Effects of Ti/RuO_2-SnO_2-Sb_2O_5 electrode for decontamination of dyes from wastewater

Bhavna D Soni, U D Patel and Jayesh P Ruparelia

***Abstract*- DSA type electrodes show good technological performance and are subject to recent review. It is attempted in the present investigation to treat synthetic dye wastewater using electrochemical process. For electro-oxidation, a ternary coating with nominal composition Ru:Sb:Sn [15:15:70] electrode was fabricated in laboratory using titanium as substrate. Titanium was coated using metal chlorides $RuCl_3$, $SbCl_3$ and $SnCl_4$ by thermal decomposition method at 550□ C. Effects of Ti/ RuO_2-Sb_2O_5-SnO_2 electrode was studied on synthetic organic dyes Reactive Black -5, Acid black-194 and Direct black-22 for degradation and decolourization. Experiments were conducted at pH 2, current density at 50 and distance between electrodes at 8mm for 50 and 100 ppm of dye solution with constant ionic strength. Colour and COD reduction were observed using UV spectrophotometer and COD reactor. Maximum colour and COD reduction was respectively 99% and 73% in Acid black-194 employing Ti/ RuO_2-Sb_2O_5-SnO_2 electrode.**

***Keywords*: Reactive Dyes, Acid Dyes, Electro-chemical degradation, Ternary oxide electrode**

I. INTRODUCTION

The day-to-day human activities and industrial revolution have influenced the flow, storage and quality of water. It is a fact that industries like dyes, textiles, plastic, metal and chemical are the most polluting industries in the world causing grave damage to the environment [1]. Because these industries use large volume of water and also produces large volume of wastewater containing synthetic organic dyes [2], chemicals, dissolved metals and organic compounds. Synthetic organic dyes contain toxic material such as organic compounds, and colour pigments. Due to their strong colour they are visible even at low concentration in wastewater. These organic compounds are responsible for high chemical oxygen demand (COD) level in wastewater and create serious problems in the environments. Since, dyes usually shows high stability under sunlight and resistance to microbial attack and temperature, conventional wastewater treatment methods are unable to degrade majority of these compounds [3].Therefore, methods for decontamination and decolourization of effluents from dyes and textile industries have received considerable attention in recent years. Advanced oxidation process, microbial and enzymatic decomposition, ozonation, membrane separation and adsorption are some of the known methods for decolourization and decontamination from textile and dyes industries [3]. The method of electrochemical oxidation for treatment of the organic contaminants contained in wastewater has become a hot focus in recent years due to various advantages over other methods. Electrochemical processes are now a day proved to be very effective method to remove petroleum hydrocarbons from produced water (refinery wastewater) [4], synthetic organic dyes from wastewater [5]-6]-[7] treatment of mixed industrial waste water [6] and treatment of paper mill waste water [8].

It is reported that in electrochemical process DSA type electrodes show good technological performance [9]. This success is due to its desirable features and they are [10] (1) High efficiency in pollutant degradation (2) high stability under anodic polarization conditions and (3) low production cost.

The electrode material is very important in electrochemical oxidation of organic pollutants. Most of reports have employed electrodes of aluminum, iron, stainless steel and titanium. Aluminum, iron and stainless steel electrodes are useful for electro-coagulation [11]-[12]-[13]-[14]. Dimensionally stable electrodes (DSA) are titanium based electrodes containing conductive metal oxide coating. For fabrication of DSA type electrode [15]-[16]-[17] transition metals such as ruthenium, tantalum, iridium, tin, antimony etc are useful. This type of electrode generally gives partial oxidation of organics. Boron doped diamond (BDD) and lead oxide are the material useful to give complete oxidation of pollutants [18].

Main aims and objectives of this study are, indigenously prepare electrode for electrochemical process, to check the potential of indigenously prepared electrode for degradation of selected dyes and optimize various parameters for electrochemical process.

II. DYES DEGRADATION MECHANISM

Decolourisation is obtained due to electrochemical oxidation using non-soluble anodes or by electro-coagulation using soluble anodes. The degradation product of dyes are different but in general they are carbon dioxide, nitrogen, sulphate compound with possible formation of esters, phenols, aromatic carboxylic acids, cyclic and aliphatic hydrocarbons, aromatic amines etc.[18]

Degradation mechanism of dyes usually depends on their strength and reactive group. In general dyes are classified as [19] acid dyes , basic dyes, mordant dyes, reactive dyes, disperse dyes, azoic dyes and sulfur dyes. Dyes contains different derivatives such as -N=N-, -NO_2, -N=O etc [19] which are responsible for imparting colour. Oxidation taking place on the electrode (anode) breaks these derivatives, and therefore decolourization of wastewater becomes possible. Reaction sequence is represented as under for generalized electrochemical process [18].

$$H_2O + MO_x \rightarrow MO_x(\bullet OH) + H^+ + e^- \qquad (1)$$

$$MO_x(\bullet OH) \rightarrow MO_x + ½O_2 + H^+ + e^- \qquad (2)$$

$$R + MO_x(\bullet OH)_{n/2} \rightarrow MOx + \text{Oxidation product} + n/2\ H^+ + n/2\ e^- \qquad (3)$$

$$H_2O + Cl^- \rightarrow HOCl + H^+ + 2e^- \qquad (4)$$

$$R + HOCl \rightarrow \text{Product} + Cl^- \qquad (5)$$

Reaction (1) indicates electrolytic discharge of water carried out due to metal oxide (MO_x) to form metal oxide hydroxide complex (MO_x (•OH)) and hydrogen. Reaction (2) is for decomposition of metal oxide hydroxide complex results in evolution of oxygen and hydrogen gas giving partial oxidation of pollutants. Complete oxidation of pollutants (R) where no oxygen gas generated is given by reaction (3). Thus reaction (3) is a desirable reaction. In presence of active chlorine, reaction (4) and (5) takes place for degradation of pollutants (R) [15].

III. MATERIALS AND METHODS

For metal oxide coating, available methods are Thermal decomposition, Chemical Vapor Deposition (CVD), Surface Modifications, Ultra micro-or Nanoscale electrode and Micro-fabrication [18]. Thermal decomposition can be done by two ways either by standard method or by polymeric precursor method. Both the methods are simple and can be carried out in laboratory without any sophisticated facilities.

1) Chemicals

Reactive Black -5 (λ_{max}-597), Acid black-194 (λ_{max}-565) and Direct black-22 (λ_{max}-500) dyes chosen for experiments were collected from dyes industry (Gayatri colour chemical, GIDC, Ahmadabad). 1N sulphuric acid and NaOH solution were prepared in laboratory to adjust pH of reaction mass. Sodium chloride (NICE make LR grade) was used to increase conductivity. $RuCl_3$. XH_2O (99.9%, Aldrich), $SbCl_3$ (98.5%, CDH) and $SnCl_4.5H_2O$ (98% Aldrich) were used to prepare precursor solution for coating on titanium substrat. Iso-propanol (99.8% CDH, AR- grade) and hydrochloric acid (37%, CDH) were used as solvent for precursor solution in electrode fabrication.

2) Apparatus and instruments

The experimental work was conducted in batch process in laboratory. The batch unit consists of a 1.0 L electrochemical glass reactor with reaction mass 500 mL. The electrodes used have same dimensions 75mm X 65mm X 3mm. Ttitanium with coating was employed as anode, stainless steel (304) as cathode and the distance between two electrodes was kept 8mm in all the experiments. The applied potential was maintained constant by means of a D.C. power supply (Aplab India, LD-3205). For each run COD and colour was measured before and after treatment to find percentage reduction in pollution levels. COD was determined by standard closed reflux method [20] using COD reactor (Hach DRB200, COD reactor, USA). Colour was determined using UV- Vis (UV-1800, Shimadzu, Japan, wavelength range (200-800 nm))

3) Preparation of anodes

Three stage procedure was followed for preparation of electrode. (1) Cleaning of metal surface (2) Precursor preparation (3) electrode coating

3.1) Ti/ RuO_2-Sb_2O_5-SnO_2

Titanium metal piece with a dimension as specified in section 2 was polished with Sic paper (400–200 grit) and etched [20] in 10 % oxalic acid at 80°C for 1 hr and then rinsed with deionized water before thermal decomposition process. Precursor solution was prepared by dissolving 0.161 g $RuCl_3$ XH_2O, 0.171 g $SbCl_3$ and 1.227 g $SnCl_4.5H_2O$ in a solvent consisting of 10 mL iso- propanol and 0.5 mL hydrochloric acid .This precursor solution was prepared with molar ratio 15: 15:70 [Ru: Sb: Sn]

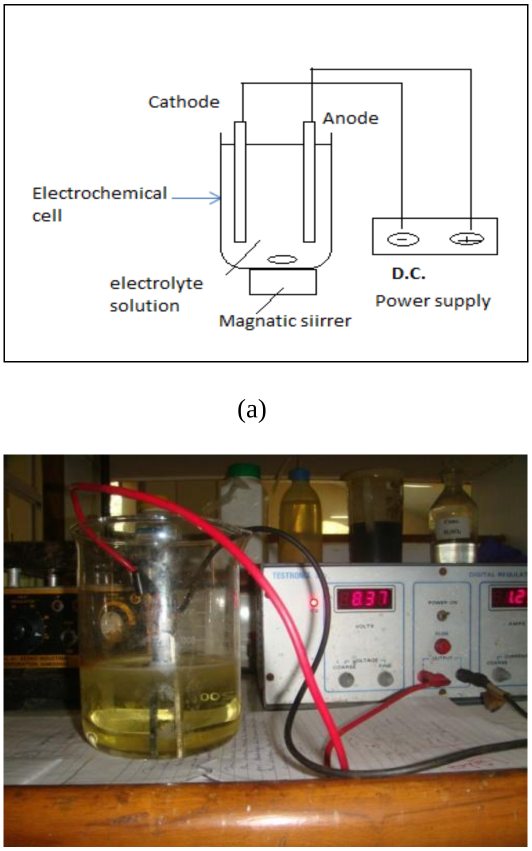
Freshly prepared precursor solution was brushed on pre-treated titanium substrate at room temperature, dried at 80° C for 5 min to allow the solvents to vaporize and then heated at 550° C for 5 min. This process was repeated about 15-20 times to provide proper coating on metal which can be ensured by measuring weight of substrate for oxide loading. After oxide loading on substrate achieved about 2-3 mg/cm^2 the electrode was heated at 550 °C in muffle furnace for an hour and cooled in desiccator up to room temperature.

3.2) Experimental protocols

500 mL dye solutions were prepared by dissolving dyes in tap water to prepare 50 and 100ppm. 2 g NaCl was added as electrolyte to raise the conductivity of solutions. The pH of the solutions was measured by pH meter and adjusted by adding NaOH or H_2SO_4 solutions. Titanium electrode with metal oxide coating was prepared as described in section (3.1) were used as anode and stain less steel (304) was used as cathode in each experiment. The electrodes were connected to a DC power supply (Fig-1) for controlling the current density. All the runs were performed at room temperature. In each run, 500 mL of the dye solution was decanted into the electrolytic cell. Electro-oxidation was carried out and samples were collected at 5, 15, 30 and 60 minutes for COD and UV analysis.

4) Analysis

The COD and decolourization were chosen as parameters in order to evaluate the effect of electrochemical treatment. Dyes concentrations were determined from their absorbance characteristics in the UV with the calibration method. The calculation of colour removal efficiency after electrochemical treatment was performed using this formula [18]-[21]



(a)

(b)

Fig-1 (a) Schematic diagram and (b) Experimental set-up for batch process

$$\%Decolorization = \frac{ABSo - ABS}{ABSo} X100 \quad \text{--- (6)}$$

Here ABS_0 and ABS are absorbance values before and after electrolysis of dye at maximum visible wavelength (λ_{max}) of the wastewater. The decontamination of dyes wastewater was monitored from the abatement of chemical oxygen demand (COD) measured for examining water and wastewater. From these data, the percentages of COD decays are calculated from following equations [18]-[21]-[22].

$$\%CODremoval = \frac{CODi - CODf}{CODi} X100 \quad \text{-- (7)}$$

Where COD_i, COD_f, are initial and final (after electrolysis) values of COD

Instantaneous current efficiency (ICE) i.e. oxidation ability of the anode material was also calculated using equation (8)

$$ICE = \frac{[CODt - CODt + \Delta t]FV}{8I\Delta t} \quad \text{---(8)}$$

Where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the COD values at t and t $+\Delta t$ (seconds) in (mol O_2 dm^{-3}), respectively, I is the applied current (ampere), F is the Faraday constant ($96487 Cmol^{-1}$), V is the volume of the electrolyte solution (m^3), 8 is a dimensional factor for unit consistence [18]-[21]-[22].

IV. RESULTS AND DISUSSION

1) Importance of DSA type electrodes: In this experiment Ti/RuO_2-SnO_2-Sb_2O_5 electrode was fabricated. Table-1 shows that there was no sludge generation with Ti/RuO_2-SnO_2-Sb_2O_5. Means reduction in COD and colour took place without sludge formation compare to electro-coagulation [11]-[12]-[13]-[14]. In this electrode precursor mixture is of three metal oxides. In which RuO_2 serves as a catalyst, SnO_2 serves as a dispersing agent and Sb_2O_5 serves as a dopent. RuO_2 also increases service life of an electrode while SnO_2 increases coating stability [18].

2) Effects of pH: Experiments were carried out at pH 2, 7 and 11 on 100 ppm (Table-1) Reactive black -5 dyes with Ti/ RuO_2-Sb_2O_5-SnO_2 electrode and influence of the initial pH on the reduction of COD concentration and colour removal with respect to time was observed. It was observed that at pH 11 neither colour nor COD reduction was taken place. At neutral pH, degradation and decolourization took place but in higher time compare to results obtained at pH 2. Means decolourization and decontamination was best carried out at pH 2.

So, the initial pH is a crucial parameter that plays important role in the oxidation of pollutants. The form of the electro generated hydroxyl radical species and its oxidation potentials are influenced by the solution pH [2]. At pH 2, generation of active hydroxyl radicals could be more compare to pH 7 and pH 11. Hence efficiency of degradation is higher at pH 2. Fig-2 is UV spectra of 100ppm untreated and treated reactive black-5 dye solution. Fig-2 (a) shows peaks in visible range while in (b) peaks disappear in visible range means colour has been removed, however it shows some peaks in UV range which may be of intermediates produced as a result of decomposition of dyes.

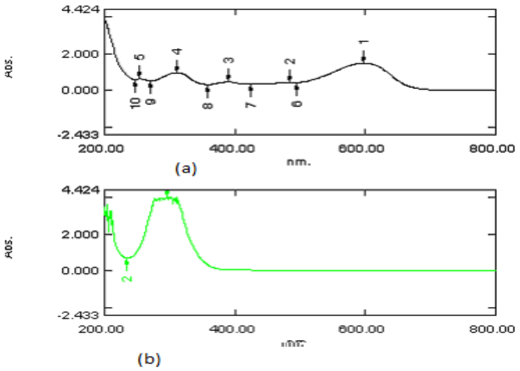


Fig-2 UV spectra of (a) 100ppm Reactive Black-5 dye sample (b) sample treated with Ti/ Ruo_2-SnO_2-Sb_2O_5 after five minutes at pH 2

TABLE-1
REDUCTION OF COD AND COLOUR ON 100 PPM REACTIVE BLACK -5 DYE AT DIFFERENT PH

Electrode	Time (minutes)	Current Density mA/cm2	pH	NaCl added in gm	%COD reduction	% colour reduction	Sludge generated gm
Ti/ RuO_2-Sb_2O_5-SnO_2	60	50	7	2	41	98	No
Ti/ RuO_2-Sb_2O_5-SnO_2	60	50	2	2	42	99	No
Ti/ RuO_2-Sb_2O_5-SnO_2	60	50	11	2	No	No	No

3) Degradation mechanism: Titanium based three dimensional electrodes includes direct and indirect oxidation process. Direct oxidation [2]-[15]-[18] takes place at the surface of the electrode while indirect oxidation takes place due to simultaneous electro generated hydroxyl radicals close to electrode could also remove the pollutants. COD reduction with respect to time for three different dyes with Ti/ RuO_2-SnO_2-Sb_2O_5 for 100 ppm and 50 ppm concentration is shown in Fig 3, 4. COD removal efficiency in synthetic wastewater is higher for 100 ppm concentration compared to 50 ppm. This may be attributed to higher concentration of pollutants available for degradation

4) Effects of initial concentration In general time to remove pollutants increases with its concentration in wastewater [2]-[14]-[22]. This phenomenon can be explained as; if other parameters like pH, amount of electrolyte are constant then amount of radicals produced for degradation would remain constant. If number of pollutants increased up to limit when radicals and pollutants become equal then there will not be any change in efficiency. As numbers of pollutants exceed radicals, efficiency starts decreasing. In this experiment for both 50 and 100 ppm concentration, colour removal efficiency is more than 90% whereas COD removal efficiency in synthetic wastewater is higher for 100 ppm concentration compared to 50 ppm as shown in Fig 3, 4, 5 and 6.

5) Effects of types of dyes: It can be observed from Table-1 that Ti/ RuO_2-Sb_2O_5-SnO_2 as an anode was able to reduce colour up to 99% for all three dyes but reduction of COD level was different for different dyes (Fig 3, 4) This can be explained as in the structure of reactive dyes [24] primary bond is covalent bonds and secondary bonds are Van-der-Waals hydrogen bonding. Covalent bonds are the strongest bonds; and thus reactive dyes are difficult to degrade whereas in acid and direct dyes, primary bonding is ionic bonding. This bonding is weaker than covalent type. Further ionic bond breaks easily compare to covalent bond, reduction of that molecule is easy therefore COD reduction is more in acid dyes compared to reactive dyes.

6) Instantaneous current efficiency(ICE) It is reported that when the applied current exceeds limiting current, organic pollutants are completely converted to CO_2, H_2O and secondary reaction (oxygen evolution or electrolyte decomposition) starts resulting decreases in instantaneous current density [18]-[21]-[22]. It means electrolysis is under mass transport control rather than the charge transport control. Fig 7, 8 shows ICE decreases maximum within five minutes, which reflects maximum oxidation takes place within this time only.

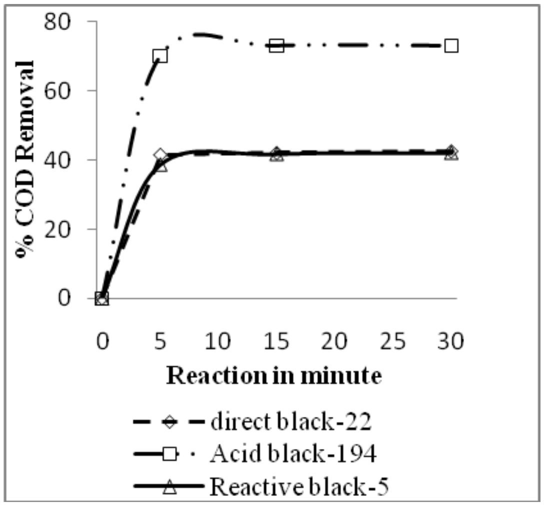


Fig-3 COD removal for 100 ppm dye solution

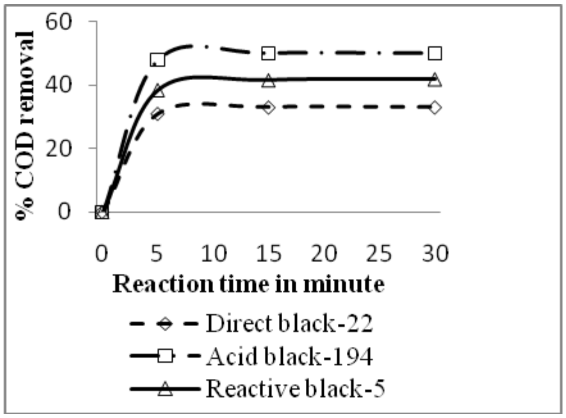


Fig-4 COD removal for 50 ppm dye solution

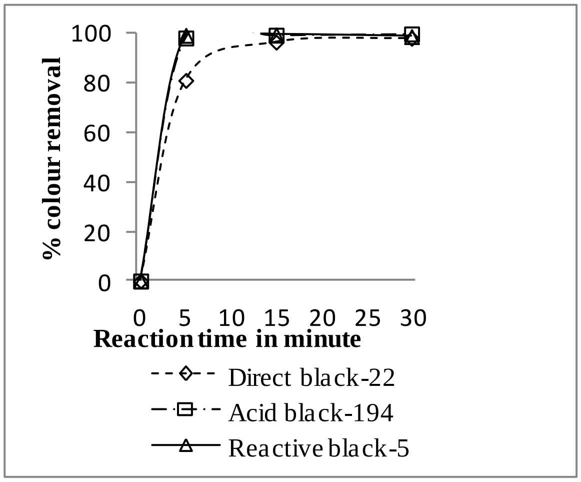


Fig-5 Colour removal efficiency for 100 ppm dye solution

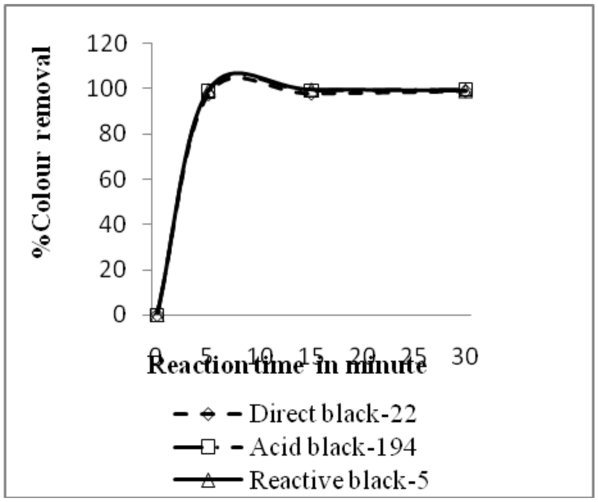


Fig-6 Colour removal efficiency for 50 ppm dye solution

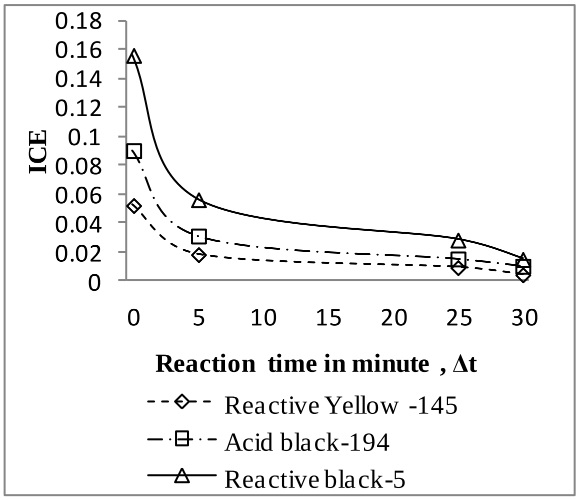


Fig-7 ICE vs. time for 100ppm dye solution

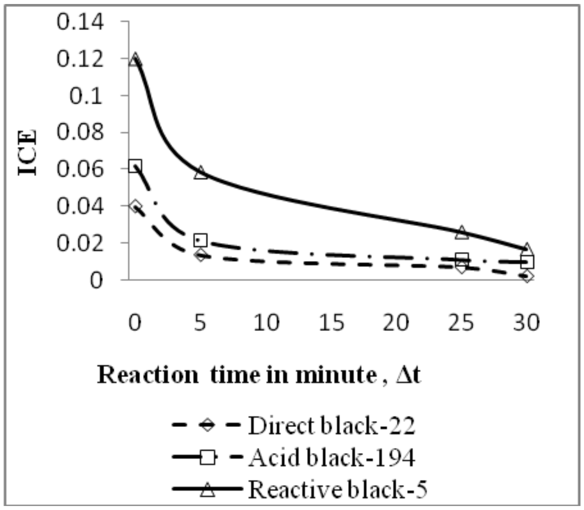


Fig-8 ICE vs. time for 50ppm dye solution

V. CONCLUSION

(1) Titanium electrode prepared by coating of oxide metals like RuO_2, SnO_2, and Sb_2O_5 on titanium substrate gave substantially good results.

For Direct black-22 and Acid black-194 dye solution it was possible to remove COD level 52%and 73% respectively while colour removal is 99%. For Reactive black-5 colour removal was possible up to 99% but COD reduction was only 42%. This may be due to stronger bonding in RB-5 compare to DB-22 and AB-194.

(2) Efficiency of Ti/Ruo2-Sb2O5-SnO2 is maximum at pH 2 compare to pH 7 and pH 11.

(3) Instantaneous current density decreases maximum within five minutes represents that the maximum degradation occurs during first five minutes of treatment.

VI. REFERENCES

[1] N. Mohan, N.Balasubramanian, C.Ahmed Basha, “Electrochemical oxidation of textile wastewater and its reuse,” *Journal of Hazardous Matterial*, vol. 147, pp. 644-651, 2007

[2] C.Efthalia, P X Nikolaos , C. Alberto, K. Nicolas, M. Dionissios, “Electrochemical treatment of textile dyes and dye house effluents,” *Journal of Hazardous Materials*, vol.137(2), pp. 998-1007, 2006.

[3] A. M. Carlos, B. Enric, “ Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review,” *Applied Catalysis B: Environmental*, vol. 87(3-4), pp. 105-145, 2009.

[4] M. Z. Adriana, A. M. Carlos, R. S. Djalma, “Application of electrochemical technology for removing petroleum hydrocarbons from produced water using a DSA type anode at different flow rates,” *Fuel*, vol. 89(2), pp. 531-534, 2010.

[5] D. Rajkumar, K. Palanivelu , “Electrochemical treatment of industrial wastewater,” *Journal of Hazardous Materials,* vol. 113(1-3), pp. 123-129, 2004.

[6] Y. Fenyun , S. Chen , Y. Chan , “Effect of activated carbon fiber anode structure and electrolysis conditions on electrochemical degradation of dye wastewater,” *Journal of Hazardous Materials,* vol. 157(1), pp. 79-87, 2008.

[7] M.C. Gutierrez, M. Crespi, “A review of electrochemical treatments for colour elimination,” *JSDC*, vol. 115, 1999.

[8] B. Wang , K. Wuping , M. Hongzhu , “Electro-chemical treatment of paper mill wastewater using three-dimensional electrodes with $Ti/Co/SnO_2$-Sb_2O_5 anode,” *Journal of Hazardous Materials*, vol. 146(1-2), pp. 295-301, 2007.

[9] J. F. Cristina, P. Olivi, A. R. Andrade, “Characterisation of DSA®-type coatings with **n**ominal composition $Ti/Ru_{0.3}Ti_{(0.7-x)}Sn_xO_2$ prepared via a polymeric precursor,” *Electrochimica Acta*, Vol. 47(6, 14), pp. 913-920, December 2001.

[10] C. Comninellis and G.Chen, “Electrochemistry for the Environment,” *New York Springer Science Business Media,* LLC 1St ed. 2010

[11] G.Chen, X. Chen, P. L. Yue , “Electro coagulation and electro flotation of restaurant wastewater” *Journal of Environmental Eng*ineering, vol. 126 (9), pp. 858–863, 2000.

[12] I. Zongo, J. Leclerc , M. H. Amadou , W. Joseph, F. Lapicque, “ Removal of hexavalent chromium from industrial wastewater by electro-coagulation,” *Separation and Purification Technology*, vol. 66(1-7), pp. 159-166, 2009.

[13] A. M. Hector, L.David, J. Cocke, A.G. Gomes, “Electro- coagulation mechanism for COD removal, *Separation and purification Technology*, vol. 56, pp. 204-211, 2007.

[14] I. L. Hernandez, D.B. Carlos, R.G. Morales, “Influence of the anodic material on electro coagulation performance,” *chemical Engineering Journal,* vol.148, pp. 97-105, 2009.

[15] C. Comninellis, C. Pulgarin , “ Electrochemical oxidation of phenol for wastewater treatment using SnO_2 anodes,” *Journa*l *of Applied. Electrochem.* Vol. 23, pp. 108–112, 1993.

[16] A.M. Polcaro S. Palmas, F. Remold , M. Mascia, “On the performance of Ti/SnO_2 and Ti/PbO_2 anodes in electrochemical degradation of 2-chlorophenol for wastewater treatment,” *Journal of Applied. Electrochem.* Vol. 29, pp. 147–151, 1999.

[17] C. Comninellis , G. P. Vercesi, “ Characterization of DSA-type oxygen evolving electrodes: choice of a coating,” *Journal of Applied Electrochem*, vol. 21, pp. 335–345, 1991.

[18] G. Chen , “Electrochemical technologies in wastewater treatment,” S*eparation and Purification Technology*, vol. 38(1), pp. 11-41, 2004.

[19] R.L. Arnold, “Dyes and Pigments: New Research,” 1st ed, *Nova Science Publishers* 2010.

[20] X. Chen, G. Chen, “Stable Ti/RuO_2–Sb_2O_5–SnO_2 electrodes for O_2 evolution,” *Electrochemical Acta,* vol. 50, pp. 4155–4159, 2005.

[21] M. Panizza, P. A. Michau, G. Cerisola, C. Comninellis, “Electrochemical treatment of wastewater containing organic pollutants on boron –doped diamond electrodes: prediction of specific energy consumption and required electrode area,” *Electrochemistry Communication*, vol. 3, pp. 336-339, 2001.

[22] S. Chen, Y. Zheng, S. Wang, X. Chen, “Ti/RuO_2–Sb_2O_5–SnO_2 electrodes for chlorine evolution from seawater,” *Chemical Engineering Journal,* vol. 172(1), pp. 47-51, 2011.

[23] F. Hong, X. Y. Song, “ The structure of azo dyes and its distribution on polyurethane fiber blend with polyester,or polyamide fiber, “*Dyes and Pigments*, vol.74 (3), pp. 672-676, 2007.