Electrochemical Treatment of organic and oily wastewaters

A Dissertation Submitted to

Thapar University, Patiala

in partial fulfillment of the Requirements
for the Award of Degree of

Master of Technology
(Environmental Science and Technology)

Under the Guidance of
Dr. A.S. Reddy
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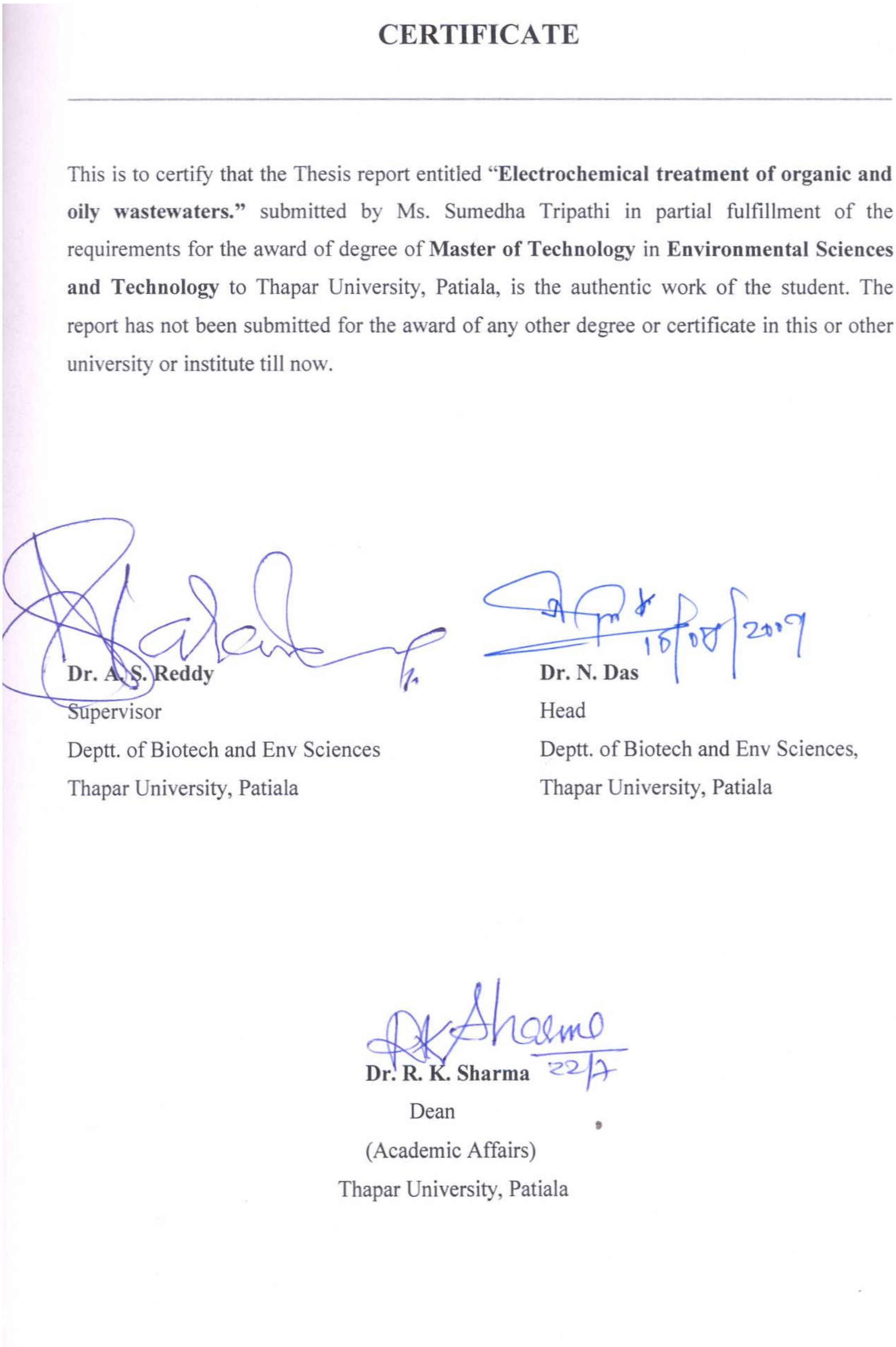
Candidate's Declaration

I, hereby declare that the thesis report entitled **"Electrochemical treatment of organic and oily wastewaters"** in partial fulfillment of the requirement for the award of the degree of Masters of Technology, Department of Biotechnology and Environmental Sciences, Thapar University, Patiala, is an authentic record of my own work during the period of eleven months from August 2008 to June 2009, under the supervision of Dr. A.S. Reddy, Assistant Professor, Department of Biotechnology and Environmental Sciences, Thapar University. The report has not been submitted for the award of any other degree or certificate in this or any other university.

Place: Patiala

Date (Sumedha Tripathi)



CERTIFICATE

This is to certify that the Thesis report entitled "**Electrochemical treatment of organic and oily wastewaters.**" submitted by Ms. Sumedha Tripathi in partial fulfillment of the requirements for the award of degree of **Master of Technology** in **Environmental Sciences and Technology** to Thapar University, Patiala, is the authentic work of the student. The report has not been submitted for the award of any other degree or certificate in this or other university or institute till now.

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(Sumedha Tripathi)

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Abstract

The study aims to investigate the treatability of acrylic fibre applicator oil wastewater from textile processing industry and first extraction stage bleach plant effluent from a pulp and paper industry by electrochemical treatment process. The set of experiments to be performed were found using Response Surface Methodology (RSM) of design expert software. The experimental results were analysed by the design expert software and the electrochemical treatment process was modelled.

For the acrylic fibre applicator oil wastewater, stainless steel electrodes were used and the treatment process was optimized for the fixed factors pH, voltage, time and chloride content, and treatment efficiency in terms of COD removal was recorded as response. Statistical modelling and the response maximization gave 5.1 pH, 14.26 V voltage, 9.25 minutes treatment time and 1067mg/l of chloride as optimal parameter values for the maximum COD removal of 77.7%.

For the treatment of bleach plant effluent, aluminium, iron and stainless steel electrodes were used. May be due the inability to properly monitor the response, statistical model development and process optimization could be done only for the SS-SS pair of electrodes. Optimum conditions for the maximum colour removal with SS-SS pair of electrodes were found to be 6.25 pH, 8.99 V voltage, and 15.69 minutes treatment time. The maximum colour removal efficiency achieved was 96.6%.

Thus above results show that electrochemical treatment can be successfully used for the treatment of acrylic fibre applicator oil wastewater and also for that of the first extraction stage bleach plant effluent.

Chapter 1

Introduction

One of the major problems faced by human race today is to provide clean water to the vast majority of population all around the world. With fresh water sources as rivers, canals and estuaries etc limited and those available being polluted by indiscriminate discharge of industrial pollutants and other processes, making fresh water much cherished commodity now a days. The widening gap between demand and supply of water comes in the way of sustainable development. Thus in the wake of 21st century ,emphasis is being laid on reduction, recycle and reuse of natural resources such as fresh water. Further there are several difficult waste waters which cannot meet the present standards by conventional waste water treatment techniques. Thus for recycling and reusing the waste water that leads to reduction of fresh water consumption and for treating difficult waste waters, there is an urgent need to develop innovative, more effective and inexpensive technique of waste water treatment. Electrochemical treatment is one such technique which can either be used as main treatment scheme or as a hybrid technique. It can also be used as a pretreatment scheme for difficult waste waters for which feasible technologies are not available. Treatment of these wastewaters may require segregation of the culprit wastewater streams at source and pretreatment prior to addition to other wastewaters for treatment and disposal. Here, objective of the pre-treatment is to make the wastewater compatible for mixing with other wastewaters and to improve the treatability of the overall wastewater of the industrial unit. This pre-treatment approach, for the segregated wastewater streams, makes the otherwise costly wastewater treatment technologies feasible. Low volumes and high strength of the segregated wastewater streams are responsible for this.

Electrochemical treatment can be used as an treatment technique for the treatment of waste water with lignin and tannic acid (Chiang et al. 1997), resorcinol and cresols (Rajkumar et al. 2001; Rajkumar and Palanivelu 2003), tannins (Buso et al. 2000), textile dye (Allen et al. 1995;Vijayaraghavan et al. 2001; Szpyrkowicz et al. 2000), landfill leachate (Chiang et al. 1995), polyaromatic organic compounds (Panizza et al. 2000), tannery (Szpyrkowicz et al. 1995), and pharmaceutical (George et al. 1995) wastewaters etc. Although the technique is not new and can be traced back of being used for the first time in 1889 in UK, still it has never been used as the main stream treatment technology. This can be attributed to its high operational cost.

So in the present report, on the basis of experimental results for acrylic waste water and bleach effluent obtained on a lab scale, attempts are being made to find out the most suitable type of electrode and optimum conditions (such as pH, Voltage, Time) to get the requisite treatment of waste water in a cost effective manner.

1.1: Objective of work

Objective of this study is to optimise the treatment conditions on laboratory scale, whose results can be used to scale up to a pilot scale treatment unit for acrylic fibre applicator oil wastewater and first extraction stage bleach effluent.

1.2: Scope of work

1. Literature has been obtained from Mr. M.S. Bhatti, lecturer of Guru Nanak Dev University, Amritsar. Some of the literature was also searched from www.sciencedirect.com, www.IEEE.com and www.googlesearch.com.

2. To work on electro-chemical treatment original industrial wastewater was used which was provided by Dr A.S. Reddy, Associate Professor of Thapar university-

   - ✓ Acrylic fibre applicator oil wastewater from textile industry.
   - ✓ First extraction stage bleach plant effluent from a pulp and paper industry.

3. It also includes the lab scale electrochemical treatment unit fabrication and standardization of the treatment process which can be used for different waste waters to get the lab scale results.

4. Main emphasis was on electro-chemical treatment of wastewater and to obtain the results under different experimental conditions.

1.3: Significance of work

1. Work was done on two types of wastewaters, so this report is of immense use for us to know about the treatability studies of these wastewaters and if any person wants to do further work then this report will be of immense use as starting material.

2. Most of the abstracts related to electrochemical treatment system, available online were gone through. Relevant research papers related to electrochemical treatment of organic and oily water were also thoroughly scanned to get the insight of the status co in the field.

3. The results obtained were used for modelling by response surface methodology (RSM).In this relevant software and the experimental results obtained, were used to chalk out optimised set of conditions for the treatment of waste water.

1.4: Limitations

Following were the limitations faced while working to reach the objectives of present thesis work.

1. The treatment scheme followed here is batch type, which is not usually the treatment mode followed in industries. Hence reliability of these results for scaling up to pilot scale plant is slightly reduced.

2. Further a dead space of 2 cm length is present below the reactor where the electrodes are not present. So there is no treatment going on in that area of the reactor which considerably reduces the efficiency of treatment.

3. Also the free board provided over the reactor was found to be quite less as compared to the volume of waste water treated, so the flocs and the scum rising above the reactor have to be periodically collected for preventing their overflow and getting the correct insight of the sludge volume produced.

4. The magnetic stirrer bead which was used to create mixing and turbulence within the reactor was useful only with aluminium and stainless steel electrodes and it was magnetically stuck to the iron electrodes when used with them, hence causing no mixing. This effects the uniformity of the experimental sets results when experimental results of different electrodes are compared.

1.5: Overview of Contents of Thesis Report

This thesis report includes abstract, five chapters and references whose contents can be briefly described as follows:

Chapter-1 It gives the brief background information and overview of the contents of thesis report along with the objectives, scope, significance and limitations of the work done.

Chapter-2 It is literature review of electrochemical treatment of organic and oily waste waters. This chapter compiles the different types of organic matter and oil rich wastewaters treated using different types of electrodes under different treatment conditions. Further the efficiency for the treatment of different wastewaters and cost effectiveness of this technology in comparison to other technology was also considered.

Chapter-3 is Methodology. This chapter gives the information about the source and characteristics of waste water; experimental set up used; procedure followed for the treatability studies and the analytical techniques used for analysing the raw and the treated effluent.

Chapter-4 is Results and Discussion. This chapter includes the experimental results along with their interpretation and further use in modelling. The details of modelling and optimised results are also quoted here.

Chapter-5 is Conclusion. Here summary of the report is presented and it also highlights the need of technology for treatment of different wastewaters.

Chapter -2

Literature Review

This thesis work is based on organic matter and oil rich waste waters hence the literature review was totally focussed on these waste waters.

Electrochemical treatment has been found to be an efficient technique for difficult and recalcitrant waste waters as soluble oils, liquid from food, cellulosic waste water, textile effluent etc for which conventional treatment techniques are either not meeting the discharge standards or are not feasible. However all the organic matter and the oil rich waste waters have different components so according to Calvo et al (2003), the treatment efficiency of electrochemical process may change dramatically from one waste water to another for instance the COD removal from landfill leachate is 73% [Peterson et al(2007)], phenolic waste water is 99% [Ma H et al(2008)], slaughter house waste water is 82% [Asselin et al(2008)], poultary waste water is 93% [Kobya M. et al (2006)], dairy waste water is 98% [Sengil A. et al (2006)], paper and pulp industry waste water is 80%[Mahesh S. Et al(2006)], distillay waste water is 89.62%[Piyareetham P. et al (2006)] etc.

Thus efficiency, applicability and even feasibility of electrochemical treatment for organic matter and oil rich waste water depends upon the different constituent present in that waste water to be treated as given below.

3.1. Organic waste waters

3.1.1. General literature

Barrera-Díaz et al. (2009) in A Comparison of Iron and Aluminium Electrodes in Hydrogen Peroxide-Assisted Electrocoagulation of Organic Pollutants studied the removal of organic pollutants from a highly complex industrial wastewater by aluminium and iron electrocoagulation assisted with hydrogen peroxide. Under optimal treatment the process reduced chemical oxygen demand (COD) by 92%, biochemical oxygen demand (BOD_5) by 89%, color by 92%, turbidity by 95%, and total coliforms by 99%. Initial and final pollutant levels in the wastewater were monitored using UV-Vis spectrometry and cyclic voltammetry.

Shibin et al. (2007) in Removal of organic pollutants from 2,2',5,5'-tetrachlorobenzidine (TCB) industrial wastewater by micro-electrochemical oxidation and air-stripping found that combined micro-electrochemical oxidation or iron-chipping filtration (ICF) and air-stripping reactor (ASR) is a feasible method for treatment of the wastewater from the two-staged neutralization in 2,2',5,5'-tetrachlorobenzidine (TCB) manufacturing processes, a refractory dye intermediate effluents. On conditions of HRT 1h, pH 3.0 in ICF and HRT 38 h, gas-liquid ratio 15, pH 6.0-8.65, temperature 26 degrees C in ASR, the overall COD, color, TCB and ammonical-N removal were 96.8%, 91%, 87.61% and 62%, respectively, during the treatment of TCB wastewater from the two-staged neutralization dissolved by methanol. The averaged 18.3%, 81.7% of the total degraded COD, 35.2%, 64.8% of TCB were carried out in ICF and ASR, respectively. Ammonical-N removal was finished mainly in ASR. The experimental results indicated that the combined micro-electrochemical oxidation and air-stripping process performed good treatment of COD, color, TCB and ammonical-N removal in TCB wastewater from the two-staged neutralization dissolved by ethanol or acetone came up the discharge standard in China.

Panizza et al. (2001) in Removal of organic pollutants from industrial wastewater by electrogenerated Fenton's reagent studied the treatment of an industrial wastewater mainly containing naphthalene and anthraquinone-sulphonic acids, by electrogenerated Fenton's reagent. The influence of cathode potential, Fe2+ concentration and electrode surface pre-treatment on chemical oxygen demand (COD) removal and colour fading were studied. Results indicated that the higher COD removal was obtained in the presence of 3 mM of ferrous ions working at a constant potential of 1 V. Moreover, it was shown that both chemical and electrochemical pre-treatments of the cathode surface resulted in a decrease of COD depletion.

Zhou et al. (2005) in Long life modified lead dioxide anode for organic wastewater treatment: electrochemical characteristics and degradation mechanism, found that the lack of ideal anodes with both good activity and stability is one of the critical problems in electrochemical oxidation for organic wastewater treatment. The electrochemical properties, the activity and stability for anodic oxidation of various phenolic compounds, and the degradation mechanism on a novel beta-PbO2 electrode modified with fluorine resin were investigated and found that the anode life after modification was greatly improved to be more than 10 yr in common electrochemical current conditions. Such an anode was effective for partial degradation of phenolic compounds, but selective because reactive activities were varied with different substituents. The active species generated during anodic oxidation were mainly hydroxyl radical and little ozone. The reactions between hydroxyl radical and phenolic compounds were proved to be electrophilic reactions, based on which a general electrochemical degradation mechanism for aromatic compounds was proposed.

Martínez-Huitle et al. (2006) in Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, summarized the results of an extensive selection of papers dealing with electrochemical oxidation of organic waste waters. Both the direct and indirect approaches are considered and the role of electrode materials is discussed together with that of other experimental parameters. Apart from discussing the possibility of removing selected contaminants from water using different anodes, efficiency rates for pollutant removal was also calculated.

Bonfatti et al. (2000) in Anodic mineralization of organic substrates in chloride-containing aqueous media investigated the electrochemical incineration of glucose in alkaline media, in the presence of NaCl. The dependence of chemical oxygen demand (COD) and total organic carbon content, on electrolysis duration, t was considered. The influence of current density, sodium chloride concentration, temperature, sodium hydroxide concentration on the rate of COD abatement was also considered. The rate of the incineration was found to increase with increasing the current density and pH and decreasing the solution temperature. With increasing the chloride concentration up to a given critical value, the mineralization rate increases while further increase causes a decrease. The critical value of the mediator concentration has been found to be lower at higher pH. On the basis of this preliminary screening, an attempt of optimization of the mediated electrochemical incineration as a function of current density and chloride concentration has been carried out, basing the analysis on the Simplex algorithm.

Jiang et al. (2008) in Simultaneous Hydrogen Production and Electrochemical Oxidation of Organics Using Boron-Doped Diamond Electrodes studied the advantages of using a boron-doped diamond (BDD) electrode for hydrogen production and wastewater treatment in a single electrochemical cell. Results indicated that the BDD electrode allowed new possibilities for both anodic and cathodic reactions to simultaneously take place. The BDD electrode exhibited high anodic potential, generating high oxidation state radicals that facilitated oxidation of toxic waste organic compounds such as 4-nitrophenols. In contrast, because of widening of potential windows, the rate of hydrogen evolution at the cathode was significantly increased. Time-on-stream concentrations of reaction intermediates were monitored to elucidate mechanism involved in 4-nitrophenol oxidation. Overall, the BDD electrode exhibits unique properties including chemical inertness, anticorrosion, and extended service life which are important in wastewater treatment. Economic advantages were attributed to the low cost and long duration BDD electrode and the valuable hydrogen byproduct produced. When combined with solar energy and fuel cells, electrochemical wastewater processing can become energy efficient and cost-effective.

3.1.2. Literature on different waste waters with organic compounds

1. Coffee curing waste water

Bejankiwar et al. (2003) in Colour and organic removal of biologically treated coffee curing wastewater by electrochemical oxidation method investigated the treatment of biologically treated wastewater of coffee-curing industry by the electrochemical oxidation using steel anode. Bench scale testing was done for several operating parameters like time, pH and current density to ascertain their effects on the treatment efficiency. Steel anode was found to be effective for the COD and colour removal with anode efficiency of 0.118 kg COD/ h x A x m^{-2} and energy consumption 20.61 kWh / kg of COD at pH 9. The decrease in pH from 9 to 3 found to increase the anode efficiency from 0.118 kgCOD / h x A x m^{-2} to 0.144 kWh / kg of COD while decrease the energy consumption from 20.61 kWh / kg of COD to 12.86 kWh / kg of COD. The pH of 5 was considered an ideal from the present treatment process as it avoids the addition of chemicals for neutralization of treated effluents and also economical with respect to energy consumption.

2. Landfill leachate treatment

Thaveemaitree et al. (2003) in Application of electrochemical process for landfill leachate treatment with emphasis on heavy metal and organic removal conducted laboratory electrochemical experiments using both synthetic wastewater and landfill leachate samples. From the synthetic wastewater experiments, the lead removal efficiencies were found to be more than 99% which was observed to be dependent on: the electrical current, ratio between reacting surface area and volume of reactor and operation time, and follows a first-order reaction. Similar results on lead removal were obtained when the landfill leachate samples were treated in the electrochemical reactor where the percent removal of soluble BOD and soluble COD concentrations from the landfill leachate during the electrochemical treatment were 30-60%, while the color removal was 70%.

Wang et al. (2001) in Electrochemical Oxidation of Leachate Pretreated in an Upflow Anaerobic Sludge Blanket Reactor studied to develop a two-stage process for the treatment of Hong Kong leachate. The leachate, containing 4750 mg l^{-1} of chemical oxygen demand (COD) and 1310 mg l^{-1} of ammoniacal nitrogen (NH_3-N), was first treated in a UASB (upflow anaerobic sludge blanket) reactor at 37°C. The process removed on average 66.1% of COD with 6.1 days of hydraulic retention time (HRT), corresponding to an organic loading rate of 0.78 g-COD $(l\cdot day)^{-1}$. The UASB effluent, which had an average pH of 8.9, COD of 1610 mg l^{-1} and NH_3-N of 1480 mg l^{-1}, was then further treated by electrochemical oxidation in a batch reactor with recirculation. With the addition of 2000 mg l^{-1} of chloride (in the form of sodium chloride) and at a current density of 32.3 mA cm^{-2}, 87% of COD and 100% of NH_3-N were removed from the UASB effluent in six hours. The energy consumption was <55 kWh kg-COD^{-1}. The final effluent contained no residual NH_3-N and only 209 mg l^{-1} of COD.

Peterson et al. (2007) in Electrodegradation of landfill leachate in a flow electrochemical reactor studied the treatment of landfill leachate by electrochemical treatment process . Leachate from a municipal landfill site was treated by electrochemical oxidation in a pilot scale flow reactor, using oxide-coated titanium anode. The experiments were conducted under a constant flow rate of 2000 l h^{-1} and the effect of current density on chemical oxygen demand, total organic carbon, color and ammonium removal was investigated. At a current density of 116.0 mA cm^{-2} and 180 min of processing, the removal rates achieved were 73% for COD, 57% for TOC, 86% for color and 49% for ammonium. Thus the process proved effective in degrading leachate, despite this effluent’s usual refractoriness to treatment.

Feki et al. (2009) in Electrochemical oxidation post-treatment of landfill leachates treated with membrane bioreactor investigated the integration of membrane bioreactor (MBR) with electrochemical process as treatment of stabilized landfill leachates, collected from Djebel Chekir (Tunisia). Results showed that at optimum conditions for the membrane and with organic loading rates of 1.9 and 2.7g COD L(-1)d(-1), MBR treated effluent is still coloured and contains high COD and ammonia concentrations. In order to reduce these high pollutant concentrations, electrochemical oxidation process using Ti/Pt, graphite and lead oxide electrodes, was tested as effluent post-treatment where Ti/Pt electrodes showed the best performance. COD, ammonia and colours removals were affected by the current density (J) and treatment time (t). At optimal operational conditions (t=1h, J=4Adm(-2)), the final COD and total kjeldahl nitrogen concentrations (TKN) were 1000 and 86mgL(-1), respectively. The final treated wastewater COD, TKN, colours, pH meet the discharge standards in the sewer. Thus the combination of MBR treatment process with electrochemical oxidation can be a technical suitable solution for stabilized landfill leachates treatment with an efficient reduction of different parameters, essentially COD (85%), TKN (94%), and colour(436) (99%).

3. Phenolic waste waters

Ma et al. (2008) in Electrochemical catalytic treatment of phenol wastewater found that the slurry bed catalytic treatment of contaminated water appears to be a promising alternative for the oxidation of aqueous organic pollutants. In this paper, the electrochemical oxidation of phenol in synthetic wastewater catalyzed by ferric sulfate and potassium permanganate adsorbed onto active bentonite in slurry bed electrolytic reactor with graphite electrode has been investigated. In order to determine the optimum operating condition, the orthogonal experiments were devised and the results revealed that the system of ferric sulfate, potassium permanganate and active bentonite showed a high catalytic efficiency on the process of electrochemical oxidation phenol in initial pH 5. When the initial concentration of phenol was 0.52g/L (the initial COD 1214mg/L), up to 99% chemical oxygen demand (COD) removal was obtained in 40min. According to the experimental results, a possible mechanism of catalytic degradation of phenol was proposed.

Korbahti et al. (2003) in Continuous electrochemical treatment of phenolic wastewater in a tubular reactor investigated the innovate process of electrochemical treatment of phenolic wastewater in a continuous tubular reactor, constructed from a stainless steel tube with a cylindrical carbon anode at the centre. The effects of residence time on phenol removal was studied at 25 degrees C, 120 g/ l electrolyte concentration for 450 and 3100 mg / l phenol feed concentrations with 61.4 and 54.7 mA cm(-2) current densities, respectively. The change in phenol concentration and pH of the reaction medium was monitored in every run and GC/MS analyses were performed to determine the fate of intermediate products formed during the electrochemical reaction in a specified batch run. For 10 and 20 min of residence time phenol removal was 56% and 78%, respectively, with 450 mg/ l phenol feed concentration and above 40 min of residence time all phenol was consumed within the column. For 1, 1.5, 2 and 3h of residence time, phenol removal achieved was 42%, 71%, 81% and 98%, respectively; at 3100 mg/l phenol feed concentration. It is noteworthy that more than 95% of the initial phenol was converted into a non-passivating polymer without hazardous end products in a comparatively fast and energy-efficient process, proving electrochemical treatment a safe treatment.

Lou et al. (2008) in Study on Treatment of the Simulation Wasterwater of Phenol with Electrochemical Process found that electrochemical treatment of organic pollutants in wastewater has the advantages of high efficiency, simple operation, compatibility with the environment etc. The experiment takes the carbon stick of discard and old No. 1 dry batteries as electrodes, uses the beaker as electrolytic cell and at room temperature by changing the concentration of supporting electrolyte by using Na_2SO_4, load voltage, pH value', the initial phenol concentration different experimental results are obtained. Electrochemically treated simulation wasterwater of phenol was analysed using the High Performance Liquid Chromatography (HPLC) and the results show that: the concentration of supporting electrolyte Na_2SO_4 at 20.0 g/L, the load voltage at 5.5 V, pH value at 8.0 etc is the best process condition for treatment of the simulation wasterwater of phenol.

4. Yellow waste waters

Lazarova et al. (2008) in Treatment of yellow water by membrane separations and advanced oxidation methods compared the performance memberane separation and advanced oxidation on purification of yellow wastewaters separated and collected in solarCity, Linz, Austria. Three membrane methods (micro-, ultra-, and nano-filtration), and two advanced oxidations (gamma radiation and electrochemical oxidation) were applied. Best results concerning the removal of pharmaceuticals and hormones from urine by membrane separation were achieved using the membrane NF-200 (FilmTec). Pharmaceuticals and hormones were removed completely from urine. NF-separation also has some disadvantages: losses of urea, and lowering the conductivity in the product (permeate). The results showed that electrochemical oxidation is more suitable than gamma radiation. Gamma-radiation with intensities higher than 10 kGy has to be applied for efficiently destroying of ibuprofen, and especially diclofenac. A high quantity of intermediate "problem" substances with oestrone structure was formed during the gamma oxidation of hormone containing urine samples. However the electrochemical oxidation can be successfully applied for elimination of pharmaceuticals such as diclofenac, and hormones(oestrone, beta-oestradiol) from yellow wastewater without loss of urea.

5. Slaughter house waste water

Asselin et al. (2008) in Effectiveness of electrocoagulation process in removing organic compounds from slaughterhouse wastewater using monopolar and bipolar electrolytic cells used electrochemical techniques at the laboratory pilot scale for organic compounds removal from poultry slaughterhouse (PS) effluent in order to produce an effluent suitable for stream discharge. Slaughterhouse wastewaters contain varied and high amounts of organic matter (e.g., proteins, blood, fat). Results showed that the best performance was obtained using mild steel BP electrode system operated at a current intensity of 0.3A, through 60 or 90 min of treatment. Under these conditions, removals of 86+/-1% and 99+/-1% were measured for BOD and oil and grease, respectively, whereas soluble COD and total COD were removed by 50+/-4% and 82+/-2%, respectively. EC is also efficient for decolorization (red-color) and clarification of the PS effluent. Removals of 89+/-4% and 90+/-4% have been measured for total suspended solids and turbidity, respectively. Electrochemical coagulation operated under the optimal conditions involves a total cost of 0.71 USD $ per cubic meter of treated PS effluent.

Tezcan et al. (2005) in Hybrid processes for the treatment of cattle-slaughterhouse wastewater using aluminium and iron electrodes found that Electrocoagulation (EC) of cattle-slaughterhouse wastewater, which is characterized by (i) high turbidity (up to 340 Nephelometric turbidity units), (ii) increased chemical oxygen demand (COD) concentration (4200 mg L^{-1}), and (iii) a dark color, served the purpose of lowering the turbidity and COD concentration to levels below the permitted direct-discharge limits. Iron and aluminium were used as electrode materials. Experiments were conducted to evaluate the effects of current density, initial pH, and supporting electrolyte (Na_2SO_4) dosage on the performance of the system. COD removal increased with increase in current density. The original pH of wastewater (7.8) was found to be preferable for both the electrode materials. Higher concentrations of Na_2SO_4 caused an increase in COD removal efficiency, and energy consumption was considerably reduced with increasing conductivity. Hybrid processes were applied in this work to achieve higher COD removal efficiencies. In the case of aluminum electrode, polyaluminum chloride (PAC) was used as the coagulant aid for the aforesaid purpose. COD removal of 94.4% was obtained by adding 0.75 g L^{-1} PAC. This removal efficiency corresponded to effluent COD concentration of 237 mg L^{-1}, which meets the legal requirement for discharge from slaughterhouses in Turkey. In the case of iron electrode, EC was conducted concurrent with the Fenton process. As a result, 81.1% COD removal was achieved by adding 9% H_2O_2. Consequently, hybrid processes are inferred to be superior to EC alone for the removal of both COD and turbidity from cattle-slaughterhouse wastewater.

Kobya et al. (2006) in Treatment of poultry slaughterhouse wastewaters by electrocoagulation investigated batchwise treatment of poultry slaughterhouse wastewater (PSW) by electrocoagulation (EC). Effects of the process variables such as medium pH, electrode material, current density, and operating time are investigated on chemical oxygen demand (COD) and oil–grease removal efficiencies, electrical energy consumption, and sacrificial electrode consumption. The highest COD removal efficiency is reached with aluminium as 93%, and maximum oil–grease removal is obtained with iron electrodes as 98%. Combined use of both electrode materials in the EC unit may yield high process performances with respect to both COD and oil–grease removals. Further work needs to be carried out at pilot scale to assess the technical end economic feasibility of the process.

6. Treated effluent (post treatment)

Buzzini et al. (2006) in Preliminary evaluation of the electrochemical and chemical coagulation processes in the post-treatment of effluent from an upflow anaerobic sludge blanket (UASB) reactor comparatively studied chemical and electrochemical coagulation processes, both followed by flocculation and sedimentation of an effluent from an upflow anaerobic sludge blanket (UASB) reactor for treating simulated wastewater from an unbleached Kraft pulp mill. The electrochemical treatment removed up to 67% (with aluminum electrodes) and 82% (with stainless-steel electrodes) of the remaining chemical oxygen demand (COD) and 84% (stainless steel) and 98% (aluminum) of the color in the wastewater. These efficiencies were achieved with an energy consumption ranging from 14 to 20 Wh/l. The coagulation-flocculation treatment with ferric chloride and aluminum sulfate removed up to 87% and 90% of COD and 94% and 98% of color, respectively. The addition of a high molecular weight cationic polymer enhanced both COD and color removal efficiencies. Hence both the post-treatment processes proved to be technically feasible.

Lei et al. (2007) in Electrochemical treatment of anaerobic digestion effluent using a Ti/Pt-IrO2 electrode evaluated the electrochemical treatment of the anaerobic digestion effluents using a Ti/Pt-IrO(2) electrode and found it feasible. The effects of electric current, NaCl dosage, and initial pH on ammonia, nitrate, total organic carbon (TOC), inorganic carbon

(IC), final pH, and turbidity variations were studied in a series of batch experiments. It was found that the electric current and NaCl dosage had a considerably larger effect on the oxidization of ammonia; this was less for the effect of the initial pH. In addition, electroflotation was the main mechanism for turbidity, TOC, and IC removals. Further, the IC removal was mainly affected by the pH of wastewater.

6. Dairy waste water

Guven et al. (2008) in Electrochemical treatment of deproteinated whey wastewater and optimization of treatment conditions with response surface methodology studied electrochemical treatment of deproteinated whey wastewater produced during cheese manufacture. Through the preliminary batch runs, appropriate electrode material was determined as iron due to high removal efficiency of chemical oxygen demand (COD), and turbidity. The electrochemical treatment conditions were optimized through response surface methodology (RSM), where applied voltage was kept in the range, electrolyte concentration was minimized, waste concentration and COD removal percent were maximized at 25 degrees C. Optimum conditions at 25 degrees C were estimated through RSM as 11.29 V applied voltage, 100% waste concentration (containing 40 g/L lactose) and 19.87 g/L electrolyte concentration to achieve 29.27% COD removal. However, highest COD removal through the set of runs was found as 53.32% within 8h proving the applicability of EC treatment for whey waste water.

Şengil et al. (2006) in Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes investigated the removal of COD and oil–grease from dairy wastewater was experimentally using direct current (DC) electrocoagulation (EC). In the EC of dairy wastewater, the effects of initial pH, electrolysis time, initial concentration of COD, conductivity and current density were examined. In batch experimental sets with iron as the sacrificial electrode material, optimum operating range for each variable was found. The overall COD and oil–grease removal efficiencies reached 98 and 99%, respectively. The optimum current density, pH and electrolysis time for 18,300 mg COD/L and 4570 mg oil–grease/L were 0.6 mA/cm^2, 7 and 1 min respectively. Mean energy consumption was 0.003 kWh/kg of COD.

Ihara et al. (2006) in Electrochemical oxidation of the effluent from anaerobic digestion of dairy manure studied the electrochemical oxidation of the digested effluent from anaerobic digestion of dairy manure. The digested effluent sample containing suspended solids was pretreated by filtration. The influence of direct anodic oxidation and indirect oxidation was evaluated through the use of dimensionally stable anode (DSA) and Ti/PbO$_2$ as anode. The decreasing rate of chemical oxygen demand (COD) was higher at lead dioxide coated titanium (Ti/PbO$_2$) electrode than at DSA, however the DSA was preferred anode for the decrease of ammonium nitrogen (NH$_4$-N) due to the control of ammonium nitrate (NO$_3$-N) accumulation. The results showed that the filtration of suspended solids as a pretreatment and addition of NaCl could improve the whole removing efficiency of NH$_4$-N in the digested effluent on electrochemical oxidation.

8. Pharmaceutical waste water

Abhijit et al. (2005) in Electrochemical oxidation of pharmaceutical effluent using cast iron electrode investigated electrochemical oxidation of low (BOD/COD) ratio pharmaceutical wastewater. The batch experimental results were assessed in terms of COD and BOD concentration while the recalcitrance was monitored in terms of change in the (BOD/COD) ratio during the process. The effects of operating parameters like pH, electrolysis duration and current density were studied on the treatment efficiency and their operating ranges were experimentally determined. The efficiency and energy consumption of anode were estimated. Cast iron electrode was found to be effective in removing 72% COD after 2hours of electrolysis. In particular, it was found that the (BOD/COD) ratio had improved from 0.18 to 0.3 after 120 min. of electrolysis indicating improvement of biodegradability of wastewater, proving that the pharmaceutical waste water can be effectively treated by EC treatment.

9. Paper and pulp industry waste water

Perng et al. (2007) in Treatment of a Specialty Paper Mill Wastewater Using a Pilot-scale Pulsed Electrocoagulation Unit used a pilot-scale pulsed electrocoagulation (EC) system capable of treating 0.5~1 m3/ h, with a hydraulic retention time (HRT) of 2.17~6.5 min, and consisting of a homogenizer tank, a pulsed EC reactor, an aerator, a flocculation tank, and a sedimentation tank to treat specialty paper mill wastewater from central Taiwan was used. The mill has a daily production of 5 t/ d, and discharges 1300 m3/ d of wastewater. The controlled parameters of the pulsed EC unit included the use of either iron or aluminum electrodes, current density, and HRT (flow rate). The wastewater quality variables examined before and after the treatment include electrical conductivity, suspended solids (SS), chemical oxygen demand (COD), and true color. The results indicated that electrical conductivity decreased with increasing current density and HRT; under all current densities, SS removal appeared to have no correlation with the flow rate, and a minimum of 85% SS removal was observed. Removal of COD was dependent on the electrode materials. Aluminum electrodes in contrast to iron achieved at least a 40% COD removal at lower current densities. With both electrodes, the higher the current density and the longer the HRT, the greater the true color removal rates became. Under the best operational conditions (a current density of 106.7 A m-2, and an HRT of 3.25 min) using aluminum electrodes achieved removals of 25.4, 97.14, 76.47 and 70.09% of electrical conductivity, SS, COD, and true color, respectively. Under any current density, however, SS removal showed no correlation with the effluent HRT, and always achieved a removal of ≥ 85%. The current dissolved air flotation unit costs NT$2.68 (US$0.0812) per ton of wastewater to operate, while the pulsed EC unit costs NT$2.42 (US$0.0733) per ton of wastewater. A proposed 5-stage mechanism of the EC system is also discussed.

Mahesh et al. (2006) in Electrochemical Degradation of Pulp and Paper Mill Wastewater. Part 1. COD and Color Removal investigated the electrochemical degradation of agri-based paper mill wastewater (black liquor) in a 2 dm^3 electrolytic batch reactor using iron plate electrodes. Of the four-, six-, and eight-plate configurations, a current density of 55.56 A/m^2 at neutral pH with a six-plate arrangement was found to be optimal, achieving a maximum chemical oxygen demand (COD) and color removal of 80% and 90% (175 platinum−cobalt units (PCU)), respectively. The chemical dissolution of iron was strongly influenced by pH_0. Electrochemical treatment at higher pH_0 ($pH_0 \geq 9$) increases the dissolution of iron electrodes by an order of magnitude. At the optimal current density, the iron electrode consumed is 31.27 $g/m^2 \cdot h$, achieving maximum COD removal. An increase in salinity reduces the treatment time significantly, and the sludge settling characteristics also improve. The addition of polyacrylamide (10 mg/dm^3) to the electrochemical reactor enhances the COD removal rate with a very short treatment time with excellent sludge settleability. Specific energy consumption (SEC) reduces from 6.64 to 5.73 kWh/kg of COD removed with the addition of NaCl (625 mg/dm^3). The posttreatment of electrochemically treated wastewater by chemical coagulation using alum (360 mg/dm^3) along with 20 mg/dm^3 polyacrylamide (PAA) further reduced COD values to <180 mg/dm^3 and a near 100% (<5 PCU) color removal. An overall COD removal of 91% and color removal of near 100% could be achieved by electrochemical treatment followed by coagulation/flocculation.

Ugurlu et al. (2008) in The removal of lignin and phenol from paper mill effluents by electrocoagulation investigated the treatment of paper mill effluents using electrocoagulation. Removal of lignin, phenol, chemical oxygen demand (COD) and biological oxygen demand (BOD) from paper mill effluents was investigated at various current intensities by using different electrodes (Al and Fe) and at various electrolysis times (1.0, 2.5, 5.0 and 7.5 min). It was observed that the experiments carried out at 12 V, an electrolysis time of 2 min and a current intensity of 77.13 mA were sufficient for the removal of these pollutants with each electrode. The removal capacities of the process using an Al electrode were 80% of lignin, 98% of phenol, 70% of BOD, and 75% of COD after 7.5 min. Using an Fe electrode the removal capacities were 92%, 93%, 80% and 55%, respectively. In addition, it was found that removal of lignin, phenol, BOD and COD increased with increasing current intensity. In the experiments carried out at different current intensities, higher removal can be explained through a decrease in intra-resistance of solution and consequently an increase at the transfer speed of organic species to electrodes. It was also found that Al electrode performs higher efficiency than Fe electrode except for COD removal. However, the time required for removal of BOD was more than that of COD. The results suggest that electrocoagulation could be considered as an effective alternative to paper mill effluents treatment.

Zaied et al. (2008) in Electrocoagulation treatment of black liquor from paper industry found that the procedure of electrocoagulation is an effective, fast and economic technique for treatment of black liquor resulting from paper industry. The effect of electrolysis time, current density, type of electrode material and initial pH were studied in an attempt to achieve a higher removal capacity. Under the optimal experimental conditions (initial pH 7, $t = 50$ min and $J = 14$ mA cm^{-2}), the treatment of black liquor by electrocoagulation has led to a removal capacity of 98% of COD, 92% of polyphenols and 99% of color intensity with a good repeatability (R.S.D. < 3%) making it possible to highlight the industrial interest of this electrochemical process.

Wang et al. (2007) in Electrochemical treatment of paper mill wastewater using three-dimensional electrodes with Ti/Co/SnO_2-Sb_2O_5 anode studied the properties of the interlayer and outer layer of Ti/Co/SnO_2-Sb_2O_5 electrode, along with the examination of electrochemical behavior. As a result of unsatisfactory treatment using Ti/Co/SnO_2-Sb_2O_5 electrode, electrochemical disposal of paper mill wastewater employing three-dimensional electrodes, combining active carbon granules serving as packed bed particle electrodes, with

$Ti/Co/SnO_2$-Sb_2O_5 anode, was performed. The outcome demonstrates that efficient degradation was achieved. The residual dimensionless chemical oxygen demand (COD) concentration reached 0.137, and color removal 75% applying 167 mA cm^{-2} current density at pH 11 and 15 g l^{-1} NaCl. The instant current efficiency, energy cost, electrochemical oxidation index (EOI) and kinetic constant of the reaction were calculated. At the same time, the influence of pH and current density on COD abatement and decolorization was also investigated, respectively.

Patel et al. (2008) in Electrochemical treatment of pentachlorophenol in water and pulp bleaching effluent studied the removal of Adsorbable organic halides (AOX) compounds produced during bleaching of pulp which are recalcitrant and known to have eco-toxic effect. The removal of pentachlorophenol (PCP) as a model AOX compound in water as well as in pulp bleaching effluent of a bamboo based mill by electrochemical treatment in batch mode was studied. It was found that 10 mg L^{-1} of PCP in water was removed almost completely in <10 min at a current density of 6 mA cm^{-2} in the presence of 1000 mg L^{-1} NaCl serving as an electrolyte and source of chloride ions. The initial rate of PCP removal was found to decrease at alkaline pH (9.3) as compared to that at acidic pH (5.5). PCP removal in neutralized raw pulp bleach effluent (containing ∼1830 mg L^{-1} of chloride) was very slow and incomplete even after 2 h of electrochemical treatment at a current density of 15 mA cm^{-2}. Various pretreatments of raw bleach effluent such as, alkaline sulfide using sodium sulfide, alkaline reduction using ferrous sulfate and coagulation using potash alum were evaluated. Electrochemical treatment of potash alum pretreated effluent (spiked with PCP) could achieve >90% removal of initial colour, COD and PCP in <1 h. Thus the treatment scheme presented may be a promising technology for removal of AOX, COD and colour from pulp bleaching effluent.

Mansour et al. (2007) did work on treatment of wastewater of paper industry containing high amount of suspended solids, COD and BOD. The experiment was done in both batch and continuous modes by using electrodes and a flotation unit. The electrodes were made up of titanium coated with ruthenium oxide as anode and stainless steel as cathode. The voltage was varied between 7 to 9 volts and the current density was varied and not fixed. The batch mode aims to optimize coagulant concentration, pH and current density at fixed electrolysis time (20 minutes). Continuous mode aims to optimize the residence time. The results demonstrated that the removal efficiency of suspended solids in both the cases was more than 95%.

10. Distillary effluent

Piya-areetham et al. (2006) in Application of electrooxidation process for treating concentrated wastewater from distillery industry with a voluminous electrode conducted experiments in a laboratory scale to reduce color and chemical oxygen demand (COD) in distillery wastewater by using electrooxidation processes. A cylindrical electrochemical reactor constructed in an axial configuration with 0.2m diameter and 0.35 m height was employed in this study. Two materials including graphite particles and titanium sponge were used as the voluminous anodes. A cathode made from Ti/RuO(2) was placed 0.04-0.05 m above the upper level of anode particles. Effect of parameters including initial pH of wastewater (1-5), time of dilution, current intensity (1-10A), type of additive (peroxide and NaCl), and additive concentration were investigated. The results indicated that the anode made from titanium sponge showed a higher potential to treat wastewater than another one. The treatment in acidic condition (pH=1) provided the maximum oxidation of organic pollutants in wastewater. The presence of additives can promote the reduction of COD and color in wastewater approximately 89.62% and 92.24%, respectively. The maximum current efficiency was reached at the first 30 min and decreased slightly as electrolysis time proceeded due to the formation of passivation on the electrode surface. The energy consumption was obtained in the range of 2.82-4.83 kWh/kgCOD or 24.08-28.07 kWh/m(3) wastewater depending upon the concentration of additive. The kinetics of COD reduction was the pseudo first-order reaction with a fast rate constant of 6.78 min^{-1}.

11. Latyx treatment waste water

Vijayaraghavan et al. (2008) in Electrolytic treatment of latex wastewater treatment was developed based on in-situ hypochlorous acid generation. The hypochlorous acid was generated in an undivided electrolytic cell consisting of two sets of graphite as anode and stainless sheets as cathode. The generated hypochlorous acid served as an oxidizing agent to destroy the organic present in the latex wastewater. For an influent COD concentration of 3,820 mg/L at an initial pH 4.5; current density of 74.5 mA/cm^2; sodium chloride content 3% and electrolysis period of 90 min, resulted in the following residual concentration pH 7.3; COD 78 mg/L; BOD_5 55 mg/L; TOC 45 mg/L; residual total chlorine 136 mg/L; turbidity 17

NTU and temperature 54°C, respectively. In the case of 2% sodium chloride content for the above, said operating condition resulted in a residual concentration of pH 7; COD 162 mg/L; BOD_5 105 mg/L; TOC 90 mg/L; residual total chlorine 122 mg/L; turbidity 26 NTU and temperature 60°C respectively. The energy requirements were found to be 35 and 50 Wh/L while treating 24 L of latex wastewater at 3 and 2% sodium chloride concentration at a current density 74.5 mA/cm^2. The observed energy difference was due to the improved conductivity at high sodium chloride content.

12. Food processing waste water

Roa-Morales et al. (2007) in Aluminum electrocoagulation with peroxide applied to wastewater from pasta and cookie processing studied the removal of organic pollutants from pasta and cookie processing industrial wastewater by aluminum electrocoagulation and combined electrocoagulation/H_2O_2 processes using a pilot batch reactor. Under optimal conditions of pH 4 and 18.2 mA/m^2 current density, the electrochemical method yields very effective removal of organic pollution. Treatment reduced chemical oxygen demand (COD) by 90%, biochemical oxygen demand (BOD_5) by 96%, total solids by 95% and fecal coliforms by 99.9%. The effect of reducing the pH of the aqueous solution with sulfuric acid on the chemical species formed and its effect on the sludge phase formation was determined. The wastewater quality was monitored using UV–vis spectrometry and cyclic voltammetry in order to characterize raw and treated wastewater.

13. Waste water with recalcitrant organic compounds

Rajkumar et al. (2004) in Combined electrochemical degradation and activated carbon adsorption treatments for wastewater containing mixed phenolic compounds studied the electrochemical degradation of mixed phenolic compounds present in coal conversion wastewater was investigated in the presence of chloride as supporting electrolyte. Initially, the degradation experiments were conducted separately with 300 mg/L of individual phenolic compound in the presence of 2500 mg/L chloride using Ti/TiO2–RuO2– IrO2 anode at 5.4 A/dm2 current density. Comparison of the experimental results of the chemical oxygen demand (COD) removal versus charge indicated that the order of decreasing COD removal for various phenolic compounds as catechol > resorcinol > *m*-cresol > *o*-cresol > phenol > *p*-cresol. Degradation of the mixture of phenolic compounds and high pressure liquid chromatography (HPLC) determinations at various stages of electrolysis showed that phenolic compounds were initially converted into benzoquinone and then to lower molecular weight aliphatic compounds. The COD and the total organic carbon (TOC) removal were 83 and 58.9% after passing 32 Ah/L with energy consumption of 191.6 kWh/kg of COD removal. Experiments were also conducted to remove adsorbable organic halogens (AOX) content in the treated solution using granular activated carbon. The optimum conditions for the removal of AOX was at pH 3.0, 5 mL/min flow rate and 31.2 cm bed height. Based on the investigation, a general scheme of treatment of mixed phenolic compounds by combined electrochemical and activated carbon adsorption treatment is proposed.

Yoon et al. (2007) in Electrochemical Degradation of Benzoquinone in a Flow through Cell with Carbon Fibers studied the anodic degradation of benzoquinone(BQ), a model compound for wastewater treatment was carried out using a home-made flow-through electrochemical cell with carbon fibers. The experimental variables affecting the degradation of BQ, such as the applying current, pH, reaction time, and flow rate of the BQ solution were examined to optimise the process and degradation products of the oxidation reaction were identified by High Performance Liquid Chromatography and Inductively Coupled Plasma Atomic Emission Spectrometer. While optimum pH was 6.56 optimum time was 12 hours respectively.Low molecular weight aliphatic acids, and CO2 were the major products in this experiment. The removal efficiency of BQ from the solution increased with the applying current and time. 99.23% of BQ was degraded to aliphatic acids and CO2 when the applying current is 175 mA in 12 hr electrolysis.

Samet et al. (2006) in Electrochemical degradation of 4-chloroguaiacol for wastewater treatment using PbO_2 anodes studied the electrochemical oxidation of 4-chloroguaiacol (4-CG) at Nb/PbO_2 anodes under different experimental conditions such as initial concentration of substrate, electrolysis time, temperature and pH. We measured the concentrations of 4-chlorocatechol (4-CC), 2-methoxyhydroquinone (2-MHQ), maleic acid (MA) and carbon dioxide as the main products. Black solid particles consisting mainly of polymers were formed during electrolysis. A mechanism of electrochemical oxidation of 4-CG was investigated. The oxidation of 4-CG can generally be described by simple pseudo first-order kinetics. The degradation of 4-CG was favoured at high temperature and lower initial concentration of 4-CG and low solution pH. However, the increase of temperature has not a significant effect on the mineralization of carboxylic acids. Moreover, these products required long electrolysis.

14. Municipal wastewater

Zheng et al. (2006) in PAH removal from spiked municipal wastewater sewage sludge using biological, chemical and electrochemical treatments found that the PAH molecules are strongly adsorbed on the particulate matters of soils, sludges or sediments because of their strong hydrophobicity which makes them less bioavailability, thus limiting their bioremediation. Different sludge treatment processes were tested to evaluate their performances for PAH removal from sludge doped with 11 PAHs (5.5 mg each PAH kg^{-1} of dry matter (DM)): two biological processes (mesophilic aerobic digestion (MAD) and simultaneous sewage sludge digestion and metal leaching (METIX-BS)) were tested to evaluate PAH biodegradation in sewage sludge. In parallel, two chemical processes (quite similar Fenton processes: chemical metal leaching (METIX-AC) and chemical stabilization (STABIOX)) and one electrochemical process (electrochemical stabilization (ELECSTAB)) were tested to measure PAH removal by these oxidative processes. Moreover, PAH solubilisation from sludge by addition of a nonionic surfactant Tween 80 (Tw80) was also tested. The best yields of PAH removal were obtained by MAD and METIX-BS with more than 95% 3-ring PAH removal after a 21-day treatment period. Tw80 addition during MAD treatment increased 4-ring PAHs removal rate. In addition, more than 45% of 3-ring PAHs were removed from sludge by METIX-AC and during ELECSTAB process were quiet good with approximately 62% of 3-ring PAHs removal. However, little weaker removal of 3-ring PAHs (<35%) by STABIOX. None of the tested processes were efficient for the elimination of high molecular weight (⩾5-ring) PAHs from sludge.

15. Algae rich waste water

Azarian et al. (2007) in Algae Removal by Electro-coagulation Process, Application for Treatment of the Effluent from an Industrial Wastewater Treatment Plant found that although stabilization ponds and lagoons are suitable treatment processes due to simplicity of operation and low per capital costs, the effluents of these systems have too high of a total suspended solids concentration to be discharged into receiving waters. This problem is mainly caused by algae. For the continuous flow electro-coagulation reactor used in these experiments three aluminum anodes were utilized. This type of metal was selected because it could introduce the flocculation agent into the effluent, thereby algae could be removed by both mechanisms of electro-flotation and electro-flocculation. The results of treatment were remarkably good and the efficiencies of total suspended solids (TSS) and chlorophyll a removal reached to as high as 99.5% and about 100% by applying a power input of about 550 W. In fact, this level of power input was needed for complete removal of algae in a low retention time of 15 minutes. Meanwhile, by applying less power input of about 100Wdm-3, the required time for a relatively same treatment was reached to 30 minutes.

3.2 Oily waste waters

3.2.1 General oil rich waste water

Yang et al. (2009) in Electrochemical coagulation for oily water demulsification studied the electrochemical treatment of oil rich waste water. Motor oil and industrial surfactants were used to prepare synthetic oily water. When stabilized with surfactant, the turbidity shows a positive correlation with the oil content in the emulsion with a correlation coefficient of 1.78 FAU/(mg/L). The oil–water emulsion was tested with gravity separation, centrifugation, flotation, and electrochemical coagulation for the effectiveness of each process on demulsification. Electrochemical coagulation was then selected for further study. A dc voltage was applied to the electrodes, dissolving ferrous ions (Fe(II)) at the anode and forming hydrogen (H_2) gas and hydroxyl (OH^-) ions at the surface of the cathode. A few 100 mg/L of sodium chloride (NaCl) were added to the solution to provide ionic conductivity and to prevent passivation of the iron electrode. The ferrous ions were oxidized into ferric ions (Fe(III)), destabilizing the emulsion. The coalesced oil droplets were adsorbed into the highly dispersed and reactive ferric hydroxide ($Fe(OH)_3$) coagulant. The oil-rich sludge that was generated in the operation was then floated to the surface forming a blanket that was removed by skimming. This complicated mechanism was completed in 4 min. When the reactor was operated for this amount of time, a measure of 165.8 mg/L of ferric ions was generated. The treatment reduced the turbidity of the emulsion from 1800 to 60 FAU. Beyond the 4-min treatment period, the addition of more iron to the system resulted in turbidity change at a much slower rate. When the operation occurred continuously with a current of 2 A and a throughput of 320 mL/min, the turbidity of the electrically treated effluent was less than 14 FAU, the detection limit of the Hach DR/4000 Spectrophotometer.

Gonclaves et al. (2008) in Electrooxidation as the anaerobic pre-treatment of fats: Oleate conversion using RuO_2 and IrO_2 based anodes studied electrochemical treatment of oleate using RuO_2 and IrO_2 type dimensionally stable anodes in alkaline medium was performed to develop a feasible anaerobic pre-treatment of fatty effluents. The results showed that the pretreated solutions over RuO_2 were faster degraded by anaerobic consortium than the raw oleate solutions or the electrolysed solutions using IrO_2. In batch experiments carried out with pre-treated solutions over RuO_2 (100–500 mg/L), no lag phases were observed before the methane production onset. On the other hand, raw oleate and pre-treated oleate over IrO_2 had originated lag phases of 0–140 and 0–210 h, respectively. This study demonstrated that it is advantageous to apply the electrochemical treatment carried out on the RuO_2 type DSA in order to achieve a faster biodegradation of lipid-containing effluent and consequently to obtain a faster methane production.

Ma et al. (2006) in Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection found that oil field produced water, by separated from crude oil can be treated by an electrochemical process in laboratory pilot-scale plant, using double anodes with active metal (M) and graphite (C) and iron as cathode and a noble metal content catalyst with big surface. Due to the strong oxidizing potential of the chemicals produced (Cl(2), O(2), OCl(-), HO and so on), when the wastewater pass through the laboratory pilot-scale plant the organic pollutants including bacteria were oxidized and coagulated by produced M(n+) ion. It can be concluded that the catalytic electrochemical treatment of oil field produced wastewater is effective. Both chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were reduced by over 90% in 6 min, suspense solids (SS) by 99%, Ca(2+) content by 22%, corrosion rate by 98% and bacteria (sulphate reducing bacteria (SRB), saprophytic bacteria (TGB) and iron bacteria) by 99% in 3 min under 15V/120A. These results indicate that this catalytic electrochemical method could be used for effective oil field wastewater treatment for injection purpose.

Xinhua et al. (2004) in Treatment of refectory oily wastewater by electro-coagulation process studied the use of electro-coagulation to treat refectory wastewater with high oil and grease contents. Different operational conditions were examined, including pH, current density, reaction time, conductivity, electrode distance and inlet concentration. The optimum current density was 10–14 A m^{-2} within 30 min depending on the wastewater properties tested. Conductivity had little effect on the treatment efficiency. Although the addition of extra salts (e.g., sodium chloride) to the wastewater did not help increase the pollutant removal efficiency, it could save the power consumption significantly. The COD_{Cr} and oil removal efficiency descended with increasing electrode distance. The optimal electrode distance was determined to be 10 mm for this equipment in consideration of the treatment cost and efficiency together. The pH effect on the performance of the electro-coagulation process was not very significant in the range of 3–10. The removal efficiency of oil and COD_{Cr} under normal condition exceeded 95% and 75%, respectively.

Tezcan et al. (2006) in Electrocoagulation of vegetable oil refinery wastewater using aluminium electrodes- found that electrocoagulation with aluminum electrodes can be used to treat the vegetable oil refinery wastewater (VORW) in a batch reactor. The effects of operating parameters such as pH, current density, PAC (poly aluminum chloride) dosage and Na_2SO_4 dosage on the removal of organics and COD removal efficiency have been investigated. It has been shown that the removal efficiency of COD increased with the increasing applied current density and increasing PAC and Na_2SO_4 dosage and the most effective removal capacity was achieved at the pH 7. The results indicate that electrocoagulation is very efficient and able to achieve 98.9% COD removal in 90 min at 35 mA cm^{-2} with a specific electrical energy consumption of 42 kWh (kg $COD_{removed})^{-1}$. The effluent was very clear and its quality exceeded the direct discharge standard.

Santos et al. (2005) in the application of electrochemical technology to the remediation of oily wastewater studied the successful application of electrochemical technology, employing a dimensionally stable anode, for the remediation of wastewater from the oil extraction industry has been demonstrated. Electrolysis of the oily wastewater lead to a time-dependent reduction in chemical oxygen demand (COD) in the sample that could be attributed to: (i) the direct oxidation of oil components at the electrode, by the metal oxide itself or by OH radicals available at the electrode surface, (ii) the indirect oxidation of oil components by intermediate oxidising agents formed in parallel reactions (ex. ClO(-)), and (iii) the aggregation of suspended oil droplets by electroflotation. The largest reduction (57%) in COD was obtained following electrolysis of an oily sample for 70 h at 50 degrees C with a current density of 100 mA cm(-2). The stability of DSA electrodes for use in oily wastewater remediation has been assessed.

3.2.2 Olive mill waste water

Chen et al. (2000) in Separation of pollutants from restaurant wastewater by electrocoagulation investigated the characteristics of restaurant wastewater and found high oil and grease contents. Different electrode materials and operational conditions were examined. Aluminum was preferred to iron. Charge loading was found to be the only variable that affected the treatment efficiency significantly. The optimum charge loading and current density were 1.67–9.95 F/m^3 wastewater and 30–80 A/m^2 depending on the wastewater tested. The removal efficiency of oil and grease exceeded 94% for all wastewaters tested. The experimental results also show that the electrocoagulation can neutralize wastewater pH. Several mechanisms associated with pH variation are proposed.

Chatzisymeon et al. (2007) in Electrochemical oxidation of model compounds and olive mill wastewater over DSA electrodes: 1. The case of Ti/IrO_2 anode, conducted experiments at 1300 mg/L initial COD, 0–1.23 V vs SHE and 1.4–1.54 V vs SHE potential windows, 50 mA/cm^2 current density, 0–25 mM NaCl, 60–80 °C temperature and acidic conditions. The reactivity of model compounds decreases in the order phenol ≈ p-coumaric acid > cinnamic acid > caffeic acid. Partial and total oxidation reactions occur with the overall rate following zero-order kinetics with respect to COD and increasing with temperature. Oxidation of OMW at 43 Ah/L, 80 °C and in the presence of 5 mM NaCl leads to complete color and phenols removal, elimination of ecotoxicity but moderate (30%) COD reduction. Similar performance can be achieved at 6 Ah/L in the presence of 15 mM NaCl. In the absence of salt, the respective color and phenols removal (at 6 Ah/L) is less than 10%. Excessive salinity (25 mM), although does not change color, phenols and COD removal, has an adverse effect on ecotoxicity.

Khoufi et al. (2007) in Detoxification of olive mill wastewater by electrocoagulation and sedimentation processes, examined the effect of a physico-electrochemical method to detoxify olive mill wastewater prior an anaerobic biotreatment process. Olive mill wastewater (OMW) is characterised by its high suspended solids content (SS), high turbidity (NTU), chemical oxygen demand (COD) concentration up to 100 gl(-1) and toxic phenolic compounds concentration up to 10 gl(-1). The proposed pre-treatment process consisted in a preliminary electrocoagulation step in which most phenolic compounds were polymerised, followed by a sedimentation step. The BOD(5)/COD ratio of the electrocoagulated OMW increased from 0.33, initial value, to 0.58. Furthermore, the sedimentation step yielded the removal of 76.2%, 75% and 71% of phenolic compounds, turbidity and suspended solid, respectively, after 3 days of plain settling. The combination of electrocoagulation and sedimentation allowed a COD reduction and decoloration of about 43% and 90%, respectively. This pre-treatment decreases the inhibition of Vibrio fisheri luminescence by 66.4%. Continuous anaerobic biomethanization experiments conducted in parallel with raw OMW and electrocoagulated OMW before and after sedimentation at a loading rate of 6g COD l(-1)day(-1), proved that the final pre-treated OMW was bioconverted into methane at high yield while raw OMW was very toxic to anaerobic microorganisms.

Kotta et al. (2007) in The effect of solids on the electrochemical treatment of olive mill effluents studied the treatment of effluent using Ti-Pt anodes which had an average total chemical oxygen demand (COD) value of 234 g L^{-1}, soluble COD of 61 g L^{-1}, soluble phenolic content 3.4 g L^{-1}, total solids of 80 g L^{-1} and pH = 5.1. Experiments were conducted in a 10 L vessel with the effluent recirculating at 1 L s^{-1}. The applied current was varied between 5 and 20 A, the salinity between 1 and 4% NaCl, and experiments were performed with the effluent diluted with water to achieve the desired initial concentration. Emphasis was given to the effect of the presence of solids as well as of varying operating conditions on process performance as assessed in terms of COD, color and phenols removal. In general, degradation of phenols occurred relatively fast with conversion increasing with increasing applied current and decreasing initial organic loading and this was accompanied by low COD removal levels and moderate decolorization. The presence of solids had practically no effect on phenols removal, which, in most cases, was complete in less than about 180 min of reaction. However, oxidation in the presence of solids resulted in a substantial solid fraction being dissolved and this consequently increased sample color and the soluble COD content. The solid content typically found in olive mill effluents may partially impede its treatment by electrochemical oxidation, thus requiring more severe operating conditions and greater energy consumption.

Gotsi et al. (2005) in Electrochemical oxidation of olive oil mill wastewaters conducted batch experiments in a flow-through electrolytic cell with internal recycle at voltage of 5, 7 and 9 V, NaCl concentrations of 1%, 2% and 4%, recirculation rates of 0.4 and 0.62 L/s and initial chemical oxygen demand (COD) concentrations of 1475, 3060, 5180 and 6545 mg/L. A titanium–tantalum–platinum–iridium anode was used and it was found that conversion of total phenols and COD as well as the extent of decolorization generally increased with increasing voltage, salinity and recirculation rate and decreasing initial concentration. In most cases, nearly complete degradation of phenols and decolorization were achieved at short treatment times up to 60 min; this was accompanied by a relatively low COD removal that never exceeded 40% even after prolonged (up to 240 min) times. The acute toxicity to marine bacteria Vibrio fischeri decreased slightly during the early stages of the reaction and this was attributed to the removal of phenols. However, as the reaction proceeded toxicity increased due to the formation of organochlorinated by-products as confirmed by GC/MS analysis. The toxicity to Daphnia magna increased sharply at short treatment times and remained quite high even after prolonged oxidation.

Inan et al. (2004) in Olive oil mill wastewater treatment by means of electro-coagulation studied the removal of chemical oxygen demand (COD), color and suspended solid (SS) from olive oil mill wastewater (OMWW). Aluminum and iron were used in the reactor simultaneously as materials for electrodes. The reactor voltage was 12 V, current density (CD) was changing between 10 and 40 mA cm^{-2}, pH was taken equal to 4, 6, 7, and 9 units, and duration varied in the limits of 2–30 min. Under the 30-min retention time, 52% COD was removed by the aluminum anode and 42% was removed by the iron anode. CD efficiency versus the percent of COD removal was examined at the 10-min retention time for pH 6.2±0.2. It appeared that with the CD increase, the percent of COD removal was increasing as well. The color removal yield was examined as the result of using different retention times, current densities, and iron and aluminum as materials for anodes. CD values in the range of 10–40 mA cm^{-2} were tested at the 10-min retention time each one; color removal was 90–97% by this. In this study the EC process was examined with the aim of determining the highest rate of SS removal from the OMWW as well.

Bellakhal et al. (2006) in Olive Oil Mill Wastewater Treatment by the Electro-Fenton Process the use of a combination of the Fentons reagent with electrochemistry (the electro-Fenton process). The electro-Fenton process is shown to fully destroy (mineralize) olive oil mill wastes in water without previous extraction and without addition of chemical reagents. This wastewater contains many organic compounds like polyphenols, which are very difficult to treat by classical techniques. An advanced electrochemical oxidation process, the electro-Fenton process, has been used as a way of removing chemical oxygen demand and colour intensity from olive oil mill wastewater. Vanillic acid, which has been selected as a model compound, and olive oil mill wastewater have been completely mineralized by the electro-Fenton process with a carbon felt cathode, using Fe(2+) ions as the catalyst

Longhi et al. (2004) in Electrochemical treatment of olive oil mill waste water studied the possibility of oxidizing at a PbO2 anode the phenols and polyphenols, present in the olive oil mill wastewater, as a pretreatment for the submission of such wastewater to the traditional biological treatments. The results obtained operating at current densities ranging 500 to 2000 A/m2 show that it is possible to reduce the concentration of the phenolic components, which interfere with the biological treatments, down to low values without decreasing too much the total organic content of the wastewater.

Panizza et al. (2006) in Olive mill wastewater treatment by anodic oxidation with parallel plate electrodes studied the applicability of electrochemical oxidation of a real olive-mill wastewater by performing galvanostatic electrolysis using parallel plate electrodes. Olive mill wastewater is characterized by very high chemical oxygen demand (COD) values and contains high concentrations of polyphenols that inhibit the activity of micro-organisms during biological oxidations. A mixed titanium and ruthenium oxide ($Ti/TiRuO_2$) was used as anode and stainless steel as cathode. The effect of chloride concentration and applied current on the removal of COD, aromatic content and colour was investigated. The experimental results showed that an effective electrochemical oxidation was achieved in which the wastewater was decolourised and the COD and aromatic content completely eliminated. In particular, the mineralisation took place by indirect oxidation, mediated by active chlorine, and the COD removal rate was enhanced by the addition of 5 g L^{-1} of NaCl to the wastewater and by increasing the applied current

Canizares et al. (2007) in Advanced oxidation processes for the treatment of olive-oil mills wastewater studied the treatment of an actual industrial waste with three advanced oxidation processes (AOP): conductive-diamond electrooxidation (CDEO), ozonation and Fenton oxidation. The wastewater comes from olive-oil mills (OMW) and contains a COD of nearly 3000 mg dm^{-3}. CDEO allowed achieving the complete mineralization of the waste with high current efficiencies. Likewise, both ozonation and Fenton oxidation were able to treat the wastes, but they obtained very different results in terms of efficiency and mineralization. The accumulation of oxidation-refractory compounds as final products excludes the use of ozonation and Fenton oxidation as a sole treatment technology. This confirms that besides the hydroxyl-radical mediated oxidation, CDEO combines other important oxidation processes such as the direct electro-oxidation on the diamond surface and the oxidation mediated by other electrochemically formed compounds generated on this electrode.

Tezcan et al. (2007) in Complete treatment of olive mill wastewaters by electrooxidation examined the efficiency of treatment scheme through the dependence of chemical oxygen demand (COD), oil-grease, phenol and turbidity on electrolysis duration. The influence of current density (25, 45, 65, 75, 85, 105, 135 mA cm^{-2}), sodium chloride concentration (1, 2, 3, 5 M), recirculation rate of OMW (1.1, 4.6, 7.9 cm^3 s^{-1}) and temperature (7, 20, 40 °C) on the rate of pollutants abatement and the response of the system and specific energy consumption were evaluated. Based on the results obtained from laboratory experiments, the removal rates of organics increased with the increase of applied current density, sodium chloride concentration, recirculation rate and temperature. The results also indicated that specific energy consumption (SEC) ranged between 5.35 and 27.02 kWh (kg COD)$^{-1}$ decreased with increasing NaCl concentration, recirculation rate and temperature whereas it increased with increasing current density. The initial COD concentration of 41,000 mg L^{-1} was reduced to 167 mg L^{-1} (corresponding to 99.6% removal) which complies with legal requirements while almost complete conversion of phenol, 99.85% turbidity removal, 99.54% oil-grease removal were achieved with the running cost of 0.88€ (kg COD)$^{-1}$ after 7 h electrolysis at the conditions of 135 mA cm^{-2}, 2 M NaCl, 7.9 cm^{3} s^{-1}, 40 °C.

Khoufi et al. (2007) in Pilot-plant results of the electro-Fenton treatment of olive mill wastewaters followed by anaerobic digestion investigated an integrated technology for the treatment of the recalcitrant contaminants of olive mill wastewaters (OMW), allowing water recovery and reuse for agricultural purposes. The method involves an electrochemical pre-treatment step of the wastewater using the electro-Fenton reaction followed by an anaerobic bio-treatment. The electro-Fenton pre-treatment process removed 66% of the total polyphenolic compounds and subsequently decreased the OMW toxicity from 100 to 66.9% which resulted in improving the performance of the anaerobic digestion. A continuous lab-scale methanogenic reactor was operated at a loading rate of 10 g COD/L day without any apparent toxicity. Furthermore, in the combined process, a high overall reduction in COD, suspended solids, polyphenols and lipids content was achieved by the two successive stages. Moreover, this combined process which was experimented at a real scale (25 m3 digester), demonstrated its technical feasibility and opens promising perspectives for industrial application in the Mediterranean countries due to its easy conception and its high energy (methane) production.

Khoufi et al. (2007) in Pilot scale hybrid process for olive mill wastewater treatment and reuse developed a novel technique at pilot scale for the treatment of olive mill wastewater (OMW), which combines electro-Fenton, anaerobic digestion and ultrafiltration. Application of electro-Fenton procedure in semi-continuous mode permitted high removal efficiencies of chemical oxygen demand (COD) (50%) and monophenolic compounds (95%). This pre-treatment was found to enhance the anaerobic activity of an up-flow anaerobic filter (300 l) significantly. In the bioreactor, COD removal efficiency of 75% was reached at a hydraulic retention time of 4.5 d and an organic loading rate of 10 g COD l^{-1} d^{-1}. The use of ultrafiltration technology as a post-treatment completely detoxified the anaerobic effluent and removed its high molecular mass polyphenols. An economic calculation of this treatment process revealed that a surplus of energy of 73.5 kWh could be recovered after the treatment of 1 m^3.

Deligiorgis et al. (2007) in Electrochemical oxidation of table olive processing wastewater over boron-doped diamond electrodes: treatment optimization by factorial design accessed the effect of operating conditions, such as initial organic loading (from 1340 to 5370 mg/L chemical oxygen demand (COD)), reaction time (from 30 to 120 min), current intensity (from 5 to 14 A), initial pH (from 3 to 7) and the use of 500 mg/L H2O2 as an additional oxidant, on treatment efficiency for implementing a factorial experimental design. Of the five parameters tested, the first three had a considerable effect on COD and total phenols removal, while the other two were statistically insignificant. In most cases, high levels of phenols degradation and decolorization were achieved followed by moderate mineralization. The analysis was repeated at more intense conditions, i.e., initial COD up to 10,000 mg/L, reaction times up to 240 min and current up to 30 A; at this level, the effect of treatment time and applied current was far more important than the starting COD concentration. Treatment for 14 h at optimal conditions (30 A and an initial loading of about 10,000 mg/L) led to 73% COD removal with a zero-order kinetic constant of 8.5mg/(L min) and an energy consumption efficiency of 16.3 g COD/(m3 A).

3. Methodology

3.1 Wastewaters Studied

Two wastewaters namely, acrylic fibre applicator oil wastewater form textile processing industry and first extraction stage bleach plant effluent from integrated pulp and paper industry were studied.

The acrylic fibre applicator oil wastewater is generated when synthetic oil in aqueous medium is applied on acrylic fibre. Prior to drying, the applied excess oil is removed by hydrosqueezing the acrylic fibre as acrylic fibre applicator oil wastewater. This wastewater has about 0.3% of oil and separation of this oil or treatment of the wastewater by conventional treatment technologies have been found difficult. Please see table-3.1 for the characteristics of the acrylic fibre applicator oil wastewater used in the present study.

S.No	**Parameter**	**Untreated value**
1	pH	5.92
2	Conductivity	1131 µS/cm
3	Turbidity	432 NTU
4	Chloride	209.81 mg/l
5	Oil and grease	331.2 mg/l
6	COD	14304 mg/l
7	BOD	3940 mg/l

Table-3.1: Characteristics of the Acrylic Fibre Applicator Oil Wastewater

Kraft pulp after brown stock washing is subjected to the first stage of bleaching usually by chlorine or chlorine and chlorine dioxide. First extraction stage bleach effluent is generated from the alkali extraction and washing of this bleached pulp. This wastewater is coloured, has chlorinated organic compounds and has high COD. Please see table-3.2 for the characteristics of the first extraction stage bleach plant effluent used in the present study.

S.No	**Parameter**	**Untreated value**
1	pH	5.57
2	Conductivity	6620 µS/cm
3	Turbidity	75.8 NTU
4	TS(Total solids)	7.5 g/l

5	TSS(Total suspended solids)	1.03 g/l
6	TDS(Total dissolved solids)	6.47 g/l
7	COD	5040 mg/l
8	Chloride	2516.95 mg/l
9	Apparent colour	4290 PCU
10	True Colour	3840 PCU

Table-3.2: Characteristics of the first extraction stage bleach plant effluent

Then the pulp is subjected to extraction washing in alkali The wastewater thus generated has approximately 0.3% oil which is difficult to treat by conventional treatment technology. Bleach effluent retrieved was the First extraction stage effluent from the large and an integrated paper and pulp mill. Pulp after brown stock washing is subjected to bleaching by Cl_2/ Cl_2, ClO_2 and the bleached pulp is further subjected extraction in alkaline solution. The wastewater generated here has colour and chlorinated organic compounds as main culprits making conventional treatment techniques not useful for the treatment of bleach effluent.

3.2 Experimental setup

The experimental electrochemical treatment system, used for the batch treatment of the wastewater, included a reactor and a DC power supply system. Please see figure-1 for details.

Reactors (fabricated by using 6 mm acrylic sheet) of 5 cm length, 3.5 cm width and 32 cm height were used in the electrochemical treatment studies. Working volume of these reactors is 400 ml. Two electrodes (anode and cathode), each of 5 cm width, 20 cm length and 2 mm thickness, are housed inside the reactor as shown in Figure-3.1. Three different types of electrodes, namely, Al-Al, Fe-Fe and SS- SS, were alternatively used in the present study. With the help of grooves in the reactor wall, spacing between the electrodes was maintained at 10 mm. For mixing the reactor contents a 1.5 cm long stirring bead was used and the reactor was placed over a magnetic stirrer. The DC power supply system (Model L-3210 of Aplab, India) used was capable of supplying DC power in the range of 0-32 volts and 0-10 amperes. It can supply DC power at the desired constant voltage (in the range of 0 to 32 V) or constant amperage (in the range of 0 to 10 Amp.). The system has provisions for the regulated and metered (voltage and amperage) supply of DC power. The ripple and noise of the instrument was less than 0.04%.

After each run, the electrodes were washed with acetone (to remove the surface grease) and dipped for five minutes in a freshly prepared solution of 100 mL of 35% HCl and 200 mL of

2.8% aqueous solution of hexamethelenetetramine (Do and Chen, 1994) for the removal of impurities from the electrode surface.

3.3 Approach followed

Electrochemical treatment of acrylic fibre applicator oil wastewater was studied using stainless steel electrodes and focused on the optimization of the parameters, pH, chloride, voltage and treatment time. COD removal was used as a measure for the treatment. Treatment of the first extraction stage bleach plant effluent was studied using three different types of electrodes, namely, Al-Al, Fe-Fe, and SS-SS. The parameters optimized in the case of first extraction stage bleach plant effluent included pH, voltage and treatment time. Colour removal was used as a measure for the treatment.

Design-Expert 7.1.5 (Stat-Ease Inc., Minneapolis, MN USA) was used for the design of experiments. Using the selected parameters and their operating ranges as inputs, the set of experiments to be carried out were obtained from running the Rotatable Central Composite Design (CCD) under the Response Surface Methodology of the Design-Expert software.

Using the laboratory scale batch electrochemical treatment system the set of experiments obtained from the design of experiments were carried out at the specified parameter values and responses were recorded.

In case of acrylic fibre applicator oil wastewater, chloride content and pH of the wastewater was adjusted to desired level by adding sodium chloride and using either sulphuric acid or sodium hydroxide solutions. Then wastewater was taken into the reactor, SS-SS electrodes were set in place, Voltage was fixed at the desired level and DC current was passed for specified period. Amperage (for facilitating estimation of power consumption), initial and final temperature and pH of the wastewater were monitored. After the treatment, the treated wastewater was allowed to settle for 2 hours, and the supernatant was sampled and analysed for COD.

In case of the first extraction stage bleach plant effluent, pH of wastewater was adjusted to desired level by using sulphuric acid or sodium hydroxide solutions. The set of electrochemical treatment experiments were carried out at the specified parameter conditions. The set of experiments were run three times, the first set with Al-Al electrodes, the second set with Fe-Fe electrodes, and the third set with SS-SS electrodes. Amperage (for facilitating estimation of power consumption), and initial and final temperature and pH of the wastewater were monitored. After the treatment, the treated wastewater was allowed to settle for 2 hours, and the supernatant was sampled and analysed for colour, COD and turbidity.

Using the responses together with the parameter values as inputs, through running design expert software, statistical models, describing and simulating the electrochemical treatment process, were developed. In case of the acrylic fibre applicator oil wastewater, COD removal efficiency and energy consumption (responses) were modelled against the parameters, pH, Chloride level, Voltage and treatment duration. And, in case of the first extraction stage bleach plant effluent colour removal and energy consumption (responses) were modelled against the parameters, pH, Voltage and treatment duration, for each of the three sets of electrodes used separately.

The model development process involved two steps: selection of model and development of the selected model. The model selection process involved calculation of the effects of all the model terms and comparison of F-values, *Lack of fit*, and coefficient of regression (R^2) values. In the model development process, first a model inclusive of all the possible terms was developed and then it was reduced through eliminating all the non-significant terms. An ANOVA (Analysis of variance) table, developed with the help of the software, was used for identifying the significant model terms (at 95% significance level) and reducing the model. *Goodness of fit* of the developed model was evaluated through estimating R^2 and CV values.

The software gave the developed model both as a standardized equation (in terms of standardized coded values for the parameters) and as an unstandardized equation (in terms of actual values for the parameters). This model included all the significant parameter terms and the parameter interaction terms. And it can be used for predicting responses, and also for simulating and optimizing the treatment process.

With the help of the design expert software, using the developed model, parameter optimization (finding values for different influencing parameters at which the response is either maximum or minimum as desired) was carried out.

3.4 Analytical techniques

pH and conductivity (in mho/cm) were measured with electronic pH meter (CP-901) by CENTURY instruments after calibrating the pH meter with buffer solutions of pH 4.0, 7.0

and 9.2. (Method number 4500-B of Standard Method, 1989) and digital conductivity meter (601-E) made by Deluxe instruments which is calibrated with standard KCl solution of 0.1N strength (Method number 2510-B of standard methods, 1989). Chemical oxygen demand (COD) was determined by closed reflux (titrimetric) method (Method number 5220-C of standard methods, 1989). Turbidity of sample was measured by using Nephalometer which uses optical properties of light as basis (Method number 2130- B of standard method, 1989) and chloride was estimated by argentometric method (Method number 4500-B of standard method, 1989). Oil and grease was determined by Partition-Gravimetric method (Method number 5520-B of standard methods, 1989) while the colour of effluent samples was determined spectrophotometrically according to Canadian Paper and Pulp Association (CPPA) Standard Method (1974). Sulphate estimation was done by gravimetric method (Method Number 4500- sulphate D of standard methods, 1989) and Biological Oxygen Demand (BOD) was estimated by standard dilution technique (Method number 5210-B of standard methods, 1989).

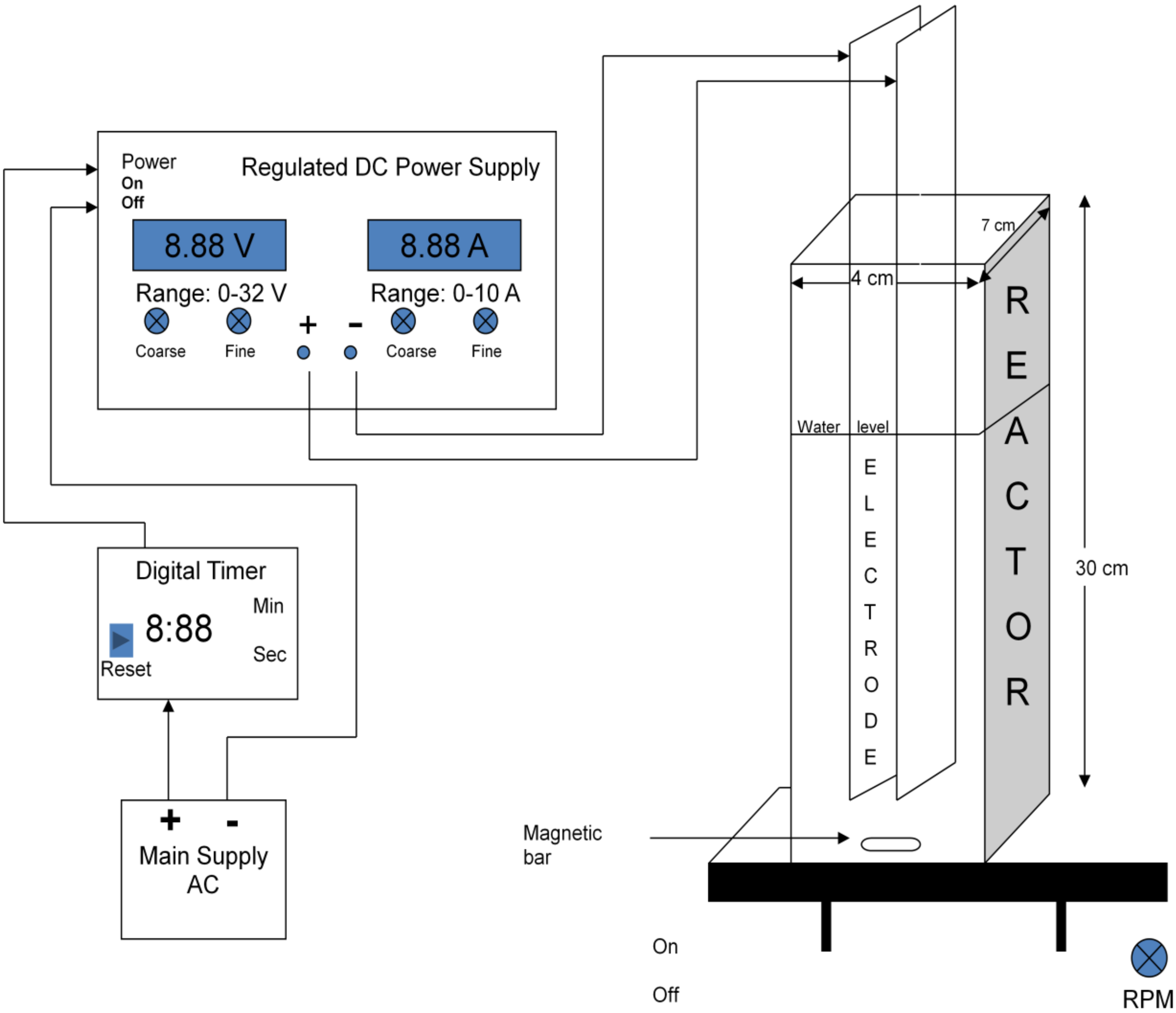


Figure 3.1 - Schematic diagram of the experimental set up

Chapter 4

Results and discussion

Both the wastewaters namely, acrylic fibre applicator oil wastewater from textile industry and first extraction stage bleach effluent from paper and pulp industry are investigated in the following study. Response Surface Methodology was used for the experimental design and Design Expert software was used for the data analysis and model building. Acrylic fibre applicator oil wastewater from the textile industry was used and the experiments were conducted using stainless steel pair of electrodes as per the experimental design and COD removal was obtained as response. Further first extraction stage bleach effluent from paper and pulp industry was treated using three pairs of electrodes (Al-Al, Fe-Fe, SS-SS electrodes) and colour removal was obtained as response.

4.1 Treatment of acrylic fibre application oil wastewater

For the treatment of acrylic fibre applicator oil wastewater based on the extensive literature review done 4 process variables were selected and their range was specified as given in the Table 4.1

Parameters	Ranges
pH	4 to 9
Chloride (mg/l)	0 to 1200
Voltage (V)	5 to 15
Time (min)	5 to 20

Table 4.1 Process variables and their ranges for acrylic fibre applicator oil wastewater

The experimental variables in terms of actual and coded values are given in Table 4.2 and the set experiments performed is given in the Table 4.3. These set of 21 experiments were obtained by using rotatable central composite design method of Response surface methodology using Design Expert Software. The responses (COD removal efficiency) or the experimental results obtained for the set of experiments conducted are shown in Annexure 1.

The response data was fitted using design expert software and the best response fitting was obtained through the linear model indicating it to be the most appropriate model for the data. Please see the Table 4.4 for details. The linear model is significant at 99.99% significance level (F value = 22.7, df = 4) and the Lack of Fit was not significant at p- value = 0.4472 (F value = 1.26, df = 12) as depicted in Table 4.4. Table 4.5 compares the actual and the predicted values showing the model to be a fitting properly. Finally based upon the press values the linear model gives the minimum value. For the linear model all the model terms are significant at the p- value < 0.05. Model gave a CV of 18.47% and R^2 of 0.8502 (acceptable above 0.80%). Also the model has low noise as compared to the signal which is evident from the precision value of 16.52 (acceptable > 4). On running the data on the software the linear model equation given in equation 4.1 was developed. This model equation has the parameters in terms of unitless regression coefficients and cannot be directly used for predictions or optimization.

COD removal = + 49.13- 7.48* pH+ 11.57* Chloride + 17.25* Voltage +7.76* Time (4.1)
where pH, chloride,voltage and time are in coded units.

For the convenience of use this linear model equation is converted into equation in terms of actual units as shown in equation 4.2.

COD removal = + 5.10834 - 3.74150 * pH + 0.025867 * Chlorides + 3.44973 * Voltage +1.55133 * Time (4.2)
where pH, chloride,voltage and time are in actual units.

Further the model is validated by comparing the actual and predicted COD removal efficiency values then the model is used for finding out the optimum treatment conditions. The numerical optimization of the model predicted COD removal efficiency of 77.7% at 5.1 pH, 1067 mg/l chloride concentration, 14.26 volts and 9.15 minutes treatment time.

The model indicates that voltage has the highest contribution in the COD removal(Graph-4.3) followed by chloride concentration(Graph - 4.2). COD removal efficiency increases with the increase in voltage and chloride concentration where as treatment time has slight effect on it(Graph – 4.4). pH has negetive effect on the COD removal efficiency infering that low pH (acidic pH condition) favours better COD removal (Graph- 4.1).

	Coded values				
Independent variables	-1.68	-1	0	1	1.68
	Actual values				
pH	3.64	5	7	9	10.36
Chloride(mg/l)	0	305.1	752.6	1200	1505.1
Voltage(volt)	1.59	5	10	15	18.41
Treatment time (min)	1.59	5	10	15	18.41

Table 4.2 Experimental range and level of independent process variables for acrylic fibre applicator oil wastewater

Experimental run	Coded values (Actual values)			
	pH	Chloride	Voltage	Time
Star points (α = ± 1)				
1	+1(9)	+1(1200)	+1(15)	-1(5)
2	+1(9)	+1(1200)	-1(5)	-1(5)
3	+1(9)	-1(305.1)	+1(15)	+1(15)
4	-1(5)	+1(1200)	-1(5)	+1(15)
5	+1(9)	-1(305.1)	-1(5)	+1(15)
6	-1(5)	-1(305.1)	+1(15)	-1(5)
7	-1(5)	+1(1200)	+1(15)	+1(15)
8	-1(5)	-1(305.1)	-1(5)	-1(5)
Axial points (α = ± 1.68)				
9	-1.68(3.64)	0(752.6)	0(10)	0(10)
10	1.68(10.36)	0(752.6)	0(10)	0(10)
11	0(7)	-1.68(0)	0(10)	0(10)
12	0(7)	1.68(1505.1)	0(10)	0(10)
13	0(7)	0(752.6)	-1.68(1.59)	0(10)
14	0(7)	0(752.6)	1.68(18.41)	0(10)
15	0(7)	0(752.6)	0(10)	-1.68(1.59)
16	0(7)	0(752.6)	0(10)	+1.68(18.41)
Center points (α = 0)				
17	0(7)	0(752.6)	0(10)	0(10)
18	0(7)	0(752.6)	0(10)	0(10)
19	0(7)	0(752.6)	0(10)	0(10)
20	0(7)	0(752.6)	0(10)	0(10)
21	0(7)	0(752.6)	0(10)	0(10)

Table 4.3 Experimental design as per CCD for acrylic fibre applicator oil wastewater

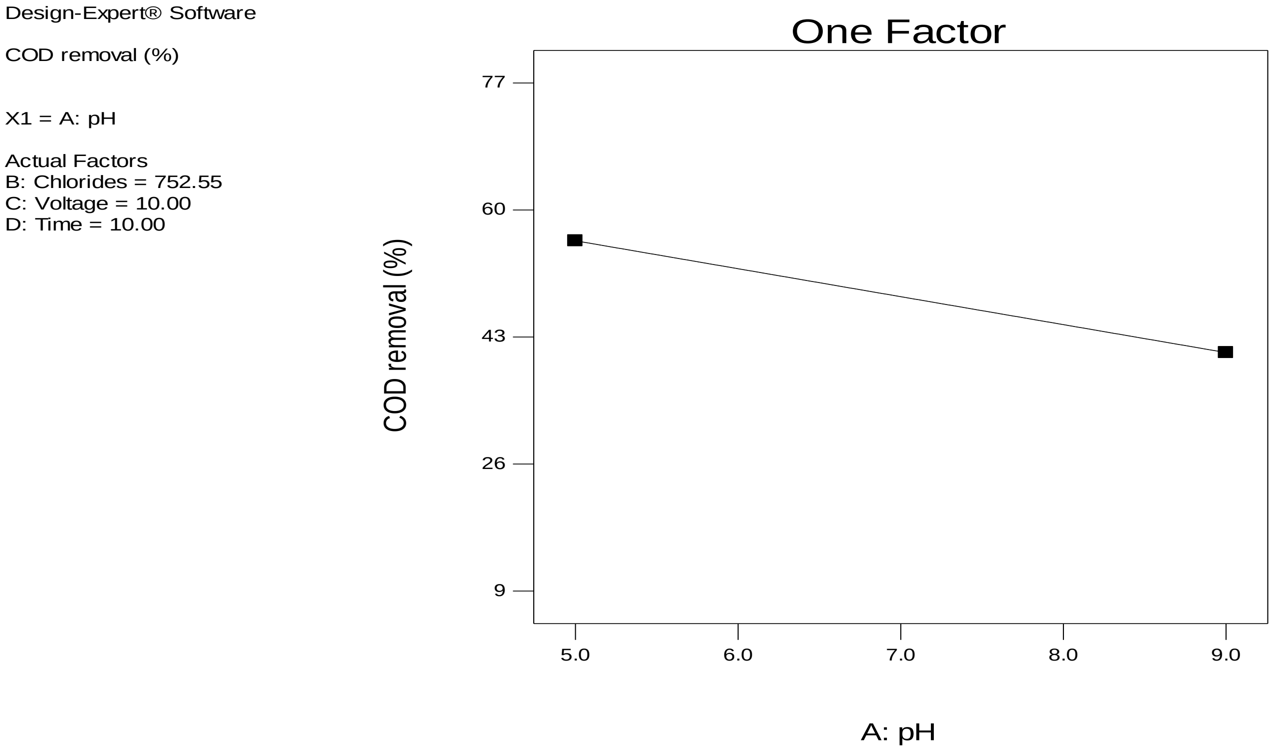
Source	Sum of square	df	mean sq	F value	P-value prob> F	
Mean vs Total	46840.6	1	46840.6			
Linear vs Mean	7478.99	4	1869.75	25.74	< .0001	Suggested

2FI vs Linear	725.37	6	120.89	2.99	0.0683	
Quadratic vs 2FI	189.09	4	47.27	1.35	0.368	
Cubic vs Quad.	53.8	2	26.9	0.67	0.5763	Aliased
Residual	121.15	3	40.38			
Total	55409	20	2770.45			

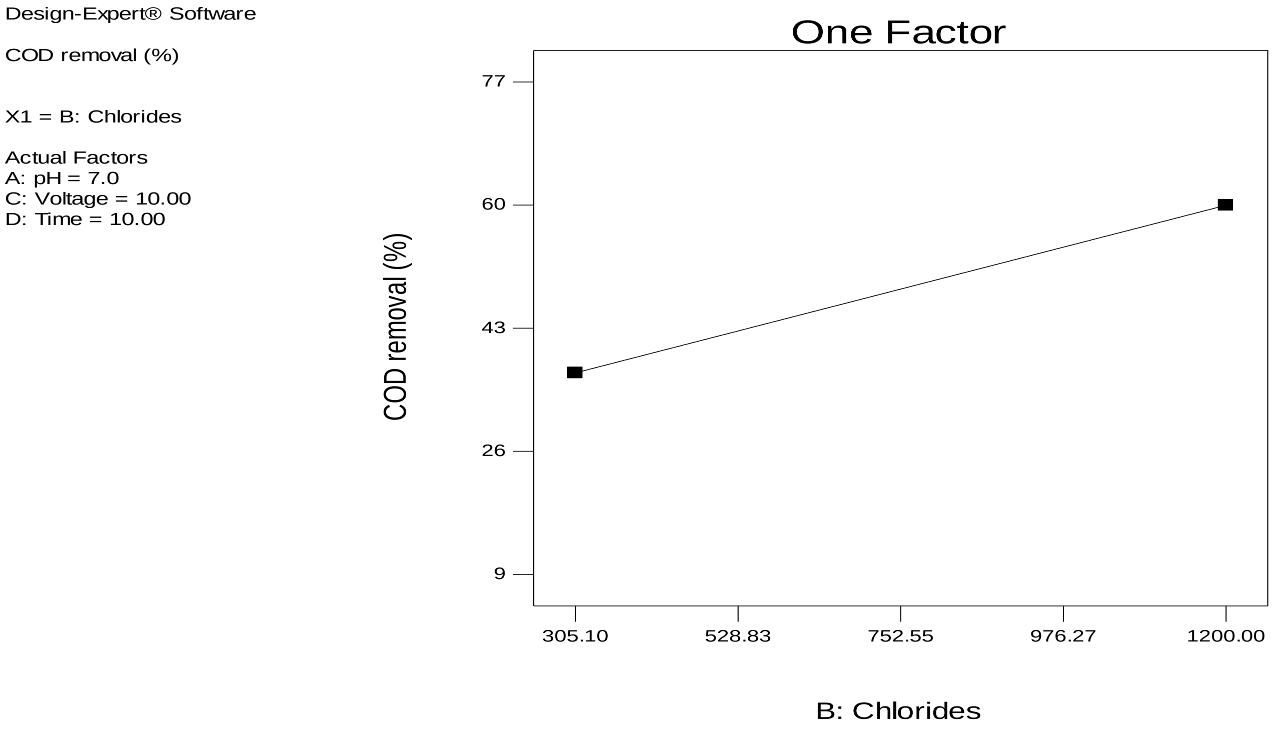
Table 4.4 Selection of model for acrylic fibre applicator oil wastewater

					Response 1	
Exp. no.	Initial pH	Chloride(mg/l)	Voltage (V)	Time(T)	COD removal Efficiency (%)	
					Actual	Predicted
1	9	1200	15	5	61.16	61.98
2	9	1200	5	5	23.97	27.48
3	9	305.1	15	15	49.2	54.34
4	5	1200	5	15	64.14	57.96
5	9	305.1	5	15	9.03	19.85
6	5	305.1	15	5	64.54	53.8
7	5	1200	15	15	76.76	92.46
8	5	305.1	5	5	16.67	19.3
9	3.64	752.6	10	10	61.82	60.98
10	10.36	752.6	10	10	47.88	35.81
11	7	0	10	10	32.27	28.93
12	7	1505.1	10	10	74.77	67.86
13	7	752.6	1.59	10	15.01	19.39
14	7	752.6	18.41	10	73.11	77.4
15	7	752.6	10	1.59	27.03	35.35
16	7	752.6	10	18.41	70.52	61.44
17	7	752.6	10	10	45.62	48.39
18	7	752.6	10	10	62.16	60.3
19	7	752.6	10	10	57.57	48.39
20	7	752.6	10	10	52.86	48.39
21	7	752.6	10	10	43.96	48.39

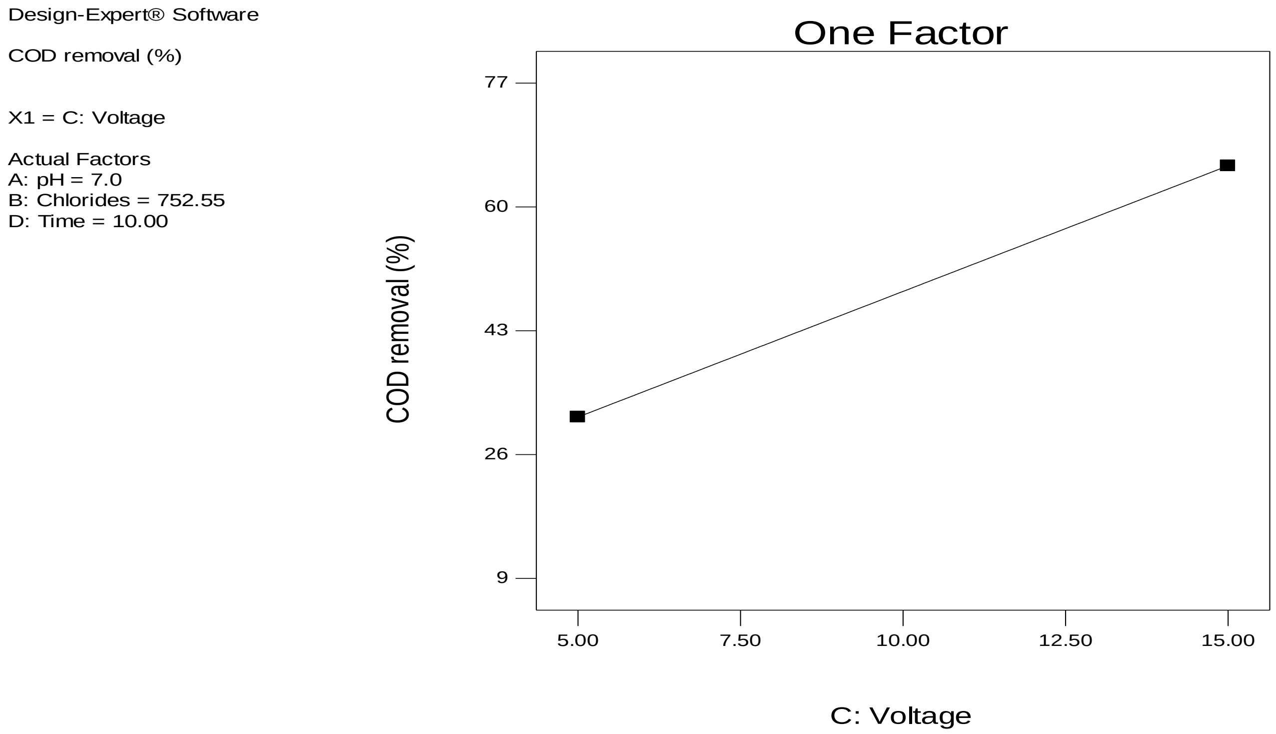
Table 4.5 Actual and predictive responses of COD removal efficiency of Acrylic fibre applicator oil wastewater



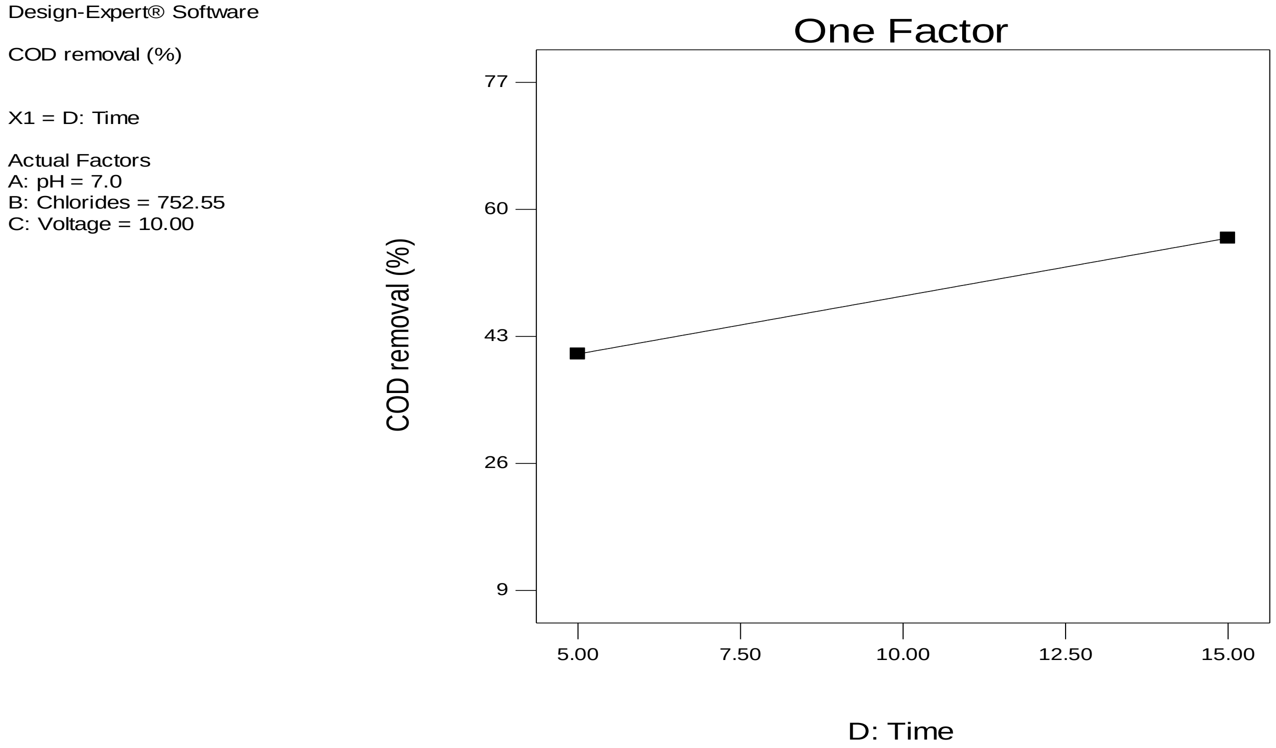
Graph 4.1 pH versus COD removal (%) for acrylic fibre applicator oil wastewater



Graph 4.2 Chlorides versus COD removal (%) for acrylic fibre applicator oil wastewater



Graph 4.3 Voltage versus COD removal (%) for acrylic fibre applicator oil wastewater



Graph 4.4 Time versus COD removal (%) for acrylic fibre applicator oil wastewater

4.2 Treatment of First extraction stage Bleach effluent

For the bleach effluent also on the basis of extensive literature review and preliminary laboratory scale testing 3 process variables namely- pH, voltage and time were selected and their range was specified as given in Table 4.6.

Parameters	Ranges
pH	2to 10
Voltage (V)	0 to 10
Time (min)	0 to 20

Table 4.6 Process variables and their ranges for Bleach effluent

In the present study, for the treatment of bleach effluent three different pairs of electrodes (Fe- Fe, Al- Al and SS- SS) were used. Further on the basis of set of 15 experiments obtained by using rotatable central composite design method of Response surface methodology using Design Expert Software the responses were obtained as COD, colour and turbidity removal efficiencies. The responses (COD, colour and turbidity removal efficiency) or the experimental results obtained for the set of experiments conducted are shown in Annexe 2, 3 and 4 for Fe- Fe, Al –Al and SS-SS pair of electrodes respectively. However the modelling done here is basically focussed on colour removal efficiency as response.

4.2.1 Using Fe-Fe pair of electrodes

The experimental results for first extraction stage bleach effluent using Fe- Fe pair of electrodes gave the responses in the form of COD, colour and turbidity removal. However for model to give reliable results R^2 value should be greater than 0.8 which was not the case here, hence modelling was not done for these results.

4.2.2 Using Al-Al pair of electrodes

For modelling to be done using Al-Al pair of electrodes again R^2 value came out to be lesser than 0.8 showing less reliability of the model. Further greater is the predicted R^2 value better is the prediction, and in the case of Al- Al pair of electrodes predicted R^2 value was highly diminished, showing that the model has low predictability. Thus modelling was not done for this case as well.

4.2.3 Using SS-SS pair of electrodes

For successful modelling to be done using SS-SS pair of electrodes, experimental range and level of independent process variables for Bleach effluent were specified as depicted in Table 4.7. The set experiments performed is given in the Table 4.8. The response data was fitted using design expert software and the best response fitting was obtained through the linear model indicating it to be the most appropriate model for the data. Table 4.9 gives the details of model selection showing linear model to be the most suitable model. For proving the selected model correct, the actual and predicted Colour removal efficiencies were compared as given in Table 4.10. Further the results for the set of experiments conducted are quoted in annexe 4.

On running the data on the software the linear model equation given in equation 4.3 was developed. As this model equation has the parameters in terms of unitless regression coefficients and cannot be directly used for predictions or optimization, hence equation 4.4 was developed which is in terms of actual units.

$$\text{Colour removal (\%)} = +48.59 + 38.33 * \text{pH} + 31.16 * \text{Voltage} + 28.97 * \text{Time} \quad (4.3)$$

where pH, voltage and time are in coded units.

$$\text{Colour removal (\%)} = -166.53949 + 13.93709 * \text{pH} + 10.38814 * \text{Voltage} + 5.26690 * \text{Time} \quad (4.4)$$

where pH, chloride,voltage and time are in actual units.

As indicated by equation 4.3, pH has the greatest influence on colour removal efficiency (Graph- 4.5) followed by voltage (Graph- 4.6). Further time has the least influence on colour removal efficiency (Graph -4.7) with no interaction being seen between the different factors. On the basis of above modelling results the optimised colour removal conditions were sorted out. Thus at 6.25 pH and 8.99 volts on giving 15.69 minutes of treatment time an optimum colour removal efficiency of 96.6% was achieved.

	Coded levels				
Independent variables	- 1.68	- 1	0	+ 1	+1.68
			Actual values		
pH	2.36	3.5	6.25	9	10.14
Voltage (volt)	2.76	4	7	10	11.24
Treatment time (min)	2.72	5	10.5	16	18.28

Table 4.7 Experimental range and level of independent process variables for first extraction stage Bleach effluent

Experimental run	Coded values (Actual values)		
	pH	Voltage	Time
Star points (α = ± 1)			
1	+1(9)	+1(10)	-1(5)
2	+1(9)	-1(4)	+1(16)
3	-1(3.5)	+1(10)	+1(16)
4	-1(3.5)	-1(4)	-1(5)
Axial points (α = ± 1.68)			
5	-1.68(2.36)	0(7)	0(10.5)
6	+1.68(10.14)	0(7)	0(10.5)
7	0(6.25)	-1.68(2.76)	0(10.5)
8	0(6.25)	+1.68(11.24)	0(10.5)
9	0(6.25)	0(7)	-1.68(2.72)
10	0(6.25)	0(7)	+1.68(18.28)
Center points (α = 0)			
11	0(6.25)	0(7)	0(10.5)
12	0(6.25)	0(7)	0(10.5)
13	0(6.25)	0(7)	0(10.5)
14	0(6.25)	0(7)	0(10.5)
15	0(6.25)	0(7)	0(10.5)

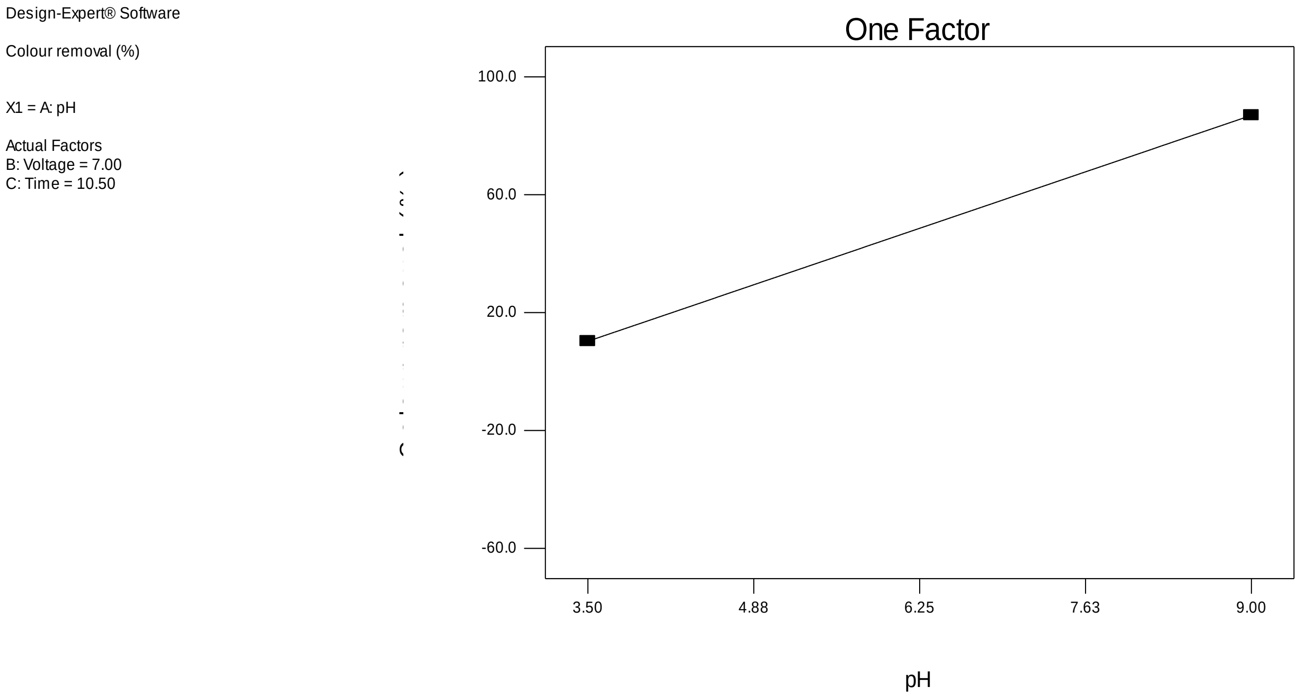
Table 4.8 Experimental design as per CCD for first extraction stage Bleach effluent

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	35410.17	1	35410.17			
Linear vs Mean	26234.59	3	8744.863	49.44888	< 0.0001	Suggested
2FI vs Linear	1047.302	3	349.1006	3.109992	0.0886	
Quadratic vs 2FI	584.5393	3	194.8464	3.107888	0.1269	
Cubic vs Quadratic	1.567574	1	1.567574	0.020103	0.8941	Aliased
Residual	311.9032	4	77.9758			
Total	63590.06	15	4239.338			

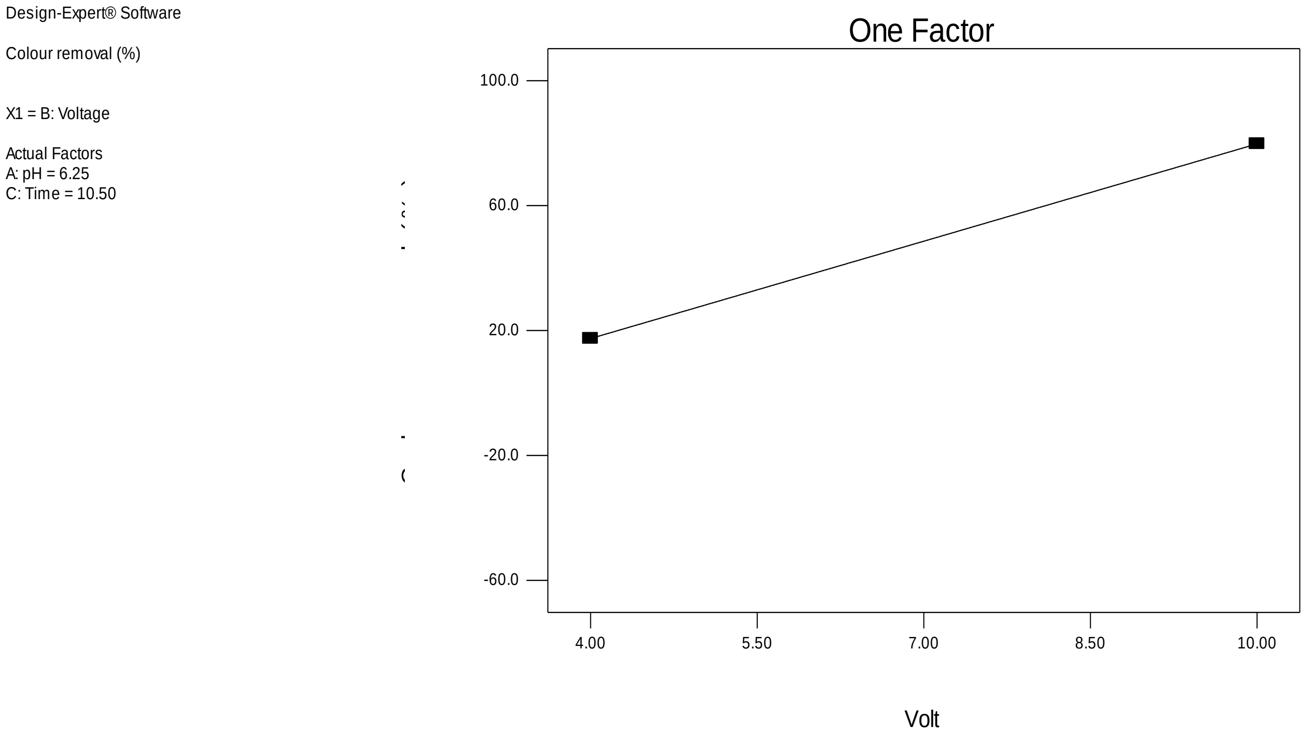
Table 4.9 Selection of model for first extraction stage bleach effluent

				Response 1	
Exp. no.	Initial pH	Voltage (V)	Time (T)	COD removal Efficiency (%)	
				Actual Value	Predicted Value
1	9	10	5	90.39	86.49
2	9	4	16	89.06	82.1
3	3.5	10	16		
4	3.5	4	5	-55.73	-52.49
5	2.36	7	10.5	10.42	5.32
6	10.14	7	10.5	92.97	97.84
7	6.25	2.76	10.5	-8.85	-0.43
8	6.25	11.24	10.5	95.05	103.6
9	6.25	7	2.72	-2.6	2.67
10	6.25	7	18.28	90.76	100.49
11	6.25	7	10.5	60.42	51.58
12	6.25	7	10.5	56.77	51.58
13	6.25	7	10.5	41.67	51.58
14	6.25	7	10.5	58.07	51.58
15	6.25	7	10.5	65.1	51.58

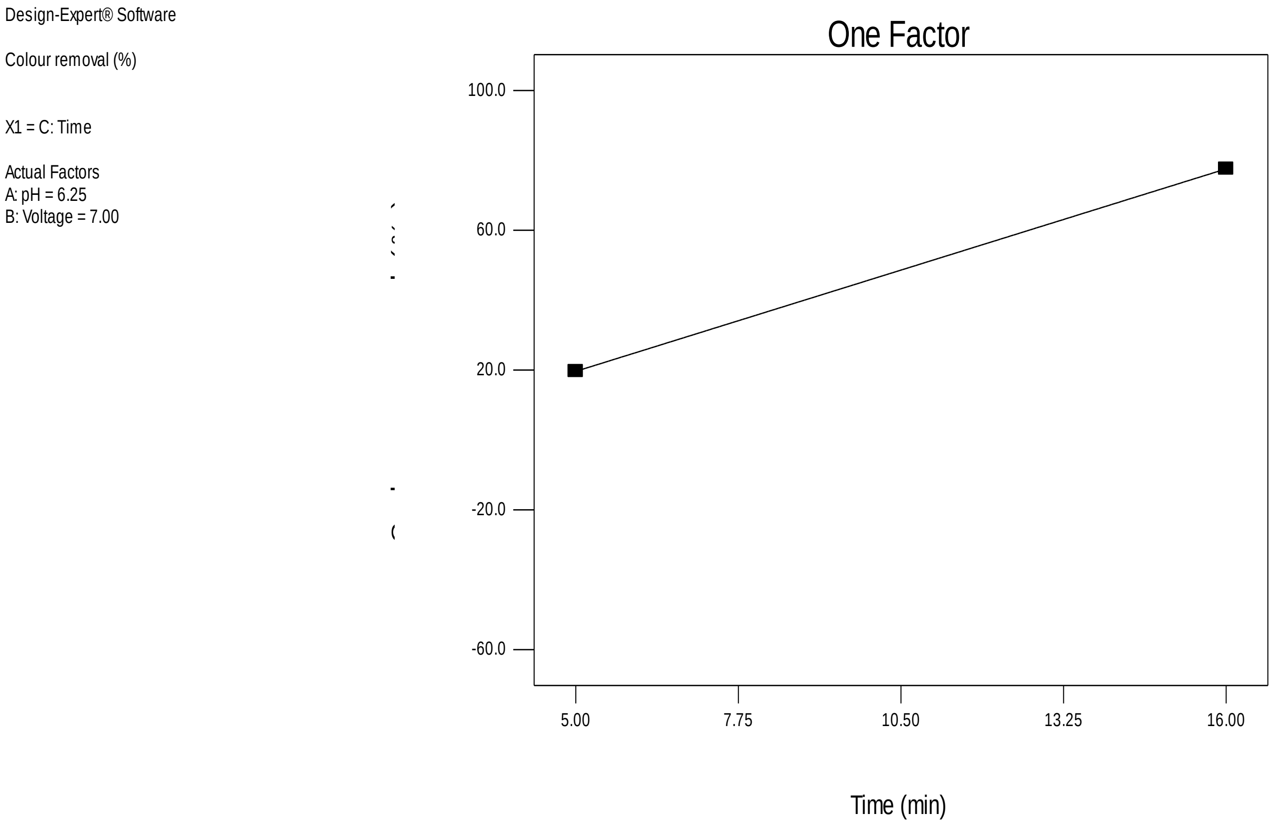
Table 4.10 Actual and predictive responses of Colour removal efficiency of First Extraction Stage Bleach Effluent using SS-SS pair of electrodes



Graph 4.5 pH versus Colour removal (%) for first extraction stage bleach plant effluent



Graph 4.6 Voltage versus Colour removal (%) for first extraction stage bleach plant effluent



Graph 4.7 Time versus Colour removal (%) for first extraction stage bleach plant effluent

Conclusion

Electrochemical treatment process was used to treat Acrylic fibre applicator oil wastewater from textile industry and 1st extraction stage bleach plant effluent from paper and pulp industry. For the acrylic fibre oil application waste water 4 factors namely pH, chloride, voltage and time were fixed and the treatment efficiency was accessed on the basis of COD removal efficiency. Based on the literature review stainless steel electrodes were used for treatment. For the interpretation of the results obtained on the laboratory scale analysis linear model was selected which gave the optimum results for COD removal at pH- 7.08, 1105.87 mg/l, 14.31 V and 13.61 minutes giving 77.72% COD removal.

In the case of Bleach effluent from paper and pulp industry three different electrodes namely aluminium, iron and stainless steel were used. Here three factors -pH, voltage and time were fixed in each experiment and the results were accessed on the basis of COD, colour and turbidity removal efficiencies. During modelling Fe-Fe and Al-Al pair of electrodes gave a low R^2 value (R^2 value< 0.8), hence model development was omitted for these. However results of treatment using SS-SS pair of electrodes gave satisfactory R^2 value and predicted R^2 showing that the model has high predictability. Hence on modelling linear model was selected which gave 96.6% as optimum colour removal efficiency at 6.25 pH and 8.99 volts on giving 15.69 minutes of treatment time.

Further as an additional advantage of the process it was found that the treatment leads to the neutralization of pH- slightly on the higher side, which cuts down the additional neutralization expenses. However, it should be noted that no feasibility analysis of the results obtained were done so the process can only be followed if it's cost effective as compared to the conventional treatment schemes.

Thus both Acrylic oil application waste water from textile industry and 1st extraction stage bleach effluent from paper and pulp industry gave encouraging results with electrochemical treatment process, so after pilot scale testing the process can be used on the industrial scale.

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