23236351, 23232701, 23237721, 23234116
23235733, 23232317, 23236735, 23239437

विश्वविद्यालय अनुदान आयोग
बहादुरशाह जफर मार्ग
नई दिल्ली-110 002
UNIVERSITY GRANTS COMMISSION
BAHADURSHAH ZAFAR MARG
NEW DELHI-110 002

UGC Reference No. & Date	F.No.41-1103/2012 (SR)/dated: 26-07-2012.
Name of the Principal Investigator	Dr. J. Narayana
Address	Office: Dr. J. Narayana Professor Principal Investigator UGC Major Project Department of Environmental Science Kuvempu University Shankaraghatta – 577 451 janaes@rediffmail.com Residential : No.71, Nesara, Sahydri Nagar, IV Main Vinobanagar (P), Shivamogga- 577204
Department and University/College where project has undertaken	Department of Environmental Science, Kuvempu University
Title of the project	Degradation and Removal of Basic Dyes by Electrochemical Method with Reference to Pulp and Paper Industry
Date of Implementation	04/01/2013
Tenure of the project	3 years from 2012 to 2015
Grants Received	1st Instalment: 6, 15,800

UGC Major Research Project Report Summary

"Degradation and Removal of basic dyes by Electrochemical method with reference to Pulp and Paper Industry "

Principal Investigator: Prof. J. Narayan

Introduction

Paper industry as one of the high priority industries of the country and considered as 15th largest in the world. It provides employment to nearly 1.5 million people and contributes to Rs 25 billion to the government's kitty. Pulp and paper industry is one of major industries which contribute a lot towards pollution of our water environment. While paper making, large amount of dyes are used as coloring agents in the dyeing process.

After the dyeing process of basic dyes, due to their poor exhaustion properties as much as 30% of initial dye applied remain unfixed and end up in effluents. The dye concentration is even lower than other pollutants, they often receive more attention due to their strong visible appearance and it will affect light penetration. Hence, their presence in wastewater is undesirable and it is essential to remove coloring material from effluents before being discharged in the environment. Because of dyes are carcinogenic and toxic it imbalances the chemical and biological nature when it is discharge into the water bodies.

Objectives of the project

- Collection of dyes and effluents from paper and pulp industry.
- Development electrochemical techniques for the degradation of dyes and effluents using different electrodes.
- Analysis of TOC and COD values of dye samples and effluents before and after the electrochemical treatment.
- Evaluating the optical density of dye samples and effluents at λ_{max} through UV-Vis studies before and after the electrochemical treatment
- Evaluating the mass reduction of dye samples and effluents through LC-MS studies after electrochemical treatment.
- Optimization of experimental procedure for the treatment of dyes and effluents.
- Scaling-up of the procedure for large-scale effluent treatment.

Materials and Methods followed

- Preparation of sample solutions using different paper mill dyes.
- Pretreatment of Graphite carbon electrodes for electrochemical treatment.
- Experimental setup for laboratory scale.
- Measurement of physico-chemical parameters, viz. *pH*, temperature, conductivity and COD by adopting the standard procedures (APHA, 1999).
- UV-vis studies for the dye solutions and effluent before and after the treatment.
- Evaluation of experimental data.

The commercial pulp and paper industrial dyes; Auromine, Brilliant green, Fast red, Direct green, Methyl violet, Pigment blue, Pigment violet were obtained from Mysore Paper Mills Ltd, Bhadravathi.

Analytical grade reagents and chemicals were used for conducting experiment. For electrochemical treatment process, cylindrical carbon electrodes (4.5 cm length and 0.8 cm diameter, Chemical composition: graphite carbon + coke: 85% and ash: 15%) were supplied by Power Cell Battery, India Limited. The effective areas of each graphite carbon electrodes, 11.82 cm^2 were used for the electrolysis.

A digital DC power supply (AESC: 30/2A CV, CC) was used as an electrical source. Double distilled water was used to prepare the desired concentration of dye solutions and the reagents.

Results and Discussion

Electrochemical degradation studies of Auromine

The electrochemical degradation under optimal electrolytes condition resulted in fast and almost complete decolourisation of the dye (Figure 4). After Electrochemical treatment the percentage of decolourisation of Auromine was found to be 90% in 40 min. The degree of decolourisation was monitored through UV-Vis absorbance studies at their λ_{max}: 437 nm.

Effect of supporting electrolytes:

From the figure 5, it can be observed that, the addition of NaCl to the dye solution during electrolysis increases the decolourisation efficiency of Auromine. From this observation it was concluded that the introduction of NaCl as an electrolyte can enhance the degradation efficiency and shortens electrolysis time, which may be attributed to the reaction between the electro generated chlorine and dye molecule. The possible mechanism of electrochemical degradation is given bellow,

Anode reaction: $2Cl^{-} \rightarrow Cl_2 + 2e^{-}$ - (1)

Cathode reaction: $2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$ - (2)

Bulk solution reaction: $Cl_2 + H_2O \rightarrow HOCl + HCl$ - (3)

$HOCl \rightarrow H^{+} + OCl^{-}$ - (4)

The above mechanism was classified as indirect electro-oxidation of pollutant. Increase in the concentration of NaCl up to 2.5g/L accelerated the decolouration rate, enabling degradation of dye effluent to the extent of 76% decolourisation efficiency of Auromine.

Further increase in NaCl concentration (> 2.5 g/L) there was a slight improvement in decolourisation efficiency, and therefore the optimal concentration of NaCl in successive degradation studied was fixed at 2.5 g/L. Moreover, the increased optimal concentration of NaCl results in a decrease in operating voltage at the given current density 100 A m^{2}.

Effect of initial *p*H

The decolouration efficiency of dye was found only 80% in acidic *p*H 3 and the final *p*H 11 decolouration efficiency was found to be 89% (Fig. 7). It indicated that the degradation of dye in basic solution is higher than that of in the acidic media. At *p*H 9 the decolouration efficiency was found 90% (Fig 7). Therefore the optimum *p*H: 9 were maintained in subsequent experiments.

Effect of Current density

Up to a current of 400 A m^2, the decolouration efficiency of both the dyes was increased almost linearly. At higher densities (>400 A m^2) the decolouration efficiency was attained almost constant.

Analysis of COD.

The standard COD measurement is known to be affected by a number of inorganic substances. In the absence of chloride containing electrolytes, the COD removal and dye degradation efficiencies were very low (Abu and Abdel, 2005). The maximum COD removal efficiency (90%) was observed at *p*H 9 .

Electric energy consumption.

The major operating cost is associated with the electrical energy consumption during electrochemical degradation process. As per the results the minimum electrical energy consumption was 0.2667 k W h m^{-3} for dye at 300 A m^2 current density.

Electrochemical degradation studies of Fast Red

The Electrochemical degradation under optimal electrolytes condition resulted in fast and almost complete decolourization of the dye (Figure 10). After Electrochemical treatment the percentage of decolouration of Fast Red was found to be 94% in 20 min. The degree of decolourisation was monitored through UV-Vis absorbance studies at their λ_{max}: 530 nm.

Effect of supporting electrolytes:

Increase in the concentration of NaCl up to 2.5g/L accelerated the decolouration rate, enabling degradation of dye to the extent of 83% decolourisation efficiency of Fast Red. Further increase in NaCl concentration (> 2.5 g/L) there was a slight improvement in decolourisation efficiency, and therefore the optimal concentration of NaCl in successive degradation studied was fixed at 2.5g/L.

Effect of initial pH:

The decolouration efficiency of dye was found 94% in acidic *p*H 3 and at initial *p*H 11 the decolouration efficiency was found to be 79% .

Effect of current density

Up to a current of 300A m^{2}, the decolouration efficiency of both the dyes was increased almost linearly.At higher densities (>300 A m^{2}) the decolouration efficiency was attained almost constant..

Analysis of COD:

The maximum COD removal efficiency (94%) was observed at *p*H 3 (Figure 15a). The percent removal of COD increased with increase in the concentration of NaCl .

Electric energy consumption

The major operating cost is associated with the electrical energy consumption during electrochemical degradation process. As per the results the minimum electrical energy consumption was 0.1732 k W h m^{-3} for dye at 300 A m^{2} current density. At higher current densities, the energy consumption was found to be increased, which may be attributed to the increased hydrogen and oxygen evolution reactions.