

# Preparation and application of TiO<sub>2</sub>/Al electrode for the removal of disperse dye in EC process

Parameswari Kalivel\*<sup>1</sup>, Jegathambal Palanichamy\*<sup>2</sup> and Vijila Moses<sup>3</sup>

<sup>1</sup>Department of Chemistry, <sup>2</sup> Water Institute, <sup>3</sup>Department of Mathematics, Karunya Institute of Technology and Sciences, Coimbatore, India

(Received 30 November, 2019; accepted 23 January, 2020)

## ABSTRACT

This research deals with electro coagulation treatment of the synthetic dye solution. The main criteria in this work are to select the right operating parameters for high efficiency of color removal with minimum energy consumption. This process was evaluated using TiO<sub>2</sub>/Al electrode by spray pyrolysis with TiCl<sub>3</sub> and the effectiveness was related with Al. SEM, XRD and EDS analysis were used to analyze the morphological, structural investigation, and percentage of the components of the electrode. The competence of the procedure for electro coagulation to treat synthetic waste water comprising Coralene Navy RDRLSR, Coralene Red 3 G, Rubru RD GLFI dye (disperse dye) has been tested for the impact of operating factors like pH, time, current and electrolyte concentration. The results showed that this method was accomplished to attain the elimination of color (97.2 percent) at pH 7.0 at the original pH of the effluent with TiO<sub>2</sub>/Al.

**Keywords:** Electro coagulation, Disperse dye, TiO<sub>2</sub>/Al, Reaction time, energy

## Introduction

The freshwater scarcity in developing countries such as India emerges due to rapid industrialization and insufficient water management. The cotton dyeing industries are one of India's major contributors to river and groundwater pollution (Rafi *et al.*, 1996). Roughly 80% of the woven apparel of the nation emanates from Tirupur town in Tamil Nadu, about 55 km east of Coimbatore. With many numbers of knitting, dyeing and bleaching, printing, embroidery and compacting, elevating and calendaring units, the effluent from these units, have high COD and salt levels. Many methods, such as physical, chemical and biological methods used to treat wastewater, have benefits and drawbacks. Most of these methods are expensive and inefficient. In recent years, research on wastewater treatment has focused on electrochemical coagulation because

it is easy to operate with less sludge production (Verma *et al.*, 2012; Nadjib Drouiche *et al.*, 2012; Alinsafi *et al.*, 2005).

Electrocoagulation system was useful to treat oil emulsion wastewater (Hooshmandfar *et al.*, 2006) and fabric wastewater (Hu *et al.*, 2005). This method was also found to be useful in treating heavy metal wastewater (Bensadok *et al.*, 2008; Zongo *et al.*, 2009; Nanseu-njiki *et al.*, 2009; Attour *et al.*, 2014; Vasudevan *et al.*, 2009; Lacasa *et al.*, 2011). But this system faces a high amount of electricity consumption and has an effect on operating costs. Since the demand for electrical energy is proportional to the treating time, this route with customary electrodes such as aluminum resulted in a double consumption of electrical energy compared to energy consumption using stainless steel electrodes (Drouiche *et al.*, 2009). Despite the fact that traditional electrode materials (Al and Fe) have better color elimi-

nation efficacy and are possible to dissolve. Therefore, a new economically viable electrode or electrode/hybrid EC device is needed that requires a lesser amount of current and time (Zhu *et al.*, 2014). In the batch process (Jegathambal *et al.*, 2015) modified electrodes such as TiO<sub>2</sub>/Al prepared by the thermal decomposition of TiCl<sub>3</sub> are used successfully.

The aim of this study is to prepare TiO<sub>2</sub>/Al from spray pyrolysis method with TiCl<sub>3</sub> and to analyze the competence of the EC process for color removal efficiency (CRE%) was assessed for the elimination of dye using TiO<sub>2</sub>/Al-TiO<sub>2</sub>/Al and compared with Al-Al. Color removal and electrode efficiencies are the methodological parameters used in this work with the optimization of operative parameters such as pH, applied current, electrolyte concentration and time.

## Materials and Methods

### TiO<sub>2</sub>/Al Electrode preparation by Spray Pyrolysis

The precursor using TiCl<sub>3</sub> was prepared in the preparation as proposed by Beck and Co-workers (Beck F *et al.*, 1985; Parameswari *et al.* 2014) was adopted by spray pyrolysis to prepare TiO<sub>2</sub>/Al electrode. The TiO<sub>2</sub> coating was done on a well-cleaned aluminum substratum, sand blasted for better adherence of the coated material and cleaned with triple distilled water, followed by coating. The precursor solution was impelled (Stroke pump) to a 100 kHz ultrasonic atomizer (Lechler Inc.) to the hot surface of the metal substrate from a tubular quartz reactor (diameter 5 cm and length 30 cm). The Al substratum was mounted on the case of the sample and raised the temperature by heating quartz bulbs positioned above and below the duct. The precursor was sprayed on the substratum at 200 °C and was 20 cm below the carrier gas such as oxygen and nitrogen with the nozzle to substrate length. The solution flow rate was 3mL/10 min for one time deposition of a 40 mL solution batch. The specimen was then gradually cooled down to room temperature by 10 °C/min. The electrodes are measured at 9cm/3.2cm/0.5 cm lengths.

### Electrocoagulation (EC) Process

**Dye Solution** - Synthetic wastewater was prepared at concentrations of 150mg/L in distilled water which was acquired from a small dyeing unit in

Coimbatore. (Commercial name of the dye; Coralene Navy RDRLSR, Coralene Red 3 G, Rubru RD GLFI)

A 500 mL beaker along with a magnetic stirrer and DC power supply was used as an electrochemical reactor. Two EC process sets were executed at 25°C with TiO<sub>2</sub>/Al—TiO<sub>2</sub>/Al and Al to achieve higher Color Removal Efficiency (CRE percent). [(These electrodes will be represented as ' A' (TiO<sub>2</sub>/Al— TiO<sub>2</sub>/Al) and ' B' (Al— Al)]. The electrode with a total active area of 28.5cm<sup>2</sup> and the distance of 10mm between both the electrodes were placed with 250 ml of sample solution for each test. Electrodes were plopped with water before each test and put in 15 percent hydrochloric acid to extract dust from the surface and thus weighed the electrodes after drying. After each experiment, the electrodes were washed with water, dried up and weighed. The test solution was filtered, and the filtrate was characterized for color removal. The test solution's pH has been attuned with 0.5N HCl or NaOH. Certain parameters were kept constant for each optimization of working parameters based on the early experimentations.

**Color Removal Efficiency (CRE)** - Efficiencies in color removal (CRE percent) were calculated from the following expression

$$CRE\% = 100 \cdot (A_b - A_t) / A_b$$

Where A<sub>b</sub> and A<sub>t</sub> were, respectively, the dye absorbance in solution prior to electrocoagulation and at time t. The spectrophotometer JascoV-670 was used to determine the dye solution's wavelength (542 nm).

**Surface Morphology and structural Investigation of electrodes**- Scanning Electron Microscope (SEM) [JEOL 6390], was used to analyze the surface morphology and structural analysis of TiO<sub>2</sub>/Al electrodes. Elemental analysis by Energy Dispersive X-Ray Spectroscopy (EDS) and micro structure of the particles present in the electrode and sludge by X-Ray diffractometer [SHIMADZU-6000] were studied.

## Results and Discussion

### Morphological study of TiO<sub>2</sub>/Al

**SEM, EDS Analysis** Fig. 1. a, b. represents the SEM and EDS spectrum of Al and TiO<sub>2</sub>/Al prepared from spray pyrolysis. SEM micrograph of TiO<sub>2</sub>/Al

showed that there are compressed units and that the size and shape of the particles are regular. The peak corresponding to 3keV for Cl appears in the metal as well in the coated electrode and the peaks corresponding to Ti and O peaks agree the presence of titanium oxide. SEM micrograph shows that the surfaces that have been obtained are permeable. In addition, the surface layer crashes are noticeable with pores, by the speedy progress in the size of the TiO<sub>2</sub> layer on the Al substratum. In Fig. 1b the peaks at 0.6, 4.3 and 4.5keV are related to the required energy of Ti and oxygen links to the TiO<sub>2</sub> particles and confirms the presence of elemental compounds in the Al substratum. The peaks are correlated to around 1.5 keV are linked to the prerequisite energies of Al with O<sub>2</sub>.

### XRD analysis of TiO<sub>2</sub>/Al

Fig. 2. is the X-ray diffractogram of Al and TiO<sub>2</sub>/Al. The TiO<sub>2</sub> phase diffraction peaks and the Al substrate are present in the electrode being investigated. Sharp peaks reached matching the planes (101), (200) established the nano-crystalline structure. It indicates TiO<sub>2</sub> nanoparticles in anatase structure. The deposition of TiO<sub>2</sub> with 2 theta values (24.8) was matched with JCPDS card no: 21-1272. Calculated using the Scherrer formula, the crystalline size ranged from 20.2 to 53.7 nm which indicates large surface area of the TiO<sub>2</sub> particle (Cullity *et al.*, 1978).

### Optimization of Operative Parameters

Working parameters such as (pH, time, concentration of electrolyte and applied current) are opti-

mized in this work for the elimination of dye. For each parameter optimization the other parameters were kept perpetually from the preliminary experiments for both TiO<sub>2</sub>/Al-TiO<sub>2</sub>/Al (electrode 'A') and Al-Al (electrode 'B') for the dye removal.

### Influence of pH on Removal of disperse dye

The optimal pH level depends on the nature and composition of the material used in the electrode. The solution's pH orders the presence of metal in its ionic state, the chemical position of additional ions in the solution, and also regulates the solution. To find the optimal pH for high color removal of the dye, under the above-mentioned condition, a se-

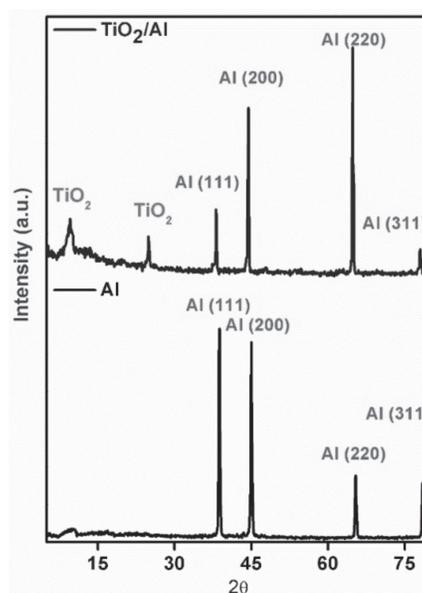


Fig. 2. XRD Configuration for Al and TiO<sub>2</sub>/Al

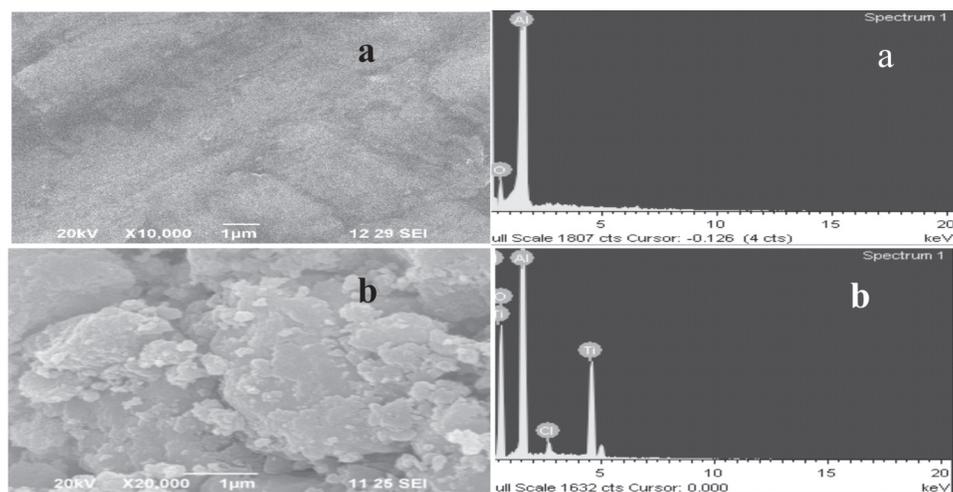


Fig. 1. SEM, EDS photograph of a. Al, b. TiO<sub>2</sub>/Al

quence of experimentations were performed with the mentioned dye solution at varying pH (4, 5, 6, 7, 8 and 9). The pH of the test solution was modified with NaOH or H<sub>2</sub>SO<sub>4</sub> to a suitable value that was varied between 4 and 9. The collection and filtering of the treated sample from which the percentage of CRE calculated. The outcomes are given in Fig. 3.a and Table 1.

**Table 1.** Influence of variable pH, NaCl, applied current, EC time on CRE (%)

pH	CRE %		NaCl (g/L)	CRE %	
	A	B		A	B
4	94.3	80.4	0.1	98.1	98.0
5	99.4	68.6	0.15	98.6	88.3
6	99.4	59.3	0.2	98.1	61.3
7	99.5	41.7	0.25	98.3	33.1
8	99.7	40.2	0.3	97.9	42.0
9	68.4	36.0	0.35	99.8	40.1

Current (A)	CRE %		Time (min)	CRE %	
	A	B		A	B
0.01	47.7	40.6	5	89.2	88.0
0.02	58.1	41.7	10	96.6	92.0
0.03	75.2	80.3	15	99.2	89.2
0.04	99.5	68.7	20	99.2	74.0
0.05	99.8	65.0	25	99.3	65.0
0.06	99.6	60.2	30	99.9	56.4

The pH of raw wastewater can affect the process's competence positively or negatively, as it interrupts the strength of various types of metal hydroxides that are formed (Ün *et al.*, 2009). The color removal effectiveness for electrode 'A' was 99.5 percent at neutral pH, probably at this level, most hydroxides like Ti(OH)<sub>2</sub><sup>+</sup> and Ti<sub>2</sub>(OH)<sub>2</sub><sup>+</sup> and unsolvable Ti(OH)<sub>3</sub> could be present and although above pH 7 CRE percent is high, but it occurred at alkaline pH. More over effluent pH at neutral, electrode 'A' is active in color removal. With Al at pH 6, the percentage of CRE was 80% as the pH augmented from 6 to 9, with a progressive and abrupt decrease in percentage of CRE, this could be attributed to the formation of further soluble metal hydroxides compared to insoluble aluminum ion compounds, as a result of which coagulation and thus precipitation are less desirable.

#### Influence of Electrolyte

Through reducing energy consumption, the supporting electrolyte in electrolysis decreases the current use there. As an addition to any electrolyte, the movement of ions in the solution can be improved

and at the identical time the adding of the same, may cause the suspension of the material from TiO<sub>2</sub>/Al due to weathering followed by Al. So the adding NaCl amount need to be optimized (Merzouk *et al.*, 2011). From the electrolyte, Cl<sup>-</sup> ions will diminution the adverse effect of other anions and thus upsurge the accessibility of hydroxides in the reaction medium. Dying units in textile industries use NaCl at different steps and the effluents pawned from them contains Na<sup>+</sup> and chloride ions, and because of which the test solution is highly mobile and therefore requires low voltage for electrocoagulation. The EC process was performed and the CRE found during the EC cycle are shown in Fig. 3b, Table 1 with changing the amount of NaCl from 0.1-0.35g / L.

At the concentration of 1g/L of NaCl, both the electrode 'A' and 'B' demonstrated almost the same percentage of dye extraction with 98% color removal. Increasing the concentration of NaCl in the electrode 'A' dye reduction was almost the same, but in the electrode 'B' CRE percentage began to decrease, may be attributable to Al metal passivation by increased chloride ions. As the conduction improved, Cl<sup>-</sup> would influence the anode and rise the dissolution of the anode (Lee *et al.*, 1999; Kobya *et al.*, 2010), so the adding NaCl further caused in lesser color elimination efficiency due to the deposition with salt film on the surface of the electrode which obstruct the contact amid the electrode and effluent thereby reducing the contact between the pollutant and hydroxides and from this 0.1g/L is found to be optimum in both electrodes.

#### Influence of Current applied

The metal ions from the anode, interacts with the hydroxyl ions and get precipitated and adsorbed with contaminants, and eliminate the dye (Ghernaout *et al.*, 2008; Khandegar *et al.*, 2013; Bazrafshan *et al.*, 2007). For the active deduction of dye molecules, all these effects are important. High-current operation in the area around the anode can cause several different side reactions, like straight oxidation of pollutants or buildup of O<sub>2</sub>, limiting the efficacy of electrocoagulation. In contrast, more current induces the passivity on the cathodic area, resulting in a high consumption of energy. Since economical parameters hinge on both energy and electrode consumption so both should be lower. Hence it is vital to circumventworking at high current to resolve the excessive group of Ti(OH)<sub>n</sub> or Al(OH)<sub>n</sub>

in the effluent. For optimization of current, experiments were performed under other optimized parameters at different applied current from 0.01 to 0.06A and the results are given in Fig. 3. (C) Table 1. As the current applied augmented from 0.01 to 0.06A, the number of  $Ti^{n+}$  ions increased, the CRE was 99.8% at 0.05A and subsequently a slight reduction in removal efficiency for the electrode 'A' and in the electrodes 'B' as the current applied increased there was a steady increase in the CRE removal, the maximum CRE was 80 percent at 0.03A. From Fig. 3. (C) it is estimated that the highest percentage of removal for electrodes 'A' was at 0.05A, with 99.8% removal. Increasing the current further at 0.06A CRE percentage reduction (99.6 percent), which caused the oxide-layered cathode surface to avertsuitabletransmission of current among the electrodes. The optimum current for 'A' 0.05A (CRE% 99.8) for 'B' 0.03A (CRE% 80.3).

#### Influence of variable EC time

To study its effect, the EC time ranged from 5 to 30 minutes and the other optimized parameters remained constant. The results obtained are illus-

trated in Fig. 3. (d), Table 1. It was clearly known that the percentage of CRE increased in the case of electrode 'A' at 15 minutes CRE percentage was 99.2 and a slight reduction in CRE occurred afterwards. Whereas in 'B' the CRE percentage is obtained at 10 minutes high (92.0) and slowly decreased. Metal ions produced at the anode are agents of destabilization. Due to the low current, fewer metal ions are released from the anode that would not be sufficient to destabilize all pollutants in the colloidal form or suspended. The optimum EC time for 'A' was 15 min (CRE% 99.2) and for 'B' 15min (CRE% 89.2)

#### Conclusion

Dye elimination efficiencies (CRE percent) were observed in all experimental parameters in short operating time using  $TiO_2/Al$ . It is also understood that, by increasing the applied current, energy consumption is increased. Due to indigenous discharge restrictions, power and electrode usage, native energy unit values and few other additional constraints, an optimum current must be considered. However, this work showed that the high CRE per-

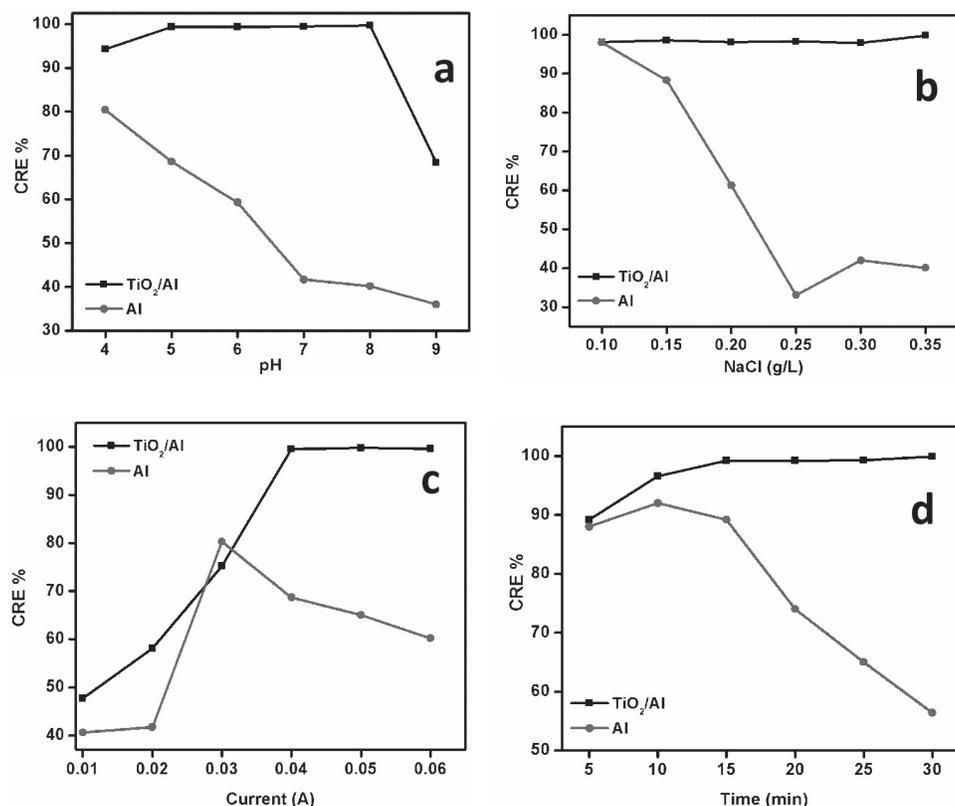


Fig. 3. Influence of (a). pH (b). NaCl (c). applied current (d). time on CRE (%)

centage of fabric dyeing effluent using  $\text{TiO}_2/\text{Al}$  was at pH 7. The EC method has the benefit of treating the fabric dyeing effluent and thereby eliminating the pollution of the surroundings by the dye molecules with the  $\text{TiO}_2/\text{Al}$  electrode and may well be used to other dyes and for the real-time effluent in the dyeing units.

## References

- Alinsafi, A., Khemis, M., Pons, M., Leclerc, J., Yaacoubi, A., Benhammou, A. and Nejmeddine, A. 2005. Electrocoagulation of reactive textile dyes and textile wastewater. *Chemical Engineering and Processing, Process Intensification*. 44 : 461–470.
- Attour, A., Touati, M. and Tilili, M. 2014. Influence of operating parameters on phosphate removal from water by electrocoagulation using aluminum electrodes. *Sep. Purif. Technol.* 123 : 124–129.
- Bensadok, K., Benammar, S., Lapique, F. and Nezzal, G. 2008. Electrocoagulation of cutting oil emulsions using aluminium plate electrodes. *J. Hazard Mater.* 152 : 423–430.
- Beck, F. and Gabriel, W. 1985. Heterogeneous Redox Catalysis on  $\text{Ti}/\text{TiO}_2$  cathodes – Reduction of nitrobenzene. *Angew. Chem. Int. Ed. Engl.* 24 : 771.
- Bazrafshan, E., Mahvi, A.H. and Nasser, S. 2007. Performance evaluation of electrocoagulation process for diazinon removal from aqueous environment by using iron electrodes. *Iran. J. Environ. Health. Sci. Eng.* 2 (4) : 127-132.
- Cullity, B.D. 1978. *Elements of X-ray Diffraction*, (2nd ed). Addison-Wesley Company, USA.
- Drouiche, S., Aoudj, M. and Hecini, N. 2009. Study on the treatment of photovoltaic wastewater using electrocoagulation: Fluoride removal with aluminium electrodes-Characteristics of products. *J. Hazard. Mater.* 169 (1-3) : 65–69.
- Gheraout, D., Badis, A., Kellil, A. and Gheraout, B. 2008. Application of electro coagulation in *Escherichia coli* culture and two surface waters. *Desalination*. 219 : 118-125.
- Hooshmandfar, A., Ayati, B. and Darban, A.K. 2006. Optimization of material and energy consumption for removal of Acid Red 14 by simultaneous electrocoagulation and electroflotation. *Water Science and Technology*. 73 (1) : 192–202.
- Hu, C.Y., Lo, S.L. and Kuan, W.H. 2005. Removal of fluoride from semiconductor wastewater by electro coagulation- flotation. *Water Research*. 39 (5) : 895-901.
- Jegathambal, P., Parameswari, K. and Vinodha, S.A. 2015. Method for Decolourization of Dyeing Waste Water by Electrocoagulation using Titanium Dioxide coated Aluminium Electrode. *Indian Patent No. Application ID 2474/CHE/2015*.
- Kobyra, M., Demirba°, E. and Dedeli, A. 2010. Treatment of Rinse Water from Zinc Phosphate Coating by Batch and Continuous Electrocoagulation Processes. *Journal of Hazardous Materials*. 173 : 326 – 334.
- Khandegar, V. and Saroha Anil, K. 2013. Electrocoagulation for the treatment of textile industry effluent - A review. *Journal of Environmental Management*. 128 : 949 – 963.
- Lacasa, E., Ca, P. and Saez, C. 2011. Removal of arsenic by iron and aluminium electrochemically assisted coagulation. *Sep. Purif. Technol.* 79 : 15–19.
- Lee, W.J. and Pyun, S.I. 1999. Effects of hydroxide ion addition on anodic dissolution of pure aluminum chloride ion-containing solution. *Electrochim Acta*. 44: 4041-4049.
- Merzouk, B., Gourich, B. and Madani, K. 2011. Removal of disperse red dye from synthetic wastewater by chemical coagulation and continuous electrocoagulation – A comparative study. *Desalination*. 272 : 246–253.
- Nadjib Drouiche, Saleh Aoudj and Hakim Lounici, 2012. Fluoride Removal from pretreated Photovoltaic Wastewater by Electrocoagulation: An Investigation of The Effect of Operational Parameters. *Procedia Engineering*. 33 : 385-391.
- Nanseu-njiki, C.P., Raoul, S. and Claude, P. 2009. Mercury (II) removal from water by electrocoagulation using aluminium and iron electrodes. *J. Hazard. Mater.* 168: 1430–1436.
- Parameswari, K. and Joseph Kennady, C. 2014. Comparative Study of Preparation, Phase formation and Application of  $\text{Ti}/\text{TiO}_2$  electrode prepared by thermal decomposition of  $\text{TiCl}_3$  with  $\text{HNO}_3/\text{H}_2\text{O}_2$ . *Chem Sci Rev Lett*. 3 (11): 388-393.
- Rafi, F., Franklin, W. and Cerniglia, C.E. 1990. Azoreductase activity of anaerobic bacteria isolated from human intestinal microflora. *Appl. Environ. Microbiol.* 56 : 2146-2151.
- Ün, Ü.T., Koparal, A.S. and Ödütveren, Ü.B. 2009. Hybrid Processes for the Treatment of Cattle Aluminum and Iron Electrodes. *J. Hazard. Mater.* 164 : 580 -586.
- Verma, A.K., Dash, R.R. and Bhunia, P. 2012. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *Journal of Environmental Management*. 93 : 154-168.
- Vasudevan, S., Lakshmi, J. and Jayaraj, J. 2009. Remediation of phosphate-contaminated water by electrocoagulation with aluminium, aluminium alloy and mild steel anodes. *J. Hazard. Mater.* 164: 1480–1486.
- Zongo, I., Hama, A. and Wethe, J. 2009. Electrocoagulation for the treatment of textile wastewaters with Al or Fe electrodes: Compared variations of COD levels, turbidity and absorbance. *J. Hazard. Mater.* 169: 70-76
- Zhu, J., Wu, F. and Pan, X. 2014. Removal of antimony from antimony mine flotation wastewater by electrocoagulation with aluminum electrodes. *J. Envi. Sc.* 23 (7): 1066–1071.