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Removal of Methylene Blue by Direct Electrochemical Oxidation Method Using a Graphite Anode

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Abstract. The present work is to degrade methylene blue dye from aqueous solution by direct electrochemical oxidation technique. For this purpose an electrochemical cell was used comprising of two electrodes made from graphite as anode and stainless steel 316 grade as cathode. Different operating parameters that affected the treatment process such as current density, electrolyte temperature and initial dye concentration had also been studied. The reaction mechanism of direct anodic oxidation of M.B. is undertaken and the kinetic follows a pseudo first order reaction. Results revealed that at 20ºC electrolyte temperature, 10 mA/cm^2 current density, 0.5 g/l Na_2SO_4 as supporting electrolyte and 60 min electrolysis time, the decolorization percents for initial concentrations of M.B. 50 and 400 mg/L were 72.51% and 77.94% respectively while at 60ºC the decolorization percent 99.75% and 99.60% respectively for the same others operating conditions. The power consumption increased from 2.055 to 11.714 Kw.h/m^3 at applied voltage 14.6 V and 28.5 V respectively.

Keywords: Methylene Blue, Electrochemical Oxidation Treatment, Direct or Anodic Electrochemical Oxidation Process, Kinetics, Industrial Wastewater Treatment.

1. Introduction

Water is an important requirement for all living bodies. It has a significant role for industrial processes [1]. One of the greatest current and future challenges that face humankind is water deficiency as the world's population and water consumption rates continue to grow [2]; therefore the protecting of the fresh water resources has become a main worry for many countries in the world [3]. Large amount of manufacturing wastewater containing nondegradable and toxic organic compounds have recently been discharged into the environments [4]. Different types of dyes are formed worldwide and are used in several industries such as textile, paper, cosmetic, food and pharmaceutical industry [5].

Colored wastewater from textile industry affected the ecosystem in many ways, color reduce penetration of high into the water bodies thus affecting the photosynthetic activity of aquatic plants[6]; so that these pollutants should be destructed before the wastewater can be discharged [7].

2. Wastewater Treatment Methods

Various techniques are being used to carry out the elimination of toxic compounds from dye wastewater. These comprise physical, chemical and biological methods such as chemical oxidation, adsorption, and coagulation, flocculation combined with flotation and membrane filtration [8]. Biological treatment are generally unsuccessful for dye degradation because of the presence of aromatic rings and high biochemical stability [9], and it is obvious that chemical treatment happens just under conditions that electrostatic property of both pollutant and coagulant is compatible[10].

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Physical methods although effective in decolorization have the disadvantage of sludge formation which requires the regular regeneration of the adsorbents [11]. These reasons pushed the scholar's efforts towards developing powerful and active treatment technologies [10].

In recent years, Electrochemical Advanced Oxidation Processes (EAOPs) have been proposed to be the alternative and effective ways for the treatment of wastewater. They are compatible for environment technologies which own advantages compared to other technics of high degradation efficiency, easy operation, no chemical reagents needed and preventing secondary pollution. Among EAOPs, one can name electro fenton oxidation $H_2O_2/Fe^{+2,}$ electro photo fenton oxidation H_2O_2/Fe^{+2} with UV, and electrochemical oxidation (EO) [7, 11]. Electrocoagulation, electroflotation, electroreduction also consider usual methods of electrochemical treatments [12].

Electrochemical oxidation has attracted wide interesting as one of the environmental friendly technologies in wastewater treatment processes. It is an effective way to treat dye wastewater and considered to be a very powerful method for breaking up most of the resistance organic compounds [12, 18]. The study of E.O. was begun in 19th century when the dissociation of cyanide into its ions was tasted [1]. Mainly used for degradation aromatic compounds, dyes, pharmaceutical waste, pesticides, and other organics [13].

3. Theory

Electrochemical oxidation of pollutants can take place through two different oxidation mechanisms as shown below:

3.1 Direct anodic oxidation:

Where the pollutants are destroyed at the anode surface as explained in figure (1)

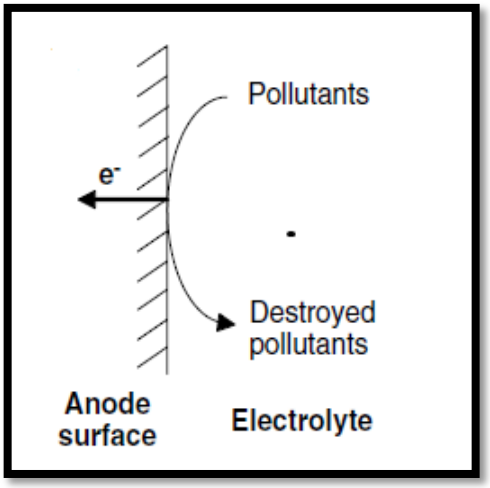


Figure 1. Direct oxidation mechanism.

Direct oxidation of pollutants takes place in two steps:

- Diffusion of pollutants from the bulk solution to the anode surface
- Oxidation of pollutants at the anode surface [14]

The organic pollutants are oxidized on the anode surface by the adsorbed hydroxyl radicals electro generated by water [11]

$$2H_2O \rightarrow 2OH^{\bullet} + 2H^{+} + 2e^{-} \quad (1)$$

3.2 Indirect anodic oxidation:

Anodically generated strong oxidizing agent such as chlorine and/or hypochlorite can be used to destroy oxidizable pollutants. In most cases, both inorganic and organic pollutants can be eliminated in the presence of a suitable amount of chloride as explained in figure (2) [14, 15].

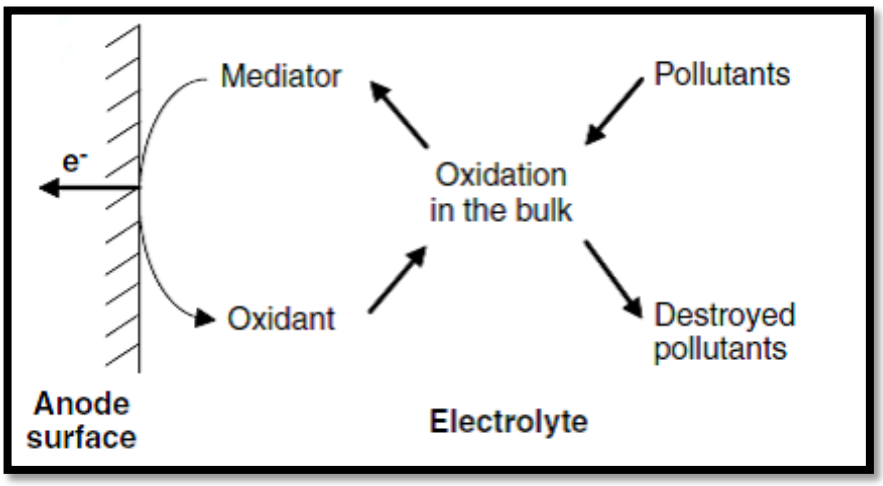


Figure 2. Indirect oxidation mechanism.

In indirect electro oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions. The reaction of anodic oxidation of chloride ions to form chlorine is given as [16, 17]:

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

At bulk solution reactions, the liberated chlorine form hypochlorous acid

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl \quad (3)$$

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

And further dissociates to give hypochlorite ion.

$$HOCl \rightarrow H^+ + OCl^- \quad (5)$$

$$M.B. + OCl^- \rightarrow \text{dye intermediate} \rightarrow CO_2 + H_2O + Cl^- \quad (6)$$

$$M.B. + HOCl \rightarrow CO_2 + H_2O + HCl \quad (7)$$

4. Experimental

4.1 Chemical materials and method

Stock solution was prepared by dissolving 1 g/L of M.B. dye ($C_{16}H_{18}ClN_3S$, Merk, Germany, M.wt:319.85 g/mole) in deionized water. Amount of Na_2So_4 salt is added for supporting electrolyte to increase conductivity. MB is a basic dye therefore pH of electrolyte solution approximately 7 and it is the same after experiment's time end. Working M.B. solution containing solutions of desired concentrations was obtained by diluting the stock solution with deionized water. 0.5g/l of Na_2So_4 added for each concentration. The molecular structure of the methylene blue is illustrated in figure (3).

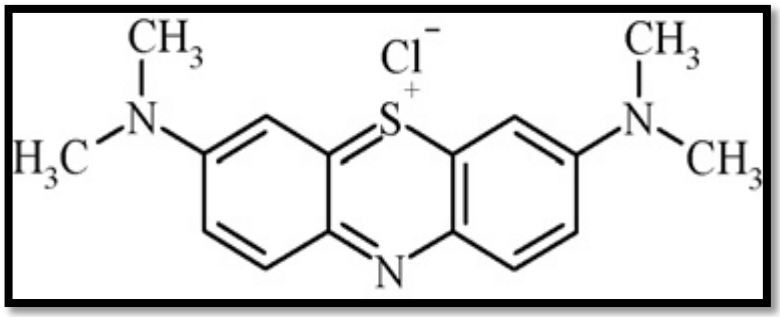


Figure 3. The molecular structure of the methylene blue.

The electrochemical oxidation of methylene blue was conducted in an electrochemical cell as shown in figure (4). The cell comprised of two compartments naming anodic and cathodic.

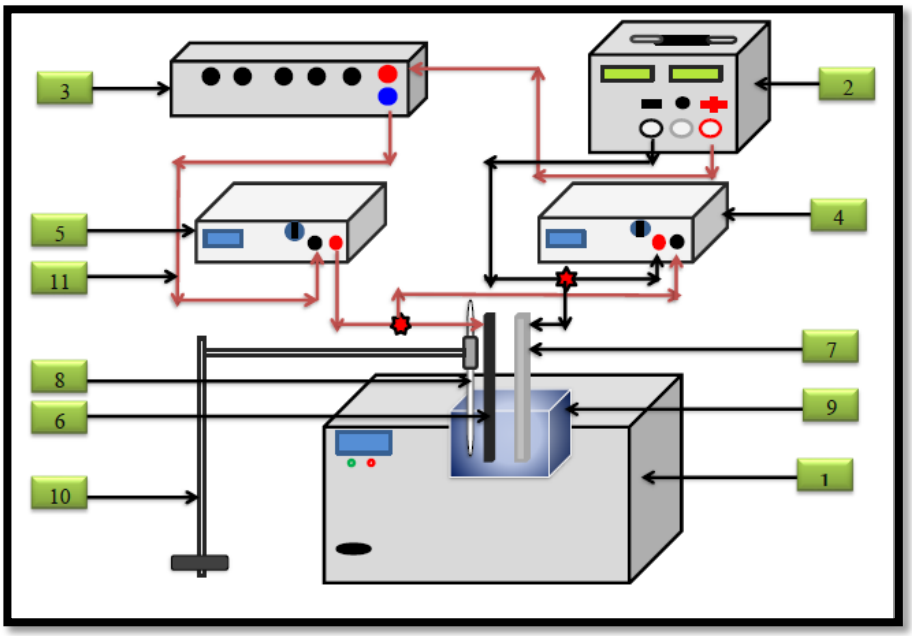


Figure 4. Experimental set-ups.
1. Water bath 2. Power supply 3. Resistance box 4. Ammeter 5.Voltmeter
6. Graphite 7. Stainless steel 8. Thermometer 9. Electrolytic cell 10. Stand
11. Electrical wires

Parallel rectangular shape (semi-cube) electrode used as the working electrode (Anode) made of special type of graphite having the dimensions, length 1.1cm, width 0.6 cm, and height 4 cm. The total surface area of electrode submerged in the electrolyte was 14.26 cm^2. Rectangular plate used as counter electrode (Cathode) made of stainless steel (316) grade having the dimensions, length 4 cm, width 5.5 cm. The side which not facing the anode was totally isolated by using self-adhesive paper to control the deposit area .The total surface area submerged was 22 cm^2. Two electrodes immersed in 0.5 L solution and the distance between them 2 cm. Total electrolysis 1 hr. Samples of M.B. solution were collected at constant interval 5 min for analysis the remaining concentration.

5. Analytical method

A UV-vis spectrophotometer (JENWAY 6800UV/VIS, Britain) was used to measure the concentration of M.B. at 661nm.the removal percent was calculated by equation (8):

$$\text{Removal } \% = \frac{Co - Ct}{Co} * 100\% \quad (8)$$

Where C_o and C_t are concentration of the M.B.initially and at time t in (mg/l) respectively.

The specific energy consumption (E_c in $kWhm^{-3}$) is determined using equation (9):

$$Ec = \frac{U.I.t}{3600V} * 10^{-3} \quad (9)$$

Where U is the average cell voltage (V), I is the current (A), t is the electrolysis treatment time (s), and V is the volume of electrolyte solution (m^3).

6. Kinetics Study of M.B. Degradation

The governing kinetic equation for color removal can be written as considering both OH radical and M.B. concentration taking part in the reaction, removal rate equation can be expressed as :

$$\frac{dC}{dt} = -K.[C_{M.B.}]^n.[OH^\bullet]^m \quad (10)$$

Working under galvanostatic condition (constant current), the concentration of $OH^\bullet$ can be approximated is constant (in steady state), thus $K[OH^\bullet]^m$ can be written as K^*. C_o^q .

$$K.[OH^\bullet]^m = K^*.C_o^q = K^{**} \quad (11)$$

Thus equation (3) can be written as :

$$-\frac{dC}{dt} = K^{**}.[C_{M.B.}]^n \quad (12)$$

In order to determine order of the reaction a plot between ln(C/C.) Vs.t was constructed.

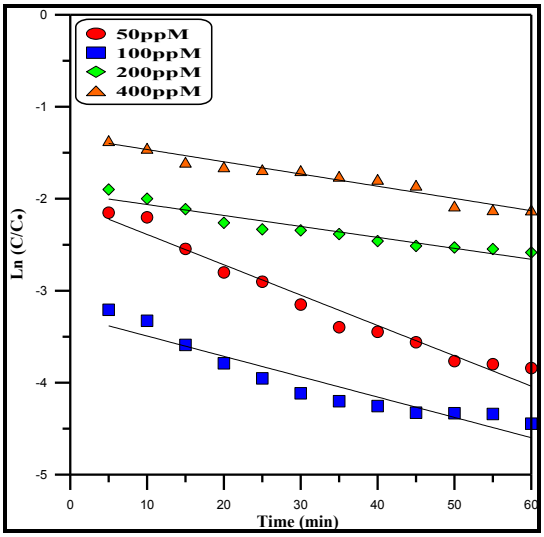


Figure 5. The kinetic fitting curve of M.B. direct removal (Na_2SO_4 0.5 g/l, current density 20 mA/cm^2, at 40°C).

Table 1. The first order reactions kinetic parameters of different concentrations of M.B. removal process.

C_o (mg/l)	K^{**}(min^{-1})	R^2
50	0.036	0.964
100	0.040	0.960
200	0.015	0.981
400	0.012	0.948

Figure (5) between ln(C/C◦) and time shows that ln(C/C◦) increase in almost linear relationship with time, so that the electrochemical reaction of methylene blue removal follows a pseudo first-order reaction, n=1, and that in a good agreement with findings by (Huimin Yang) [7].
Integrate equation (12) with following boundary conditions:
$C=C_\circ$ at t=0
$C=C_t$ at t=t

$$-\int_{C_\circ}^{C_t}\frac{dC}{C} = K^{**}.\int_0^t t\ .dt \tag{13}$$

$$-\ln\left(C - C_o\right) = K^{**}.t \tag{14}$$

By taken ln to equation (11) equation (15) can be obtained:

$$\ln K^{**} = \ln K^{*} + q\ln C_o \tag{15}$$

By fitting ln K^{**} □□and ln C. in figure (6) to get intercept lnK^{*}□□□ and the slope q of equation (15).

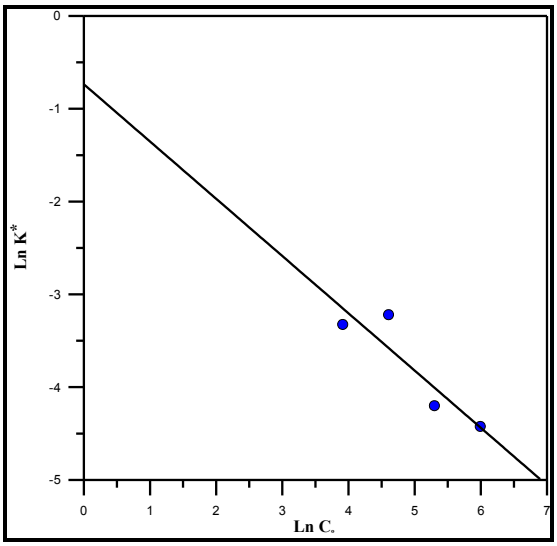


Figure 6. fitting between ln$C_\circ$ and ln K□**

Slop (q) = -0.5283
Intercept (ln K^{*}) = -0.7, taken exponetional to get value of K^{*}
K^{*}= 0.4965 mg/L.min = 8.2764*10^{-3} mg/L.s.
The values of the correlation coefficient (R^2) implies that equation (15) is acceptable and the relation between $OH^{\bullet}$ conc. and M.B conc.is credible. M.B. removal rate equation can be expressed as:

$$-\frac{dC}{dt} = 8.2764 * 10^{-3}.C_o^{-0.5283}\ .C_{M.B.} \tag{16}$$

7. Results and Discussion

7.1. Effect of current density
The effect of current density was tested for initial dye concentration of 50-400 mg/l in the range 10-30 mA/cm^2. Figure (7) shows the effect of current on removal percent. it has been noticed that the decolorization rate or the oxidation rate of Methylene Blue increase linearly with increase in current density, due to the fact that by increasing the current density, it means a large amount of charge entering the electrochemical cell and electro-generating more of hydroxyl radicals from electrolysis of water at anode surface according to the following equation (1):

$$2H_2O \rightarrow 2OH^{\bullet} + 2H^{+} + 2e^{-} \qquad E^{o} = -2.8V \tag{17}$$

Which is in turn will increase the oxidation rate of M.B.

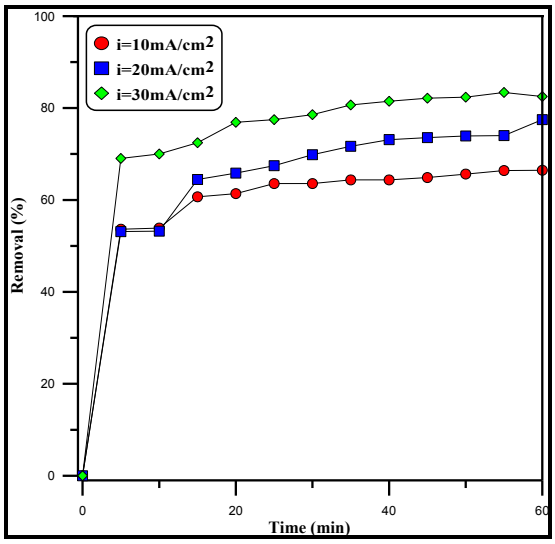


Figure 7. Effect of current density on removal percent for 200 mg/l at 20ºC

7.2. Effect of electrolyte temperature

The electrochemical reaction of M.B. is highly electrolyte temperature dependent and shows an increase of it will strongly expedite the removal of M.B., Thus the effect of electrolyte temperature considers one of the most important parameters that are effect on the anodic oxidation process. It can be seen from figure (8) that an increase of electrolyte temperature leads to an increase the decolorization rate. A sharp increase was happened especially when electrolyte temperature increase from 20°C to 40°C. On the other hand a slight increase can be noticed at 60°C, removal of methylene blue is nearly completely. The main influence of the electrolysis temperature on the decolorization rate is the production of hydroxyl radicals so that it may be obvious to operate at higher temperatures for complete removal of M.B.

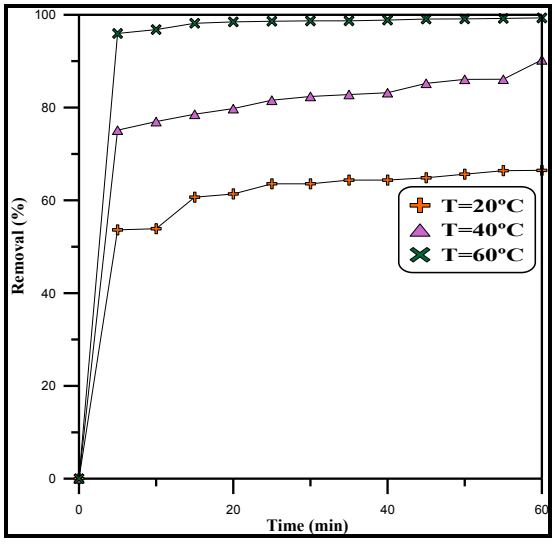


Figure 8. Effect of electrolyte temperature on removal percent for 200 mg/l and 10 mA/cm^2.

7.3. Effect of initial dye concentration

Figure (9) shows that as the initial M.B. concentration varied from 50 to 400 mg/l and there is no very evident effect of increasing concentration on the removal and that was in a good agreement with findings by (Yao Xing Liu) [9] for, example at 20°C when the initial concentrations were 50 and 400 mg/l, the decolorization rates were 76.590% and 77.709% respectively after 60 min of electrochemical treatment for the same others operating conditions i= 20 mA/cm^2 while at 60°C high M.B removal rates were obtained for all four dye concentrations studied almost complete removal at all current densities 10, 20 and 30 mA/cm^2.

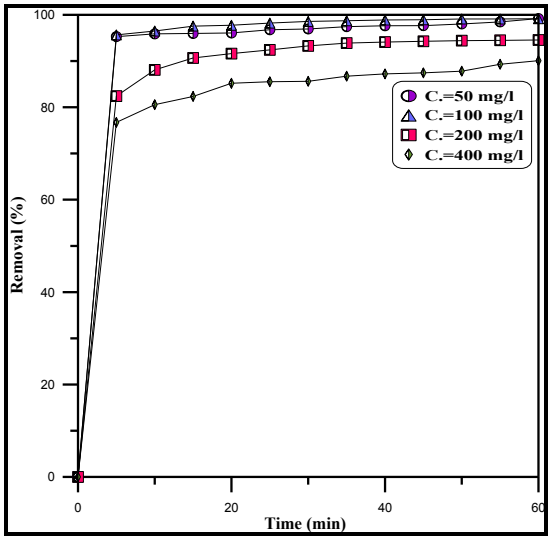


Figure 9. Effect of initial dye concentration on removal percent at 40ºCand 30 mA/cm^2

8. Conclusion

Direct electrochemical oxidation of methylene blue with sodium sulphate as supporting electrolyte is used to treat the textile industrial effluents. The process was carried out using graphite as anode and stainless steel 316 grade as cathode. The optimal conditions were 0.5 g/l from Na_2SO_4 salt and 60 min for electrolysis time. Under these experimental conditions, the removal percent in creased with increasing current density and electrolyte temperature while initial dye concentration had no evident effect on the decolorization percent.

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References

[1] Asghar H, Ahmad T, Hussain S and Sattar H 2015 Electrochemical oxidation of methylene blue in aqueous solution *J.Chem. Eng. and Appl.* 352-55

[2] Moussa D, El-Naas M, Nasser M and Al-Marri M 2016 A comprehensive review of electrocoagulation for water treatment: Potentials and challenges J. *Envi. Man*. 1-18

[3] Aimer Y, Benali O, Salghi R, Latapie L and Serrano K 2017 Removal of Pesticides by electrochemical oxidation using a boron doped diamond anode *J. Mate. and Envi.Sci.* 777-83

[4] Hyun Lee C, Seok Lee E, Kyun Lim Y, Hee Park K, Deung Park H and Soon Lim D 2017 Enhanced electrochemical oxidation of phenol by boron-doped diamond nanowire electrode J.*The Royal Soci. of Chem*. 6229-35

[5] Khandegar V and Saroha A 2013 Electrocoagulation for the treatment of textile industry effluent *J.of Envi.Man*. 949-63

[6] Indu M, Gupta A and Sahoo C 2014 Electrochemical oxidation of methylene blue using lead acid battery anode *J. of Sci. Dir.* 70-74
[7] Yang H, Liang J, Zhang L and Liang Z 2016 Electrochemical oxidation degradation of methyl orange wastewater by Nb/PbO_2 electrode *J. Electro. Sci.* 1121-34
[8] El Hajj Hassan M and El Jamal M 2012 Kinetic study of the electrochemical oxidation of methylene blue with Pt electrode *J. Portugalete Electro. Acta* 351-59
[9] Liu Y, Liao Z, Yun X, Zhao C, Lei Y and Bin D 2014 Electrochemical degradation of methylene blue using electrodes of stainless steel net coated with single-walled carbon nanotubes *J. Desalin. and Wat. Treat.* 1-9
[10] Najafpoor A, Davoudi M, and Salmani E, 2017 Decolorization of synthetic textile wastewater using electrochemical cell divided by cellulosic separator *J. of Envi. Heal. Sci. and Eng.* 2-11
[11] Panizza M, Barbucci A, Ricotti R and Cerisola G 2007 Electrochemical degradation of methylene blue *J. Separa.and Purifi. Techno.* 1-7
[12] Feng Y, Yang L, Liu J and Logan B 2016 Environmental science: water research and technology *J. of The Roy. Soci. of Chem.* 41
[13] Dimitrijevic S, Dimitrijevic S and Vukovic M 2013 Modren water treatment by electrochemical oxidation *International Research/Expert Conference* 1-4
[14] Anglada A, Urtiaga A and Ortiz I 2009 Contributions of electrochemical oxidation to wastewater treatment: fundamentals and review of applications *J. of Chem. Techno. Biotechno*. 1747–55
[15] Carlos A, Huitle M and Ferro S 2006 Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes *J. of Ro. Soci. of Chem.* 1324–40
[16] Mohan N, Balasubramanian N and Ahmed Basha C 2007 Electrochemical oxidation of textile wastewater and its reuse *J.of Haza. Mater.* 644–51
[17] Tahir h, Shah a, Iqbal S and Kifayatullah H 2017 The statistical optimization of indirect electrochemical oxidation process for the treatment of dye from simulated textile discharge *J. of Envi. Sci. and Natu. Resou*. 2 1-18
[18] Gu Q and Zheng J 2015 Study on the electrochemical oxidation treatment of coking wastewater by DSA anode *J.of Atla. Pre.*1-5