ELECTROCHEMICAL OXIDATION OF 4-NITROPHENOL BEARING WASTEWATER

A DISSERTATION

*Submitted in the partial fulfillment of the
requirements for the award of the degree
of*

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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June, 2014

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented by me in this dissertation report entitled "**ELECTROCHEMICAL-OXIDATION OF 4-NITROPHENOL BEARING WASTEWATER**" in partial fulfilment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization in "Industrial Pollution Abatement" submitted to the Department of Chemical Engineering, Indian Institute of Technology Roorkee, is an authentic record of my own work carried out under the supervision of**Dr. V.C. Srivastava**, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India.

The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my belief and knowledge.

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ACKNOWLEGEMENT

ABSTRACT

The electrochemical oxidation is an effective treatment technology for wastewater treatment. In this method, use of the electrical energy can produce complete oxidation of pollutants on high oxidation potential. In present study, oxide coated metal electrode (Ti/RuO_2) was used for the electrochemical oxidation of 4-nitrophenol treatment on laboratory scale under the different experiment condition of current density (j=56.3 to 225.2 A/m^2), initial pH (pH_o=3-9) and initial electrolyte (NaCl) concentration (m=150 to 500 mg/L) and initial concentration of 4-nitrophenol (C_o=50-500 mg/L) within 150 min of treatment. The removal efficiency was determined in terms of chemical oxygen demand (COD) and total organic carbon (TOC). 4-NP was oxidized by both direct (hydroxyl radical generated water electrolysis on anode surface) and indirect (via mediators, hypochlorous acid and active chlorine generated chlorine oxidation in solution) EC oxidation. Various powerful oxidizing species generated during direct and indirect oxidation were capable of rapidly oxidizing 4-NP. Maximum removal COD and TOC efficiencies were found to be 98.87% and 81.92%, respectively, at j=168.9 A/m^2, pH_o=6, C_o=100 mg/L and m=300 mg/L.

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NOMENCLATURE

4-NP	4-Nitrophenol
BOD	Biological Oxygen Demand, mg/l
COD	Chemical Oxygen Demand, mg/l
TOC	Total Organic Compound, mg/l
DO	Dissolved Oxygen, mg/l
DW	Distilled Water
EO	Electrochemical Oxidation
AOPs	Advanced Oxidation Processes
C_o	Initial concentration, mg/l
C_t	Final concentration, mg/l
pH_o	Initial pH value
j	Current Density, A/m^2

INTRODUCTION

1.1. GENERAL

Today we are facing big problem for clean water. This is very difficult task to provide clean water for most of the population throughout the world. Approximate billions of liters wastewater produced by industries every day and this quantity increasing day by day and usually flow these wastes into the canals, rivers, sea, wells and other natural sources. The need is massive in particularly in Third World countries. And in the concluding, some of the geochemical processes have injured the ground water by arsenic and other harmful chemicals in the world [Rajeshwar et al., 1994].

The effluent of many industries may contain very harmful chemicals like poisonous, carcinogenic and mutagenic in a variety of microbiologic and unlike species of fish. A lot of problems due to urbanization and climate changes even in the most developed countries. There is an important time to take action for the reclaim of wastewater [Daneshvara et al., 2003]. Especially dye industries waste are very aesthetic by nature because of their colour and sometimes they form a thick cover on water surface hence causing less passage of light to the related water bodies [Daneshvara et al., 2006].

There are many methods, which are uses for the treatment of wastewater in developed and developing countries such as chemical, biological and physical, which are certain extent not insufficient. But in the third world countries, the wastewaters are generally discharged directly into ponds, rivers, sea and other natural water foundation which in container causes solemn difficulty for the aquatic lives. The biological techniques are low-priced but cannot be used for a multiplicity of wastewaters. It is very successful for handling waste, highly innovative, affordable and effective ways to develop a mandatory obligation [Daneshvara et al., 2003].

A dangerous indication has raised due to the increasing industrialization and increasing population and decrease in quality and quantity of usable water, so the industries which produce set of poisonous and very dangerous waste which is left unprocessed in water sources and which later becomes useless for the human beings. So

definitely we want to urgent need of some new technologies for wastewater treatment [Daneshvara et al., 2006].

Rapid industrialization and urbanization often flowing into rivers and streams that meet their end have given rise to the generation of chemical waste. The presence of toxic organic pollutants such as phenols, nitrophenols, chlorophenols and hexachlorobenzenes in these water bodies poses a health threat, not only to humans, but also to the aquatic flora and fauna. Many of these organic pollutants are persistent in the environment and are biomagnified in the food chain. The major concern is the disposal of toxic organic wastes and treatment methods have been proposed [Cestarolli and Andrade, 2007].

1.2. CHARACTERISTIC OF PHENOLS

Phenol and its other compounds are multifaceted and very important organic chemicals of many industries. Runge found it from coal tar [Runge, 1834]. Firstly a product was isolated by heating salicylic acid with lime by C.F. Gerhardt in 1843 and that was known as 'phenol' [Gerhardt, 1843].

According to demand of phenol, synthetic methods were used for more production. Currently, when we wants to small amount of phenol, we found from coal tar, and more quantity are being produced by coking at the low pressure wood carbonization and brown coal, as well as from oil cracking. Alkali fusion of benzenesulfonic acid is used as latest methods of phenol production [McMurry, 1995]. See fig.1.1
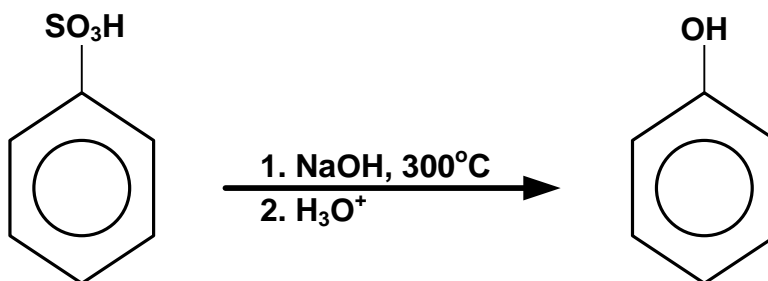
Figure 1.1. Synthesis of Phenol from benzenesulphonic acid (alkali fusion)

[Source: McMurry, 1995**]**

Phenol also prepared via chlorobenzene in presence of hydronium ion and aqueous sodium hydroxide at 340°C, 2500 psi as shown in fig.1.2 [McMurry, 1995].
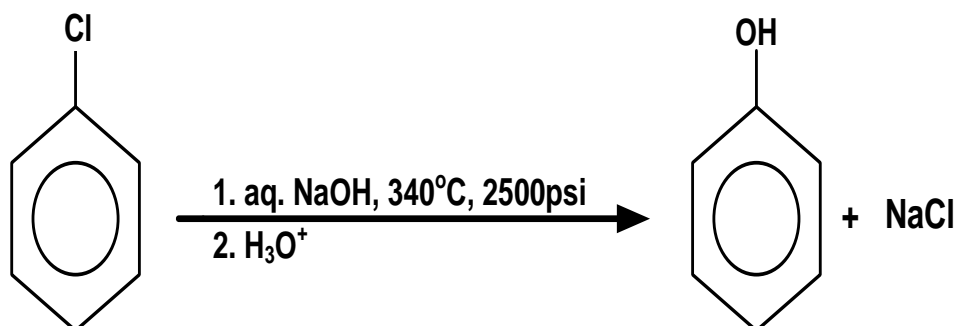
Figure 1.2. Synthesis of phenol from chlorobenzene [Source:McMurry, 1995]

Hock process is more economically and environment friendly, which utilizes cumene as substrate. The main byproduct of Hock process is acetone, but it's not a disadvantage of method since acetone is also highly demanded product worldwide. Oxidation of terthydroperoxide, gives the product as phenol and acetone [Frank and Stadelhofer, 1987] See figure1.3.

Cumene   Cumene   Acetone
                hydroperoxide
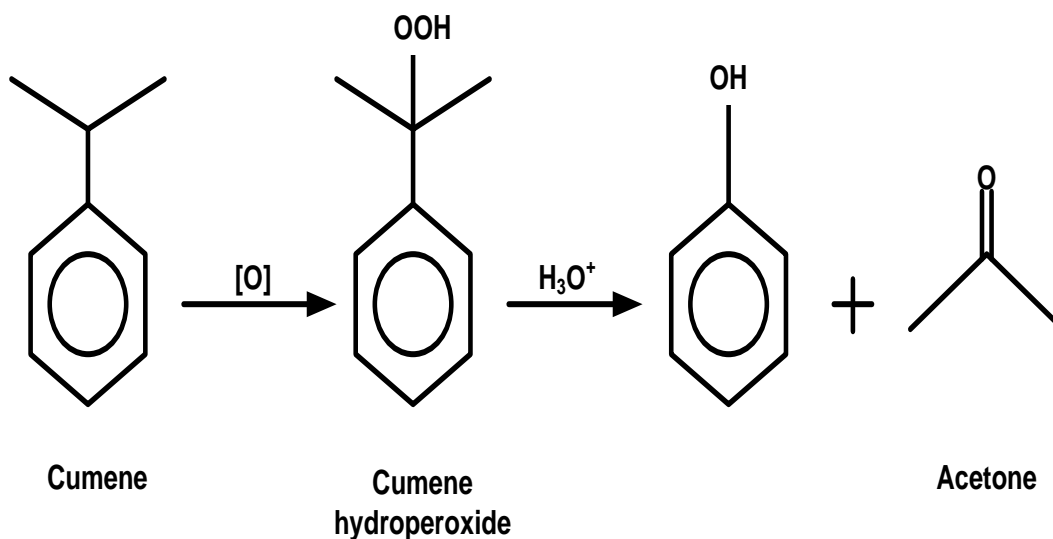
Figure-1.3. The Hock process for synthesis of phenol [Frank and Stadelhofer, 1987]

1.3. PROPERTIES OF PHENOL

Table-1.1. Properties of phenol (Source: http://en.wikipedia.org/wiki/Phenol)

Properties	
General formula	C_6H_6O (C_6H_5-OH)
IUPAC name	Phenol
Other name	Carbolic acid, phenylic acid, benzenol, hydroxybenzene, phenic acid
Appearance	Transparent crystalline solid
Density	1.07 g/cm^3
Molar mass	94.11 g mol−1
Boiling point	181.7 °C, 455 K, 359 °F
Melting point	40.5 °C, 314 K, 105 °F
Solubility inwater	8.3 g/100 mL (20 °C)
Acidity (pKa)	9.95 (in water), 29.1 (in acetonitrile)

1.4. PROPERTIES OF 4-NITROPHENOL

4-nitrophenol crystalline state shows two polymorphs. Alpha form is colorless pillars, volatile at 25°C and stable to sunlight. The beta-form is yellow pillars, stable at 25°C and gradually turns red radiation of sunlight. Generally 4-nitrophenol exists as mixture of two forms. At 22°C, dissociation constant (pKa) of 4-nitrophenol has 7.16. 4-

nitrophenol solution likely develop a bright yellow colour. The color changing properties of this compound makes it useful as a pH indicator [Internet-http://en.wikipedia.org/wiki/4-nitrophenol].

4-nitrophenol is soluble in water and more soluble in hot water and more dense as compare to water. This is moderately toxic, crystalline substance and it also be explode when mix with Diethyl phosphate with heated. It is decompose exothermally and also emits toxic fumes of nitrogen oxides. 4-nitrophenols is used as reagents for production of herbicides, pesticides, explosives [www.chemicalbook.com/ChemicalProductProperty].

Table-1.2. Properties of nitrophenol
(Source: http://www.chemicalbook.com/ChemicalProductProperty_EN_CB7852550.htm)

General formula	$C_6H_5NO_3$
Appearance	Colorless or yellow pillars
Density	1,27 g/cm3
Molar mass	139.11 g mol−1
Boiling point	279 °C
Melting point	113–114 °C
Vapor pressure	0.6 mm Hg at 120°C
Sensitive	Light Sensitive
Solubility in water	16 g/L (25°C), 11.6 g/L (20°C), 10 g/L (15°C),
Acidity (pKa)	29.1 (in acetonitrile), 9.95 (in water)

1.5. PHENOLS AS POLLUTANT

For many reasons phenol was used as a model pollutant. This is a pharmaceutical and petrochemical industries, oil refineries, pesticides and textiles, chemicals and plastics plants, coal tar distillation plants and industries involved in the production of polymeric resin that is representative of many industrial wastes [Rajkumar and Palanivelu, 2004]. Also, the biochemical and chemical degradation pathways are well studied and the metabolites have been characterized [Canizares et al., 2005].

In waste water treatment terminology includes not only phenol (C_6H_5OH), but all derivatives of the aromatic ring that contain one or more hydroxyl group. Phenols are constituents of many industrial waste water streams. The main sources of phenolic waste

are coke plants and oil refineries. Phenols are finding increasing use in solvents, paints, coating, fertilizers, stripping agent, explosives, vehicles, drugs. plastics, wood preservatives and rubber substitutes. There are some usefulness of phenolic compound, they will undoubtedly continue to be a major product of the chemical industry. Unfortunately, some of the chemical characteristic that makes phenols so useful is also responsible for their pollution potential.

Chlorine, which used in drinking water combines with phenols to form chlorophenols which are persistent pollutants, since they are not easily degradable in the environment. In drinking water, concentration as low as 5 µg/l of phenols will impact objectionable tastes and odours when phenols are combined with chlorine [Throop, 1977].

Due to this reason, U.S. Public Health Service has set the allowable phenols concentration in drinking water at 1 µg/l [Siegerman, 1971]. At the above level of 2 µg/l, phenols are toxic to fish, but can cause in fish flesh at concentrations far below the toxic level [Lanouette, 1977].

The chemical oxygen demand (C.O.D.) of phenols is relatively high (theoretically 2.4 mg O_2 per mg phenol) and in sufficient concentration can deplete the oxygen of a receiving body of water causing the death of vegetable and animal species.

Permissible levels of phenols have been established by U.S. Environment Protection Agency (E.P.A.) for different industrial wastes. These guideline generally limited phenolic concentration to 0.1 mg/l in 1977 and project a standard of 0.02 mg/l for 1983 [Lanouette, 1977].

1.6. PARAMETERS REFLECTING WATER QUALITY

Different parameters have been exposed which reflect on the quality of the water and gives us the information of its usability. Some of the wide-ranging parameters for the industrial wastewater include pH, COD, organic acid concentration, heavy metal concentration etc. The waste is monitored using the parameters and only after certain agreeable the standard results conventional by the regulation making bodies can safely be disposed or may be returned to the environment as the case as it may be. There are other

physic-chemical methods or parameters involve a very detailed analysis which gives us the possibility of a particular treatment process for a particular or type of the wastewater.

1.7. WASTEWATER TREATMENT TECHNOLOGIES

Industrial wastewater treatment actually covers the mechanism used to treat the waste water that have been contaminated in some way or the other by either anthropogenic or commercial behavior prior to its release into environment or may be its reuse. Many waste water methods have reached a lot in investigate which has been reported later in the literature. New methods have been made very useful by scientifically studying their applicability and mechanism for the different kinds of wastewater. Some of the various methods are:
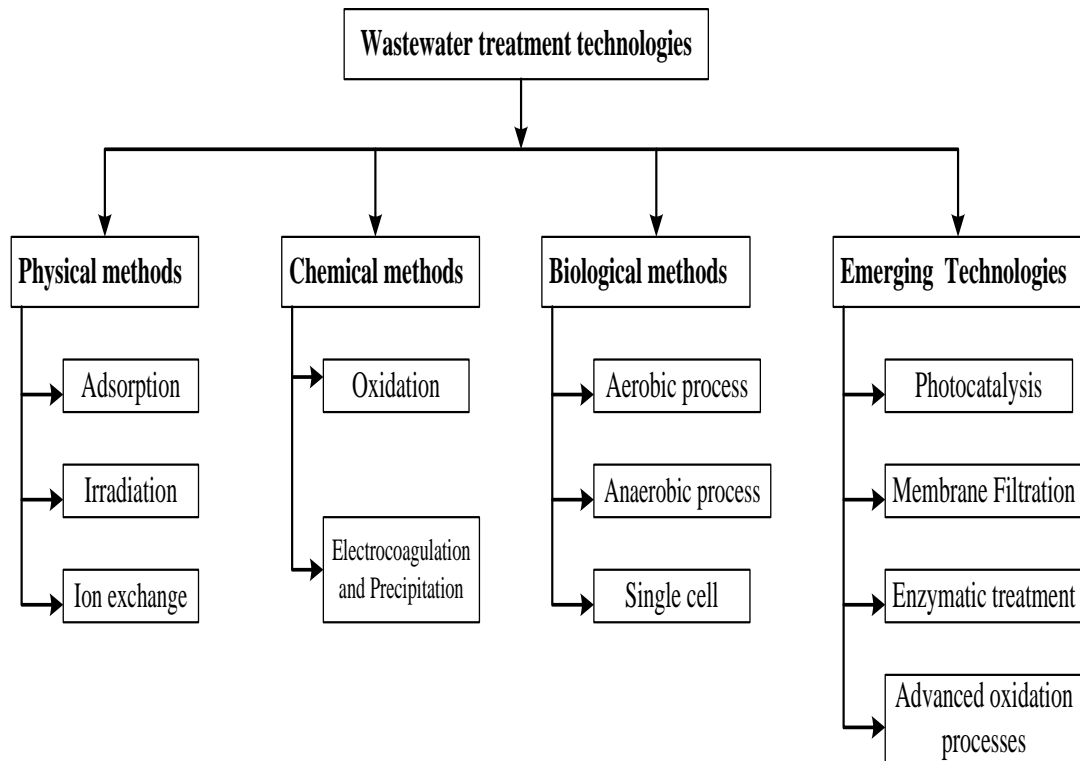
Figure 1.4. Various methodology of wastewater treatment

Incineration, adsorption, biological treatment, electro-catalytic oxidation, and electrochemical oxidation are a few of the technologies available to treat organic pollutants in wastewater. The economy of operation of the treatment process, ease of control, reliability and efficiency are the factors that govern the selection of a treatment process for a given application [Comninellis and Pulgarin, 1991].

In physical and chemical process, electrochemical (EC) treatment is advanced processes which provide simple tools for process control and operation of high removal efficiency in compact reactors. For the treatment of varieties of industrial wastewater, various researchers have utilized it. EC methods has been very successful for nutrient rich wastewater like restaurant wastewater [Kushwaha et al., 2010].

EC treatment is an best upcoming wastewater treatment technology. The major Check-off area among the EC treatment is electro-flotation, electro-coagulation and electro oxidation. In Electro-flotation process, generated O_2 and H_2 from water electrolysis move upwards and takes the pollutant particles to the surface of liquid body. Electro-coagulation is a simple process in which oxidation occurs in the anode surface and various metal hydrolyzed species are produced. These metal hydroxides recapture organic compounds from wastewater by sweep coagulation and/or by aggregating with colloidal particles present in the waste water to form bigger size flocs and ultimately get removed by settling. Electro coagulation method is very efficient in COD removal and discoloration with low energy consumption [Kushwaha et al., 2010].

Electro-oxidation process is two type:

1. Direct oxidation (anodic oxidation) at which pollutant first absorbed on anode surface then destroyed by anodic electron transfer reaction *(Vlyssides et al., 1999)*.

2. Indirect oxidation strong oxidants like chlorine, ozone, hydrogen per oxide, hydroxyl ions (OH^-) are generated at cathode *(Pletcher et al., 1990)*.

In short, in the electrochemical-oxidation process of wastewater treatment, Organics contained presented in wastewater are oxidized directly at surface of electrode or oxidizing agent is electrochemically generated to carry out oxidation.

EC treatment of wastewater is an effective technique. In this technique, not only smaller colloidal particles can be removed but also this technique of treatment produces relatively low amount of sludge. Therefore, it has been successfully applied for treatment of various types of industrial wastewaters. Thus, wastewater can be treated efficiently at neutral conditions using various electrodes [Singh, et al., 2013].
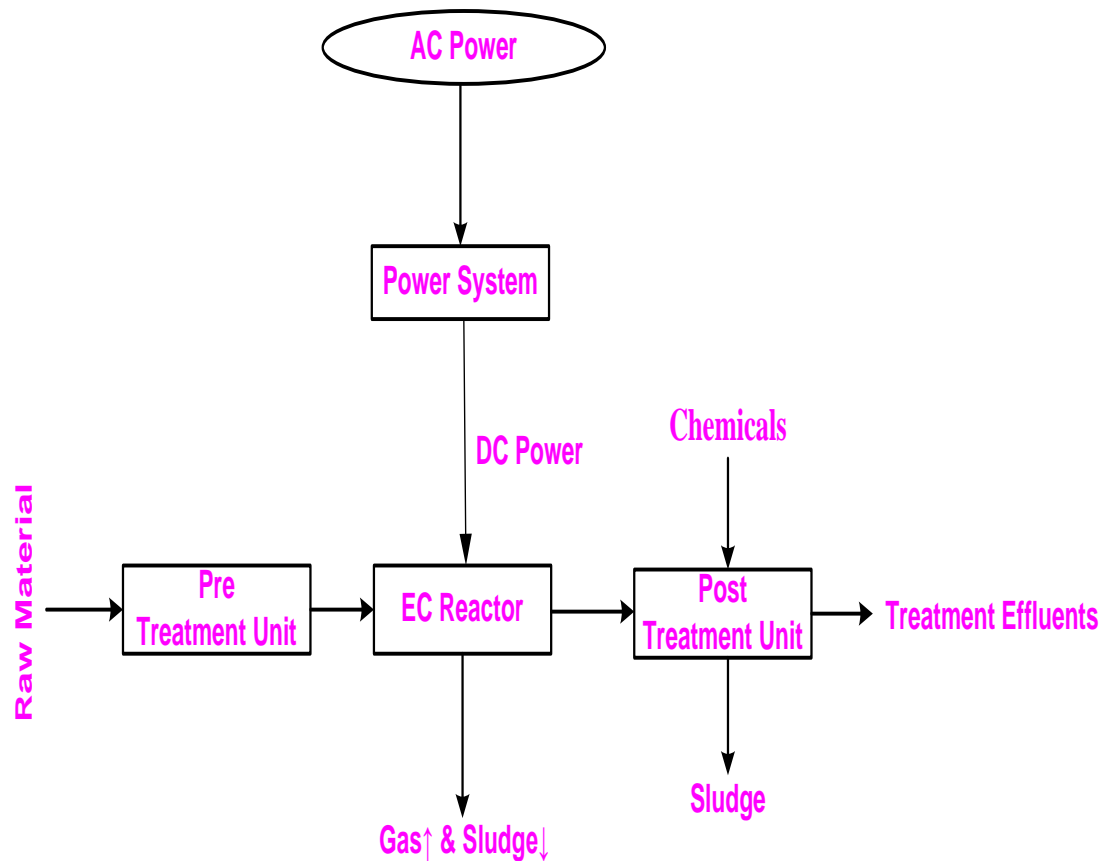
Figure-1.5. Schematic diagram of EC treatment process

1.8. ENVIRONMENTAL POLLUTION STANDARDS

Table-1.4 Minimal national standards for oil refineries, petrochemical, organic chemical industries [Source: CPCB, 2011]

Oil Refineries	Maximum permissible limit (mg/l)	Maximum permissible quantity (kg/100 kg of crude oil)
Oil and Grease	10	7
Phenol	1	0.7
Sulphide	0.5	0.35
BOD(3 days at 27 ^{o}C)	15	10.5
Suspended Solid	20	14
pH	6 - 8.5	

Table-1.5. Maximum permissible concentration of pollutants in effluent discharge [Source: CPCB, 2011]

Oil Refineries	mg/l	MINAS Standard kg/1000 tonnes of crude processed
Oil and grease	10	7.0
Phenol	1	0.7
Sulphide	0.5	0.35
Suspended Solid	20.0	14.0
BOD (3 days at 27 ^{o}C)	15.0	10.5

Table-1.6. USEPA (U.S. environment protection agency) maximum discharge standards for land and surface water (USEPA, 2006)

Parameter	Permissible Limit (ppm)
Phenolic Compounds (as C6H5OH)	0.5
Cyanide (as CN -)	0.1
Ammonical Nitrogen	1
Total Kjeldahl Nitrogen (TKN	25
Sulphide	0.002
Biochemical Oxygen Demand (BOD5)	40
Chemical Oxygen Demand (COD)	120
Oil & Grease	10

1.9. AIMS AND OBJECTIVE

4-NP has been subjected to a lot of research particularly because of its toxicity and importance in many industries. Electrochemical oxidation has already proved its worth as a wastewater treatment technology for a wide variety of pollutants. However, literature review of 4-NP indicates more work on electrochemical treatment specially electro-coagulation, but very few work done in electro-oxidation with coated electrodes.

Hence, keeping this in mind, the main aim of this work is to study the electrochemical oxidation of 4-nitrophenol bearing wastewater using ruthenium oxide coated titanium (Ti/RuO_2) electrodes. Following objectives were set forth for the present study:

1. To study the effects of operational parameters namely initial pH, current density, inter electrode distance, initial 4-NP concentration and time for COD and TOC removal.

2. To optimize the COD and TOC removal efficiency and to understand the mechanism of 4-NP electrochemical oxidation.

3. To carry out detailed physio-chemical analysis of electrodes and samples (before, during and after process) to understand the feasibility of the process. To perform FE-SEM study so as to determine the change in structure of electrode before and after the process. To perform FTIR (Fourier transform infrared spectroscopy), and GCMS (Gas chromatography mass spectroscopy) so as to understand the degradation process.

LITERATURE REVIEW

2.1 ELECTROCHEMICAL OXIDATION OF PHENOLIC WASTEWATER

Several methods have been proposed for the treatment of industrial effluent containing phenolic compounds. The recalcitrant and bio-refractory nature of such organics inhibits the normal functioning of microorganisms and limits the application of biological methods for their treatment. Phenol removal from aqueous wastewater by liquid-liquid extraction methods does not prove to be economical for concentrations below 4000 ppm. Though several alternatives like electro-catalytic oxidation, separation by electro-flocculation, photo-chemical degradation, peroxide, UV or ozone oxidation, electrochemical oxidation have been proposed for treatment of organics in wastewater, electrochemical treatment of wastewaters is finding application in the water treatment industry owing to the various advantages it offers. It can be a cost –effective addition to the plant for pretreatment of wastewater by removing or decreasing the toxicity and levels of persistent organics and making the effluent stream suitable for biological treatment processes.

2.2. ADVANCED OXIDATION PROCESSES

Advanced Oxidation Processes (AOPs) can be defined as aqueous phase oxidation methods intermediated of highly reactive species such as hydroxyl radicals in the mechanisms leading to destruction of the pollutants [Comninellis et al., 2008 and Poyatos et al., 2010].

$$\text{AOPs} \rightarrow \text{OH}^\bullet + \text{Pollutant} \rightarrow CO_2 + H_2O + \textbf{inorganic compounds}$$
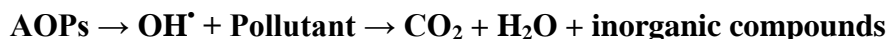
AOPs can be classified as homogenous or heterogeneous processes. Homogenous processes rubricated into processes with or without the requirement of energy input [Poyatos et al., 2010] and heterogeneous photocatalysis based on near ultraviolet (UV) or solar visible irradiation, alkaline ozonation, Fenton's or modify Fenton's chemistry, and combinations of UV irradiation and chemical oxidants.

2.3. ELECTROCHEMICAL OXIDATION (EO)

EO of organic compounds in aqueous solution can be obtained without electrode fouling by performing electrolysis at high anodic potentials in the region of water

discharge due to the participation of intermediates of oxygen evolution [Comninellis et al., 2008]. This process results in partly conversion or full mineralization of the organics, does not need to add oxidation catalysts to the solution and does in principle not produce any by-products. However, current efficiencies are diminished by the secondary reaction of oxygen evolution during oxidation, and generally, removal efficiencies are related to operating conditions and selected electrode materials.

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                    ADVANCED OXYDATION
                         PROCESSES

    HOMOGENEOUS PROCESSES              HETROGENEOUS PROCESSES

                                                    ( Catalytic Ozonation )

    USING ENERGY       WITHOUT ENERGY              ( Photocatalytic
                                                      ozonation )

                          ( O3 in alkaline
                              medium )             ( Hetrogeneous
                                                      Photocatalysis )
 Ultraviolet  Ultrasound  Electrical
 Radiation    Energy      Energy
                          ( O3/H2O2 )

 ( O3/UV )   ( O3/US )  ( Electro-
                          Fenton )    ( H2O2/Catalyst )

 ( H2O2/UV ) ( H2O2/US ) ( Anodic
                           Oxidation )

 ( O3/H2O2/UV )          ( Electrochemical
                           Oxidation )

 ( Photo-Fenton
   Fe2+/H2O2/UV )
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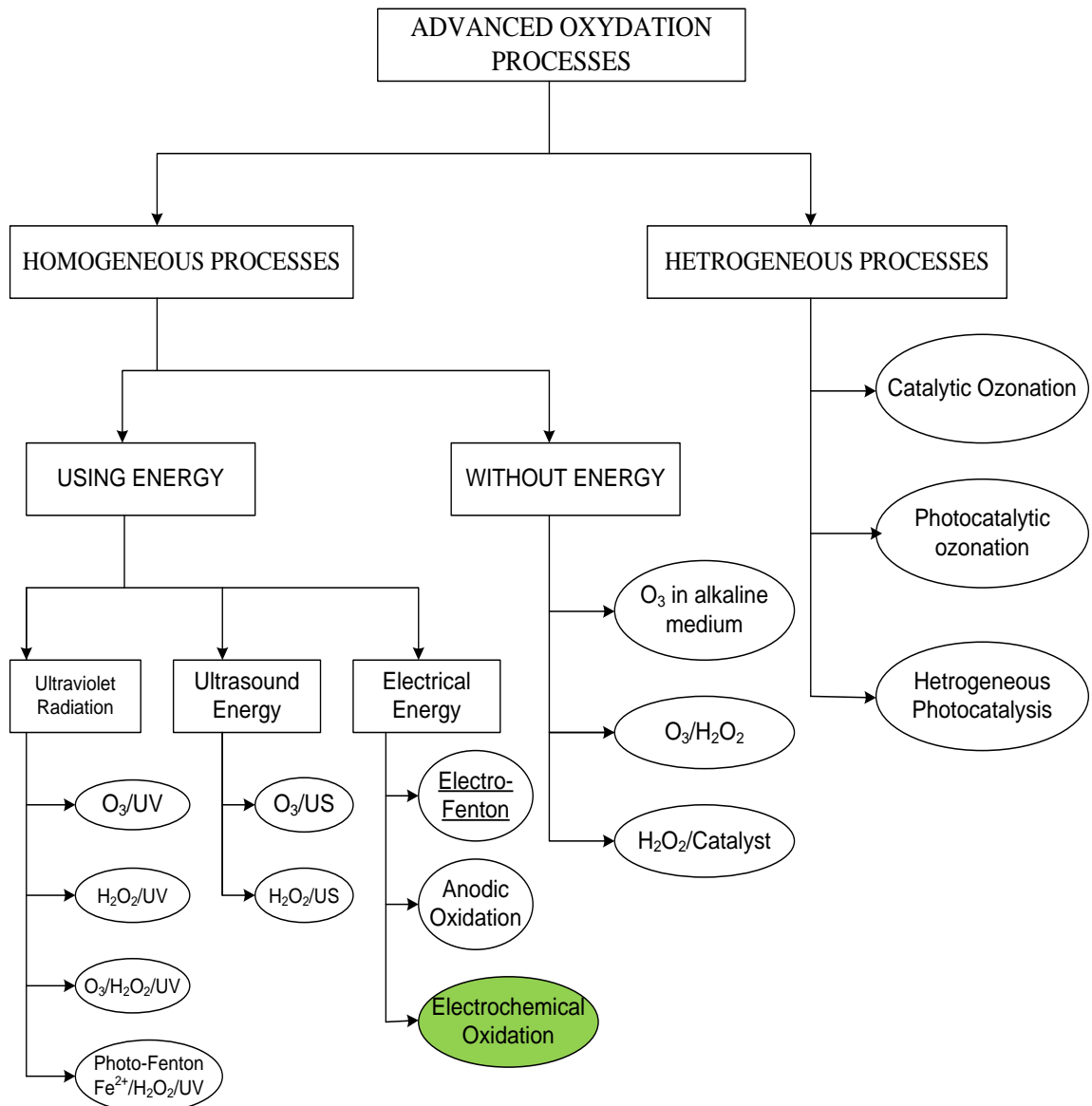
Figure 2.1. Classification of advanced oxidation processes [Poyatos et al., 2010]

Cestarolli*et al.* [2007] investigated oxidation of phenol at $Ti/Ru_{0.3}Pb_{(0.7-x)}Ti_xOy$ oxide electrodes in acidic media and found that higher lead oxide content provided faster degradation of phenol and faster aromatic ring opening. They noticed highest TOC

removal and 45% phenol mineralization in 5 hours for the $Ti/Ru_{0.3}Pb_{0.5}Ti_{0.2}O_2$ composition.

Iniesta*et al.* [2001] conducted a small scale experiment for the biorefractory solutions treatment with higher concentration of phenol (1000 ppm) and obtained complete degradation at bismuth-doped and pure lead dioxide electrodes in the presence of sodium chloride. They noticed greater COD reduction at alkaline pH, lower final concentration of phenol in acidic media, and that an increase in chloride concentration increased COD and phenol removal.

Abuzaid*et al.* [1999] studied oxidation of phenol at a graphite electrode, found that an increase in current led to increased phenol removal efficiency, and concluded that when ionic transport increases, the rate of electrode reactions increase for phenol removal.

Inesta*et al*. [2001] reported that, during bulk electrolysis of phenol in perchloric acid and at a boron-doped diamond electrode, oxidation of phenol is occurs into hydroquinone, benzoquinone and catechol type aromatic compounds at low current density and high phenol concentration while complete combustion of phenol to carbon dioxide takes place at high current density and low phenol concentration owing to the fact that the concentration of hydroxyl radicals generated at the anode surface is high. They also noticed that electrode fouling could happen due to formation of polymeric film in the potential region of water stability while indirect oxidation takes place in the potential region of water decomposition that can avoid electrode fouling. Though several electrodes are capable of decreasing phenol concentration in the effluent, literature suggests that the extent of oxidation of phenol should not be overlooked because intermediates like quinones and chlorophenols are more toxic than phenol.

Patnaik*et al.* [2004] found in their experiments that phenol at ambient temperatures reacted completely with chlorine to form chlorophenols and detected no residual phenol in a mixture of phenol and chlorine after a contact time of one minute. The EO of phenol has been extensively studied at several electrodes using different electrolytes. Comninellis and Nerini report in their paper that Mieluch*et al.* have studied the direct oxidation of organics in the presence of NaCl and reported the formation of

chlorinated by-products which can increase the toxicity of the effluent and make it more hazardous than the original waste stream [Comninellis and Nerini, 1995]

Canizares*et al.* [2005] found that apart from carbon dioxide as the final product, there was formation of volatileorgano-chlorinated compounds and polymeric materials while working with chlorinated phenolsand nitro-substituted phenols respectively.

In a study conducted by Rajkumar*et al.* [2005] using a Ti/Ti-RuO$_2$-IrO$_2$ anode, it was found that indirect electrochemical oxidation of phenol with chloride as the supporting electrolyte lead to complete degradation of phenol while only a small amount was oxidized by direct EO. During their study, they also observed noticeable formation of chlorinated compounds at the beginning of the electrolysis process that later were lost after extended electrolysis Comninellis and Nerini, [1995] studied indirect electrochemical oxidation of phenol using sodium chloride as the supporting electrolyte with Ti/IrO$_2$ and Ti/SnO$_2$ anodes and found that current density and chloride concentration did not influence the rate of elimination of phenol and that NaCl catalyzed the anodic oxidation only at the Ti/IrO$_2$ anode. They also drew a conclusion that the electrogenerated ClO$^-$ was responsible for the catalytic action of NaCl in the oxidation of phenol and its oxidation products both near the anode and in the bulk electrolytic solution.

In another study by Lin *et al.* [1991] involving the treatment of saline wastewater by electrolysis using phenol as the pollutant and cast iron as the anode, it was noticed that at medium salinity, direct oxidation at the anode surface dominated the electrochemical process whereas in electrolytes with salinity over 3%, the phenol removal was due to the indirect oxidation by hypochlorousacid.

Iniesta*et al.* [2001] suggest the use of an alkaline medium during the oxidation of phenol to prevent or reduce the formation of halocompounds. In alkaline medium, the electrogenerated chlorine is converted to hypochlorite and hypochlorite is known for its strong oxidizing properties. However, there is not much literature pertaining to the production, control and impact of chlorinated inorganics such as chlorates on the process efficiency.

In study of Amrane et al. [2011], EO of phenol on Pb/ PbO$_2$ electrode was accomplished to evolve for future model. A central composite design (CCD) was

employed to investigate the key operating parameters and to identify the most relevant interaction. The model equations derived from these parameters lead to a classification based on their level of significance, as current density, initial concentration of phenol, temperature and agitation speed. In addition, we were found the three relevant interactions, initial concentration of phenol-current density, current density-temperature, and initial concentration of phenol-temperature. After performing a screening of different factors, the response surface analysis to yield the optimum conditions for phenol degradation. In this study, current density 19.66 mA/cm^2, 600 rpm agitation speed and 608°C temperature were used. Under these conditions, the obtained phenol degradation yield was 71% and (COD) was reduced approximate to 45%.

In the study of Yavuz Yusuf et al. [1991], ruthenium mixed metal oxide electrode were used in EO for phenol removal which was proceeded in a parallel plate reactor. The effects of various parameters like current density, initial pH, flow rate, temperature, electrolyte concentration and initial concentration of phenol on the removal efficiency were calibrated. Synthetic wastewater of phenol prepared in distilled water, which was recirculated to the electrochemical reactor by a peristaltic pump. Supporting electrolyte like Sodium sulfate was used for the increase of conductivity. During the study, the Microtox bioassay was used to the measurement of toxicity of the synthetic wastewater. As a result study, Phenol and COD removal efficiency of 99.7% and 88.9% were found for the initial phenol concentration of 200 mg/L and initial COD of 480 mg/L, respectively. Mass transfer coefficient and specific energy consumption were found 8.62×10^{-6}m/s and 1.88kWh/g at the current density of 15mA/cm^2. The amount of electrochemically formed oxygen used for the oxidation of organic pollutants was 2.13 g O_2/g phenol which is also known as electrochemical oxygen demand (EOD). EO of petroleum refinery wastewater was also studied at the optimum conditions. Phenol and COD removal of 94.5% and 70.1% were achieved at the current density of 20mA/cm^2.

Table 2.1. Various types of electrodes used in organic containing wastewater during electrochemical oxidation:

Anode materials	Nature of wastewater	Operating parameters		Process performance		Refs.
		Experimental conditions	Nature of reactor and electrode	Process efficiency	Removal efficiency	
Ti/RuO$_2$	DCP & PHB	C$_o$: 1000 gL^{-1}; pH: 7.0; T: 40°C; m: 0.2 M phosphate buffer; j: 200 Acm^{-2}	Undivided EC flow reactor; g: 1.0 cm; Q: 0.5 and 10 cm^{3}s^{-1}		100% color	Polcaro et al., 2005
Sb-doped SnO$_2$	ketoprofen	C$_o$: 50 mgL^{-1};V$_{sol}$: 100 mL; pH: 7.0 to 9.0; T: 25°C; m: 0.1 M Na$_2$SO$_4$; j: 20 mAcm^{-2}; tEC: 60 min; P: 1.2 V	Conventional three-electrode reactor; g: 10 mm; A: 8.8 cm^2	K=0.93 h^{-1} v: 100mVs^{-1}	63.4% ketoprofen	Fan et al., 2013
Eu doped Ti/SnO$_2$/Sb	Phenol	C$_o$: 100 mgL^{-1}; V$_{sol}$: 80 mL; T: 25°C; m: 0.25 M Na$_2$SO$_4$; j: 1.12 A; t$_{EC}$: 150 min; P: 1.2 V	Batch reactor; g: 15 mm; A: 6.0 cm^2		97% Phenol 90%TOC	Feng et al., 2010
Ta/PbO$_2$	1,3,5-trimethoxybenzene (TMB)	C$_o$: 78 mgL^{-1}; V$_{sol}$: 200 mL; T: 35°C; m: 0.5 MH$_2$SO$_4$; j: 65mAcm^{-2}; t$_{EC}$: 120 min	Batch reactor; g: 15 mm; A: 9.0 cm^2	Pseudo first-order EC: 38 kWhm^{-3} (0.655 kWh (g TOC)$^{-1}$); v: 50mVs^{-1}	65%TOC	Hamza et al., 2011
Sb dopant Ti/Sb-SnO$_2$	4-chlorophenol	C$_o$: 78 mgL^{-1}; V$_{sol}$: 400 mL; pH: 12; m: 0.2 molL^{-1} Na$_2$SO$_4$; j: 20mAcm^{-2}; 1mmolL^{-1} 4-chlorophenol; t$_{EC}$: 180 min	Batch reactor; g: 10 mm; A: 9.0 cm^2; v: 50mVs^{-1}; Q: 1.0 mL min^{-1}	v: 50mVs^{-1}	51.0% 4-chlorophenol; 48.9% COD	Kong et al., 2007
RuO$_2$	Phenol	C$_o$: 200 mgL^{-1}; V$_{sol}$: 500 mL; pH: original; T: 30°C; m: 0.5 gL^{-1} Na$_2$SO$_4$; j: 15 mAcm^{-2}; t$_{EC}$: 90 min; σ: 100mScm^{-1}	Batch Parallel plate reactor; Q: 24.83×10^{-3} L min^{-1}	CE: 74.1%; EC: 0.752 kWhg^{-1}; EOD: 2.05 g O$_2$g^{-1} phenol. SEC:1.88 kWhg^{-1}	99.7% Phenol; 88.9% COD	Yavuz and Koparal 2006

Electrode	Pollutant	Conditions	Reactor	Kinetics/Energy	Removal	Reference
Pb/PbO$_2$	Phenol	C$_o$: 200 mgL^{-1}; V$_{sol}$: 500 mL; [pOH]$_o$: 53.11 mg L^{-1}; pH: 2.0; T: 50°C; m: 0.5 gL^{-1} Na$_2$SO$_4$; j: 25 mAcm^{-2}; t$_{EC}$: 30 min	Batch reactor: r: 600 rpm		71% Phenol; 45%COD	Yahiaoui et al., 2011
Graphite	Phenolic wastewater	C$_o$: 37.24 mM; V$_{sol}$: 100 mL; pH: 9.0; T: 25°C; m: 124 gL^{-1} NaCl; j: 329 Am^{-2}; t$_{EC}$: 12 h; V: 6 V	Batch reactor; g: 8 cm; r: 450 rpm	First-order kinetic	99%	Korbahti and Tanyolac 2003
BDD	p-substituted phenols	C$_o$:300 gL^{-1}; V$_{sol}$: 250 mL; m: 0.2M Na$_2$SO$_4$; pH: 12 ; T: 30°C; j: 20 mAcm^{-2}; t$_{EC}$: 300 min; P: 2.8V	Batch reactor; g: 10 mm; A: 4.0 cm^2; Q: 1.6 AhL^{-1}; v: 100 mV s^{-1}		99%PNP, 78% PHB, 71% P, 67% PC, 66% PMP	Zhu et al., 2007
β-PbO$_2$	Polynitrophenol(PNP)	C$_o$: 400 mgL^{-1}; V$_{sol}$: 500 mL; m: 0.2M Na$_2$SO$_4$; pH: 3.0 ; T: 25°C; j: 30 mAcm^{-2}; t$_{EC}$: 120 min	Batch reactor	ICE: 0.641		Zhou et al., 2005
β–PbO$_2$	4-Chlorophenol	C$_o$: 10,000 mgL^{-1}COD; V$_{sol}$: 10L; pH: 4.5 ; T: 35°C; j: 30 A; t$_{EC}$: 12h σ: 111.5 mScm^{-1}	Batch reactor; g: 5 mm; A: 70 cm^2; Q: 10.5 AhL^{-1}			Cong and Wu et al., 2007
Graphite	Bisphenol-A (BPA)	C$_o$: 500 mgL^{-1}; V$_{sol}$: 675mL; T: 25°C; pH: 5.0; m: 0.05M NaCl; j: 12 mAm^{-2}; t$_{EC}$: 120 min σ: 111.5 mScm^{-1}	Batch undivided reactor; g: 5 mm A: 102 cm^2	44.8 kWhm^{-3}		Govindaraj et al., 2012
BDD	Polyhydroxy benzenes	C$_o$: 10 mmolL^{-1}; V$_{sol}$: 2.5 mmol L^{-1}; T: 25°C; pH: 2.0; m: 5000 mgL^{-1}Na$_2$SO$_4$; j: 30 mAm^{-2}	Single-compartment EC flow cell; g: 9 mm A: 78 cm^2 v: 100 mV s^{-1}		Carboxylic acids C$_4$ and C$_2$	Canizares et al., 2004

p-nitrophenol (PNP), p-hydroxybenzaldehyde (PHB), phenol (P), p-cresol(PC), and p-methoxyphenol (PMP); k: rate constant; 2,6–dichloro phenol (DCP) & p–hydroxybenzoic acid (PHB)

Table2.2. Various types of electrodes used in organic containing wastewater during electrochemical oxidation:

Anode materials	Nature of wastewater	Operating parameters		Process performance		References
		Experimental conditions	Nature of reactor and electrode	Process efficiency	Removal efficiency	
Ti/SnO$_2$-Sb, Ti/RuO$_2$, and Pt.	Phenol	C$_o$: 490 mgL^{-1}; V$_{sol}$: 80 mL; pH: 8.0; T: 25°C; m: 0.25 M Na$_2$SO$_4$; j: 200 mAm^{-2}; t$_{EC}$: 22 h; P: 4.6 V	Batch reactor: g: 8.0 mm; A: 6.0 cm^2; Q: 0.9 ml min^{-1}		89% COD and 78%TOC removal efficiency	Lin et al., 2005
Nano-PbO$_2$ anode (NT/PbO$_2$) and (Ti/PbO$_2$)	Isopropanol and 4-chlorophenol (4-CP)	C$_o$:1.0 gL^{-1}; V$_{sol}$: 200 mL; pH: 11.5; T: 25°C; m: 5.84 gL^{-1}NaCl; j: 15 mAcm^{-2}; t$_{EC}$: 180 min	Batch reactor: g: 1.0 cm; A: 16 cm^2; Q: 60 ml min^{-1}			Tan et al., 2011
Ti/SnO$_2$, Ti/IrO$_2$ and Ti/PbO$_2$	bisphenol-A (BPA)	C$_o$:200 mgL^{-1}; V$_{sol}$: 200 mL; pH: 11.5; T: 25°C; m: 250 mgL^{-1} Na2SO4; j: 2.0 A; tEC: 100 min	Batch reactor: g: 10 mm; A: 45 cm^2; r: 1000 rpm; Q: 2.0 L min^{-1}	v: 150 mVs^{-1}	90%	Zaviska et al., 2012
Ti/BDD, Ti/SnO$_2$–Sb/PbO$_2$, & Ti/SnO$_2$–Sb	Polynitrophenols	C$_o$:250 mgL^{-1}; V$_{sol}$: 100 mL; pH: 7.1; T: 25°C; m: 0.2 M Na$_2$SO$_4$; j: 20mAcm^{-2} A; tEC: 30 min	Batch reactor: g: 10 mm; A: 4.0 cm^2		98% Ti/BDD, 34 Ti/SnO$_2$–Sb/PbO$_2$ 25% Ti/SnO$_2$–Sb TOC	Zhu et al., 2008
PbO$_2$ or F-, Co- and Co,F-doped PbO$_2$	Phenol	C$_o$: 1000 mg L^{-1}; V$_{sol}$: 1 L; T: 45°C pH: 7.0; m: 0.5 M H$_2$SO$_4$; j: 100 mAcm^{-2}; t$_{EC}$: 20 min	Filter press reactor: g: 1.0 cm; A: 63 cm^2; Q: 120 Ah L^{-1}	16% and 70 k Wh kg^{-1} 18% and 105 kWh kg^{-1}COD,	65% COD 45% TOC 75% COD 50% TOC	Andrade et al., 2008

MATERIAL AND METHODS

3.1. GENERAL

In the present study, Ruthenium oxide coated titanium (Ti/RuO$_2$) electrodes were used for the treatment of 4-nitrophenol bearing wastewater. Experimental details of the study have been presented in this chapter. These details include characterization of electrode and samples taken during run, reactor design and batch electrochemical oxidation study with Ruthenium oxide coated titanium (Ti/RuO$_2$) electrodes.

3.2. CHEMICALS

3.2.1. 4-nitrophenol: The Laboratory reagent Grade 4-nitrophenol, (pure) used in this experiment was purchased from HIMEDIA$^{®}$ Laboratories Pvt. Ltd. (REF RM1182-500G) Mumbai, India. The molecular structure of 4-nitrophenol is shown in Fig. 3.1 and properties of 4-nitrophenol are summarized in Table 3.1.
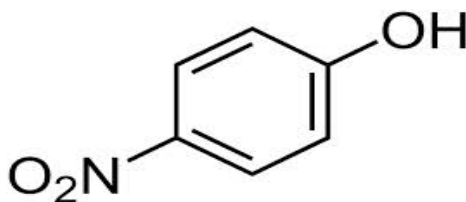

Fig 3.1. Molecular structure of 4-nitrophenol

3.2.2. Silver Sulfate (Ag$_2$SO$_4$): It was used for the preparation of stock solution for measurement of COD. Silver sulfate was obtained from RANKEM (Product code-S0660, Batch- P048B05), RANBAXY Fine Chemicals Limited, New Delhi, India.

3.2.3. Sulfuric Acid (H$_2$SO$_4$): It was also used for the preparation of stock solution for measurement of COD. Sulfuric Acid, 98% AR was obtained from S.D. Fine Chem. Limited (IMDG Code -8/11, UN: 1830 IATA: 8).

Table 3.1. Physical and Chemical Properties

Molecular formula	C6H5NO3
Appearance	Colorless or yellow pillars
Density	1,27 g/cm3
Molar mass	139.11 g mol−1
Boiling point	279 °C, 552 K, 534 °F
Melting point	113–114 °C
Vapor pressure	0.6 mm Hg (120 °C)
Sensitive	Light Sensitive
Solubility in water	10 g/L (15°C) 11.6 g/L (20°C) 16 g/L (25°C)
Acidity (pKa)	9.95 (in water), 29.1 (in acetonitrile)

In this experiment, 4-nitrophenol is used for the preparation of synthetic wastewater for the treatment.

3.2.4. Potassium Dichromate ($K_2Cr_2O_7$): It was also used for the preparation of stock solution for measurement of COD. Potassium Dichromate was obtained from RANBAXY Laboratory Limited (Batch no.-6CCV0712), Punjab, India.

3.2.5. Mercuric Sulfate (Hg_2SO_4): It was also used for the preparation of stock solution for measurement of COD. Mercuric sulfate (Mercury (II) sulfate) was obtained from HIMEDIA® Laboratories Pvt. Ltd. Mumbai, India.

3.2.6. Sodium Chloride (NaCl): It was used for maintain the conductivity of solution during the electro-oxidation. Sodium Chloride, extrapure AR was obtained from SISCO Research Laboratories Pvt. Ltd. (Batch no.T/83122E), Mumbai, India.

3.2.7. Other Chemicals: Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Potassium chloride (KCl), Phosphoric acid (H_3PO_4), Potassium hydrogen phthalate ($C_8H_5KO_4$), etc. also be used during experiment and analysis.

3.3. SYNTHETIC WASTEWATER

Firstly prepared synthetic wastewater for the electrochemical oxidation treatment of 4-nitrophenol (4-NP). Synthetic wastewater having initial concentration of 100 mg/l was used for experiment. Solution was prepared by adding 100 mg of 4-NP in 1 liter distilled water (DW). The solubility of 4-NP is 1.6g/100ml at 25°C. As 4-NP is sparingly soluble in cold water, so it is easily mix in DW at room temperature.

3.4. PREPARATION OF REAGENTS FOR COD MEASUREMENT
3.4.1. Standard Potassium Dichromate Reagent (Digestion Solution): Accurately weighted 10.216 g of potassium dichromate (previously dried in oven at 103ºC for 2 hours) and transferred it to a beaker. Then weighted exactly 33.3g of mercuric sulfate and add to the same beaker. Measure accurately 167 ml of concentrated sulfuric acid using clean dry measuring cylinder and transferred it to the beaker. Dissolve the contents and cool to room temperature. Then 1000 ml standard measuring flask was taken and a funnel was placed over it and make up to 1000 ml using distilled water.

3.4.2. Sulphuric Acid Reagent (Catalyst Solution)

Weighted accurately 5.5 g silver sulphate crystals to a dry clean 1000 mL beaker and carefully add 500 mL of concentrated sulphuric acid and allow to stand for 24 hours (For completely dissolve of silver sulphate crystals).

3.5. INSTRUMENTATION
The instruments, which are used in my dissertation, described as follow:

3.5.1. pH meter: pH adjustment was carried out by HI 2211 pH/ORP meter and purchased from HANNA Instruments.

3.5.2. UV-Spectrophotometer: The initial 4-NP and residual concentrations concentration was determined by UV- Spectrophotometer (UV-1800, SHIMADZU, Serial No.-A114548) with maximum wavelength (λ_{max}) of 319 nm for 4-NP. As the curve is linear upto 30mg/l, so the sample was diluted to measurable concentration.

It works on the Beer-Lambert law, which is given as follows

$$A = \log\left(I / I_0\right) = eCL$$

Where, A is the absorbance measured in Absorbance Unit (AU), I_0 is the influent intensity, I is the intensity transmitted, E is molar absorptivity, C is the concentration of the solution, and L is the length through which the rays are passed.

3.5.3. Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) was determined by COD analyzer (HACH/ DR 5000). The digestion of the sample was done in CSB/COD reactor AL 38 SC, Aqualytic, (Serial No. 0908/ 2210) of 400W. The digestion period was 2 hour at 150°C.

Procedure for measurement of COD

1. Take COD vials with stopper (one extra vial for the blank).
2. Add 3.5 mL of the sample to each of the COD vials and the remaining COD vial is for blank; to this COD vial add 3.5 ml of distilled water.
3. Add 1.5 mL of potassium dichromate reagent - digestion solution to each of the vials.
4. Add 3.5 mL of sulphuric acid reagent - catalyst solution in the same manner.
5. CAUTION: COD vials are hot now.
6. Cap tubes tightly switch on the COD Digester and fix the temperature at 150º C and set the time at 2 hours.
7. Place the COD vials into a block digester at 150°C and heat for two hours.
8. The digester automatically switches off. Then remove the vials and allow it to cool to the room temperature.
9. Clean vials with tissue paper, and determined COD value by COD analyzer.

3.5.4. TOC Analyser

The Total Organic Carbon (TOC) was measured by TOC-VCPH, Total Organic Carbon Analyser Shimadzu and ASI-V Shimadzu (Serial No.- 521048).

3.5.5. Others instruments

Fourier transform infrared spectroscopy (FTIR), Gas chromatography mass spectroscopy (GCMS). Thermo gravimetric analysis (TGA) and Scanning electron microscope (SEM) etc. also be used for the analysis of sample (before, during and after the treatment).

3.6. EXPERIMENTAL PROCEDURES

Experiments were carried out at room temperature in 1.0 Liter beaker of 11 cm diameter inside equipped with two electrodes , 10×8.5 cm^2 piece of Ruthenium dioxide (RuO$_2$) coated titanium base (Ti/ RuO$_2$) electrode (cathode and anode). Electrolysis were carried out under current controlled electrolysis conditions and monitored by a D.C. power supply (4818A10) potentiostat/galvanostat schematic representation shown in Figure 3.3(a), The applied current was 3A studies, Solutions are stirred magnetically in a rate of 600 rpm.
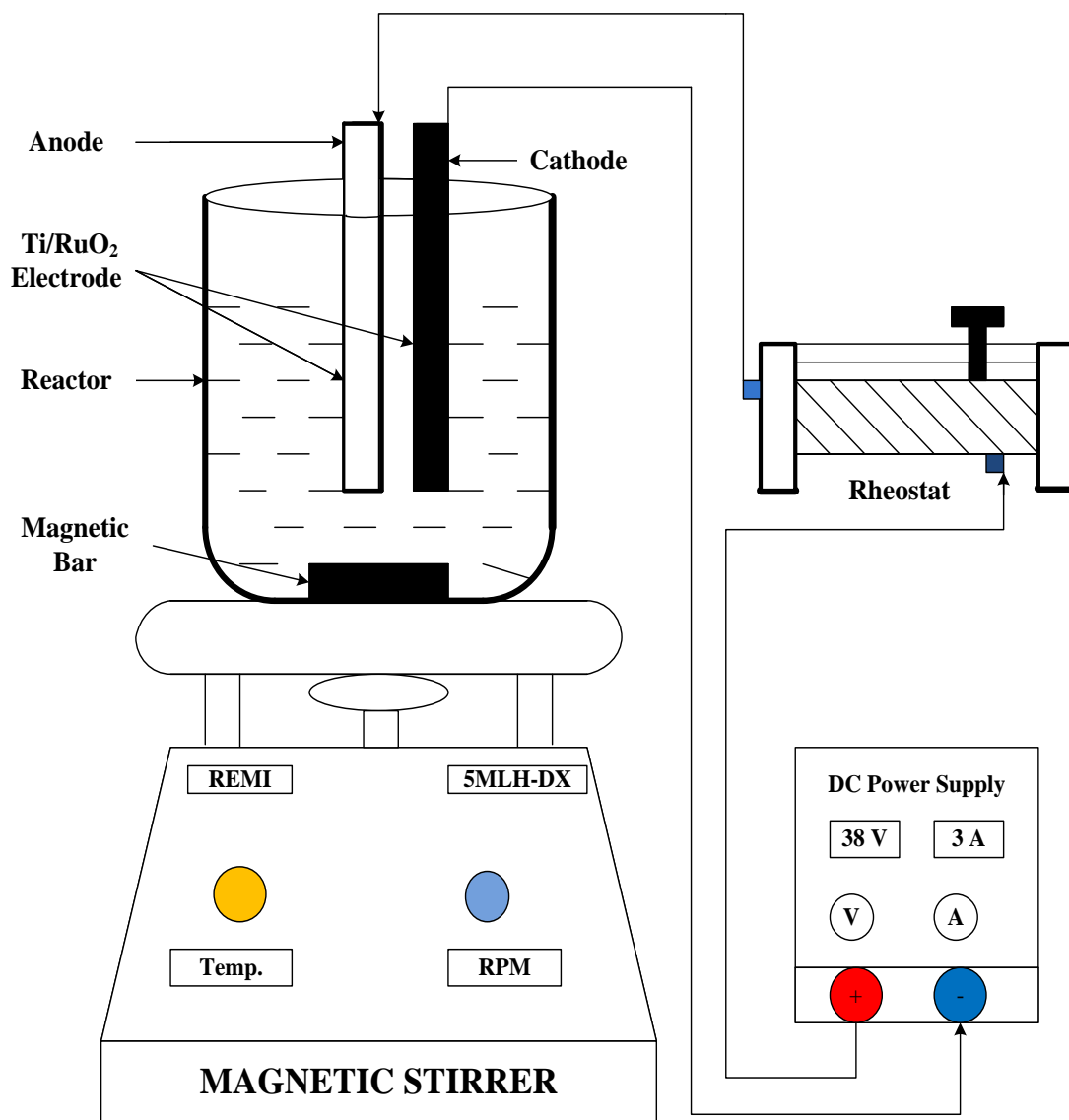

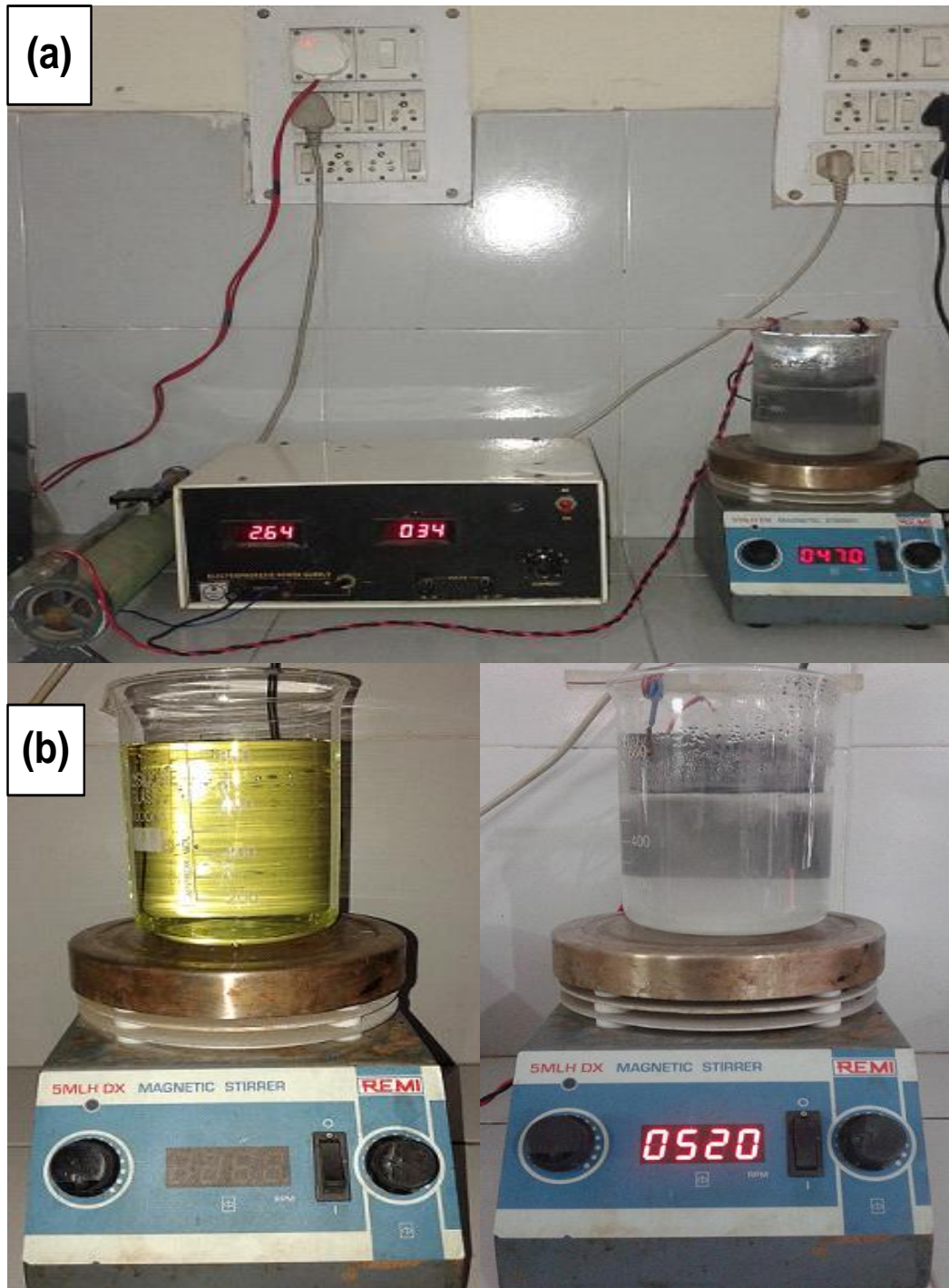**Figure 3.2. Schematic experimental setup**

Figure 3.3(a). Schematic representation of complete electrochemical treatment setup (b). Before and after treatment during the laboratory treatment of 4-nitrophenol bearing wastewater

3.7. ANALYSIS PROCEDURES

The initial concentration of 4-nitrophenol taken as 100 mg/L for treatment in 1.0 Liter beaker and mix 300 mg/L NaCl for conductivity, then supply the DC current of 3A. Measure Initial COD of 4-nitrophenol is 180 mg/L. Sample taken in every 15 min, and find out the COD and TOC removal. The decrease of COD and TOC during treatment and maximum removal find out in 90 min. The change in removal efficiency during the treatment was shown in the fig. 3.3(b)

3.7.1. Current efficiency

Current efficiency is generally defined as the ratio of the charge used for the oxidation of each compound to the total charge passed during electrolysis, and hence states if the electrons in the electrical circuit all come from oxidation of the target organics or if side reaction are dominant. In the literature, different expressions of current efficiency have been proposed: instantaneous current efficiency (ICE), electrochemical oxidation index (EOI) and general current efficiency (GCE) [Panizza and Cerisola, 2009].

Two methods for the determination of ICE and GCE have been proposed, the oxygen flow rate (OFR) method and the chemical oxygen demand (COD) method. Determination of COD is a common parameter in wastewater treatment monitoring, measuring the amount of chemically added oxygen needed in order to oxidize all compounds in a sample amendable for oxidation. This parameter then provides the number of electrons needed to be removed from the solution in order to obtain full mineralization (4 mole e$^-$ per mole O_2).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
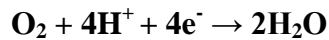
The COD method is the one applied in the current research and ICE is calculated using the following relationship:

$$ICE = \left(\frac{COD_t - COD_{t+\Delta t}}{8I\Delta T} FV \right)$$

Where, COD_t and $COD_{t+\Delta t}$ are the chemical oxygen demand at times t and t + Δt (g L^{-1}), I is the current intensity (A), F is the Faraday's Constant (96485 C mol^{-1}), V is the electrolyte volume (L), and 8 is the oxygen equivalent mass (32 g O2 mol^{-1} / 4 e$^-$).

In the same way, GCE represents an average value of the current efficiency between initial time t = 0 and t.

$$GCE = \left(\frac{COD_0 - COD_t}{8IT} FV \right)$$

The electrochemical oxidation index (EOI) is the average value of the current efficiency during overall oxidation and is determined based on ICE.

$$EOI = \frac{\int_0^t ICEdt}{\tau}$$

The parameter τ represents the time at which ICE is almost zero. If considered during a period of sufficiently short time, particular in the beginning of electrolysis, the EOI can to some extend be considered specific for the compound investigated and supply information of the reactivity of the compound.

3.7.2. Specific energy consumption

An important cost optimization parameter is the determination of the amount of energy needed in order to reach removal goals. The energy consumption, E_{sp} of the EO process is typically expressed as the energy consumed in kWh for removal of one kilogram of COD. It is based on the average cell voltage, U (V), applied in order to reach the desired current intensity.

$$E_{sp} = \frac{tUI/V}{\Delta COD}$$

t(h) is the time of electrolysis and ΔCOD is the difference in initial and final COD (g L^{-1}).

RESULTS AND DISCUSSION

4.1 CALIBRATION CURVE

For Nitrophenol bearing wastewater treatment, prepare 100mg/l solution for finding the absorbance and λ_{max}. With the help of Specto-photometer, found the value of λ_{max} is 319, and absorbance of Nitrophenol for different-different concentrations of sample shown below in Table-4.1 and the calibration curve between concentrations Vs. absorbance was drawn as below see Figure- 4.1

Table-4.1: Data found from Spectrophotometer for calibration of 4-nitrophenol

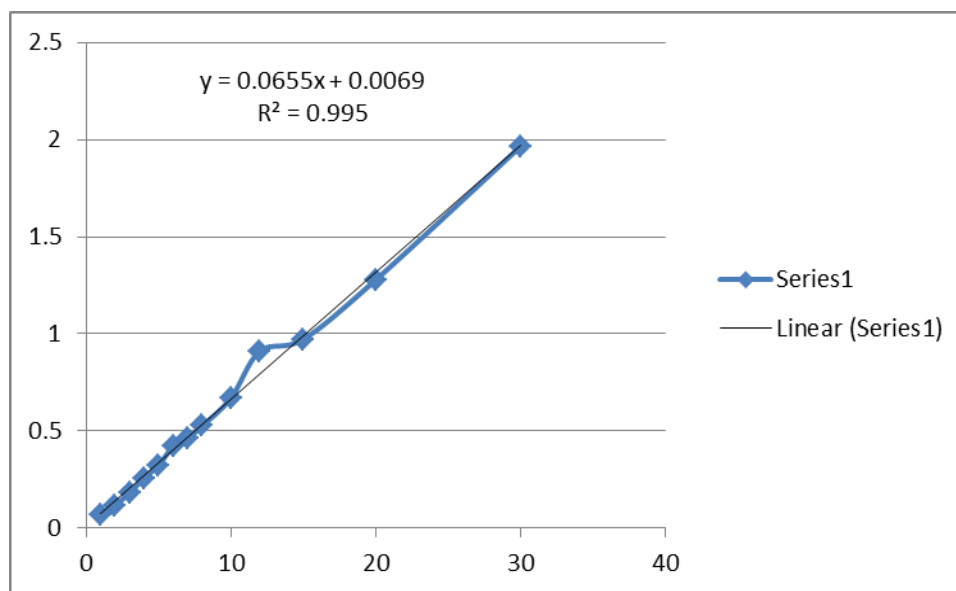| Concentration (PPM)	Absorbance
1	0.066
2	0.117
3	0.183
4	0.258
5	0.323
6	0.421
7	0.461
8	0.526
10	0.669
12	0.911
15	0.972
20	1.277
30	1.963

Figure 4.1. Calibration curve (concentrations Vs. absorbance)

4.2. EFFECT OF CURRENT

Figure 4.2 shows that the effect of current on COD and TOC removal efficiencies decreased for 4-nitrophenol degradation during the electrochemical treatment with Ti/RuO$_2$ coated electrodes. The 4-nitrophenol degradation was increase from 27% to 71% within 15 to 150 min treatment time at 53.6A/m^2 current density. Similarly TOC removal efficiency was also increase from 21% to 64.29% within 15 to 150 min of electrochemical oxidation process.

Same process when applied at 112.6 and 168.9 A/m^2 current density, then 4-nitrophenol degradation was increase from 30% to 83% and 36% to 98.87% respectively and TOC removal efficiency was also increases from 23.37% to 71.34 and 31.17 to 81.92 respectively within 15 to 150 min treatment time. But when we applied 225.2A/m^2 current, we found degradation of 4-nitrophenol increases 33.51% to 95.86% and TOC removal efficiency 29.82% to 79.73% within 15 to 120 min treatment time. The removal efficiency of COD and TOC was schematic reported in Fig. 4.2(a) and 4.2(b) at 100 mg/l initial 4-nitrophenol concentration and electrolyte concentration (NaCl) 300 mg/L at 6 pH of 4-nitrophenol in aqueous solution.

Fig. 4.2(a) and 4.2(b) denoted that the COD and TOC removal efficiency of 4-nitrophenol for both parameters it does accelerate at 300 mg/L NaCl concentration and 100 mg/l initial 4-nitrophenol concentration, but removal efficiency decreases at

225.2A/m^2 current density. COD and TOC removal efficiency at 100 mg/l initial concentration of 4-nitrophenol and electrolyte concentration (NaCl) 300 mg/L at pH 6. The maximum removal efficiency 98.87% COD and 81.92% TOC was obtained with Ti/RuO$_2$ at 150 min of treatment time due to active chlorine species concentration was higher at Ti/RuO$_2$.

At the maximum removal level the co-existence of oxy-chloro radicals, hydroxyl radicals and other intermediate that participate in the chlorine evaluation increase which increase the electrochemical mineralization of 4-nitrophenol concentration solution.

4.3. EFFECT OF INITIAL 4-NITROPHENOL CONCENTRATION (C$_O$)

Figure 4.3 shows the effect of initial concentration of 4-nitrophenol on COD and TOC removal efficiencies for 4-nitrophenol degradation during the electrochemical treatment with Ti/RuO$_2$ coated electrodes. The 4-nitrophenol degradation was increase from 28% to 98.87% within 15 to 150 min treatment time at 100 mg/L initial concentration of 4-nitrophenol. Similarly TOC removal efficiency was also increase from 21% to 81.92% within 15 to 150 min of electrochemical oxidation process. The removal efficiency of COD and TOC was schematic reported in Fig. 4.3(a) and 4.3(b) at constant current density 168.9A/m^2 and electrolyte concentration (NaCl) 300 mg/L at pH 6 of 4-nitrophenol in aqueous solution. Ti/RuO$_2$ electrodes was shows the poor performance at direct oxidation. Therefore, new indirect electrochemical oxidation approach was select for the study of these DSA type electrodes. Indirect oxidation of 4-nitrophenol was study by applying the current density 168.9A/m^2 in presence of 300 mg/L NaCl in 1.0 Liter 4-nitrophenol solution. Fig. 4.3(a) and 4.3(b) denoted that the COD and TOC removal efficiency of 4-nitrophenol for both parameters it does accelerate at 300 mg/L NaCl concentration at current density 168.9A/m^2 during the indirect electrochemical oxidation. The rate of removal efficiency is decrease with increase the 4-nitrophenol. The reaction involve in the indirect EC oxidation and some of the active species such as active chlorine, ozone, or persulfates and hydrogen peroxide are required for act as mediator for electron travelling between the electrode and pollutant and help to avoiding the electrodes fouling during direct electron travelling between electrodes surface and pollutants. The complete mineralization was observed when the hydroxyl radical discharge through H$_2$O at anode and interact with oxygen already present in oxide coated anode and converted into higher oxide and active oxygen.
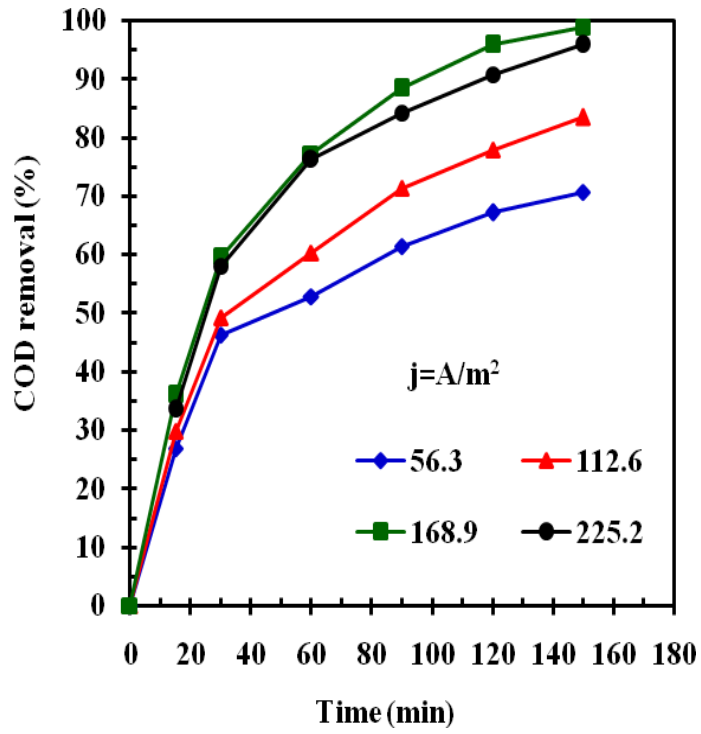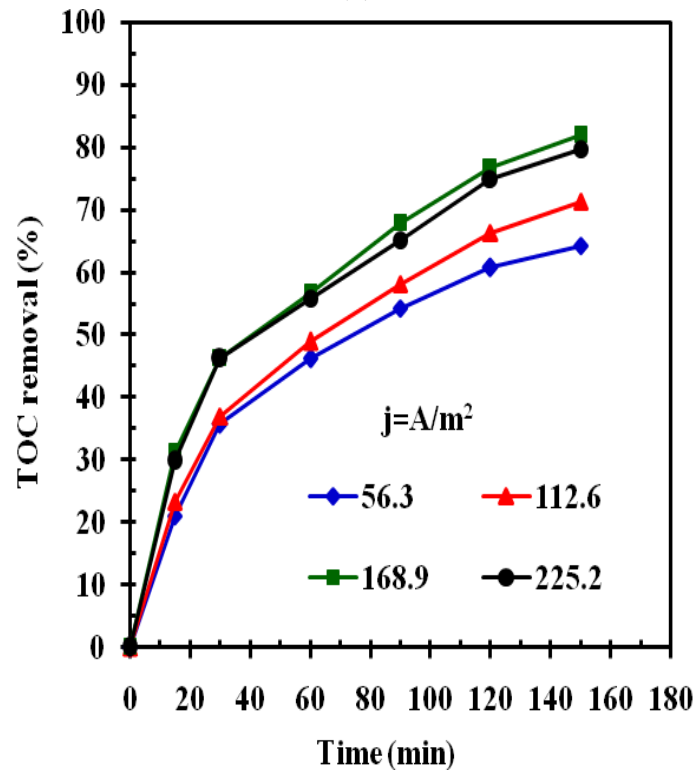
Figure 4.2. Effect of current density on (a) COD and (b) TOC removal efficiency

The active hydroxyl species interact with Cl ions generated by NaCl and convert into active chloride species which then again interact with Cl ions and oxygen already present on the surface of anode oxide. The physiosorption active species (hydroxyl radical) participate in the complete combustion and chemisorbed species undergo selective oxidation. Hence the indirect electrochemical oxidation of 4-nitrophenol solution is a physiosorption and chemisorption phenomenon of absorption. The higher oxidation power containing i.e. Ti/RuO_2 electrodes shows the physiosorption behavior and exhibit complete oxidation with higher intention current efficiency (ICE) for 4-nitrophenol degradation. Some of the author already reported the indirect oxidation in presence of chlorine reduces the amount of dissolved organic matter. Fig. 4.3(a) and 4.3(b) presented that COD and TOC removal efficiency at current density $168.9 A/m^2$ is directly influence by the 4-nitrophenol concentration and electrode materials. The maximum removal 98.8% COD and 81.9% TOC removal was obtained with Ti/RuO_2 at 100 mg/L 4-nitrophenol concentration and constant amount of electrolyte (NaCl) 300mg/L at 150 min of treatment time due to active chlorine species concentration was higher at Ti/RuO_2.
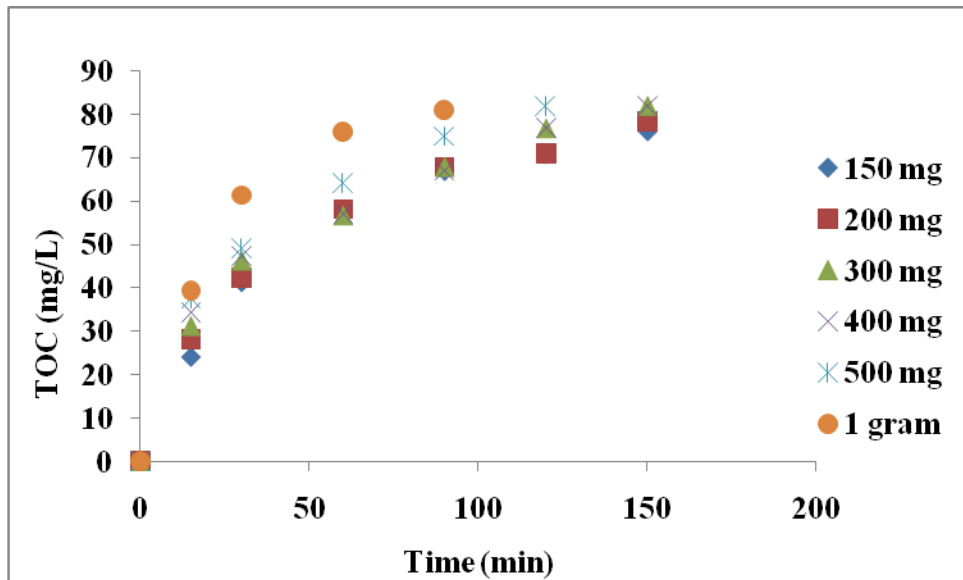
4.4. EFFECT OF pH

Figure 4.4 shows the effect of pH on COD and TOC removal efficiencies for 4-nitrophenol degradation during the electrochemical treatment with Ti/RuO_2 coated electrodes. Many experiments were conducted at various pH value and found best results at pH 6. At this pH value, the 4-nitrophenol degradation was increase from 31.2% to 98.8% within 15 to 150 min treatment time at 100 mg/L initial concentration of 4-nitrophenol. Similarly TOC removal efficiency was also increase from 21% to 81.9% within 15 to 150 min of electrochemical oxidation process. The removal efficiency of COD and TOC was schematic reported in Fig. 4.4(a) and 4.4(b) at constant current density $168.9 A/m^2$ and electrolyte concentration (NaCl) 300 mg/L at various pH value of 4-nitrophenol in aqueous solution.

During the experiments, when we taken the simples at various time interval observed pH value increases with experiment time. The 4-nitrophenol degradation and TOC removal shown in figure 4.4(a) and 4.4(b) at various pH value and at pH 6 gave best result.
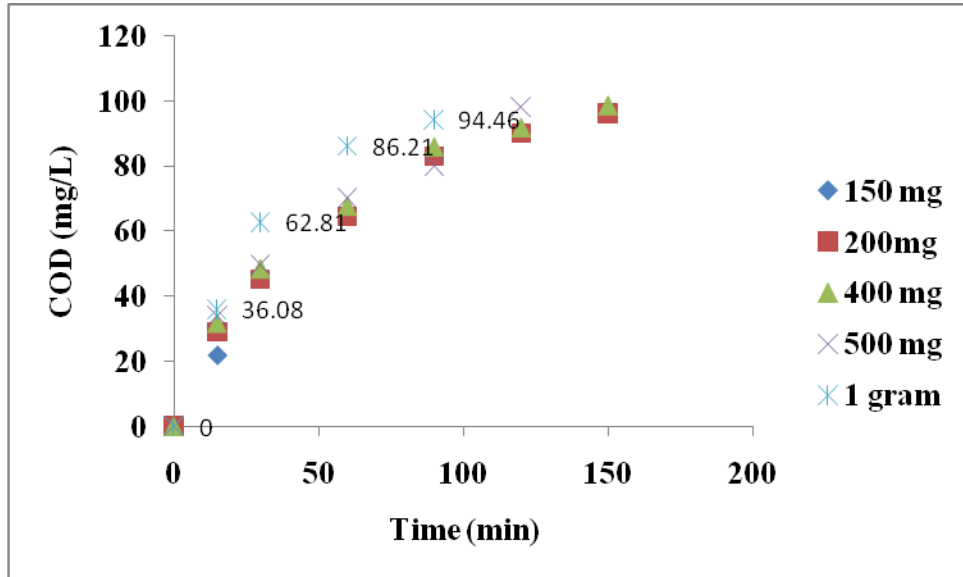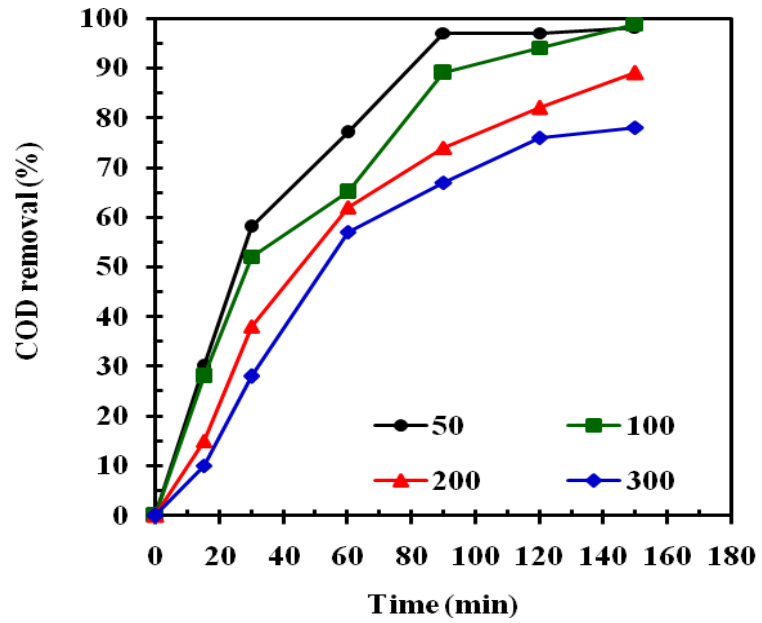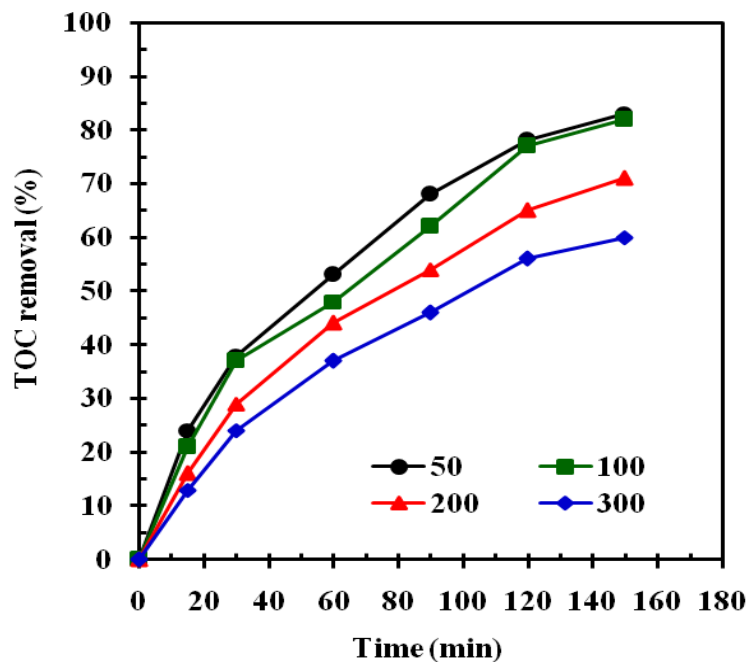
(a)

(b)

Figure 4.3: Effect of initial concentration of 4-nitrophenol on (a) COD and (b) TOC removal efficiency.

(a)

(b)

Figure 4.4. Effect of pH on (a) COD and (b) TOC removal efficiency.

4.5. CHARACTERIZATION OF Ti/RuO$_2$ ELECTRODE

Path I

Path III
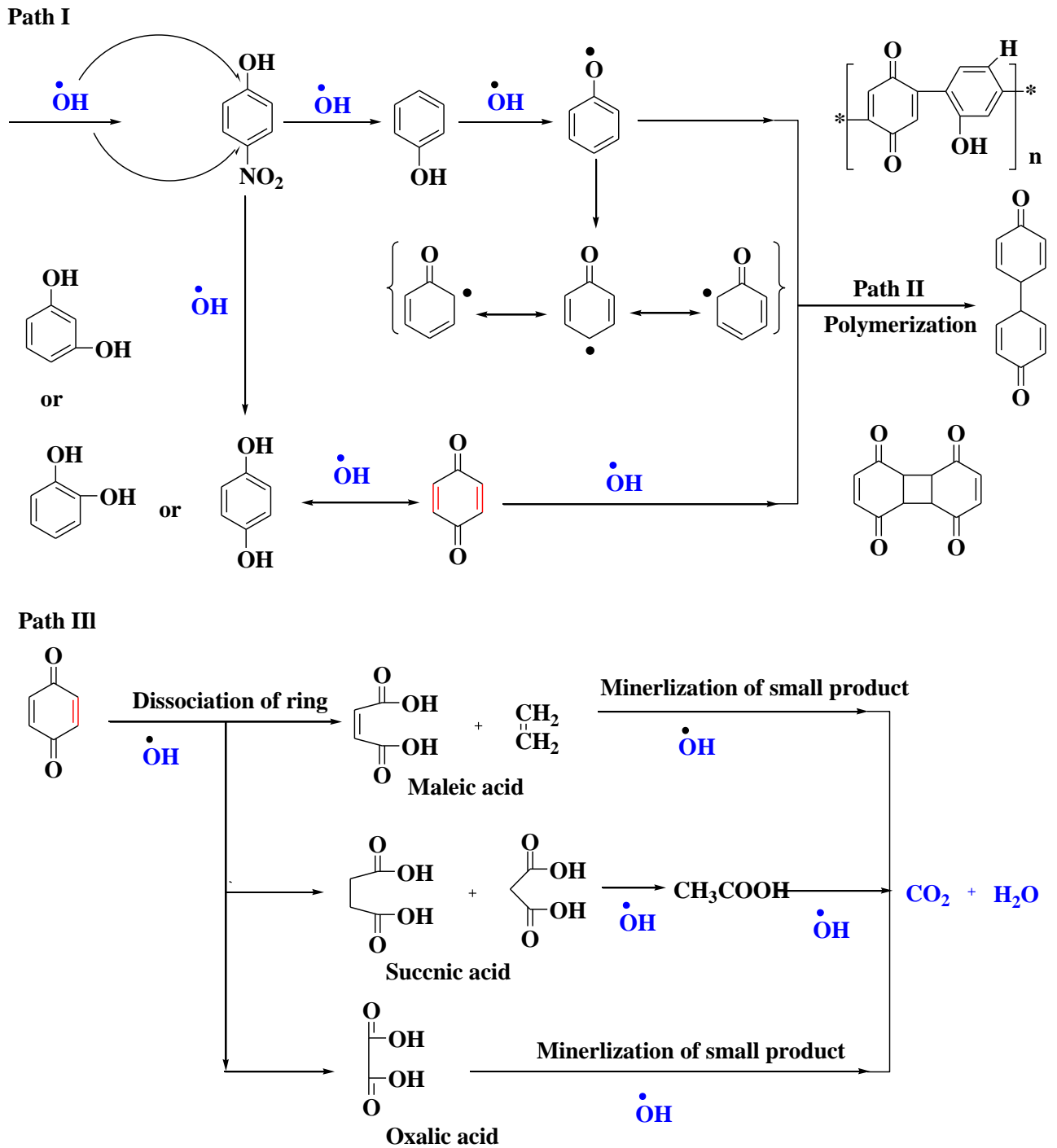
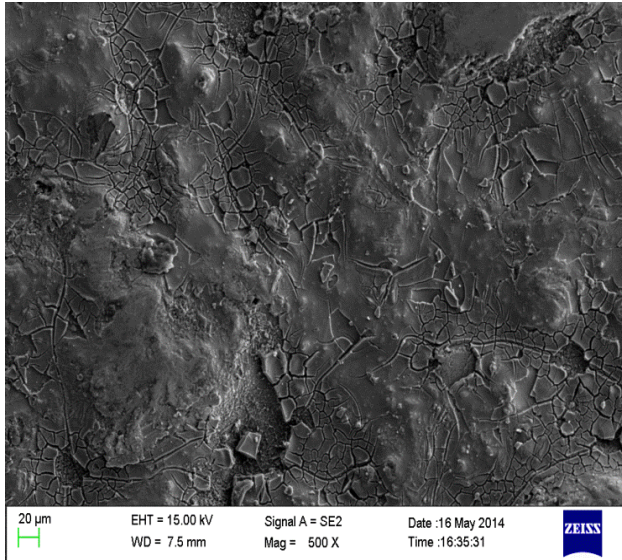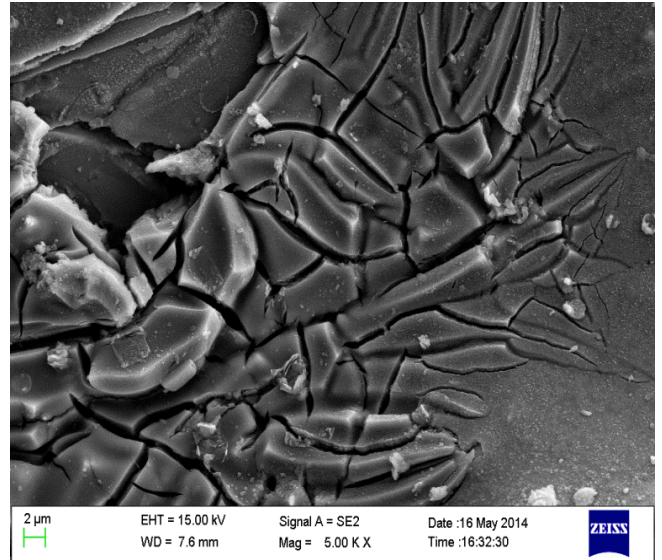**Figure 4.5. Schematic representation of 4-NP degradation during electro oxidation process**

(a)   (b)

Figure 4.6(A). SEM micrographs of Ti/RuO$_2$ (a) before treatment, (b) after treatment.
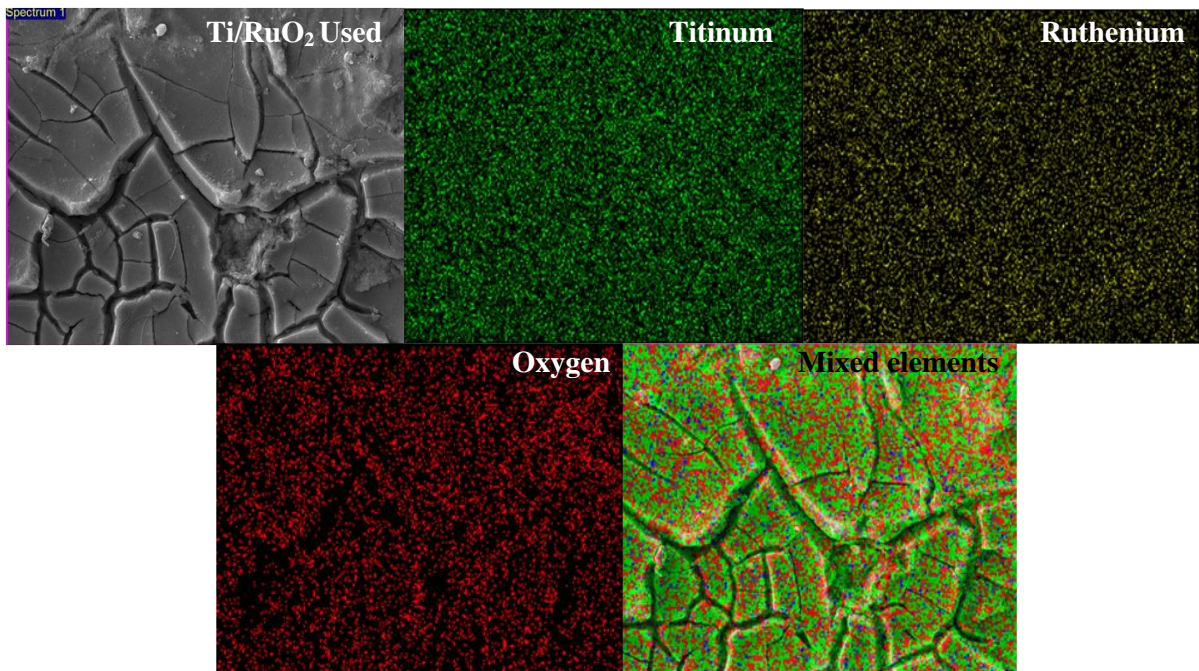

Figure 4.6(B). X-ray dot-mapping of Ti/RuO$_2$ electrode (a) Ti, (b) Ru, and (c) O elements

CONCLUSIONS

The present study involves the removal of 4-NP from the synthetic wastewater from electrochemical oxidation process. Following conclusions can be drawn from the experimental studies:

➢ The optimum value of parameters:

- pH value = 6
- Contact time = 150 min
- Current density (j) = 168.9 A/m^2
- Electrode Spacing = 1cm
- Electrolyte Concentration = 300 mg/l

➢ The removal efficiency of COD and TOC were found to be 98.8% and 81.9% respectively.

➢ The following value of pH, COD and TOC were found during before and after experiment.

Parameter	Initial Value (before experiment)	Final Value (after experiment)
pH	6	9.3
COD	177 mg/l	2 mg/l
TOC	58 mg/l	10.5 mg/l

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