Design and Application of Electrochemical Processes for Decolorization Treatment of Nylanthrene Red dye Bearing Wastewaters

D. Marmanis[1,3,*], K. Dermentzis[2,3] and A. Christoforidis[1,3]

[1]*Laboratory of Environmental Protection, Department of Petroleum and Mechanical Engineering, Eastern Macedonia and Thrace Institute of Technology, EMaTTech, 65404 Agios Loukas, Kavala, Hellas*
[2]*Laboratory of General and Physical Chemistry, Department of Petroleum and Mechanical Engineering, Eastern Macedonia and Thrace Institute of Technology, EMaTTech, 65404 Agios Loukas, Kavala, Hellas*
[3]*Hephaestus Advanced Research Laboratory, Eastern Macedonia and Thrace Institute of Technology, EMaTTech, 65404 Agios Loukas, Kavala, Hellas*

___

Abstract

The purpose of this paper is the investigation of the capability of electrochemical methods, such as electrocoagulation, electrooxidation and electro-Fenton for decolorization and degradation of synthetic aqueous solutions and actual dye house effluents containing nylanthrene red reactive dye. All electrochemical experiments with the synthetic dye solutions were conducted in electrochemical cell of volume 500 ml containing 200 mL of dye solution at concentration 50 mg/L and inter-electrode distance of 1 cm. The three different electrochemical processes were analyzed, and their removal efficiencies were measured and evaluated. In addition, a flow diagram is designed for a continuously operated electrochemical process for remediation of synthetic and actual dye house effluents laden with nylanthrene dye.

In the electrocoagulation process with aluminum electrodes, the colored aqueous dye solution was treated at the applied current densities of 5, 10 and 15 mA/cm2 and was quantitatively decolorized in 11, 9 and less than 6 minutes of electroprocessing time respectively. The electrooxidation process conducted with Ti/Pt and boron doped diamond (BDD) electrodes, at the applied current density of 10 mA/cm2 led to the quantitative decolorization and destruction of the dye in 25 and 15 min respectively. In the electro-Fenton process with iron electrodes, supply of added hydrogen peroxide and applied current density of 10 mA/cm2, complete decolorization and degradation of the nylanthrene red dye occurred in 6 min. The actual polyamide textile dyeing effluent of same volume 200 mL with initial turbidity of 114 NTU and COD of 1755 mg/L was treated by electrocoagulation at the same applied current density of 10 mA/cm2. The turbidity was quantitatively eliminated in only 10 min, while COD was reduced by 74.5 % in 40 minutes of electrolysis time.

Keywords: dye house effluents, electrochemical coagulation, electrooxidation, electro Fenton, BDD - Ti/Pt anodes.

___

1. Introduction

Nylanthrene dyes are used for dyeing polyamide textiles. The textile industry discharges into the environment large quantities of water during dyeing and finishing operations every year. Textile wastewater is among the most polluted wastewaters due to its strong color, toxicity and large amounts of suspended solids. It also contains organic compounds, such as dyes and high values of chemical oxygen demand (COD). These toxic wastes, when discharged to the eco-system, create enormous environmental problems that cannot be acceptable by society. Because of this situation, it is necessary for textile industries to search for 'greener' methods and processes. In order to achieve lower level of pollution, the textile industries must treat textile effluents prior to discharge into the environment. Many techniques have been used till now, such as biological methods, adsorption, oxidation, flocculation, chemical coagulation and combination treatments, in order to solve the aforementioned problem.

The conventional biological treatment processes are often not suitable because most dyes are barely or non biodegradable [1,2].

The chemical coagulation produces large amounts of sludge and leads to extra pollution. Electrochemical processes for pollution abatement have been proved viable alternatives or complementary to biological treatment in some instances, especially when pollutants are recalcitrant to biological processing. They are based mainly on the direct anodic oxidation at dimensionally stable electrodes [3,4], advanced electrochemical oxidation [6,7] and electrocoagulation with sacrificial aluminum or iron electrodes [8].

The electrochemical treatment of textile dyes has numerous advantages as for instance immobilization of the catalyst/electrode i.e. without the need to separate the catalyst from the reaction mixture, the variables of electrical current and potential are easily controlled presuming that the process has been automated.

The present paper aims to present an integrated electrochemical decolorization/degradation treatment of colored nylanthrene red dye contained in synthetic and real dye house wastewaters. The following wastewater treatment processes are examined: (1) electrocoagulation with aluminum sacrificial electrodes; (2) direct anodic oxidation at dimensionally stable platinized titanium (Ti/Pt) and boron

_____

doped diamond (BBD) electrodes; (3) advanced electrochemical oxidation using the electro-Fenton process with sacrificial iron anode and added hydrogen peroxide. The decolorization of the treated solutions was followed by spectrophotometry, turbidity and COD measurements. The efficiencies of the three different electrochemical processes are compared and evaluated.

2. Materials and Methods

2.1. Materials
NaCl, Na_2SO_4 H_2SO_4, NaOH and H_2O_2 were of analytical grade (Merck). The value of pH was adjusted with 0.1 M solutions of H_2SO_4 and NaOH when it was required. The actual polyamide textile dyeing effluent was received from a dye house located in Northern Greece. The reactive dye nylanthrene red B-2BSA was purchased from Kyke (CB Number: CB5412967). Its structure is shown in Figure 1.
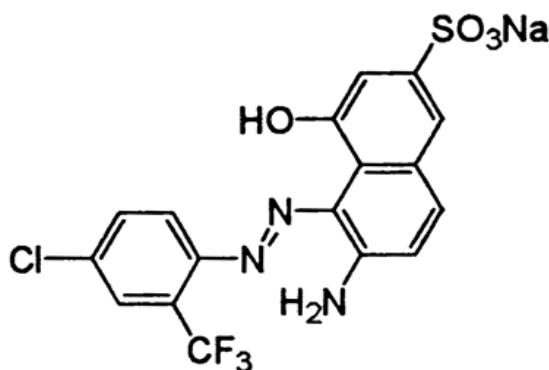

Fig. 1. Chemical structure of reactive dye Nylanthrene Red B-2BSA, Mr: 467.78, Molecular Formula: $C_{17}H_{10}ClF_3N_3NaO_4S$

2.2. Apparatus
A laboratory DC power supply apparatus (Agilent E3612A, USA) was used to maintain constant DC current. Voltage and current were measured by a multimeter (PHYWE). Conductivity was measured by means of a conductivity meter (inoLab Cond. Level 1, WTW). The pH and the temperature were measured using a WTW pH-meter. Electrolyses were conducted at room temperature in a cylindrical glass cell under slow stirring with a magnetic bar at 500 rpm.

The electrodes used for electrooxidation were two platinized titanium plates (Ti/Pt) each one serving as anode and cathode or one BDD anode and one graphite cathode. For the electrocoagulation and electro-Fenton experiments two aluminum and two iron plates were used, respectively. All electrodes used were of the same dimensions 5x10x0.1 cm, they were immersed 6 cm deep in the treated solution, and their effective area was 30 cm^2.

2.3. Analytical Procedures
UV-VIS Spectrophotometry (HITACHI U- 2000, Japan) was used for measuring dye concentrations. Known concentrations of the nylanthrene red B-2BSA dye solution were scanned at optimum absorption wavelength of 496 nm for generating the calibration plot. Samples were diluted using distilled water if the absorbance exceeded the range of calibration curve. All samples were filtered using polytetrafluorethylene filters with a pore size of 0.45 μm (Whatman). The COD was measured using a COD reactor (Thermoreaktor TR 420, MERCK) and a direct reading spectrophotometer (Spectroquant Pharo100, MERCK). The

turbidity of treated wastewater samples was analyzed with a turbidimeter (AQUALYTIC AL-100).

2.4. Experimental Procedures
All electrochemical experiments: electrocoagulation, electrooxidation and electro-Fenton were conducted in the 500 ml electrochemical reactor with solutions of 200 mL and 50 mg/L dye. The interelectrode distance was 1 cm. H_2O_2 was added to the reactor during the electro-Fenton process. The concentrations of Na_2SO_4 and NaCl were 2 g/L and 0.5 g/L. The applied current densities were 5, 10 and 15 mA/cm^2 for electrocoagulation and 10 mA/cm^2 for electrooxidation and electro-Fenton. The near neutral pH of the synthetically prepared and the actual wastewater samples needed no adjustment for the electrocoagulation treatment, whereas it was adjusted to 3 for the electro-Fenton and electrooxidation experiments.

3. Results and discussion

3.1. Removal of nylanthrene red by electrocoagulation
Electrocoagulation (EC) is an electrochemical method closely related to chemical coagulation. EC is a process consisting of creating metallic hydroxide flocs inside the wastewater by electrodissolution of soluble anodes made of aluminum or iron. The main reactions occurring during electrocoagulation produce aluminum ions at the sacrificial anode and hydroxide ions as well hydrogen gas at the cathode according to reactions (1-2):

$$Al \quad \rightarrow \quad Al^{3+} + 3e- \qquad \text{(anode)} \quad (1)$$

$$2H_2O + 2e- \quad \rightarrow \quad H_2 + 2OH- \qquad \text{(cathode)} \quad (2)$$

The generated Al^{3+} and OH- ions react to form the known gelatinous coagulant $Al(OH)_3$, effecting the coagulation and coprecipitation of particulates from the solution by adsorption.

The effect of current density and operating time are presented using two sacrificial aluminum electrodes as anode and cathode at different current densities. Na_2SO_4 (2 g/L) and NaCl (0.5 g/L) were used as supporting electrolyte to increase the solution conductivity (1980 mS/cm) and therefore reduce the resistance and the electrical energy consumption. The value of pH needed no adjustment as it lies in the optimum near neutral region [9].

According to Fig. 2, for the three current densities 5, 10 and 15 mA/cm^2 the initial concentration of 50 mg/L nylanthrene red fell under the detection limit (0.008 mg/L) in 11, 9 and 6 minutes of electrolysis time respectively. The removal rate is faster with increasing current density [10], because the current density determines the coagulant dosage rate, the bubble production rate and size and the flocs growth resulting in a faster removal of pollutants.

During the electrocoagulation process the molecules of nylanthrene red dye are not destructed. The dye molecules are absorbed and relocated as a whole in the electrogenerated $Al(OH)_3$ precipitate. The electrical energy consumption for the current density of 10 mA/cm^2 was calculated to 1.63 kWh/m^3 of treated dye solution.
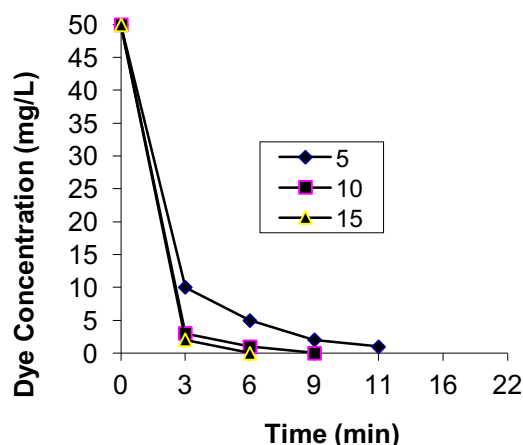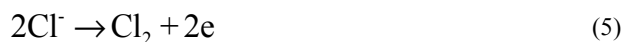
Fig, 2. Effect of applied current density on residual dye concentration versus timeduring electrocoagulation treatment of aqueous nylanthrene red due solution.

3.2. Degradation of Nylanthrene Red by electro-oxidation.

Organic matter can be anodically destroyed in two different mechanisms: A) direct oxidation, where the pollutants are adsorbed on the anode surface and destroyed by the electron transfer reaction and B) indirect oxidation in the liquid bulk by the electrochemically generated intermediate oxidants, such as free hydroxyl radicals OH^*, hydrogen peroxide H_2O_2, chlorine Cl_2 and peroxodisulfate, $S_2O_8^{2-}$, according to reactions (3-6):

$$H_2O \rightarrow OH^* + H^+ + e \qquad (3)$$

$$2OH^* \rightarrow H_2O_2 \qquad (4)$$

$$2Cl^- \rightarrow Cl_2 + 2e \qquad (5)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e \qquad (6)$$

In anodic oxidation organic pollutants are attacked mainly by the absorbed free hydroxyl radicals formed as intermediates from water oxidation at the surface of dimensionally stable anodes (BDD, TiO_2, IrO_2, PbO_2, Pt or graphite).

The most powerful oxidant in water is the hydroxyl radical with a redox potential of 2.8 V versus the normal hydrogen electrode (NHE). Chemical Advanced Oxidation Processes (AOPs) and Electrochemical Advanced Oxidation Processes (EAOPs), therefore, are characterized by the production and use of these hydroxyl radicals for oxidative destruction of organic substances. BDD electrodes show the largest overvoltage for oxygen production and the widest potential window in water ever found for an electrode material [11-13]. These electrodes are also chemically and mechanically stable. Therefore, BDD electrodes, compared to Ti/Pt are more suited for producing free OH^* radicals and performing EAOPs with very high current efficiencies [3,12].

The degradation of nylanthrene red B-2BSA from aqueous solution of 50 mg/L was investigated by direct electro-oxidation at platinized titanium Ti/Pt and BBD anodes. Na_2SO_4 (2 g/L) and NaCl (0.5 g/L) were used as supporting electrolytes. H_2SO_4 was added to the dye solution until it reached the optimum value of pH = 3. As it has been shown, [3], acidic electrolyte solutions favor the electrooxidation process by increasing the oxidation power of the intermediate oxidants (OH^*, H_2O_2, Cl_2, $S_2O_8^{2-}$) which are produced during the electrooxidation treatment of organic pollutants. Thus the optimum acidic solution of pH = 3 was selected as the operation pH. The applied current density was held at 5 mA/cm^2. It can be shown in Fig. 3 that the nylanthrene red dye concentration of 50 mg/L was completely reduced in 15 and 25 minutes of electrolysis time with BDD and Ti/Pt anodes respectively.   The electrical energy consumption for the current density of 10 mA/cm^2 was calculated to 3.52 kWh/m^3 of treated dye solution.
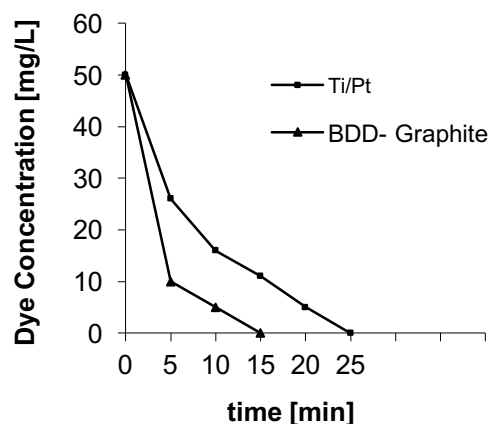

Fig. 3. Residual dye concentration versus time during electrooxidation of nylanthrene red solution at Ti/Pt and BBD anodes

3.3. Degradation of nylanthrene red by electro-Fenton

Fenton's reagent is an acidic mixture of hydrogen peroxide and Fe^{2+} ions, where free hydroxyl radicals with high oxidative power are produced according to reaction (7):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH \qquad (7)$$

Recently, the Fenton's reagent has been produced in situ electrochemically (electro-Fenton by addition of H_2O_2 and electrochemical production of Fe^{2+} ions with a sacrificial Fe anode according to the anodic reaction (8):

$$Fe \rightarrow Fe^{2+} + 2e- \qquad (8)$$

A part of OH^- ions produced from Fenton's reaction (3) react with the electroregenerated Fe^{2+} ions and precipitate as $Fe(OH)_3$. Therefore, the organic pollutants can be removed by electrooxidation with OH^* radicals and simultaneously by electrocoagulation with the $Fe(OH)_3$ precipitate [6,14].

Fenton reagent is generally conducted in acidic solutions with pH values ranging from 2 to 4 with the optimal value of pH=3. Hence, the dye solution was acidified with H_2SO_4 for pH value equal to 3. The electro-Fenton experiment was conducted at the applied current density of 5 mA/cm^2 with iron plate electrodes as anode and cathode and addition of 2 ml H_2O_2 1M solution every 2 minutes during electroprocessing. The solution pH tending to increase slightly during the process was monitored and adjusted with a dilute H_2SO_4 solution to the optimal pH value of 3. It can be shown in Fig. 4 that the initial concentration of 50 mg/L

Nylanthrene Red dye was completely decolorized and degraded in 6 minutes of electrolysis time. The electro-Fenton process is faster compared to the direct electrooxidation due to the fast reaction of the nylanthrene dye and its molecule fragments with the very reactive OH* radicals generated from corresponding reaction equation (7).

In addition to electro-Fenton degradation, the nylanthrene red dye and its molecule fragments can partially be absorbed and co-precipitate with the generated $Fe(OH)_3$ flocs and therefore be removed by electrocoagulation as pointed out in section 3.1.
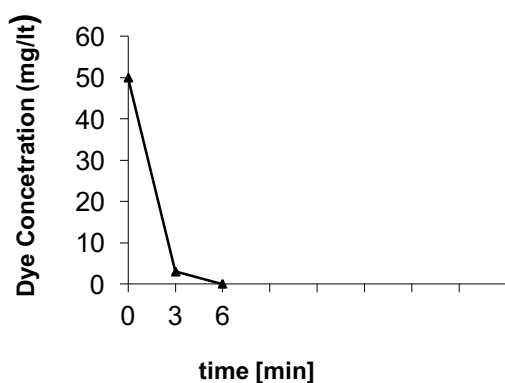

Fig. 4. Residual dye concentration versus time during electro-Fenton treatment of nylanthrene red solution

The electrical energy consumption for the current density of 10 mA/cm^2 was calculated to 3.52 kWh/m^3 of treated dye solution.

3.4. Treatment of actual dye house effluent
The applicability of the electrocoagulation processes for treating actual dye house wastewaters was validated by treating an industrial effluent sample collected from a polyamide textile dyeing unit. The main characteristics of the effluent sample before and after the electrocoagulation treatment are shown in Table 1.

Table 1. Main characteristics of the treated actual dye house effluent.

Parameter	Before treatment	After treatment
Color	reddish	colorless
pH	6.3	7.8
Turbidity (NTU)	114	0.2
COD (mg/L)	1755	448

The relatively high COD content of the wastewater indicates the presence of organic compounds added to the dyeing baths as dyeing auxiliaries e.g. brighteners, levelers, complexing and wetting agents.

At a constant current density of 10 mA/cm^2 the initial turbidity of 114 NTU was quantitatively reduced (>99.8 %) to 0.2 NTU in only 10 minutes of electroprocessing time. COD was reduced from the initial value of 1755 to a final value of 448 mg/L, showing a reduction of 74.5 % in 40 minutes. It reached then a plateau and remained almost constant at longer electrolysis time. The value of pH showed a slight increase from 6.3 to 7.8. The reddish color of the wastewater sample was completely disappeared in 40 minutes. Compared to color removal from synthetic solutions, the decolorization rate of the treated actual wastewater seems to be slower. This should be attributed to the presence of the organic compounds, which also compete for absorption on the $Al(OH)_3$ coagulant flocs resulting in a substantial reduction of the dye removal. The electrical energy consumption for the current density of 10 mA/cm^2 was calculated to 8.74 kWh/m^3 of treated wastewater.

3.5. Prespectives
A flow diagram is designed for treatment of actual industrial dye house effluents by continuously operated electrochemical process.

Wastewater generated by textile dyeing processes is channeled to a cylindrical wastewater deposit point. Next, it is transferred to an electrochemical reactor (EC- reactor) by means of a feed pump, following the wastewater's having passed through a flow meter for measuring purposes and a filter for removal of undesirable impurities.

Many are the electrochemical processes that wastewater undergoes within an EC-Reactor (such as electrocoagulation; electrooxidation; and electro-Fenton), at room temperature and via moderate magnetic stirring. Additionally, electrodes connected to a DC power supply are used for the provision of direct electric current flow and the monitoring of voltage and current limits. Photometric, pH, conductivity, temperature, and COD (Chemical Oxygen Demand) measurements are performed to check the progress of the wastewater cleaning and discoloration processes. Especially when it comes to electroflocculation, many flocculating agents at the beginning of the process are generated, leading to particle (pollutant) coagulation and to hydrogen evolution which carries a part of pollutants away to the surface of the treated liquid due to electroflotation.

Treated wastewater is transferred from the reactor to the sedimentation tank where the coagulated particles settle, while part of those pollutants is channeled to the surface of the solution. In that manner, two layers of sludge are produced: one at the bottom of the tank and one on the surface of the liquid. The sludge is transferred to a sludge tank by means of two pumps, while the intermediate cleaned liquid is filtered and then channeled to a treated solution tank.
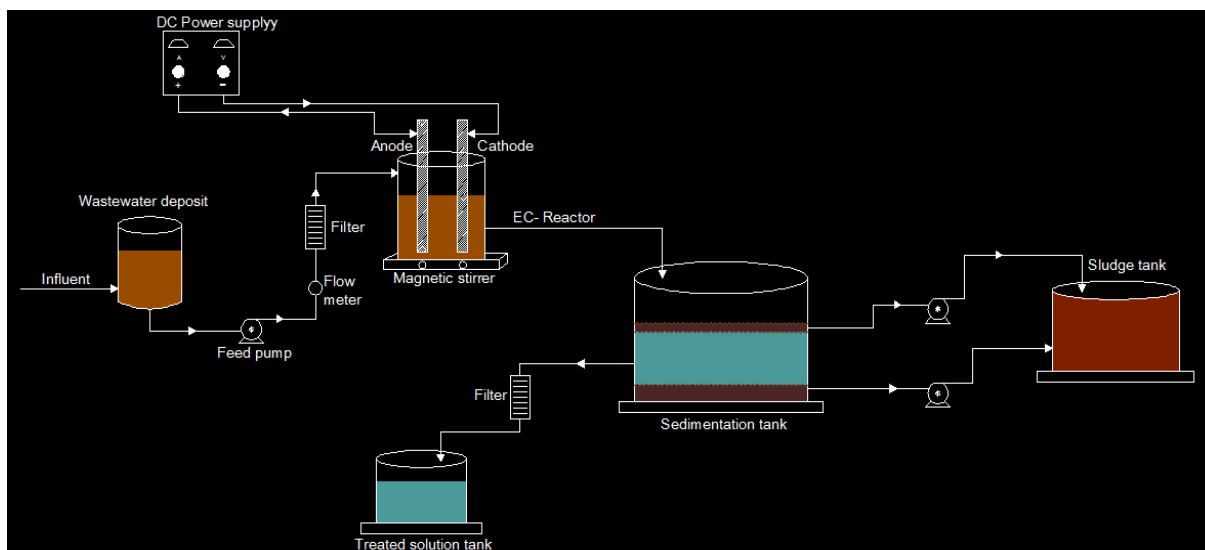
Fig. 5. Flow sheet of a continuously operated electrochemical process

4. Conclusions

The electrocoagulation process with Al electrodes is a fast and efficient method for decolorization of aqueous Nylanthrene Red solutions achieving 100% color removal in 11, 9 and less than 6 minutes of electroprocessing at the applied current densities of 5, 10 and 15 mA/cm^2. The dye decolorization rate increases with increasing applied current density. The electrical energy consumption for the current density of 10 mA/cm^2 was calculated to 1.63 kWh/m^3 of treated aqueous dye solution.

The electrooxidation process using Ti/Pt and BBD anodes in acidic medium of pH 3 and Na$_2$SO$_4$/NaCl mixture as supporting electrolyte is an effective method for decolorization and degradation of the Nylanthrene Red dyes. In 15 and 25 minutes of electrorocessing at BDD and Ti/Pt anodes respectively, the dye was completely decolorized and destructed. The electrical energy consumption for the current density of 10 mA/cm^2 using a BDD anode was calculated to 3.52 kWh/m^3 of treated aqueous dye solution.

The electro-Fenton process with Fe electrodes and supplied H$_2$O$_2$ in acidic solution of pH=3 is the most rapid and energy efficient method. The dye was completely decolorized and degraded in only 6 minutes of electrolysis time. The electrical energy consumption for the current density of 10 mA/cm^2 was calculated to 1.05 kWh/m^3 of treated dye solution.

For the electrochemical treatment by electrocoagulation of the real dye house effluent of same solution volume and same current density were needed 40 minutes of electroprocessing and 8.7 kWh/m^3 of treated wastewater.

It can be concluded that the proposed electrochemical treatment processes are safe and efficient methods for remediation of wastewater from polyamide dyeing plants. The generated free hydroxyl radicals increase the process efficiency as it is realized by the processes of electro-Fenton and electrooxidation at BDD electrodes.

_____

References

1. Cailean D., Barjoveanu G., Musteret C.-P., Sulitanu N., Manea L.R., Teodosiu C., Reactive dyes removal from wastewater by combined advanced treatment, *Environmental Engineering and Management Journal, 8, 503-511* (2009).
2. Beydill M.I., Matthews R.D., Pavlostathis S.G., Decolorization of a reactive copper-phthalocyanine dye under methanogenic conditions, *Water Science and Technology, 43, 333-340* (2001).
3. Chatzisymeon E., Xekoukoulotakis N.P., Coz A., Kalogerakis N., Mantzavinos D., Electrochemical treatment of textile dyes and dye house effluents, *Journal of Hazardous Materials,, B137, 998- 1007* (2006).
4. Dermentzis K., Stergiopoulos D., Moumtzakis A., Electrochemical degradation of indigo carmine textile dye powered by solar photovoltaic energy, *Global Journal of Energy Technology Research Updates* 1, 90-95 (2014).
5. Senthilkumar P., Umaiyambika N., Gayathri R., Dye removal from aqueous solution by electrocoagulation process using stainless steel electrodes, *Environmental Engineering and Management Journal, 9, 1031-1038* (2010).
6. Oturan M.A., Brillas E., Electrochemical Advanced Oxidation Processes (EAOPs) for Environmental Applications, *Portugaliae Electrochimica Acta, 25, 1- 18* (2007).
7. El-Desoky H.S., Ghoneim M.M., El-Sheikh R., Zidan N.M., Oxidation of Lewafix CA reactive azo-dyes in industrial wastewater of textile dyeing by electrogenerated Fenton's reagent, *Journal of Hazardous Materials, 175, 858-6,* (2010).
8. Kobya M., Can O.T., Bayramoglu M., Treatment of textile wastewaters by electrocoagulation using iron and aluminium electrodes, *Journal of Hazardous Materials, B100, 163-7* (2003).
9. Secula M.S., Cretescu I., Petrescu S., *Environ. Eng. Manage. J., 11,* 1485-1491 (2011).
10. Koshla N.K., Venkachalam S., Sonrasundaram P., Pulsed electrogeneration of bubbles for electroflotation, *Journal of Applied Electrochemistry, 21, 986-990* (1991).
11. Troster I., Fryda M., Herrmann D., Schafer L., Hanni W., Perret A., Blaschke M., Kraft A., Stadelmann M., Electrochemical advanced oxidation process for water treatment using DiaChem^R eledtrodes, *Diamond and Related Materials, 11,* 640-645 (2002).
12. Kraft A., Stadelmann M., Blaschke M., Anodic oxidation with doped diamond electrodes: a new advanced oxidation process, *Journal of* Hazard*ous Materials* **B103** 247-261 (2003).
13. Stergiopoulos D., Dermentzis K., Giannakoudakis P., Sotiropoulos S., Electrochemical decolorization and removal of indigo carmine textile dye from wastewater, *Global NEST Journal* **16** 499-506 (2014).
14. Brillas E., Casado J., Aniline degradation by electro-Fenton and peroxi-coagulation processes using a flow reactor for wastewater treatment, *Chemosphere, 47, 241-248* (2002).