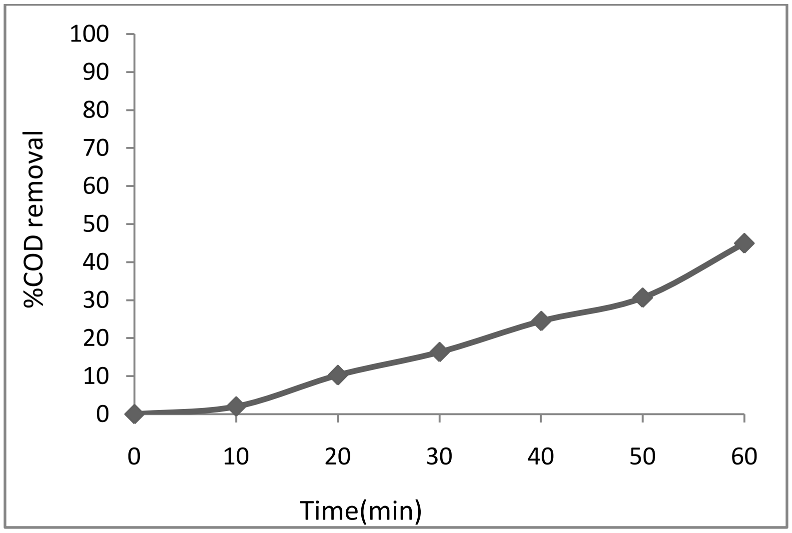


Figure5.8.2 f %COD removal for RR195 using Ti/CeO-RuO_2-SnO_2-Sb_2O_5

Above figure 5.2.8 e and f shows the performance assessment of Ti/Ce-4D for mineralization of dye in terms of %COD removal for both the dyes RR2 and RR195 respectively. It can be observed from the above graph that in case of RR2 the %COD removal was 46.19% higher than that of RR195. In case of RR195 sludge formation was also observed where as no such sludge was noticed in case of RR2.

5.8.3Treatment performance of Ti/SnO_2-Sb_2O_5

The performance assessment of Ti/Sn-Sb electrode for mineralization of RR2 and RR195 was analyzed in terms of %color removal, %TOC removal and %COD removal. As shown in Figure 5.3.8 a and b the color removal for RR2 was 100% at the end of 10 min whereas for RR195 only 25% color is removed at the end of 60 min using this MMO electrode. But in both the cases sludge formation was an additional issue accompanied with this electrode.

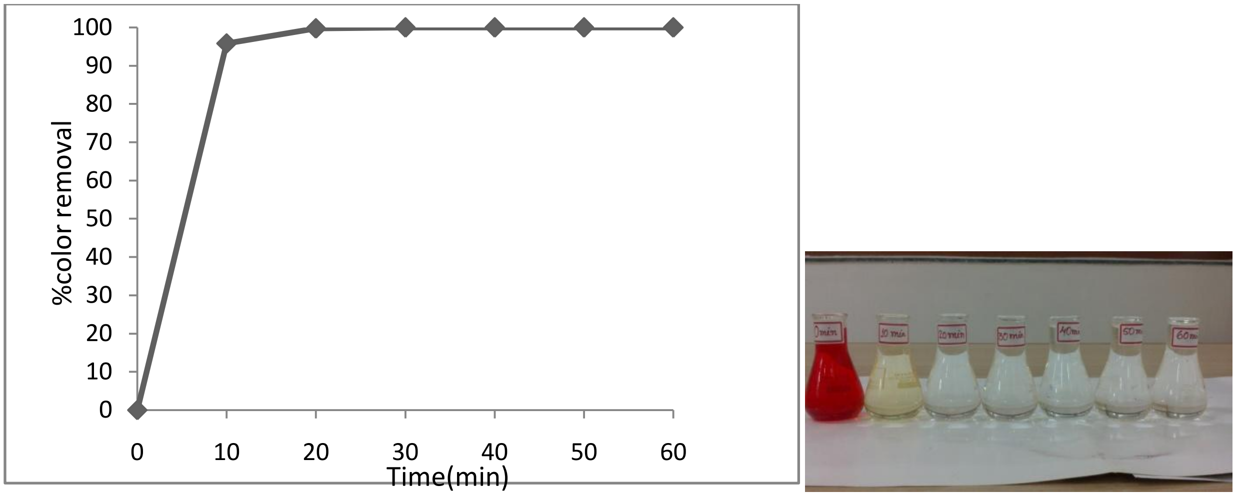


Figure 5.8.3a %color removal for RR 2 using Ti/SnO_2-Sb_2O_5

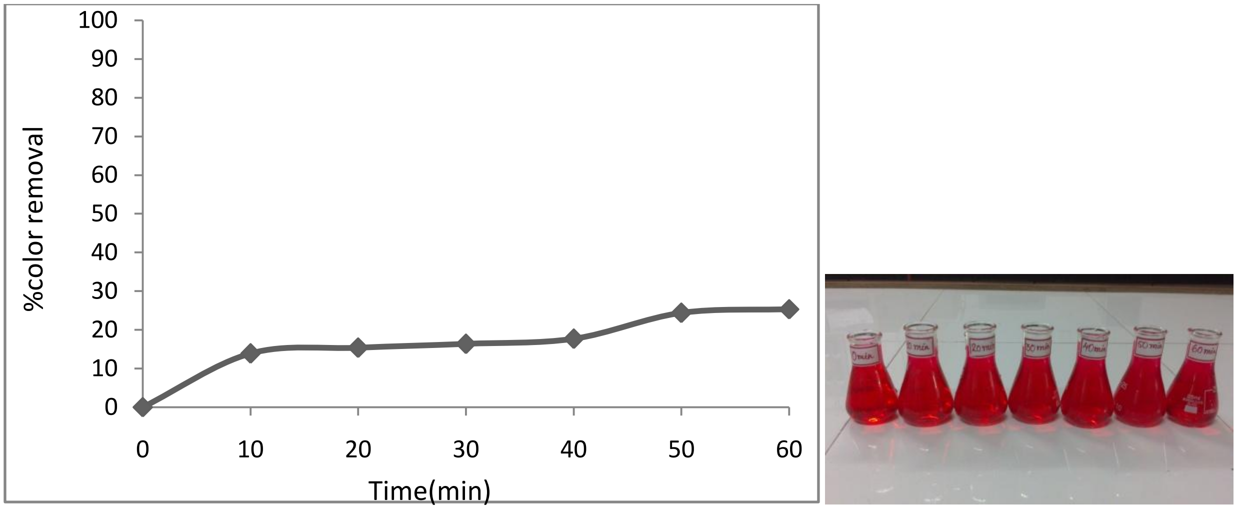


Figure 5.8.3b % color removal for RR195 using Ti/SnO_2-Sb_2O_5

Figure 5.8.3 c and d represents the % TOC removal for RR2 and RR195 respectively using Ti/Sn-Sb electrode. It was observed that % TOC removal was 29% higher in case of RR2 dye than that of RR195 dye.

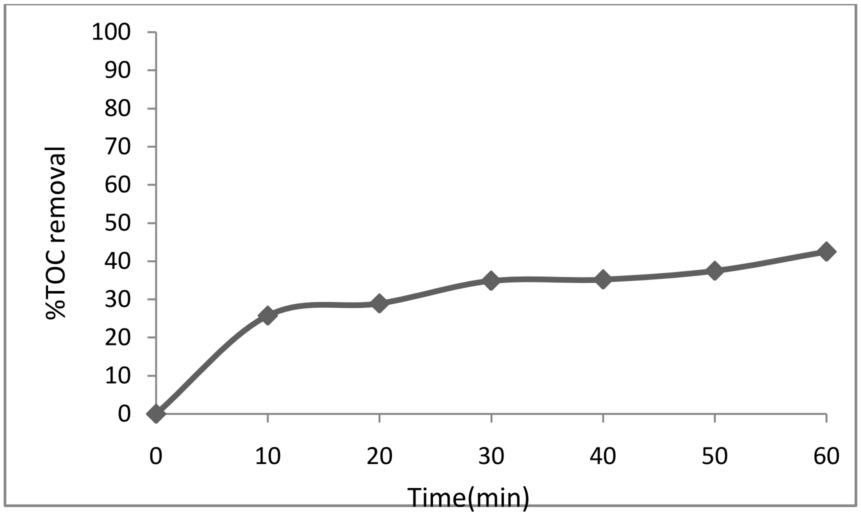


Figure 5.8.3 c %TOC removal for RR2 using Ti/SnO_2-Sb_2O_5

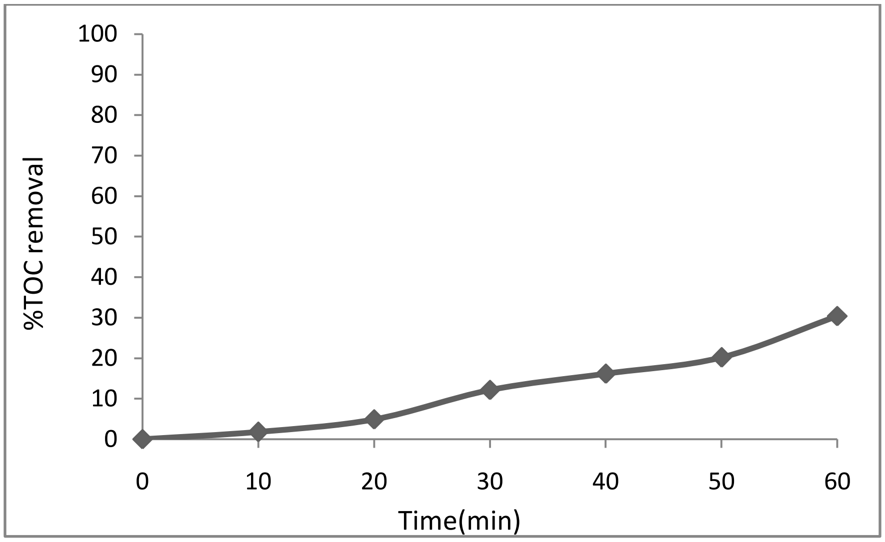


Figure 5.8.3 d %TOC removal for RR195 using Ti/SnO_2-Sb_2O_5

As shown in figure 5.8.3 e and f % COD removal was almost similar for both the dyes. Almost 25% COD removal was obtained using this MMO as electrode. The major issue related to RR195 dye was sludge generation, as good quantity of sludge is generated in this process.

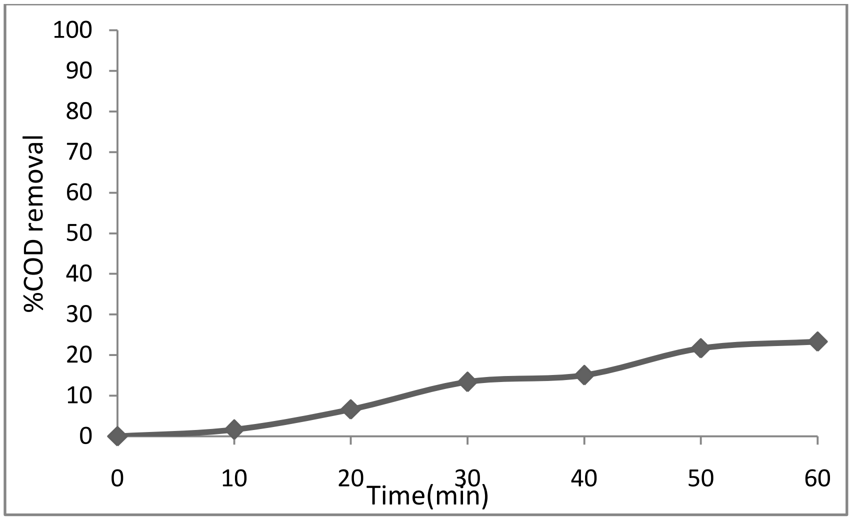


Figure 5.8.3 e %COD removal for RR2 using Ti/SnO_2-Sb_2O_5

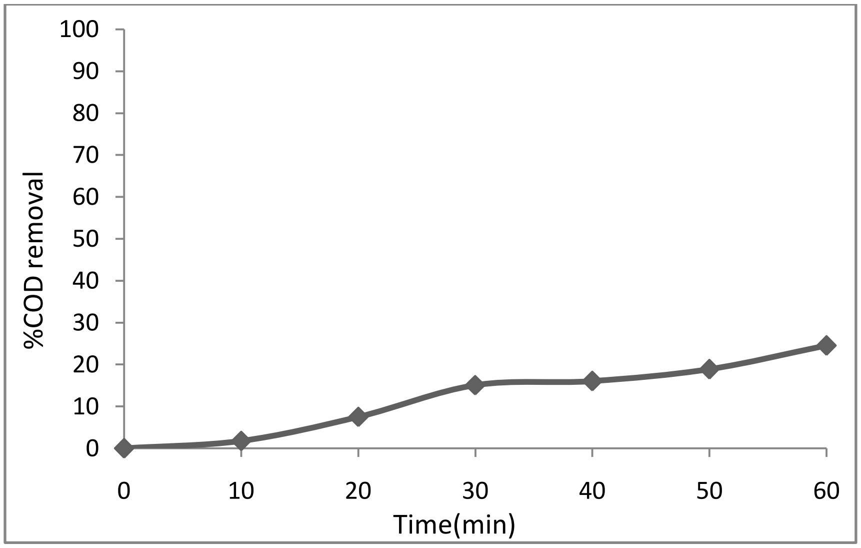


Figure 5.8.3 f %COD removal for RR195 using Ti/SnO_2-Sb_2O_5

5.8.4 Treatment Performance of Ti/Ceo-RuO_2

Ti/Ce-2D is a mixed metal oxide of Cerium and Ruthenium coated on Titanium substrate. The performance of this MMO was analyzed on the basis of % color removal, % TOC removal, %COD removal. Minimum amount of sludge generation was noticed for both the dyes. As shown in figure 5.3.8 a and b almost 100% color removal is achieved in both the cases but in case of RR2 almost 99% color removal is achieved in 30 min only whereas in case of RR195 it takes complete 60 min to achieve 99% color removal.

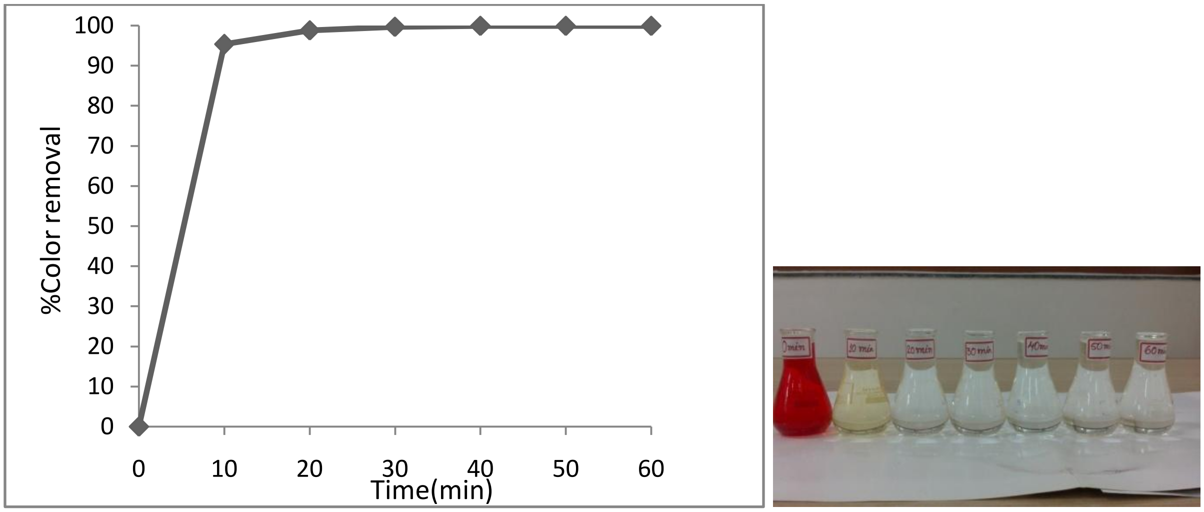


Figure5.8.4a % Color removal for RR2 using Ti/Ceo-RuO$_2$

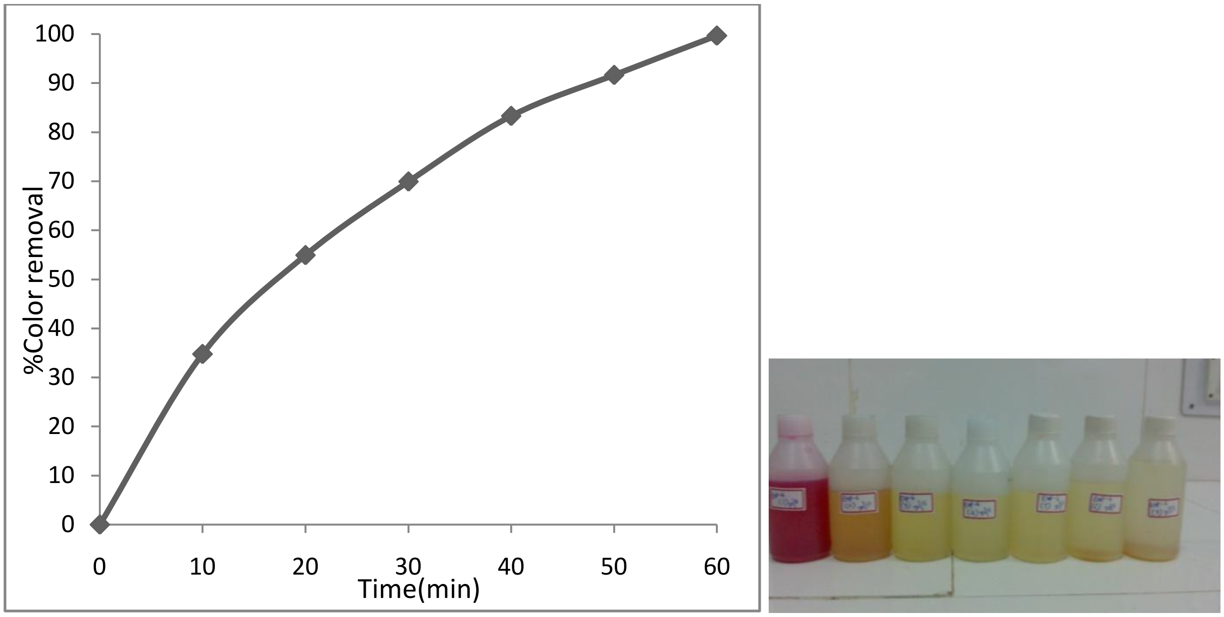


Figure 5.8.4 b %Color removal for RR195 using Ti/Ceo-RuO$_2$

Figure 5.8.4 c and d represents %TOC removal for RR2 and RR195 dye respectively using Ti/Ce-2D MMO electrode. In case of RR2 dye %TOC removal was 59% greater than that of RR195. Minimum amount of sludge generation was also observed in this process.

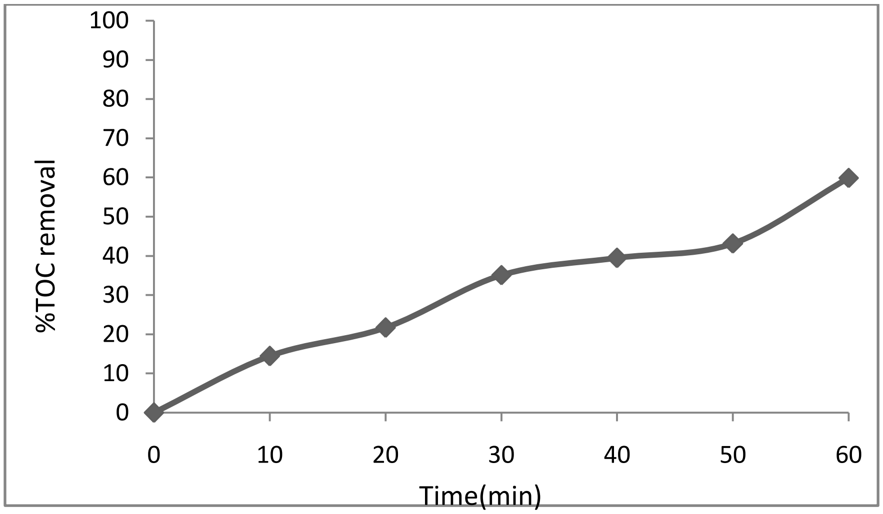


Figure 5.8.4 c %TOC removal for RR2 using Ti/Ceo-RuO$_2$

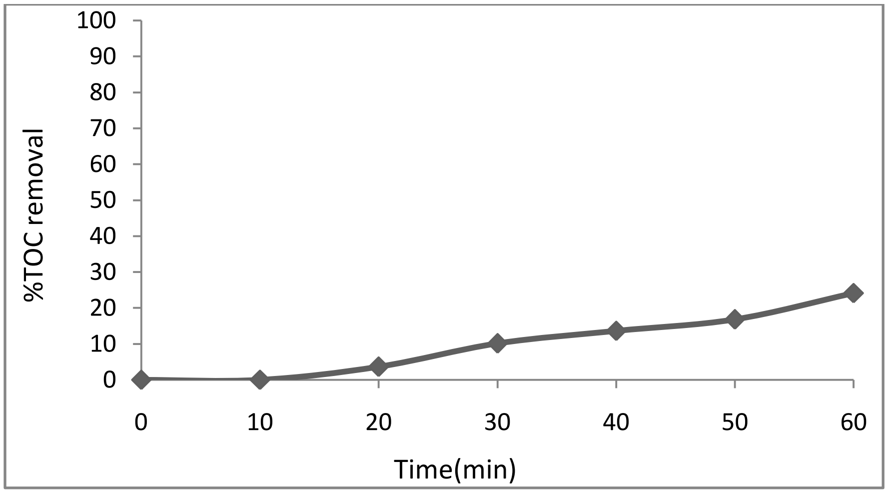


Figure 5.8.4 d %TOC removal for RR195 using Ti/Ceo-RuO$_2$

As shown in figure 5.8.4 e and f % COD removal for RR195 was 14.76% greater than that of RR2. It shows that Ti/Ce MMO gives better COD removal for RR195 dye than that of RR2 dye. It was also observed that minimum amount of sludge was generated using this MMO electrode.

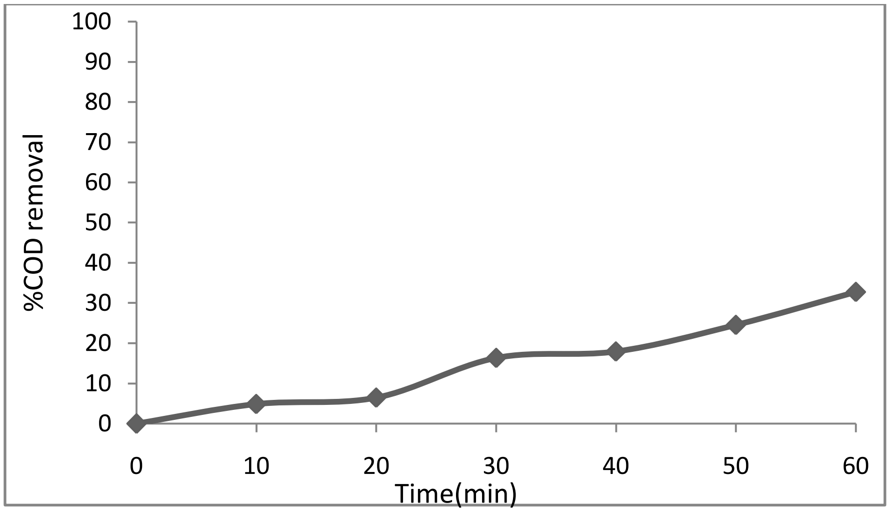


Figure5.8.4 e % COD removal for RR2 using Ti/Ceo-RuO$_2$

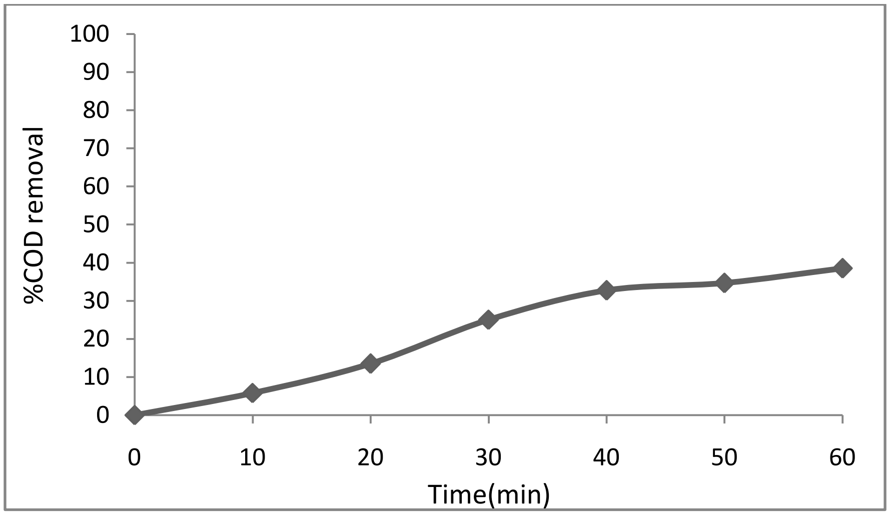


Figure 5.8.4f %COD removal for RR195 using Ti/Ceo-RuO$_2$

5.8.5 Effect of pH variation on treatment of RR195 dye

To optimize the pH for RR195 set of experiments have been performed in which other parameters such as salt concentration and current density are kept constant. Results reveal that at all three pH values i.e. 3, 7, 11 %color removal was almost 100%. So it can be concluded that varying the pH does not considerably affects the color removal rate for RR195. But it has a noticeable effect on %TOC removal and %COD removal. As shown in Figure5.8.5 a and b , 43% TOC removal was achieved in case of pH 7 which was almost 50% higher than that of %TOC removal achieved at pH 3 and 11. Similarly at pH 7 %COD removal was 84% which was almost four and eight fold greater that %COD removal which was achieved at pH 3 and 11 respectively.

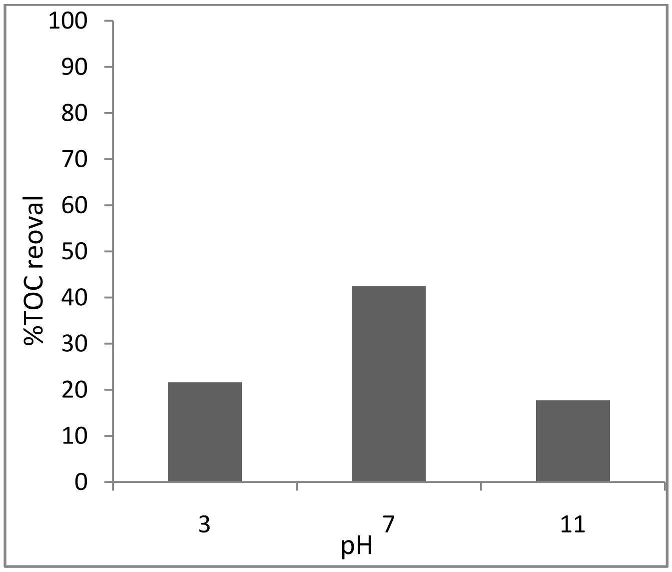


Figure 5.8.5 a %TOC removal for RR195 with respect to pH

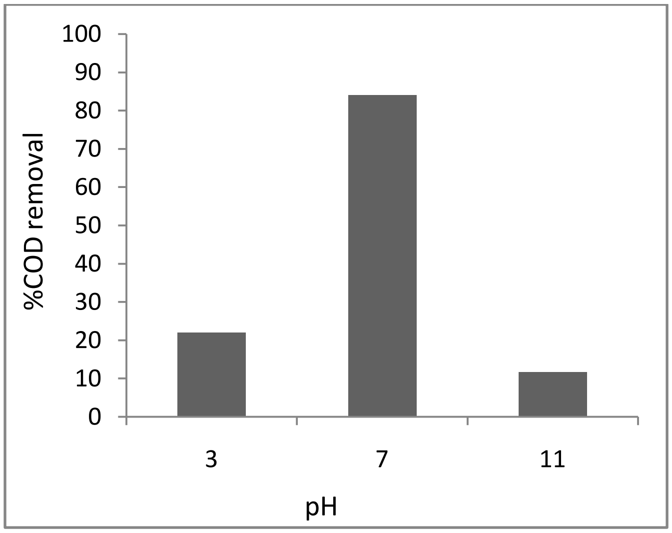


Figure 5.8.5 b %COD removal with respect to pH

5.8.6 Effect of Electrolyte concentration on treatment of RR195

To determine the effect of salt which was added as electrolyte in the process, experiment was conducted using RR195 dye, Ti/Ni-4D as MMO electrode and without adding electrolyte (salt) so as to determine performance efficiency of the process in absence of electrolyte. The performance was analyzed in terms of %color removal, %TOC removal and %COD removal. As shown in Figure 5.8.6 a in absence of electrolyte only 25% color removal was possible, where according to figure5.8.6b and c 44% TOC removal and 22% COD removal were achieved respectively. However foremost drawback for this case was to maintain the high voltage. In absence of electrolyte almost three times higher voltage is required to maintain the constant current as per requirement.

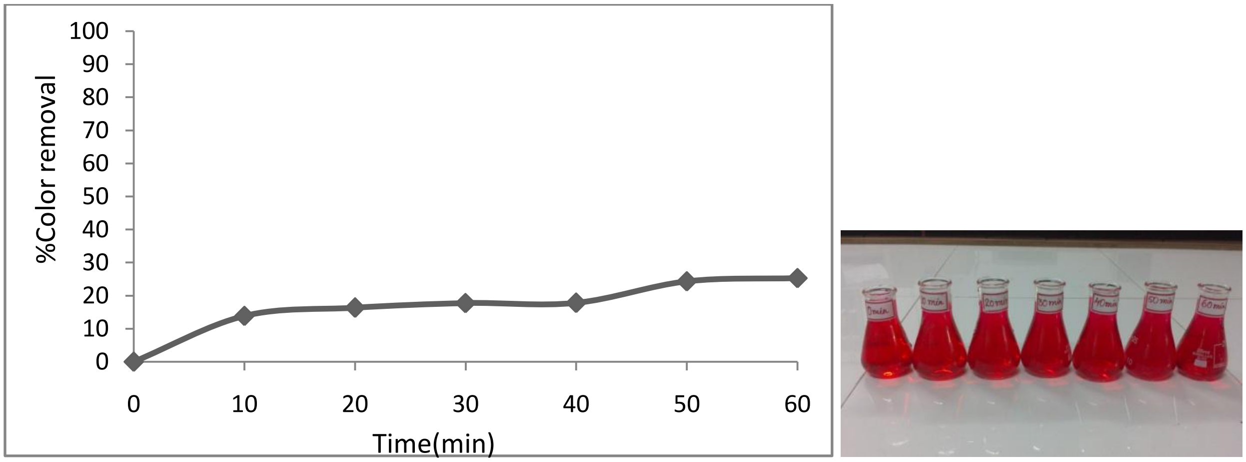


Figure 5.8.6a % Color removal for RR195 in absence of electrolyte

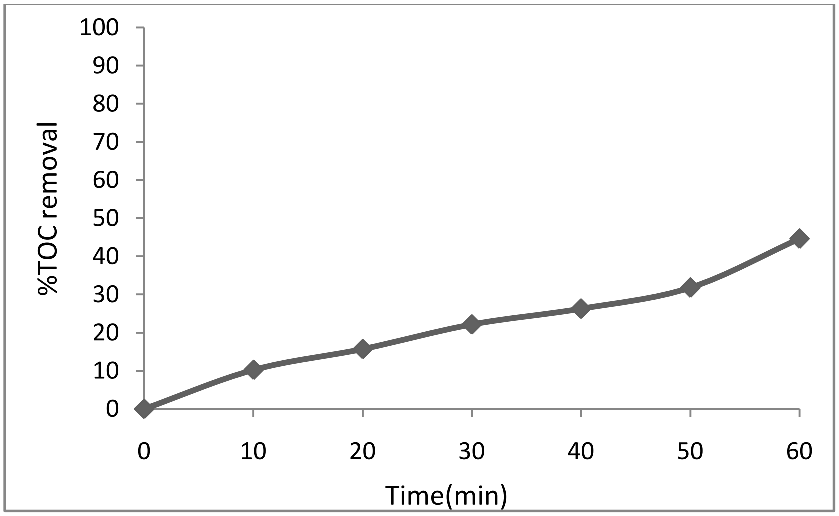


Figure 5.8.6 b %TOC removal for RR195 in absence of electrolyte

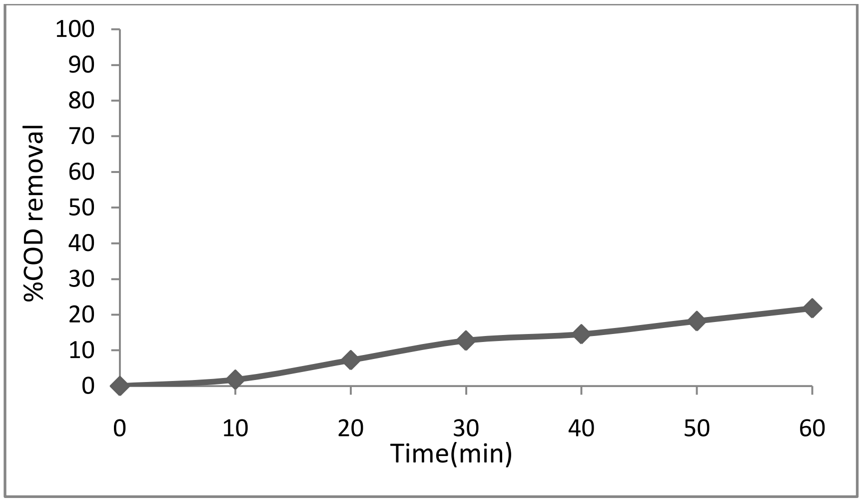


Figure 5.8.6 c %COD removal %TOC removal for RR195 in absence of electrolyte

5.9 Conclusion

From the present work it can be concluded that out of all the four MMOs, Ti/Ni-4D electrode gives better results with 100% color removal, 64%TOC removal and 85%COD removal. Also, while using Ti/Ni-4D electrode no sludge generation was noticed. So it can be concluded that performance of all the four MMOs follows following pattern Ti/NiO-RuO_2-SnO_2-Sb_2O_5>Ti/CeO-RuO_2-SnO_2-Sb_2O_5>Ti/Ce- Sb_2O_5>Ti/ SnO_2-Sb_2O_5.

Phase- III

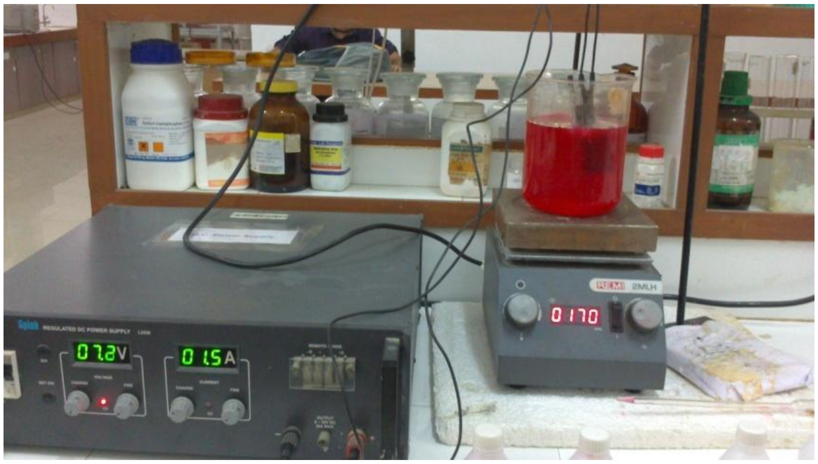
5.10 Materials and Methods

5.10.1 Chemicals

Reactive Red2 and Reactive Red195 dye were used as model pollutants. The dyes were procured from GIDC Vatva. Sodium chloride was used as supporting electrolyte. In phase III of experiment two different MMOs were used to compare its performance with commercial MMO. Nickle chloride hexahydrate ($NiCl_26H_2O$), Cobaltous chloride hexahydrate, Ruthenium trichloride ($RuCl_3xH_2O$), Antimony chloride ($SbCl_3$), Tinchloride pentahydrate ($SnCl_4.5H_2O$) were purchased from CDH and used without further purification. Commercial MMO was purchased from Titanium anode fabricators Pvt. Ltd Chennai. Isopropanol (99.8% CDH) and hydrochloric acid (37% CDH) were used as solvents to prepare precursor solution.

5.10.2 Experimental Set-up

All experiments were conducted using laboratory unit of 1L capacity. Experiments were conducted using three different electrodes and two different dyes. MMO electrode was prepared by applying respective coating of mixed metal oxide over titanium substrate and it was used as DSA type anode, Stainless Steel (SS 304) was used as cathode. The distance between anode and cathode was 8 mm. A constant DC Power supply was applied (Aplab India, LD-3205). Both the electrodes were fabricated using thermal decomposition method as discussed in Phase I.



5.10.3 Methodology

All the experiments were conducted at optimized conditions obtained from Phase I and Phase II of this study, salt concentration (4g/L), pH (7), current density (40mA/cm^2). The dye concentration was maintained at 200ppm.

5.11 Observations

5.11.1 Ti/NiO-RuO$_2$-SnO$_2$-Sb$_2$O$_5$

Table VI: Performance of Ni-4D electrode for mineralization of RR2 and RR195

S.No	Time (min)	pH		%COD Reduction		%Color Removal		% Concentration Reduction		Energy Consumption, KWh/g COD	
		RR2	RR195	RR2	RR195	RR2	RR195	RR2	RR195	RR2	RR195
1	0	7.0	7.0	0	0.00	0.00	0	198.48	195.24	0.00	0.00
2	10	7.0	7.3	21	2.04	99.23	100	0.70	0.24	8.00	13.37
3	20	7.2	7.3	48	10.20	99.73	100	0.24	0.05	6.90	26.51
4	30	7.3	7.7	53	16.33	99.77	100	0.21	0.00	9.30	37.44
5	40	7.5	7.9	69	24.49	99.97	100	0.03	0.00	9.60	48.35
6	50	7.8	8.0	71	30.61	99.97	100	0.03	0.00	11.70	56.53
7	60	8.1	8.0	74	44.90	100.0	100	0.00	0.00	13.50	66.09

5.11.2 Co/4D MMO

Table VII: Performance of Co-4D electrode for mineralization of RR2 and RR195

S.No	Time (min)	pH		%COD Reduction		%Color Removal		% Concentration Reduction		Energy Consumption, KWh/g COD	
		RR2	RR195	RR2	RR195	RR2	RR195	RR2	RR195	RR2	RR195
1	0	7.0	7.0	0.00	0	0.00	0	197.87	0	0.0	0
2	10	7.4	7.30	20.68	2.77	98.56	97.83	1.30	98.43	8.0	26.01

3	20	7.4	7.60	44.26	5.66	98.96	98.69	0.90	99.05	7.5	39.69
4	30	7.7	7.70	48.55	10.06	99.73	99.69	0.24	99.78	10.2	48.99
5	40	7.8	7.90	62.48	14.47	99.86	99.72	0.12	99.80	10.6	64.71
6	50	7.8	8.20	69.45	20.50	99.93	99.79	0.06	99.85	11.9	79.79
7	60	8.3	8.40	70.73	32.08	99.93	99.83	0.06	99.88	14.0	84.38

5.11.3 Commercial MMO

Table VIII: Performance of Commercial electrode for mineralization of RR2 and RR195

S.No	Time (min)	pH		%COD Reduction		%Color Removal		% Concentration Reduction		Energy Consumption, KWh/g COD	
		RR2	RR195	RR2	RR195	RR2	RR195	RR2	RR195	RR2	RR195
1	0	7.0	7.0	0.0	0.0	0.0	0.00	0.0	0.00	0.0	0
2	10	7.7	7.5	3.26	1.78	96.27	99.83	98.29	99.88	54.4	162.11
3	20	7.7	7.7	10.54	9.15	99.90	100	99.95	100	33.7	49.20
4	30	8.0	7.8	15.22	11.69	99.97	100	99.98	100	35.0	42.19
5	40	8.1	8.0	20.43	16.39	100.0	100	100.00	100	34.8	55.35
6	50	8.1	8.2	29.02	25.54	100.0	100	100.00	100	30.6	66.32
7	60	8.1	8.3	40.98	30.62	100.0	100	100.00	100	26.0	77.71

5.12 Results and Discussions

5.12.1 Effect of Ni/4D, Co/4D and commercial electrode on COD Reduction

The performance of three MMOs was analyzed on the basis of COD reduction. RR2 and RR 195 were selected as model pollutant for synthetic wastewater. For both the dyes Ni/4 D MMO give better results as compared to Co/4D and Commercial MMO.

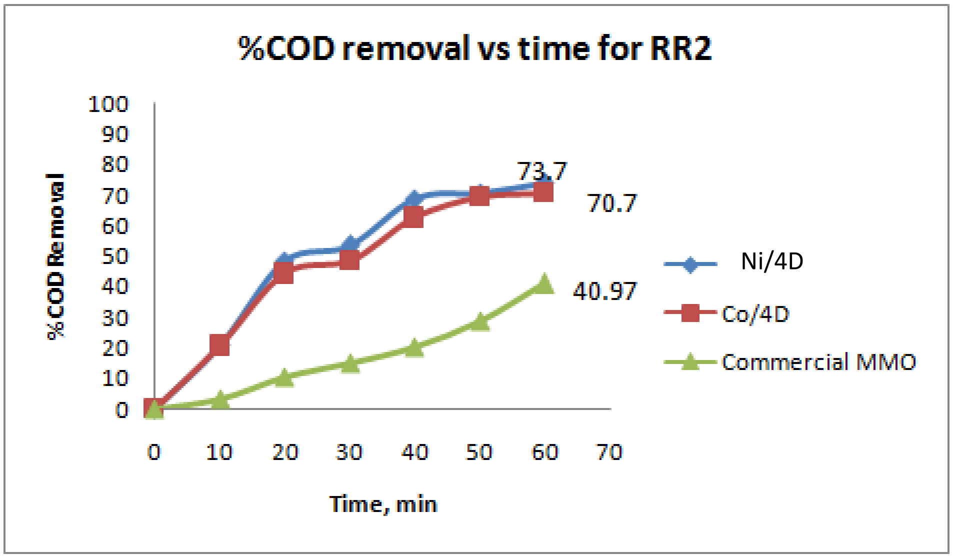


Figure 5.12.1 a COD removal vs Time for RR2

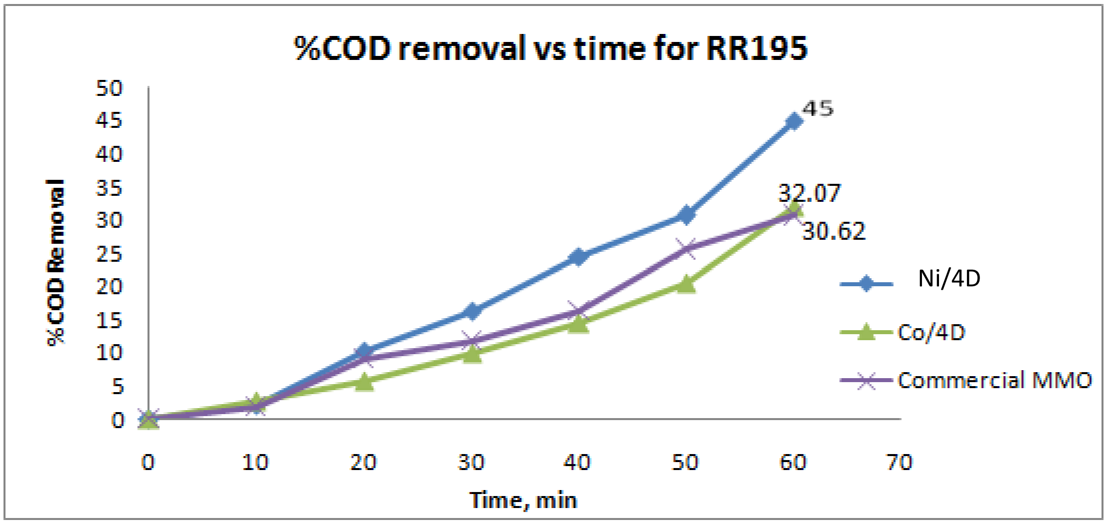


Figure 5.12.1b %COD removal vs time for RR195

It is quite evident from above results that Ni/4D MMO gives better performance for COD removal than Co/4D and Commercial MMO with 73.7 % and 45 % COD removal for RR2 and RR195 respectively.

5.12.2 Effect on pH variation during electrolysis

The present study also analyzed effect of time on pH of solution. It was found that for both the dye pH is not much affected with change in time. For all three MMOs pH at the end of 60 min was around 8.0 to 8.2. This indicates that pH is not much affected with experimental time.

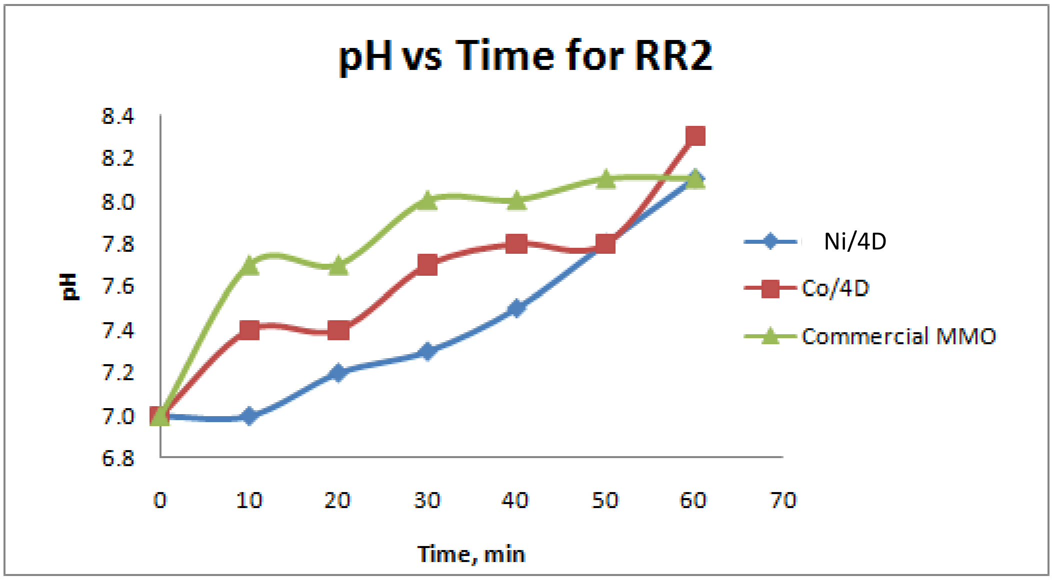


Figure 5.12.2 a pH vs Time for RR2

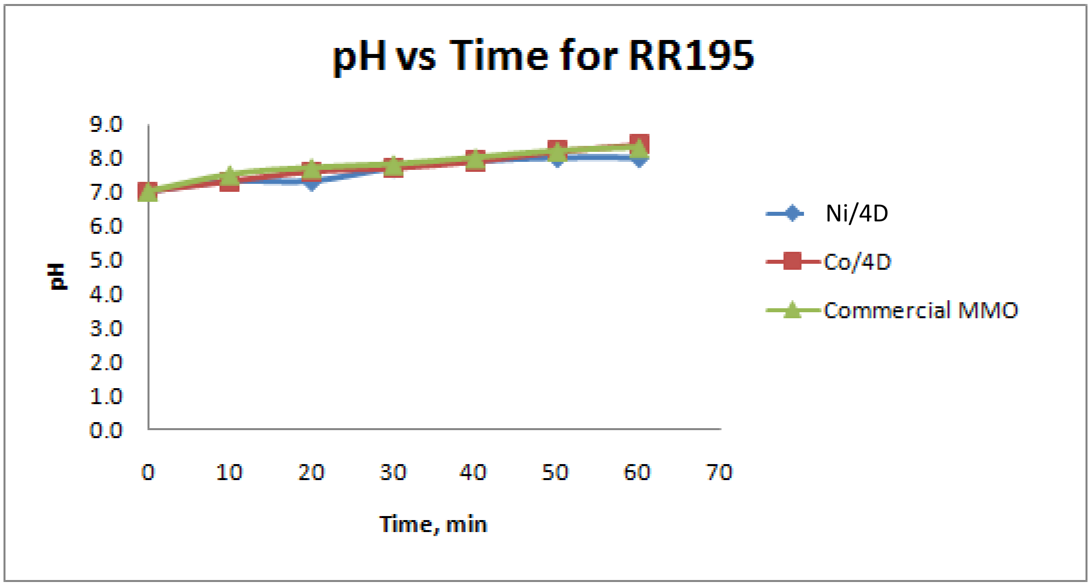


Figure 5.12.2 b pH vs Time for RR195

5.12.3 Effect on Color Removal

MMOs were also analyzed on the basis of decolorization of both the dyes. It was found that almost 99% color is removed within 10 min of experiment by all three MMOs and for both the dyes (i.e. RR2 and RR195).

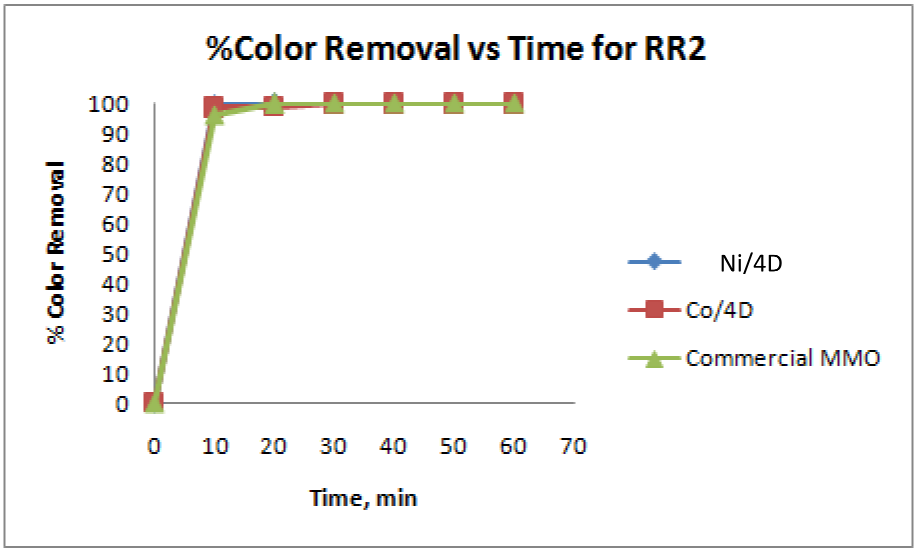


Figure 5.12.3 a % Color removal vs Time for RR2

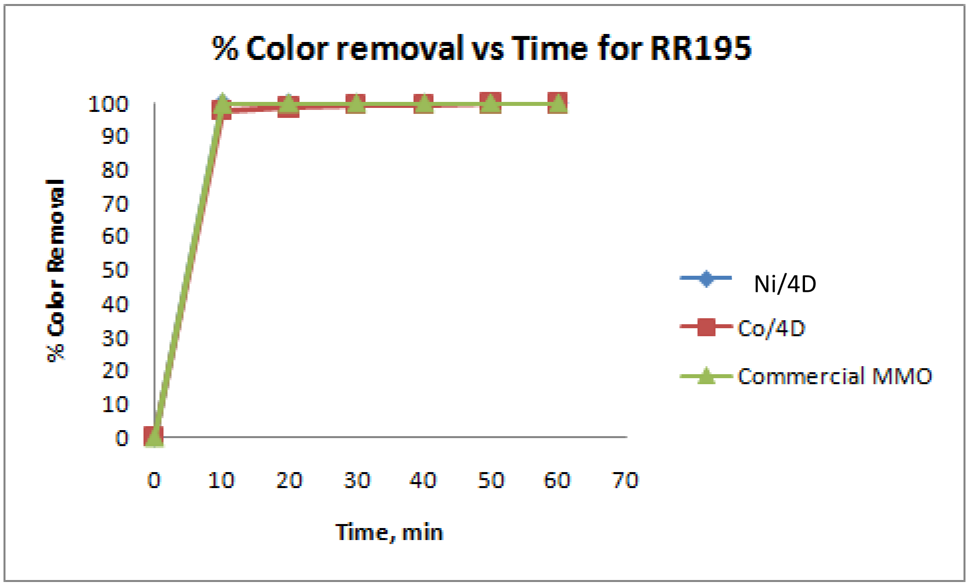


Figure 5.12.3 b % Color removal vs Time for RR195

5.12.4 Effect on Concentration Reduction

Effect of MMOs on concentration reduction of dye was also analyzed in this study. It was found that around 98 to 99% initial concentration was reduced within 10 min of experiments only. All three MMOs have shown similar performance in terms of concentration reduction for both the dyes.

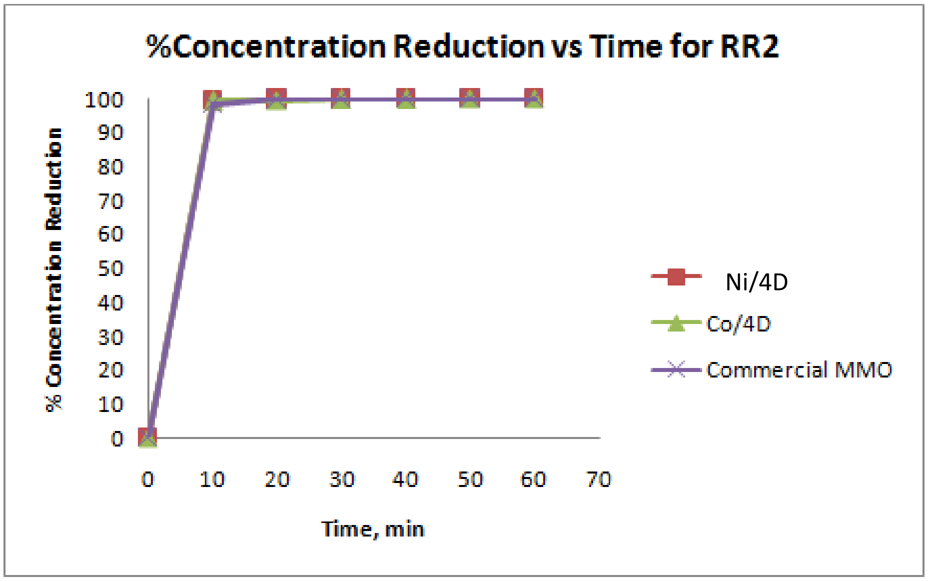


Figure 5.12.4 a % Concentration reduction vs Time for RR2

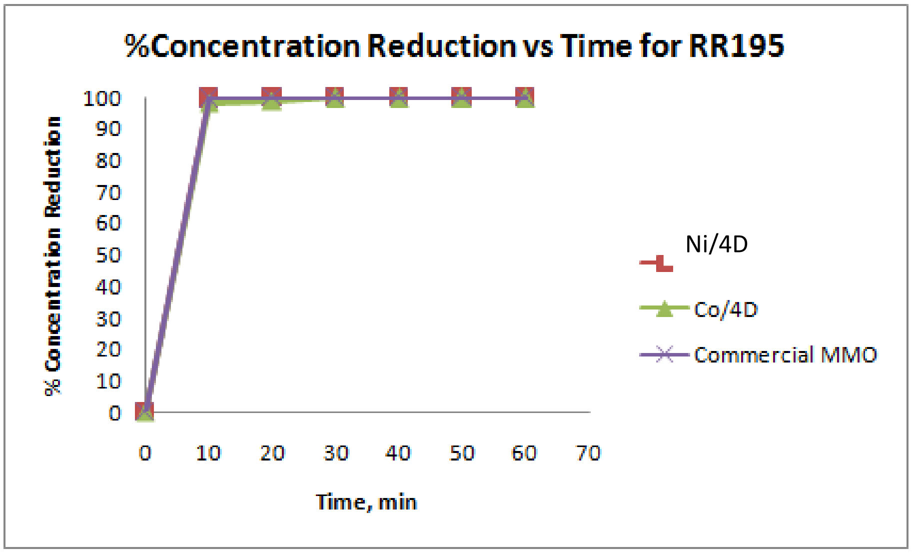


Figure 5.12.4 b % Concentration reduction vs Time for RR195

5.12.5 Effect on Energy Consumption

Energy consumption is essential to determine to assess the viability of electrochemical treatments of dye wastewater. Specific energy consumption per unit volume (EC) for unit COD mass is calculated to evaluate performance of various MMOs.

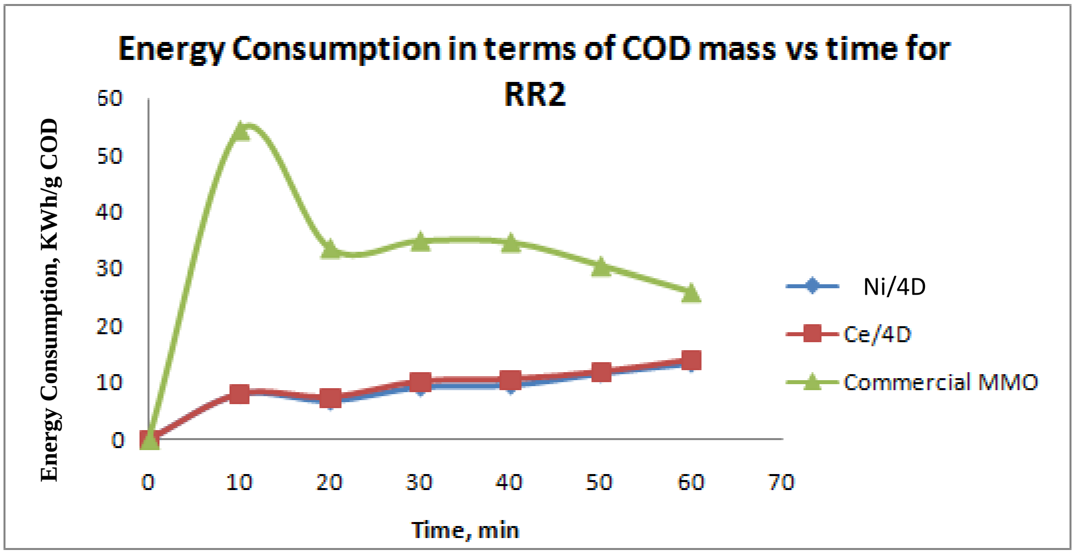


Figure 5.12.5a Energy Consumption vs Time for RR2

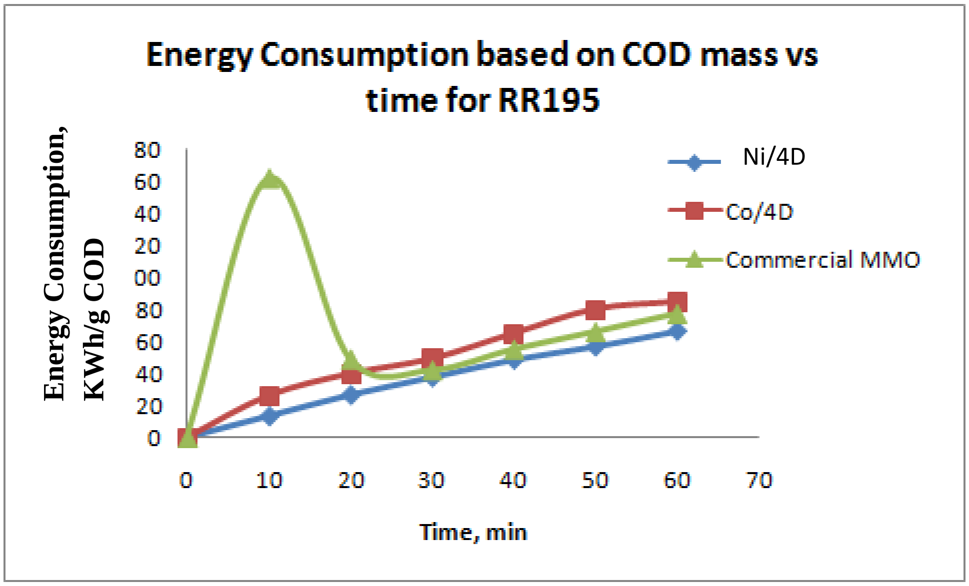


Figure 5.12.5b Energy Consumption vs Time for RR195

From Figure 5.12.5a and b it is quite evident that energy consumption for unit mass of COD removal is less in case of Ni/4D MMO, which is 13.5 and 66.05 kWh/g COD, for RR2 and RR195 respectively. It is also noteworthy that in case of RR195 more energy is consumed for removal of unit mass of COD as compared to the case of RR2. The above result may be attributed to the fact that RR195 is more complex in nature due to presence of compounds like nitrobenzene, 1-(3,6,8-Trihydroxy-1-naphthyl)urea, Benzo-1,4-quinone, (3,6,8-Trihydroxy-1-naphthyl)carbamic acid, etc.

5.12.6 Characterization of Electrodes

For determining surface morphology of MMOs Scanning Electron Microscopy (SEM) characterization was done. The morphological structure obtained for $Ti/NiO\text{-}RuO_2\text{-}SnO_2\text{-}Sb_2O_5$and $Ti/CoO\text{-}RuO_2\text{-}SnO_2\text{-}Sb_2O_5$ MMO prepared by thermal decomposition method was of cracked pattern and was similar to that reported in literature. And for MMO prepared by PPTD method, plate like structure was obtained which resembles to the reporting of literature.

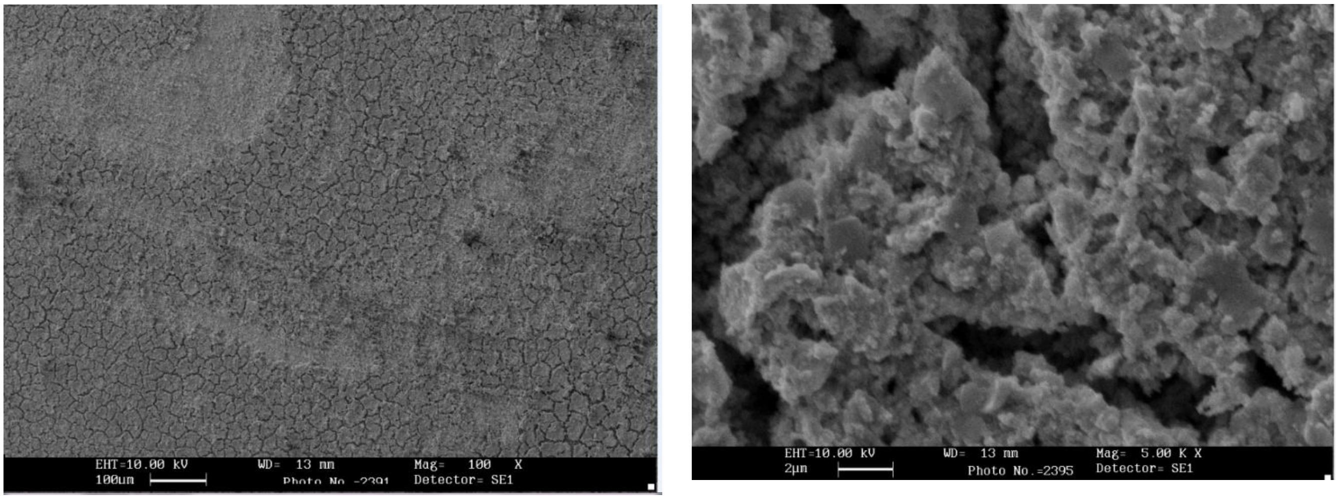


Figure 5.12.6a SEM images of Ni/4D STD MMO

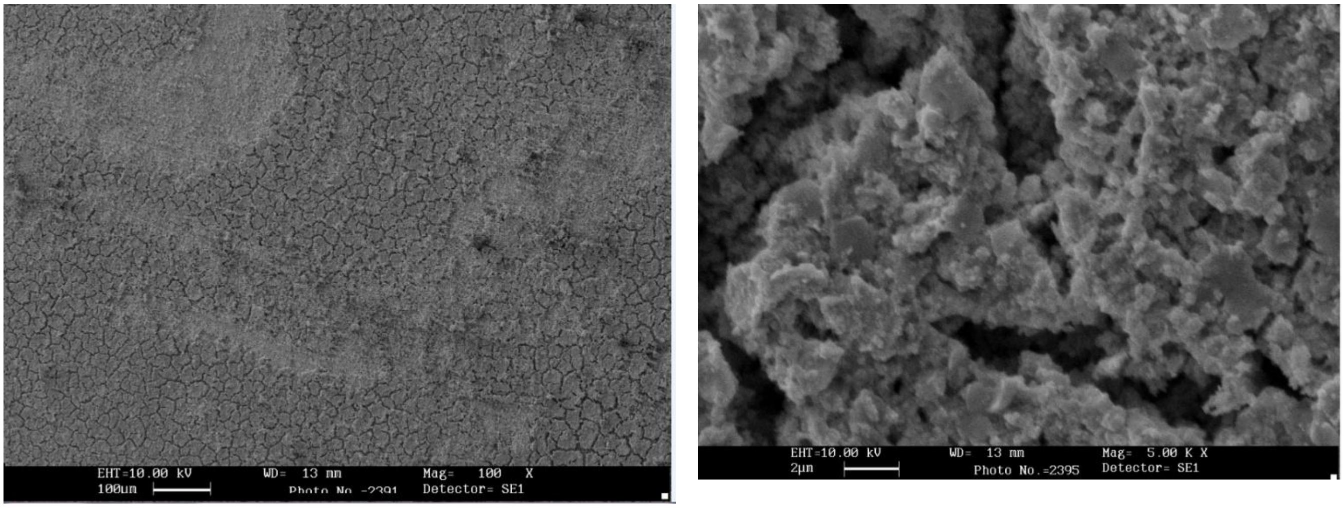


Figure 5.12.6b SEM image of Co/4D STD MMO

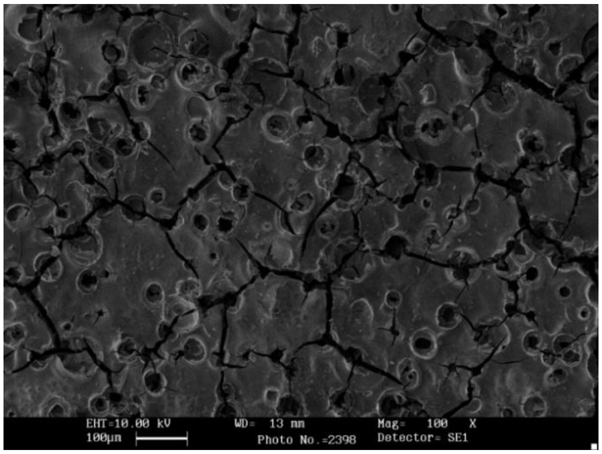


Figure 5.12.6c SEM image of Ni/4D PPTD MMO

5.13 Conclusion

It can be concluded from present study that performance of Ni/4D MMO is better as compared to Co/4D and Commercial MMO. It gives 73.7 % and 45% COD removal and almost 99% color removal for RR2 and RR195 respectively. Energy consumption was 13.5 and 66.05 kWh/kg COD for RR2 and RR195 respectively, which was much lower as compared to Co/4D and Commercial MMO.

Phase- IV

5.14 Materials and Methods

5.14.1 Chemicals

Reactive Red 2 and Reactive Red195 dye were used as model pollutant. The selected dyes were purchased from GIDC Vatva. Sodium chloride was used as supporting electrolyte. In phase IV of experiment Ti/NiO-RuO-SnO_2-Sb_2O_5 MMO anode was used to analyze the effect of time on treatment of synthetic wastewater containing two single dyes. Nicklechloride hexahydrate ($NiCl_26H_2O$), Ruthenium trichloride ($RuCl_3xH_2O$), Antimony chloride ($SbCl_3$), Tin chloride pentahydrate ($SnCl_4.5H_2O$) were purchased from CDH and used without further purification. Commercial MMO was purchased from Titanium anode fabricators Pvt. Ltd Chennai. Isopropanol (99.8% CDH) and hydrochloric acid (37% CDH) were used as solvents to prepare precursor solution.

5.14.2 Experimental Set-up for Batch and Continuous Runs

Experiments of batch extended time run were carried out using laboratory unit of 1L capacity. For continuous run holdup tank of 5L capacity and two laboratory unit of 1L capacity were used. Peristaltic pump was used to maintain the flowrate. Ti/NiO-RuO-SnO_2-Sb_2O_5 MMO anode was used for carrying out all experiments. MMO electrode was prepared by applying respective coating of mixed metal oxide over titanium substrate and it was used as DSA type anode, Stainless Steel (SS 304) was used as cathode. Electrode was fabricated as discussed in Phase I. The distance between anode and cathode was 8 mm. A constant DC Power supply was applied (Aplab India, LD-3205).

Figure 5.14.1 Set up of Batch run for extended time period

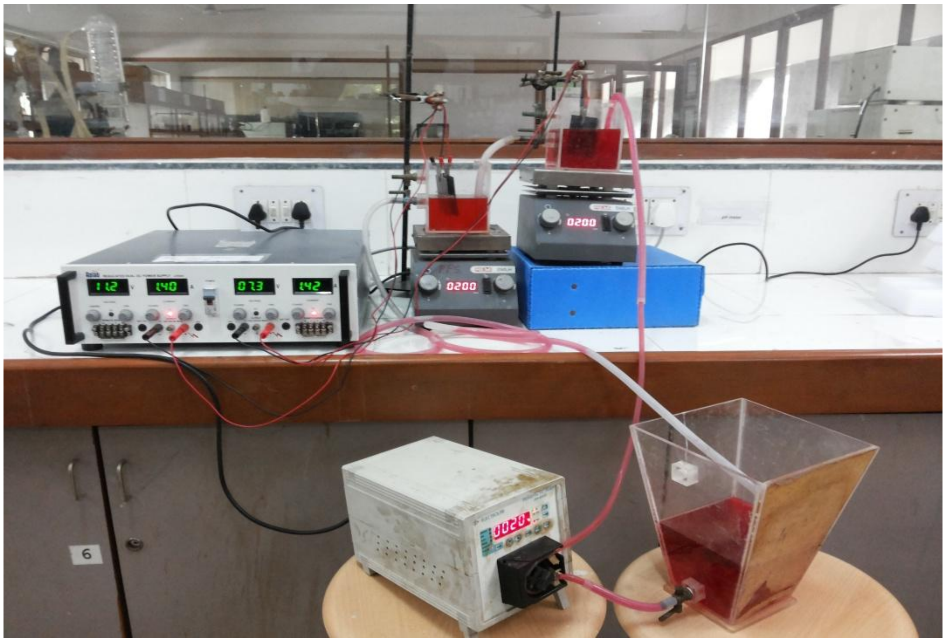


Figure 5.14.2 Set up of continuous run

Calculations Involved

$$\%\text{COD Removal} = \left(\frac{COD_0 - COD_t}{COD_0} \right) \times 100 \tag{10}$$

where, COD_0 and COD_t represent COD values at initial and electrolysis time t respectively.

$$\%\text{TOC Removal} = \left(\frac{TOC_0 - TOC_t}{TOC_0} \right) \times 100 \tag{11}$$

where, TOC_0 and TOC_t represent TOC values at initial and electrolysis time t respectively.

Energy consumption based on COD mass is calculated using following equation,

$$EC = \left(\frac{UI\Delta t}{COD_t - COD_{t+\Delta t}} \right) \times V \tag{12}$$

where $(COD)_t$, $(COD)_{t+\Delta t}$, $(TOC)_t$, and $(TOC)_{t+\Delta t}$ are the COD and TOC 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 (A), and V is the volume of the electrolyte solution (L), to get energy consumption in kWh/g of COD reduction.

5.15 Observations

Table IX. Performance of Ti/NiO-RuO_2-SnO_2-Sb_2O_5 in batch run for RR2 extended time period

S.No	Time (min)	%COD Removal	% TOC Removal	Energy Consumption (KWh/g COD)
1	0	0	0	0
2	5	9.27	7.13	8.28
3	10	20.69	15.69	7.41
4	15	48.28	28.47	4.77
5	30	53.45	44.84	8.61
6	45	68.97	52.48	10.01
7	60	70.69	55.88	13.02
8	75	73.71	69.08	15.61
9	90	74.68	72.16	18.48
10	105	76.29	76.27	21.11
11	120	77.91	77.37	23.62
12	135	78.66	81.66	26.32
13	150	79.20	82.23	29.05
14	165	79.63	83.03	31.78
15	180	79.96	85.11	34.53

Table X. Performance of Ti/NiO-RuO_2-SnO_2-Sb_2O_5 in batch run for RR195 extended time period

S.No	Time (min)	%COD Removal	% TOC Removal	Energy Consumption (KWh/g COD)
1	0	0	0	0
2	5	3.85	3.33	28
3	10	5.77	7.87	37.33

4	15	7.69	14.49	42
5	30	10.90	22.90	59.29
6	45	12.18	28.02	79.58
7	60	18.97	32.16	68.11
8	75	23.33	34.19	69.23
9	90	30.13	41.15	64.34
10	105	37.18	47.47	60.83
11	120	45.51	48.71	56.79
12	135	50.64	59.03	57.42
13	150	55.77	63.75	57.93
14	165	60.90	64.18	58.63
15	180	64.10	65.96	60.48

Table XI. Performance of Ti/NiO-RuO_2-SnO_2-Sb_2O_5 in Continuous run for RR2 at 20mL/min flowrate

S.No	**Time (min)**	**%COD Removal**		**% TOC Removal**		**Energy Consumption (KWh/g COD)**	
		Tank 1	**Tank 2**	**Tank 1**	**Tank 2**	**Tank 1**	**Tank 2**
1	0	0	0	0	0	0	0
2	5	10.16	11.02	3.10	4.55	7.49	6.19
3	10	10.37	21.28	4.32	7.28	14.67	7.15
4	15	16.15	19.79	9.51	14.92	14.14	11.54
5	30	22.46	25.67	20.13	23.23	20.33	17.79
6	45	26.84	32.41	23.84	25.18	25.52	21.14
7	60	32.09	37.54	27.91	35.25	28.47	24.33
8	75	36.36	41.71	30.90	32.57	31.40	27.37
9	90	38.72	46.74	36.00	42.33	35.39	29.31
10	105	48.45	51.87	44.65	46.40	32.99	30.81
11	120	50.27	56.36	49.16	51.34	36.34	32.41
12	135	57.57	62.78	51.34	54.52	35.72	32.73
13	150	61.07	65.56	57.50	64.64	37.39	34.83
14	165	69.52	71.76	58.64	70.78	36.13	35.00
15	180	73.26	80.11	68.35	73.65	37.40	34.21

Table XII. Performance of Ti/NiO-RuO_2-SnO_2-Sb_2O_5 in Continuous run for RR2 at 67mL/min flowrate

S.No	**Time (min)**	**%COD Removal**		**% TOC Removal**		**Energy Consumption (KWh/g COD)**	
		Tank 1	**Tank 2**	**Tank 1**	**Tank 2**	**Tank 1**	**Tank 2**
1	0	0	0	0	0	0	0
2	5	1.07	3.32	0.39	4.55	71.17	22.96

3	10	1.93	4.06	4.32	7.28	79.07	37.46
4	15	3.85	5.24	5.30	9.20	59.31	43.57
5	30	6.10	8.77	8.76	12.30	74.91	52.07
6	45	8.66	10.80	13.97	21.83	79.07	63.42
7	60	11.34	13.80	19.27	22.81	80.57	66.20
8	75	16.04	18.29	19.88	23.81	71.17	62.43
9	90	17.75	19.47	23.26	20.02	77.17	70.83
10	105	22.57	22.99	29.06	32.77	70.83	69.51
11	120	25.88	25.88	38.96	44.09	70.58	70.58
12	135	31.02	31.55	41.30	48.83	66.26	65.14
13	150	32.73	33.37	46.12	50.33	69.77	68.43
14	165	38.72	39.25	48.22	54.49	64.88	63.99
15	180	42.25	43.10	50.14	55.16	64.86	63.57

5.16 Results and Discussion

5.16.1 Batch study for extended time period

Experiments were conducted to investigate the effect of time on removal of COD and TOC as well as its effect on energy consumption. For both the dyes (RR2 and RR195) it was found that after 3 hours there is no noticeable change in COD and TOC removal. Additionally complete color removal was noticed at the end of 30 min.

Figure 5.16.1a depicts that almost after of 150min of reaction time there is no such noticeable change in COD and TOC values of synthetic wastewater containing RR2. Similar observations were recorded for synthetic wastewater containing RR195 dye. 85% TOC removal was obtained for RR2 dye whereas only 66% TOC removal was achieved in case of RR195.

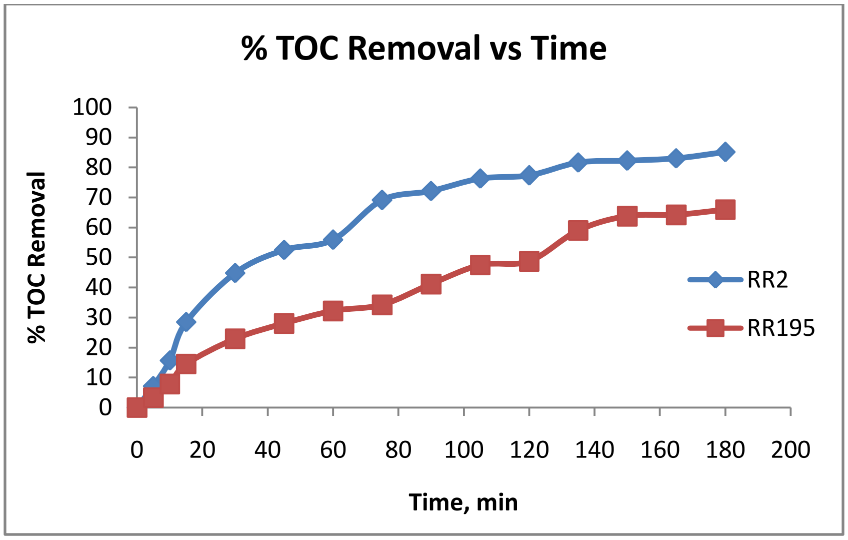


Figure 5.16.1 a %TOC Removal vs Time

As depicted in Figure 5.16.1 b at the end of 105min almost similar removal rate of COD was obtained till 180 min of time. For RR2 dye almost 80% COD was removed whereas in case of RR195 dye only 64% COD removal was obtained. It also indicates that RR195 is stronger dye with complex structure which makes it more complicated to degrade.

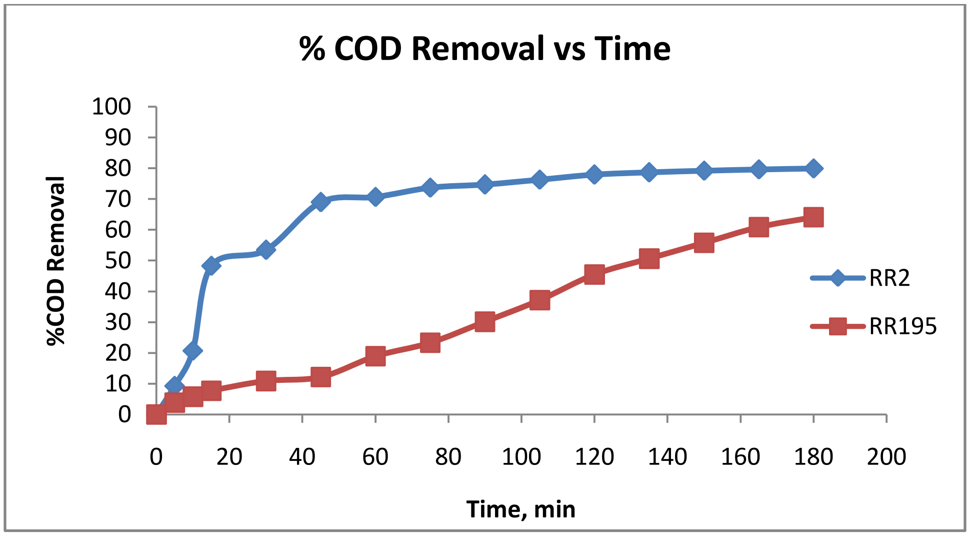


Figure 5.16.1 b %COD Removal vs Time

As shown in Figure 5.16.1 c energy consumption based on unit mass of COD removal was higher in case of RR195 dye as compared to that of RR2 dye. It was observed that for removal of 80% COD in case of RR2 dye 35KWh/g COD of energy was consumed. In case of RR195 dye 64% COD removal almost 61% KWh/g COD of energy was consumed.

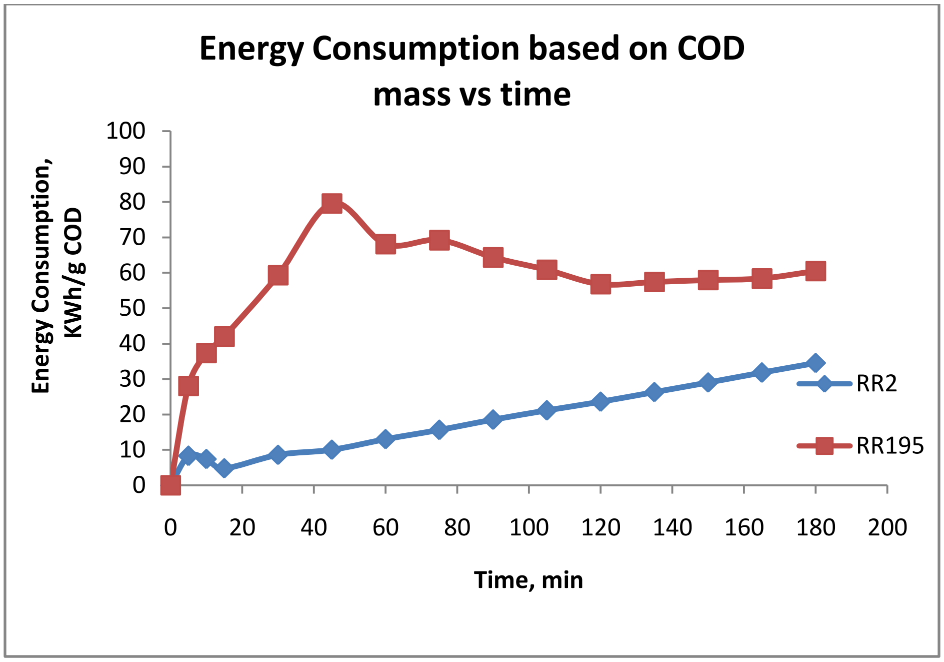


Figure 5.16.1 c Energy consumption vs Time

5.16.2 Continuous study

Experiments of continuous study were conducted at two different liquid flowrate i.e. 20mL/min and 67mL/min using 200 ppm RR2 dye and Ti/NiO-RuO-SnO_2-Sb_2O_5 MMO anode. The performance was analyzed in terms of %COD removal, %TOC removal and energy consumption based on unit mass of COD removal. It was found 20mL/min flowrate gives better results than that of 67mL/min of flowrate. This is attributed to the fact that at lower flow rate retention time increases and thereby increasing the mineralization efficiency.

It is clearly depicted in Figure 5.16.2 a and b that at lower liquid flowrate TOC removal was much more effective than that at higher flowrates. At 20mL/min of flowrate almost 74% of TOC is removed whereas only 55% TOC is removed in case of 67mL/min flowarte.

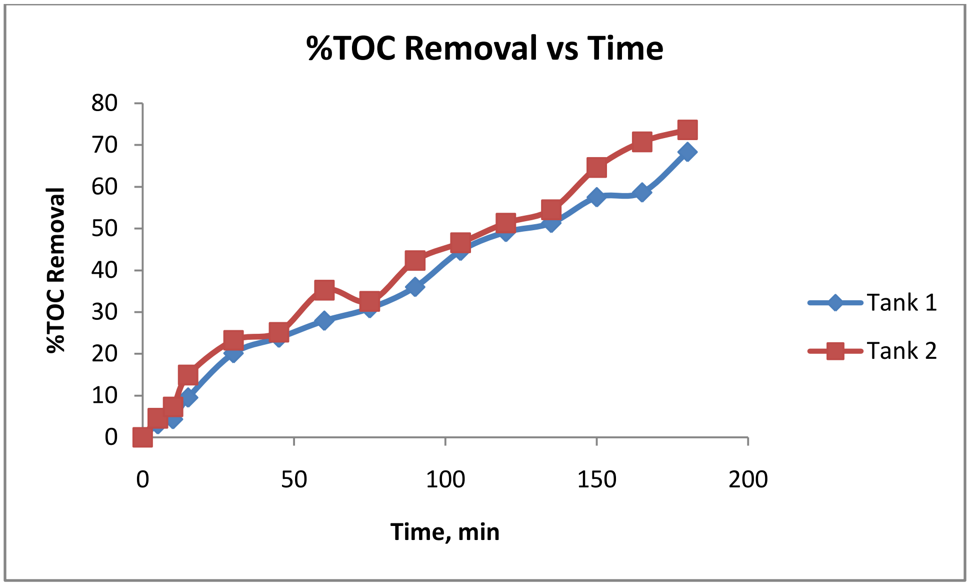


Figure 5.16.2 a %TOC removal vs Time at 20mL/min flowrate.

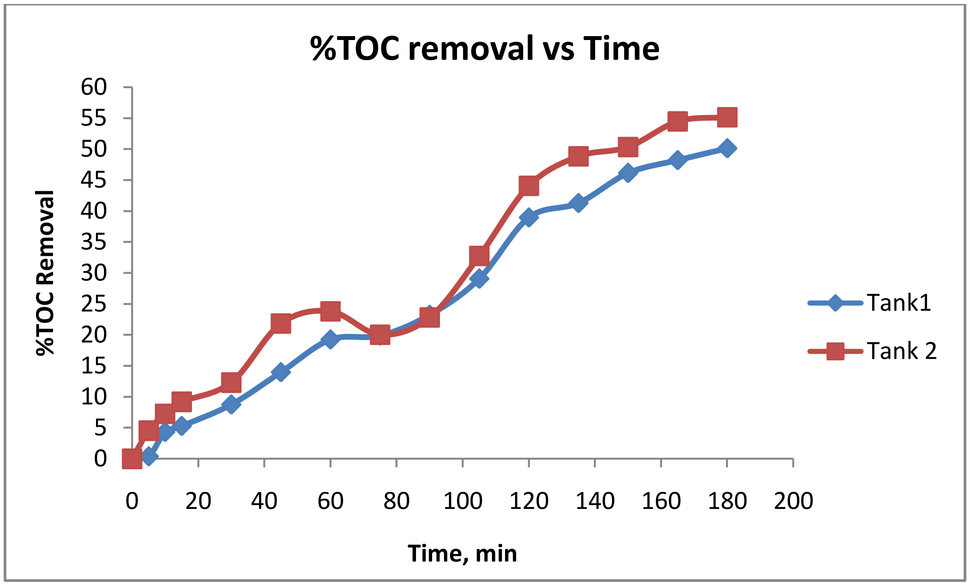


Figure 5.16.2 b %TOC removal vs Time at 67 mL/min flowrate.

Figure 5.16.2 c and d shows that almost double COD removal was obtained when flowrate was changed from 20mL/min from 67 mL/min. At 20mL/min flowrate 80% COD was removed whereas only 43% COD was removed in case of 67mL/min flowrate.

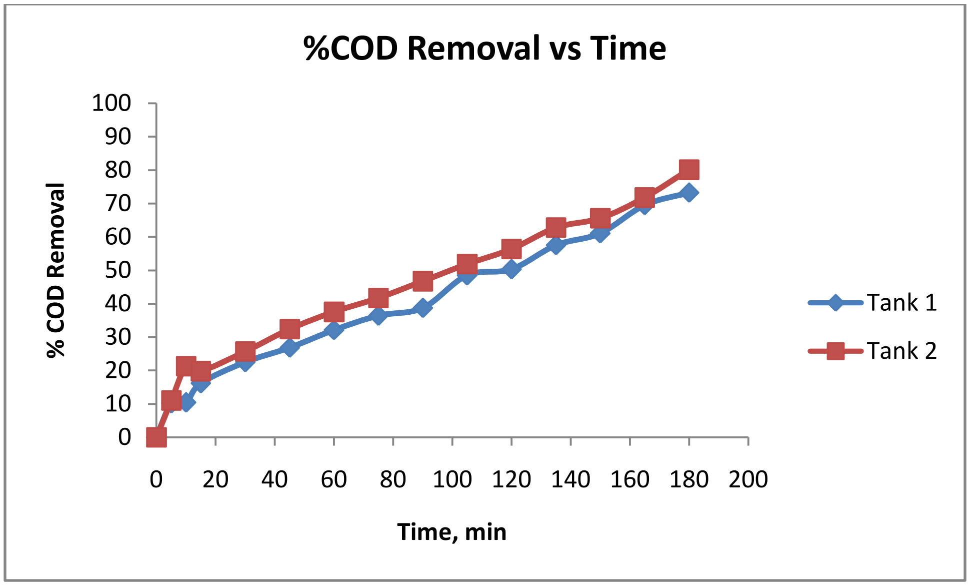


Figure 5.16.2 c %COD removal vs Time for 20mL/min

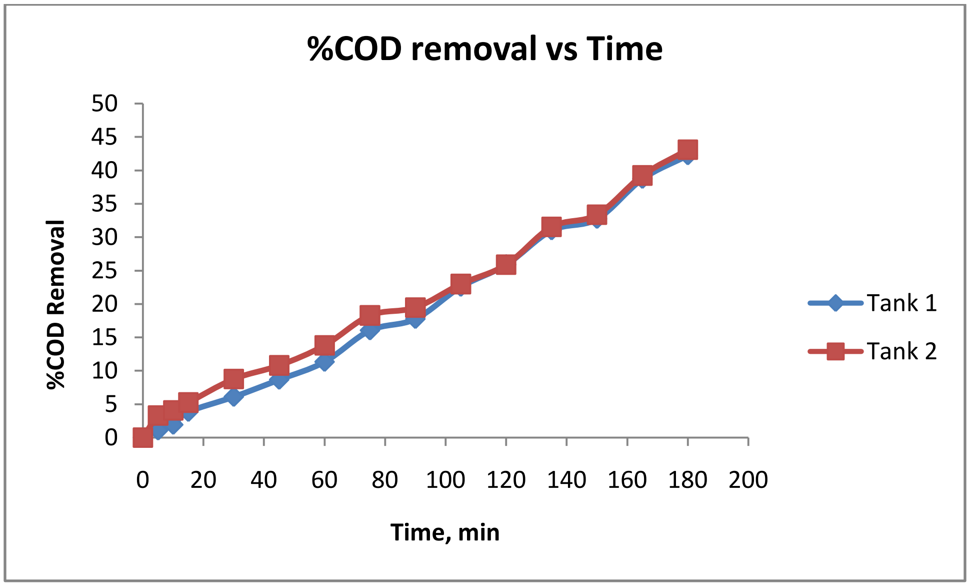


Figure 5.16.2 d % COD removal vs Time for 67 mL/min

Energy consumption was also affected with change in flowrate. In case of 20mL/min flowrate energy consumption for removal of 43% COD from synthetic wastewater was nearly 28 KWh/g COD whereas in case of 67mL/min flowrate for same removal of COD 64 KWh/g COD energy was consumed.

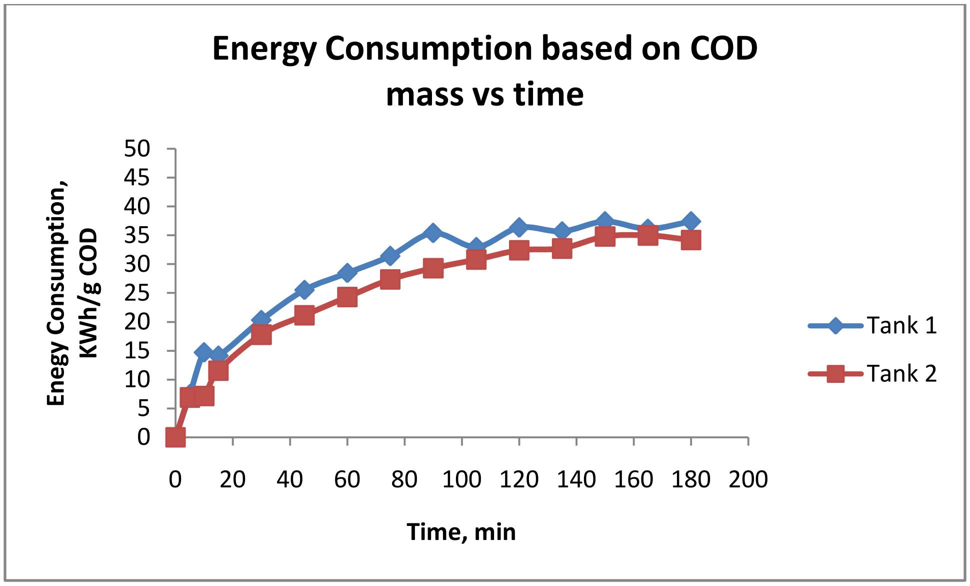


Figure 5.16.2 e Energy Consumption vs Time for 20mL/min flowarte

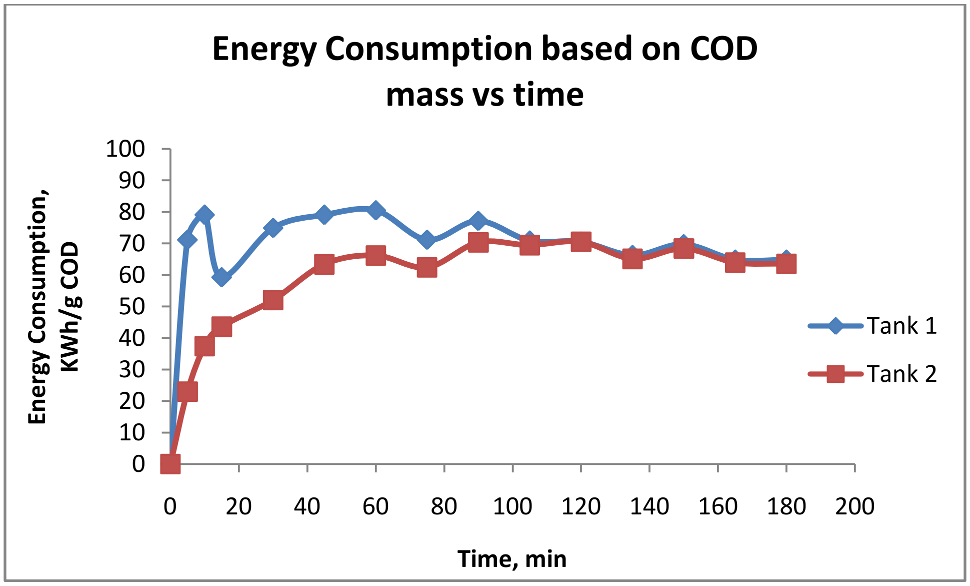


Figure 5.16.2 f Energy consumption vs Time for flowrate of 67mL/min

5.17 Life Test

Life test of Ti/NiO-RuO$_2$-SnO$_2$-Sb$_2$O$_5$ MMO anode was conducted at extreme salt conditions to determine the working life of an electrode. Synthetic wastewater containing 200ppm RR2 dye, 200g/l of NaCl electrolyte and 1.4A current was used to perform the life test. It was observed that it took 56 hours to raise the potential by 2V. Hence, it can be concluded that these MMOs have a longer working life and higher durability of film was observed.

5.17 Conclusion

From all the four phases of present study it can be concluded that MMO electrode can be served to be better alternative for treatment of recalcitrant organic compound. It is also evident from present work that various operating parameters affect the mineralization efficiency of synthetic wastewater containing dyes. pH plays dominant role in degradation efficiency of organic molecules and it highly depends on the nature of dye. Current efficiency and supporting electrolyte also helps to improve the effectiveness of process. Therefore it is suggested to optimize the various operating parameters. From present study it can be concluded that Ti/NiO-RuO_2-SnO_2-Sb_2O_5 serves to be better MMO anode amongst various MMO selected for present study. It mineralize both the dyes, RR2 and RR195 with higher Color, TOC and COD removal as compared to other MMO electrodes studied during different phases of present study. At the same time energy consumption for removal of unit of COD was also lower for Ti/NiO-RuO_2-SnO_2-Sb_2O_5 anode than that of all other MMOs.

APPENDIX

INTRODUCTION

Various analyses have been used for determining the performance of the electrochemical method. Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), UV Spectrophotometer have been learned during the training process.

COD Analysis

Standard potassium dichromate digestion solution, 0.04167M (0.25N): In 500 ml distilled water; 12.259 g $K_2Cr_2O_7$ primary standard grade, previously dried at 150°C for 2 h was added. In this solution 167 ml concentrated H_2SO_4, and 33.3g $HgSO_4$ was dissolved, cooled to room temperature, and diluted to 1000 ml.

Sulphuric acid reagent: Ag_2SO_4, reagent or technical grade, crystals or powder was added to concentrated H_2SO_4 at the rate of 5.5g Ag_2SO_4/kg H_2SO_4 and allowed to stand 1 to 2 days to dissolve it properly.

Standard ferrous ammonium sulphate (FAS), approximately 0.10M: 39.2 g $Fe\ (NH_4)_2\ (SO_4)_2 \cdot 6H_2O$ was dissolved in distilled water and 20ml concentrated H_2SO_4 was added in the solution further cooled and diluted to 1000 ml.

Molarity of FAS: For that 5 ml digestion solution was taken in to beaker and 10 ml reagent water was substituted for sample. After adding 1 to 2 drops diluted Ferroin indicator, mixture was titrated with FAS titrant.

In COD test, 2.5ml sample, 1.5ml digestion solution and 3.5mlsulphuric acid reagent was taken in 16 ×100 mm culture tubes. The mixtures in vials were digested for 2h at 150°C in a heating block. The samples were allowed to cool and analyzed by the titration method. In this method the residual potassium dichromate in the digestion vial was titrated with 0.1M ferrous ammonium sulphate (FAS) in the presence of ferroin indicator until the color of the solution changes from a blue green color to a red brown color. The amount of FAS used to achieve the color change was recorded and used in the calculation of COD. For blank reading in above mixture, sample was substituted by distilled water, digested for 2 h at 150˚C and titrated against standard 0.1M FAS. Molarity of FAS was made according to Eq. (3.2) while COD was calculated using Eq. (3.3).

$$Molarity\ of\ FAS\ solution = \frac{Volume\ of\ 0.0416\ M\ K_2Cr_2O_7\ solution\ titrated}{Volume\ of\ FAS\ used\ in\ titration\ (mL)} \times 0.1 \tag{3.2}$$

$$COD\,(mg/L) = \frac{(A-B)\times M \times 8000}{mL\ sample}$$

Figure 1 COD analyzer

TOC Analysis

TOC analysis is used to determine the total amount of organic carbon present wastewater. It is measured by taking difference of total carbon present in wastewater to that of inorganic carbon present in wastewater.

Total Organic Carbon (TOC)= Total Carbon (TC)- Inorganic Carbon(IC).

Figure2 TOC analyzer

Calibration verification: Calibration needs to be performed periodically to ensure the effectiveness and correctness of TOC. It should be repeated on fixed time period interval or depending upon fixed number of sample testing. It is performed by analyzing sample near midpoint of calibration range. The difference in values so obtained in initial calibration and at the time of verifying the calibration will give the error or deviation. If the error or deviation is above acceptable limit it should be rectified and erected by performing new calibration curve.

UV Analysis

In UV- analysis, has learned the procedure of using UV Spectrophotometer. The procedure of developing the calibration curve for various dyes was also covered and R^2 value for the same is also demonstrated. The calibration curve for Reactive Red 2 dye and Reactive Red 195 is shown the figure

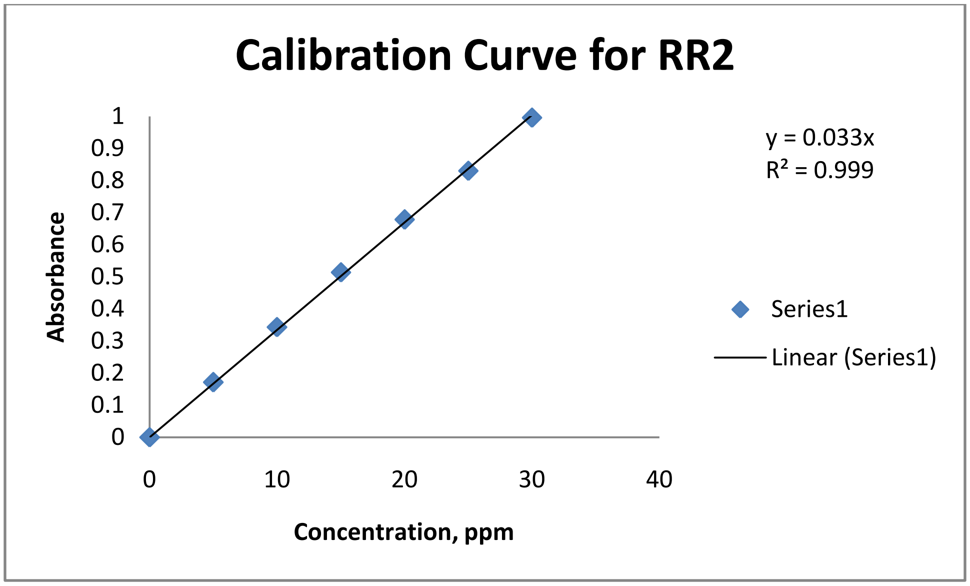


Figure 3: Calibration curve of Reactive Red 2 dye.

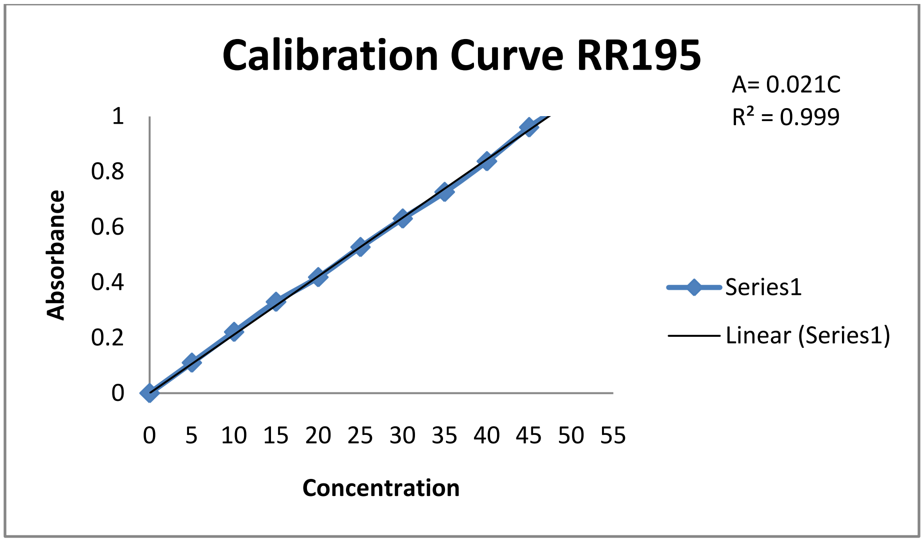


Figure 4: Calibration curve of Reactive Red 195 dye.

Figure 6 UV analyzer

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