TREATMENT OF INDUSTRIAL WASTEWATER CONTAINING NITROGENOUS COMPOUND BY ELECTRO-OXIDATION PROCESS

A dissertation report submitted
in partial fulfillment of the requirement for
the award of degree of

Master of Science
In
Chemistry

By

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CERTIFICATE

This is to certify that the dissertation entitled **"Treatment of industrial wastewater containing nitrogenous compound by electro-oxidation process"**is an authentic record of my own work carried out as requirement for the award of the degree of Master of Science in Chemistry in the Department of Chemical Engineering, Thapar Institute of Engineering and Technology, Patiala under the supervision of Dr. J.P. Kushwaha, Associate professor, Department of Chemical Engineering and Dr. Neetu Singh, Associate professor, Department of Chemical Engineering. No part of this project has been submitted for award of any other degree by me.

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It is certified that the above statement made by the student is correct to the best of our knowledge and belief.

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DECLARATION

I hereby declare that the research work being presented in the dissertation report named,**“TREATMENT OF INDUSTRIAL WASTEWATER CONTAINING NITROGENOUS COMPOUND BY ELECTRO-OXIDATION PROCESS”** by me in the partial fulfillment of the requirements for the award of the degree of **Master of Science in Chemistry** at School of Chemistry and Biochemistry, Thapar Institute of Engineering & Technology, Patiala, Punjab, is an authentic record of my work carried under the supervision of **Dr. J.P. Kushwaha** and **Dr. Neetu Singh**, Associate Professors, Department of Chemical Engineering, Thapar Institute of Engineering & Technology, Patiala. The results presented under this dissertation have not been submitted in any other Institute or University for the certification of any other degree or diploma.

Dated: 15-07-2019

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ABSTARCT

The dissertation demonstrates the electro-oxidative treatment of nitrogenous compound and its significance in the removal. As proliferation of hazardous organic pollutants in the environment becomes the greatest manifestation of industrial wastewater, development of effective chemical strategies have intervened. The toxic nitrogenous pollutants pose environmental and health implications like persistence, biomagnification, mutagenic or carcinogenic nature, endocrine disruption and genotoxicity. Using Aluminium(Al) and Ti/RuO_2 electrodes, the study has been investigated. Synthetic Industrial Wastewater(SIW) was prepared by an aromatic compound with ethanol and NaCl mixed in distilled water(DW). For experimental design and analysis of data based on response surface methodology (RSM), central composite design (CCD) was used. These organic pollutants cannot be effectively treated with biological wastewater treatment methods or physical separation methods due to non-biodegradable or bio-recalcitrant nature. Also, chemical coagulation, adsorption and incineration cannot be effectively implemented. Against this backdrop, the electrochemical treatment methods are significant and relevant. Many pollutants undergo direct oxidation at the anode through electrochemical charge transfer while others follow indirect oxidation. The anode material, the inter-electrode potential, current density and the supporting electrolyte have all been found to affect the process. Thus, synthetic wastewater containing a carcinogenic aromatic compound was prepared for each run and its removal efficiency was studied under thirty different conditions of pre-defined varying current, pH and initial concentration. By keeping voltage usage in notice, energy consumption was derived for each reaction condition.

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NOMENCLATURE

EC	Electro-coagulation
EDC	Endocrine Disruptor Chemicals
CPCB	Central Pollution Control Board
EO	Electro-oxidation
CCD	Central Composite Design
RSM	Response Surface Methodology
ANOVA	Analysis of variance
R_1	Percentage removal
R_2	Energy consumption
IW	Industrial wastewater
AOP	Advanced Oxidation Processes
SS	Suspended solids

CHAPTER 1

INTRODUCTION

1.1. General

Water has been the biggest sign of many attributes and it constitute as one of the vital asset for our country [19]. It has qualities of a good solvent and the capability to transport particles. Its properties incorporate in itself various impurities that characterize it as polluted. Water pollution is a result of the acts of human beings [7]. Countless new developments have increased the water demand while preventing enough water getting to the right place due to its toxicities. Hence, the rapid urbanization, industrialization and population growth have taken a larger toll on our environment than to give boost to the quality of human life [2]. Water is required at nearly every step of production across a multitude of different food, beverages, textile or paper industries. In reality though, water pollution has threatened the human existence and is making an immediate action a priority. India and China along with the countries in Europe and Africa are expected to encounter water scarcity by 2025 if sustainable water treatment initiatives are not sufficiently advocated. Industrial wastewater is water that has been used as part of making a commercial product. The release of possible toxic wastewater having alkaline pH, very dark brown display, unpleasant odor, high BOD as well as COD and a mixture of other organic pollutants has ignited an outcry in opposition to the industries. The resulting wastewater must be carefully managed [7]. The EO processes degrade pollutants more effectively than other methods and have caused increased interest due to their outstanding technical characteristics. Investments in energy consumption and experimental costs sometimes slow down its large scale implementation. Conventional processes are either replaced by electrochemical oxidation or integrated with it. The contaminants containing BOD, COD, suspended solids and other organic-inorganic substances are common toxic materials [1-3]. To comply with environmental protection laws, certain pollutants must be removed from the wastewater like organic matter, inorganics (sodium, potassium, calcium, magnesium, copper, lead, nickel, and zinc), pathogens, and nutrients (most notably nitrogen and phosphorus).

The treated wastewater can then be safely discharged into water bodies, applied to land, or even reused in plant operations. Organic compounds are becoming an indispensable part of human health systems as their production as well as consumption has risen in past few decades. Many of organic substances are classified as priority pollutants such as polychlorinated biphenyls (PCBs), polycyclic aromatic compounds, acetaldehyde, formaldehyde, 1,3-butadiene, 1,2-dichloroethane, dichloromethane, hexachlorobenzene (HCB), etc.

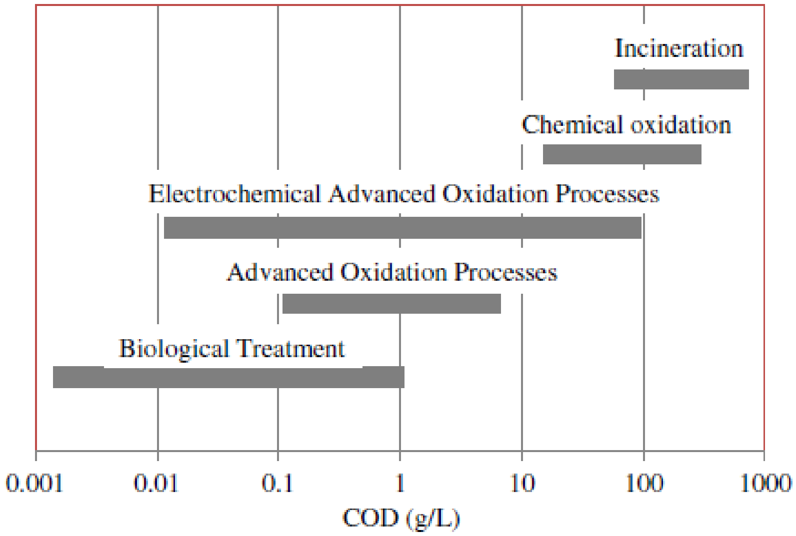


Figure 1.1 The applicability of water treatment technologies based on organic load, Source: Fryda et al. (2003)

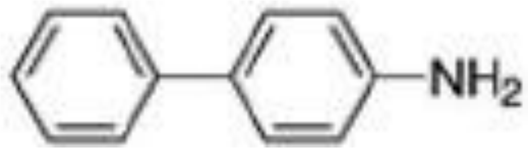


Figure 1.2 Chemical structure of 4-ABP

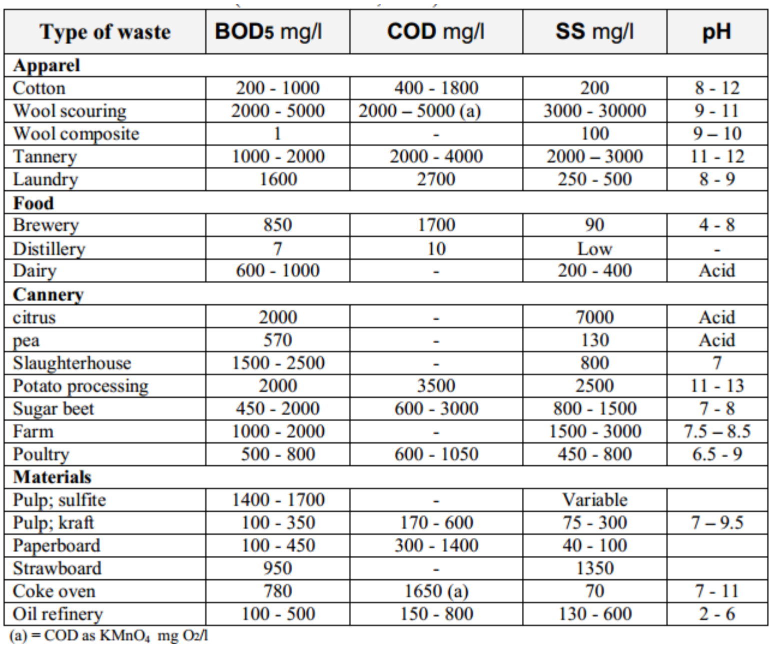
The model pollutant, 4-ABP has been frequently used over the years as a rubber antioxidant and a high-quality dye intermediate. Critic examination stated that 4-ABP is in charge for bladder cancer in humans and dogs by causing destruction to their DNA which is completely unacceptable. Other alarming effects are lethargy, cyanosis, headache and urinary tract burning sensations [11]. Owing to its carcinogenic effects, commercial production of 4-ABP was ceased in the United States in 1950s as toxic fumes aroused from this compound when heated to decomposition [3]. The advantage of EO method is that final products are mainly CO_2 and H_2O. Since 1895, the carcinogenicity and toxicity of aromatic amines are in notice but the relationship of 4-ABP to urinary bladder cancer was first reported in early 1950. The European Union Standards (1907/2006) outlawed few aromatic amines of concentration above 30 ppm among the 22 known, due to their carcinogenic and mutagenic effects [19]. Aromatic amines are released in effluents discharged by various industries such as polymer, tanneries [7], oil refining, dyes, textile, pesticides, herbicides, adhesives, rubber, pharmaceuticals, food industries, etc. The final disposal problem has always been imminent to the environment check. In such cases, the application of an Advanced Oxidation Processes (AOP) proves to be a promising alternative. AOPs provide very high degree of mineralization in many cases as they generate highly reactive radical species like hydroxyl radicals [1-3]. Electrochemical treatment via oxidation is a very significant development in AOPs that has provided several benefits and satisfactory results. For the removal of various pollutants, as per Environmental Management Bureau, Phillipines(1998), several powerful tools based on principles of electrochemistry are electro-dialysis, electro-coagulation, electro-flotation, anodic processes, cathodic processes and electrochemical advanced oxidation processes.

1.2. Industrial wastewater characteristics and environmental impact

To determine the organic content of industrial wastewater, the tests may be divided into those used to measure gross concentrations of organic matter greater than about 1 mg/l and those used to measure trace concentrations. Specific organic compounds are determined to assess the presence of priority pollutants [20]. Some key parameters include BOD, COD and TOC which measures the gross concentrations of the industrial wastewater as shown in Tab.1.1

The amount of dissolved oxygen needed by aerobic biological organisms to break down organic material present in a given wastewater sample at a certain temperature over a specific time period is Biological Oxygen Demand (BOD). Therefore, BOD indicates indirectly the amount of organic compounds in wastewater. Also, specifying indirectly organic compounds' amount in wastewater and oxygen consumption in mg/L gives Chemical Oxygen Demand (COD). However, COD is less specific because it measures everything that can be chemically oxidized rather than just levels of biodegradable organic matter. The total solid in wastewater consists of insoluble or suspended solids and the soluble compounds dissolved in bulk .The organic matter is generally volatile. Color gives qualitative characteristic to wastewater, IW which is light brown in color is less than 6 hours old while light-to-medium grey color shows some degree of decomposition. And dark grey or black tells about wastewater being typically septic, having undergone bacterial decomposition. These pollutants have many environmental implications like persistence, biomagnifications and ecotoxicity. Being mostly non- biodegradable or biorecalcitrant, bioaccumulation is also seen through the food web. Quite a few organic substances are said to be mutagens and carcinogens and some are endocrine disruptors.

Table.1.1. Effluent characteristics of industrial wastewater:



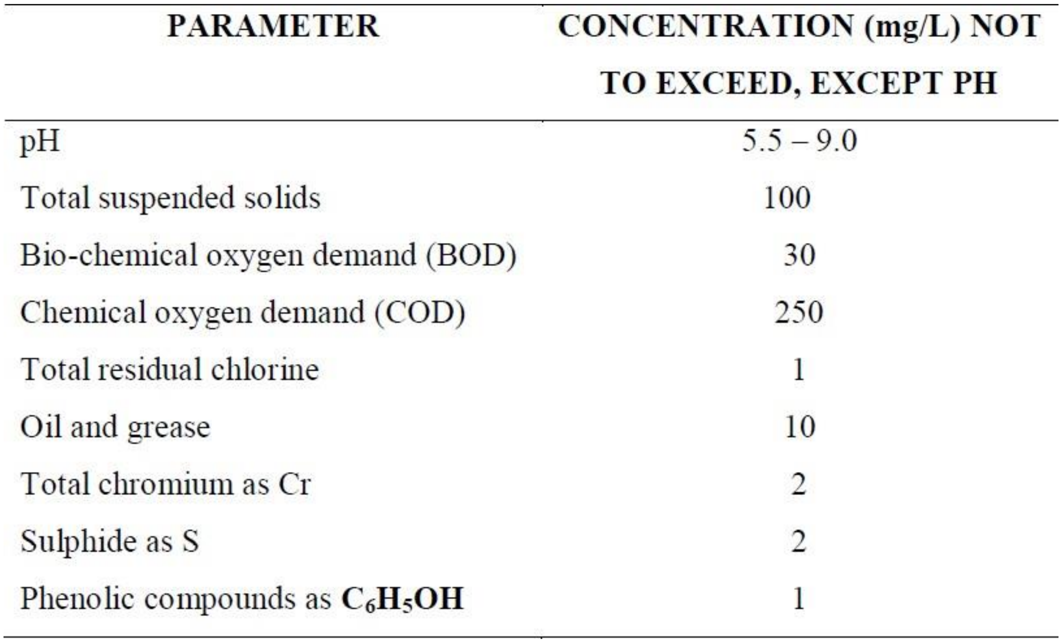
Type of waste	**BOD5** mg/l	**COD** mg/l	**SS** mg/l	pH
Apparel				
Cotton	200 - 1000	400 - 1800	200	8 - 12
Wool scouring	2000 - 5000	2000 – 5000 (a)	3000 - 30000	9 - 11
Wool composite	1	-	100	9 – 10
Tannery	1000 - 2000	2000 - 4000	2000 – 3000	11 - 12
Laundry	1600	2700	250 - 500	8 - 9
Food				
Brewery	850	1700	90	4 - 8
Distillery	7	10	Low	-
Dairy	600 - 1000	-	200 - 400	Acid
Cannery				
citrus	2000	-	7000	Acid
pea	570	-	130	Acid
Slaughterhouse	1500 - 2500	-	800	7
Potato processing	2000	3500	2500	11 - 13
Sugar beet	450 - 2000	600 - 3000	800 - 1500	7 - 8
Farm	1000 - 2000	-	1500 - 3000	7.5 – 8.5
Poultry	500 - 800	600 - 1050	450 - 800	6.5 - 9
Materials				
Pulp; sulfite	1400 - 1700	-	Variable	
Pulp; kraft	100 - 350	170 - 600	75 - 300	7 – 9.5
Paperboard	100 - 450	300 - 1400	40 - 100	
Strawboard	950	-	1350	
Coke oven	780	1650 (a)	70	7 - 11
Oil refinery	100 - 500	150 - 800	130 - 600	2 - 6

(a) = COD as $KMnO_4$ mg O_2/l

Source:Bond and Straub,1974

In recognition of the environmental implications of these substances the ‘International Conventions’ and government regulatory authorities of most of the countries have included them in their priority lists. The objective of the Stockholm Convention (2001) on persistent organic pollutants was to protect human health and the environment from these organic pollutants. It has listed 26 regulated organic chemicals and also 5 more chemical classes are under review for possible inclusion. Concise International Chemical Assessment Documents (CICADs) from International Program on Chemical Safety lists about 60 odd organic chemicals with associated environmental issues. The United States Environmental Protection Agency (USEPA) under its National Waste Minimization Program provides a list of 31 priority chemicals, 28 of which are organic chemicals . Environment Canada has provided two priority substances lists containing 34 and 16 organic chemicals, respectively, many of which are conclusively proven to be toxic. The manufacture, storage and import of hazardous chemical (Amendment) rules, 2000, of the Ministry of Environment and Forests, Government of India, regulate the use of 94 toxic organic chemicals (MoEF, GOI, 2000).

Table 1.2 Standards for effluents by CPCB



PARAMETER	CONCENTRATION (mg/L) NOT TO EXCEED, EXCEPT PH
pH	5.5 – 9.0
Total suspended solids	100
Bio-chemical oxygen demand (BOD)	30
Chemical oxygen demand (COD)	250
Total residual chlorine	1
Oil and grease	10
Total chromium as Cr	2
Sulphide as S	2
Phenolic compounds as C_6H_5OH	1

1.3. Industrial wastewater treatment processes

The varieties of chemically generated actions, physiochemical and natural methods are developed for industrial pollutant treatment. The physical separation techniques comprises of mechanical screening, sedimentation, magnetic separation, flotation, stripping, ion exchange, adsorption and attrition scrubbing [15-18]. The conventional methods are precipitation, oxidation-reduction, coagulation and incineration [1,3]. Biological methods rely upon living micro-organisms which play a vital role in organic or inorganic substances removal [7]. Many a times, toxic sludge is produced which doesn't settle in the physical separation.

Every industrial wastewater treatment application has its own set of variables that make it unique, these are as follows.

1.3.1. Advanced Oxidation Processes

1.3.1.1. Electrochemical Method: These are energy intensive processes as they involve application of electrical power for generation of free radicals from water discharge. Electrochemical method for wastewater treatment can broadly be classified into two categories: (i) electro–Fenton (EF) method, and (ii) electro–oxidation (EO) method.

i) Electro-Fenton method: EF method involves heterogeneous catalytic reactions of hydrogen peroxide with ferric or ferrous ions, acting as catalysts, for generation of hydroxyl radicals via free radical chain reactions. As compared to traditional Fenton's process, addition of iron salts in EF is limited because of regeneration of ferrous ions at the cathode surface. The produced hydroxyl radicals then non-selectively destroy the organic content in the wastewater. Efficiency of EF is further improved when assisted by UV radiation/sunlight (photo-electro Fenton) or ultrasonic radiation (sono-electro Fenton) [30]. However, the major drawback of EF method is its dependency on pH (efficient in pH value ≈ 3) and possibility of generation of some iron sludge [31].

(ii) Electro-oxidation method: EO method is based on electrochemical generation of powerful oxidising agents, such as hydroxyl radicals (•OH) directly on-site using only water, salt and energy, which are then able to destroy organics up to their mineralization to carbon dioxide and water. It is also termed as green method for wastewater treatment. Major advantages of EO are listed below [31]:

- No sludge generation, hence environmentally benign technology
- Minimum or no addition of chemicals required
- Easy handling because of simple equipment
- Safety – operates under mild conditions (room temperature and pressure)
- Robustness – the reaction can be terminated easily in seconds by cutting off the power and resumed immediately after solving any operational problem

Hence, EO represents a useful solution when the presence of bio-refractory and toxic pollutants prevents the use of conventional treatment techniques.

EO technique destroys organic pollutants by two different oxidation mechanisms, i.e., “direct oxidation” at the anode surface, and “indirect oxidation” in the bulk solution by oxidizing agents generated on the anode surface(Fig. 1.3) [20,21]. Direct anodic oxidation of pollutants occurs after pollutant adsorption on anode surface and its destruction via electron transfer.The mechanism of direct oxidation of target pollutant strongly depends on process conditions and type of electrodes (active or non-active) employed for the purpose. The hydroxyl radicals generated by water discharge either get physisorbed on the anode surface or chemisorbed by forming a covalent bond with the anode (Eq. 1.3)[21]. Physisorption is predominant in non-active anodes. Whereas, chemisorption dominates in case of active anodes [36]. Physisorbed •OH leads to complete mineralization of organic pollutant to CO_2(Eq. 1.2). However, the chemisorbed radicals lead to electrochemical conversion of organic pollutants (Eq. 1.4)[36,3].

$M + H_2O \rightarrow M(\bullet OH) + H^+ + e^-$ (*Physisorption*) **(1.1)**
$M(\bullet OH) + R \rightarrow nCO_2 + mH^+ + ze^- +$ Inorganic ions + M (*Combustion*) **(1.2)** M
$+ H_2O \rightarrow MO + 2H^+ + 2e^-$ (*Chemisorption*) (**1.3)** MO
$+ R \rightarrow RO + M \rightarrow$ Reaction intermediates + M (C*onversion*) **(1.4)**

In case of indirect oxidation, strong oxidant species are generated in-situ through oxidant precursor or mediator, which instantly destroy the organic pollutants in the bilk solution. Commonly generated oxidant species include hydrogen peroxide (H_2O_2) and ozone (O_3).

In wastewaters comprising chlorides, reactive chlorine species (Cl_2, HOCl, ClO^-) play an imperative part in pollutant degradation via indirect oxidation. The dominance of these species is highly pH dependent [2,21] Apart from generation of oxidants and pollutant destruction, the undesirable but inevitable reactions of oxygen and hydrogen evolution occur simultaneously in the electrochemical cell, resulting in curtailed performance of EO process.

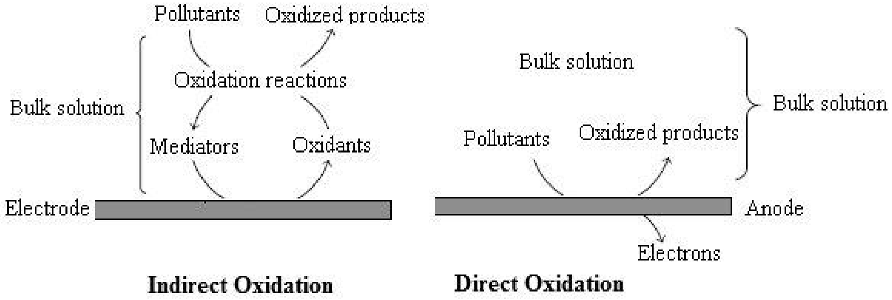


Fig.1.3 Direct and indirect electrolytic treatment scheme
Source: (Chiang et al., 1995)

1.3.1.2. Photo chemical oxidation

Detoxification of air and water can be done using photo chemical oxidation. Pure semiconductors act as microscopic photo chemical cells to promote catalytic oxidation reaction. The semi conductor is in electric contact with a counter electrode. One classic example is the oxidative degradation of organic contaminants by the H_2O_2/UV processes. The principal is to provide low-energy activation pathways.

1.3.2 Adsorption

The establishment of adsorbed segment having dissimilar composition from bulk fluid forms foundation of this method. Adsorption is a surface phenomenon which has widespread mechanism for organic and inorganic pollutant removal [12]. The surface buildup of adsorbate on adsorbent causes adsorption. It mixes the wastewater and porous granules.Through the filter bed, wastewater comes out. A lot of people have given substantial importance aimed at developing good removal competence of organic pollutants by adsorption technique. Inexpensive substitute is activated carbon (AC) which also decreases treatment costs.

Also, clay minerals have high surface areas and molecular sieve structure are effective adsorbents for organic contaminants [13]. Between the solution and adsorbent, equilibrium of adsorption of solute occurs as adsorption progresses. Langmuir and Freundlich isotherms usually describe the adsorption data. There are natural and synthetic adsorbents in use like charcoal, clay, zeolite and ones prepared from agricultural or industrial wastes respectively. There is a complex process involved, posing difficulty for activated carbon to be widely used as adsorbent[14]. Majorly large number of variables involved as intrinsic properties of solute, interactions, solution properties and temperature are the cause.

1.3.3 Aerobic and anaerobic biological treatment

Using aerobic or facultative bacteria, water is purified under these main classes: Activated sludge process and bio-film progression. The bacteria gets divided according to their oxygen requirement. The macromolecules, cyclic organic matter and other biodegradable organic matter can be rotten into smaller organic substances through anaerobic biological treatment using facultative and anaerobic bacteria. Upflow Sludge Bed (UASB), Upflow Anaerobic Fluidized Bed (UABF) and Anaerobic Baffled Reactor (ABR) are also used to treat industrial wastewater [3].

1.3.4 Chemical precipitation of heavy metals

The simple handling operation of this process makes it most widely used for heavy metals in industrial wastewater [5]. Sulfides or hydroxides are the precipitates formed which are not soluble in IW. The fine particles formed are enhanced in size by flocculation or coagulation to move out as sludge for later solid disposal. By pH and initial concentration change, % removal is optimized [6].

CHAPTER 2

LITERATURE REVIEW

2.0. GENERAL

The appearance of water pollutants, intractable to conformist treatments has brought the most intellectual minds across the globe to focus on its handling by processes like EO or AOP. This is an environmentally benign technology, mineralizing the non-biodegradable organic matter wholly and eradicating the nitrogen species. All of the approaches used have various positive and negative aspects. Besides, wastewater treatment processes exist for % pollutant, dye, color, BOD, COD and TOC removal.

Nashev et al.,(2010) identified the target of action in endocrine disruptor chemicals(EDC) by developing a database. All the virtual screening approaches were based on 3D structures. Due to ascending gain in male reproductive disorders and cancer, the removal of EDCs is required. Benzophenone (BP) UV-filters were taken as potential 17β-HSD3 inhibitors. The pharmacophores of 17β-hydroxysteroid dehydrogenase type 3 (17β-HSD3) that catalyzes final step of testosterone synthesis and is vital for male sexual development was used for database screening. The 3-benzylidene camphor (3-BC) and 4-methylbenzylidene camphor (4-MBC) are preferably low micro-molar 17β- HSD2 inhibitors as suggested by UV-filters used on estrogen or androgen-metabolizing 17β-HSD enzymes. The aromatic or other compounds interfering with hormonal action were embattled by screening of virtual structural libraries. Their work requires more thorough investigations parallel to safety assessments [10,11].

Moreas et al.,(2013) studied about aromatic amines [24] which characterizes one of the most important class of industrial as well as natural chemicals and still are not fully efficiently treated. Some types of complex effluents comprising these chemical species, mainly those originated from chemicals plants are in this work.

The use of electrochemical technology through an electrolytic pilot scale flow reactor is measured for treatment of wastewater of a chemical industry manufacturer of antioxidant and anti-ozonant substances used in rubber. Experimental results exhibited that it was possible to eradicate between 65% and 95% of apparent color and COD removal between 30 and 90% in 60 min of treatment, with energy consumption rate from 26 kWh m^3 to 31 kWh m^3. Absorbance, TOC and toxicity analyses don't give formation of toxic by-products. The results suggest that the presented electrochemical process is a fit method for treating this type of wastewater, mainly when pre-treated by aeration.

Chen et al.,(2014) studied eco-toxicological evaluation of 4-ABP using a test battery [22]. Eco-toxicological models are used for discovery, direction, and monitoring of the existence of pollutants which cause bladder cancer [23]. Bioassays were used for evaluation of risk of any new chemical or its effects. A complete test battery was made because single essay does not depicts a full picture of environment quality. For the study, the effects of 4-ABP were investigated. The complete battery of eco-toxicological model systems was used. The included immobilization of *Daphnia magna* was most sensitive to pollutant than development of zebra fish embryos or inhibition of mammalian cell proliferation. The results indicated 4-ABP's toxicity for aquatic organisms and mammal cells.

Pacheco et al.,(2010) investigated electrochemical oxidation of four aromatic amines of diverse substituent groups [38]. 3-amino-4-hydroxy-5-nitrobenzenesulfonic acid (A1), 5-amino-2-methoxybenzenesulfonic acid (A2), 2,4-dihydroxyaniline hydrochloride (A3) and benzene-1,4-diamine (A4) weresubjected to perform electrochemical oxidation using as anode a boron-doped diamond electrode. All the tests were run at room temperature with model solutions of the different amines with concentrations about 200 ppm, using as electrolyte 0.035 M Na_2SO_4 aqueous solutions. In a batch cell with recirculation, at different current densities (200 and 300 A m^{-2}), experiments were run. UV–Vis spectrophotometry, chemical oxygen demand (COD), total organic carbon (TOC), total Kjeldahl nitrogen, ammonia nitrogen, nitrates and HPLC analyses were performed .

Results have shown a good electrodegradation of all the amines tested. The COD removal after 6 hours assays wasadvanced than 90% and TOC removals between 60 and 80%. Combustion efficiency (η_C), which measures the tendency to adapt organic carbon to CO_2, which was also determined for all the amines being, $\eta_{CA1} < \eta_{CA2} < \eta_{CA3} < \eta_{CA4} = 0.99$.

Lopez et al.,(2013) noticed four amines (aniline, *o*-toluidine, 4-chloroaniline and 4-aminobiphenyl) by GC-MS in the residual azo dye baths. The occurrence of aromatic amines in effluent from dyeing processes of the textile industry was seenas an additional problem to the high coloration typical of this type of effluent. For the analysis of amines, a liquid–liquid extraction method was developed as an easier and faster substitute to the method described in the standards and widely used in analytical laboratories. The chief objective of the present work was to eliminate these two problems simultaneously by electrochemical treatment using bath solutions containing three azo dyes. A total amine concentration of between 2.5 and 1 ppm was detected, 4-aminobiphenyl being the main compound. Both residual color and amines were removed by electrochemical treatment carried out at three current densities (3, 24 and 40 mA/cm^2). At 24 mA/cm^2, more than 90% of color removal was accomplished, and the total amine concentration was reduced to below 0.15 ppm.

Panizza et al.,(2009) studied direct and mediated anodic oxidation of organic pollutants [21]. The assessment of process selection depending on the nature and structure of the electrode material, experimental conditions and electrolyte composition was carried out. They focused on recent progress and the literature. Energy consumption was seemingly reduced using “advanced electrochemical oxidation processes” which is the combination of anodic and cathodic electrogeneration of highly oxidizing hydroxyl radicals. There were two main strategies for anodic electro-oxidation of organiccompounds to achieve electrolysis at a highanodic potential in the region of water discharge. The part aking of intermediates of electrogenerated hydroxylradicals and to oxidize pollutants by indirectelectrolysis, generating a redox reagent in situ as a chemicalreactant has been discussed.

Alexander et al.,(1981) studied treatment of aqueous solution(IW) comprising of carcinogenic aromatic amines with horseradish peroxidase and hydrogen peroxide as pollutants [35].

The treatment with horseradish peroxidase catalyzes the oxidation of various organic substances by hydrogen peroxide. A supreme precipitation of carcinogenic aromatic amines from water due to enzymatic cross linking was observed. This method was used to remove 4- ABP and benzidine along with other eight human carcinogens . The removal effectiveness of peroxidase treatment depends on concentration of enzyme, H_2O_2, a carcinogen, pH and duration of treatment. There was an optimal H_2O_2 concentration for the removal. This particular approach has been used to remove over 30 different phenol and aromatic amines from IW. Later, the carcinogen removal from water was chemically and toxicologically confirmed by essays. The enzymatic precipitation was accelerated in the presence of easily removable phenyl or aromatic amines for those treatments having low removal competence.

Raghu et al.,(2007) varied the current densities for conducting experiment with Ti/RuO_2 [41] as anode and stainless steel as cathode in a cylindrical flow reactor with selected electrolyte. In NaCl medium, the best condition for maximum redox reaction rate was found by cyclic voltammetric analysis. At the various stages in the electrolysis, parameters like COD, color, FTIR, UV-VIS spectra studies, energy consumption and mass transfer coefficient were measured and presented. The results showed effective removal of color and COD from synthetic effluents. The maximum COD reduction was 74%. Modeling and reaction mechanism were proposed too. The result obtained reveals many feasibilities of application of electrochemical treatment for desired degradation.

Raghu et al.,(2009) highlighted the energy consumption of the EO method [33] and its cost efficiency as the high energy cost of this method gives a drawback to large-scale application. Traditionally, single chamber EC method used for treatment focused on anodic oxidation, whereas hydrogen produced on cathodic part of electrode system and indirect electro-oxidation method converted chloride to chlorine or hypochlorite [32]. In the new reactor developed, there was 2 compartment electrolytic cell parted by an anion exchange membrane. In this, indirect oxidation at anode, while hydrogen peroxide and UV\Hydrogen peroxide ($UV\backslash H_2O_2$) generation at cathodic part occured simultaneously. Hence, ‘Dual electrochemical oxidation’ in one electrochemical reactor was idealized.

This reduced approximate 24% - 40% energy cost as compared to cell reactor. This method became substantial because of low cost. For anode, Ti/RuO_2 and for cathode, carbon felt gas diffusion electrodes was used. For the experiment to be carried out at different current densities, electrode was fed with O_2 containing gases to produce H_2O_2, pH effects, COD, color, energy consumption during electrolysis. FTIR and HPLC studies evaluated the degradation efficiency with UV treatment. The energy consumption were decreased by 25% (13.58 kWh\kg of COD) and without UV, a decrease by 40% (10.97 Kwh\kg of COD) was seen.

Djilani et al.,(2013) established an adsorption phenomenon [39] of new activated carbon adsorbent from lignocellulosic wastes of vegetable origin , melon seeds and orange peels.With organic pollutants like o-nitrophenol and p-nitrotoulene, adsorption efficiency was tested. 70%-90% elimination ratio was obtained. In 75-135 minutes, adsorption equilibrium was achieved.

Jieying et al.,(2016) studied the degradation of aromatic amines in textile-dyeing sludge by combining the ultrasound technique [26] with potassium permanganate treatment for the first time as the best practical method[25]. The combined technique (US-$KMnO_4$) examined reaction mechanisms and degradation kinetics for different operating parameters and indicated a synergistic effect. On an average, 58.7% of monocyclic anilines, 88.3% of other forms of aromatic amines, and 24.0% of TOC were seen eradicated at optimum condition($KMnO_4$ dosage of 12 mM, an US power density of 1.80 W/cm^3 and pH 5).

Korbahti et al., (2008) used iron electrodes in the presence of NaCl electrolyte to study electro-chemical treatment of simulated IW in a batch reactor. The reaction optimization was done at 8V applied potential within 183 minute of run [30]. Highest removal for COD, color and turbidity were 93.9%, 99.5% and 82.9% respectively while under optimized conditions (35.5mA/cm^2 current density, 8V, 25 g/l electrolyte concentration, 183 min) the COD, turbidity and color removal were 66.7%, 72.6% and 100% respectively.

Bahadir et al.,(2007) studied EC oxidation of wastewater from paint industry in a batch wise reaction procedure using RSM optimization [40]. 51.8% COD removal and complete color-turbidity removal was seen at optimum condition of 64.37 mA/cm^2 current density.

35g/L electrolyte concentration was present. Such study with RSM was done for the first time . The results gave a better alternative to physiochemical treatment techniques.

- Electrochemical technology has a vital role to play as part of an modern integrated approach to the evading of pollution, monitoring of pollution, process efficiency and cleaner processing.

2.1. RESEARCH GAP

EO for degradation of various aromatic amine have been reported using BDD electrode by a number of researchers. BDD is reported to be an excellent anode material for degradation and mineralization various organic compounds. Nonetheless, its high cost makes its application at large-scale dubious. Therefore, there is need of alternative anode material which is comparatively cheaper and surmount the limitations of BDD. Cost effective Al-Ti/RuO_2 electrodes have shown promising results in terms of organic pollutants removal from wastewater. Efficacy of the electrodes material further needs to be explored for degradation of aromatic amines in water matrices.

2.2. OBJECTIVES

In view of literature survey and research gap, following objectives have been set for present study:

- To study the effect of Al-Ti/RuO_2 electrodes on 4-ABP removal and energy consumed.
- To study the effect of various operating parameters such as pH, current, electrolysis time and 4-ABP concentration on 4-ABP removal and energy consumed.
- To identify final degradation products of 4-ABP and propose degradation mechanism

CHAPTER 3

MATERIALS AND METHODS

3. EXPERIMENTAL

3.1. Materials

The 4-aminobiphenyl (4-ABP) (CAS no. 92–67–1) was purchased from Sigma-Aldrich, India and its predefined quantity of 0.1g was dissolved in 1.5L of double distilled water. To the mixture, NaCl (LobaChemie Pvt.Ltd., Mumbai, India) was also added for enhancement of conductivity of the solution, as it works as a supporting electrolyte. The mixture was placed on a magnetic stirrer (IKA C-MAG HS7 digital) for almost an hour. The D.C. power supply (DIGITECH, Roorkee, India, Model:4818A10;0-20V,0-5A) regulated current in controlled conditions for electrolysis. The pH was maintained in each run with variation from 2 to 10 using 0.1M HCl or 0.1M NaOH. Aluminum and Ti/RuO_2 electrodes were picked from Titanium Tantalum Products Ltd. Company, Chennai, India.

Fresh wastewater was prepared synthetically for each run in the EO method and every chemical used was of analytical grade.

3.2. Experimental setup and Procedure and Analysis

A cuboid shaped reactor of 13cm x 13cm x13cm dimensions made of acrylic sheet was designed, and electro-oxidation was performed in it (Fig. 3.1). A set of Ti/RuO_2-Al electrodes was arranged in the reactor, Ti/RuO_2 as cathode and Al as anode. 1cm gap was taken as a standard between the electrodes. The magnetic stirrer mixed the 1.5L synthetic fresh wastewater in the reactor placed on it. A magnetic bead was also introduced. The solution was kept for mixing throughout the experiment on the stirrer at 4-5mot speed. Before performing each experiment, electrodes and reactor were washed properly once or twice. Proper rotation of magnetic bead at desired speed was ensured by 2.5cm gap from lower edge of the electrodes to the bottom of reactor. The oxidation began when power supply was switched on. A stock solution was prepared by 0.1 g of 4-ABP being dissolved in 100 ml ethanol, and it was preserved at 4°C in refrigerator. To conduct the experiments, dilution of the stock 4-ABP solution with suitable volume of double distilled water was done to have desired concentration of the final solution in ppm. NaCl used was 3g for each run.

Four factors and five level full factorial central composite design (CCD) underlying response surface methodology (RSM) was used to design the experiment, and data obtained was analyzed by Design-Expert. Total 30 experiments were suggested and performed over a range of parameters: pH (2–10), applied current, I (0.5-2.0A), time (10-110 min) and initial 4-ABP solution concentration, C_o (10-90ppm)(Table 3.1). The %removal of 4-ABP and energy consumption (kWh/mg pollutant removal) were set as response of the system.

Fig 3.1. Actual setup of the experiment

Table 3.1. Variables range and their levels

Factor	Variable	Range of actual and coded variables		
		-1	0	1
A	Initial pH	4	6	8
B	Time of electrolysis, *t* (min)	35	60	85
C	Current, I(A)	0.5	1.0	1.5
D	4-ABP concentration, C_0 (mg/L)	30	50	70

In order to conduct the experiments, desired concentration and volume of 4-ABP solution was adjusted to desired *pH*, as per the predefined run. Time, *t*, was measured when power supply was switched on. Current *(I)* was constantly maintained during the run.

Samples were withdrawn from the reactor during the experiment at pre-set time intervals, and analyzed for the responses.

Treated samples were analysed for their residual concentration of 4-ABP using double beam UV–Vis spectrophotometer (Prekin Elmer Lambda 35) at λ max = 272 nm. For this purpose a calibration curve was prepared (Fig. 3.2), and unknown concentration of 4-ABP was calculated using following calibration equation 3.1.

$$y = 0.0955x \tag{3.1}$$

The % removal of 4-ABP was calculated according to the equation (Eq. 3.2).

$$\%\text{Removal} = \frac{(C_i - C_e)100}{C_i} \tag{3.2}$$

where, C_i and C_e are the concentration of 4-ABP in mg/L at t = 0 and at any time t, respectively.

Energy consumption which evaluates the economic feasibility of the EO process using Ti/RuO_2-Al electrodes was calculated using equation 3.3.

$$Energy\ consumed\ (Y_1) = IVt \tag{3.3}$$

Here, V is average voltage, I is current and t is electrolysis time in hour.

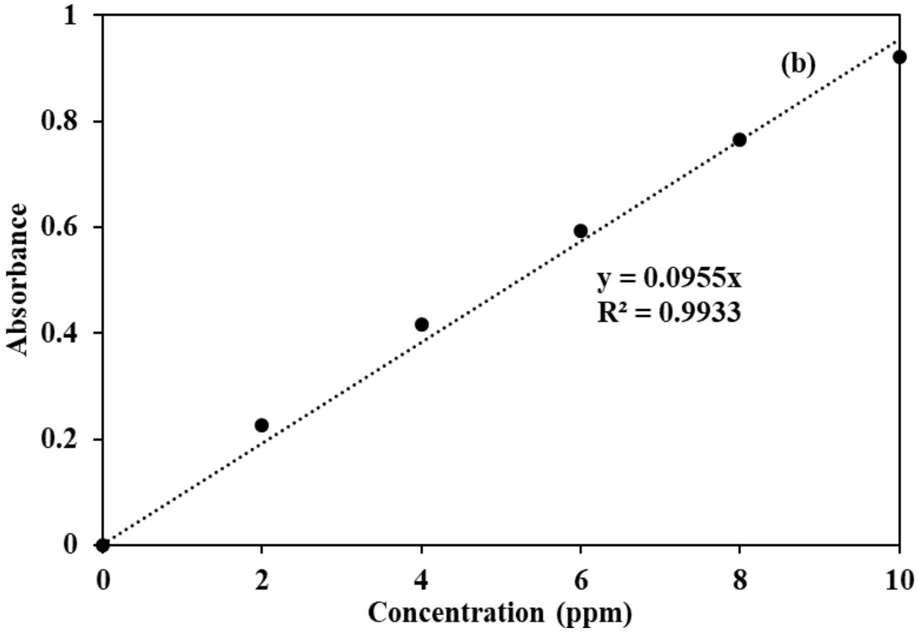


Fig. 3.2. Calibration Curve of 4-ABP

3.3 Electrode material and its types

The selectivity and efficiency of the whole process depends on how capable are the electrodes. The rougher and porous surface provides more activity site and higher specific surface area for the oxidation treatment. There must be resistance to anodic corrosion and low operation costs. Without any modification to the electrode, it should anodically produce hydroxyl radicals and attain complete mineralization of pollutant with high current efficiency. Degradation of nitrogenous organic pollutant in the wastewater needs specific electrodes.

BDD, the most efficient material for EO of wastewater has very high over potential for oxygen, hydrogen evolution, quite low capacitance, absence of surface oxide formation, reduction reactions between oxygen-hydrogen evolution and high electrochemical stability in severe conditions.

However, BDD is less efficient for diluted wastes, also due to mass transport limitations for small concentrations of pollutants and high price thwarts the widespread use of BDD on large scale.

IrO_2 and RuO_2 are electro-catalysts whereas SnO_2 and TiO_2 acts as modulator agents to promote mechanical stability. SnO2 has slow resistivity and high stability with good phenol removal efficiency. RuO_2 is more active than IrO_2 in chlorine evolution.

Ti/RuO_2–Al is chosen because of its longer lifetime, lower costs and greater electrochemically active area than others.

3.4 Advantages and disadvantages of electro-oxidation

Direct or indirect EO is capable of treating even high toxic water at room or atmospheric temperature. A very simple and easy to operate equipment is needed for experimental run, requiring less maintenance as the process is controlled by power supply with no moving parts. Neutralisation of excess chemicals and disposal of secondary pollutants is avoided with least use of chemicals at any concentration.

The sacrificial electrodes are made to replace on a regular basis. The electricity expenses are generally very high. The efficiency of this unit is lowered by the formation of an impermeable oxide film at the cathode surface. The electrodes are dissolved into stream of synthetic wastewater. The suspension is required to have very conductivity which is not feasible. Electrode fouling due to some material deposition on surface has been noticed.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. GENERAL

As not reported earlier, the treatment process shows a considerable aromatic amine (4-ABP) removal, the results and their interpretation have been discussed in detail. Dimensionally stable Ti/RuO$_2$-Al electrodes were used to degrade 4-ABP. Finally, EO degradation products of 4-ABP were identified and a suitable degradation mechanism was proposed.

4.2. RSM Application and Responses

4.2.1. Central composite design (CCD)

Central composite design by RSM was accustomed for the investigational study. The methodical steps followed were, adequacy of various models test which is sequential model sum of squares and model summary statistics, ANOVA, which is analysis of variance and the 3-D response surface graphs explanation. Further, steps were performed to establish an optimum condition suitable for all the responses. Optimization is required for the stimulated data obtained. Four operation parameter variables, current (I) 0.0-2.0 A, electrolysis time (t) 10-110 minutes, concentration (Co) 10-90ppm and pH 2-10 were considered as input parameters and percentage removal of 4-ABPand electrical energy consumption (kWh) was taken as responses of the system. Total 30 experiments were designed by RSM(Table 4.1). Accordingly, effects of pH, current, time and concentration on percentage removal (R_1) and energy consumption (R_2) were studied and reported.

4.2.2. Statistical analysis

The background of different input parameters provided by design matrix (Table 4.1) gave calculated responses as R_1 and R_2. To obtain the regression equation, quadratic model was suggested for the simulated data. Sequential model sum of squares presented quadratic model as the best fit for responses R_1 and R_2 .The adequacy of model was tested by sequential model sum of squares and model summary statistics (Table 4.2-4.3). Higher order models were aliased for R_1 and R_2.

Table 4.1 Full factorial design matrix used for electro-oxidation of 4-ABP

Std	Run	pH	I (A)	T (min)	C_o (mg/L)	%Removal (R_1)	Energy Consumed (R_2)
1	4	4	0.5	35	30	46.35	0.002
2	27	8	0.5	35	30	28.54	0.002
3	30	4	1.5	35	30	62.68	0.0092
4	6	8	1.5	35	30	21.3	0.0082
5	19	4	0.5	85	30	49.55	0.005
6	24	8	0.5	85	30	25.14	0.005
7	5	4	1.5	85	30	64.96	0.027
8	2	8	1.5	85	30	28.5	0.0197
9	8	4	0.5	35	70	27.97	0.0025
10	3	8	0.5	35	70	31.66	0.002
11	13	4	1.5	35	70	40.25	0.011
12	11	8	1.5	35	70	40.41	0.011
13	29	4	0.5	85	70	32.57	0.005
14	17	8	0.5	85	70	43.67	0.006
15	9	4	1.5	85	70	50.32	0.029
16	10	8	1.5	85	70	51.84	0.026
17	18	2	1	60	50	50.14	0.008
18	1	10	1	60	50	31.17	0.009
19	16	6	0	60	50	5.2	0
20	20	6	2	60	50	44.62	0.029
21	7	6	1	10	50	30.81	0.0015
22	15	6	1	110	50	40.79	0.016
23	22	6	1	60	10	44.67	0.009
24	28	6	1	60	90	53.55	0.009
25	14	6	1	60	50	38.28	0.009
26	12	6	1	60	50	39.12	0.009
27	23	6	1	60	50	39.16	0.009
28	21	6	1	60	50	38.64	0.009
29	26	6	1	60	50	38.87	0.009
30	25	6	1	60	50	38.68	0.009

Table 4.2 Sequential model sum of squares for % removal (R_1)

Source	**Sum of squares**	**DF**	**Mean square**	**F value**	**Prob> F**	
Mean	36542.39	1	36542.39			
Linear	7690.68	4	1922.67	35.79	< 0.0001	
2FI	469.88	6	78.31	1.70	0.1744	
Quadratic	867.43	4	216.86	579.22	<0.0001	Suggested
Cubic	5.03	8	0.63	7.55	0.0075	Aliased
Residual	0.58	7	0.083			
Total	45575.99	30	1519.20			

Table 4.3 Sequential model sum of squares for energy consumption (R_2)

Source	**Sum of squares**	**DF**	**Mean square**	**F value**	**Prob> F**	
Mean	8.32	1	8.32			
Linear	4.04	4	1.01	11.78	< 0.0001	
2FI	0.85	6	0.14	2.08	0.1041	
Quadratic	1.29	4	0.32	6344.74	<0.0001	Suggested
Cubic	5.813E-004	8	7.267E-005	2.79	0.0972	Aliased
Residual	1.824E-004	7	2.606E-005			
Total	14.50	30	0.48			

The model gives coefficient of determination R^2 value of 0.999 and 0.999 for R_1 and R_2 respectively.Predicted R^2 value of 0.997 and 0.999 for R_1 and R_2, respectively, adjusted R^2 value of 0.998 and 0.999 for R_1 and R_2, respectively. All these values focus on a very good correlation between the observed and predicted data values. All the actual values were very near to the predicted value. The graphs (Figure 4.1) shows a very close relation between % Normal probability and studentised residual.

4.2.3 Analysis of variance

The ANOVA for response surface quadratic model of % Removal (R_1) and energy consumption (R_2) for EO of 4-ABP are shown in Table 4.4 and 4.5, respectively.The quadratic model best fitted the experimental response values. Various response values were calculated according to the suggested experiments performed as per CCD. The value of Prob>F less than 0.05 shows corresponding model term to be significant. The “Lack of fit” values of the model were found to be insignificant. All the results were desired. The analysis of variance (ANOVA) depicted F-value of 14.3 and 69.52 for R_1 and R_2, respectively. All these values indicate that model considered is significant for R_1 and R_2 responses. Table 4.4 and 4.5 shows significant model terms having values of “prob>F” to be less than 0.05. Whereas, “Prob>F” values larger than 0.100 usually give insignificant model terms. The "Lack of Fit F-value" for R_1 and R_2 of 275.53 and 375.41, respectively, implies there is a 5.65% chance that a "Lack of Fit F-value" could occur due to noise. In this case pH, I, t, I^2, C_o^2, pH×I and pH×C_o are hoghly significant model terms for response $R_{1,}$% removal; and I, t, I^2, pH×I and I x t are the high significant model terms for response R_2, energy consumption.The equation for quadratic model representing R_1 and R_2 obtained in terms in terms of parameters are given below.

$$R_1 =+38.79-5.90 \times pH +6.40 \times I +2.81 \times t +0.39 \times C_0+0.92 \times pH^2-3.01 \times I^2-0.29 \times t^2+3.04 \times C_o^2-3.05 \times pH \times I +0.44 \times pH \times t +8.53 \times pH \times C_o +0.91 \times I \times t + 1.19 \times I \times C_o +1.80 \times t \times C_0 \qquad \textbf{(4.1)}$$

$$R_2 = 8.5 \times 10^{-3}-4.5 \times 10^{-4} \times pH + 7.2 \times 10^{-3} \times I + 4.3 \times 10^{-3} \times t +4.8 \times 10^{-4} \times C_0+1.08 \times 10^{-4} \times pH^2+1.6 \times 10^{-3} \times I^2+8.7 \times 10^{-5} \times t^2+1.7 \times 10^{-4} \times C_o^2-8.7 \times 10^{-4} \times pH \times I -5.02 \times 10^{-4} \times pH \times t - 3.37x10^{-4} \times pH \times C_0-3.12 \times 10^{-3} \times I \times t +7.2 \times 10^{-4} \times I \times C_o+3.2 \times 10^{-4} \times t \times C_0 \qquad \textbf{(4.2)}$$

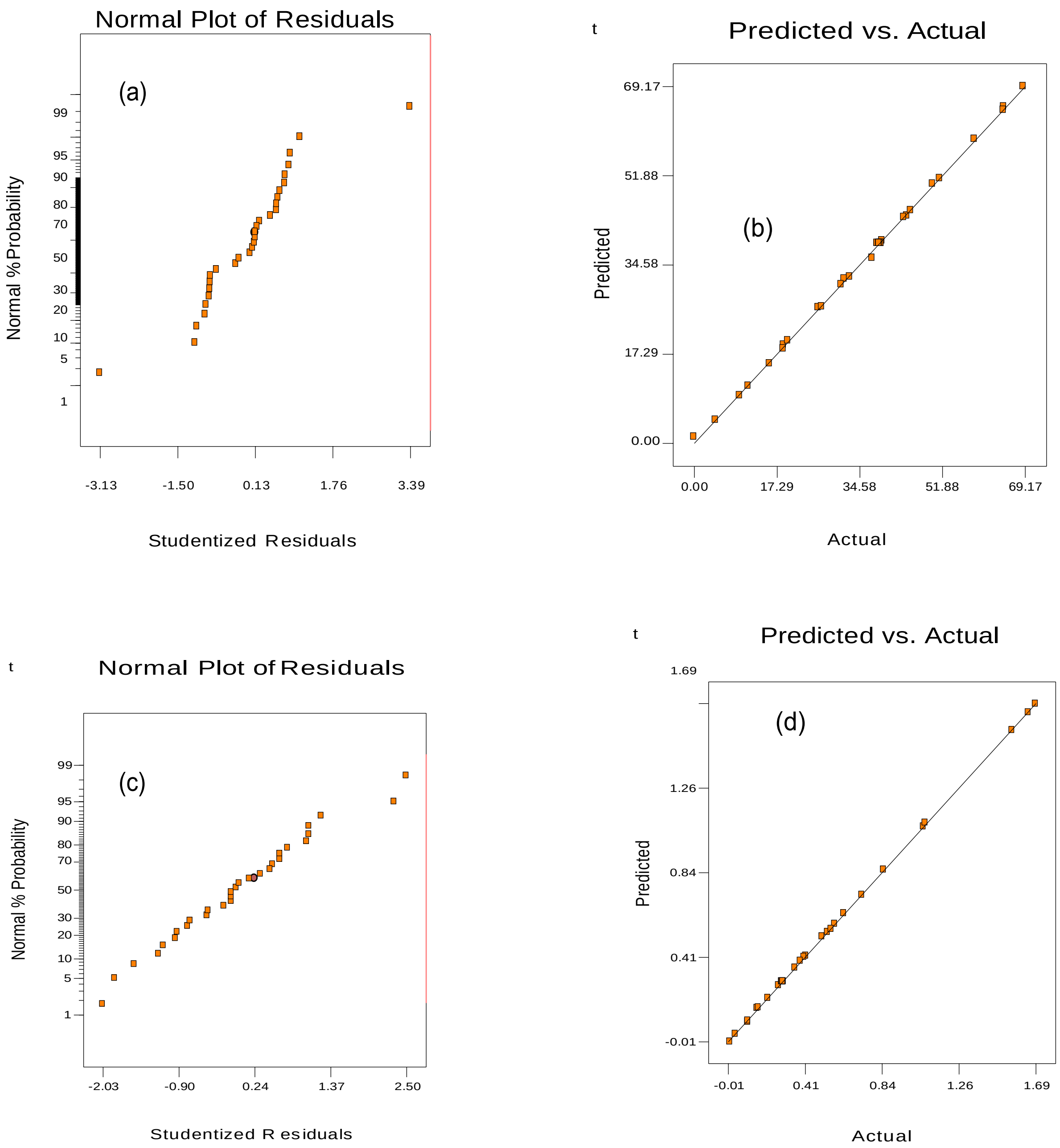


Figure 4.1. Residual plots (a) and (b)for response R_1; (c) and (d) for R_2

Table 4.4. ANOVA for response surface quadratic model for % Removal of 4-ABP

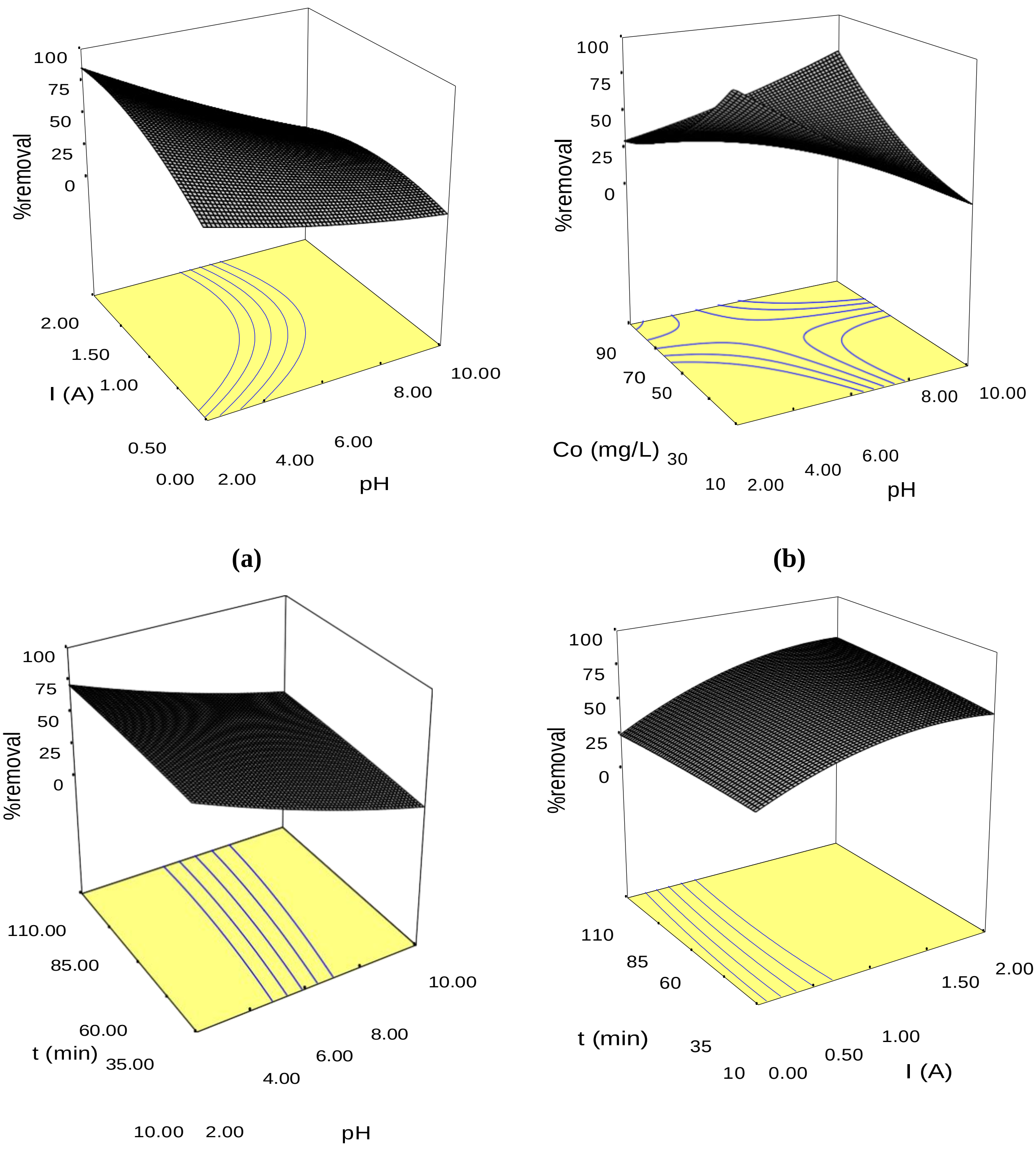
Source	Sum of Squares	DF	Mean Square	F Value	Prob> F	
Model	4029.8	14	287.84	14.30	< 0.0001	Significant
A	834.61	1.00	834.61	41.47	< 0.0001	
B	983.68	1.00	983.68	48.87	< 0.0001	
C	189.00	1.00	189.00	9.39	0.0079	
D	3.71	1.00	3.71	0.18	0.6740	
A^2	23.33	1.00	23.33	1.16	0.2987	
B^2	249.18	1.00	249.18	12.38	0.0031	
C^2	2.33	1.00	2.33	0.12	0.7383	
D^2	252.81	1.00	252.81	12.56	0.0029	
AB	148.41	1.00	148.41	7.37	0.0160	
AC	3.14	1.00	3.14	0.16	0.6983	
AD	1165.03	1.00	1165.03	57.88	< 0.0001	
BC	13.27	1.00	13.27	0.66	0.4295	
BD	22.78	1.00	22.78	1.13	0.3043	
CD	51.95	1.00	51.95	2.58	0.1290	
Residual	301.91	15.00	20.13			
Lack of Fit	301.37	10.00	30.14	275.53	< 0.0001	Significant
Pure Error	0.55	5.00	0.11			
Cor Total	4331.71	29.00				

Table 4.5. ANOVA for response surface quadratic model for response R_2 (Energy consumption)

Source	Sum of Squares	DF	Mean Square	F Value	Prob> F	
Model	0.001951	14	0.000139	69.52	< 0.0001	significant
A	0.000005	1.00	0.000005	2.44	0.1390	
B	0.001242	1.00	0.001242	619.41	< 0.0001	
C	0.000445	1.00	0.000445	222.08	< 0.0001	
D	0.000005	1.00	0.000005	2.711	0.1205	
A^2	0.000000	1.00	0.000000	0.160	0.6951	
B^2	0.000069	1.00	0.000069	34.285	< 0.0001	
C^2	0.000000	1.00	0.000000	0.104	0.7515	
D^2	0.000001	1.00	0.000001	0.398	0.5377	
AB	0.000012	1.00	0.000012	6.143	0.0256	
AC	0.000004	1.00	0.000004	2.014	0.1763	
AD	0.000002	1.00	0.000002	0.908	0.3558	
BC	0.000156	1.00	0.000156	77.793	< 0.0001	
BD	0.000008	1.00	0.000008	4.198	0.0584	
CD	0.000002	1.00	0.000002	0.850	0.3712	
Residual	0.000030	15.00	0.000002			
Lack of Fit	0.000030	10.00	0.000003	375.409	< 0.0001	significant
Pure Error	0.000000	5.00	$8x10^{-9}$			
Cor Total	0.001981	29.00				

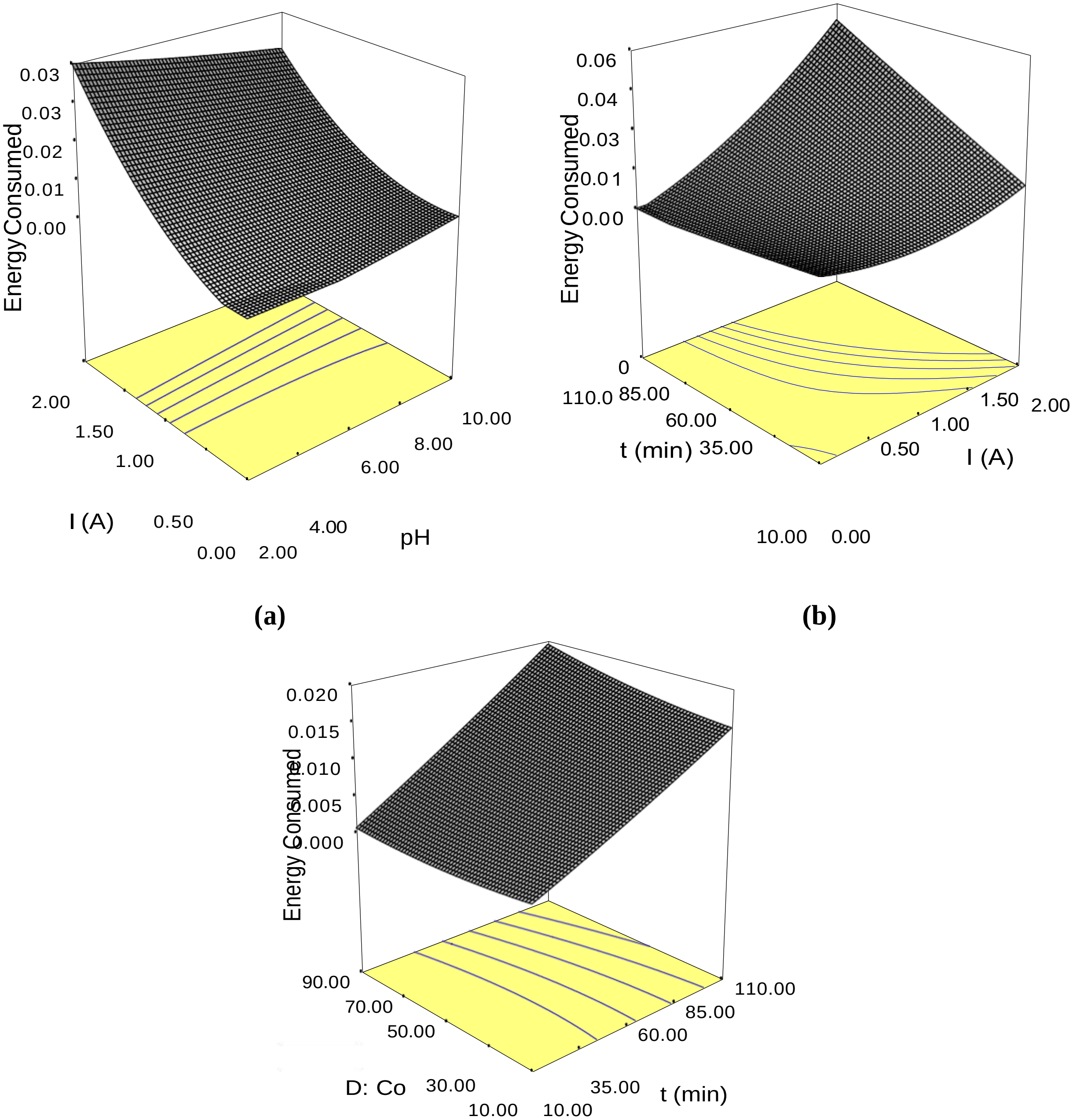
4.2.4. Effects of pH, time, current on responses R_1 and R_2

The 3D contour plots enumerates how fitted are the response values based on a model equation to the two continuous variables in consideration. The geometric illustration of 3D relationship is very concisely plotted in two dimensions. The relationship of current density, intial concentration, time, pH on responses as %removal (R_1) and energy consumption (R_2) can be drawn from Figure 4.2-4.3. This projection of 3D graph on a 2D plot also shows minimum and maximum points of the independent variables taken. Efficiency of EO process for organic pollutants abatement is highly pH dependent as shown in Fig.4.2(a)(b)(c). The contour surface indicates the response on z-axis according to the predictors (I, pH, C_o or t) on x-y axis,. In Fig.4.2(a)(b)(c), R_1 can be seen higher at 2-4pH(acidic) with further sharp decrease in alkaline medium as depicted a fitted response by the predictors (I, pH, C_o or t) on z-axis. After 85 min of EO process, 68.85% of 4-ABP was degraded at pH 4, whereas, at pH 6, almost 50% removal was achieved in just 10 min of EO (Fig.4.2-d). Just 4.52% of 4-ABP is removed in an hour of EO at pH10 with quite high energy consumption. 38.87%, 4.52% and 64.68% 4-ABP was degraded in 60 min of electrolysis for pH values of 6, 10 and 2 respectively. With further higher concentration 70-90ppm(Fig.4.2-b), there was no improvement in removal efficiency. The enrichment in R_1 value is well observed with time(Fig.4.2-d) which was outstanding for higher values of applied current (1.5–2.0 A), than low applied current value≈0.5 A. For every C_o, t and current density, highest % removal could be seen in acidic pH only (Fig.4.2-a,b,c). Further, based on the same quadratic polynomial equation as in Figure 4.2, the R_2 response was evaluated as shown in Fig.4.3. The variables I, pH, t, C_o affect energy consumption of the EO, with increase in pH (Fig.4.3a), (R_2) elevates and for high applied current (I>1.00A), R_2 value can be seen decreasing gradually as interpreted from Fig.4.3(a)(b). Least energy consumption (0.03kWh/mg pollutant removal) was seen at 10min (Fig.4.3-b) where current density is 1A. For t(110min), 0.58kWh/mg removal can be drawn from Fig.4.3b. A very high value of R_2 (1.69 kWh/mg pollutant removal) is numerated at lower C_o (30ppm), large time (85min) and high pH(8).



(a) (b) (c) (d)

Figure 4.2. 3-D response surface graphs for % removal as function of independent variables pH, I, t and C_o.



(a) **(b)**

(c)

Figure 4.3. 3-D response surface graphs for EC (kWh) as function of independent variables pH, I, t and C_o.

4.2.5. Optimization analysis

EO treatment has been optimized for R_1 and R_2 responses, where the former is maximized and later minimized. In order to confirm the optimization results which were predicted for R_1 and R_2, verification runs were conducted at 30ppm and 100ppm, keeping other operational parameters similar. To get the simultaneous maximum R_1 and minimum R_2,the desirability approach was applied.

Table 4.6. Constraints applied for optimization of electro-oxidation

Variables	**Goal**	**Lower limit**	**Upper limit**
pH	Is in range	2	10
I(A)	Is in range	0.5	2
Time	Is in range	10	110
%removal	maximize	50	100
Energy consumption (kWh)	maximize	0.03	1.56

Table 4.7. Optimum conditions for EO process

Variables	**Optimum values**
I (A)	1.2
pH	4
Time (min)	10
Concentration	30
Expected Response, R_1	57.1
Expected Response, R_2	0.0581
Predicted Response, R_1	60.25
Predicted Response, R_2	0.0674

Maximization of % removal and minimization of energy consumption with desirability function approach (D) optimized the whole process.

The optimum values suggested by RSM with D as 1.000 were 4pH, 10 min, 1.2A and 30ppm concentration. For these, suggested % removal was 57.1% and predicted 60.25%, energy consumption was 0.0581 kWh/mg while predicted was 0.0674 kWh/mg.

4.2.6. 4-ABP degradation products and LC-MS Analysis

The degradation of 4-aminobiphenyl using electrooxidation technique by Ti/RuO_2 electrodes was further evaluated by performing LC-MS analysis of synthetic wastewater samples before and after 30 min of the treatment process. As shown in Fig.4.5, the retention time of 4-aminobiphenyl came out to be 5.16 min. The corresponding mass spectra of initial sample reveals the peak at mass/charge ratio (m/z) value of 170.1 (Fig. 4.4), which corresponds to protonated 4-aminobiphenyl molecule $[M+H]^+$. However, the LC chromatogram (Fig. 4.6) of treated sample revealed the formation of three major reaction intermediates (RIs) of 4-aminobiphenyl (Table 4.8). A plausible degradation mechanism was proposed on the basis of identified RIs (Fig.4.7). The hydroxyl radicals generated at the Ti/RuO_2 anode surface reacted with 4-aminobiphenyl molecule to form RI 1. Further attack of hydroxyl radicals on amine group formed an instable molecule, resulting in opening of the benzene ring and formation of RI 2. Similarly, RI 3 was formed by action of •OH on RI 2. After the opening of benzene rings, further attack of oxidant species resulted into mineralization of reaction intermediates to CO_2 and H_2O.

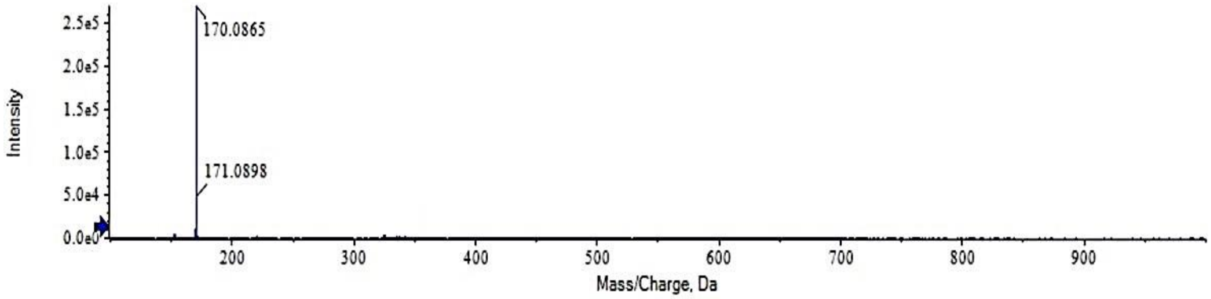


Fig. 4.4 Mass spectrum of initial sample of synthetic wastewater comprising 4-aminobiphenyl

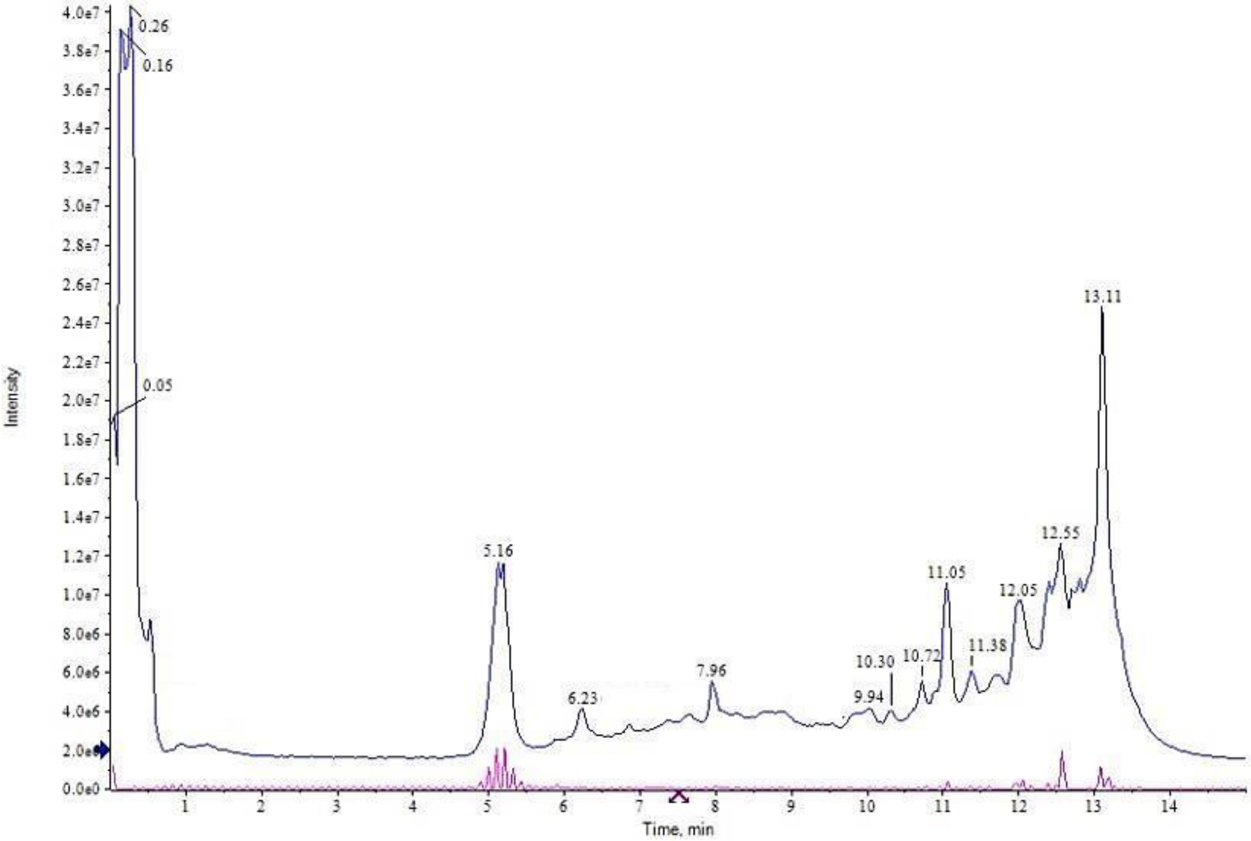


Fig. 4.5 LC chromatogram of initial sample of synthetic wastewater comprising 4-aminobiphenyl (Retention time = 5.16)

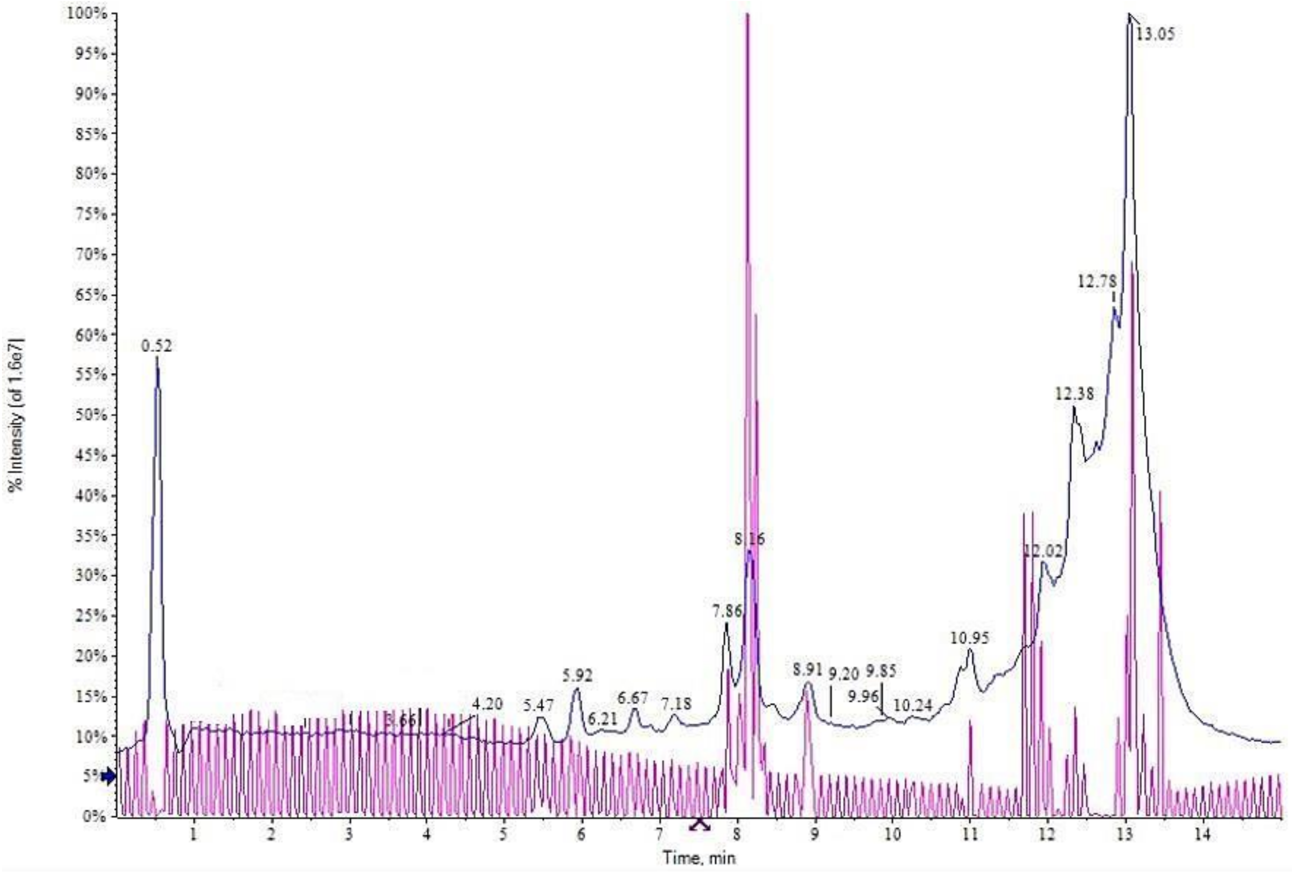
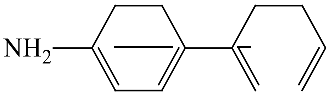
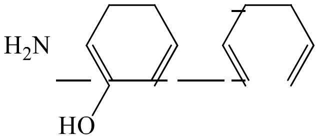
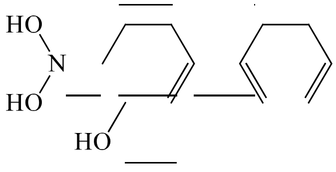
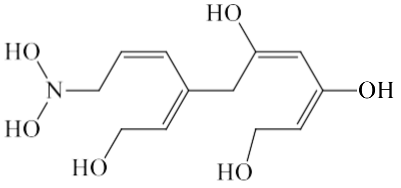


Fig. 4.6. LC chromatogram of synthetic wastewater sample after 30 min of electrooxidation treatment using Ti/RuO$_2$ electrodes

Table 4.8. Reaction intermediates (RIs) formed during batch electrooxidation treatment of 4-aminobiphenyl

Compound	R_T (min)	m/z $[M+H]^+$	Elemental composition	Proposed structure
4-aminobiphenyl	5.16	170	$C_{12}H_{11}N$	
RI 1	5.47	185	$C_{12}H_{11}NO$	
RI 2	5.92	221	$C_{12}H_{15}NO_3$	
RI 3	6.67	273	$C_{12}H_{19}NO_6$	

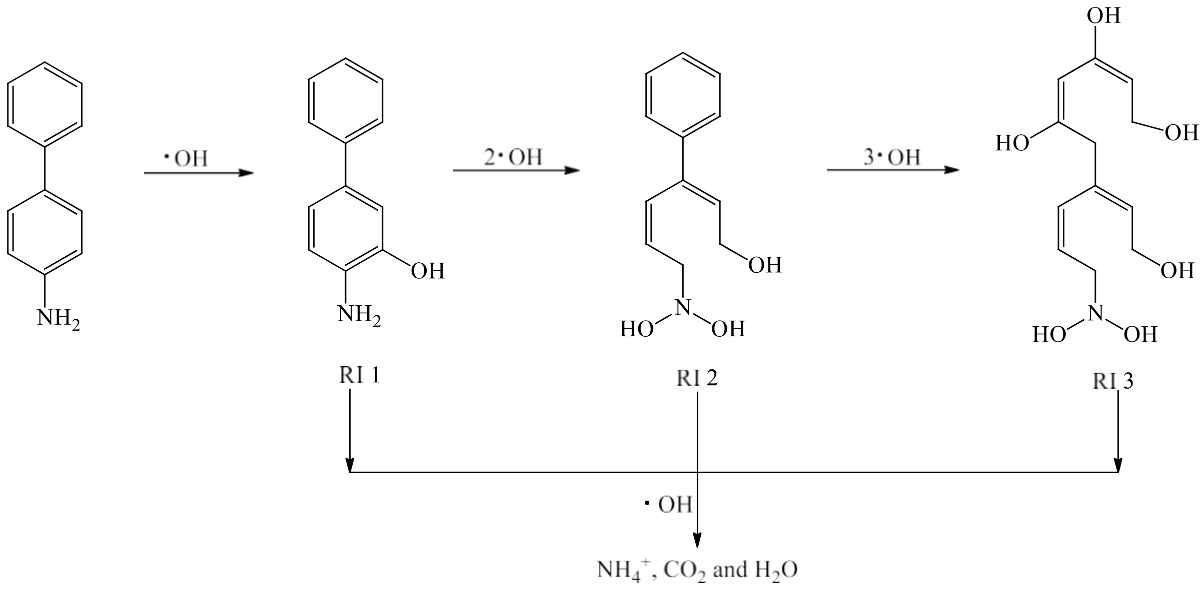


Fig. 4.7 Plausible degradation mechanism of 4-aminobiphenyl by electro-oxidation treatment

CHAPTER 5

CONCLUSION

The electro-oxidation process has become a captivating alternative which is successfully applied for IW treatment as it does not produce the undesired reaction co-products, neither use toxic materials nor the hazardous ones. It has also eliminated the use of oxidation reagents in carrying out processes that are useful and suitable for on-site treatment in small-scale facilities. This could be an ideal finishing step in amine and treatment combinations with all existing technologies and IW treatment systems. From the present study for the degradation of 4-ABP wastewater by EO method with Ti/RuO_2-Al electrodes, following major conclusions were drawn:

a) Only a small portion of current intensity (1.5A) was used in degradation/ mineralization of 4-ABP in synthetic IW. Furthermore, it decreased the energy consumption from 1.65 to 0.73 kWh/mg pollutant removed while lowering pH from 10 to 4.

b) With increasing ‘t’ value and applied current, % removal was always enhanced.

c) According to RSM, pH, I, t, Co, pH^2, I^2, t^2, Co^2, pH×I, pH×t, pH×Co, I×t and $t \times C_o$ are significant model terms for both % removal and energy consumption. There is no term which is not significant for the model.

d) At optimum conditions for EO treatment of 4-ABP (pH 4.0, t-10min, 1.2A), 0.067 kWh of electrical energy was consumed for removal of 1 mg pollutant from wastewater. For these, suggested % removal was 57.1% and predicted 60.25%. The average cost of electrical energy in India is INR 5 per kWh. Therefore, the price of electrical energy consumption comes out to be INR 0.335/mg pollutant removal.

e) The coefficient of determination R^2 value of 0.9994, 0.999 were of R_1 and R_2 respectively. These values point a very good correlation between the observed and predicted values.

f) Ti/RuO_2-Al electrode pair was successful in aromatic amine degradation electrochemically.

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